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THE CRYSTAL AND MOLECULAR STRUCTURES OF SELECTED ORGANOMETALLIC COMPOUNDS AND SOME DIRECT METHODS

Ph. D. Thesis Submitted to Iowa State University, August 1970

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THE CRYSTAL AND MOLECULAR STRUCTURES OF
SELECTED ORGANOMETALLIC COMPOUNDS AND SOME DIRECT METHODS

by

Leslie Leon Martin

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August 1970

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ABSTRACT

The crystal structure of 2-[tetra(trimethylsilyl)cyclohexene-1-yl]heptamethyltrisilane has been determined from three-dimensional single-crystal x-ray diffraction data collected by counter methods. The crystals are orthorhombic, space group $Pna2_1$ with unit cell parameters $a = 24.081 \pm 0.008$, $b = 9.839 \pm 0.007$, $c = 15.973 \pm 0.009 \text{ \AA}$, $\alpha_0 = 0.967$, $\alpha_c = 0.984 \text{ g/cm}^3$ for $Z = 4$. Block-diagonal anisotropic least-squares refinement led to a conventional R of 0.07 for 1225 observed reflections. The molecular structure is composed of a tetrasubstituted cyclohexene ring with the carbon-carbon double bond vinylic to the trisilane moiety. The average Si-Si bond distance is $2.35 \pm 0.01 \text{ \AA}$, and the average Si-C(sp^3) bond distance is $1.88 \pm 0.04 \text{ \AA}$.

The crystal and molecular structure of cis-dichlorobis(dimethylphenylphosphine)palladium(II) has been determined from 2027 independent, non-zero reflections using conventional three-dimensional single crystal techniques. The

compound crystallizes in the space group $P4_2/n$ with four molecules in a unit cell of dimensions $a = b = 9.324 \pm 0.004$ and $c = 21.485 \pm 0.004 \text{ \AA}$ ($\rho_{\text{calc}} = 1.62 \text{ g/cc}$ and $\rho_{\text{obs}} = 1.61 \text{ g/cc}$). The calculated volume is 1868 \AA^3 . The structure is approximately cis, square-planar with a slight tetragonal distortion of 4.3° . The Pd-P and the Pd-Cl distances are $2.259 \pm 0.002 \text{ \AA}$ and $2.362 \pm 0.002 \text{ \AA}$, respectively. The shortest Pd-Pd distance is 6.6 \AA .

The crystal and molecular structure of nitrilotriacetato-diaquopraseodymium(III)-monohydrate has been determined from 1111 independent, non-zero intensities using conventional heavy atom techniques. The compound crystallizes in the space group $Pbca$ with eight molecules in a unit cell of dimensions $a = 13.21 \pm 0.01 \text{ \AA}$, $b = 20.98 \pm 0.01 \text{ \AA}$, $c = 8.132 \pm 0.006 \text{ \AA}$ and $V = 2254 \text{ \AA}^3$. The praseodymium is nona-coordinate with six carboxylate oxygen atoms, two waters and one nitrogen atom in the coordination sphere. The spatial arrangement of the coordinating atoms can be described as either a distorted tri-capped trigonal prism or a distorted, capped, square anti-prism. Each nitrilotriacetate (NTA) is hepta-dentate with one carboxylate oxygen coordinating to two adjacent metal atoms. One carboxylate oxygen is uncoordinated and there is one water of crystallization.

The crystal and molecular structure of nitrilotriacetato-diaquodysprosium(III)-dihydrate has been determined from 3067

independent, non-zero intensities using a combination of heavy atom and superposition techniques. The compound crystallizes in the space group $Pca2_1$ with eight molecules in a unit cell of dimensions $a = 21.535 \pm 0.013$, $b = 9.028 \pm 0.004$, $c = 12.186 \pm 0.007 \text{ \AA}$ and $V_c = 2369 \text{ \AA}^3$. The two independent dysprosium atoms are octa-coordinate with five acetate-oxygen atoms, two water molecules and one nitrogen atom in the coordination sphere. The eight atoms reside at the corners of a distorted dodecahedron with triangular faces. Each nitrilotriacetate ligand is hexadentate with one acetate-oxygen atom not coordinated to any metal atom. Also, there are two waters of crystallization.

A new method for relating the phases of reflections in a centric structure is described. The derivation of the basic equations, a description of the procedure, and the application of the procedure to a structure solution are presented.

TABLE OF CONTENTS

	Page
ABSTRACT	iv
INTRODUCTION	1
STRUCTURE OF 2[TETRA(TRIMETHYLSIYL)CYCLOHEXENE-1-YL]HEPTAMETHYLTRISILANE	3
Introduction	3
Experimental	3
Results and Discussion	10
STRUCTURE OF <i>cis</i> -DICHLOROBIS(DIMETHYLPHENYLPHOSPHINE) PALLADIUM(II)	23
Introduction	23
Experimental	23
Solution and Refinement of the Structure	26
Description of the Structure	38
Discussion	39
STRUCTURE OF NITRILOTRIACETODIAQUOPRASEODYMIUM(III)-MONOHYDRATE	44
Introduction	44
Experimental	45
Solution of the Structure	47
Results and Discussion	48
STRUCTURE OF NITRILOTRIACETODIAQUODYSPROSIUM(III)-DIHYDRATE	67
Introduction	67
Experimental	67
Solution of the Structure	70
Discussion	81

	Page
THE QUADRUPLE PRODUCT	101
Introduction	101
Description of the Method	103
Application of the Method	110
LITERATURE CITED	115
ACKNOWLEDGMENTS	119
APPENDIX A. A LISTING OF QUADS	120
APPENDIX B. A LISTING OF RELATE	124
APPENDIX C. RESEARCH PROPOSALS	130

INTRODUCTION

The term "organometallic" is used to describe a wide range of compounds in which the organo-group is bonded directly to a metal atom. In addition, this term is often used to indicate compounds in which the organo-group is bonded to such atoms as silicon, boron, or phosphorus. The four compounds, $\text{Si}_7\text{C}_{26}\text{H}_{55}$, $\text{Pd}(\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5)_2\text{Cl}_2$, $\text{Pr}(\text{N}(\text{C}_2\text{H}_2\text{O}_2)_3)_3\text{H}_2\text{O}$, $\text{Dy}(\text{N}(\text{C}_2\text{H}_2\text{O}_2)_3)_4\text{H}_2\text{O}$ all fall into this category. An attempt was made to select compounds for study for which there was relatively little structural information available or the information was inconclusive and a crystal structure study would remove the ambiguity.

The silicon compound was selected for study due to the dearth of structural information available on multiple Si-Si bonding. In fact, this is, to my knowledge, the first crystal structure report of a compound with multiple Si-Si bonds. The silicon atoms were found to have a normal tetrahedral type configuration with little evidence for d-orbital contribution to the bonding despite the presence of a carbon-carbon double bond adjacent to the trisilane moiety. In the case of the palladium structure, information available on the structure was inconclusive. This study determined the configuration of the compound to be cis, square-planar, with a significant lengthening of the Pd-Cl bond and a shortening of the Pd-P bond. The amount of structural information available for the

rare earth complexes is limited; especially on structural changes across an entire series of rare earths complexed to one particular ligand. The purpose of the study of the lanthanon(III)-nitrilotriacetate complexes was to provide good structural information on the nature of the changes in the complexes across the series and to determine the causes of these changes. The two structures, which are presented here, show a gross structural change from nona-coordinate to octa-coordinate with additional, minor changes in bond distances. The results indicate that these changes are probably due to the decreased metal-ion size.

In addition, we have attempted to extend the normal "direct methods" by use of a new phase relationship called the "quadruple product". The method has been tried successfully on $\text{Cs}_3\text{Sb}_2\text{Cl}_9$.

STRUCTURE OF 2[TETRA(TRIMETHYLSILYL)CYCLOHEXENE-
1-YL]HEPTAMETHYLTRISILANE

Introduction

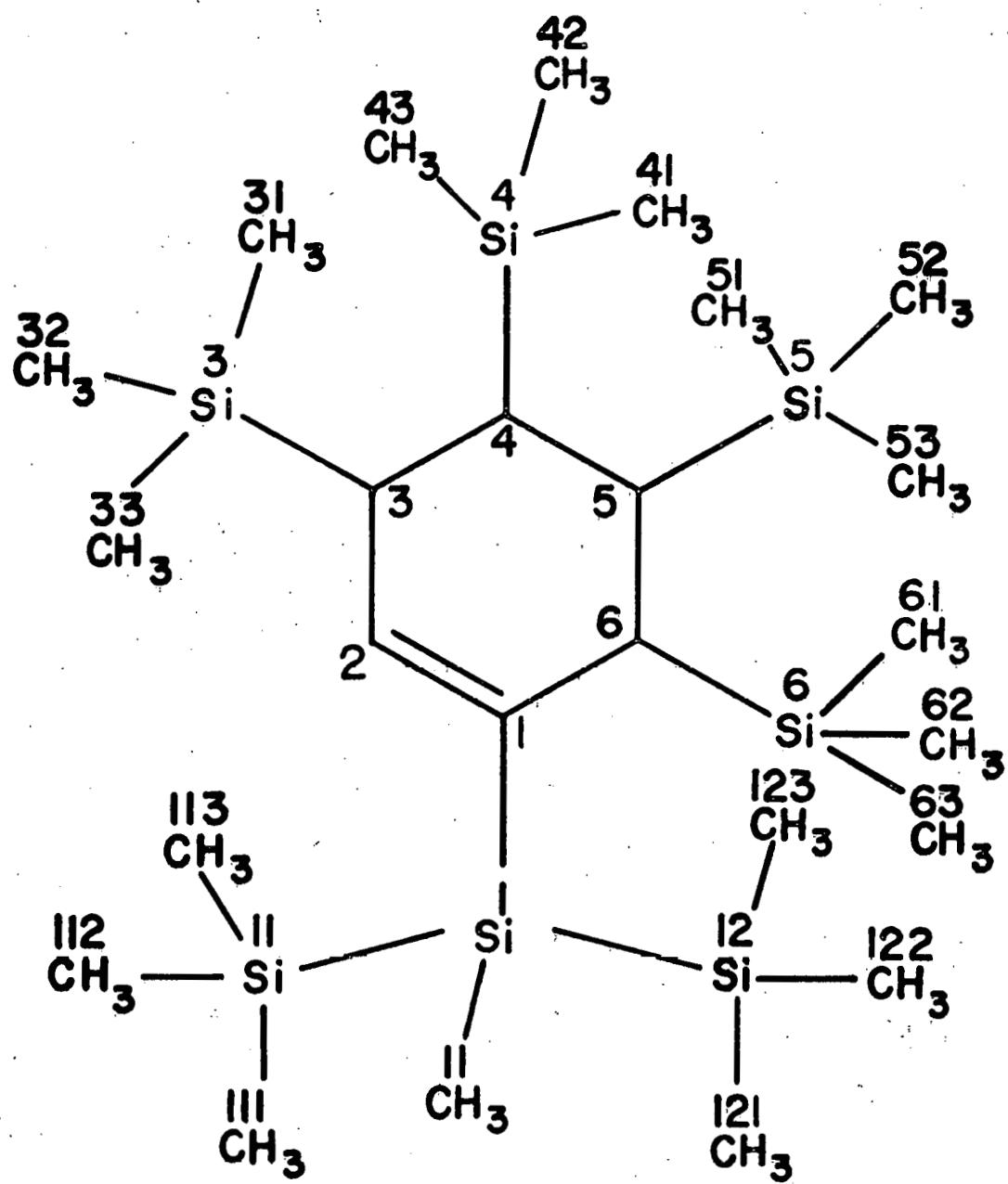
Although the structures of inorganic silicon compounds as well as a number of organic siloxanes and silsesquioxanes have been studied extensively, relatively little structural information is available for organosilicon compounds which contain Si-Si bonds. Gas phase electron diffraction was used to investigate the structures of disilane¹ and hexamethyldisilane², but the only compound of this type to be investigated by single-crystal X-ray diffraction techniques prior to the present study was bistetramethyldisilane-dioxide, $((\text{CH}_3)_4\text{Si}_2\text{O})_2$ ³. The title compound, 2-[tetra(trimethylsilyl)cyclohexene-1-yl]heptamethyltrisilane, hereafter referred to as TTCH, is of interest because of the trisilane moiety. The molecular configuration and the numbering scheme used in this investigation are seen in Figure 1. TTCH was obtained as the major product⁴ in the reaction of phenylmethyldichlorosilane and chlorotrimethylsilane with metallic lithium in tetrahydrofuran, and was unambiguously characterized only after this structural investigation.

Experimental

A sample of TTCH, mp 121°, was kindly supplied by Professor Gilman of this department. After recrystallization

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Figure 1. The molecular structure of TTCH (the ring carbons are numbered from 1 through 6 and the silicon atoms which are bonded to them have the same number as the carbon to which they are attached. Substituents on each silicon atom are identified by moving the silicon number one digit to the left)



from a 1:1 solution of methanol and ethyl acetate, many small, colorless crystals were obtained and were used without further purification. Weissenberg and precession photographs made with $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiation, respectively, indicated orthorhombic symmetry. Systematic absences observed for $\text{Ok}\bar{l}$ reflections with $k + l$ odd, and for $\text{h}\bar{0}\text{l}$ reflections with h odd, limited the choice of space groups to $\text{Pna}2_1$ or Pnma . Accurate unit cell parameters were obtained from a least-squares refinement based on the 2θ values for 16 reflections which had been carefully measured on a General Electric diffractometer using $\text{CrK}\alpha$ radiation. The a_1 and a_2 components were unresolved. Hence the wavelength used was the weighted mean of a_1 and a_2 , $\lambda = 2.291 \text{ \AA}$. The unit cell parameters and their standard deviations based on the elements of the least-squares inverse matrix are $a = 24.081 \pm 0.008$, $b = 9.839 \pm 0.007$, $c = 15.973 \pm 0.009 \text{ \AA}$, and $V = 3784 \text{ \AA}^3$. The density as measured by flotation in a methanol-glycerol mixture was 0.97 g/cm^3 ; the density calculated with $Z = 4$ was 0.98 g/cm^3 . A General Electric XRD-5 X-ray unit equipped with a single-crystal orienter and scintillation counter was used with $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) in the moving-crystal-moving-counter mode (θ , 2θ coupling) to measure intensities. A 100-sec scan covering 1.67° in 2θ was used for each reflection. The take-off angle was 1.0° . Since the backgrounds were seen to be a function of θ only,

the backgrounds for individual reflections were obtained from a plot of background versus 2θ . One crystallographically independent octant of data was measured within a 2θ sphere of 45° ($\sin\theta/\lambda = 0.538$) beyond which no reflections were observed to have intensities significantly above the background. These data, after correction for noncharacteristic radiation streaks⁵ and Lorentz-polarization factors, were reduced to structure factors. The crystal used for intensity measurements had approximate dimensions $0.2 \times 0.2 \times 0.4$ mm. The minimum and maximum transmittances were 91% and 97% based on $\mu = 2.50 \text{ cm}^{-1}$. Consequently no absorption correction was made. In an attempt to account for systematic as well as random errors standard deviations were assigned to the intensity data according to the formula:

$$\sigma(I) = [C_T + C_B + C_S + (0.04C_T)^2 + (0.04C_B)^2 + (0.06C_S)^2]^{1/2}$$

where C_T , C_B , and C_S are, respectively, the total counts, background counts, and streak counts. The quadratic terms correspond to estimated systematic errors of 4% in intensity and background measurements, and 6% in the streak correction. The estimated standard deviation for each structure factor was obtained by the method of finite differences⁵

$$\sigma(F) = ([I + \sigma(I)]^{1/2} - I^{1/2})/(L_p)^{1/2}$$

where L_p is the Lorentz-polarization factor. Of the 1423

measured reflections, 198 had $F < 3\sigma(F)$ and were excluded from the refinement.

Since the general multiplicity of the centrosymmetric space group, Pnma, is 8, four molecules of TTCH could occupy one unit cell in this space group only if each possessed either a center of symmetry or a mirror plane. The improbability of either symmetry in TTCH molecules indicated the noncentrosymmetric space group Pna₂1. The successful solution of the structure verified this space group assignment. The Si atoms were located by the use of a three-dimensional, superposition procedure starting with a well resolved peak in the Harker section of the sharpened Patterson map (the thermal parameter, B, used for sharpening was 2.0 \AA^{02}). In the resultant map, a center of symmetry relating two images was readily found. Utilizing one additional superposition and a knowledge of the space group symmetry, six of the seven Si atoms were located. Because of the large number of apparently equal peaks in the three-dimensional electron density map, the final silicon atom, Si₅, could not be distinguished from the many, as yet unassigned, carbon peaks. A centrosymmetric projection of this Fourier map along the c-axis, however, clearly yielded the x and y coordinates of Si₅. The z coordinate was readily obtained by searching the three-dimensional map along the line defined by x and y. Subsequent three-dimensional Fourier syntheses revealed

the locations of all of the carbon atoms. Calculations were performed on IBM/360 models 50 and 65 computers using a series of unpublished programs developed at Iowa State University, the Oak Ridge least-squares program⁶, and the block-diagonal least-squares program of the National Research Council of Canada⁷. Scattering factors for neutral silicon and carbon atoms were those of Hanson *et al.*⁸. Only the x and y parameters of Si₁₁ were varied in the least-squares refinement in order to fix the origin of the polar unit cell. The full-matrix isotropic refinement converged to a conventional R, $R = \Sigma ||\underline{F}_o|| - ||\underline{F}_c|| / \Sigma ||\underline{F}_o||$, of 0.116. The function minimized was $\Sigma w (||\underline{F}_o|| - ||\underline{F}_c||)^2$ in which the weight, w, was $1/\sigma^2(\underline{F})$. The anisotropic refinement of 287 positional and temperature factors necessitated use of the block-diagonal approximation. In the final stages of refinement a modified weighting function was used in order to remove the dependence of $\langle w (||\underline{F}_o|| - ||\underline{F}_c||)^2 \rangle$ on \underline{F}_o . The modified weighting function was $w = 1/(\sigma^2(F) + 0.005F^2)$. Convergence was achieved with a conventional R factor of 0.07 and a weighted R factor, $R_w = (\Sigma w (||\underline{F}_o|| - ||\underline{F}_c||)^2 / \Sigma w \underline{F}_o^2)^{1/2}$, of 0.10. The standard deviation of a reflection of unit weight was 1.009. A consideration of the isotropic and anisotropic R factors permits rejection at the 0.005 level of the hypothesis that all atoms vibrate isotropically⁹. A difference map was calculated in an attempt to determine the positions of the hydrogens. How-

ever, due to the large thermal vibrations in the molecule, the hydrogen atoms could not be located. Final positional and thermal parameters along with their estimated standard deviations are listed in Figure 2. The neglect of interatomic correlations in the block-diagonal approximation leads to underestimation of the standard deviations. Experience in this laboratory has shown that the block-diagonal standard deviations and quantities calculated from them should be multiplied by 1.2 for comparison with full-matrix values. Calculated structure factors are compared with the observed values in Figure 3.

Results and Discussion

The molecular structure of TTCH is shown in Figure 4 which was prepared by the computer utilizing Johnson's ORTEP program¹⁰. TTCH absorbs in the ultraviolet with a maximum at 241 μm ¹¹ whereas trisilanes usually absorb at 215 μm ¹². Such a shift toward the visible is common in the spectra of silanes which have phenyl or vinyl substituents and has been explained in terms of $\text{p}\pi$ - $\text{d}\pi$ interactions with the unoccupied 3d orbitals on silicon^{13,14}. Accordingly the carbon-carbon double bond in TTCH was placed vinylic to the trisilane moiety by Gilman *et al.*⁴. The carbon-carbon double bond of the cyclohexene system is unambiguously located between C₁ and C₂ on the basis of interatomic distances. Thus the structure proposed by Gilman *et al.*⁴ is verified.

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Figure 2. Fractional atomic coordinates and anisotropic temperature coefficients ($10^4 \times \sigma$ is given in parentheses. β 's are times 10^4 and have the form $\exp [-(h^2 \cdot \beta_{11} + k^2 \cdot \beta_{22} + l^2 \cdot \beta_{33} + kl \cdot \beta_{23} + hl \cdot \beta_{13} + hk \cdot \beta_{12})]$)

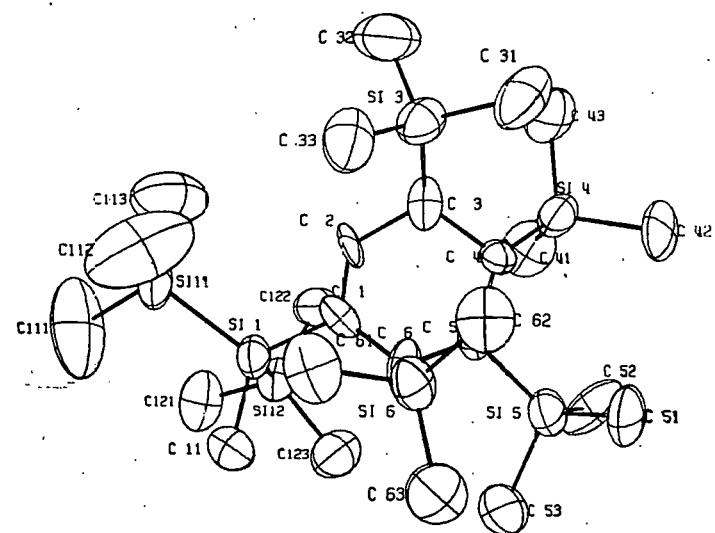
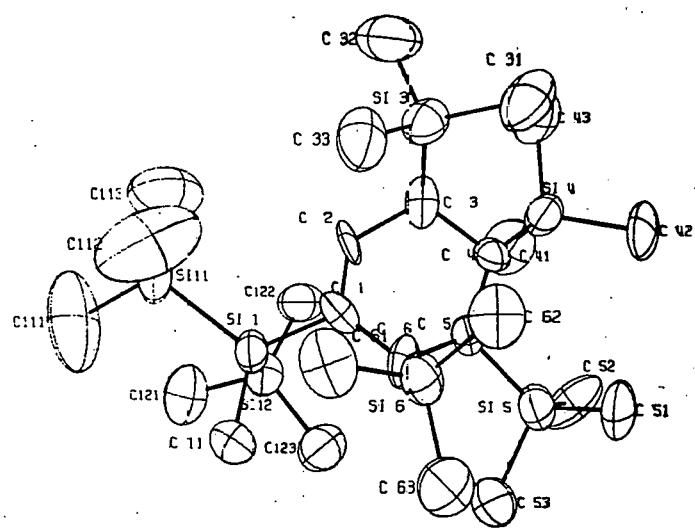
ATOM	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{23}	β_{13}	β_{12}
SI 1	-0.0173(2)	0.4391(6)	0.3002(4)	14(1)	134(7)	60(3)	11(9)	-4(3)	4(4)
SI 11	-0.0854(2)	0.2947(6)	0.3541(-)	16(1)	157(8)	101(4)	-8(12)	9(4)	-14(5)
SI 12	-0.0302(2)	0.6653(5)	0.3455(5)	21(1)	114(7)	66(3)	-2(10)	1(4)	2(5)
SI 3	0.1297(2)	0.1504(6)	0.4857(4)	25(1)	124(7)	66(4)	27(10)	-12(4)	-8(5)
SI 4	0.2050(2)	0.5079(6)	0.5019(4)	19(1)	143(7)	62(3)	-31(10)	-15(4)	-3(5)
SI 5	0.2005(2)	0.6148(6)	0.2787(5)	17(1)	160(8)	74(4)	43(11)	10(1)	-4(5)
SI 6	0.1301(2)	0.2862(6)	0.2092(4)	18(1)	169(8)	58(3)	-32(10)	-1(4)	24(5)
C 1	0.0554(6)	0.3917(16)	0.3328(11)	18(3)	115(21)	37(9)	-39(26)	-18(9)	34(14)
C 2	0.0619(6)	0.3504(16)	0.4112(12)	6(3)	133(24)	59(11)	8(30)	-22(9)	21(14)
C 3	0.1180(6)	0.3369(18)	0.4571(13)	14(3)	147(25)	72(12)	-29(32)	-1(11)	-7(15)
C 4	0.1697(6)	0.4194(16)	0.4142(11)	17(3)	95(22)	50(10)	54(28)	-20(10)	-17(14)
C 5	0.1486(6)	0.5090(16)	0.3394(11)	13(3)	124(21)	43(9)	-11(28)	-6(9)	1(14)
C 6	0.1047(6)	0.4360(17)	0.2817(14)	10(3)	118(22)	81(13)	-18(34)	16(11)	16(14)
C 11	-0.0246(8)	0.4398(25)	0.1813(14)	27(5)	310(44)	56(13)	-62(42)	-16(13)	16(24)
C 31	0.2062(8)	0.1025(19)	0.4837(17)	32(5)	140(26)	116(18)	38(43)	-34(18)	13(19)
C 32	0.0999(11)	0.1218(27)	0.5892(17)	54(8)	236(40)	76(15)	94(45)	27(19)	14(30)
C 33	0.0934(8)	0.0335(20)	0.4144(19)	25(4)	142(29)	128(19)	28(42)	-4(15)	12(19)
C 41	0.1702(10)	0.6748(24)	0.5245(15)	41(6)	232(38)	76(16)	-68(42)	-11(16)	23(26)
C 42	0.2820(7)	0.5208(29)	0.4790(16)	12(3)	400(50)	87(15)	33(50)	-22(13)	-42(22)
C 43	0.1999(9)	0.4151(23)	0.6029(14)	30(5)	233(37)	65(13)	-19(39)	-29(14)	-2(23)
C 51	0.2652(7)	0.5210(24)	0.2431(16)	13(3)	277(39)	106(17)	56(45)	12(13)	14(19)
C 52	0.2235(10)	0.7722(22)	0.3395(17)	48(6)	165(32)	103(17)	29(44)	53(20)	-84(24)
C 53	0.1659(8)	0.6967(26)	0.1788(16)	24(5)	308(45)	87(17)	100(48)	-1(14)	51(25)
C 61	0.0714(9)	0.1635(22)	0.1983(16)	34(5)	193(35)	92(16)	-92(43)	-12(17)	16(22)
C 62	0.1873(9)	0.1820(19)	0.2461(15)	32(5)	130(26)	85(15)	-64(34)	2(14)	10(19)
C 63	0.1477(9)	0.3565(30)	0.1009(15)	29(5)	406(55)	58(14)	-36(49)	30(14)	68(28)
C 111	-0.1553(10)	0.3457(30)	0.3133(33)	27(5)	310(51)	297(48)	175(89)	-31(27)	-84(27)
C 112	-0.0673(17)	0.1144(30)	0.3257(29)	98(15)	224(46)	232(41)	175(75)	158(42)	-202(44)
C 113	-0.0856(13)	0.2938(37)	0.4675(20)	62(10)	459(73)	87(19)	-119(65)	41(25)	-97(45)
C 121	-0.1044(9)	0.7195(25)	0.3359(19)	33(5)	237(39)	117(19)	48(68)	6(19)	37(25)
C 122	-0.0065(9)	0.6859(23)	0.4564(16)	38(6)	217(35)	59(12)	-62(37)	-16(14)	44(24)
C 123	0.0147(9)	0.7800(23)	0.2772(17)	31(5)	206(34)	93(19)	68(43)	19(17)	27(23)

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Figure 3. Observed and calculated structure factors (each group of data contains, going from left to right, h , l , F_o , w , F_c while the data are headed by the value of k . Structure factors are in electrons times 10. A negative F_o indicates a reflection which is considered unobserved)

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Figure 4. Stereoscopic representation of TTCH (anisotropic thermal vibration is indicated by 50% probability ellipsoids)



The bond distances and angles in TTCH are listed in Table 1. Anisotropic thermal vibration is indicated in Figure 4 by the ellipsoids which are drawn to a scale such that the atomic centers are found within them 50% of the time. Root-mean-square amplitudes of thermal vibration along the principal axes 1-3 of the ellipsoids are presented in Table 2. There are 23 crystallographically independent Si-C(sp³) bonds in TTCH all of which should be chemically equivalent. However, a rather large scatter is observed in these Si-C bond lengths (1.81 - 1.97 Å). Such a range is not uncommon in organosilicon compounds^{3,15} and, in the case of the methyl-carbon to silicon distances, can be attributed to the large amplitudes of thermal motion and methyl-methyl group steric interactions. The ring-carbon atoms to silicon atom distances are in much better agreement (1.86 - 1.91 Å) with exception of the Si₆-C₆ distance of 1.97(2) Å which is apparently lengthened due to steric interactions with the adjacent trisilane moiety. In addition, the inability to silyate the last ring-carbon atom can be attributed to this effect in agreement with mechanisms proposed by Harrell¹¹ and Weyenberg and Toporger.¹⁶ The mean Si-Si distance is 2.35 ± 0.01 Å which is in agreement with the value of 2.3517 ± 0.0001 Å in metallic silicon.¹⁷ With respect to the approximate plane of the ring, the four trimethylsilyl groups are bonded β , α , β , β , to ring carbons C₃, C₄, C₅,

Table 1. Distances (\AA) and angles (deg) with standard deviations in parentheses

Bond	Value	Angle	Value	Angle	Value
Non-methyl bond distances and angles					
Si ₁ -Si ₁₁	2.335(7)	Si ₁₁ -Si ₁ -Si ₁₂	111.6(0.2)	Si ₄ -C ₄ -C ₃	105.4(0.9)
Si ₁ -Si ₁₂	2.361(8)	Si ₁₁ -Si ₁ -C ₁	115.6(0.5)	Si ₄ -C ₄ -C ₅	117.3(0.9)
Si ₁ -C ₁	1.884(17)	Si ₁₂ -Si ₁ -C ₁	105.7(0.5)	C ₃ -C ₄ -C ₅	110.6(1.2)
Si ₃ -C ₃	1.912(19)	Si ₁ -C ₁ -C ₂	116.5(1.0)	Si ₅ -C ₅ -C ₄	119.1(0.9)
Si ₄ -C ₄	1.856(17)	Si ₁ -C ₁ -C ₆	120.7(1.0)	Si ₅ -C ₅ -C ₆	113.2(0.9)
Si ₅ -C ₅	1.893(17)	C ₆ -C ₁ -C ₂	120.4(1.3)	C ₅ -C ₅ -C ₆	113.9(1.6)
Si ₆ -C ₆	1.971(18)	C ₁ -C ₂ -C ₃	125.4(1.3)	Si ₆ -C ₆ -C ₅	118.4(0.9)
C ₁ -C ₂	1.325(22)	Si ₃ -C ₃ -C ₄	117.7(1.0)	Si ₆ -C ₆ -C ₁	110.3(0.9)
C ₂ -C ₃	1.544(24)	Si ₃ -C ₃ -C ₂	107.3(1.0)	C ₅ -C ₆ -C ₁	110.1(1.2)
C ₃ -C ₄	1.635(24)	C ₂ -C ₃ -C ₄	115.1(1.2)		
C ₄ -C ₅	1.569(23)				
C ₅ -C ₆	1.577(23)				
C ₆ -C ₁	1.504(24)				

Table 1. (Continued)

Bond	Value	Bond	Value	Bond	Value
Bond distances involving methyl groups					
Si ₁ -C ₁₁	1.908(23)	Si ₄ -C ₄₃	1.857(23)	Si ₆ -C ₆₃	1.911(25)
Si ₃ -C ₃₁	1.903(23)	Si ₅ -C ₅₁	1.899(23)	Si ₁₁ -C ₁₁₁	1.873(35)
Si ₃ -C ₃₂	1.824(27)	Si ₅ -C ₅₂	1.878(25)	Si ₁₁ -C ₁₁₂	1.882(39)
Si ₃ -C ₃₃	1.840(24)	Si ₅ -C ₅₃	1.971(24)	Si ₁₁ -C ₁₁₃	1.811(33)
Si ₄ -C ₄₁	1.878(25)	Si ₆ -C ₆₁	1.889(24)	Si ₁₂ -C ₁₂₁	1.873(27)
Si ₄ -C ₄₂	1.895(24)	Si ₆ -C ₆₂	1.814(24)	Si ₁₂ -C ₁₂₂	1.871(23)
				Si ₁₂ -C ₁₂₃	1.906(23)

Table 1. (Continued)

Angle	Value	Angle	Value	Angle	Value
Bond angles involving methyl groups					
C ₁₁ -Si ₁ -C ₁	112.0(0.9)	C ₄₁ -Si ₄ -C ₄₃	103.6(1.0)	C ₆₂ -Si ₆ -C ₆₃	109.3(1.0)
C ₁₁ -Si ₁ -Si ₁₁	107.7(0.7)	C ₄₂ -Si ₄ -C ₄₃	105.4(1.0)	Si ₁ -Si ₁₂ -C ₁₂₁	111.7(0.8)
C ₁₁ -Si ₁ -S ₁₂	106.8(0.7)	C ₅ -Si ₅ -C ₅₁	115.3(0.9)	Si ₁ -Si ₁₂ -C ₁₂₂	110.6(0.7)
C ₃ -Si ₃ -C ₃₁	112.1(0.9)	C ₅ -Si ₅ -C ₅₂	113.6(0.9)	Si ₁ -Si ₁₂ -C ₁₂₃	107.9(0.7)
C ₃ -Si ₃ -C ₃₂	107.9(1.0)	C ₅ -Si ₅ -C ₅₃	111.2(0.9)	C ₁₂₁ -Si ₁₂ -C ₁₂₂	109.7(1.1)
C ₃ -Si ₃ -C ₃₃	112.4(0.9)	C ₅₁ -Si ₅ -C ₅₂	107.7(1.0)	C ₁₂₂ -Si ₁₂ -C ₁₂₃	107.8(1.0)
C ₃₁ -Si ₃ -C ₃₂	111.0(1.1)	C ₅₁ -Si ₅ -C ₅₃	107.6(1.0)	C ₁₂₁ -Si ₁₂ -C ₁₂₃	109.0(1.1)
C ₃₁ -Si ₃ -C ₃₃	107.2(1.0)	C ₅₂ -Si ₅ -C ₅₃	100.3(1.0)	Si ₁ -Si ₁₁ -C ₁₁₁	109.9(1.1)
C ₃₂ -Si ₃ -C ₃₃	106.1(1.0)	C ₆ -Si ₆ -C ₆₁	110.4(0.9)	Si ₁ -Si ₁₁ -C ₁₁₂	108.8(1.2)
C ₄ -Si ₄ -C ₄₁	110.6(0.9)	C ₆ -Si ₆ -C ₆₂	117.9(0.9)	Si ₁ -Si ₁₁ -C ₁₁₃	111.9(1.0)
C ₄ -Si ₄ -C ₄₂	109.5(0.9)	C ₆ -Si ₆ -C ₆₃	109.3(0.9)	C ₁₁₁ -Si ₁₁ -C ₁₁₂	112.1(1.6)
C ₄ -Si ₄ -C ₄₃	113.3(0.9)	C ₆₁ -Si ₆ -C ₆₂	105.3(1.0)	C ₁₁₁ -Si ₁₁ -C ₁₁₃	110.3(1.5)
C ₄₁ -Si ₄ -C ₄₂	114.5(1.1)	C ₆₁ -Si ₆ -C ₆₃	103.7(1.0)	C ₁₁₂ -Si ₁₁ -C ₁₁₃	103.7(1.6)

Table 2. Root-mean-square amplitude of vibration (angstroms $\times 10^3$)

Atom	Min.	Med.	Max.	Atom	Min.	Med.	Max.
Si ₁	200	252	282	C ₃₃	250	280	406
Si ₁₁	207	280	362	C ₄₁	277	330	382
Si ₁₂	235	250	291	C ₄₂	160	335	450
Si ₃	238	255	310	C ₄₃	237	331	344
Si ₄	216	259	302	C ₅₁	191	337	399
Si ₅	216	265	327	C ₅₂	200	340	445
Si ₆	218	262	310	C ₅₃	238	310	426
C ₁	178	190	297	C ₆₁	260	311	386
C ₂	94	261	289	C ₆₂	227	308	348
C ₃	200	259	312	C ₆₃	204	324	461
C ₄	178	198	301	C ₁₁₁	229	390	637
C ₅	188	231	252	C ₁₁₂	218	393	703
C ₆	155	246	328	C ₁₁₃	300	377	535
C ₁₁	240	292	401	C ₁₂₁	285	347	402
C ₃₁	241	293	407	C ₁₂₂	248	293	383
C ₃₂	256	359	421	C ₁₂₃	281	288	386

and C_6 , respectively. The torsion angles about the three $C(sp^3)-C(sp^3)$ bonds within the cyclohexene ring are listed in Table 3. Methyl groups on adjacent silyl groups are meshed as follows: C_{11} is between C_{61} and C_{63} ; C_{51} , between C_{62} and C_{63} ; C_{52} , between C_{41} and C_{42} ; and C_{43} , between C_{31} and C_{32} . In this way intramolecular nonbonded repulsions are minimized. TTCH is obviously a racemate as is required by the presence of improper symmetry elements in the space group. The molecular packing is apparently governed entirely by steric factors because there exists no possibility for hydrogen bonding. The shortest intermolecular distances were 3.86 \AA between C_{11} and C_{122} (molecule at $\bar{x}, \bar{y}, 1/2 + z$) and 3.88 \AA between C_{53} and C_{113} (molecule at $\bar{x}, \bar{y}, 1/2 + z$).

Table 3. Torsion angles

Bond	Torsion angle (degrees)
$C_3 - C_4$	84.8
$C_4 - C_5$	59.3
$C_5 - C_6$	69.5

STRUCTURE OF *cis*-
DICHLOROBIS(DIMETHYLPHENYLPHOSPHINE)PALLADIUM(II)

Introduction

It has been observed that square planar complexes of the type PdX_2Y_2 , where X is a halide, very often adopt the trans configuration.¹⁸ In fact, only recently have any cis complexes of this type been characterized. The cis, chloro complexes usually form pale yellow or colorless crystals while crystals of the trans complexes are more decidedly yellow.¹⁹ However, a recent far-infrared study²⁰ by R. Keiter of $PdCl_2(P(CH_3)_2C_6H_5)_2$ which forms distinctly yellow crystals, indicated that this compound unlike $PdI_2(P(CH_3)_2C_6H_5)_2$ ²¹ was probably not trans but no configuration could be assigned from the spectra. Therefore we undertook a crystal structure investigation to determine if the complex is square-planar and, if so, which isomer is present.

Experimental

A sample of this compound was kindly supplied by R. Keiter and the yellow crystals were used without further purification. Inspection of the crystals showed them to be square plates with sharply-defined faces. Weissenberg and precession photographs indicated a tetragonal space group with systematic extinctions of the type $00\bar{l}, \bar{l} = 2n + 1$; $h\bar{k}0, \underline{h} + \underline{k} = 2\underline{n} + 1$. These conditions indicate the space

group to be $P4_2/n$. In addition, systematically weak reflections of the type $h + k = 2n + 1$ and $l = 2n + 1$ for general hkl reflections were observed.

The unit cell dimensions were determined by least-squares fit of 13 independent reflections whose 2θ values were determined from Weissenberg photographs calibrated with Al powder lines. The values obtained were $a = b = 9.324 \pm 0.004 \text{ \AA}$ and $c = 21.485 \pm 0.004 \text{ \AA}^{\circ}$. The measured density was 1.61 g/cc obtained by flotation techniques in a solution of diiodomethane and 1-bromopropane. The calculated density with four molecules per unit cell ($V_c = 1868 \text{ \AA}^3$) is 1.62 g/cc.

A crystal of approximate dimensions $0.2 \times 0.2 \times 0.1 \text{ mm}$ was selected for use in data collection. The crystal was mounted such that the (110) axis would be coincident with the phi axis of the diffractometer. Data were collected at room temperature using a Hilger-Watts four circle diffractometer equipped with a scintillation counter employing Zr-filtered Mo-K α ($\lambda = 0.7107 \text{ \AA}^{\circ}$) radiation. All data within a 2θ sphere of 60 deg ($\sin\theta/\lambda = 0.70$) were measured using a $\theta-2\theta$ coupled scan with a five deg take-off angle. Stationary-counter measurements of the background were made at the beginning and the end of each scan. The scan range was over 50 steps of 0.01 deg, one step per 0.4096 sec, and was increased by 1 step per deg increase in 2θ to insure complete integration over the entire peak. The length of the back-

ground measurement was adjusted accordingly. No appreciable decrease in the intensities of three standard reflections which were measured periodically throughout the data taking period was observed.

The measured intensities were corrected for background, Lorentz and polarization effects, and for adsorption⁷ ($\mu = 14.2 \text{ cm}^{-1}$); minimum and maximum transmission factors were 0.67 and 0.87, respectively. The standard deviations were assigned to the intensities according to the following formula:

$$\sigma(I) = (c_t + c_b + (0.05 c_t)^2 + (0.10 c_b)^2 + (0.05 c_n)^2)^{1/2}$$

where c_t , c_b , c_n and A are the total counts, background counts, net counts, and the absorption factor. The quadratic terms correspond to the estimated systematic errors in the intensity, background and absorption correction of 5, 10 and 5% respectively. The standard deviations in the structural amplitudes were obtained by the method of finite differences⁵,

$$\sigma(F_O) = ((I + \sigma(I))^{1/2} - I^{1/2})/(Lp)^{1/2}$$

where Lp is the Lorentz-polarization factor. Of the 2877 measured reflections, 850 were found to have values of F_O less than $2.0 \times \sigma(F_O)$. These reflections were considered

to be unobserved and were not included in the refinement.

Solution and Refinement of the Structure

Since the space group $P4_2/n$ has eightfold general positions, it was necessary to place the palladium atoms in special positions. From a consideration of the systematically weak reflections of the type $\underline{l} = 2n + 1$, the palladiums were placed in the fourfold special position denoted by the Wycoff symbol 'e'; that is on the twofold axis perpendicular to the ab plane. Analysis of the Patterson map confirmed this supposition and allowed ready determination of the z-coordinate of the palladium. Three possible sets of chlorine and phosphorus positions were present due to pseudo mirroring. The correct set was determined by trial and error. These atoms gave a value of the discrepancy factor, $R = \sum |F_o| - |F_c| | / \sum |F_o|$, of 28% for a structure factor calculation with the heavy atoms alone. The remaining carbon atoms were located from a three-dimensional electron density map. The structure was refined isotropically to an $R = 15.4\%$ using a modified version of ORFLS^{6,8,22} and unit weights. At this point weights were changed to those based on individual statistics of the reflection ($w = 1/\sigma(F_o)^2$). The ring hydrogen atoms were added in calculated positions assuming 1.0 \AA^0 for the C-H distance. No attempt was made to refine hydrogen positions. A final statistical analysis of the F_o and F_c values indicated a dependence on the scattering angle. The

relative weights were adjusted to remove this dependence. An additional 134 reflections were removed from the refinement because they failed to fulfill one of the following criteria:

$$||\underline{F}_o|| - ||\underline{F}_c|| < 10 \times \sigma(\underline{F}_o) , \quad \left| \frac{\underline{F}_o}{\underline{F}_c} \right| < 5.0 \text{ or } \left| \frac{\underline{F}_c}{\underline{F}_o} \right| < 5.0.$$

The structure was refined anisotropically to a final $R = 8.8\%$ and a final weighted discrepancy index, $R = (\sum w(\underline{F}_o - \underline{F}_c)^2)^{1/2}/(\sum w\underline{F}_o^2)^{1/2}$, of 7.9%. Convergence was assumed when no parameter shift was greater than 0.1 of that parameter's estimated-standard deviation. A final difference electron density map showed no residual electron density above $1.4 \text{ e}^-/\text{\AA}^3$.

In Figure 5 are the final values of the positional and thermal parameters and their respective estimated standard deviations.²³ Estimated standard deviations were derived from the inverse matrix. In Table 4 are given the root-mean-square amplitudes of vibration while in Figure 6 are listed the values of the observed and calculated structure factors on an absolute scale. The configuration of the molecule along with the numbering scheme used is shown in Figure 7.¹¹ Selected intramolecular distances and angles are given in Table 5 (see also Figure 8).

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Figure 5. Fractional atomic coordinates and thermal parameters (estimated standard deviation are given in parentheses right adjusted to the least significant figure of the preceding number. β 's are times 10^4 and have the form $\exp[-(\beta_{11}\underline{h}^2 + \beta_{22}\underline{k}^2 + \beta_{33}\underline{l}^2 + \beta_{12}\underline{hk} + \beta_{13}\underline{hl} + \beta_{23}\underline{kl})]$.)

ATOM	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
PD	0.75000	0.25000	0.25309(3)	69(1)	79(1)	12(0)	-1(1)	0	0
P	0.8863(2)	0.3716(2)	0.3222(1)	66(2)	74(2)	16(0)	-12(2)	2(1)	-2(1)
CL	0.8977(2)	0.3462(2)	0.1742(1)	151(3)	145(3)	17(0)	-26(2)	17(1)	2(1)
C 1	0.8162(7)	0.4163(7)	0.3973(3)	79(8)	79(8)	17(2)	-21(7)	0(3)	-5(3)
C 2	0.702(1)	0.511(1)	0.4011(4)	122(12)	164(14)	25(2)	6(10)	3(4)	-10(5)
C 3	0.650(1)	0.556(1)	0.4583(6)	159(15)	186(16)	35(3)	27(12)	22(6)	-21(6)
C 4	0.712(1)	0.513(1)	0.5114(5)	185(18)	287(23)	20(2)	-67(17)	19(6)	-38(6)
C 5	0.823(1)	0.417(1)	0.5103(4)	212(18)	239(20)	15(2)	-87(16)	-13(5)	11(5)
C 6	0.8759(9)	0.3678(9)	0.4527(4)	113(11)	165(13)	18(2)	-43(10)	-11(4)	6(4)
C 7	0.933(1)	0.5498(9)	0.2942(4)	187(15)	107(11)	22(2)	-75(10)	4(5)	7(4)
C 8	0.4411(8)	0.2143(9)	0.3340(4)	74(9)	170(14)	37(3)	35(9)	17(4)	16(5)
H 2	0.655	0.544	0.360	5.0					
H 3	0.570	0.631	0.463	5.0					
H 4	0.668	0.550	0.552	5.0					
H 5	0.872	0.382	0.550	5.0					
H 6	0.964	0.301	0.453	5.0					

Table 4. Root-mean-square amplitude of vibration ($\text{\AA} \times 10^3$)

Atom	Min.	Intermed.	Max.
Pd	169	174	187
P	158	185	199
Cl	175	245	284
C ₁	157	196	215
C ₂	224	240	279
C ₃	202	296	324
C ₄	176	259	397
C ₅	179	246	376
C ₆	180	215	294
C ₇	158	234	320
C ₈	160	251	325

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Figure 6. Observed and calculated structure amplitudes
(in electrons x 10) for $\text{PdCl}_2(\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5)_2$

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Figure 7. A perspective drawing of cis-dichlorobis(dimethylphenylphosphine) palladium(III). Anisotropic thermal vibration is indicated by 50% probability ellipsoids

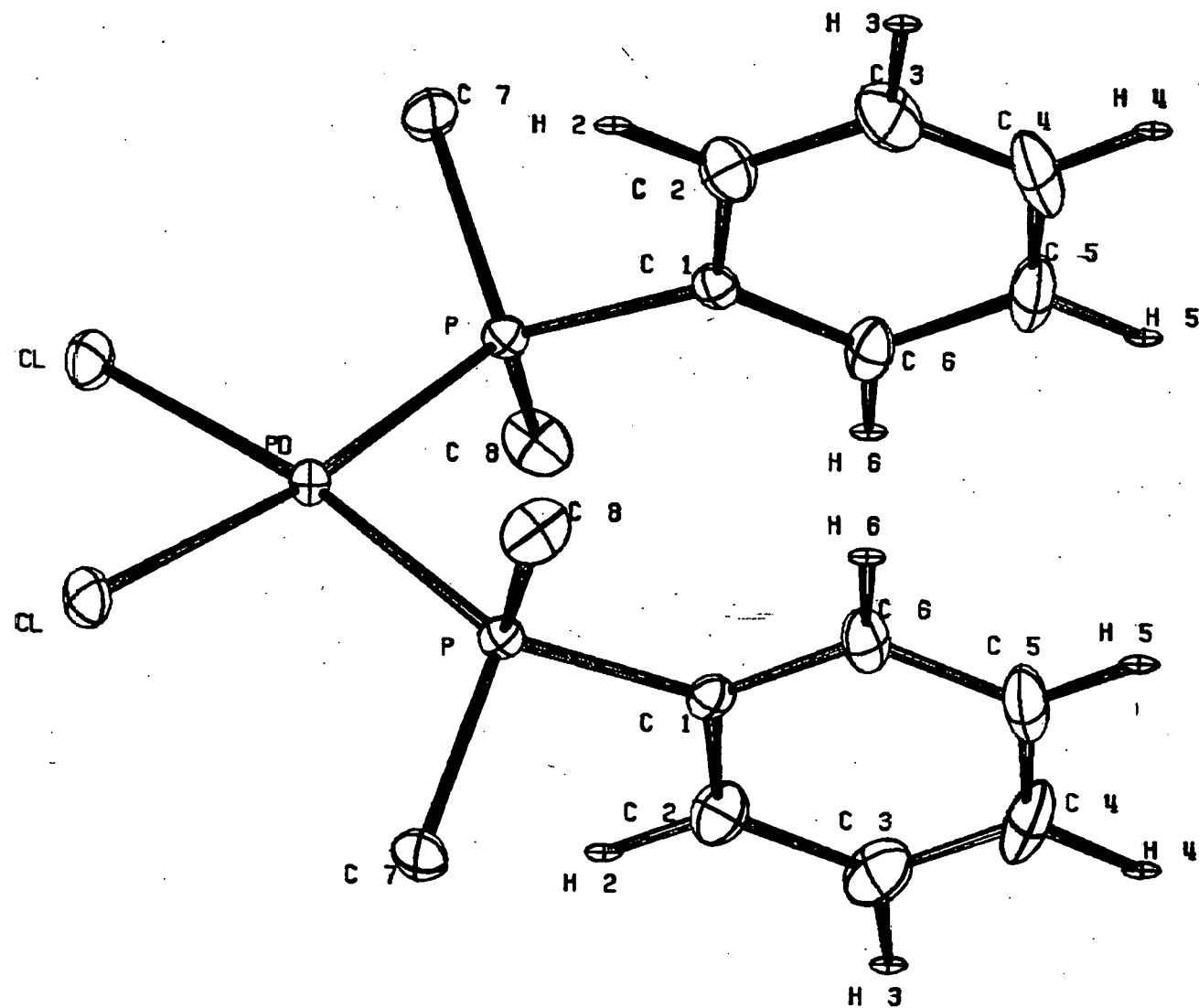
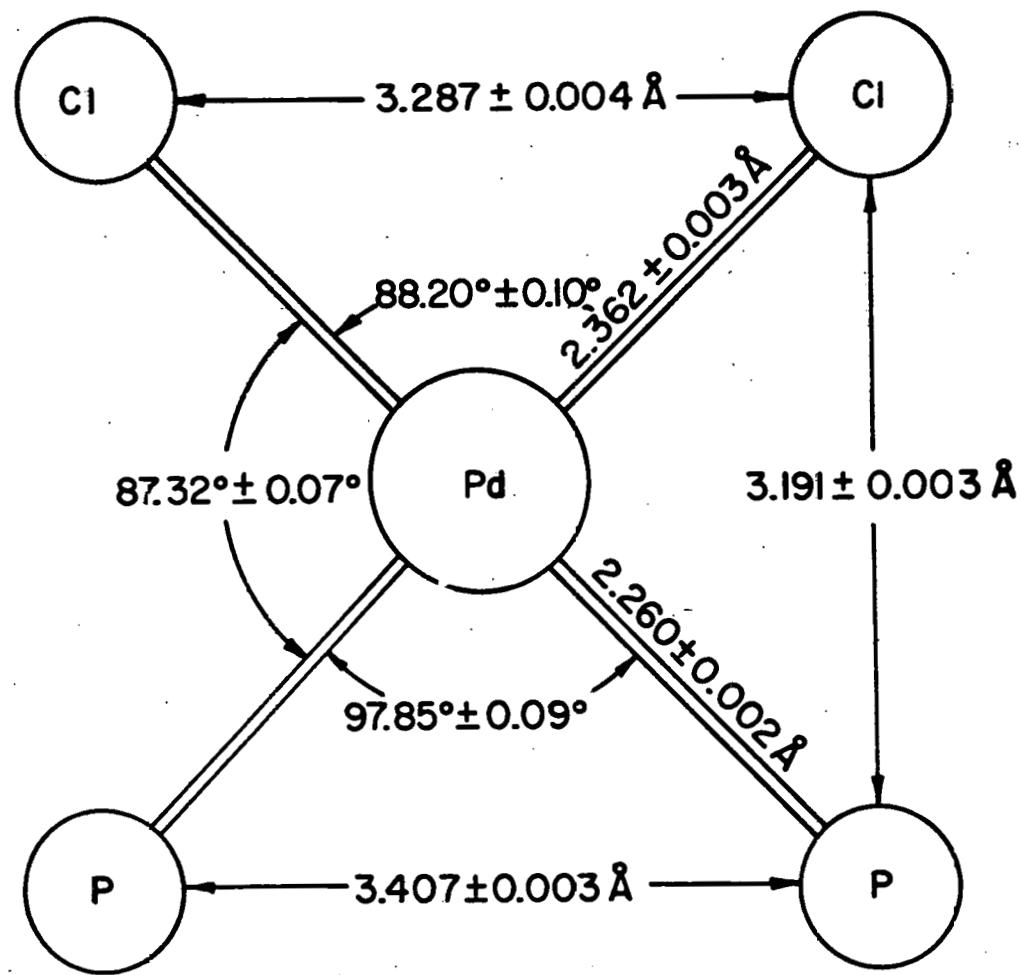


Table 5. Selected distances (\AA) and angles (deg) with standard deviations in parentheses

Bond	Value	Angle	Value	Angle	Value
P-Cl	3.191(3)	Cl-Pd-Cl'	88.2(1)	P-C ₁ -C ₂	118.8(6)
P-P'	3.407(3)	Cl-Pd-P	87.32(7)	P-C ₁ -C ₆	123.4(5)
Cl-Cl'	3.287(4)	P-Pd-P'	97.85(9)	P-C ₁ -C ₄	174.6(5)
P-C ₁	1.791(7)	Pd-P-C ₁	120.2(2)	C ₆ -C ₁ -C ₂	117.7(7)
P-C ₇	1.819(7)	Pd-P-C ₇	112.0(3)	C ₁ -C ₂ -C ₃	121.0(8)
P-C ₈	1.815(8)	Pd-P-C ₈	111.7(3)	C ₂ -C ₃ -C ₄	120.6(9)
C ₁ -C ₂	1.38(1)	C ₁ -P-C ₇	100.0(3)	C ₃ -C ₄ -C ₅	120.6(9)
C ₂ -C ₃	1.39(1)	C ₁ -P-C ₈	107.4(4)	C ₄ -C ₅ -C ₆	119.4(8)
C ₃ -C ₄	1.34(2)	C ₇ -P-C ₈	103.8(6)	C ₅ -C ₆ -C ₁	120.6(8)
C ₄ -C ₅	1.37(2)				
C ₅ -C ₆	1.41(2)				
C ₆ -C ₁	1.39(1)				

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Figure 8. The arrangement of palladium and its four neighbors along with
coherent distances and angles



Description of the Structure

The complex is best described as approximately cis, square-planar. However there are slight, but significant distortions since the $\angle \text{Cl-Pd-Cl}'$ ("'" denotes atom at \bar{x} , \bar{y} , \bar{z}) has closed two deg and the $\angle \text{P-Pd-P}'$ has opened some eight deg from their theoretical value of 90 deg. The Cl's are $+0.13^\circ \text{ \AA}$ and -0.13° \AA from the least-squares plane defined by the palladium and its four nearest neighbors while the P's are $\pm 0.12^\circ \text{ \AA}$ from the plane. This is best viewed as a tetragonal distortion of 4.3 deg. The dihedral angle between the planes defined by the two phosphorus atoms and the palladium, and the two chlorine atoms and the palladium is 171.3 ± 0.1 deg. The equations of the two planes in the form $ax + by + cz - d = 0$ are ($a = -0.66$, $b = 0.746$, $c = 0.00$, $d = -2.92$) and ($a = -0.546$, $b = 0.838$, $c = 0.00$, $d = -1.86$), respectively.

The six carbon atoms in the phenyl ring showed no significant deviations from the best least-squares plane ($a = 0.642$, $b = 0.766$, $c = -0.025$, $d = 7.64$). The largest deviation from the plane was 0.02° \AA by C_4 which is not statistically significant. The angles within the ring are all within three e.s.d.'s of the normal value of 120 deg. The ring bond distances also agree well with the expected value²⁴ of 1.41° \AA with the exception of the C_3-C_4 distance which is slightly short.

Discussion

The apparent deviations in this complex from the ideal square-planar configuration can be primarily attributed to overcrowding caused by the bulky phosphorus ligands cis to each other. The phenyl rings of the different phosphorus ligands on the same palladium interact sterically with one another. This accounts for the fact that the P-Pd-P' angle is 98 deg and the Pd-P-C₁ angle is found to be 120 deg since in this way steric interactions can be reduced. However, the two rings still approach each other within 3.2 Å, (C₆-C'₆); somewhat less than the sum of the van der Waals radii.²⁴ This interaction could also easily explain the slight screwing of the phenyl rings as indicated by the \angle P-C₁-C₄ of 174.6 deg. In order to accommodate the bulky phosphorus ligands, the chlorine atoms are forced closer together as shown by the \angle Cl-Pd-Cl' of 88.2 deg. The Cl-Cl' distance of 3.287 Å is still greater than the distance of 2.88 Å which is the sum of the van der Waals radii of two chlorine atoms bonded to a common atom.²⁵ The slight tetragonal distortion may also be attributed to this overcrowding.

The agreement between the three nonequivalent P-C distances is good. The two phosphorus-methyl distances (1.819, 1.815 Å) are similar while the phosphorus-ring distance (1.791 Å) is just slightly shorter as would be expected from the slightly smaller covalent radii for the

ring carbon. The C-C distances are within 3σ of their normal values and the Pd-Pd distance of 6.6°\AA is so great that any interaction is precluded despite an apparent alignment of the atoms.

The Pd-P bond in this compound ($2.260 \pm 0.003^{\circ}\text{\AA}$) is significantly shorter than that found by Bailey and Mason²¹ of $2.333 \pm 0.007^{\circ}\text{\AA}$ in the trans-iodo complex, while the Cl-Pd bond ($2.362 \pm 0.003^{\circ}\text{\AA}$) is significantly longer than that found by Bennett, Cotton and Weaver²⁶ of $2.290 \pm 0.002^{\circ}\text{\AA}$ in $\text{PdCl}_2(\text{DMSO})_2$. The predicted values from the sum of the covalent radii are 2.38°\AA and 2.28°\AA for the Pd-P and Pd-Cl distances, respectively. Our results generally agree with those expected from a strong "trans-effect".²⁷ That is, the bond trans to a strongly "trans-direction" ligand such as phosphorus is weaker and therefore longer than a bond trans to the somewhat less "trans-directing" chlorine. As has already been noted by Messmer, Amma and Ibers,²⁸ these distances may be sensitive to the substituents on the phosphorus as well as variations in the halide used. However, it would be expected that as long as the ligands are similar with respect to their "trans-directing" ability, the effect on either the M-Cl or M-P distance would be the same whether M is Pd or Pt. In Table 6 are listed a number of M-Cl and M-P bond lengths involving ligands of similar "trans-directing" ability.²⁹ As would be expected from the different covalent radii and electro-negativities of palladium and platinum,

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Table 6. Selected metal-phosphorus and metal chloride bond lengths

Pd <u>trans</u>			
Bond	Distance (Å)	Compound	Ref.
Pd-P	2.333 \pm 0.007	PdI ₂ (P(CH ₃) ₂ C ₆ H ₅) ₂	21
Pd-Cl	2.287 \pm 0.002	PdCl ₂ (DMSO) ₂	26
Pd <u>cis</u>			
Bond	Distance (Å)	Compound	Ref.
Pd-P	2.260 \pm 0.003	PdCl ₂ (P(CH ₃) ₂ C ₆ H ₅) ₂	this work
Pd-Cl	2.362 \pm 0.003	"	"
Δ <u>trans</u> to <u>cis</u> Pd			
Bond	Δ (Å)		
Pd-P	- 0.073		
Pd-Cl	+ 0.075		

Pt trans

Bond	Distance (Å)	Compound	Ref.
Pt-P	2.315 \pm 0.004	Pt P(C ₂ H ₅) ₃ 2 ^{Br}	28
Pt-Cl	2.294 \pm 0.009	Pt P(C ₂ H ₅) ₃ 2 ^{Cl} ₂	28

Pt cis

Bond	Distance (Å)	Compound	Ref.
Pt-P	2.247 \pm 0.008	PtCl ₂ (P(CH ₂) ₃) ₂	29
Pt-Cl	2.376 \pm 0.009	"	

 Δ trans to cis Pt

Bond	Δ (Å)
Pt-P	- 0.068
Pt-Cl	+ 0.082

the M-Cl and M-P distances are somewhat different. However, the changes in the bond distances are identical within l e.s.d. in going from the trans to the cis configuration.

STRUCTURE OF

NITRILOTRIACETODIAQUOPRASEODYMIUM(III) -MONOHYDRATE

Introduction

The complexes formed by the reaction of the trivalent lanthanons with nitrilotriacetate (NTA) in aqueous solution have been studied for some time.³⁰ The crystalline complexes formed by precipitation from saturated solution have been found to form one of several hydrates depending upon the temperature at which recrystallization is carried out and the rare earth used. Our preliminary study of the series of complexes formed at 25° C indicates that the series is divided into three crystallographically distinct groups: (1) the La-Ce group, (2) the Pr-Tb (Pm?) group and (3) the Dy-Lu group. Crystals of the first group are so poorly formed that they could not be characterized. Crystals of the second group belong to the space group Pbca with $a = 13.21 \pm 0.01$, $b = 29.98 \pm 0.01$ and $c = 8.132 \pm 0.006 \text{ \AA}$. Those of the third group are in space group Pca₂₁ with $a = 21.535 \pm 0.013 \text{ \AA}$, $b = 9.02 \pm 0.004 \text{ \AA}$, $c = 12.186 \pm 0.007 \text{ \AA}$.

This division into groups also coincides with observed changes in hydration number across the series from 5 to 3 to 4.³¹ The break between groups at Tb occurs near a sudden change in thermodynamic properties of these as well as other lanthanon (III) complexes.³² Coordination numbers ranging from 6 to 12 have been observed in various com-

plexes.³³⁻³⁶ The smaller coordination numbers are usually associated with the heavier rare earths while coordination numbers of 9 or greater are not uncommon for the light rare earths. We therefore undertook a three-dimensional X-ray structural study of $\text{Pr}(\text{NTA}) \cdot 3\text{H}_2\text{O}$ in order to determine its coordination. In the next chapter the structure of $\text{Dy}(\text{NTA}) \cdot 4\text{H}_2\text{O}$ is described.

Experimental

Well formed, rectangular prismatic crystals of the $\text{Pr} \cdot \text{NTA} \cdot 3\text{H}_2\text{O}$ complex M.W. = 383.1 g), were kindly supplied by J. E. Powell of this Laboratory. Preliminary Weissenberg and precession photographs indicated orthorhombic symmetry. Systematic absences were observed for $0kl$, k odd; $h0l$, l odd; $hk0$, h odd and are consistent with space group Pbca (D_{2h}^{15}). Accurate unit cell parameters were obtained from a least-squares fit of 16 independent reflections whose 2θ values were obtained from Weissenberg photographs calibrated with Al powder using $\text{CuK}\alpha$ radiation ($\lambda = 1.54051 \text{ \AA}^{\circ}$). The unit cell parameters and their standard deviations calculated from the inverse matrix are $a = 13.21 \pm 0.01$, $b = 20.98 \pm 0.01$, $c = 8.132 \pm 0.006 \text{ \AA}^{\circ}$ and $V = 2254 \text{ \AA}^3$. The density determined by flotation techniques in a diiodomethane-1-bromopropane mixture is 2.24 g/cc, while the calculated density with $Z = 8$ is 2.26 g/cc.

A crystal having approximate dimensions $0.07 \times 0.05 \times$

0.26 mm was mounted so that its long axis (100) was coincident with the phi axis of the diffractometer. A General Electric, XRD-6, X-ray diffractometer equipped with single crystal orienter and scintillation counter was used with Zr-filtered, MoK α radiation ($\lambda = 0.717 \text{ \AA}$) in the moving-crystal-moving-counter mode ($\theta/2\theta$ coupled) to measure the intensities. A 40 sec scan covering 1.36° in 2θ was employed with a take-off angle of 2° . Since the background was seen to be a function of θ only, individual reflections were obtained from a plot of 2θ vs. background. One crystallographic independent octant of data was collected within a 2θ sphere of 45° ($\sin\theta/\lambda = 0.538$). No appreciable decrease in the intensities of three independent reflections which were remeasured periodically throughout the data taking period was observed.

The measured intensities were also corrected for Lorentz and polarization effects and for absorption⁷ with minimum and maximum transmission factors of 0.74 and 0.76 ($\mu = 43.2 \text{ cm}^{-1}$). The standard deviations were assigned to the intensities according to the formula:

$$\sigma(I) = (C_t + C_b + (0.05 \times C_t)^2 + (0.10 \times C_b)^2 + (0.05 \times C_n)^2)^{1/2} \times A$$

where C_t , C_b , C_n and A are the total count, background count, net count and absorption factor, respectively. The quadratic

terms correspond to estimated systematic errors of 5, 10, and 5% in the total count, background count, and net count, respectively. The standard deviations of the structure amplitudes ($\sigma(\underline{F})$) were obtained by the method of finite differences.⁵ Of the 1494 measured reflections, 368 had a value of $\underline{F}_o < 2 \sigma(\underline{F})$. They were considered to be unobserved and were not included in the refinement.

Solution of the Structure

The structure was solved by normal heavy atom techniques. The heavy atom was readily located in the Patterson map and the light atoms were found in a series of structure factor-electron density map calculations. Scattering factors used were those of Cromer and Waber³⁷ for the praseodymium(III) atom corrected for anomalous scattering²² and those of Hanson et al.⁸ for the light atoms. All atoms were refined⁶ isotropically to a value of the discrepancy indicator ($R = \Sigma \Delta / \Sigma |\underline{F}_o|$ where $\Delta = ||\underline{F}_o| - |\underline{F}_c||$) of 0.13. At this point weights were introduced based on the individual statistics of the reflections ($w = 1/\sigma^2(\underline{F})$). These weights were later adjusted slightly to remove a dependence of $w \Delta^2$ on $|\underline{F}_o|$. In addition, 15 reflections with values of $\Delta > 6.0 \times \sigma(\underline{F})$ were excluded from the refinement. The large isotropic temperature factor of 0_{w3} suggested occupational disorder. However, refinement of the occupational parameter yielded a value near unity. An attempt was then made to refine all

atoms anisotropically but was aborted when no physically meaningful results were obtained. With only the Pr^{3+} anisotropic final values of \underline{R} and the weighted discrepancy index, \underline{R}_w ($\underline{R}_w = (\sum_w \Delta^2 / \sum_w F_0^2)^{1/2}$), of 0.085 and 0.080 were obtained. The final difference electron density map contained no residual density greater than $0.8 \text{ e}^-/\text{\AA}^2$ and confirmed that all nonhydrogen atoms had been located. In Table 7 are listed the final atomic positional parameters and temperature factor coefficients along with their estimated standard deviation (esd) as derived from the inverse matrix.²³ For praseodymium, the maximum, intermediate and minimum root-mean-square amplitudes of vibration are 0.145, 0.144 and 0.135. The magnitudes of the observed and calculated structure factors are shown in Figure 9.

Results and Discussion

The configuration of the NTA ligand around the Pr^{3+} is shown in Figure 10.¹¹ There are six carboxylic oxygens (O_c), two waters (O_w) and one nitrogen coordinated to the metal atom. Relevant distances and angles are given in Table 8. There are no discrete molecular units in the complex. One bridge is formed by O_{21} by which two different adjacent metal atoms are coordinated. In addition, O_{22} and O_{31} coordinate to metal atoms other than the one to which the remainder of the NTA ligand is coordinated. Two oxygen atoms O_{w3} and O_{12} are not coordinated to any metal atom.

Table 7. Fractional atomic coordinates and thermal parameters^{a,b}

Atom	X	Y	Z	B_{iso} (\AA^2)
N	0.330(1)	0.1444(8)	0.021(2)	2.0(3)
O ₁₁	0.137(1)	0.1719(8)	0.117(2)	2.4(3)
O ₁₂	0.158(1)	0.2753(8)	0.073(2)	3.3(3)
C ₁₁	0.307(2)	0.211(1)	0.073(3)	2.3(4)
C ₁₂	0.190(2)	0.220(1)	0.089(3)	2.5(4)
O ₂₁	0.283(1)	0.0271(6)	-0.105(2)	1.8(3)
O ₂₂	0.328(1)	0.0551(7)	-0.352(2)	3.1(3)
C ₂₁	0.307(2)	0.137(1)	-0.154(3)	2.7(4)
C ₂₂	0.307(1)	0.0691(9)	-0.204(2)	1.4(3)
O ₃₁	0.541(1)	0.0544(7)	0.201(2)	2.6(3)
O ₃₂	0.377(1)	0.0410(6)	0.219(2)	2.2(3)
C ₃₂	0.452(2)	0.072(1)	0.171(3)	2.8(4)
C ₃₁	0.441(2)	0.130(1)	0.055(3)	2.6(5)
O _{W1}	0.252(1)	0.1286(7)	0.409(2)	2.7(3)

^aEstimated standard deviations are given in parentheses right adjusted to the least significant figure of the preceding number.

^bAnisotropic temperature factors are given for Pr only. They are times 10^5 and have the form

$$\exp[-(\underline{\alpha}_{11} \underline{h}^2 + \underline{\alpha}_{22} \underline{k}^2 + \underline{\alpha}_{33} \underline{l}^2 + \underline{\alpha}_{12} \underline{hk} + \underline{\alpha}_{13} \underline{hl} + \underline{\alpha}_{23} \underline{kl})].$$

Table 7. (Continued)

Atom	X	Y	Z	B_{iso} (\AA^2)
O_{W2}	0.076(1)	0.0576(8)	-0.075(2)	3.0(3)
O_{W3}	0.508(2)	0.299(1)	0.183(3)	7.2(5)
Pr	0.19901(8)	0.06427(5)	0.16546(13)	
\underline{g}_{11} 234(7)	\underline{g}_{22} 83(3)	\underline{g}_{33} 619(19)	\underline{g}_{12} 6(4)	\underline{g}_{13} -1(13)
				\underline{g}_{23} -8(8)

Figure 9. Observed and calculated structure factors (in electrons times 10)
for $\text{Pr} \cdot \text{N}(\text{C}_2\text{H}_2\text{O}_2)_3 \cdot 3\text{H}_2\text{O}$

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Figure 10. The perspective drawing of nitrilotriacetate-triaquopraseodymium III-monohydrate. (The numbering in the NTA ligand is such that the left number indicates the acetate group to which the atom belongs. In the case of the carbon atoms the right number indicates its position relative to the nitrogen and in the case of the oxygen atoms, is solely for uniqueness. The primes indicate atoms related to those of the coordinate list by symmetry operations which are described elsewhere)

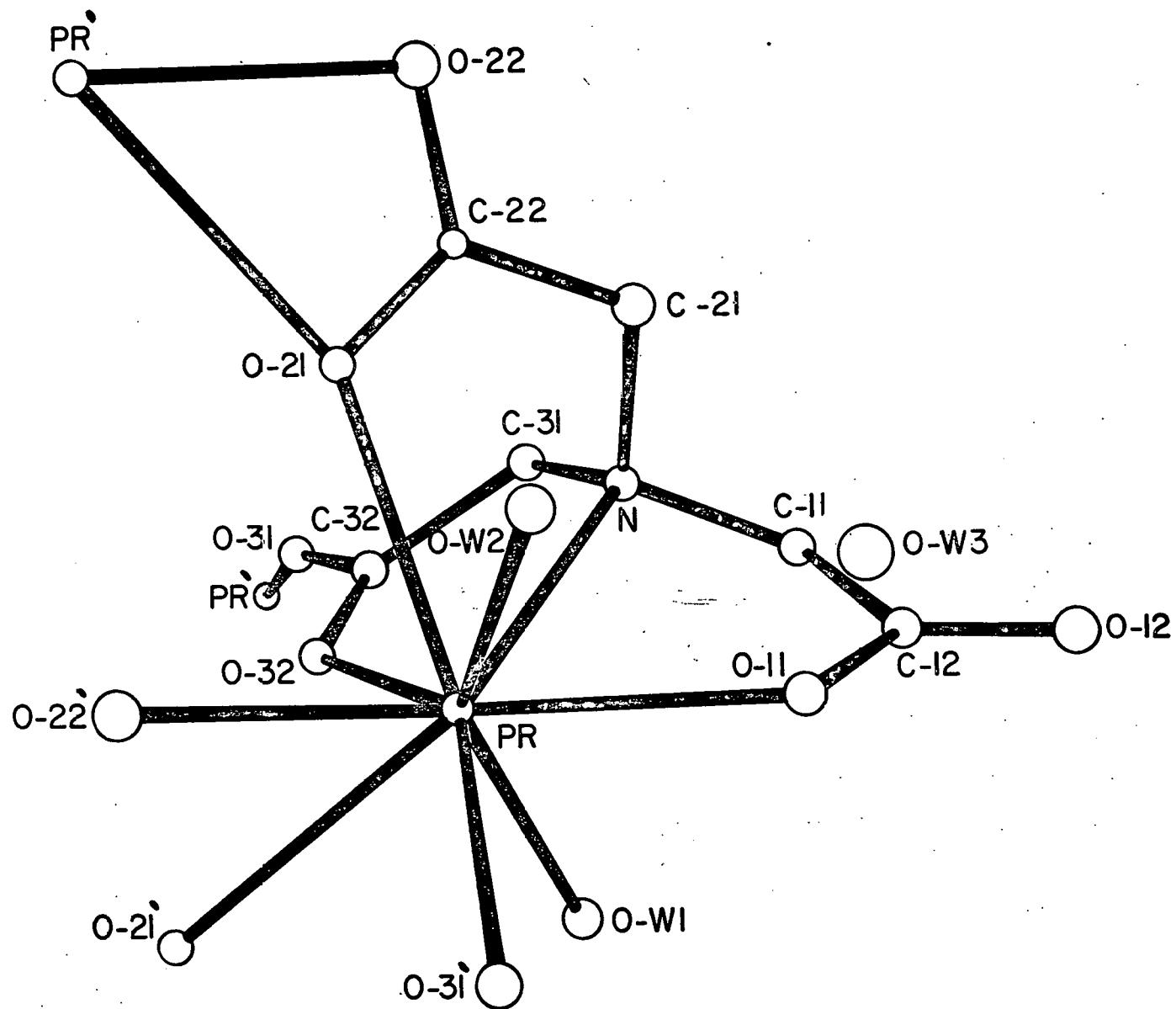


Table 8. Selected distances (\AA) and angles (deg) with associated standard errors as calculated from the parameters in Table 7^a

Distances					
Pr-O ₁₁	2.43(1)	N-C ₁₁	1.48(2)	C ₂₂ -O ₂₂	1.27(2)
Pr-O ₂₁	2.59(1)	N-C ₂₁	1.49(3)	C ₃₂ -O ₃₁	1.25(2)
Pr-O ₂₁ ¹	2.69(1)	N-C ₃₁	1.53(3)	C ₃₂ -O ₃₂	1.25(2)
Pr-O ₂₂ ¹	2.53(1)	C ₁₁ -C ₂₂	1.57(3)	O ₁₂ -O _{w3} ²	2.85(3)
Pr-O ₃₁ ²	2.37(1)	C ₂₁ -C ₂₂	1.47(3)	O ₁₂ ³ -O _{w3} ²	2.72(2)
Pr-O ₃₂	2.44(1)	C ₃₁ -C ₃₂	1.55(3)	O ₂₁ -O _{w2}	2.82(2)
Pr-O _{w1}	2.50(1)	C ₁₂ -O ₁₁	1.25(2)	O ₃₂ -O _{w2} ¹	2.73(2)
Pr-O _{w2}	2.54(1)	C ₁₂ -O ₂₂	1.24(2)	O ₂₁ -O ₂₂	2.18(2)
Pr-N	2.68(2)	C ₂₂ -O ₂₁	1.24(2)	O ₁₁ -O ₁₂	2.21(2)
				O ₃₁ -O ₃₂	2.19(2)

^aSuperscripts indicate symmetry operations which relate the atom to the original coordinates: 1) $1/2 - x, y, 1/2 + z$; 2) $-1/2 + x, y, 1/2 - z$; 3) $x, 1/2 - y, 1/2 + z$; 4) $1/2 - x, \bar{y}, -1/2 + z$; 5) $1/2 + x, y, 1/2 - z$.

Table 8. (Continued)

Angles around Pr					
O_{11} -Pr- O_{31}^2	82.0(5)	O_{31}^2 -Pr- O_{21}	138.1(4)	O_{w2} -Pr- O_{22}^1	79.1(5)
O_{11} -Pr- O_{w1}	73.9(4)	O_{31}^2 -Pr- O_{22}^1	79.3(5)	O_{w2} -Pr- O_{21}^1	123.4(4)
O_{11} -Pr- O_{w2}	73.3(5)	O_{31}^2 -Pr- O_{21}^1	72.3(4)	N-Pr- O_{32}	65.3(5)
O_{11} -Pr-N	64.1(5)	O_{w1} -Pr- O_{w2}	145.0(5)	N-Pr- O_{21}	62.6(5)
O_{11} -Pr- O_{32}	122.5(5)	O_{w1} -Pr-N	80.0(5)	N-Pr- O_{22}^1	133.3(5)
O_{11} -Pr- O_{21}	106.6(4)	O_{w1} -Pr- O_{32}	72.2(4)	N-Pr- O_{21}^1	134.0(4)
O_{11} -Pr- O_{22}^1	149.4(5)	O_{w1} -Pr- O_{21}	135.8(4)	O_{32} -Pr- O_{21}	71.3(4)
O_{11} -Pr- O_{21}^1	143.6(4)	O_{w1} -Pr- O_{22}^1	128.2(5)	O_{32} -Pr- O_{22}^1	87.1(4)
O_{31}^2 -Pr- O_{w1}	86.1(5)	O_{w1} -Pr- O_{21}^1	79.0(4)	O_{32} -Pr- O_{21}^1	69.4(4)
O_{31}^2 -Pr- O_{w2}	77.6(5)	O_{w2} -Pr-N	96.3(5)	O_{21} -Pr- O_{21}^1	109.8(1)
O_{31}^2 -Pr-N	145.7(5)	O_{w2} -Pr-N	137.8(5)	O_{21} -Pr- O_{22}^1	73.4(4)
O_{31}^2 -Pr- O_{32}	138.7(4)	O_{w2} -Pr- O_{21}	66.7(4)	O_{21} -Pr- O_{22}	49.2(4)

Table 8. (Continued)

Angles in NTA ligand					
C_{11} -N- C_{21}	110(2)	N- C_{31} - C_{32}	111(2)	C_{21} - C_{22} - O_{22}	119(2)
C_{11} -N- C_{31}	109(2)	C_{11} - C_{12} - O_{11}	118(2)	O_{21} - C_{22} - O_{22}	120(2)
C_{21} -N- C_{31}	110(2)	C_{11} - C_{12} - O_{22}	117(2)	C_{31} - C_{32} - O_{31}	116(2)
N- C_{11} - C_{12}	110(2)	O_{11} - C_{12} - O_{22}	126(2)	C_{31} - C_{32} - O_{32}	122(2)
N- C_{21} - C_{22}	112(2)	O_{21} - C_{22} - O_{21}	120(2)	O_{31} - C_{32} - O_{32}	122(2)
Angles involving NTA and Pr					
C_{12} - O_{11} -Pr	126(1)	C_{22} - O_{22} -Pr ⁴	98(1)	C_4 -N-Pr	110(1)
C_{22} - O_{21} -Pr	117(1)	C_{31} - O_{31} -Pr ²	153(1)	C_{21} -N-Pr	103(1)
C_{22} - O_{21} -Pr ⁴	92(1)	C_{31} - O_{32} -Pr	128(1)	C_{31} -N-Pr	115(1)

Thus two of the six O_C 's in each NTA molecule are coordinated to the same metal atom as the nitrogen, two are coordinated to adjacent metal atoms, one is simultaneously coordinated to two adjacent metal atoms and the last is uncoordinated.

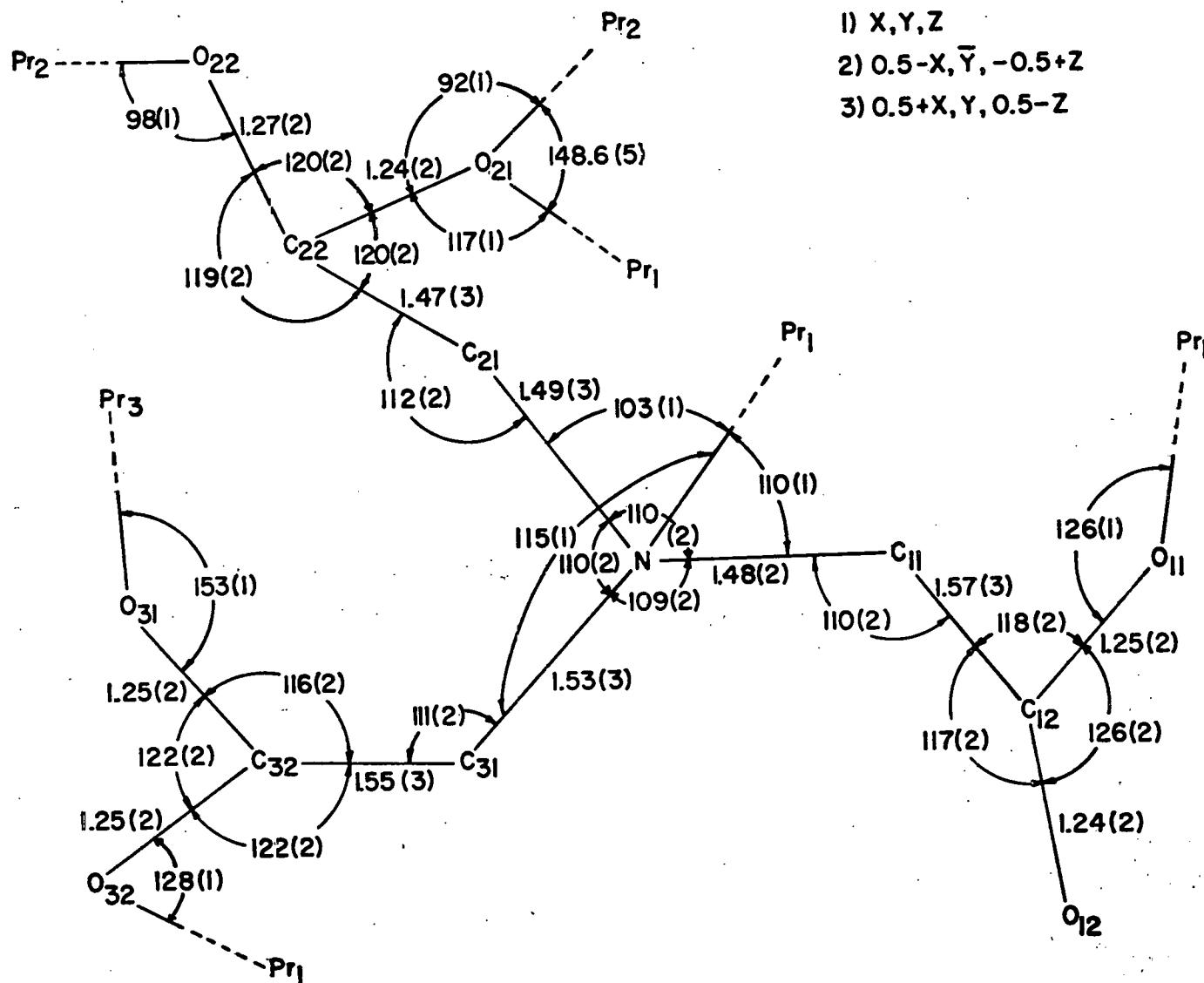
The average for the six independent terminal carbon to carboxylic oxygen bond distances is $1.25 \pm 0.02 \text{ \AA}$. This is in excellent agreement with the expected value for the C-O distance in a carboxylate ion.^{38,39} Moreover, none of the C-O distances vary from this value by more than one esd which indicates the acid is completely deprotonated and that the $O_{12}-C_{12}$ bond ($1.24 \pm 0.02 \text{ \AA}$) has no significantly greater double bond character than the rest. The three acetate groups are planar to within 0.1 \AA , while the angles around the carboxylate carbons are $120^\circ \pm 3^\circ$ with the exception of the $O_{11}-C_{12}-O_{12}$ angle which is slightly larger ($126 \pm 2^\circ$). This increase in angle can be attributed to steric strain in the unsymmetric environment caused by single coordination of this carboxylate group. The angles around the nitrogen are essentially tetrahedral with the "lone pair" directed approximately towards the metal atom (see Figure 11).

There are four short O_W-O_C distances ranging from 2.72 to 2.85 \AA which are suggestive of possible hydrogen bond formation. The large thermal parameters of O_{W3} suggests that it is involved in only a weak hydrogen bond.

The arrangement of the atoms in the coordination sphere

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Figure 11. The conformation of the NTA ligand (bond distances (\AA) and angles (deg) are shown along with their estimated errors right adjusted to the least significant figure of the preceding number. The subscripts of the Pr atoms indicate their relation to the Pr in the coordinate list)



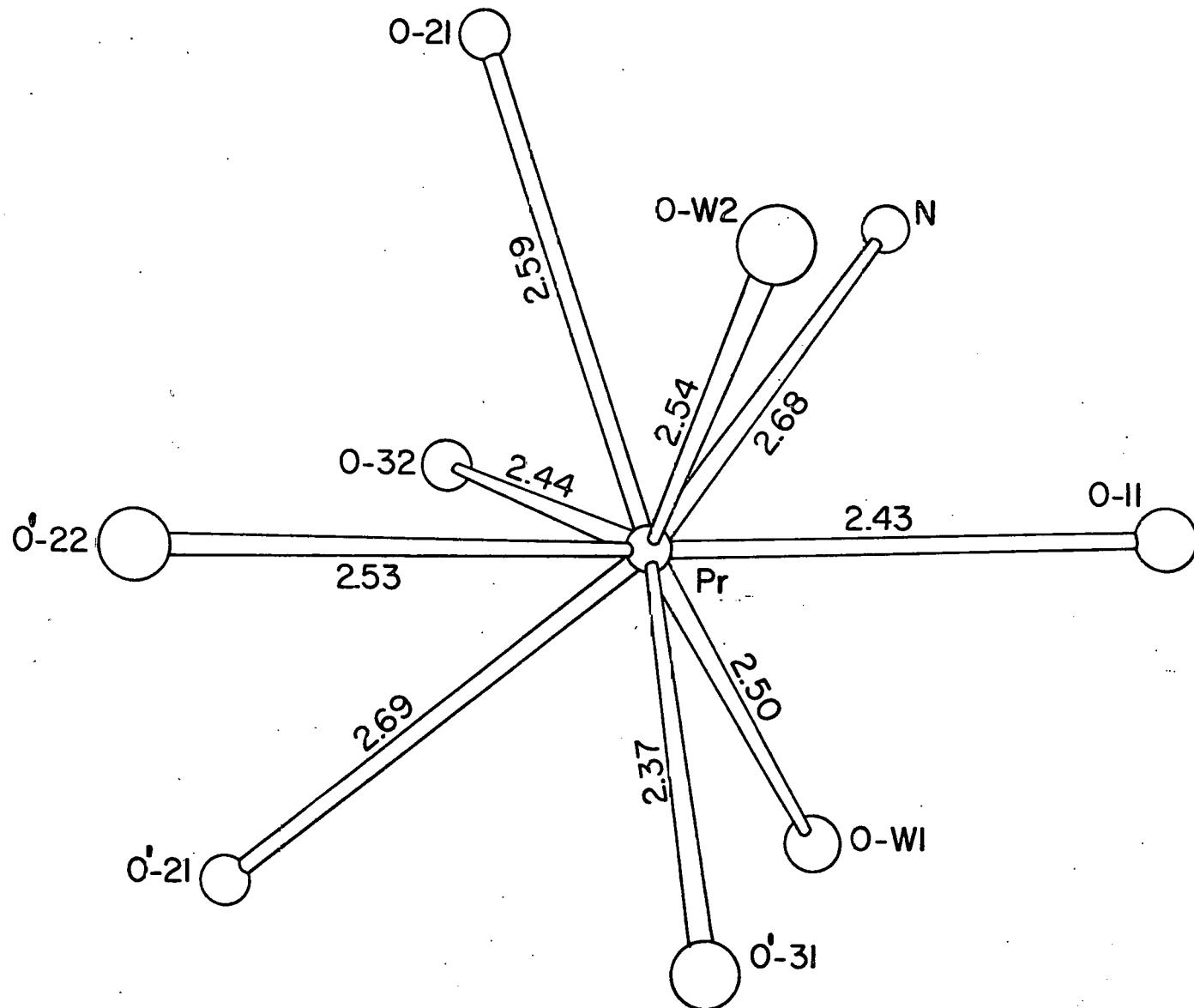
is shown in Figure 12. The average $\text{Pr}-\text{O}_c$ distance is $2.47 \pm 0.02 \text{ \AA}$ while the average $\text{Pr}-\text{O}_w$ distance is $2.52 \pm 0.02 \text{ \AA}$.

The $\text{Pr}-\text{O}_{21}$ distances have been excluded from this calculation since they are significantly longer than the other $\text{Pr}-\text{O}_c$ distances due to the different coordination mode exhibited by O_{21} . The $\text{Pr}-\text{N}$ distance is $2.68 \pm 0.02 \text{ \AA}$. The average metal-oxygen distance is in reasonable agreement with the value predicted either from the sum of the covalent radii²⁴ or from the sum of the crystal radii.⁴⁰ The $\text{Pr}-\text{N}$ distance is $\sim 0.1 \text{ \AA}$ longer than would be expected, indicating weaker coordination. These values are 0.04 to 0.08 \AA shorter than those observed by Hoard *et al.*⁴¹ in the nine coordinate $\text{La} \cdot \text{EDTA}$ complex (2.51 \AA , 2.58 \AA , 2.76 \AA for the average $\text{La}-\text{O}_c$, $\text{La}-\text{O}_w$ and $\text{La}-\text{N}$ distances). This general shortening is consistent with a decrease in the rare earth ionic radius from 1.15 \AA to 1.09 \AA . In fact, assuming the average oxygen-metal-oxygen angle remains constant (72 to 74°), a continued decrease in the metal-oxygen bond distance of 0.10 \AA to 0.14 \AA would cause significant oxygen-oxygen steric interactions. This would occur at Dy^{3+} (0.99 \AA) or Ho^{3+} (0.97 \AA) and a change in coordination number from 9 to 8 would be expected.

The arrangement of atoms around the Pr^{3+} can be described equally well in any of three ways: (1) as a distorted, tri-capped trigonal prism, (2) as a capped square anti-prism or (3) as in the description by Hoard *et al.* of

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Figure 12. A perspective drawing of the Pr coordination. (The orientation is the same as in Figure 11. The primes indicate atoms related to those in the coordinates list: (1) O_{21}' : $1/2 - x, \bar{y}, 1/2 + z$, (2) C_{22}' : $1/2 - x, \bar{y}, 1/2 - z$ and (3) O_{31}' : $-1/2 + x, y, 1/2 - z$)



the La·EDTA complex.

The tri-capped, trigonal prism arrangement has been observed for many nona-coordinate structures and have been described in some detail in a review by Muetterties and Wright.⁴² Typical of these are the anhydrous, rare earth tri-chlorides.⁴³ Referring to Figure 12, the three rectangular faces of the trigonal prism are as follows: $O_{22}'-O_{32}-N-O_{w2}-O_{22}'$, $O_{w2}-N-O_{w1}-O_{31}'-O_{w2}$, and $O_{31}'-O_{w1}-O_{32}'-O_{22}'-O_{31}'$. The two triangular faces of the prism are described by $O_{22}'-O_{w2}-O_{31}'-O_{22}'$ and $O_{32}'-N-O_{w1}-O_{32}'$. The atoms O_{21} , O_{21}' and O_{11} occupy the capping positions.

The capped square anti-prism is observed somewhat less frequently than is the tri-capped trigonal prism;⁴² however, the square anti-prism is a very common arrangement for octa-coordination. In Figure 12, the rectangular faces of the square anti-prism are defined by O_{22}' , O_{32}' , O_{w1} , O_{31}' , O_{22}' and O_{21} , N, O_{11} , O_{w2} , O_{21}' . The atom in the capping position (O_{21}') shows a significant distortion towards O_{22}' .

The description favored by Hoard *et al.*⁴¹ for the nona-coordinate La·EDTA complex, due to the large distortions from any regular geometric figure, is a one, five, three arrangement where one atom (O_{31}') is located 1.9 ± 0.2 Å below a plane of five atoms, O_{21}' , O_{22}' , O_{w2} , O_{11} , O_{w1} . The equation of this plane along with selected distances from the plane are given in Table 9. The average O-Pr-O angle in

Table 9. Selected distances to and equations of the planes

Atom	Distance \textcircled{o} from plane (Å)	Atom	Distance \textcircled{o} from plane (Å)
Plane 1			
O_{22}	0.22	O_{31}	1.90
O_{21}	0.23	Pr	0.46
O_{w1}	0.14	N	2.54
O_{11}	0.06	O_{21}	2.47
O_{w2}	0.05	O_{32}	2.31

Equation:

$$(0.881)x + (0.005)y - (0.474)z - 1.229 = 0$$

Plane 2			
O_{21}	0.0	O_{22}	2.10
O_{32}	0.0	O_{21}	2.44
N	0.0	O_{w1}	2.23
O_{31}	4.31	O_{11}	2.66
Pr	1.97	O_{w2}	2.61

Equation:

$$(0.907)x - (0.052)y - (0.418)z - 3.720 = 0$$

the plane is 71° while the average O-O distance is 2.97 \AA . The most significant distortions from these averages occur in the O_{22}' -Pr- O_{21}' angle of 49.2° and O_{21}' - O_{22}' distance of $2.18 \pm 0.02 \text{ \AA}$. This appears to be a result of both carboxylate oxygens being in the same acid moiety. The Pr^{3+} is located 0.5 \AA above the approximate center of this plane away from the O_{31}' . In the $\text{La} \cdot \text{EDTA}$ complex, the distance from the similar plane to La^{3+} is 0.6 \AA ; some increase being expected due to the longer oxygen- La^{3+} distances.

At a distance of 2.0 \AA from the Pr^{3+} and opposite the first plane is a second plane of three atoms: O_{21} , N, O_{32} . The equation of this plane and some selected distances from the plane are given in Table 9. The two planes are within 9° of being parallel.

In complexes such as ceric ammonium nitrate⁴⁴ considerable distortion of the N-O bonds and O-N-O angles have been observed and have been attributed to the presence of metal-oxygen covalent bonding. However, in the $\text{La} \cdot \text{EDTA}^-$ complex the bonding has been described as primarily electrostatic in nature. In the title compound no systematic distortions in C-O distances or O-C-O angles are observed. This, coupled with the wide range in Pr-O-C angles (92° to 153°), would imply primarily electrostatic bonding effects.

STRUCTURE OF
NITRILOTRIACETODIAQUODYSPROSIUM(III)-DIHYDRATE

Introduction

The diversity in types of coordination found in the rare-earth complexes is large (45-49). In an endeavor to determine the effect of changing metal-ion size on coordination, we have investigated the structures of the lanthanon (III)-nitrilotriacetate (NTA) complexes from Pr-Lu. The series is broken into two groups--the Pr group and the Dy group. In the previous chapter the structure of the Pr group has been discussed. In this chapter the structure of the Dy NTA complex will be discussed and comparisons made to the Pr structure.

Experimental

Well formed rectangular-prismatic crystals of Dy·NTA·4H₂O (M.W. = 422.7 g) were supplied by J. E. Powell and were used without additional purification. Weissenberg and precession photographs indicated an orthorombic space group with systematic extinctions of the type 0kl, l odd and h0l, h odd. These conditions indicate the space group to be either Pca₂₁ or Pcam (No. 57-Pbcm). In addition the 0k0, k odd reflections were unobserved. However, there are no special positions in Pca₂₁ or Pcam which can account for this type of extinction. The light lanthanon(III) NTA com-

plexes crystallize in space Pbca, and $Pca2_1$ can be obtained from Pbca by removal of the center of symmetry, interchanging the a and b axes, and translation of the origin to the 2_1 . In addition, the $0k0$ extinction condition suggests that the y , $1/2 + y$ relationship has been retained from Pbca. Therefore, it was decided to initially assume $Pca2_1$ as the space group, which was later justified by successful refinement in this space group.

The unit cell dimensions were determined by least-squares fit of 29 independent reflections whose 2θ values were obtained from Weissenberg photographs calibrated with Al powder lines at $25^\circ C$ using Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$). The values obtained along with the estimated errors are: a = $21.535 \pm 0.013 \text{ \AA}$, b = $9.028 \pm 0.004 \text{ \AA}$, c = $12.186 \pm 0.007 \text{ \AA}$ and $V_c = 2369 \text{ \AA}^3$. The measured density was 2.3 g/cc while the calculated density with eight molecules per unit cell is 2.4 g/cc.

A crystal with approximate dimensions $0.12 \times 0.12 \times 0.26 \text{ mm}$ was selected for use in data collection. The crystal was mounted along its long axis with the (001) axis coincident with the phi axis of the diffractometer. Data were collected at room temperature using a Hilger-Watts, four circle diffractometer equipped with a scintillation counter employing Zr-filtered Mo-K α ($\lambda = 0.7107 \text{ \AA}$) radiation. All data in one octant within a 2θ sphere of 60° ($\sin\theta/\lambda =$

0.70) were measured using a θ -2 θ coupled scan with a 5° take-off angle. Stationary counter measurements of the background were made at the beginning and the end of each scan. The scan range was over 50 steps of 0.01° , one step per 0.4096 sec., increased by 1 step per deg in 2θ to insure complete integration over the entire peak. The length of the background measurements were adjusted accordingly. No appreciable decrease in the intensities of three standard reflections which were remeasured periodically throughout the data taking period was observed.

The measured intensities were corrected for Lorentz and polarization effects and for absorption⁸ with minimum and maximum transmission factors of 0.43 and 0.47 ($\mu = 65.5 \text{ cm}^{-1}$). The standard deviations were assigned to the intensities according to the following formula:

$$\sigma(I) = (c_t + c_b + (0.03 \times c_t)^2 + (0.06 \times c_b)^2 + (0.06 \times c_n)^2)^{1/2} \times A$$

where c_t , c_b , c_n and A represent the total count, background count, net count and the absorption factor, respectively. The quadratic terms correspond to the estimated systematic errors in the intensity, background, and absorption correction of 3, 6, and 6% respectively. The standard deviations in the structural amplitudes were obtained by the method of finite differences,⁵ $\sigma(F) = ((I + \underline{I})^{1/2} - \underline{I}^{1/2})/(\underline{L_p})^{1/2}$, where

L_p is the Lorentz-polarization factor. Of the 3407 measured reflections, 375 had values of F less than $\sigma(F)$ and were considered to be unobserved. They were not used in the refinement.

Solution of the Structure

The structure was determined using a combination of heavy atom and superposition⁵⁰ techniques. Since the space group $Pca2_1$ has only four general positions, two independent molecules must be present in the unit cell. From the Patterson map the two heavy atom positions were readily located. However, due to the placement of the heavy atoms at almost exactly 0 and $1/2$ in y , the phasing was such that two sets of light atoms appeared in the electron density maps which were related by mirroring at 0 and $1/2$ in the y direction. Because of the large number of light atoms and their small individual contributions to the scattering, it was very difficult to consistently select atoms in the same image. Therefore, a superposition procedure was used starting with a known heavy atom vector. This superposition enabled us to locate single heavy atom-light atom vectors around the heavy atoms. A second superposition eliminated a number of the pseudo peaks. Using vectors from this second superposition, two more superpositions were carried out. The resultant map had, in addition to the peaks corresponding to the heavy atoms, seven peaks which appeared at chemically reasonable

positions for oxygen atoms. By successive electron density map-structure factor calculations, the remaining light atoms positions were determined. In the process, it was found that all but one of the original seven light atoms were correct. Scattering factors used were those of Cromer and Waber³⁷ for dysprosium³⁺ corrected for anomalous scattering²² and those of Hanson *et al.*⁸ for the light atoms.

All atoms were refined⁶ isotropically with unit weights resulting in a value for the discrepancy factor, $\underline{R} = \frac{\sum ||\underline{F}_o| - |\underline{F}_c||}{\sum |\underline{F}_o|}$ of 0.089. Weights were then introduced based on the individual statistics of the reflections ($w = 1/\sigma^2(\underline{F})$). In addition, 65 reflections were removed from the refinement since they did not fulfill the requirement $||\underline{F}_o| - |\underline{F}_c|| < 9 \times \sigma(\underline{F})$. The refinement was continued with anisotropic temperature factors for the dysprosium atoms to an \underline{R} of 0.057 and of the weighted discrepancy factor $\underline{R}_w = (\sum w(|\underline{F}_o| - |\underline{F}_c|)^2 / \sum w |\underline{F}_o|^2)^{1/2}$ of 0.082. In order to further refine the structure, it was necessary to use a variation of a block diagonal procedure. In successive cycles, the parameters of one and then the other of the independent molecules were allowed to vary with all temperature factors anisotropic. This procedure seemed appropriate since the correlation matrix in the isotropic refinement had indicated that the interaction between atoms in nonequivalent molecules were small. In addition, in two final cycles of refinement,

first all positional parameters, and then all temperature factors were allowed to vary to minimize as much as possible any dependence of the parameters on intermolecular correlations. In these two final cycles no parameter shift was greater than 0.5 of the associated estimated standard deviation (esd). Final values of \underline{R} and \underline{R}_w were 0.050 and 0.070. A final difference electron density map showed no residual electron density greater than $0.5 \text{ e}^-/\text{\AA}^3$.

An attempt was made to determine the absolute configuration of the molecules. One image, the positional parameters of which are listed in Table 10, gave a value of \underline{R} 0.1 lower than the other image, which suggests the former to be the correct configuration. A larger difference was not observed due to the approximate centrosymmetric relationship between the two independent molecules. The independence of the two molecules is indicated by the fact that only 8 out of a possible 108 correlations between terms related by the approximate centering had values greater than 0.1 and no term exceeded 0.36.

Previous experience on the trisilane structure using a 9×9 block diagonal procedure indicated that the method may lead to an underestimate of the esd's by 0.20. This is probably a maximum value for the esd's in Table 10 since much larger blocks were used. In Table 11 are listed the root-mean-square amplitudes of vibration while in Figure 13

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Table 10. Atom positions and anisotropic temperature factors^a

Atom	x	y	z	β_{11}
Dy1	61202(2)	-130(5)	0	60(1)
Dy2	19555(2)	49940(5)	18663(5)	60(1)
O1E1	415(5)	3745(11)	-1868(9)	20(3)
O1E2	166(7)	52(11)	-3300(8)	26(3)
O1D1	889(4)	-2259(9)	748(8)	17(2)
O1D2	1080(4)	-4690(8)	625(8)	14(2)
O1U1	470(4)	456(11)	-203(10)	11(2)
O1U2	-1416(5)	-545(14)	-88(13)	9(2)
C1E1	-43(6)	-205(14)	-2033(11)	17(3)
C1E2	68(6)	-440(15)	-2454(12)	10(3)
C1D1	363(7)	-3673(14)	-628(15)	18(3)
C1D2	810(5)	-3540(12)	363(9)	6(2)
C1U1	-574(6)	-2241(14)	-325(15)	16(3)
C1U2	-847(6)	-636(14)	-181(12)	12(3)
O2E1	2269(5)	5158(8)	3748(8)	15(2)
O2E2	2702(4)	4106(10)	5198(7)	17(2)
O2D1	1450(3)	2723(7)	1796(8)	7(2)
O2D2	1491(5)	496(11)	1067(9)	15(2)
O2U1	3019(3)	5570(10)	1850(10)	7(2)

^aHeavy atom parameters are times 10^5 while light atom parameters are times 10^4 .

β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
380(7)	242(4)	17(2)	-17(2)	-37(4)
421(8)	229(4)	16(2)	-13(2)	-52(4)
85(11)	36(7)	-5(5)	-5(4)	20(8)
169(19)	13(6)	-15(5)	-12(3)	26(8)
68(11)	45(7)	6(4)	-14(33)	-12(7)
28(8)	41(6)	7(3)	-9(3)	-5(6)
79(11)	69(8)	-3(4)	-3(3)	-32(9)
127(15)	135(15)	-1(5)	7(5)	-10(14)
64(15)	50(10)	4(6)	-10(5)	-8(10)
86(15)	39(9)	9(5)	2(4)	-1(11)
74(16)	82(15)	22(6)	-17(6)	-7(13)
55(12)	29(7)	3(4)	-3(4)	-9(8)
52(16)	74(13)	-8(5)	3(5)	-14(12)
59(14)	66(10)	49(5)	6(4)	22(11)
73(11)	26(6)	8(3)	-1(3)	-3(6)
101(13)	29(6)	-1(4)	-4(3)	-23(8)
30(8)	61(7)	1(3)	-1(3)	3(6)
78(10)	57(8)	-10(4)	-17(4)	-10(8)
54(10)	72(8)	12(3)	-9(3)	-5(9)

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Table 10. (Continued)

Atom	x	y	z	β_{11}
O2U2	3997(5)	4988(9)	1811(14)	9(2)
C2E1	2547(6)	2603(13)	3616(11)	13(3)
C2E2	2500(6)	4218(14)	4244(12)	5(2)
C2D1	2402(5)	1415(10)	1905(12)	6(2)
C2D2	1719(5)	1611(13)	1568(9)	9(2)
C2U1	3294(6)	3056(11)	2814(12)	13(3)
C2U2	3444(6)	4659(12)	1941(10)	17(3)
OW11	1501(4)	-633(14)	-1046(10)	8(2)
OW12	634(4)	2596(9)	-232(9)	21(2)
OW21	1100(4)	5684(12)	2951(8)	11(2)
OW22	2041(4)	7570(9)	1705(11)	13(2)
OW13	-2352(5)	1721(12)	-386(14)	14(3)
OW14	-1547(6)	1463(12)	1925(13)	44(4)
OW23	4907(4)	3347(11)	2705(11)	14(2)
OW24	4108(7)	6634(14)	-36(11)	57(6)
N1	41(4)	-2228(9)	-871(8)	14(2)
N2	2625(4)	2764(9)	2460(7)	5(2)

β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
124(15)	97(11)	-13(4)	-9(5)	5(11)
77(15)	45(10)	-5(5)	-10(4)	29(11)
115(17)	38(9)	-7(6)	-7(4)	-2(11)
42(11)	60(10)	-2(4)	-14(4)	-5(10)
64(13)	17(7)	5(5)	-6(3)	-16(8)
28(11)	60(11)	2(4)	5(4)	8(9)
56(12)	12(6)	-1(4)	-4(4)	2(8)
202(18)	66(9)	1(5)	8(3)	-23(12)
41(10)	76(8)	-1(4)	-27(4)	5(8)
161(16)	38(7)	31(5)	-2(3)	-10(9)
46(10)	114(12)	-1(4)	-10(4)	8(10)
169(18)	141(15)	22(6)	-8(5)	58(15)
79(14)	103(12)	12(6)	5(7)	18(12)
96(13)	98(10)	-1(4)	-5(4)	22(10)
136(19)	71(13)	-41(8)	-1(7)	-7(12)
29(10)	29(7)	1(4)	-4(3)	-4(7)
6(10)	21(6)	-9(3)	4(3)	-21(7)

Table 11. Root-mean-square thermal displacement (Å)

Atom	Min.	Med.	Max.	Atom	Min.	Med.	Max.
Dy1	0.118	0.121	0.144	Dy2	0.115	0.120	0.145
N1	0.115	0.138	0.188	N2	0.078	0.114	0.179
C1E1	0.136	0.179	0.226	C2E1	0.124	0.161	0.230
C1E2	0.130	0.175	0.200	C2E2	0.095	0.181	0.215
O1E1	0.142	0.190	0.241	O2E1	0.141	0.157	0.202
O1E2	0.083	0.229	0.281	O2E2	0.129	0.204	0.220
C1D1	0.091	0.203	0.288	C2D1	0.068	0.136	0.226
C1D2	0.102	0.114	0.179	C2D2	0.091	0.133	0.185
O1D1	0.133	0.174	0.232	O2D1	0.113	0.122	0.212
O1D2	0.104	0.145	0.211	O2D2	0.121	0.173	0.258
C1U1	0.134	0.195	0.240	C2U1	0.105	0.166	0.220
C1U2	0.132	0.165	0.217	C2U2	0.101	0.154	0.195
O1U1	0.133	0.174	0.237	O2U1	0.133	0.153	0.227
O1U2	0.143	0.226	0.325	O2U2	0.130	0.187	0.303
OW11	0.115	0.201	0.309	OW21	0.108	0.170	0.280
OW12	0.130	0.139	0.279	OW21	0.143	0.170	0.296
OW13	0.155	0.252	0.353	OW23	0.177	0.192	0.276
OW14	0.177	0.274	0.319	OW24	0.209	0.236	0.377

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Figure 13. Observed and calculated structure factors for
 $\text{Dy}(\text{N}(\text{C}_2\text{H}_2\text{O}_2)_3)^4\text{H}_2\text{O}$ in electrons $\times 10$

Figure 13. (Continued)

are listed the values of the observed and calculated structure factors. Selected intramolecular distances, both corrected and uncorrected for thermal motion, and angles are given in Table 12. Their estimated errors²³ were determined from the inverse matrix obtained when only the positional parameters were allowed to vary.

Discussion

The thermal parameters of the atoms in the NTA ligand exhibit a general increase as the distance from the nitrogen increases. Therefore, a correction for thermal motion using a riding model⁵¹ seemed appropriate and was applied to the intraligand distances. Corrections using both a riding model and an independent atom model were made to the metal-oxygen distances.

The molecular configurations of the two independent Dy. NTA·4H₂O molecules are shown in Figure 14. The two ligands exhibit similar metal coordinations. The three acetate groups in each independent ligand can be placed in one of three categories dependent upon the acetate-oxygen atom (O_a)-metal atom coordination. For a given ligand, one O_a atom in each of the three acetate groups, along with the nitrogen atom, coordinate to the same metal atom. Of the remaining three O_a atoms in each ligand, one is coordinated to an adjacent, symmetry-equivalent dysprosium atom (E type), one is coordinated to an adjacent, nonequivalent metal atom

Table 12. Selected interatomic distances (\AA) and angles ($^\circ$)^a

Atoms	Uncorr.	Riding	Independent
Metal-light atom distances			
Dy1-O1E1	2.342(10)	2.354	2.368
Dy1-O1E2	2.283(10)	2.304	2.317
Dy1-O1D1	2.303(9)	2.311	2.326
Dy1-O2D2	2.345(9)	2.350	2.373
Dy1-O1U1	2.376(9)	2.385	2.400
Dy1-OW11	2.371(9)	2.392	2.406
Dy1-OW12	2.373(8)	2.386	2.400
Dy1-N1	2.575(9)	2.578	2.592
Dy2-O2E1	2.394(9)	2.401	2.414
Dy2-O2E2	2.307(8)	2.319	2.333
Dy2-O2D1	2.323(7)	2.329	2.343
Dy2-O1D2	2.438(9)	2.453	2.434
Dy2-O2U1	2.348(7)	2.356	2.371
Dy2-OW21	2.352(9)	2.366	2.380
Dy2-OW22	2.341(8)	2.359	2.372
Dy2-N2	2.580(8)	2.580	2.592

^aStandard deviations are given in parentheses right justified to the last significant figure of the preceding number.

Table 12. (Continued)

Atoms	Uncorr.	Riding	Atoms	Uncorr.	Riding
Intraligand distances					
C1E2-O1E1	1.27(2)	1.28	C2E2-O2E1	1.22(1)	1.22
C1E2-O1E2	1.20(2)	1.23	C2E2-O2E2	1.24(1)	1.25
C1E2-C1E1	1.56(2)	1.56	C2E2-C2E1	1.58(2)	1.58
C1D2-O1D1	1.26(1)	1.27	C2D2-O2D1	1.19(1)	1.20
C1D2-O1D2	1.23(1)	1.24	C2D2-O2D2	1.28(1)	1.30
C1D2-C1D1	1.51(1)	1.53	C2D2-C2D1	1.53(1)	1.53
C1U2-O1U1	1.28(2)	1.29	C2U2-O2U1	1.24(1)	1.25
C1U2-O1U2	1.23(1)	1.27	C2U2-O2U2	1.24(2)	1.27
C1U2-C1U1	1.57(2)	1.57	C2U2-C2U1	1.50(1)	1.50
N1-C1E1	1.44(2)	1.44	N2-C2E1	1.43(2)	1.44
N1-C1D1	1.51(1)	1.53	N2-C2D1	1.47(1)	1.48
N1-C1U1	1.48(2)	1.50	N2-C2U1	1.50(1)	1.51
Intraligand angles					
O2E1-C2E2-O2E2	128(1)		O1E1-C1E2-O1E2		124(1)
O2E1-C2E2-C2E1	117(1)		O1E1-C1E2-C1E1		119(1)
O2E2-C2E2-C2E1	115(1)		O1E2-C1E2-C1E1		116(1)
C2E2-C2E1-N2	113(1)		C1E2-C1E1-N1		114(1)
O2D1-C2D2-O2D2	126(1)		O1D1-C1D2-O1D2		128(1)
O2D1-C2D2-C2D1	120.0(9)		O1D1-C1D2-C1D1		116(1)
O2D2-C2D2-C2D1	113.9(9)		O1D2-C1D2-C1D1		115(1)

Table 12. (Continued)

Atoms	Angles	Atoms	Angles
Intraligand angles cont.			
C2D2-C2D1-N2	109.9(8)	C1D2-C1D1-N1	112(1)
O2U1-C2U2-O2U2	123(1)	O1U1-C1U2-O1U2	126(1)
O2U1-C2U2-C2U1	120(1)	O1U1-C1U2-C1U1	118(1)
O2U2-C2U2-C2U1	117(1)	O1U2-C1U2-C1U1	116(1)
C2U2-C2U1-N2	114.6(9)	C1U2-C1U1-N1	112(1)
C2E1-N2-C2D1	109.3(9)	C1E1-N1-C1D1	110(1)
C2E1-N2-C2U1	110.6(9)	C1E1-N1-C1U1	109(1)
C2D1-N2-C2U1	110.8(8)	C1D1-N1-C1U1	108(1)
Angles involving a metal atom			
N2-Dy2-OW21	119.1(3)	OW11-Dy1-O1U1	141.1(4)
O2D1-Dy2-O2E1	102.8(3)	N1-Dy1-O1E1	68.2(3)
O2E2-Dy2-OW22	104.2(4)	O2D2-Dy1-O1E2	80.3(4)
O2U1-Dy2-O1D2	136.4(4)	O1D1-Dy1-OW12	156.3(3)
N2-Dy2-O1D2	134.3(2)	O2D2-Dy1-O1E1	130.9(3)
O2D1-Dy2-O2E2	79.1(3)	OW11-Dy1-OW12	98.8(4)
O2E1-Dy2-OW22	89.8(4)	N1-Dy1-O1E2	101.2(3)
OW21-Dy2-O2U1	135.2(4)	O1D1-Dy1-O1U1	116.9(3)
O2E2-Dy2-O2E1	140.9(3)	O1U1-Dy1-O1E1	72.3(4)
OW22-Dy2-O2D1	155.5(3)	O1D1-Dy1-O2D2	75.1(3)
N2-Dy2-O2U1	68.3(3)	OW12-Dy1-N1	137.1(3)
OW21-Dy2-O1D2	73.2(3)	O1E2-Dy1-OW11	146.4(4)

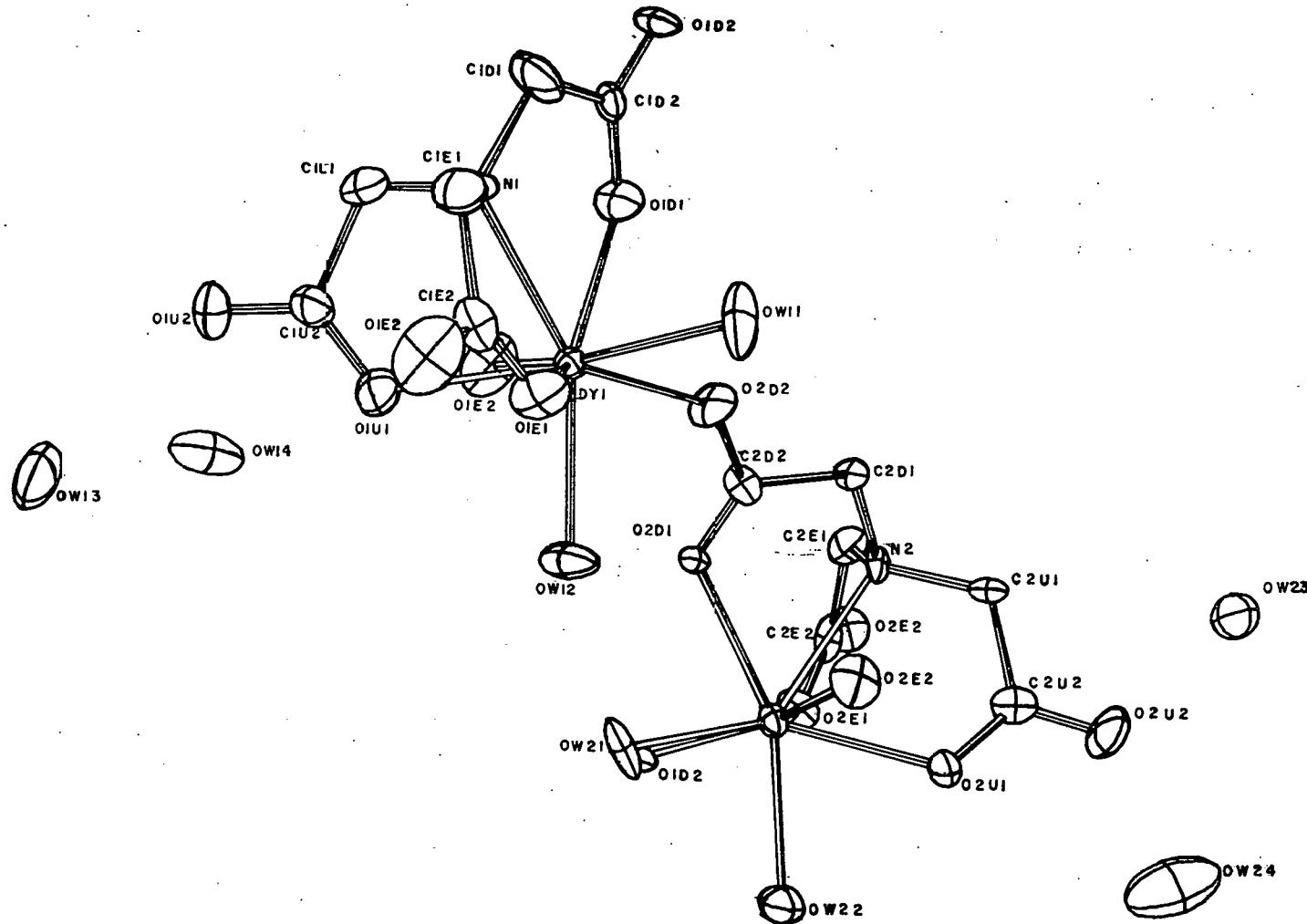
Table 12. (Continued)

Atoms	Angles	Atoms	Angles
Angles involving a metal atom cont.			
C2U2-O2U1-Dy2	125.0(8)	C1U2-O1U1-Dy1	118.9(9)
C2E2-O2E1-Dy2	123.0(8)	C1E2-O1E1-Dy1	124.5(8)
C2E2-O2E2-Dy2 ^b	159(1)	C1E2-O1E2-Dy2 ^b	164(1)
C2D2-O2D2-Dy2	121.5(7)	C1E2-O1D1-Dy1	128.7(7)
C2D2-O2D1-Dy1	134.0(8)	C1D2-O1D2-Dy2 ^b	128.7(7)
Atoms	Distance	Atoms	Distance
Additional interatomic distances			
O1E1-O1E2	2.18(1)	OW13-O1U2	2.89(2)
O2E1-O2E2	2.24(1)	OW14-OW11	2.59(2)
O1D1-O1D2	2.23(1)	OW14-O1U2	3.06(2)
O2D1-O2D2	2.21(1)	OW23-O2U2	2.69(2)
O1U1-O1U2	2.20(1)	OW23-OW12	2.85(1)
O2U1-O2U2	2.17(1)	OW24-O2U2	2.71(2)
OW13-OW11	2.78(2)	OW23-OW21	2.64(2)

^bFor an explanation of symmetry related positions see Figures 15 and 16.

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Figure 14. Configuration of the two independent molecules. (The two metal atoms are numbered for uniqueness. The nitrogen atoms have the same number as the metal to which they are coordinated which is also the left-most number for the remaining atoms in the ligand. The letters specify the type of metal-oxygen coordination (see text), while the right-most number indicates a skeletal position for the carbon atoms. In the case of the oxygen atoms, a one in the right-most position indicates coordination to the same metal atoms as the nitrogen atom while a two indicates a different interaction)



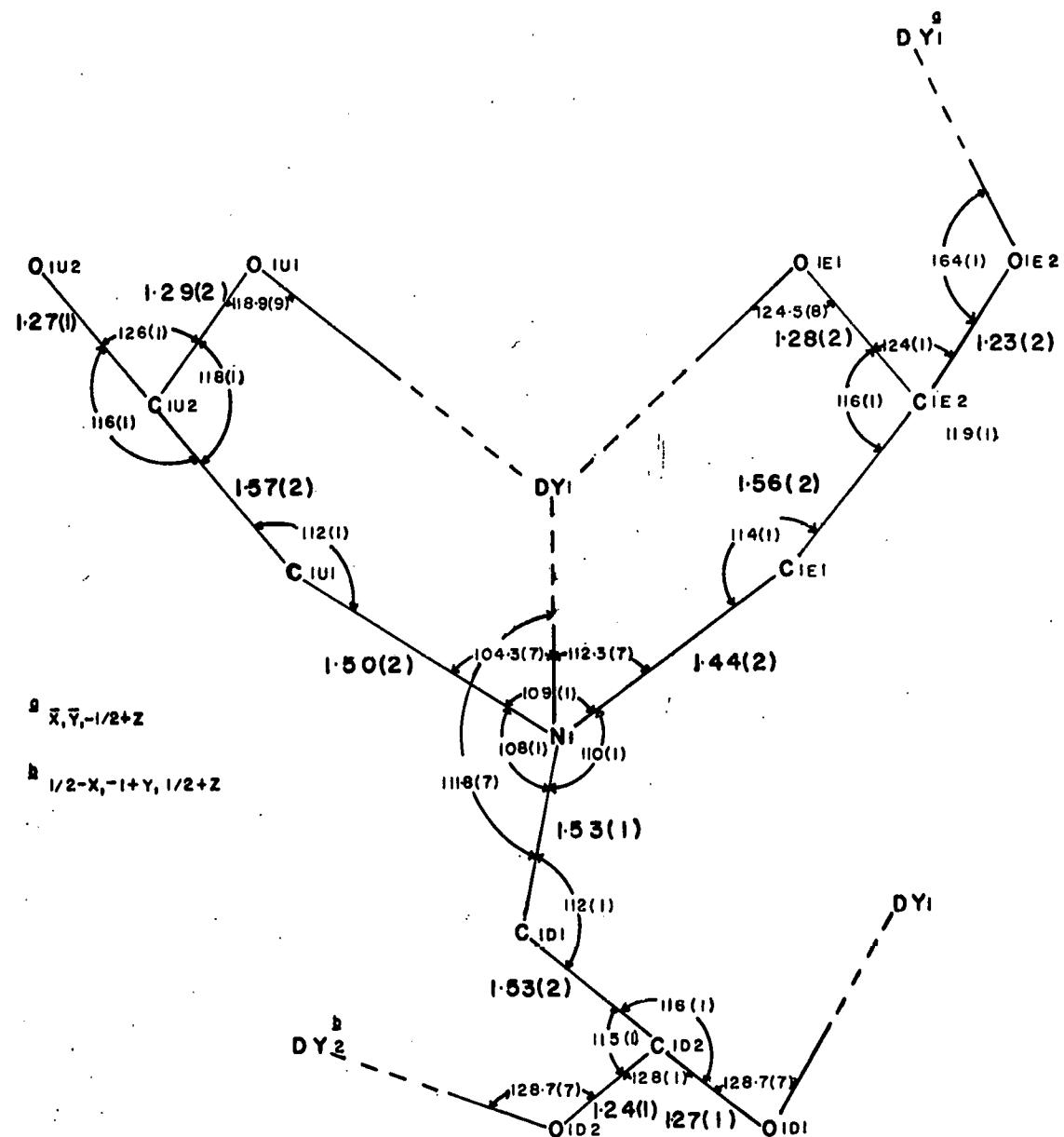
(D type), and one is not coordinated to any metal atom (U type). Schematic drawings of the two independent NTA ligands are shown in Figures 15 and 16. The acetate groups are all planar to within 0.03 Å; the O_a -C- O_a angles average 126° (123 - 128°) while the O_a -C-C angles average 117° (114 - 120°). The average carbon-oxygen (1.26 Å), carbon-carbon (1.55 Å) and carbon-nitrogen (1.48 Å) bond distances, corrected for thermal motion are all within 0.01 Å of the expected values.³⁹

The variation in C-C and C-N bond distances does not appear to be significant. The systematically large O_a -C- O_a angles are apparently the result of intermolecular steric interactions and intracarboxylate oxygen-oxygen repulsions.²⁵ Also, the wide range in metal-oxygen and C- O_a distances probably is a result of a combination of steric and electrostatic effects. There does not appear to be any correlation between lengthenings and shortenings of C-O distances in a manner which would suggest covalent effects. In addition, the C- O_a distance for the two uncoordinated oxygens are 0.01 Å longer than the average; a shortening of this bond would be expected in the presence of covalent bonding.⁴⁴

Five acetate oxygen atoms, two water molecules and one nitrogen atom are in the coordination sphere of each metal atom. These coordinating atoms reside at the corners of a distorted dodecahedron with triangular faces with approximate

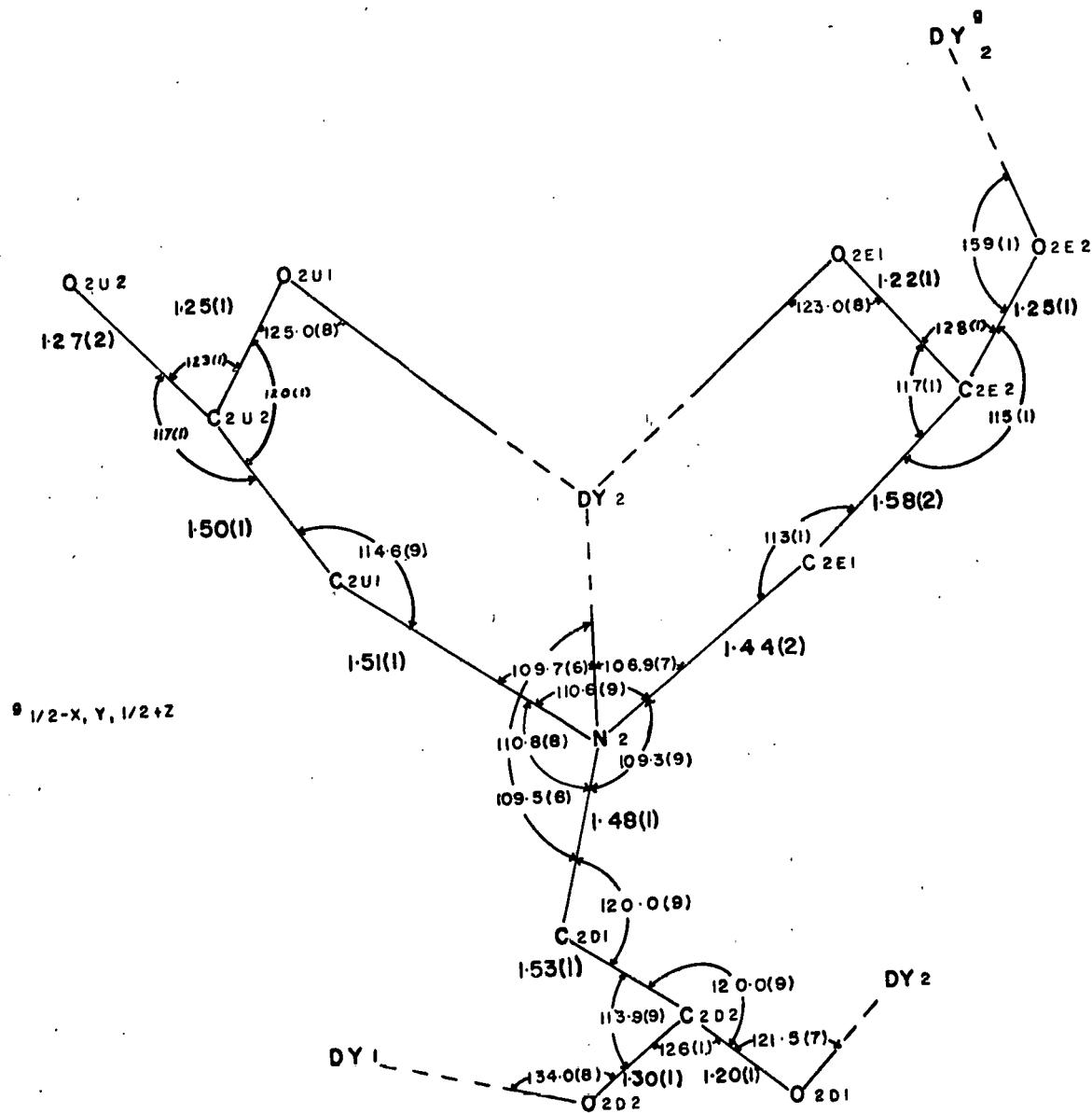
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Figure 15. Schematic drawing of NTA ligand one



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Figure 16. Schematic drawing of NTA ligand two



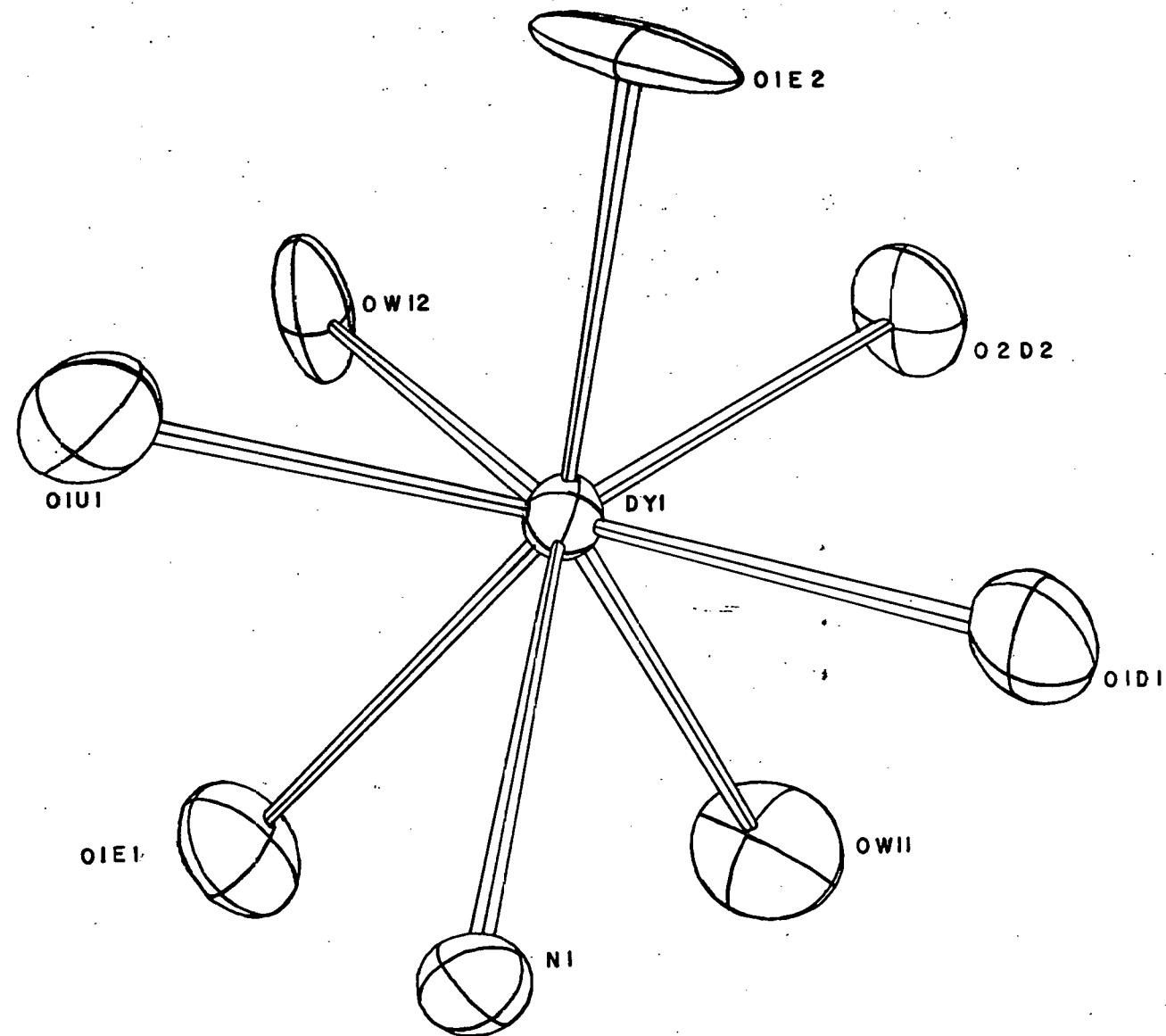
D_{2d} symmetry. A projection down one of the two folds in molecule one and a projection showing the fourfold inversion axis in molecule two are given in Figures 17 and 18. The good agreement, in most cases, between symmetry equivalent distances (see Table 13) illustrates the approximate D_{2d} symmetry. The nona-coordinate, capped, square antiprism found in the $\text{Pr}\cdot\text{NTA}\cdot3\text{H}_2\text{O}$ can be converted to the octa-coordinate dodecahedron by removal of the atom in the capping position and relatively minor changes in angles. The NTA ligand in the Pr complex would then be hexadentate as it is in the title compound with no doubly coordinated oxygen atom.

The coordination can also be described as a distorted one-five-two complex similar to the one-five-three description given by Hoard *et al.*⁴¹ for the $\text{La}\cdot\text{EDTA}$ complex. The distortions are much greater in this case than for the dodecahedron and we prefer the latter.

The average $\text{Dy}-\text{O}_a$, $\text{Dy}-\text{N}$ and $\text{Dy}-\text{O}_w$ distances, uncorrected for thermal motion are 2.346, 2.578, and 2.359 \AA . This corresponds to a decrease of approximately 0.1 \AA compared to the corresponding praseodymium distances for the $\text{M}-\text{O}_a$ and $\text{M}-\text{N}$ bonds. This is in good agreement with the decrease in the ionic radius.⁴⁰ The $\text{Dy}-\text{O}_w$ distances average approximately 0.06 \AA shorter than expected. However, there are a large number of O_w-O distances which are in the range typical of

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Figure 17. Coordination of Dy_1 (viewed down a pseudo, twofold axis)



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Figure 18. Coordination of Dy_2 (viewed perpendicular to a pseudo, $\overline{4}$ axis)

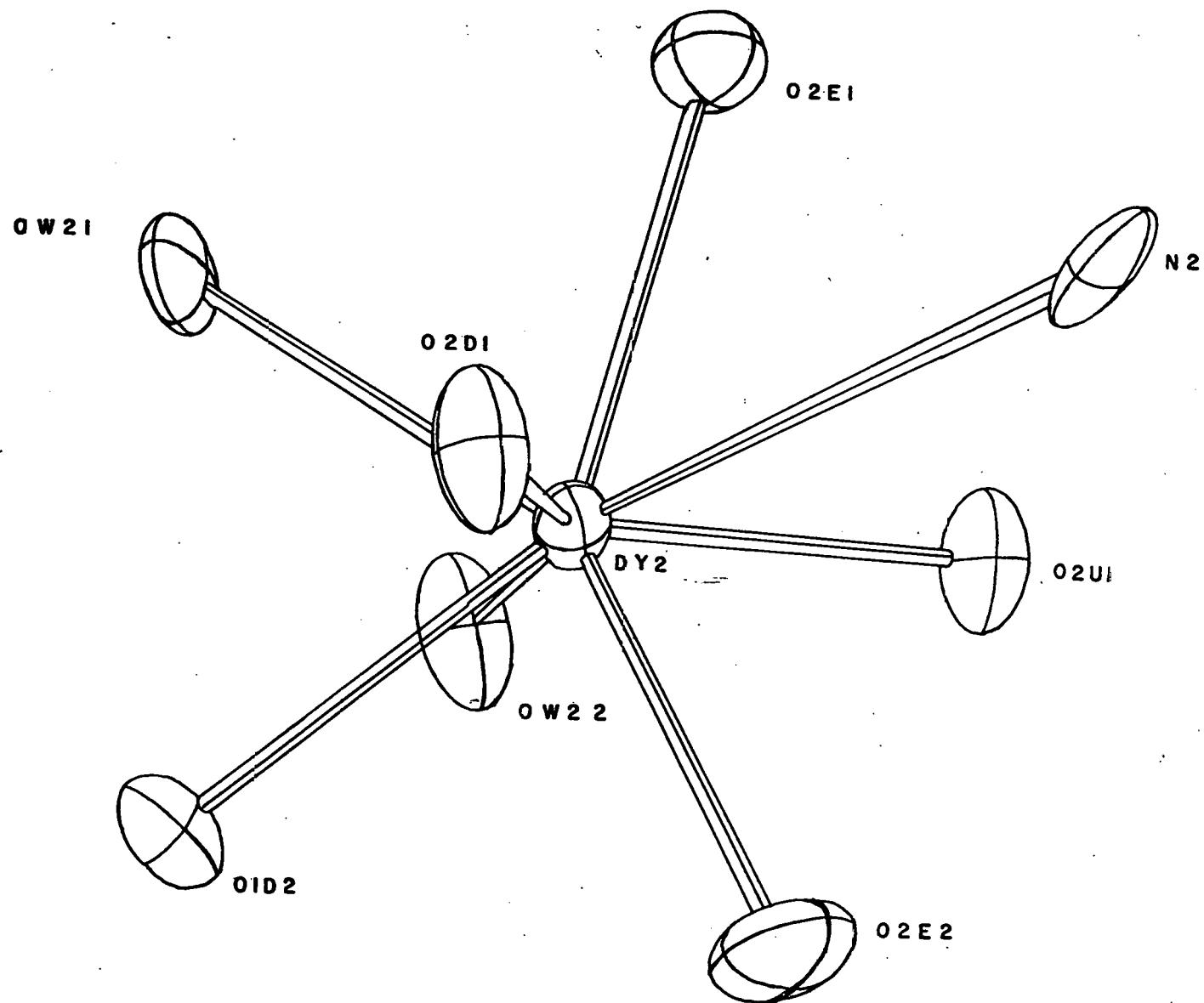


Table 13. Atoms and distances^a related by pseudo-symmetry

Atoms related by a twofold			
Molecule 1		Molecule 2	
N1-O1E1	O2D2-O1E1	N2-OW21	OW21-O2U1
OW11-O1U1	OW11-OW12	O1D2-O2U1	O2D1-O2E2
O2D2-O1E2	N1-O1E2	O2D1-O2E1	N2-O1D2
O1D1-OW12	O1D1-O1U1	O2E2-OW22	O2E1-OW22

Atoms related by 4			
Molecule 1		Molecule 2	
O1U1-O1D1-O1E1-O2D2		O2E2-OW22-O2E1-O2D1	
OW12-O1E2-N1-OW11		N2-OW21-O2U1-O1D2	

Equivalent distances related by pseudo-symmetry					
Molecule 1				Molecule 2	
Atoms	Dist.	Ave.		Atoms	Dist.
O1E1-O1U1	2.78			O1D2-OW21	2.85
		2.80			
O1D1-O2D2	2.83			O2U1-N2	2.77
O1E1-N1	2.77			O1D2-O2D1	2.85
O1D1-O1E2	2.85			OW21-OW22	3.05
O1U1-OW12	3.06			N2-O2E1	2.78
O2D2-OW11	2.78			O2E2-O2U1	2.87
		2.88			2.97
O1E1-OW12	2.87			O1D2-OW22	3.19
O1E1-N1	2.77			OW21-O2D1	3.11

^aAverage standard deviation in distances is 0.02 Å.

Table 13. (Continued)

Atoms	Dist.	Ave.	Atoms	Dist.	Ave.
O1D1-OW11	2.95		N2-02E2	3.09	
O2D2-01E2	2.98		O2U1-02E1	2.85	
N1-01E2	3.76		O2D1-02E1	3.69	
OW11-OW12	3.60		O2D1-02E2	2.95	
		3.57			3.41
N1-OW11	3.47		OW22-02E1	3.34	
OW12-01E2	3.44		OW22-02E2	3.67	
O1E1-OW11	2.70		O1D2-02E2	2.89	
O1U1-01E2	2.72		OW21-02E1	2.94	
		2.80			2.77
O1D1-N1	2.69		N2-02D1	2.67	
O2D2-OW12	3.08		O2U1-OW22	2.78	

hydrogen bonding (Tables 12 and 13) and such hydrogen bonding might be expected to increase the metal-O_W interactions on electrostatic grounds.

THE QUADRUPLE PRODUCT

Introduction

The basis for the method to be described below as well as for any of the so called "direct methods" is the Sayre⁵² squared equation

$$V \times S \times \underline{F}_{\underline{h}} = \sum_k \underline{F}_{\underline{k}} \underline{F}_{\underline{h}-\underline{k}} \quad (1)$$

where V is the volume of the unit cell and S is a function to correct for a difference in peak-shape between $\underline{F}_{\underline{h}}$ and $\underline{F}_{\underline{k}}$.

This function is a direct result of the self-convolution of the structure factor, $\underline{F}_{\underline{h}}$.⁵³ It is apparent for centrosymmetric space groups, where phases are limited to integral values (± 1), that in order for $\underline{F}_{\underline{h}}$ to be large, the values within the summation must tend strongly towards terms with the same sign.

Therefore, for most terms in Equation 1,

$$s(\underline{F}_{\underline{h}}) = s(\underline{F}_{\underline{k}})s(\underline{F}_{\underline{h}-\underline{k}}) \quad (2)$$

where s represents "the sign of". The larger the values of $\underline{F}_{\underline{h}}$, $\underline{F}_{\underline{k}}$, and $\underline{F}_{\underline{h}-\underline{k}}$, the more probable that (2) will hold. A more useful measure of a particular reflections "largeness" is its E value.⁵⁴ This is simply the value of \underline{F} corrected for $\sin\theta/\lambda$ fall-off in the scattering power

$$\underline{E}_{\underline{h}}^2 = \underline{F}_{\underline{h}}^2 / \epsilon \sum_j^N f_j^2 \quad (3)$$

where f_j is the scattering factor, ϵ is a term which is introduced to correct for symmetry, and $\underline{F}_{\vec{h}}$ is corrected for thermal motion. The use of $\underline{E}_{\vec{h}}$ instead of $\underline{F}_{\vec{h}}$ makes possible meaningful size comparisons between reflections at different values of θ . When the size of a particular reflection is expressed in terms of $\underline{E}_{\vec{h}}$'s, then the probability that (2) will hold is given by⁵⁵

$$P(+) = 1/2 + 1/2 \tanh \rho_3/\rho_2^{3/2} |\underline{E}_{\vec{h}-\vec{k}} \underline{E}_{\vec{h}-\vec{k}}| \quad (4)$$

where $\rho_q = \sum_i^N n_i^q$ and $n_i = f_i/\sum_j^N f_j$. If there are multiple relations which yield $\underline{E}_{\vec{h}}$, then

$$P(+) = 1/2 + 1/2 \tanh \sum_k \rho_3/\rho_2^{3/2} |\underline{E}_{\vec{h}-\vec{k}} \underline{E}_{\vec{h}-\vec{k}}| \quad (5)$$

The normal manner in which the signs of the various reflections are determined in a centrosymmetric structure is to use a "symbolic addition procedure".⁵⁶⁻⁵⁹ In this procedure initial signs are given to a few reflections (three or less) with larger values of \underline{E} to fix the origin and additional algebraic symbols are given to a few other reflections as needed. By the application of Equation (2), additional signs may be determined. Failure in this method usually is a result of either poor data, difficulty in choosing a good starting set, or few type (2) relationships with high probability. The last case is especially important in triclinic systems because of the low symmetry. In the method

described below, an attempt was made to develop additional phase relationships between the various reflections. In this manner, the dependency of the solution upon the choice of a good starting set can be eliminated and the problems caused by only a few type (2) relationships may be reduced.

Description of the Method

When \underline{E}_h is large, all the individual signs of the terms in Equation (1) are equated; this results in a series of equations of the type

$$s(\underline{E}_{\vec{k}})s(\underline{E}_{\vec{h}-\vec{k}}) = s(\underline{E}_{\vec{k}'})s(\underline{E}_{\vec{h}-\vec{k}'}) \quad (6)$$

for all possible values of \vec{k} and \vec{k}' , $\vec{k} \neq \vec{k}'$. The probability that these equations hold is just the product of the probabilities that each individual relation of the type (2) holds. Upon rearrangement of (6)

$$s(\underline{E}_{\vec{k}})s(\underline{E}_{\vec{h}-\vec{k}})s(\underline{E}_{\vec{k}'})s(\underline{E}_{\vec{h}-\vec{k}'}) = +1 \quad (7)$$

is obtained. This relationship we have chosen to call the quadruple product. In every centrosymmetric structure there will be at least one set, and sometimes several sets, depending upon the amount of symmetry present, of \vec{h} , \vec{k} , \vec{k}' values where two of the unknowns can be eliminated from Equation (7). For example, two sets of \underline{E} 's which satisfy Equation (2) for a value of $\vec{h} = 1, 3, 3$ are $\underline{E}_{111} \cdot \underline{E}_{022}$ and

$E_{111} \cdot E_{244}$. These two sets would then give rise to the quadruple product

$$s(E_{111}) \cdot s(E_{022}) \cdot s(E_{111}) \cdot s(E_{244}) = +1 \quad (8)$$

For a centrosymmetric structure $E_{111} = E_{111}$ and

$$s(E_{111}) \cdot s(E_{111}) = +1 \quad (9)$$

Upon substitution of Equation (9) into Equation (8)

$$s(E_{022}) \cdot s(E_{244}) \cdot (+1) = +1 \quad (10)$$

is obtained, or, upon rearrangement

$$s(E_{022}) = s(E_{244}) \quad (11)$$

The probability that the relationship given by Equation (11) holds is the same as that of the parent quadruple relation holding.

As soon as the relationship between two E_{η} 's is known with high probability (~ 0.95), then this relation can be fed back into the sign determining process and the number of quadruple products, from which two unknowns can be eliminated, rapidly increases. The probability that these new relationships will hold is just equal to the product of the probabilities that the quadruple product holds and the relation between the two E_{η} 's, which are eliminated, is valid. Since this new probability is the product of four numbers all less

than one, it is apparent that a single relationship may well have a probability which is small ($\ll 0.95$). However, as the number of relationships between \underline{E}_h 's increases, so will the number of multiple indications of a particular relationship between two \underline{E} 's. For two indications, the probability that an indication is correct is

$$P(c) = P_1 \times P_2 / (1 - P_1 - P_2 + 2P_1 \times P_2) \quad (12)$$

where P_1 and P_2 are the probabilities of the individual relationships being valid. In general, for n indications the probability can be expressed as

$$P(c) = \frac{\prod_{i=1}^n P_i}{\prod_{i=1}^n (1 - P_i) + \prod_{i=1}^n (P_i)} \quad (13)$$

It is apparent that with only a few indications of moderate probability (~ 0.8), Equation (13) will rapidly approach unity.

A particular reflection may be placed in any one of eight parity groups: eee, eeo, eoe, oee, eoo, oeo, ooe, and ooo where e indicates even and o indicates an odd index. The parties are seen to form a group with respect to multiplication (Table 14). It is readily seen that, in order to satisfy Equation (2) for a given parity of \vec{h} , \underline{E} 's of appropriate parity must be used. For example, if \vec{h} has parity eoe, there will be four combinations of two \underline{E} 's which will yield this parity (oeo, ooo; eee, eoe; ooe, oee;

Table 14. Parity group multiplication table

	eee	eeo	eo _e	oe _e	oo _e	oe _o	eo _o	oo _o
eee	eee	eeo	eo _e	oe _e	oo _e	oe _o	eo _o	oo _o
eeo	eeo	eee	eo _e	oe _e	oo _e	oe _o	eo _o	oo _e
eo _e	eo _e	eo _o	eee	oe _e	oo _e	oo _o	eo _o	oe _e
oe _e	oe _e	oe _o	oe _e	eee	eo _e	eo _o	oo _o	eo _e
oo _e	oo _e	ooo	oe _e	eo _e	eee	eo _o	oe _o	ee _e
oe _o	oe _o	oe _e	ooo	eo _o	eo _e	eee	oe _e	eo _e
eo _o	eo _o	eo _e	eo _o	ooo	oe _o	oe _e	ee _e	oe _e
oo _o	ooo	oe _e	oe _o	eo _o	eo _e	oe _o	oe _e	eee

eo_o, eo_o). In addition, if two of the three parity groups are specified then, obviously, the parity of the third term is determined. This is important since it dictates that only terms of like parity may be related through Equation (11) before the origin is defined.

When relationships within the various parity groups are known, the origin may be specified. Using the known intra-parity relationships, absolute signs may be assigned to the E's in the parity groups of the origin defining E's. Since there are now many new relationships between E's in the different parity groups, there will be many additional quadruple products where two of the unknowns, now of dif-

ferent parity classes, may be eliminated.

Absolute signs may be determined for the remaining parity groups by two different procedures. The first procedure is to make use of type (2) relationships. When two \underline{E}_h 's have known absolute signs and the third \underline{E}_h is of a parity class for which absolute signs are not known, the absolute signs of the third parity group can be obtained. For example, the necessary relationships needed to relate relative signs of the undetermined parity groups to those of the three parity groups eee, oee, eoe are shown in Table 15.

Table 15. Parities which relate relative signs

	\vec{h}	\vec{k}	$\vec{h} - \vec{k}$
Cycle 1	ooo	oee	eoe
	oeo	oee	eee
	ooo	eoe	ooo
	eee	oee	eee
	eee	ooo	ooo
	eee	eoe	eoe
Cycle 2	ooo	ooo	ooo

In order to determine the ooo parity group, it would be necessary to recycle using relative signs generated in the first cycle. The probability that these new signs are

correct would be the probability that Equation (2) holds, times the probability that the relationship between the two known E_h 's, as determined from the quadruple product, is valid. Only relationships of very high probability (~ 0.99) need be used in this process since there will be numerous indications for the absolute signs of each of the unknown groups and these probabilities will rapidly approach certainty by the use of equations similar to (13).

The second procedure, which can be used to determine the absolute signs of the unknown parity classes, utilizes the absolute signs of the eee-type reflections which can be determined before the origin is defined. When two E 's with the same parity are involved in a type 2 relation, the parity of the third E must be eee. If the E 's are of the same parity, their relative signs will be known and Equation (2) can be uniquely solved for the absolute sign of the eee- E . There are usually a number of these types of relations for every eee- E and the associated probabilities will approach certainty by the use of equations similar to (13). After the origin is defined, there are a number of quadruple products which involve two E_h 's of a parity class with known absolute signs, an E_h of eee parity with known absolute sign, and one E_h from an unknown parity group. The absolute sign for this E_h is then uniquely determined. The types of parities needed to relate the absolute signs of the undeter-

mined parity groups to the three parity groups eeo, eoe, oee by the use of the quadruple product and known signs for the $\underline{E}_{\vec{h}}$'s are shown in Table 16. The quadruple products are, of course, formed with \vec{k} and $\vec{h}-\vec{k}$ terms. It is also seen in

Table 16. Types of parities needed to relate undetermined signs

	\vec{h}	\vec{k}	$\vec{h}-\vec{k}$		\vec{h}	\vec{k}	$\vec{h}-\vec{k}$		\vec{h}	\vec{k}	$\vec{h}-\vec{k}$
	oee	oeo			oee	oeo			oee	eee	
eeo	eoe	eoo		eo	eoe	eee		oee	eo	ooe	
	eeo	eee			eeo	eo			eeo	eo	
	eeo	ooo			eo	ooo			oee	ooo	
ooe	eoe	oee		eo	oe	eo		eo	eo	eo	
	oee	eo			eo	oe			eo	eo	

Table 16 that the absolute signs of one of the parity groups (in this case the ooo type) is determined directly from the origin defining parity groups.

In practice a mixture of the two methods described above is used. The second method is routinely used in an automated procedure since it is easier to program and, in addition, it leads to new relationships between $\underline{E}_{\vec{h}}$'s which are not found through symmetry alone. The first procedure is used only if

the automated procedure fails. This only occurs when there are a small number of E's in a particular parity group or when small sub-groups form where a few of the E's have no interrelations with the bulk of the E's in a particular parity group. In these cases the (2)-type relationships may be used to find the unknown signs.

Application of the Method

To facilitate the application of this method two programs, Quads and Relate have been written. The calculation of the quadruple products is carried out by the use of the program Quads. A listing of this Fortran IV program is supplied in Appendix A. Input to this program is a tape containing all relations of the type (2). The actual sign determination process is carried out using Relate. Relate is a PL-1 program written for the 360-65 system. It uses 22K words of high speed core with some dynamic allocation of arrays plus an additional 50K words of slow core. A listing of this program can be found in Appendix B.

Relate searches through the entire list of quadruple products for relationships where the relative signs of two of the four members are known. The remaining two members are then given the appropriate relative sign and the probability is stored, or if there is already some indication known between these E_h 's, a new probability is calculated. At the end of each cycle, the probabilities are searched for values

exceeding a cut-off value (~ 0.95). These relationships are then output along with their associated probabilities. This list of related \underline{E}_h 's is then searched for relationships of the type $a = \pm b$ and $b = \pm c$. Then a is set equal to c with the appropriate relative sign. Finally, the list of relationships of type (2) involving eee reflections is searched for cases where two of the three unknowns may be eliminated. If the cumulated probability exceeds a given cut-off value (~ 0.99), the \underline{E}_h , where h is eee, is given the appropriate absolute sign. Then if any of the type (2) relations which contain this $s(\underline{E}_h)$ are not known, the remaining two members are given the appropriate relative sign and probabilities. The program then recycles using these newly determined relations. Whenever most of the relations for the various parity groups are known, the origin is defined by assigning absolute signs to appropriate reflections. The program then recycles through the type (2) relations and determines the signs of the remaining groups. It also continues to cycle through the quadruples since in so doing the signs of some previously undetermined \underline{E}_h 's may be found.

The method has been tested on the structure of $Cs_3Sb_2Cl_9$ which crystallizes in the space group Pnma (No. 62) with $Z = 4$. This structure was previously solved by W. Pflaum using normal direct methods. Values of the \underline{E} 's were calculated using a scale factor of 0.20 and an overall thermal parameter

of 2.65 determined by the method of Hackert.⁶⁰ The relations of type (2) were calculated⁸ for $E_{\vec{h}}$'s above 1.5. The value of $\rho_3/\rho_2^{3/2}$ used in calculating the probabilities was 0.143. Due to the limited core size of 50K words, only the 196 $E_{\vec{h}}$'s above 2.28 were used in the calculation of some 62,560 quadruple products. In Relate, quadruple products were accepted only if their probability exceeded 0.80. A relationship between two $E_{\vec{h}}$'s had to exceed a probability of 0.95 before it was accepted. Before signs were accepted for groups of reflections or for eee type reflections, the associated probability had to exceed 0.99. After three cycles through Relate, absolute signs were given appropriate members of the oee, ooe and eoo parity groups. In this case, all signs of the remaining groups were obtained automatically. Of the 196 inputs $E_{\vec{h}}$'s, 194 were successfully assigned signs. Of these 194 signs, all were correct. From an E-map using these signs the positions of the Cs and Sb atoms were readily located. In Table 17 are listed the hkl values, and the signed $E_{\vec{h}}$ values.

Table 17. Signed E values as determined by Relate(h,k,l,E)

0	0	6	-3.00	4	2	10	2.96	8	4	2	-2.50	15	1	14	2.56	
0	0	12	5.07	4	2	14	2.47	8	4	4	3.65	15	2	2	3.34	
0	0	18	-3.10	4	4	4	3.15	8	4	8	3.24	15	2	4	2.28	
0	1	3	2.28	4	4	8	2.87	8	4	16	2.33	15	2	10	-3.20	
0	1	9	-2.80	4	6	2	3.09	8	5	1	-2.40	15	2	14	3.51	
0	1	15	2.49	4	6	10	2.62	8	6	2	3.23	15	3	14	-2.40	
0	2	0	-2.90	4	8	4	2.66	8	6	10	2.90	15	4	4	-2.90	
0	2	6	4.15	4	8	8	2.69	8	6	14	2.59	15	4	8	2.85	
0	2	12	-2.70	4	10	2	2.44	8	8	4	2.76	15	6	10	-2.50	
0	2	18	3.73	5	0	11	2.48	8	8	8	2.82	16	0	4	3.35	
0	3	3	-2.60	5	0	16	-2.40	8	10	2	2.61	16	0	8	2.91	
0	3	9	2.37	5	0	17	-4.40	9	0	8	-2.30	16	2	2	3.15	
0	3	15	-2.30	5	1	14	2.85	9	0	13	-2.70	16	2	10	2.43	
0	4	0	4.69	5	2	11	-2.40	9	1	10	2.28	16	4	4	2.58	
0	4	6	-2.50	5	2	17	3.17	9	1	16	-3.00	17	0	11	2.87	
0	4	12	3.74	5	3	14	-2.70	9	2	13	2.36	17	0	8	-2.40	
0	5	3	2.65	5	5	14	2.77	9	3	16	3.02	17	2	11	-2.80	
0	5	9	-2.50	5	5	6	11	-2.40	10	0	8	-2.30	17	4	11	2.31
0	6	0	-2.70	5	5	8	11	2.55	10	0	16	-3.10	18	0	0	-2.30
0	6	6	3.93	6	0	0	-2.40	10	2	14	-2.30	18	0	12	-3.60	
0	7	3	-2.70	6	0	12	-3.70	12	0	0	4.25	18	2	6	-3.00	
0	8	0	3.91	6	2	6	-3.00	12	0	6	-3.80	19	0	7	2.67	
0	8	6	-2.50	6	4	12	-2.40	12	0	12	5.84	19	1	10	3.23	
0	8	12	3.57	7	0	4	2.90	12	1	3	3.73	19	3	4	2.23	
0	9	3	2.63	7	0	8	-2.80	12	1	9	-3.20	19	3	10	-2.60	
0	9	9	-2.80	7	0	14	2.44	12	2	0	-2.50	20	0	2	-2.50	
0	10	0	-2.40	7	0	16	3.27	12	2	6	5.80	20	0	4	3.59	
0	10	6	3.85	7	1	17	2.40	12	2	12	-2.90	20	0	8	3.14	
3	0	4	-3.40	7	2	2	-2.60	12	3	3	-3.40	20	1	1	-2.50	
3	0	8	5.04	7	2	10	2.59	12	3	9	2.74	20	1	5	-2.40	
3	0	13	-2.50	7	2	16	-2.30	12	4	0	3.47	20	2	2	3.12	
3	0	14	-2.40	7	4	4	2.40	12	4	6	-3.00	20	2	10	2.75	
3	0	16	-2.90	7	4	16	2.72	12	4	12	4.45	20	4	4	2.73	
3	1	16	-2.50	8	0	2	-2.80	12	5	2	2.78	20	4	8	2.53	
3	2	2	3.19	8	0	4	4.22	12	5	9	-2.80	21	0	9	-2.40	
3	2	10	-2.60	8	0	8	4.19	12	6	6	4.24	22	0	6	-3.20	
3	2	14	3.05	8	0	10	-2.30	12	7	3	-2.40	22	1	3	2.77	
3	3	16	2.51	8	0	14	-2.60	13	0	13	-3.50	22	1	9	-2.80	
3	4	4	-2.70	8	0	16	3.34	13	0	15	2.50	22	2	6	2.49	
3	4	8	2.75	8	1	1	-2.80	13	2	13	2.39	22	3	3	-2.40	
3	5	16	-2.40	8	1	5	-2.50	13	4	13	-3.00	22	4	6	-2.50	
3	6	2	2.60	8	1	7	2.42	15	0	2	-2.30	24	0	2	-2.50	
3	6	14	2.36	8	2	2	4.14	15	0	4	-3.60	24	0	4	2.66	
3	8	8	2.32	8	2	4	-2.40	15	0	8	3.73	24	1	1	-2.50	
4	0	4	3.74	8	2	8	-2.40	15	0	10	2.62	24	1	5	-2.40	

Table 17. (Continued)

4	0	8	3.93	8	2	10	3.38	15	0	14	-2.70	24	2	2	2.30
4	0	10	-2.40	8	2	14	3.05	15	1	1	2.30				
4	0	16	2.65	8	3	1	2.57	15	1	7	-2.30				
4	2	2	3.65	8	3	5	2.29	15	1	13	2.50				

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APPENDIX A. A LISTING OF QUADS

121

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C QUADS IS A FORTRAN IV PROGRAM TO CALCULATE THE QUADRUPLE PRODUCTS QUA 0010
C AND THE ASSOCIATED PROBIBILITIES.....INPUT TO THIS PROGRAM QUA 0020
C IS THREE TAPES AND ONE CARD.....INFORMATION SUPPLIED ON THE QUA 0030
C INPUT TAPE IS THE SAME AS THAT OUTPUT FROM NRC-SAP-2 QUA 0040
C INFORMATION SUPPLIED BY THE USER ON CARDS IS AS FOLLOWS..... QUA 0050
C NTAP-SPECIFIES ON WHICH UNIT THE INPUT TAPE SHOULD BE MOUNTED QUA 0060
C IOTAP-SPECIFIES ON WHICH UNIT THE OUTPUT TAPE 1 SHOULD BE MOUNTED QUA 0070
C NOTAP-SPECIFIES ON WHICH UNIT THE OUTPUT TAPE 2 SHOULD BE MOUNTED QUA 0080
C AMIN-THE MINUMUN ACCEPTABLE PROBABILITY QUA 0090
C MH-MAXIMUM SERIAL NUMBER TO BE CONSIDERED IN EVEN PARITY SEARCH QUA 0100
C MK-MAXIMUM SERIAL NUMBER TO BE CONSIDERED QUA 0110
C ML-DUMMY VARIABLE QUA 0120
C SIGMA-VALUE OF SIGMA3/SIGMA2 TO THE 3/2 POWER QUA 0130
C FORMAT 3I10,F10.5,3I5,F10.5 QUA 0140
C OUTPUT FROM PROGRAM IS AS FOLLOWS.....HKL VALUES FOR ALL E'S QUA 0150
C ALONG WITH AN INDICATOR FOR EEE PARITY QUA 0160
C ALL OF THE QUADRUPLE PRODUCTS QUA 0170
C THE TOTAL NUMBER OF QUADS CALCULATED QUA 0180
C THE MAGNETIC TAPES CONTAIN THE FOLLOWING INFORMATION..... QUA 0190
C TAPE 1 HAS ALL OF THE QUADRUPLE PRODUCTS AND THEIR ASSOCIATED QUA 0200
C PROBABILITIES..... QUA 0210
C TAPE 2 CONTAINS ALL THE EEE TRIPLES..... QUA 0220
C BOTH OF THESE TAPES WILL BE NEEDED REPEATEDLY..... QUA 0230
C DIMENSION N1(200),N2(200),A(200),TITLE(20),NQ(24),NNA(12),NNB(12) QUA 0240
C DIMENSION MMM(401),NNC(12),NND(12),SIGG(12) QUA 0250
C IZ=0 QUA 0260
C II=0 QUA 0270
C IN=0 QUA 0280
C INPUT INFORMATION..... QUA 0290
C READ(1,100)TITLE QUA 0300
100 FORMAT(20A4) QUA 0310
C WRITE(3,101)TITLE QUA 0320
101 FORMAT(1H ,20A4//) QUA 0330
C READ(1,102)NTAP,IOTAP,NOTAP,AMIN,MH,MK,ML,SIGMA QUA 0340
102 FORMAT(3I10,F10.5,3I5,F10.4) QUA 0350
C ND=0 QUA 0360
C WRITE(3,1001)NTAP,IOTAP,AMIN QUA 0370

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1001 FORMAT(1H , 'INPUT TAPE IS',I5,'OUTPUT TAPE IS',I5,'AMIN IS',F10.3) QUA 0380
C   CALCULATE PARITY..... QUA 0390
  8 READ(NTAP)IH,IK,IL QUA 0400
  IF(IH.GE.99)GO TO 93 QUA 0410
  II=II+1 QUA 0420
  NH=(IH/2)*2 QUA 0430
  NK=(IK/2)*2 QUA 0440
  NL=(IL/2)*2 QUA 0450
  IF(NH.NE.IH)GO TO 90 QUA 0460
  IF(NK.NE.IK)GO TO 90 QUA 0470
  IF(NL.NE.IL)GO TO 90 QUA 0480
  MMM(II)=1 QUA 0490
  GO TO 91 QUA 0500
  90 MMM(II)=0 QUA 0510
  91 WRITE(3,1003)II,IH,IK,IL,MMM(II) QUA 0520
1003 FORMAT(1H ,I5,5X,4I5) QUA 0530
  GO TO 8 QUA 0540
  93 READ(NTAP) QUA 0550
  WRITE(3,1004) QUA 0560
1004 FORMAT(1H , 'I AM HERE') QUA 0570
  5 I=0 QUA 0580
  IN=0 QUA 0590
  6 READ(NTAP,END=60)NA,NB,ES,PS QUA 0600
C   CALCULATE PROBABILITIES..... QUA 0610
  VAL=ABS(ES) QUA 0620
  ARG=SIGMA*VAL QUA 0630
  PROB=0.5+0.5*TANH(ARG) QUA 0640
  PROB=PROB*VAL/ES QUA 0650
  IF(NA)20,20,7 QUA 0660
  7 IF(NA.GT.MH)GO TO 6 QUA 0670
  IF(NB.GT.MH)GO TO 6 QUA 0680
  IZ=IZ+1 QUA 0690
  NNA(IZ)=NA QUA 0700
  NNB(IZ)=NB QUA 0710
  SIGG(IZ)=PROB QUA 0720
  IF(IZ.LT.8)GO TO 23 QUA 0730
  WRITE(3,1006)(NNA(N),NNB(N),SIGG(N),N=1,8) QUA 0740

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1006 FORMAT(1H ,8(2I4,F5.3,2X)) QUA 0750
   IZ=0 QUA 0760
23  IN=IN+1 QUA 0770
   IF(IN.GT.100)GO TO 6 QUA 0780
   I=I+1 QUA 0790
   N1(I)=NA QUA 0800
   N2(I)=NB QUA 0810
   A(I)=PROB QUA 0820
   GO TO 6 QUA 0830
20  NB=NB-1 QUA 0840
   IF(NB.GT.MK)GO TO 60 QUA 0850
   DO 21 N=1,I QUA 0860
   IF(MMM(NB).NE.1)GO TO 92 QUA 0870
   IF(N1(N).EQ.0)GO TO 92 QUA 0880
C   OUTPUT EEE-TRIPLES..... QUA 0890
   WRITE(NOTAP)NB,N1(N),N2(N),A(N) QUA 0900
92  DO 21 K=1,I QUA 0910
   IF(N.GE.K) GO TO 21 QUA 0920
C   CALCULATE QUADRUPLES..... QUA 0930
   SIGN=A(N)*A(K) QUA 0940
   ASIGN=ABS(SIGN) QUA 0950
   IF(ASIGN.LT.AMIN)GO TO 21 QUA 0960
C   OUTPUT QUADRUPLES..... QUA 0970
   WRITE(IOTAP)N1(N),N2(N),N1(K),N2(K),SIGN QUA 0980
24  ND=ND+1 QUA 0990
22  FORMAT(1H ,4I5,F10.2) QUA 1000
21  CONTINUE QUA 1010
   IF(NA)60,5,5 QUA 1020
60  WRITE(3,999)ND QUA 1030
999 FORMAT(1H ,'TOTAL NUMBER OF QUADS=',I9) QUA 1040
   END QUA 1050

```

APPENDIX B. A LISTING OF RELATED

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(SUBRG,STRG):                               REL00010
    RELATE: PROC OPTIONS(MAIN);             REL00020
/* *****REL00030
    RELATE: A PL-1 PROGRAM TO CALCULATE THE SIGNS OF THE E'S USING THE REL00040
        QUADRUPLE PRODUCT METHOD.....L.L.MARTIN             REL00050
                                                               REL00060
THIS PROGRAM REQUIRES THE FOLLOWING INPUT INFORMATION:             REL00070
1) ADFS-THE CUTOFF PROBABILITY-USUALLY THE SAME AS AMIN IN QUADS REL00080
2)NOES-THE LARGEST SERIAL NUMBER TO BE CONSIDERED<200           REL00090
3)NTOTCY-TOTAL NO. OF CYCLES TO BE DONE                         REL00100
4)ITRIC-1 IF PROCEDURE CROSS IS TO BE AVOIDED-ONLY USED IN      REL00110
EARLY STAGES OF A TRICLINIC SOLUTION                         REL00120
5)NOSI-NO. OF SIGNED E'S TO BE INPUT                         REL00130
THE FORMAT USED IS F(5,3),4 F(5)                           REL00140
    THE REMAINDER OF THIS CARD AND ANY OTHER CARDS HAVE          REL00150
    THE SIGNED SERIAL NUMBERS OF THE INPUT E'S                  REL00160
    WITH FORMAT N F(5)                                         REL00170
    IN ADDITION, THE TWO TAPES WRITTEN IN QUADS ARE NEEDED      REL00180
***** */REL00190
DCL TITLE CHAR(80); DCL IOTAP FILE SEQUENTIAL;                 REL00200
DCL CARD CHAR(80);                                         REL00210
DCL NIN(*) CTL;                                         REL00220
DCL NOES,LA,II,JJ,NTOTCY,NIL,JA,NINA,NINB,NOSI;           REL00230
DCL ARRAY[198,198] FLOAT DEC(6) EXTERNAL;                  REL00240
DCL AEQ,ADFS,CUM,DPROB;                                     REL00250
DCL ABEL(7) LABEL;                                         REL00260
DCL NCYCLES INITIAL(1);                                     REL00270
DCL 1 QUAD,2 NA(4) FIXED BINARY(31),2 SIGN;             REL00280
DCL KIND;                                         REL00290
/* INPUT INFORMATION */
    GET EDIT(TITLE)(A(80));
    PUT EDIT(TITLE)(SKIP, A(80));
        GET EDIT(ADFS,NOES,NTOTCY,ITRIC,NOSI)(F(5,3),4 F(5)); REL00330
    PUT EDIT('PROB. LIMIT=',ADFS,'NO. OF E S=',NOES,'NO. OF CYCLES=', REL00340
        NTOTCY,'NO. OF INPUT SIGNS',NOSI)(SKIP,A(12),F(5,3),A(11),F(5), REL00350
        A(14),F(5),A(19),F(5));
        ARRAY=0.0;                                         REL00360
                                                               REL00370

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```

ON ENDFILE(IOTAP) GO TO NUEQUAL; REL00380
IF NOSI=0 THEN GO TO CYCLE; REL00390
ALLOCATE NIN(NOES); REL00400
  NIN=0; REL00410
    DO N=1 TO NOSI; GET EDIT(NIN(N))( F(5)); END; REL00420
CYCLE: IF NCYCLES=3 THEN GO TO CYCLE1; IF NOSI=0 THEN GO TO CYCLE1; REL00430
  DO N=1 TO NOSI; DO J=N TO NOSI; REL00440
    NINA=ABS(NIN(J)); NINB=ABS(NIN(N)); REL00450
    ARRAY(NINA,NINB)=((NIN(J)*NIN(N))/(NINA*NINB)); REL00460
    ARRAY(NINB,NINA)=((NIN(J)*NIN(N))/(NINA*NINB)); REL00470
  END; REL00480
    PUT EDIT( NIN(N))(SKIP, F(5)); END; REL00490
CYCLE1: DO N=1 TO NOES; ARRAY(N,N)=1.0; END; REL00500
ST: READ FILE(IOTAP) INTO (QUAD); REL00510
/* START CALCULATION OF THE SIGNS */
  DO K=1 TO 4; IF NA(K)>NOES THEN GO TO ST; REL00520
    IF NA(K)=0 THEN GO TO ST; END; REL00530
    DO L=1 TO 3; DO N=2 TO 4; KIND=0; REL00540
      IF L>= N THEN GO TO CONT; REL00550
      CALL CHECK; REL00560
        IF KIND=1 THEN GO TO LABLER; REL00570
        ELSE GO TO CONT; REL00580
LABLER: NIL=(L+2*N)-4; REL00590
  GO TO ABEL(NIL); REL00600
  ABEL(1): JA=NA(3); LA=NA(4); GO TO SIGNER; REL00610
  ABEL(3): JA=NA(2); LA=NA(4); GO TO SIGNER; REL00620
  ABEL(4): JA=NA(1); LA=NA(4); GO TO SIGNER; REL00630
  ABEL(5): JA=NA(2); LA=NA(3); GO TO SIGNER; REL00640
  ABEL(6): JA=NA(1); LA=NA(3); GO TO SIGNER; REL00650
  ABEL(7): JA=NA(1); LA=NA(2); GO TO SIGNER; REL00660
  ABEL(2): PUT EDIT(' ERROR IN SEARCH')(SKIP,A(16)); GO TO OUT; REL00670
SIGNER: IF ARRAY(JA,LA)=0 THEN GO TO ASSIG; BCUM=ABS(ARRAY(JA,LA)); REL00680
  ACUM=ABS(CUM); IF ARRAY(JA,LA)*CUM<0.0 THEN GO TO DIFFER; REL00690
  DPR0B=1.0-ACUM-BCUM+2.0*ACUM*BCUM; REL00700
  CUM=(CUM*ACUM*BCUM)/(DPR0B*ACUM); REL00710
  GO TO ASSIG; REL00720
DIFFER: CUM=0; REL00730

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ASSIG: ARRAY(JA,LA)=CUM;
        ARRAY(LA,JA)=CUM;
CONT: END; END; GO TO ST;
/* DETERMINATION OF SIGNIFICANCE OF E RELATIONS */
NUEQUAL: DO II=1 TO NOES; DO JJ=1 TO NOES;
           IF II>=JJ THEN GO TO ELOOP;
           AEQ=ARRAY(II,JJ); IF ABS(AEQ)>AOFS THEN
/* OUTPUT OF RELATED E'S */
           PUT EDIT(' THE SIGN OF',II,'EQUALS THE SIGN',JJ,'****',AEQ,
           'PROBS')(SKIP, A(12),F(4),A(15),F(4),A(3),F(8,4), A(5));
           ELSE DO; ARRAY(II,JJ)=0.0; ARRAY(JJ,II)=0.0; END;
ELOOP: END; END;
SKIP3:  NCYCLES=NCYCLES+1;
        IF ITRIC=1 & NCYCLES< NTOTCY THEN GO TO TRIC;
        CALL PARITY;
        IF NCYCLES>NTOTCY THEN GO TO OUT;
        CALL CROSS;
TRIC: CLOSE FILE(IOTAP);
        PUT EDIT(' END OF CYCLE',NCYCLES)(SKIP, A(14),F(5));
        GO TO CYCLE;
/* CHECK: PROCEDURE FOR CALCULATING PROBABILITIES */
CHECK: PROC;
        CUM=ARRAY(NA(L),NA(N));
        CUM=CUM*SIGN;
        IF ABS(CUM)>0.80 THEN KIND=1;
        RETURN; END CHECK;
/* CROSS: PROCEDURE TO RELATE E'S EQUAL TO A COMMON
   E BUT NOT EQUAL TO EACH OTHER */
CROSS: PROC;
        DCL IA,IB,IC,ID;
        DCL AJ,BJ,CJ,DJ,EJ,FJ,GJ;
        DCL CRS(9); DCL NCR(9),MCR(9); DCL KKK INITIAL(0);
        PUT EDIT('OUTPUT FROM CROSS CHECK IN CYCLE',NCYCLES)(SKIP, A(32)
           ,F(3));
        DO IA=1 TO NOES; ID=IA+1; DO IB=ID TO NOES;
           AJ=ARRAY(IA,IB); IF ABS(AJ)<AOFS THEN GO TO DONE;
           DO IC=1 TO NOES; IF IC=IA|IC=IB THEN GO TO DONEA;

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REL00750
 REL00760
 REL00770
 REL00780
 REL00790
 REL00800
 REL00810
 REL00820
 REL00830
 REL00840
 REL00850
 REL00860
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 REL00880
 REL00890
 REL00900
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 REL00930
 REL00940
 REL00950
 REL00960
 REL00970
 REL00980
 REL00990
 REL01000
 REL01010
 REL01020
 REL01030
 REL01040
 REL01050
 REL01060
 REL01070
 REL01080
 REL01090
 REL01100
 REL01110

```

        BJ=ARRAY(IB,IC); IF ABS(BJ)<AOFS THEN GO TO DONEA;           REL01120
        CJ=ARRAY(IA,IC);                                         REL01130
        IF ABS(CJ)<0.01 THEN DO; CJ=0.5; GO TO BEGAN; END;          REL01140
        IF CJ*AJ*BJ <0.0 THEN DO; ARRAY(IA,IC)=0.0;                REL01150
        ARRAY(IC,IA)=0.0; ARRAY(IC,IB)=0.0; ARRAY(IC,IA)=0.0;      REL01160
        ARRAY(IB,IC)=0.0; ARRAY(IA,IC)=0.0;                         REL01170
        PUT EDIT('INCONSISTENCY INOUNTERED',IA,IB,IC)(SKIP,A(25),
            3 F(5)); GO TO DONEA; END;                               REL01180
BEGAN:FJ=ABS(AJ*BJ); EJ=ABS(CJ); GJ=1.0-FJ-EJ+2.0*FJ*EJ;      REL01190
        IF GJ=0.0 THEN PUT EDIT(FJ,EJ,IA,IB,IC)(SKIP,2 F(5,3),3 F(5)); REL01200
        IF FJ>1.01|EJ>1.01 THEN DO; PUT EDIT(' ERROR IN CROSS ',FJ,
            IA,IB,IC)(SKIP,A(16),2 F(6,3),3 F(5)); GO TO DONEA; END; REL01210
        IF FJ<0.01 THEN FJ=1.0;                                     REL01220
        DJ=(FJ*EJ*AJ*BJ)/(GJ*FJ);                                REL01230
        IF ABS(DJ)>0.98 THEN DO;                                REL01240
        KKK=KKK+1;
        ARRAY(IA,IC)=DJ;                                         REL01250
        ARRAY(IC,IA)=DJ;                                         REL01260
        IF NCYCLES>NTOTCY THEN DO;                                REL01270
NCR(KKK)=IA; MCR(KKK)=IC; CRS(KKK)=DJ;                         REL01280
        IF KKK=9 THEN DO;                                         REL01290
        PUT EDIT((NCR(IK),'=',MCR(IK),CRS(IK),'*' DO IK=1 TO 9))
            (SKIP,9( F(3),A(1),F(3),F(5,3),A(2))); KKK=0; END; END; END; REL01300
        DONEA: END; DONE: END; RETURN; END CROSS;                REL01310
/*  PARITY: PROCEDURE TO DETERMINE ABSOLUTE SIGNS OF EEE TYPE E'S */ REL01320
PARITY: PROC;
        DCL NOTAP FILE SEQUENTIAL;                                REL01330
        DCL 1 EVENS,2 NNN(3) FIXED BINARY(31),2 PRD;             REL01340
        DCL JN INITIAL(0);                                         REL01350
        DCL INN(300,3); DCL PROD(300);                           REL01360
        DCL ABCD,DET,ASUM,BDTT;                                    REL01370
        DCL SUM INITIAL(0.0);                                     REL01380
        DCL I INITIAL(1);                                         REL01390
        DCL CAR CHAR(1);                                         REL01400
        INN(1,1)=99;                                            REL01410
        ON ENDFILE(NOTAP) GO TO PINK;                            REL01420
RED: READ FILE(NOTAP) INTO(EVENS); IF NNN(1)>NOES(NNN(1)=0 THEN REL01430

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GO TO PINK; REL01490
 IF NCYCLES=NTOTCY THEN PUT EDIT(EVENS)(SKIP,3 F(5),F(5,3)); REL01500
 DO K=1 TO 3; IF NNN(K)>NOES THEN GO TO RED; END; I=I+1; REL01510
 INN(I,1)=NNN(1); INN(I,2)=NNN(2); INN(I,3)=NNN(3); PROD(I)=PRD; REL01520
 SKIP2: IF INN(I,1)=INN(I-1,1) THEN GO TO WORK; REL01530
 BLUE: ABCD=ABS(ARRAY(INN(I,2),INN(I,3))*PRD); ASUM=ABS(SUM); REL01540
 IF SUM=0.0 THEN GO TO STRIKE; IF ABCD<0.01 THEN GO TO RED; REL01550
 IF SUM*ARRAY(INN(I,2),INN(I,3))*PRD>0.0 THEN REL01560
 SUM=(SUM*ASUM*ABCD)/((1.0-ASUM-ABCD+2.0*ASUM*ABCD)*ASUM); ELSE REL01570
 SUM=0.0; GO TO RED; REL01580
 STRIKE: SUM=ARRAY(INN(I,2),INN(I,3))*PRD; GO TO RED; REL01590
 WORK: IF SUM>0.0 THEN CAR='+'; ELSE CAR='-';
 PUT EDIT (' THE PROBABILITY THAT',INN(I-1,1),' IS ',CAR,' IS',
 SUM)(SKIP,A(21),F(3),A(4),A(1),A(3),F(5,3)); REL01600
 IF ABS(SUM)<0.99 THEN GO TO SMALL; REL01610
 DO N=1 TO I-1;
 DET=ARRAY(INN(N,3),INN(N,2)); REL01620
 IF DET=0.0 THEN DO; DET=PROD(N)*SUM; GO TO EVALU; END; REL01630
 IF DET*SUM*PROD(N)<0.0 THEN DO; DET=0.0; GO TO EVALU; END; REL01640
 BOTT=1.0-ABS(PROD(N)*SUM)-ABS(DET)+2.0*PROD(N)*SUM*DET; REL01650
 DET=(PROD(N)*DET*SUM*DET)/(BOTT*ABS(DET)); REL01660
 EVALU: IF DET> A0FS THEN DO;
 ARRAY(INN(N,3),INN(N,2))=DET; REL01670
 ARRAY(INN(N,2),INN(N,3))=DET; END; REL01680
 PUT EDIT(DET)(SKIP, F(6,3)); END; REL01690
 SMALL: IF JN=1 THEN GO TO COMP; REL01700
 INN(1,*)=INN(I,*); PROD(1)=PROD(I); I=1; SUM=0.0; GO TO BLUE; REL01710
 PINK: JN=1; IF I=1 THEN I=2; GO TO WORK; REL01720
 COMP: CLOSE FILE (NOTAP); RETURN; END PARITY; REL01730
 OUT: END RELATE; REL01740
 REL01750
 REL01760
 REL01770
 REL01780

APPENDIX C. RESEARCH PROPOSALS

In this appendix are presented a few proposals of additional structure work which are of interest to the author. These are intended to be preliminary in nature and no experimental details will be given.

It would seem unlikely in solution that the bridging NTA oxygen-rare earth bonds would be formed. Instead, these coordination sights would probably be occupied by solvent molecules. The act of crystallization could well involve replacement of these solvent molecules which are then trapped in the forming lattice. It would be of interest to carry out a diffraction study of these complexes in aqueous solution to test this hypothesis. In addition, the large number of apparent hydrogen bonds would make a neutron diffraction study of interest.

Most of the rare earth compounds which have been studied by diffraction techniques have been complexes formed with highly electronegative species such as oxygen or chlorine atoms. To be better able to evaluate the role of covalent bonding, complexes formed with less electronegative ligands, such as urotropin or thiocyanate, could be studied.

Many antibiotics are of moderate molecular weight and are crystalline in nature. Therefore, they would lend well to study by diffraction techniques. In addition, many are well characterized as to their mode of inhibition of bacterial growth. Several antibiotics with similar modes

of inhibition could be selected for structural study to determine what features they have in common. Idealistically, this information could be used in the synthesis of biologically active analogs.