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 2*θ* 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 K*α* (λ 0.7107 Å) radiation. All data in one octant within a 2*θ* sphere of 60° ((sin *θ*)/λ = 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°, 1 step/0.4096 sec, increased by 1 step/deg in 2*θ* 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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TABLE I

ATOM POSITIONS AND ANISOTROPIC TEMPERATURE FACTORS[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Dy1	6120 (2)	−130 (5)	0	60 (1)	380 (7)	242 (4)	17 (2)	−17 (2)	−37 (4)
Dy2	19555 (2)	49940 (5)	18663 (5)	60 (1)	421 (8)	229 (4)	16 (2)	−13 (2)	−52 (4)
O1E1	415 (5)	374 (11)	−1868 (9)	20 (3)	85 (11)	36 (7)	−5 (5)	−5 (4)	20 (8)
O1E2	166 (7)	52 (11)	−3300 (8)	26 (3)	169 (19)	13 (6)	−15 (5)	−12 (3)	26 (8)
O1D1	889 (4)	−2259 (9)	748 (8)	17 (2)	68 (11)	45 (7)	6 (4)	−14 (33)	−12 (7)
O1D2	1080 (4)	−4690 (8)	625 (8)	14 (2)	28 (8)	41 (6)	7 (3)	−9 (3)	−5 (6)
O1U1	470 (4)	456 (11)	−203 (10)	11 (2)	79 (11)	69 (8)	−3 (4)	−3 (3)	−32 (9)
O1U2	−1416 (5)	−545 (14)	−88 (13)	9 (2)	127 (15)	135 (15)	−1 (5)	7 (5)	−10 (14)
C1E1	−43 (6)	−2051 (14)	−2033 (11)	17 (3)	64 (15)	50 (10)	4 (6)	−10 (5)	−8 (10)
C1E2	68 (6)	−440 (15)	−2454 (12)	10 (3)	86 (15)	39 (9)	9 (5)	2 (4)	−1 (11)
C1D1	363 (7)	−3673 (14)	−628 (15)	18 (3)	74 (16)	82 (15)	22 (6)	−17 (6)	−7 (13)
C1D2	810 (5)	−3540 (12)	363 (9)	6 (2)	55 (12)	29 (7)	3 (4)	−3 (4)	−9 (8)
C1U1	−574 (6)	−2241 (14)	−325 (15)	16 (3)	52 (16)	74 (13)	−8 (5)	3 (5)	−14 (12)
C1U2	−847 (6)	−636 (14)	−181 (12)	12 (3)	59 (14)	66 (10)	49 (5)	6 (4)	22 (11)
O2E1	2269 (5)	5158 (8)	3748 (8)	15 (2)	73 (11)	26 (6)	8 (3)	−1 (3)	−3 (6)
O2E2	2702 (4)	4106 (10)	5198 (7)	17 (2)	101 (13)	29 (6)	−1 (4)	−4 (3)	−23 (8)
O2D1	1450 (3)	2723 (7)	1796 (8)	7 (2)	30 (8)	61 (7)	1 (3)	−1 (3)	3 (6)
O2D2	1491 (5)	496 (11)	1067 (9)	15 (2)	78 (10)	57 (8)	−10 (4)	−17 (4)	−10 (8)
O2U1	3019 (3)	5570 (10)	1850 (10)	7 (2)	54 (10)	72 (8)	12 (3)	−9 (3)	−5 (9)
O2U2	3997 (5)	4988 (9)	1811 (14)	9 (2)	124 (15)	97 (11)	−13 (4)	−9 (5)	5 (11)
C2E1	2547 (6)	2603 (13)	3616 (11)	13 (3)	77 (15)	45 (10)	−5 (5)	−10 (4)	29 (11)
C2E2	2500 (6)	4218 (14)	4244 (12)	5 (2)	115 (17)	38 (9)	−7 (6)	−7 (4)	−2 (11)
C2D1	2402 (5)	1415 (10)	1905 (12)	6 (2)	42 (11)	60 (10)	−2 (4)	−14 (4)	−5 (10)
C2D2	1719 (5)	1611 (13)	1568 (9)	9 (2)	64 (13)	17 (7)	5 (5)	−6 (3)	−16 (8)
C2U1	3294 (6)	3056 (11)	2814 (12)	13 (3)	28 (11)	60 (11)	2 (4)	5 (4)	8 (9)
C2U2	3444 (6)	4659 (12)	1941 (10)	17 (3)	56 (12)	12 (6)	−1 (4)	−4 (4)	2 (8)
OW11	1501 (4)	−633 (14)	−1046 [10]	8 (2)	202 (18)	66 (9)	1 (5)	8 (3)	−23 (12)
OW12	634 (4)	2596 (9)	−232 (9)	21 (2)	41 (10)	76 (8)	−1 (4)	−27 (4)	5 (8)
OW21	1100 (4)	5684 (12)	2951 (8)	11 (2)	161 (16)	38 (7)	31 (5)	−2 (3)	−10 (9)
OW22	2041 (14)	7570 (9)	1705 (11)	13 (2)	46 (10)	114 (12)	−1 (4)	−10 (4)	8 (10)
OW13	−2352 (5)	1721 (12)	−386 (14)	14 (3)	169 (18)	141 (15)	22 (6)	−8 (5)	58 (15)
OW14	−1547 (6)	1463 (12)	1925 (13)	44 (4)	79 (14)	103 (12)	12 (6)	5 (7)	18 (12)
OW23	4907 (4)	3347 (11)	2705 (11)	14 (2)	96 (13)	98 (10)	−1 (4)	−5 (4)	22 (10)
OW24	4108 (7)	6634 (14)	−36 (11)	57 (6)	136 (19)	71 (13)	−41 (8)	−1 (7)	−7 (12)
N1	41 (4)	−2228 (9)	−871 (8)	14 (2)	29 (10)	29 (7)	1 (4)	−4 (3)	−4 (7)
N2	2625 (4)	2764 (9)	2460 (7)	5 (2)	6 (10)	21 (6)	−9 (3)	4 (30)	−21 (7)

[a] Heavy atom parameters are 10^5 while light atom parameters are 10^4. [b] β's have the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE II

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	OW22	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

375 had values of F less than $\sigma(F)$ and were considered to be unobserved. They were not used in the refinement.

Solution and Refinement of the Structure

The structure was determined using a combination of heavy atom and superposition[5] 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 interrelated by mirrors 0 and $^1/_2$ in the y direction. Because of the larger number of light atoms and their small individual contribution 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.

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TABLE III

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)[a]

Metal–Light Atom Distances

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

Intraligand Distances

Atoms	Uncor	Riding	Atoms	Uncor	Riding
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

Angles

Atoms	Angles	Atoms	Angles
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)
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)
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)

Additional Interatomic Distances

Atoms	Distance	Atoms	Distance
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)

[a] Standard deviations are given in parentheses, justified to the last significant figure of the preceding number. [b] For an explanation of symmetry related positions see Figures 2A and 2B.

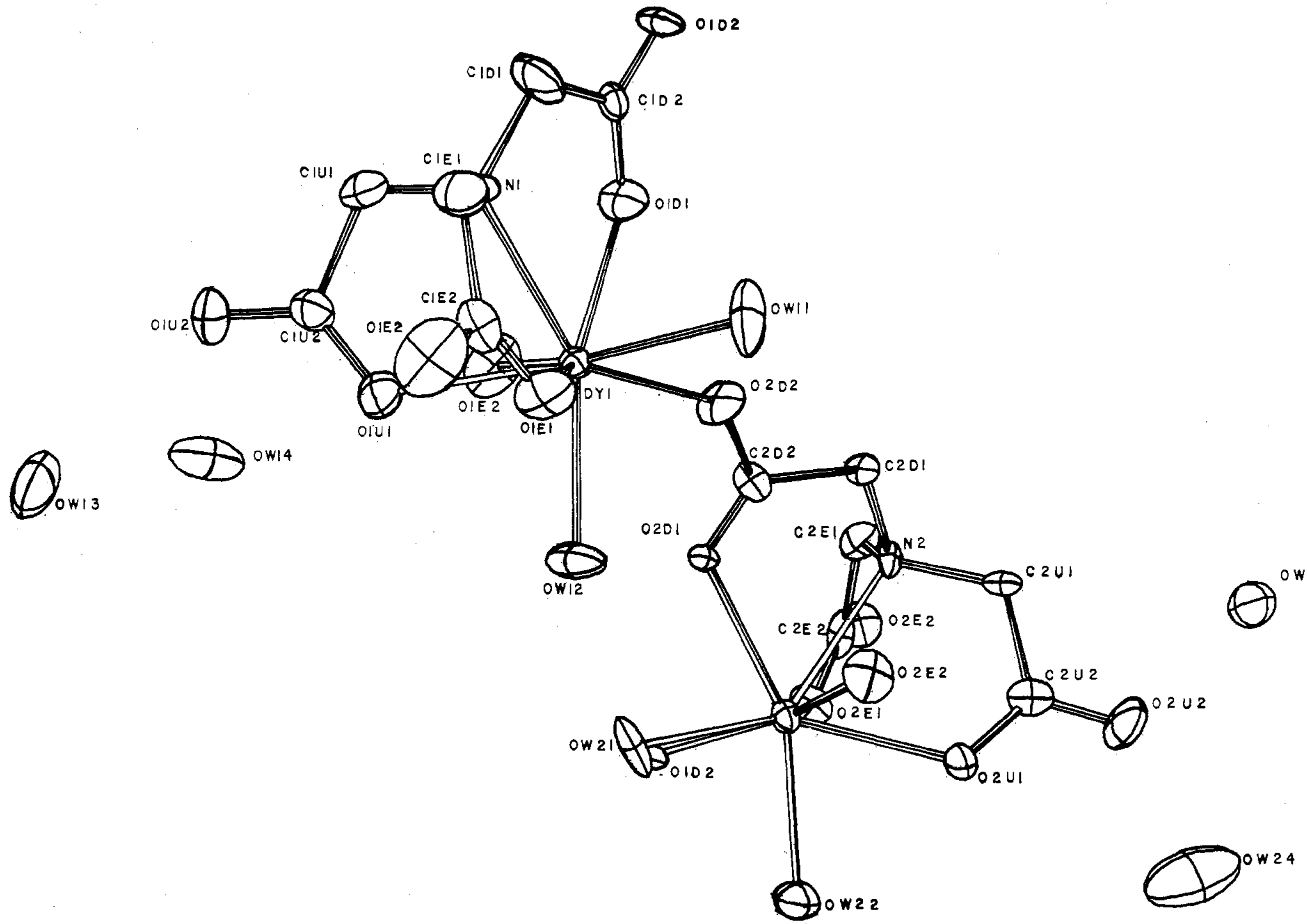

Figure 1.—Configuration of the two independent molecules. The two metal atoms are numbered for uniqueness. The nitrogen atoms have the same number as the metal atoms to which they are coordinated which is also the left-most number for the remaining atoms in the ligand. The letters specify the type of metal–oxygen interaction (see text). In the case of an oxygen atom, a one in the right-most position indicates coordination to the same metal atom as the nitrogen atom while a two indicates a different interaction. For carbon atoms, the right-most number indicates relative skeletal position.

By successive electron-density map–structure-factor calculations, the remaining light atom 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 Waber[6] for dysprosium^{3+} corrected for anomalous scattering[7] and those of Hanson, *et al.*,[8] for the light atoms.

All atoms were refined[9] isotropically with unit weights resulting in a value for the discrepancy factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.089. Weights were then introduced based on the individual statistics of the reflections ($w = 1/\sigma^2(F)$). The refinement was continued with anisotropic temperature factors for the dysprosium atoms to an R of 0.057 and of the weighted discrepancy factor $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$ of 0.082. In order to refine the structure further, 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 interactions 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 R and R_w were 0.050 and 0.070. A final difference electron-density map showed no residual electron density greater than 0.5 e/Å^3.

An attempt was made to determine the absolute configuration of the molecules. One image, the positional parameters of which are listed in Table I, gave a value of R 0.002 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 eight out of a possible 108 corrections between terms related by the approximate centering had values greater than 0.1 and no term exceeded 0.36.

Experience at this laboratory using a 9 × 9 block diagonal procedure[10] has 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 I since much larger blocks were used. In addition, the pronounced anisotropic motion of some of the atoms in proximity to the Dy atom could well be an artifact of the refinement procedure to some extent. In Table II are listed the root-mean-square amplitudes of vibration while in reference 11 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

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

[7] "International Tables for X-ray Crystallography," Vol III, Kynoch Press, Birmingham, 1965.

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

[9] W. R. Busing, K. O. Martin, and H. A. Leavy, Report ORNL-TM-305, "A Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[10] T. A. Beineke and L. L. Martin, *J. Organometal. Chem.*, **80**, 65 (1969).

[11] A listing of the structure factor amplitudes will appear 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-72-2789. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

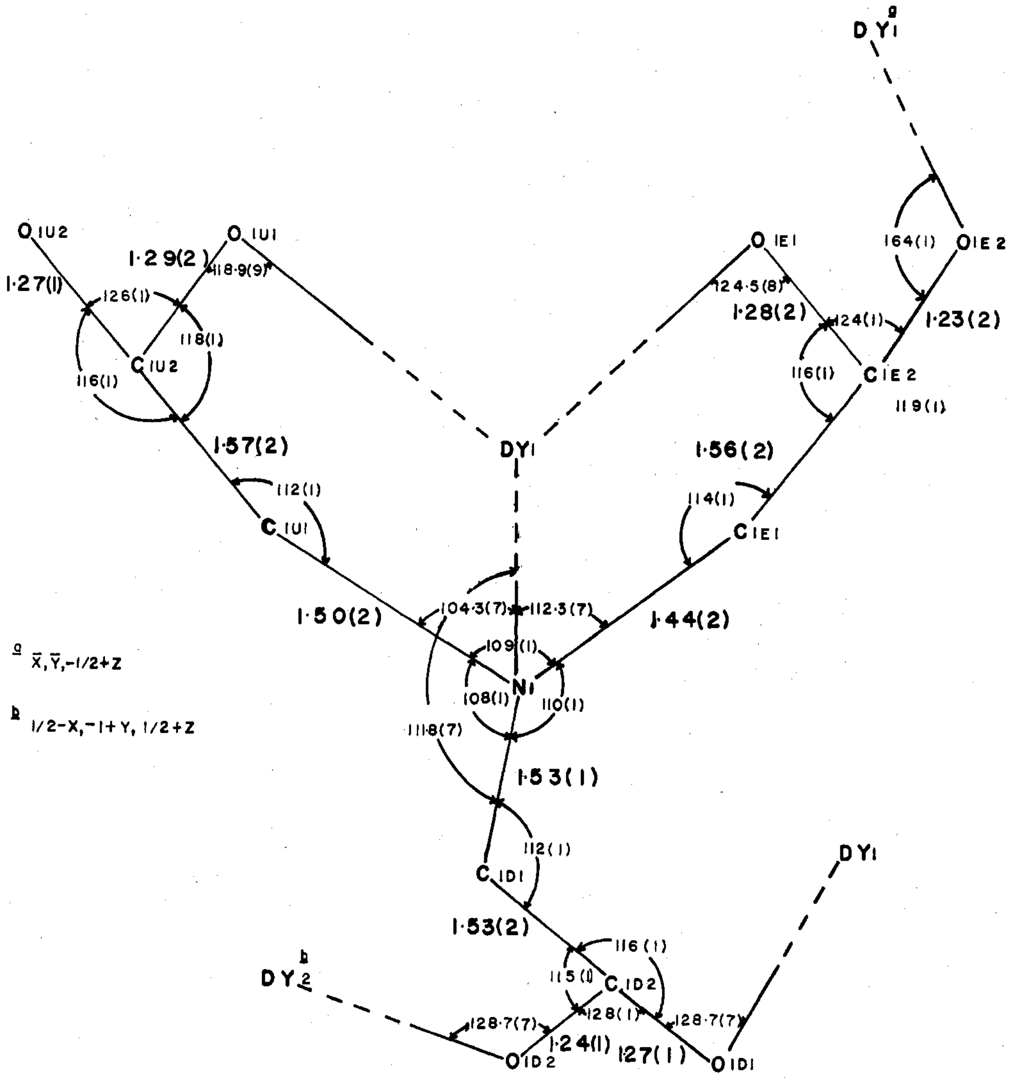

Figure 2A.—Schematic drawing of NTA ligand 1.

III. Their estimated errors[12] 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 model[13] 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. Both corrected and uncorrected intramolecular distances are listed in Table III.

The molecular configurations of the two independent Dy·NTA·$4H_2O$ molecules are shown in Figure 1. The two ligands exhibit similar metal coordination. 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 acetate oxygen 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 (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 2A and 2B. In Figure 3 is seen the packing of the two, independent molecules in the unit cell. 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.[14]

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.[15] Also, the wide range in metal–oxygen and C–O_a distances probably is a result

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(12) 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.

(13) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

(14) *Chem. Soc., Spec. Publ.*, **No. 18**, S21s (1965).

(15) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

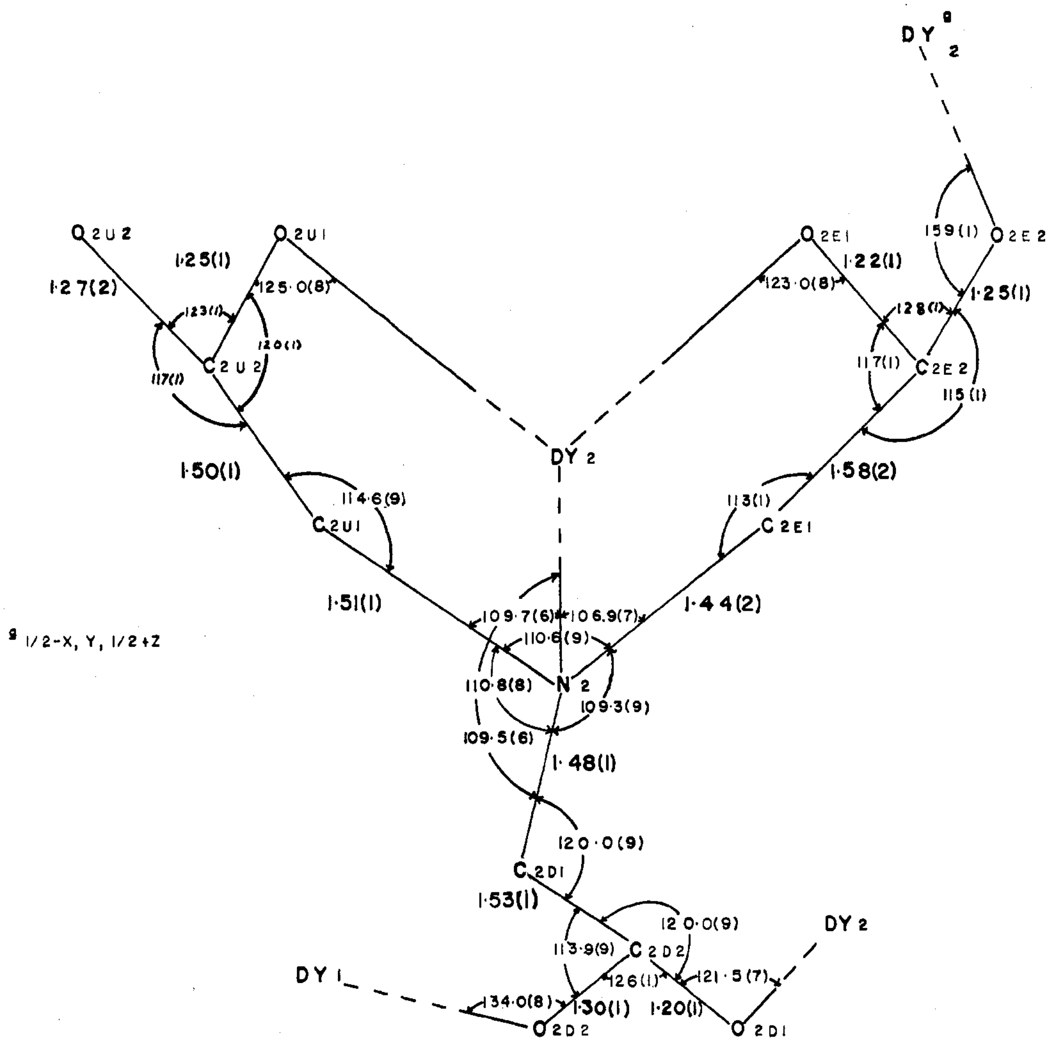

Figure 2B.—Schematic drawing of NTA ligand 2.

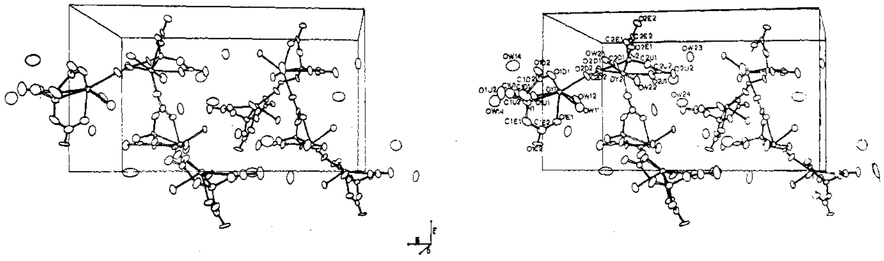

Figure 3.—Stereoscopic view down the *b* axis of the unit cell.

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 distances 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.[16]

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 which is a distorted, square antiprism where the symmetry has been reduced from D_{4d} to approximately D_{2d}.

A projection down one of the twofold axes in molecule one and a projection perpendicular to the approximate fourfold inversion axis in molecule two are given in Figures 4 and 5. The good agreement, in most cases, between symmetry equivalent distances (see Table IV) illustrates the approximate D_{2d} symmetry. The nonacoordinate, capped, square antiprism found in the Pr·NTA·$3H_2O$ can be converted to the octacoordinate 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.

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(16) T. A. Beineke and J. Del Gaudio, *Inorg. Chem.*, **7**, 715 (1968).

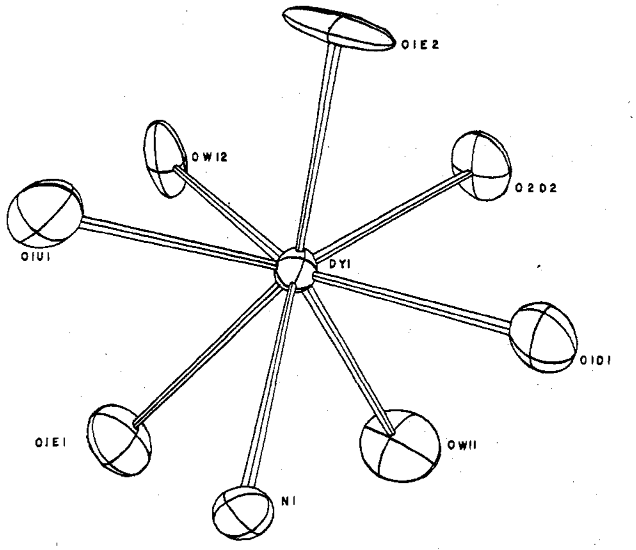

Figure 4.—Coordination of Dy1 as viewed down a pseudo-C_2 axis.

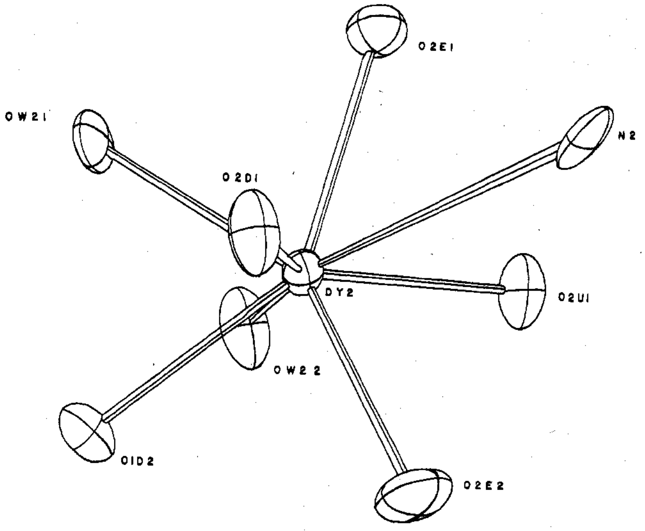

Figure 5.—Coordination of Dy2 as viewed perpendicular to the pseudo-$\bar{4}$ axis.

TABLE IV
ATOMS AND DISTANCES[a] RELATED BY PSEUDOSYMMETRY

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 $\bar{4}$

O1U1–O1D1–O1E1–O2D2 O2E2–OW22–O2E1–O2D1
OW12–O1E2–N1–OW11 N2–OW21–O2U1–O1D2

Equivalent Distances Related by Pseudosymmetry

Molecule 1			Molecule 2		
Atoms	Dist	Av	Atoms	Dist	Av
O1E1–O1U1	2.78	2.80	O1D2–OW21	2.85	2.81
O1D1–O2D2	2.83		O2U1–N2	2.77	
O1E1–N1	2.77	2.88	O1D2–O2D1	2.85	2.97
O1D1–O1E2	2.85		OW21–OW22	3.05	
O1U1–OW12	3.06		N2–O2E1	2.78	
O2D2–OW11	2.78		O2E2–O2U1	2.87	
O1E1–OW12	2.87		O1D2–OW22	3.19	
O1U1–N1	2.77		OW21–O2D1	3.11	
O1D1–OW11	2.95		N2–O2E2	3.09	
O2D2–O1E2	2.98		O2U1–O2E1	2.85	
N1–O1E2	3.76	3.57	O2D1–O2E1	3.69	3.41
OW11–OW12	3.60		O2D1–O2E2	2.95	
N1–OW11	3.47		OW22–O2E1	3.34	
OW12–O1E2	3.44		OW22–O2E2	3.67	
O1E1–OW11	2.70	2.80	O1D2–O2E2	2.89	2.77
O1U1–O1E2	2.72		OW21–O2E1	2.94	
O1D1–N1	2.69		N2–O2D1	2.67	
O2D2–OW12	3.08		O2U1–OW22	2.78	

[a] Average standard deviation in distances is 0.02 Å.

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.*,[17] for the La·EDTA$^-$ complex. The distortions are much greater in this case than for the dodecahedron and we prefer the latter.

The average Dy–O_a, Dy–N, and Dy–O_w distances, uncorrected for thermal motion, are 2.345, 2.578, and 2.359 Å. This corresponds to a decrease of approximately 0.1 Å compared to the corresponding praseodymium distances for the M–O_a and M–N bonds. This is in good agreement with the decrease in the ionic radius.[18] The Dy–O_w distances average approximately 0.06 Å shorter than expected. However, there are a large number of O_w–O_a distances which are in the range typical of hydrogen bonding (Table III) and such hydrogen bonding might be expected to increase the metal–O_w interactions on electrostatic grounds.

In solution it would seem unlikely that the intermolecular bridges found in these crystalline complexes would be formed. It would seem more reasonable that the positions which are occupied by bridging oxygen atoms in both the praseodymium and dysprosium crystal structures are occupied by solvent molecules in solution. The process of crystallization may well involve a replacement of these solvent molecules by the carboxylate oxygen atoms resulting in the displaced solvent molecules being trapped in the lattice. A liquid diffraction study of these compounds in aqueous solution is planned.

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(17) J. L. Hoard, B. Lee and M. D. Lind, *J. Amer. Chem. Soc.*, **87**, 1612 (1965).

(18) D. H. Templeton and C. H. Danben, *ibid.*, **76**, 5237 (1954).