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The Crystal and Molecular Structure of Nitrilotriacetatodiaquopraseodymium(III) Monohydrate

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The crystal and molecular structure of nitrilotriacetatodiaquopraseodymium(III) monohydrate has been determined. The structure was refined by full-matrix least-squares to a conventional discrepancy factor of 8.5% and a weighted R factor of 8.0% for 1126 reflections. The compound crystallizes in the space group *Pbca* with eight molecules in a unit cell of dimensions $a = 13.21 \pm 0.01$, $b = 20.98 \pm 0.01$, $c = 8.132 \pm 0.006$ Å. The praseodymium is nonacoordinated with six carboxylate oxygen atoms, two waters, and one nitrogen in the coordination sphere. The spatial arrangement of the coordinating atoms can be described as either a distorted, tricapped, trigonal prism or a distorted, capped, square antiprism. Each nitrilotriacetate (NTA) is heptadentate with one carboxylate oxygen atom which coordinates to two adjacent metal atoms and two carboxylate oxygen atoms which coordinate to metal atoms in adjacent molecules. This gives rise to a polymeric structure. Average distances for atoms which coordinate to the Pr are 2.47 ± 0.02 Å to the carboxylate oxygens, 2.52 ± 0.02 Å to the waters, and 2.68 ± 0.02 Å to the nitrogen.

Introduction

The complexes formed by the reaction of the trivalent lanthanons with nitrotriacetate (NTA) in aqueous solution have been studied for some time.[1] 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 what rare earth is used. Our preliminary study of the series of complexes formed at 25° indicates that the series is divided into three crystallographically distinct groups: (i) the La–Ce group, (ii) the Pr–Tb (Pm?) group, and (iii) 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 $a \cong 13.2$, $b \cong 21.0$, and $c \cong 8.1$ Å. Those of the third group are in space group $Pca2_1$ with $a \cong 21.5$, $b \cong 9.0$, and $c \cong 12.2$ Å.

This division into groups also coincides with observed changes in hydration number across the series from 5 to 3 to 4.[2] The break between groups at Tb occurs near a sudden change in thermodynamic properties of these as well as other lanthanon(III) complexes.[3] This so-called Gd break has been attributed to some, as yet undefined, change in the lanthanon(III) coordination. Coordination numbers ranging from 6 to 12 have been observed in various complexes.[4–7] 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. Packing forces certainly play an important role in stabilizing a particular coordination in the solid and hence this coordination number might, in general, be different than that found in solution. In the case of the NTA complexes, the coincident changes in thermodynamic properties in solution and crystal structure in the solid across the rare earth series, along with a consideration of the bulk of the ligand, strongly indicate that coordination changes in both phases are of a similar nature. We therefore undertook a three-dimensional X-ray structural study of $Pr \cdot NTA \cdot 3H_2O$ in order to determine its coordination. In a companion paper the structure of $Dy \cdot NTA \cdot 4H_2O$ is described.

Experimental Section

Well formed, rectangular prismatic crystals of the $Pr \cdot NTA \cdot 3H_2O$ complex (mol wt = 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 the 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 ($a_0 = 4.03310$ Å) using Cu Kα_1 radiation (λ 1.54051 Å). The unit-cell parameters and their standard deviations calculated from the inverse matrix are $a = 13.21 \pm 0.01$, $b = 20.98 \pm 0.01$, $c = 8.132 \pm 0.006$ Å, and $V = 2254$ Å^3. The density determined by flotation techniques in a diiodomethane–1-bromopropane mixture is 2.24 ± 0.02 g/cm^3, while the calculated density with $Z = 8$ is 2.26 ± 0.01 g/cm^3.

A crystal having approximate dimensions 0.07 × 0.05 × 0.26 mm was mounted so that its long axis (100) was coincident with the ϕ axis of the diffractometer. A General Electric, XRD-6, X-ray diffractometer equipped with a single-crystal orienter and scintillation counter was used with Zr-filtered, Mo Kα radiation (λ 0.7107 Å) in the moving-crystal–moving-counter mode (θ, 2θ 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 backgrounds 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 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 absorption[8] with minimum and maximum transmission factors of 0.74 and 0.76 ($\mu = 43.2$). The standard deviations were assigned to the intensities according to the formula

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

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[1] F. T. Fitch and D. S. Russel, *Can. J. Chem.*, **29**, 363 (1951).

[2] S. C. Levy and J. E. Powell, Report No. IS-421, "Some Properties of Rare Earth-Nitrilotriacetato Complexes," Ames Laboratory, Ames, Iowa, 49 (1961).

[3] T. Moeller, E. R. Birnbaum, J. H. Forsberg, and R. B. Gaghart, *Progr. Sci. Technol. Rare Earths*, **3**, 61 (1968).

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[6] J. F. Urgo, Ph.D. Thesis, Iowa State University, Ames, Iowa 1968.

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[8] F. R. Ahmed, S. R. Hall, M. E. Pippy, and C. P. Saunderson, "NRC Crystallographic Programs for the IBM 360 System," National Research Council of Canada, Ottawa, 1966.

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 error limits of 5, 10, and 5% in the total count, background count, and net count, respectively. The standard deviations of the structure amplitudes ($\sigma(F)$) were obtained by the method of finite differences.[9] Of the 1494 measured reflections, 368 had a value of $F_o < 2\sigma(F)$. 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 *via* a series of structure factor–electron density map calculations. Scattering factors used were those of Cromer and Waber[10] for the praseodymium(III) atom corrected for anomalous scattering[11] and those of Hanson, *et al.*,[12] for the light atoms. All atoms were refined[13] isotropically to a value of the discrepancy indicator ($R = \Sigma\Delta/\Sigma|F_o|$ where $\Delta = ||F_o| - |F_c||$) of 0.13. At this point weights were introduced based on the estimated standard deviations of the reflections ($w = 1/\sigma^2(F_o)$). These weights were later adjusted slightly to remove a dependence of $w\Delta^2$ on $|F_o|$. The large isotropic temperature factor of O_{w3} suggested some occupational disorder. However, refinement of the occupational parameter yielded a value near unity. With the Pr atom anisotropic, final values of R and R_w, the weighted discrepancy index ($R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$), of 0.085 and 0.080 were obtained (1125 data, 70 variables). The final difference electron-density map contained no residual density greater than 0.8 e/Å^3 and confirmed that all nonhydrogen atoms had been located. In Table I are listed the final atomic positional parameters and temperature factor coefficients along with their estimated standard deviations (esd) as derived from the inverse matrix.[14] For praseodymium, the maximum, intermediate, and minimum root-mean-square amplitudes of vibration are 0.145, 0.144, and 0.135 Å. The magnitudes of the observed and calculated structure factors are given.[15]

TABLE I

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS[a,b]

Atom	x	y	z	B_{iso}, Å^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}	0.452 (2)	0.072 (1)	0.219 (2)	2.2 (3)
C_{31}	0.441 (2)	0.130 (1)	0.055 (3)	2.8 (4)
O_{w1}	0.252 (1)	0.1286 (7)	0.409 (2)	2.7 (3)
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 (18)	0.06427 (5)	0.16546 (13)	

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
234 (7)	83 (3)	619 (19)	6 (4)	−1 (13)	−8 (8)

[a] Estimated standard deviations are given in parentheses right adjusted to the least significant figure of the preceding number. [b] Anisotropic temperature factors are given for Pr only. They are times 10^5 and have the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

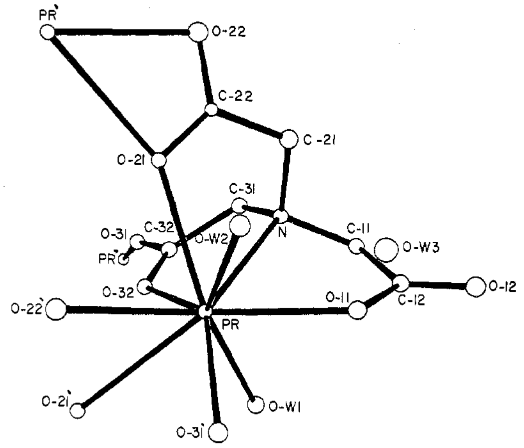

Figure 1.—The perspective drawing of nitrilotriacetatotriaquopraseodymium(III) monohydrate. The numbering in the NTA ligand is such that the left number indicates to which acetate group the atom belongs. In the case of the carbon atoms the right number indicates its position relative to the nitrogen 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.

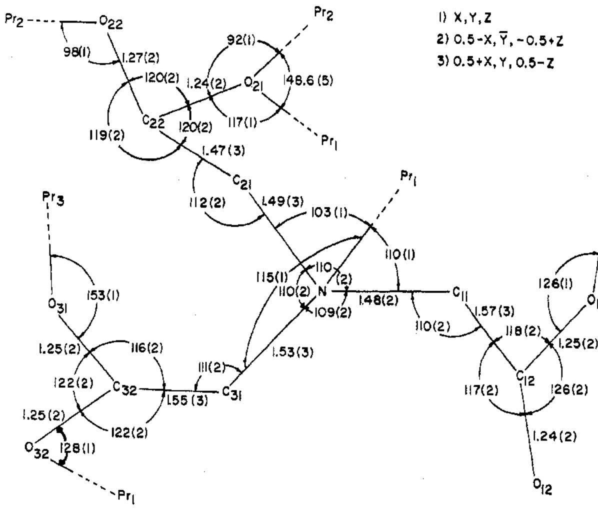

Figure 2.—The drawing of the conformation of the NTA ligand. Bond distances (Å) and angles (deg) are shown along with their estimated errors right adjusted to the least significant figure of the preceding number. The subscripts of the Pr atoms indicate their relation to the Pr in the coordinate list.

Description of the Structure

The configuration of the NTA ligand around the Pr is shown in Figure 1.[16] There are six carboxylic oxygens (O_c), two waters (O_w), and one nitrogen atom coordinated to the metal atom. Relevant distances and angles are given in Table II. For each NTA ligand, the nitrogen and one of the two oxygen atoms in each

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[9] D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

[10] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

[11] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1965.

[12] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

[13] W. R. Busing, K. O. Martin, and H. A. Levy, Report No. ORNL-TM-305, "A Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[14] W. R. Busing, K. O. Martin, and H. A. Levy, Report No. ORNL-TM-306, "A Fortran Crystallographic Function and Error Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[15] A listing of structure factor amplitudes will appear immediately following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-2785. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[16] C. K. Johnson, Report No. ORNL-3799, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

TABLE II

SELECTED DISTANCES (Å) AND ANGLES (DEG) WITH ASSOCIATED STANDARD ERRORS AS CALCULATED FROM THE PARAMETERS IN TABLE I[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_{22}	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)
		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_{22}^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_{21}^1	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)
		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)

[a] Superscripts indicate symmetry operations which relate the atom to the original coordinates: (1) $^1/_2 - x, \bar{y}, ^1/_2 + z$; (2) $-^1/_2 + x, y, ^1/_2 - z$; (3) $x, ^1/_2 - y, ^1/_2 + z$; (4) $^1/_2 - x, y, -^1/_2 + z$; (5) $^1/_2 + x, y, ^1/_2 - z$.

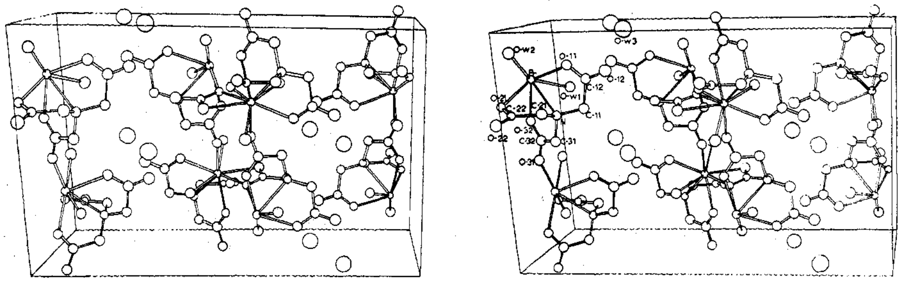

Figure 3.—The perspective drawing of the packing of $Pr(N(C_2H_2O_2)_2)_3(H_2O)_3$.

carboxylate group coordinate to the same metal atom. Two of the remaining carboxylate oxygen atoms, O_{22} and O_{31}, coordinate to adjacent metal atoms (see Figure 2). In addition O_{21} which is coordinating to the original metal atom also coordinates to an adjacent metal atom. Thus, there are no discrete molecular units in the complex. Instead metal atoms are connected by intermolecular bridges formed by the coordination of O_{22}, O_{21}, and O_{31} to adjacent metal atoms (*e.g.*, $-Pr_3-O_{31}-C_{32}-O_{33}-Pr_1-$, $-Pr_2-O_{22}-C_{22}-O_{21}-Pr_1-$ and $-Pr_2-O_{21}-Pr_1$). The packing of these molecules is seen in Figure 3. Two oxygen atoms O_{w3} and O_{12} are not coordinated to any metal atom. 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 ± 0.02 Å. This is in excellent agreement with the expected value for the C–O distance in a carboxylate ion.[17] 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 ± 0.02 Å) has no significantly greater double bond character than the rest. The three acetate groups are planar to within 0.1 Å, while the angles around the carboxylate carbons are 120 ± 3° with the exception of the O_{11}–C_{12}–O_{12} angle which is slightly larger (126 ± 2°). This increase in

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[17] *Chem. Soc., Spec. Publ.*, **No. 18**, S21s (1965).

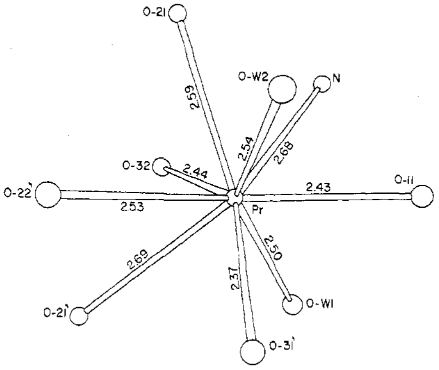

Figure 4.—The perspective drawing of the Pr coordination. The orientation is the same as in Figure 1. The primes indicate atoms related to those in the coordinate list: (i) O_{21} $^1/_2 - x, \bar{y}, {}^1/_2 + z$; (ii) O_{22} $^1/_2 - x, \bar{y}, {}^1/_2 + z$; (iii) O_{31} $-{}^1/_2 + x, \bar{y}, {}^1/_2 - z$.

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 2).

There are four short O_w–O_c distances ranging from 2.72 to 2.85 Å which is suggestive of possible hydrogen bond formation. The large thermal parameters of O_{w3} suggest that it is involved in only weak hydrogen bond formation.

The arrangement of the atoms in the coordination sphere is shown in Figure 4. The average Pr–O_c distance is 2.47 ± 0.02 Å while the average Pr–O_w distance is 2.52 ± 0.02 Å. The Pr–O_{21} distances have been excluded from this calculation since they are significantly longer than the other Pr–O_c distances due to the different coordination mode exhibited by O_{21}. The Pr–N distance is 2.68 ± 0.02 Å. The metal–oxygen distance is in reasonable agreement with the value predicted either from the sum of the covalent radii[18] or from the sum of the crystal radii.[19] The Pr–N distance is ~0.1 Å longer than would be expected, indicating weaker coordination. These values are 0.04–0.08 Å shorter than those observed by Hoard, *et al.*,[20] in the nine-coordinate La·EDTA complex (2.51, 2.58, 2.76 Å for the average La–O_c, La–O_w, and La–N distances). This general shortening is consistent with a decrease in the rare earth ionic radius from 1.15 to 1.09 Å. In fact, assuming the average oxygen–metal–oxygen angle remains constant (72–74°), a continued decrease in the metal–oxygen bond distance of 0.10–0.14 Å would cause significant oxygen–oxygen steric interactions. This would occur by Dy^{3+} (0.99 Å) or Ho^{3+} (0.97 Å) and a change in coordination number from nine to eight would be expected.

The arrangement of atoms around the Pr can be described equally well in any of the following three ways: (i) as a distorted, tricapped trigonal prism, (ii) as a capped square antiprism, or (iii) as in the description by Hoard, *et al.*, of the La·EDTA complex.

The tricapped, trigonal prism arrangement has been observed for many nonacoordinate structures which have been described in some detail by Muetterties and Wright.[21] Typical of these are the anhydrous, rare earth trichlorides.[22] Referring to Figure 4, the three rectangluar faces of the trigonal prism are as follows: O_{22}'–O_{32}–N–O_{w2}, O_{w2}–N–O_{21}–O_{31}', and O_{31}'–O_{w1}–O_{32}–O_{22}'. The two triangular faces of the prism are described by O_{22}'–O_{w2}–O_{31}' and O_{32}–N–O_{w1}. The atoms O_{21}, O_{21}', and O_{11} occupy the capping positions.

The capped square antiprism is observed somewhat less frequently than is the tricapped trigonal prism.[21,23] However, the square antiprism is a very common arrangement for octacoordination. In Figure 4, the rectangular faces of the square antiprism are defined by O_{22}', O_{32}, O_{w1}, O_{31}', and O_{21}, N, O_{11}, O_{w2}. The atom in the capping position (O_{21}') shows a significant distortion toward O_{22}'.

The description reported by Hoard, *et al.*,[20] for the nonacoordinate La·EDTA complex, which was later recognized by Hoard and Day[24] to be a distorted capped, square antiprism, 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 III. The average O–Pr–O angle in the plane is 71° while the average O–O distance is 2.97 Å. The most significant distortions from these averages occur in the O_{22}'–Pr^{3+}–O_{21}' angle of 49.2° and O_{21}'–O_{22}' distance of 2.18 ± 0.02 Å. This appears to be a result of both carboxylate oxygens being in the same acid moiety. The Pr is located 0.5 Å above the approximate center of this plane away from the O_{31}'. In the La·EDTA complex, the distance from the similar plane to La^{3+} is 0.6 Å, some increase being expected due to the longer oxygen–La distances.

TABLE III

Atom	Distance from plane, Å	Atom	Distance from plane, Å
	Plane 1		
Equation:	$(0.881)x + (0.005)y - (0.074)z - 1.229 = 0$		
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
	Plane 2		
Equation:	$(0.907)x - (0.052)y - (0.418)z - 3.720 = 0$		
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

At a distance of 2.0 Å from the Pr atom 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 III. The two planes are within 9° of being parallel.

In complexes such as ceric ammonium nitrate,[25] considerable distortions of the N–O bonds and O–N–O

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angles have been observed and have been attributed to the presence of metal–oxygen covalent bonding. However, in the La·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 (92–153°), would imply primarily electrostatic bonding effects.

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The Crystal and Molecular Structure of Nitrilotriacetatodiaquodysprosium(III) Dihydrate

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The crystal and molecular structure of nitrilotriacetatodiaquodysprosium(III) dihydrate has been determined from a combination of heavy atom and superposition techniques. The structure was refined by block-diagonal least squares to a conventional discrepancy index of 5.0% and a weighted R of 7.0% for 3032 reflections. The compound crystallizes in the space group $Pca2_1$ with two independent molecules in a unit cell of dimensions $a = 21.535 \pm 0.013$, $b = 9.028 \pm 0.004$, $c = 12.186 \pm 0.007$ Å. Both independent dysprosium atoms are octacoordinate 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 uncoordinated to any metal atom and two carboxylate oxygen atoms coordinated to metal atoms in adjacent molecules. This gives rise to a polymeric structure. Average distances for atoms coordinated to the dysprosium are 2.36 ± 0.01, 2.35 ± 0.01, and 2.58 ± 0.01 Å for water molecules, carboxylate oxygens, and nitrogen atoms, respectively.

Introduction

It has been speculated that a change in coordination is responsible for the nonmonotonic behavior of the thermodynamic properties of the nitrilotriacetate (NTA) and other rare earth complexes across the series.[1] In an endeavor to determine the plausibility of such arguments, we have investigated the crystal structure of the lanthanon(III) nitrilotriacetate complexes. In this paper the structure of the dysprosium complex is described and then compared to the structure of the Pr·NTA complex reported in the preceding paper.[2] This comparison illustrates coordination change which takes place and is probably responsible for the observed nonmonotonic behavior of the thermodynamic properties.

Experimental Section

Well formed rectangular-prismatic crystals of Dy·NTA·4H_2O (mol wt = 422.7 g) were supplied by J. E. Powell and were used without additional purification. Weissenberg and precession photographs indicated an orthorhombic space group with systematic extinctions of the type 0*kl*, *l* odd and *h*0*l*, *h* odd. These conditions indicate the space group to be either $Pca2_1$ or *Pcam* (no. 57-*Pbcm*). In addition the 0*k*0, *k* odd reflections were weak. However, there are no special positions in $Pca2_1$ or *Pcam* which can account for this type of condition. The light lanthanon(III) NTA complexes crystallize in space group *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 0*k*0 extinction condition suggests that there remains an x_1, y, z_1; x_2, $^1/_2 + y$, z_2 relationship between the two independent molecules which has been retained from *Pbca*. Space group $Pca2_1$ was assumed and 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° (a_0 = 4.03310 Å) using Cu Kα_1 radiation (λ 1.54051 Å). The values obtained along with the estimated errors are $a = 21.535 \pm 0.013$, $b = 9.028 \pm 0.004$, $c = 12.186 \pm 0.007$ Å, and $V_0 = 2369 \pm 1$ Å^3. The density, determined by flotation techniques, was 2.3 ± 0.1 g/cm^3 while the calculated density with eight molecules per unit cell is 2.24 ± 0.02 g/cm^3.

A crystal with approximate dimensions 0.12 × 0.12 × 0.26 mm was selected for use in data collection. The crystal was mounted along its long axis with the (001) axis coincident with the ϕ 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 Kα (λ 0.7107 Å) radiation. All data in one octant within a 2θ sphere of 60° ($(\sin \theta)/\lambda = 0.70$) were measured using a θ–2θ 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°, 1 step/0.4096 sec, increased by 1 step/deg in 2θ to ensure complete integration over the entire peak. The lengths 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 absorption[3] with minimum and maximum transmission factors of 0.43 and 0.47 (μ = 65.5 cm^{-1}). The standard deviations were assigned to the intensities according to the formula

$$\sigma(I) = (C_t + C_b + (0.03C_t)^2 + (0.06C_b)^2 + (0.06C_n/A)^2)^{1/2}$$

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,[4] $\sigma(F) = [(I + \sigma(I))^{1/2} - I^{1/2}]/(L_p)^{1/2}$, where L_p is the Lorentz–polarization factor. Of the 3407 measured reflections,

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