IS-434

Contribution No. 1134 from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

Stability Constants and Intrinsic Solubility of Several Nickel(II)-*vic*-Dioxime Complexes[1]

By Charles V. Banks and Samuel Anderson*

Introduction

It was suggested by Godycki and Rundle[2] that the nickel-nickel bonding which occurs in the crystals of the nickel(II)-*vic*-dioxime complexes makes a significant contribution to the stability of these crystals and thus explains their limited solubility. Frasson, Bardi, and Bezzi[3] have shown that in copper(II) dimethylglyoxime, Cu(DMG)$_2$, the copper is bonded to four nitrogen atoms and with an oxygen atom in a nearby molecule

---

(1) Paper No. XXIX in a series on "Chemistry of the *vic*-Dioximes." Previous paper in this series was No. XXVIII, "Proceedings of the Symposium." Abstracted from dissertation submitted by Samuel Anderson to graduate faculty of Iowa State University in partial fulfillment of requirements for the degree of doctor of philosophy, 1962.

(2) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, *6*, 487 (1953).

(3) E. Frasson, R. Bardi, and S. Bezzi, *Acta Cryst.*, *12*, 201 (1959).

* Present address: Department of Chemistry, Tennessee A and I State University, Nashville 8, Tennessee.

Facsimile Price $ 1.60
Microfilm Price $ .80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

DISCLAIMER

forming a dimer. Fleischer[4] and also Dyrssen and Hennichs[5] have concluded that the large difference in water-solubility between $Cu(DMG)_2$ and nickel dimethylglyoxime, $Ni(DMG)_2$, must be due to the greater tendency of the $Cu(DMG)_2$ to become solvated.

Frasson and Panatoni[6] have shown that in nickel ethylmethylglyoxime, $Ni(EMG)_2$, the packing system is completely different from that in $Ni(DMG)_2$. The nickel-nickel direction is not perpendicular to the plane of the molecule and the nickel-nickel distance (4.75 Å.) is so great that nickel-nickel bonding is not possible. Also the distance between the nickel and the closest oxygen of an overlying molecule is much too great (3.44 Å.) to involve coordination. Banks and Anderson[7], in a study of the heats of solution of $Ni(DMG)_2$ and $Ni(EMG)_2$, found that the crystal of $Ni(DMG)_2$ is about 10 kcal. more stable than that of $Ni(EMG)_2$. This difference in the stabilities of the crystals was attributed to nickel-nickel bonding in $Ni(DMG)_2$.

Banks and Barnum[8] determined the solubility product constant,

---

(4) D. Fleischer, Ph.D. Thesis, Univ. Pittsburgh, 1959. Univ. Microfilms 59-2396, Ann Arbor, Michigan.

(5) D. Dyrssen and M. Hennichs, Acta Chem. Scand., 15, 47 (1961)

(6) E. Frasson and C. Panatoni, Acta Cryst., 13, 893 (1959).

(7) C. V. Banks and S. Anderson, Unpublished work.

(8) C. V. Banks and D. W. Barnum, J. Am. Chem. Soc., 80, 3579 (1958).

and the nickel-nickel bond length for several nickel(II) vic-dioximes in order to ascertain if and how these properties were related. They suggested that the limited correlation which they obtained might be caused by the fact that the solubility product constant depends on the instability constant and on the intrinsic solubility constant of the nickel complex, i.e., $K_{sp} = \frac{K_s}{K_2}$ where K_{sp} = solubility product, K_s = intrinsic solubility constant, and K_2 = over-all stability constant.

The value of the intrinsic solubility of the nickel(II) vic-dioxime complexes can be calculated from a knowledge of the solubility product constant and the stability constant. The purpose of this work was to determine the stability constants for several nickel(II)-vic-dioximes and calculate their intrinsic solubility constants.

The low solubility of the nickel(II) complexes of the vic-dioximes in water makes it desirable to use mixtures of water and organic solvents to determine their stability. Calvin and Wilson[9] employed the glass electrode in 50% (v/v) dioxane-water mixtures for pH measurements in order to determine the stability constants of metal-ligand complexes of low solubility.

Charles and Freiser[10] have measured the stability constants

---

(9) M. Calvin and K. W. Wilson, J. Am. Chem. Soc., 67, 2003 (1945).

(10) R. G. Charles and H. Freiser, Anal. Chim. Acta, 11, 101 (1954).

of the nickel(II) complexes of dimethylglyoxime and its monomethyl ether in 50% (v/v) dioxane-water mixtures. They found that the nickel(II) complex of dimethylglyoxime is more stable than the corresponding complex with the monomethyl ether, presumably because no hydrogen bonding could be present in the latter case.

Christopherson and Sandell[11] have determined the stability constant of nickel(II) dimethylglyoxime in water solution using solubility data.

Bochkova and Peshkova[12] have used pH measurements to determine the stability constants of the nickel(II), copper(II), and cobalt(II) complexes of dimethylglyoxime in 50% (v/v) dioxane-water mixtures.

Van Uitert and Fernelius[13] determined the stability constant for $Ni(DMG)_2$ in 75% dioxane-25% water (v/v) mixtures at 30°C.

In order to use pH measurements to determine the stability constants of a metal-ligand complex, it is necessary that the acid dissociation constant of the ligand be known. Banks and Carlson[14] have determined the acidic dissociation constants of

---

(11) H. Christopherson and E. B. Sandell, Anal. Chim. Acta, 10, 1 (1954).

(12) V. M. Bochkova and V. M. Peshkova, Zhur. Neorg. Khim., 3, 1131 (1958).

(13) L. G. Van Uitert and W. C. Fernelius, J. Am. Chem. Soc., 76, 375 (1953).

several vic-dioximes in water solution. Several other workers[8,11,15,16] also have determined the acid dissociation constants for several vic-dioximes in water.

Several workers[10,12,13] have determined the acid dissociation constant of dimethylglyoxime in dioxane-water mixtures.

Theory

The stability constants of nickel(II)-vic-dioxime complexes are defined as follows:

$$k_i = \frac{[M(HD)_i^{2-i}]}{[M(HD)_{i-1}^{3-i}][HD^-]} \qquad (1)$$

$$K_i = \frac{[M(HD)_i^{2-i}]}{[M^{+2}][HD^-]^i} \qquad (2)$$

where M = divalent metal ion,
HD^- = the singly ionized species of any of the vic-dioximes,
k_i = the step-wise stability constant of the ith complex,
K_i = the over-all stability constant of the ith complex.

The formation function[17] is given by equation 3,

---

(14) C. V. Banks and A. B. Carlson, Anal. Chim. Acta, 7, 291 (1952)

(15) A. K. Babko and P. B. Mikhelson, Zhur. Anal. Khim., 6, 267 (1951).

(16) P. E. Wenger, D. Monnier, and W. Bachmann-Chapuis, Anal. Chim. Acta, 15, 473 (1956).

(17) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

$$\bar{n} = \frac{K_1[HD^-] + 2K_2[HD^-]^2}{1 + K_1[HD^-] + K_2[HD^-]^2} = \frac{[H_2D]_T - [HD^-][1 + H/Ka]}{(M)_T} \qquad (3)$$

where the subscript T refers to the total concentration of the species in the system. The stability constants may be calculated from appropriately selected pairs of $\bar{n}$ and $[HD^-]$ values.

The extremely low solubility of the nickel(II)-vic-dioxime complexes precludes the determination of the stability constants by pH measurements in aqueous solution or by the extrapolation of values measured in various concentrations of mixed solvents to pure water. A 75% dioxane-25% water (v/v) solvent was chosen because it dissolved all of the nickel(II)-vic-dioxime complexes studied.

The relationship between the stability of metal-ligand complexes in water solution and in organic solvent-water mixtures has been investigated by Irving and Rossotti[18]. They have shown that equation 4 expresses approximately this relationship,

$$\log K_1 = \log \bar{K}_1 - (p\bar{K}a_1 - pKa_1) \qquad (4)$$

where K_1 represents the constant in water and $\bar{K}_1$ represents the constant in the mixed solvent. This same symbolism will be used for all equilibrium constants discussed in this work.

Equation 4 applies only to the stability of the 1:1 complex but approximations for 1/2 log K_2 can be obtained by using 1/2 log $\bar{K}_2$.

---

(18) H. Irving and H. Rossotti, Acta Chem. Scand., 10, 72 (1956).

The solubility product constant, K_{sp}, the over-all stability constant, K_2, and the intrinsic solubility constant, K_s, for the nickel(II)-vic-dioxime complexes are related as follows:

$$\begin{tikzcd}
Ni(HD)_{2(c.)} \arrow[r, "K_s"] \arrow[d, "K_{sp}"'] & Ni(HD)_{2(aq.)} \\
Ni^{++}_{(aq.)} + 2HD^{-}_{(aq.)} \arrow[ur, "K_2"'] &
\end{tikzcd}$$

The equations for the derivation of the solubility product constant of nickel(II)-vic-dioximes have been reported by Banks and Barnum[8]. The expression for the solubility product constant is then

$$K_{sp} = \frac{K_{a_1}^{2}}{a_{H^+}^{2}}\left[[Ni]_T f_{Ni^{++}} - \frac{a_{H^+} f_{Ni^{++}}}{2f_{H^+}}\right]\left[2[Ni]_T - \frac{a_{H^+}}{f_{H^+}}\right]^2 \qquad (5)$$

where K_{a_1} is the first acid dissociation constant for the vic-dioxime, and $[Ni]_T$ is the total amount of nickel in mole per liter, regardless of the species in which it exists.

Experimental Work

Apparatus and Reagents. - The pH measurements were made with a Beckman Model G pH meter. Beckman Type E glass and Beckman No. 1190-80 calomel electrodes were used. The pH meter was calibrated with Beckman standard buffer solution (pH 7.00) and with solutions prepared from Beckman buffer powders (pH 4.01, pH 9.18). All work was performed at a thermostatically controlled room temperature of 25°C. All glassware used was of class A specification. Rapid mixing of solutions was achieved by means of a magnetic stirrer which was stopped during the actual pH measurements.

Calculations of stability constants were made on a Magnetic Drum Data-Processing Machine, Type 650, manufactured by International Business Machines Corporation. The programing system used was a floating decimal interpretive system designed by Wolontis[19].

Dimethylglyoxime was obtained from the Matheson Company. Nioxime[20], heptoxime[21], 3-methylnioxime, 4-methylnioxime, and 4-isopropylnioxime[22], diethylglyoxime and di-*n*-propylglyoxime[23,24,25] were prepared by published procedures. Each of

---

(19) V. M. Wolontis, International Business Machines Corporation Technical Newsletter, No. 11 (1956).

(20) C. C. Hach, C. V. Banks, and H. Diehl, *Organic Synthesis*, **32**, 35 (1952).

(21) R. W. Vander Haar, R. C. Voter, and C. V. Banks, *J. Org. Chem.*, **14**, 836 (1949).

(22) C. V. Banks, D. T. Hooker, and J. J. Richard, *J. Org. Chem.*, **21**, 547 (1956).

(23) J. M. Snell and S. M. McElvain, *Organic Synthesis Collective*, **2**, 114 (1943).

(24) J. Wegmann and H. Dahn, *Helv. Chim. Acta*, **29**, 111 (1946).

(25) W. M. D. Bryant and D. M. Smith, *J. Am. Chem. Soc.*, **57**, 57 (1935).

the vic-dioximes was recrystallized at least three times from alcohol-water mixtures and dried in a vacuum oven at 40°C. before use.

A standard solution of nickel(II) perchlorate was prepared by dissolving Mond nickel in aqua-regia, evaporating to near dryness with perchloric acid, diluting and standardizing by precipitation with dimethylglyoxime. The sodium perchlorate which was used for controlling the ionic strength of all equilibrium solutions was reagent-grade sodium perchlorate obtained from the G. Frederick Smith Chemical Company. All solutions were prepared by weight.

Sodium hydroxide solutions were prepared from Fisher Chemical Company "certified reagent grade" and were standardized against primary standard potassium acid phthalate. The perchloric acid was standardized by comparison with the standard sodium hydroxide solution.

The dioxane was purified by using the method described by Vogel[26].

Cobalt(II) and copper(II) solutions were standardized by titrating with standard ethylenediaminetetraacetic acid.

$\bar{n}$ and [HD^-] Values. - The values of $\bar{n}$ and [HD^-] were determined at an ionic strength of 0.1 in 75% dioxane-25% water (v/v) mixtures.

---

(26) A. I. Vogel, "A Text-Book of Practical Organic Chemistry," Longmans, Green and Co., New York, 1948.

A solution containing nickel(II) perchlorate and a large excess of ligand was titrated with a sodium hydroxide solution. A second solution containing the same amount of ligand as was present in the above solution was titrated with the same sodium hydroxide solution. In the presence of a large excess of ligand, the difference in the amounts of base required to reach the same pH in the two titrations, ΔV, is a measure of the amount of ligand bound to the metal because under these conditions $[HD^-]$ is negligible in comparison with $[H_2D]_T - \left[[Ni(HD)^+] + 2[Ni(HD)_2]\right]$. The change in ionic strength due to addition of base and dioxane was about 7%. According to Ringbom[27], the corrections to be applied for change in activity coefficients can be neglected for solutions which have an ionic strength of the order of 0.1 or higher, provided the volume change is small. The hydrolysis of the nickel(II) ion is not appreciable at the pH values used in this study[28]. No precipitation of the metal-ligand complex occurred during any of the titrations except for nickel(II)-nioxime mixtures. No data taken after precipitation had occurred were used in the calculations.

Values for $\bar{n}$ were calculated from the amount of ligand complexed and the total analytical concentration of nickel ions in solution. The concentration of the ligand, $[HD^-]$, was

---

(27) A. Ringbom, *J. Chem. Educ.*, *35*, 282 (1958).

(28) F. Achenza, *Ann. Chim.*, *49*, 624 (1959).

calculated from equation 6.

$$[HD^-] = \frac{Ka_1[H_2D]}{[H^+]} = \frac{Ka_1\left[[H_2D]_T - [NiHD^+] - 2[Ni(HD)_2]\right]}{[H^+]}$$

$$= \frac{Ka_1\left[[H_2D]_T - \frac{(\Delta V)N}{V}\right]}{[H^+]} \qquad (6)$$

$p\overline{K}a_1$ and pKa_1 Values. - The first acid dissociation constants of the various vic-dioximes were measured in dioxane-water mixtures by titration with sodium hydroxide solutions under the same conditions used for titrating the metal and the ligand. The change in the volume of the solutions was never greater than 4% so that corrections for changes in activity coefficients were considered negligible. In order to avoid the replacement of more than one of the dioxime hydrogen, only about one tenth mole of base per mole of vic-dioxime was added. During the titration, increments of dioxane were added in order to keep the dioxane content constant. Nitrogen, saturated with water vapor, was passed over the solution during the titration. The magnetic stirrer used for mixing was turned off during the actual measurements of pH.

The acid dissociation constants of the vic-dioximes in water were determined by measurements in several concentrations of dioxane. The $p\overline{K}a_1$ was plotted against the percentage of dioxane and extrapolated to zero concentration of dioxane. Linear functions were obtained for all the vic-dioximes studied.

$p\overline{K}_{NH}$ Values. - The $p\overline{K}_{NH}$ (basicity of the oxime nitrogen) was determined in dioxane-water mixtures for each vic-dioxime studied by titrating a known amount of vic-dioxime with a standard acid solution. In all cases, the $p\overline{K}_{NH}$ was less than 2 which indicated negligible basicity of the oxime nitrogen.

Calculation of log $\overline{K}_i$ Values. - The data for the calculations of the stability constants for the nickel(II)-dimethylglyoxime complexes are given in Table 1. Similar data were obtained for the other nickel(II)-vic-dioxime complexes. The equilibrium constants calculated from these data are given in Table 2. The stability constants were calculated by using appropriately selected pairs of $\bar{n}$ and $[HD^-]$ values and solving a system of two simultaneous equations. For a single titration, a value of $\overline{K}_1$ and $\overline{K}_2$ may be calculated for each pair of $\bar{n}$ and $[HD^-]$ values selected.

Table 1

Titration of Nickel(II)-Dimethylglyoxime Mixtures with Sodium Hydroxide[a]

Ml. NaOH, ΔV^b	pH	$\bar{n}$	$-\log [HD^-]$
		Titration I[c]	
0.500	3.97	0.437	11.69
0.600	3.99	0.524	11.67
0.700	4.01	0.611	11.65
0.800	4.03	0.698	11.64
0.900	4.03	0.787	11.64
1.000	4.04	0.874	11.63
1.100	4.06	0.966	11.61
1.200	4.12	1.05	11.55
1.300	4.16	1.13	11.51
1.400	4.22	1.22	11.45
1.500	4.28	1.31	11.40
1.600	4.34	1.40	11.34
1.700	4.42	1.48	11.25
1.800	4.48	1.57	11.20

Table 1 (Concluded)

Ml. NaOH, ΔV^b	pH	$\bar{n}$	-log [HD^-]
		Titration II[d]	
0.050	3.75	0.319	11.92
0.080	3.95	0.510	11.72
0.090	4.00	0.574	11.67
0.120	4.10	0.766	11.57
0.140	4.15	0.893	11.52
0.165	4.20	1.05	11.47
0.200	4.30	1.276	11.37
0.240	4.40	1.53	11.27
0.280	4.50	1.786	11.17
		Titration III[d]	
0.080	3.75	0.510	11.92
0.120	3.90	0.766	11.77
0.140	4.00	0.893	11.67
0.180	4.10	1.15	11.57
0.210	4.20	1.34	11.47
0.230	4.25	1.47	11.42
0.250	4.30	1.59	11.37

[a] 75% dioxane-25% water, $\mu = 0.1$, T = 25°, $[H_2D]_T = 7.18 \times 10^{-4}$ M, $[Ni]_T = 1.162 \times 10^{-4}$ M.

[b] [NaOH] = 0.01014 M.

[c] The difference in volume of sodium hydroxide solution required to titrate the ligand alone and the nickel(II)-ligand mixture to the same pH.

[d] [NaOH] = 0.07410 M.

Table 2

Acid Dissociation Constants of Several *vic*-Dioximes and the Stability Constants of Their Nickel(II) Complexes in 75% Dioxane-25% Water Mixtures[a]

vic-Dioxime	$p\bar{K}a_1$	log $\bar{K}_1$	log $\bar{K}_2$
Dimethylglyoxime	13.53	10.96 ± .34	23.10 ± .14
Diethylglyoxime	13.93	12.43 ± .20	23.69 ± .13
Di-*n*-propylglyoxime	14.18	13.14 ± .35	23.86 ± .65
Ethylmethylglyoxime	13.55	10.41 ± .52	23.97 ± .03

Table 2 (Concluded)

vic-Dioxime	$p\bar{K}a_1$	log $\bar{K}_1$	log $\bar{K}_2$
4-Isopropylnioxime	12.27	10.06 ± .31	20.44 ± .18
Nioxime	13.11	11.08 ± .19	22.46 ± .10
4-Methylnioxime	13.07	10.76 ± .30	23.00 ± .27
3-Methylnioxime	13.23	11.28 ± .12	23.52 ± .09
Heptoxime	13.33	12.26 ± .19	24.68 ± .23

[a] All constants were determined at 25°C. and at ionic strength 0.1.

Calculation of log K_i Values. - Values for log K_1 and 1/2 log K_2 were calculated from the corresponding values for log $\bar{K}_1$ and 1/2 log $\bar{K}_2$ by means of equation 4. In order to show that equation 4 gives a good approximation for the stability constant of $Ni(DMG)_2$ in water solution, the stability constants of $Cu(DMG)_2$ and $Co(DMG)_2$ were determined in water, in 50% dioxane-water (v/v) and in 75% dioxane-25% water (v/v) mixtures. Thus, a comparison of the values of ($p\bar{K}a_1$ - pKa_1) for dimethylglyoxime as determined experimentally and as determined from the stability constants of $Cu(DMG)_2$ and $Co(DMG)_2$ in water and in dioxane-water mixtures should serve as a good check on the applicability of equation 4. These results are shown in Table 3. The average value of the term, ($p\bar{K}a_1$ - pKa_1), calculated from equation 4 for 50% dioxane-water (v/v) is 2.13 compared to the value of 2.07 which was determined experimentally. The average calculated value of the term for 75% dioxane-25% water (v/v) is 2.83 compared to the value of 3.05 which was determined experimentally.

Table 3

Stability Constants of Copper(II)- and Cobalt(II)-Dimethylglyoxime Complexes in Dioxane-Water Mixtures and Values of $(p\bar{K}a_1 - pKa_1)$

% Dioxane	log K_1	1/2 log K_2	$(p\bar{K}a_1 - pKa_1)^a$	$(p\bar{K}a_1 - pKa_1)^b$
		Copper(II)		
0	9.05	9.25	-	-
50	11.94[c]	11.66[c]	2.41	2.07
75	12.23	12.17	2.92	3.05
		Cobalt(II)		
0	8.35	8.49	-	-
50	11.01	10.34	1.85	2.07
75	12.20	11.22	2.73	3.05

[a] Calculated using equation 4 and values of 1/2 log K_2.

[b] Calculated from experimentally determined values of $p\bar{K}a_1$ and pKa_1.

[c] Values taken from work of Charles and Freiser[10].

Because the various *vic*-dioximes included in this study are very similar, the assumption is made that equation 4 is also applicable for other nickel(II)-*vic*-dioxime complexes.

The stability constants in water were calculated from the stability constants in 75% dioxane-25% water (v/v) and $(p\bar{K}a_1 - pKa_1)$. The results are given in Table 4.

Table 4

Acid Dissociation Constants of vic-Dioximes and Stability Constants of Nickel(II)-vic-Dioxime Complexes in Water Solution

vic-Dioxime	pKa_1	$(p\bar{K}a_1-pKa_1)$	$\log k_1$	$\log k_2$	$\log K_2$	Ref.
Dimethylglyoxime	10.48	3.05	7.91	9.09	17.00	a
	10.6					14
	10.46				17.23	29
	10.66					11
	11.1					15
Ethylmethylglyoxime	10.41	3.14	7.27	9.99	17.26	a
Diethylglyoxime	10.67	3.26	8.97	8.20	17.17	a
Di-n-propylglyoxime	10.81	3.27	8.77	8.35	17.12	a
4-Isopropylnioxime	10.53	1.74	8.42	8.34	16.76	a
Nioxime	10.55	2.56	8.52	8.82	17.34	a
	10.6					14
	10.4					16
3-Methylnioxime	10.61	2.62	8.66	9.62	18.28	a
4-Methylnioxime	10.54	2.53	8.27	9.71	17.94	a
Heptoxime	10.71	2.62	9.62	9.81	19.44	a
	10.7					14

[a] Values from this work.

---

(29) D. Dyrssen, F. Krasovec, and L. G. Sillen, Acta Chem. Scand., 13, 50 (1959).

Calculation of pK_s. - The intrinsic solubility constants for the nickel(II) complexes of dimethylglyoxime, nioxime, 4-isopropylnioxime, 3-methylnioxime, 4-methylnioxime, and heptoxime were calculated from the values of K_{sp} from this work, the work of Banks and Barnum[8] and the calculated values of K_2. These values for pK_s are reported in Table 5.

Table 5

Values of the Intrinsic Solubility, Nickel-Nickel Bond Length, Solubility Product and Over-All Stability Constant for the Nickel(II) Complexes of Several _vic_-Dioximes

vic-Dioxime	pK_s	Ni-Ni Bond Length in Å.[a]	pK_{sp}	$\log K_2$
Dimethylglyoxime	6.66	3.233	23.66	17.00
Ethylmethylglyoxime	5.70	b	23.27	17.57
Diethylglyoxime	6.96	c	24.21	17.17
Dipropylglyoxime	8.02	c	25.14	17.12
4-Isopropylnioxime	11.08	3.19	27.84	16.76
Nioxime	11.06	3.237	28.39	17.34
4-Methylnioxime	10.32	3.24	28.25	17.94
3-Methylnioxime	9.34	3.47	27.62	18.28
Heptoxime	7.20	3.596	26.64	19.44

[a] Values taken from work of Banks and Barnum[8].
[b] Does not form nickel-nickel bonds[6].
[c] Crystal structure has not been determined.

Solubility Product Constants. - Nickel perchlorate and the _vic_-dioxime were mixed in stoichiometric amounts, shaken at a room temperature of 25° for two hours and the pH measured. Between 0.100 and 1.00 ml. of 0.05874 _M_ nickel solution was added with a micro-pipet to a solution of the _vic_-dioxime. The volume of the sample was adjusted by adding a known amount of water. The ionic strength was adjusted by using a solution of sodium perchlorate. The values of the activity coefficients are those reported by Kielland[30]. The pH of the mixture was measured without filtering.

---

(30) J. Kielland, _J. Am. Chem. Soc._, _59_, 1675 (1937).

The values for pK_{sp} are reported in Table 5.

Results and Discussion

The $p\overline{K}a_1$ values for the vic-dioximes vary in a linear manner with the dioxane content of the solvent mixture. As is to be expected, the acid dissociation constant decreases as the dielectric constant of the solvent mixture decreases.

When a comparison is made of the stability constants of the nickel(II)-vic-dioxime complexes in Table 2, one observes that all have values of the same order of magnitude. This is to be expected because the nature of the ligand does not change significantly. If the alicyclic and the aliphatic series are considered separately, one observes that, in general, an increase in stability constant follows a decrease in the acid dissociation constant.

Excluding $Ni(DMG)_2$ and nickel(II) 4-methylnioxime, there appears to be a smooth relationship between the intrinsic solubility constant and nickel-nickel bond distance in the crystals of the nickel(II) complexes of nioxime, 4-isopropylnioxime, 3-methylnioxime, and heptoxime (Table 5 and Figure 1). A similar relationship is shown for the solubility product constant and the nickel-nickel bond distance for the complexes. A long nickel-nickel bond distance results in a weak bond and less interaction between nickel atoms. Consequently, the intrinsic solubility constant of the complex would be expected to increase with increasing nickel-nickel bond distance.

The exceptionally low value of K_2 for nickel(II) isopropylnioxime causes K_{sp} to be low and could explain why this complex does not correlate with the solubility product constant. The reason for the failure of nickel(II) 4-methylnioxime to exhibit a smooth relationship with the other alicyclic <u>vic</u>-dioxime complexes is not known. It is possible that there is an error in the nickel-nickel distance or an error in the intrinsic solubility or both.

$Ni(DMG)_2$ is much more soluble than the corresponding complexes for the alicyclic <u>vic</u>-dioximes studied. This may be due in part to the nature of the ligand. It may be that $Ni(DMG)_2$ is more soluble because of greater solvation of the complex. The complexes of nickel diethylglyoxime, $Ni(DEG)_2$, and nickel dipropylglyoxime, $Ni(DPG)_2$, are not included on Figure 1 because their x-ray powder patterns indicate that they are not isostructural with $Ni(DMG)_2$.

The intrinsic solubility of $Ni(EMG)_2$ is greater than that of $Ni(DMG)_2$. This is not an unexpected result in view of the fact that $Ni(EMG)_2$ does not form nickel-nickel bonds[6]. Furthermore, it has been shown[7] that the crystal of $Ni(DMG)_2$ is more stable than that of $Ni(EMG)_2$ by about 10 kcal. and that this difference in the crystal energies is believed to be due to nickel-nickel bonding in the former complex.

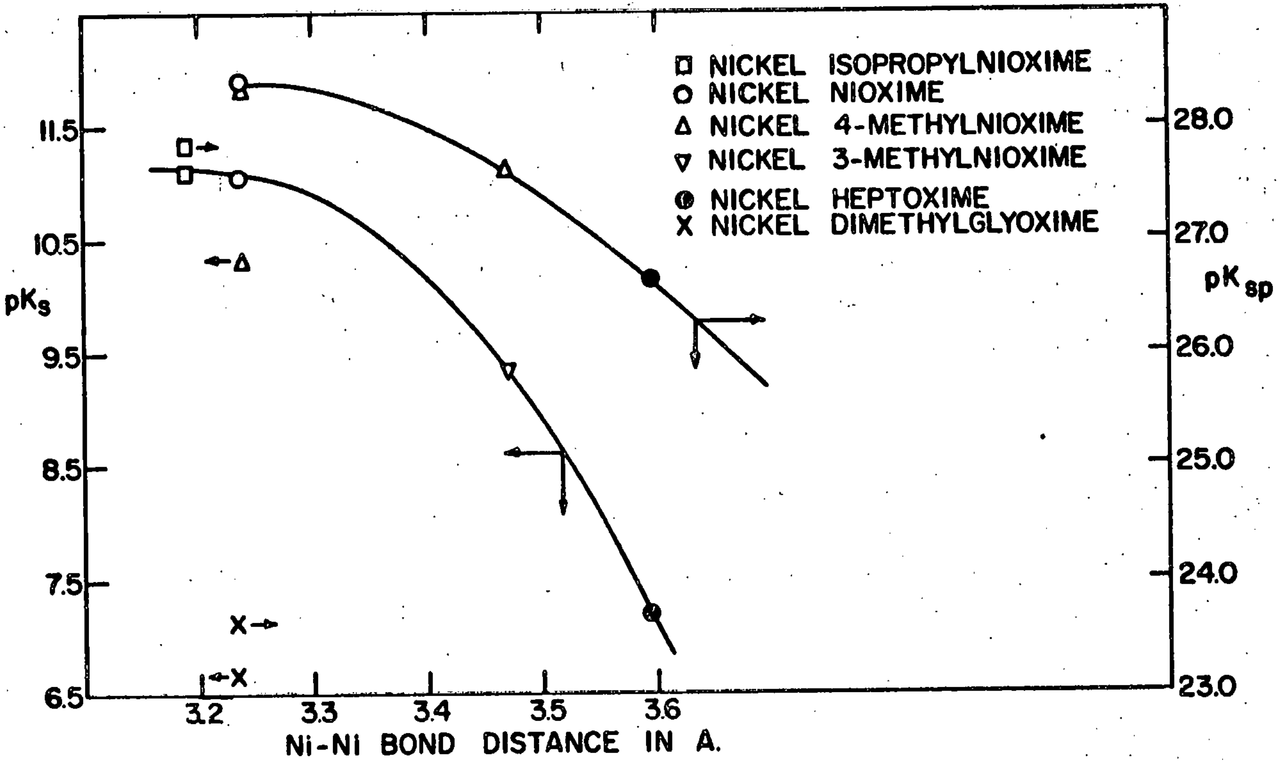

Fig. 1. - Dependence of pK_{sp} and pK_s on nickel-nickel bond distance in several nickel(II)-vic-dioxime complexes.