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A comparative study of the complexation of Np(V) with *N,N*-dimethyl-3-oxa-glutaramic acid and related ligands: thermodynamics, optical properties and structural aspects

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Complexation of Np(V) with *N,N*-dimethyl-3-oxa-glutaramic acid (DMOGA) was studied in comparison with its diamide analog, *N,N,N′,N′*-tetramethyl-3-oxa-glutaramide (TMOGA), and dicarboxylate analog, oxydiacetic acid (ODA). Thermodynamic parameters, inclduing the stability constant and the enthalpy of complexation, were determined by spectrophotometry and calorimetry. Single-crystal structure of $NpO_2(H_2O)(DMOGA)\cdot H_2O$(c) was identified by X-ray diffractometry using synchrotron radiation. Like ODA and TMOGA, DMOGA forms a tridentate Np(V) complex, with three oxygen atoms coordinating to the linear NpO_2^+ moiety *via* the equatorial plane. The stability constants, enthalpy and entropy of complexation generally decrease in the order ODA > DMOGA > TMOGA, suggesting that the complexation is entropy driven and the substitution of a carboxylate group with an amide group reduces the strength of complexation with Np(V) due to the decrease in the entropy of complexation.

Introduction

Alkyl-substituted amides have the potential to be used as extractants for actinide separations, making the separation processes more efficient and environmentally-benign than the traditional processes using organophosphorus compounds such as tributylphosphate. The products of radiolytic and hydrolytic degradation of amides are less detrimental to the separation processes and stripping of actinides from the amide-containing organic solvents is relatively easy. In addition, the amides consist of only C, H, O and N so that they are completely incinerable. Therefore, the amount of solid radioactive wastes generated in the amide-based processes could be significantly reduced.

A group of alkyl-substituted oxa-diamides, including tetraoctyl-3-oxa-glutaramide,[1,2] tetraisobutyl-oxa-glutaramide[3] and *N,N′*-dimethyl-*N,N′*-dihexyl-3-oxaglutaramide,[4] have been studied for actinide separation. These ligands form chelate complexes with actinides that can be effectively extracted from nitric acid solutions into organic solvents.[1-9] To help understand the thermodynamic principles and structural factors governing the complexation of actinides with oxa-amides, we have started systematic studies of three structurally-related ligands, including *N,N,N′,N′*-tetramethyl-3-oxa-glutaramide (TMOGA), *N,N*-dimethyl-3-oxa-glutaramic acid (DMOGA) and their dicarboxylate analog - oxydiacetic acid (ODA).[10,11] Thermodynamic parameters (stability constants, enthalpy and entropy of complexation) and structural data (crystal structure, coordination modes and vibration frequency) were obtained to establish a structure – property relationship.

DMOGA is the smallest homologue of dialkyl-oxa-glutaramic acids, a major group of hydrolytic and radiolytic products of tetraalkyl-oxa-glutaramides that also form complexes with actinides and affect their separation.[12] Thermodynamic parameters and the crystal structure of an Np(V) complex with DMOGA were obtained in this work. As shown in Figure 1, DMOGA is structurally related to TMOGA and ODA. Comparison of the thermodynamic trends for the Np(V) complexes with this series of ligands could provide insight into the energetics and driving force of the complexation (e.g., enthalpy, entropy or both) and help to design effective extractants for actinide separations.

Experimental

Chemicals

N,N-dimethyl-3-oxa-glutaramic acid (DMOGA) was synthesized from diglycolic anhydride and dimethyl ammonia (gas) in 1,4-dioxane with vigorous stirring below 5°C; and purified by re-crystallization from water. H-NMR(D_2O): 2.7-2.8, double peak (6H, -C(O)N-(C***H***$_3$)$_2$); 4.1, single peak (2H, HOOC-CH_2-O-C***H***$_2$-C(O)N-(CH_3)$_2$); 4.2, single peak (2H, HOOC-C***H***$_2$-O-CH_2-C(O)N-(CH_3)$_2$). Melting point: 80-82°C. All other chemicals were reagent grade or higher.

Milli-Q water was used in the preparation of all solutions. The stock solution of Np(V) in perchloric acid was prepared according to previous procedures.[13] Absorption spectra were collected to confirm that Np(V) was the only oxidation state in the stock solution. The concentration of Np(V) was determined by the absorbance at 980.2 nm (ε = 395 $M^{-1}\cdot cm^{-1}$). Gran's titration method[14] was used to determine the concentration of free acid in the Np(V) stock solution. The stock solution of DMOGA was prepared by dissolving appropriate amounts of DMOGA in water. The concentration of DMOGA was determined potentiometrically with a standard carbonate-free NaOH solution. The ionic strength of all working solutions used in spectrophotometry and calorimetry was adjusted to 1.0 $mol\cdot dm^{-3}$ at 25°C by adding appropriate amounts of sodium perchlorate as the background electrolyte.

Thermodynamic measurements

Spectrophotometry. Spectrophotometric titrations were carried out with a Cary 5G spectrophotometer from 950 to 1150 nm (0.2 nm interval) to determine the stability constants of Np(V) complexes with DMOGA. The stability constants were calculated by non-linear regression using Hyperquad 2000.[15]

Calorimetry. The enthalpy of the complexation of Np(V) with DMOGA was determined with an isothermal microcalorimeter (ITC 4200, Calorimetry Sciences Corp.). Calorimetric experiments were also conducted on the complexation of Np(V) with the related ligand TMOGA. Information on the microcalorimeter, its calibration and the titration procedure has been provided previously.[16] Multiple titrations using different concentrations of the reagents (C_L, C_H and C_{Np}) were performed to reduce the uncertainty of results. The reaction heats measured by microcalorimetry were used, in conjunction with the equilibrium constants obtained by spectrophotometry, to calculate the enthalpy of complexation with the computer program Letagrop.[17]

Single crystal X-ray diffractometry

Pale blue crystals of the Np(V)/DMOGA complex, $NpO_2(H_2O)(L)\cdot H_2O$ where L stands for the deprotonated DMOGA, were obtained by slow evaporation from an aqueous $NpO_2(ClO_4)$ solution containing the ligand. Representative crystals were chosen and sealed in glass capillary tubes and mounted on the goniometer. Diffraction data were collected on a Brüker AXS APEX II diffractometer using a silicon (111) monochromator at 0.77490 Å on Beamline 11.3.1 of the Advanced Light Source (ALS). The structure solution and refinement were performed using the SHELXTL crystallographic software package of the Brüker Analytical X-ray System.[18] Details of the crystallographic data are provided in Table 1.

Results

Stability constant of the Np(V)/DMOGA complex

A representative set of absorption spectra for the titration of Np(V) with DMOGA is shown in Figure 2. As the concentration of DMOGA was increased, the intensity of the absorption band of NpO_2^+ at 980.2 nm decreased and a new band appeared at 988.6 nm. An isobestic point was observed at around 984 nm, indicating the presence of two absorbing species, i.e., the free NpO2+ and an Np(V)/DMOGA complex. This is confirmed by the factor analysis with the Hyperquad program and the spectral were fitted with the formation of the 1:1 Np(V)/DMOGA complex. The stability constant of the complex and the molar absorptivities of NpO_2^+ and $NpO_2(L)(aq)$ (where L stands for the deprotonated DMOGA) were accordingly calculated with the Hyperquad program. The molar absorptivities are shown in Figure 2, while the stability constant of the Np(V)/DMOGA complex is shown in Table 2 in comparison with those of the Np(V)/TMOGA and Np(V)/ODA complexes previously published.

Enthalpy of Np(V)/DMOGA complexation

A representative thermogram of the calorimetric titrations is shown in Figure 3 (top). Integration of the peaks in the thermogram results in the reactions heat during the titration. The reaction heat, shown as a function of the titrant volume in Figure 3 (bottom), is dependent on the equilibrium constants and enthalpies of all reactions occurring in the titration system, as well as the concentrations of all reagents participating in the reactions. From the results of multiple titrations with different concentrations of Np(V), the ligand and acidity, the enthalpy of complexation for the 1:1 Np(V) complex with DMOGA was calculated and shown in Table 2. A value of ΔH (0.83 ± 0.01 kJ·mol^{-1}) for the protonation reaction of DMOGA, determined in a previous study,[19] was used in the calculation. Results of the calorimetric titrations of the Np(V)/TMOGA system that have not been previously published are also shown in Figure 3 (bottom) and Table 2.

Crystal structure of the Np(V)/DMOGA complex

The crystal structure of $NpO_2(H_2O)(L)\cdot H_2O$, where L stands for the deprotonated DMOGA, is shown in Figure 4. Selected bond lengths and angles are given in Table 3. As shown in Figure 4, the 1:1 Np(V)/DMOGA complex crystallized in an orthorhombic space group, Cmc21. The previously published structural parameters of the Np(V) complexes with related ligands, TMOGA and ODA, are also given in Table 3 for comparison.

Discussion

Thermodynamic trends: amide group vs. carboxylate group

Clear trends in thermodynamic parameters of complexation can be observed for the three related ligands in Table 2 and Figure 5. For the 1:1 Np(V) complex, the stability constant ($\ln\beta_1 = -\Delta G/(RT)$), the enthalpy ($\Delta H$, kJ·mol^{-1}), and the entropy (ΔS, J·K^{-1}·mol^{-1}) all decrease in the order ODA > DMOGA > TMOGA. This means that, when the carboxylate group is replaced with an amide group, the enthalpy of complexation becomes less endothermic and more favorable to the complexation while the entropy of complexation becomes smaller and less favorable to the complexation. It is because the entropy term ($T\Delta S$) is significantly larger than the enthalpy (Figure 5), the complexation with Np(V) becomes weaker when the carboxylate group is replaced with the amide group. In other words, the complexation of Np(V) with DMOGA, as well as TMOGA and ODA, is thermodynamically entropy-driven. Same trends have been observed for the complexation of U(VI) with the three ligands.[19]

The thermodynamic trends observed for the complexation of Np(V) (this work) and U(VI)[19] imply that the –C=O moiety in the amide group is less hydrated than the –C(O)O- moiety in the carboxylate group. When forming complexes with NpO_2^+ or UO_2^{2+}, less energy is required to dehydrate the amide group and fewer water molecules are released from the hydration sphere of the amide group than the carboxylate group, resulting in less endothermic enthalpy and smaller entropy of complexation along the series from ODA (two carboxylate groups), to DMOGA (one carboxylate, one amide), and further to TMOGA (two amide groups).

Structural aspects of $NpO_2(H_2O)(L)\cdot H_2O$(c)

The axial O=Np=O moiety in $NpO_2(H_2O)(L)\cdot H_2O$(c) is slightly bent (178.4° angle), differing from the perfectly linear O=Np=O configuration in the 1:2 Np(V)/TMOGA and Np(V)/ODA complexes (Table 3). This difference is understandable because, in the 1:2 complexes, six oxygen atoms coordinate to the center Np atom in the equatorial plane in a highly symmetrical manner. In contrast, the 1:1 complex of Np(V)/DMOGA has no such symmetry and the Np atom is coordinated by five oxygen atoms, among which three are from the carboxylate, ether and amide groups of one DMOGA ligand, one from a water molecule in the primary hydration sphere and another from the carboxylate group of a second DMOGA ligand connecting to a second Np atom and forming a chain-like structure (Figure 4).

Because the 1:2 complexes of Np(V) with TMOGA and ODA were observed in aqueous solutions and crystal structures[20,22] and because the equatorial plane of NpO_2^+ is expected to be able to accommodate a second tridentate ligand such as DMOGA, efforts were made to identify the 1:2 Np(V)/DMOGA complex but were unsuccessful. In the spectrophotometric titrations of the Np(V)/DMOGA system in aqueous solutions, no spectra changes suggesting the formation of the 1:2 complex was observed even when the ratio of [DMOGA]/[Np] was high. Likewise, preparation of crystals of a 1:2 Np(V)/DMOGA complex has not succeeded. The reason underlying the structural difference between the complexes of DMOGA and the two related ligands remains to be explored in future studies.

Conclusion

N,N-dimethyl-3-oxa-glutaramic acid (DMOGA) forms a 1:1 tridentate complexes with Np(V) in aqueous solutions and in crystal solids, with the three oxygen atoms from the carboxylate, ether and amide groups coordinating to NpO_2^+ in the equatorial plane. The stability of the 1:1 Np(V)/DMOGA complex is weaker than that of Np(V)/ODA (an oxa-dicarboxylate), but stronger than that of Np(V)/TMOGA (an oxa-diamide). Results show that substitution of a carboxylate group with an amide group in the series of ODA-DMOGA-TMOGA makes the enthalpy of complexation less endothermic and more favorable to the formation of the Np(V) complexes, but still results in weaker complexation due to the larger decrease in the entropy of complexation.

Though 3-oxa-glutaramic acid may appear to be a weaker ligand than its dicarboxylate analog in aqueous solutions, it could still be a highly effective extractant in solvent extraction because the great ease of attaching alkyl (or aryl) groups to the amide group makes the ligand readily soluble in many organic solvents. Besides, thermodynamic data from this work indicate that the binding strength of the ligand can be improved by increasing the entropy of complexation (e.g., increasing the denticity). Further studies are underway to optimize the structure of related ligands and develop efficient extractants for actinide separations.

Acknowledgments

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Notes and references

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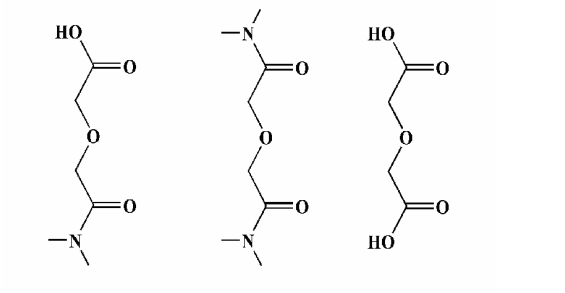

Fig. 1 DMOGA (left), TMOGA (center), and ODA (right).

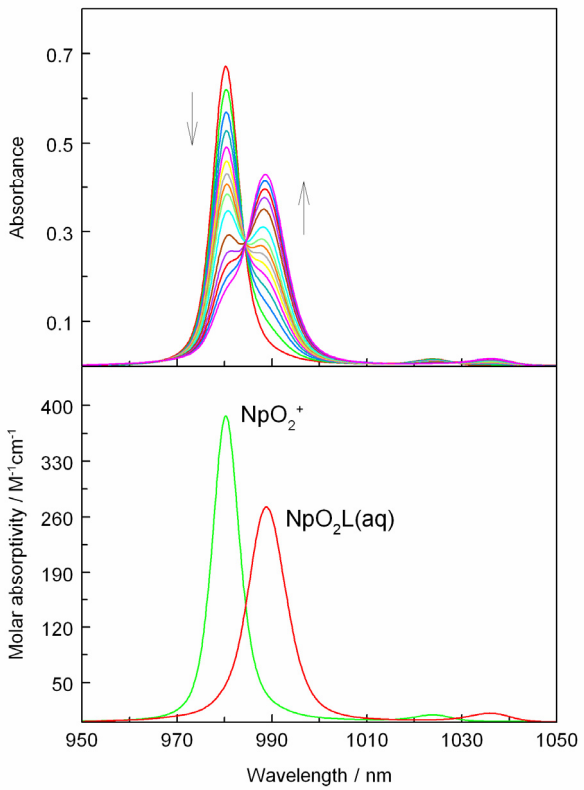

Fig. 2 Spectrophotometric titrations of Np(V)/DMOGA complexation (I = 1.0 mol·dm^{-3}, t = 25°C), (top) normalized absorption spectra, (bottom) molar absorptivities. V^o = 2.50 mL, $C_{Np}{}^o/C_H{}^o$ = 1.74/0.0006 mmol·dm^{-3}; DMOGA titrant: C_L/C_H = 0.0346/0.0148 mol·dm^{-3}, 0.300 mL total volume added.

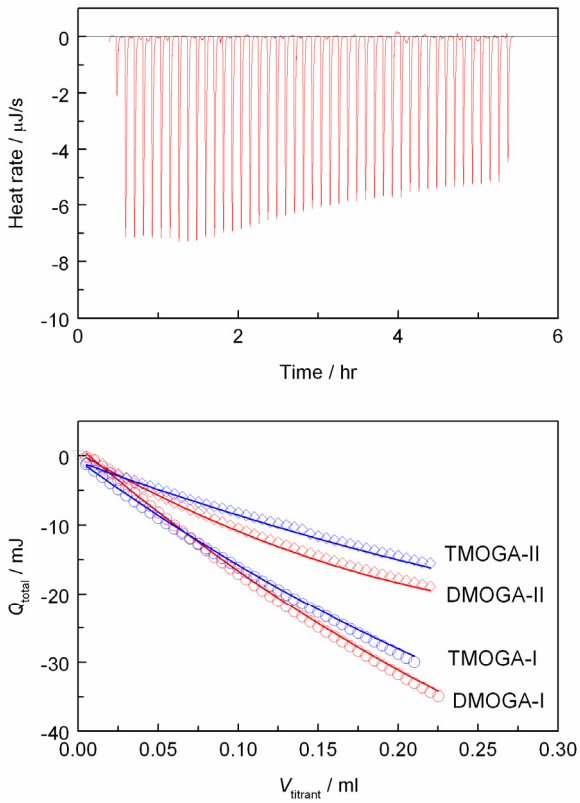

Fig. 3 Calorimetric titrations of Np(V)/DMOGA and Np(V)/TMOGA complexation (I = 1.0 mol·dm^{-3}, t = 25°C), (top) an example thermogram, (bottom) experimental heat (○) and fit (—). V^o = 0.900 mL, $C_{Np}{}^o/C_H{}^o$ = 1.74/0.0006 (I) and 1.16/0.0004 (II) mmol·dm^{-3}; titrant: C_{DMOGA}/C_H = 0.0570/0.00273 mol·dm^{-3}, C_{TMOGA} = 0.400 mol·dm^{-3}, about 0.225 mL total volume added.

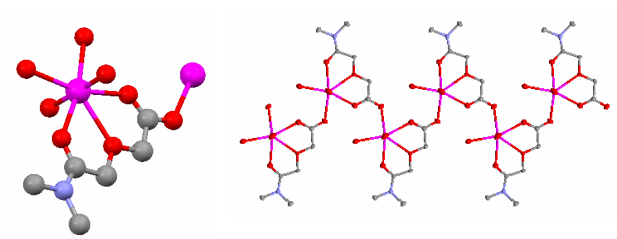

Fig. 4 Crystal structure of the Np(V)/DMOGA complex; (left) $NpO_2(H_2O)(L)\cdot H_2O$; (right) chain-like structure in the equatorial plane. Color: Np – magenta, O – red, N – blue, C- gray. Hydrogen atoms and non-coordinated water molecules are not shown for clarity.

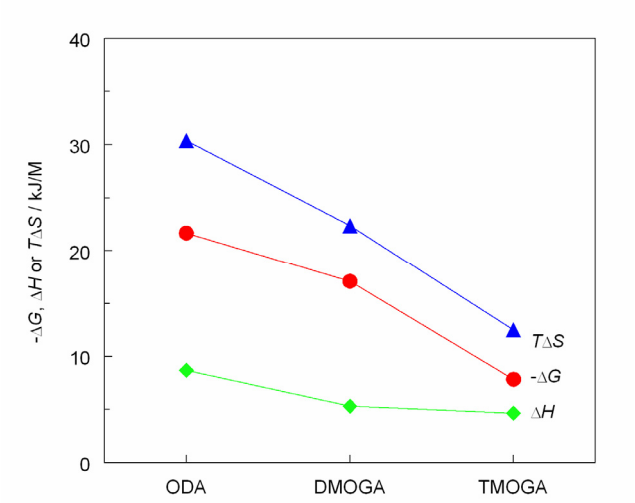

Fig. 5 Thermodynamic trends of Np(V) complexes with ODA, DMOGA and TMOGA (I = 1.0 mol·dm^{-3} $NaClO_4$, t = 25°C).

5

Table 1 Crystal data and structure refinement for the $NpO_2(H_2O)(L)\cdot H_2O$ complex (L stands for deprotonated DMOGA).

Chemical formula	$C_6H_{14}NNpO_8$
Formula weight	465.18
Temperature	90(2) K
Radiation, wavelength	synchrotron, 0.77490 Å
Crystal system, space group	orthorhombic, $Cmc2_1$
Unit cell parameters	a = 7.161(2) Å α = 90°
	b = 16.659(5) Å β = 90°
	c = 9.536(3) Å γ = 90°
Cell volume	1137.6(6) Å^3
Z	4
Calculated density	2.716 g/cm^3
Absorption coefficient μ	7.679 mm^{-1}
F(000)	856
Crystal colour and size	pale blue, 0.03 × 0.02 × 0.02 mm^3
Reflections for cell refinement	6073 (θ range 4.10 to 33.49°)
Data collection method	Bruker APEX II CCD diffractometer
	ω rotation with narrow frames
θ range for data collection	4.10 to 33.53°
Index ranges	h −10 to 10, k −23 to 23, l −13 to 13
Completeness to θ = 30.00°	98.8 %
Reflections collected	8249
Independent reflections	1824 (R_{int} = 0.0500)
Reflections with $F^2>2\sigma$	1758
Absorption correction	semi-empirical from equivalents
Min. and max. transmission	0.74 and 0.81
Structure solution	direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting parameters a, b	0.0469, 0.0000
Data / restraints / parameters	1824 / 67 / 94
Final R indices [$F^2>2\sigma$]	R1 = 0.0287, wR2 = 0.0728
R indices (all data)	R1 = 0.0295, wR2 = 0.0733
Goodness-of-fit on F^2	1.065
Absolute structure parameter	0.03(4)
Extinction coefficient	0
Largest and mean shift/su	0.001 and 0.000
Largest diff. peak and hole	1.029 and −1.486 e Å^{-3}

Table 2 Thermodynamic parameters of the complexation of Np(V) with DMOGA, TMOGA and ODA. I = 1.0 mol·dm^{-3} $NaClO_4$, t = 25ºC. The uncertainties are 3σ. Legends: pot – potentiometry, cal – calorimetry, sp- spectrophotometry, p.w. – present work.

Ligand	Reaction	Method	log β	ΔH kJ·mol^{-1}	ΔS J·K^{-1}·mol^{-1}	ref
DMOGA	$H^+ + L^- = HL(aq)$	pot, cal	3.49 ± 0.03	0.83 ± 0.01	70 ± 1	[19]
	$NpO_2^+ + L^- = NpO_2L(aq)$	sp, cal	2.99 ± 0.01	5.32 ± 0.08	75 ± 1	p.w.
TMOGA	$NpO_2^+ + L = NpO_2L^+$	sp	1.38 ± 0.01			[20]
		cal		4.65 ± 0.86	42 ± 3	p.w.[a]
	$NpO_2^+ + 2L = NpO_2L_2^+$		2.47 ± 0.01			[20]
		cal		43.5 ± 1.5	193 ± 3	p.w.[a]
ODA	$NpO_2^+ + L^{2-} = NpO_2L^-$	sp, cal	3.79 ± 0.01	8.7 ± 0.3	102 ± 1	[21]
		sp	3.89 ± 0.05			[22]
	$NpO_2^+ + 2L^{2-} = NpO_2L_2^{3-}$		4.40 ± 0.05			

[a] The values of ΔH and ΔS from this work differ from the preliminary results [11] that were obtained from a single titration..

Table 3 Caption Comparison of selected bond lengths (Å) and bond angle (deg) in Np(V) complexes with DMOGA, TMOGA and ODA.

	$NpO_2(H_2O)DMOGA)\cdot H_2O$ (this work)	$NpO_2(TMOGA)_2(ClO_4)_2$ [20]	$Na_3NpO_2(ODA)_2$ [22]
$Np{=}O_{axial}$	1.833 (5), 1.833 (5)	1.731 (5), 1.731 (5)	1.841 (4), 1.841 (4)
$Np\text{-}O_{amide}$	2.476 (7)	2.433 (3), 2.433 (3) 2.433 (3), 2.433 (3)	
$Np\text{-}O_{carboxylate}$	2.484 (7), 2.466 (7)		2.543 (5), 2.577 (7) 2.543 (5), 2.577 (7)
$Np\text{-}O_{ether}$	2.552 (6)	2.588 (5), 2.588 (5)	2.651 (7), 2.651 (7)
$Np\text{-}O_{water}$	2.526 (8)		
∠O=Np=O	178.4 (10)	180.0 (4)	180.0 (2)
$Np{=}O_{axial}$	1.833 (5), 1.833 (5)	1.731 (5), 1.731 (5)	1.841 (4), 1.841 (4)