

Structural Studies on the Rare Earth Carboxylates. 23.

The Crystal Structure of Tetra-aquobis(hydrogeniminodiacetato)-iminodiacetatodiprasedymium(3+) Dichloride Trihydrate at -50 °C

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In a systematic study of various lanthanoid dicarboxylate compounds, the crystal structure of $[Pr_2(H_2O)_4(C_4H_5NO_4)_2(C_4H_5NO_4)]Cl_2 \cdot 3H_2O$ has been determined using X-ray intensity data collected at $-50^{\circ}C$ with a four-circle single crystal diffractometer. The structure of an iso-topic neodymium analogue has been reported previously. The space group is $P2_1/m$, and there are two formula units in the cell. The lattice parameters are $a = 8.7198(9)$, $b = 18.4218(27)$, $c = 9.2725(6)$ Å and $\beta = 108.248(6)^{\circ}$. The structure has been refined to $R = 0.087$. Each of the hydrogeniminodiacetate and iminodiacetate ions is coordinated to four praseodymium ions forming a three-dimensional network. The coordination polyhedron around each metal ion is a distorted monocapped square antiprism formed by seven carboxylate oxygens and two water oxygens. The Pr–O distances are in the range 2.34–2.75 Å. The chloride ions are connected by hydrogen bonds via two water molecules and two nitrogen atoms, forming chains running in the a -direction.

The lanthanoid elements Ce–Gd form an iso-topic series of iminodiacetate compounds with the composition $[M_2(H_2O)_4(C_4H_5NO_4)_2(C_4H_5NO_4)]Cl_2 \cdot 3H_2O$. The crystal structure of the neodymium compound has previously been determined¹ from three-dimensional intensity data recorded with the Weissenberg multiple film technique. Although the main features of the structure were obtained, the accuracy needed for a more quantitative description of it was not achieved. Such a description is desirable for a discussion of the shape of the coordination polyhedron around the metal ion and the geometry

of the iminodiacetate ligand in various solid complexes as will be given in a following publication.²

The crystal quality is poor for all compounds in the series. Since the crystals of the praseodymium compound were judged to be the most suitable in the series, this compound, referred to as PRIMIN below, was chosen to be investigated with an automatic single crystal diffractometer. To facilitate location of the water molecule not found in the previous analysis, the intensity data were collected at $-50^{\circ}C$.

EXPERIMENTAL

Preparation and analysis. The compounds $[M_2(H_2O)_4(C_4H_5NO_4)_2(C_4H_5NO_4)]Cl_2 \cdot 3H_2O$, M = Ce–Gd, were prepared from an aqueous solution of $M_2(C_4H_5NO_4)_3$ by adjusting the pH to 2.5 with HCl. Crystals were then obtained by slow evaporation of the solution at room temperature. The neodymium compound was analyzed for neodymium, carbon, nitrogen, hydrogen, and water. The results were 32.2(32.6)% Nd, 16.3(16.3)% C, 4.7(4.8)% N, 3.8(3.5)% H and 14.0(14.3)% H_2O , where the number in parentheses are the calculated values for $[Nd_2(H_2O)_4(C_4H_5NO_4)_2(C_4H_5NO_4)]Cl_2 \cdot 3H_2O$. The praseodymium compound was analyzed only for the metal, the result being 32.0(32.2)% Pr. Powder photographs of all preparations were nearly identical.

The weight loss was determined as a function of the temperature in the range 25–200°C using a Mettler thermogravimetric analyser equipped with a DTA unit. The heating rate used was 2 K/min.

Single crystal work. A single crystal with the dimensions $0.13 \times 0.06 \times 0.13$ mm was used for collecting data at -50 ± 2 °C on a Nonius computer-controlled four-circle diffractometer of type CAD-4, equipped with a commercial low temperature device modified as will be described in a forthcoming communication.³ Intensity data were measured at a take-off angle of 5° using $\text{CuK}\alpha$ radiation. A graphite monochromator was used. The $\omega - 2\theta$ scan technique was employed, with a scan range $\Delta\omega = 0.80 + 0.50 \tan \theta$. A fast pre-scan was used to determine the scan speed at which a predetermined minimum number of counts (3000) was received by the detector. However, the recording time for a reflexion was limited to 3 min. The scan range, $\Delta\omega$, was extended 25% at both ends for the background measurement. Of the 2443 independent reflexions in the interval $5^\circ < \theta < 70^\circ$ and with $h \leq 6$, 2392 were measured. All the reflexions with $h > 6$ and 51 of those with $h \leq 6$ were not attainable due to obscuration by the low temperature device. Another 620 reflexions with $I < 3\sigma_c(I)$ were considered not to be significantly different from the background and were excluded from the following calculations. The values of $\sigma_c(I)$ were based only on counting statistics. The reflexions 045, 191, and 045 were selected as standards, and their intensities were recorded after every 50 reflexion measurements. The intensities of the standard reflexions decreased 20% during the experiment. The variations could be described with a linearly decreasing function of the recording time and this function was used for scaling the data set. The values of I and $\sigma_c(I)$ were corrected for Lorentz, polarization and absorption effects. The expression $p = (1 + \cos^2 2\theta_M \cos^2 2\theta) / (1 + \cos^2 2\theta_M)$ with $\theta_M = 13.3^\circ$ was used in the correction of the polarization effects. The transmission factors evaluated by numerical integration varied from 0.034 to 0.297.

UNIT CELL AND SPACE GROUP

PRIMIN crystallizes in the monoclinic system. The systematically absent reflexions are $0k0$ with $k \neq 2n$, indicating the space group to be $P2_1$ (No. 4) or $P2_1/m$ (No. 11).⁴

Accurate unit cell dimensions were determined by measuring θ -values for 60 reflexions on the diffractometer. The technique will be described later.³ The measured θ -values were used for a least-squares refinement of the unit cell dimensions. The density, D_m , was determined from the loss of weight in benzene. The following crystal data were obtained:

$$a = 8.7198(9) \text{ \AA}^* \quad D_m = 2.07 \text{ g cm}^{-3}$$

* Numbers within parentheses represent e.s.d.'s in the last significant digits.

$b = 18.4218(27) \text{ \AA}$	$D_x = 2.05 \text{ g cm}^{-3}$
$c = 9.2725(6) \text{ \AA}$	$Z = 4$
$\beta = 108.248(6)^\circ$	$\mu(\text{CuK}\alpha) = 270.7 \text{ cm}^{-1}$
$V = 1414.6 \text{ \AA}^3$	

REFINEMENT OF THE STRUCTURE

Preliminary atomic parameters were taken from Ref. 1 for all non-hydrogen atoms except the water oxygen atoms O(9) and O(10). Assuming the centrosymmetric space group $P2_1/m$, these parameters, together with a scale factor, were improved by a full matrix least-squares refinement. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, with weights $w = 1/[\sigma_c^2(F) + a|F_o|^2 + b]$. The constants a and b were chosen so that the average values of $w(|F_o| - |F_c|)^2$ were fairly constant between different $|F_o|$ and $\sin \theta$ intervals. After the last cycle of the refinement the variations of $w(|F_o| - |F_c|)^2$ were in the ranges 0.9–1.5 and 0.9–1.4 for the various $|F_o|$ and $\sin \theta$ intervals, respectively. In the last cycles of refinement $a = 0.003$ and $b = 7.0$ were used. A difference electron density map calculated using data with $\sin \theta/\lambda \gtrless 0.4 \text{ \AA}^{-1}$ revealed the positions of remaining water oxygen atoms O(9) and O(10). As the maximum electron density for O(10) was 3 e\AA^{-3} compared to 6 e\AA^{-3} for O(9), the occupancy for O(10) was included as a variable in the further refinements. The final occupancy was 0.81(3). This small number was considered to be caused by a dynamic disorder of this molecule, as will be discussed later. The occupancy number was at a fixed value of 1.0 in the following calculations. The final structural model included anisotropic thermal parameters for the praseodymium ion and an isotropic extinction parameter $g = 0.03 \times 10^4$.⁵ The value of g corresponds to a mosaic spread of $171''$ or a domain size of $0.05 \times 10^{-4} \text{ cm}$. In the last cycle of refinement, the shifts in all parameters were less than 5% of their corresponding e.s.d.'s. The agreement index was 0.087. A final difference electron density map was featureless.

The atomic scattering factors used were taken from the International Tables⁶ (Cl, O, N, and C) and from Cromer *et al.*⁷ (Pr). The atomic scattering factor for Pr was corrected for anomalous dispersion. The final positional and thermal parameters are given in Table 1. Observed and calculated structure amplitudes

Table 1. Atomic parameters with e.s.d.'s in parentheses. B denotes the isotropic temperature factor.

Atom	$x/a(\times 10^4)$	$y/b(\times 10^4)$	$z/c(\times 10^4)$	$B(\text{\AA}^2)$
Pr	-89(2)	240(1)	2179(1)	a
Cl(1)	3601(17)	2500	4129(13)	3.7(2)
Cl(2)	8058(15)	2500	3986(11)	2.9(2)
O(1)	7701(25)	108(10)	5759(19)	2.6(3)
O(2)	8162(24)	524(9)	3642(18)	2.4(3)
O(3)	2556(22)	320(9)	-521(17)	1.9(3)
O(4)	2323(24)	790(9)	1633(18)	2.2(3)
O(5)	-805(24)	646(9)	-812(18)	2.3(3)
O(6)	-1785(26)	1322(10)	776(19)	2.6(3)
O(7)	700(26)	1414(10)	3751(19)	2.7(3)
O(8)	-737(25)	-950(9)	3245(19)	2.7(3)
O(9)	4485(31)	2500	9780(23)	1.5(4)
O(10)	6113(57)	-1367(22)	2863(43)	10.2(11)
N(1)	5327(30)	1281(11)	2668(22)	2.4(4)
N(2)	-2196(59)	2500	-844(46)	4.7(9)
C(1)	7279(34)	455(12)	4493(25)	1.9(4)
C(2)	5644(37)	820(13)	4085(27)	2.4(5)
C(3)	4859(40)	854(15)	1208(30)	3.1(6)
C(4)	3049(34)	647(13)	740(25)	2.1(4)
C(5)	-1928(45)	1821(17)	-1649(33)	3.7(6)
C(6)	-1499(36)	1216(13)	-495(27)	2.3(4)

^a The anisotropic thermal parameters for praseodymium, calculated from the expression $\exp[-(h^2\beta_{11} + 2hk\beta_{12} + \dots)]$, are $\beta_{11}=0.0099(3)$, $\beta_{22}=0.0010(1)$, $\beta_{33}=0.0031(2)$, $\beta_{12}=0.0002(1)$, $\beta_{13}=0.0017(1)$ and $\beta_{23}=0.0000(1)$.

are compared in Table 2, and selected interatomic distances and angles are shown in Table 3.

All computations were made on the UNIVAC 1108 computer in Lund, Sweden and a list of the programmes used is given in Ref. 8.

DESCRIPTION OF THE STRUCTURE

There are two crystallographically different ligands in the structure. Their atoms are designated in Figs. 1 and 2 and they are referred to below as ligand 1 or 2, depending upon whether

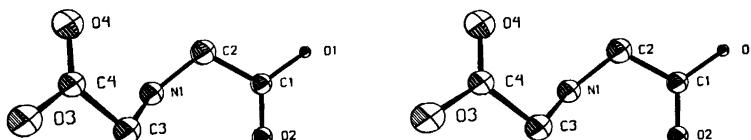


Fig. 1. A stereoscopic pair of drawings showing the hydrogeniminodiacetate ion. The view is perpendicular to a least-squares plane through N(1), C(2), C(1), O(1) and O(2). The Figs. 1–4 have been drawn by the programme ORTEP.

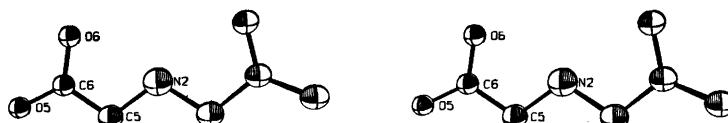


Fig. 2. A stereoscopic pair of drawings showing the iminodiacetate ion. The view is perpendicular to a least-squares plane through N(2), C(5), C(6), O(5), and O(6).

Table 2. Continued.

12	25	24	L = S H = 5	1	51	47	11	77	A1	11	11	L = 7 H = 4	L = 8 H = 3	L = 9 H = 2	
13	26	20	0 124 125	2	22	27	13	58	60	12	42	0 37 44	2 12 10	0 81 76	
15	43	41	0 25 12	3	74	72	15	56	52	13	24	2 58 64	3 29 30	2 79 79	
16	45	41	0 29 71	4	20	17	16	32	33	4	46	4 66 74	4 23 25	4 63 61	
17	17	18	0 23 22	5	27	R1	L = A, H = 4	16	54	51	6	50	5 49 69	5 24 18	5 36 35
18	59	59	7 18 21	6	29	35	0 23	35	17	22	17	8 22 23	7 56 58	6 36 35	
			8 20 22	7	43	58	7 20	21				9 63	60	7 28 29	
L = S H = 5	9 23 22	R 19 12	5 29 34	L = 7 H = 1	L = 7 H = 5	L = 8 H = 4	L = 9 H = 3								
0 92 93	11 17 15	9 101 107	4 19 24	0 145 141	0 58 50	0 55 52	0 53 50								
1 22 24	11 12 10	5 77 83	5 41 42	2 90 92	2 53 56	2 46 47	2 46 47								
2 88 7R		13 76 79	7 74 77	4 66 68	4 46 46	4 46 46	4 46 46								
3 72 15	L = S H = 6	15 66 65	0 55 54	6 46 46	6 38 38	3 22 25	3 22 25								
4 65 67	6 57 58	9 72 48	11 75 74	7 28 27											
6 74 75	2 50 44	R 12 10	14 66 54	R 43 42	L = R H = 0	5 46 49	L = 10 H = 0								
7 14 16	4 48 52			11 74 24	2 28 25	6 11 8	0 27 31								
8 57 59	4 30 34	L = 6 H = 2	I = A, H = 5	13 12 13	2 23 22	7 51 52	2 20 19								
9 49 53	I = 6 H = 0	1 24 16	1 23 20	14 52 33	3 47 50	3 20 21									
11 15 17	0 99 96	2 25 20	5 46 72	16 35 36	5 52 54	L = 9 H = 0	4 32 34								
12 22 22	1 30 26	3 48 59	7 54 51	L = 7 H = 2	9 100 104	0 65 67	5 51 51								
13 24 27	2 47 45	5 78 79	8 16 18	0 102 105	9 95 98	2 88 89	6 12 12								
14 22 24	3 46 44	7 84 83	9 63 62	2 85 82	13 62 60	3 11 9	7 64 66								
15 44 42	4 53 55	9 95 102	11 54 47	4 100 100	6 42 74	8 19 18									
17 23 19	5 70 72	10 18 16		6 62 57	6 50 54										
	6 17 17	11 81 86	L = A, H = 6	R 37 35	R 30 36	L = 10 H = 1									
L = S H = 4	7 84 86	13 63 72	5 24 28	14 43 42	3 46 43	8 23 22	L = 10 H = 1								
Po 21	9 43 44	15 57 54	5 48 56	15 15 12	5 66 69	9 21 26	0 35 35								
9 101 101	0 91 101	16 18 19	7 51 56		11 14 12	10 15 15	2 33 34								
4 83 90	11 25 26	17 34 35	I = 7 H = 3	9 77 77	11 14 12	3 23 26									
5 19 20	11 72 77	L = 6 H = 3	0 115 117	0 79 78	10 15 15	0 87 87									
6 73 72	11 71 75	0 36 35	1 39 42	2 83 84	11 76 76	2 93 88									
7 24 28	14 13 12	1 23 20	2 120 122	4 76 75	13 66 66	3 20 19									
Po 20 27	15 61 61	2 26 22	4 76 75	5 14 18	4 74 77										
9 30 31	17 43 41	5 51 50	6 68 70	6 56 65	L = P H = 2	5 15 13									
*2 24 26	18 30 27	7 69 71	R 19 22	7 21 20	5 49 70	6 45 44									
14 30 30		L = A H = 1	7 69 71	8 19 22	9 64 67	R 19 19									
	C 20 17	9 66 67	R 2R 34	11 60 60	9 26 22										

they contain N(1) or N(2), respectively. Each ligand is coordinated to four different praseodymium ions. Together with the praseodymium ions ligand 1 forms a two-dimensional network in the *ac*-plane. Ligand 2 connects these layers in the *b*-direction. The resulting three-dimensional arrangement is shown in Fig. 3.

The coordination polyhedron. It was suggested previously¹ that the lanthanoid ion was eight-coordinated, with metal-oxygen distances in the range 2.3–2.6 Å. The coordination polyhedron was described as a square antiprism. By including O(5) in the coordination sphere [the Pr–O(5) distance is 2.75(2) Å] each lanthanoid ion is surrounded by nine oxygen atoms forming a distorted monocapped square antiprism (Fig.

4). The atom O(5) is situated at a corner of the square antiprism in one polyhedron (the distance Pr–O(5)ⁱⁱⁱ) is 2.34(2) Å] but caps the antiprism of the neighbouring polyhedron. A similar situation is found in the iminodiacetate compound Nd(C₄H₈NO₄)(H₂O)₃Cl⁺ where the nine-coordinated neodymium ion is surrounded by a tricapped trigonal prism of one nitrogen and eight oxygen atoms. One of the oxygen atoms is situated at a corner of the trigonal prism in one polyhedron but in the equatorial ("capping") plane of the neighbouring polyhedron. The corresponding metal-oxygen distances are 2.52(2) and 2.78(2) Å, respectively. Bond distances in the coordination polyhedron are given in Table 3a. There are 12 oxygen-

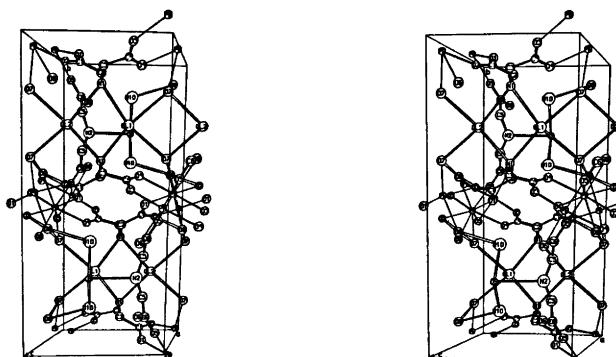


Fig. 3. A stereoscopic pair of drawings showing the structure of PRIMIN.

Table 3. Selected interatomic distances (\AA) and angles ($^\circ$) with estimated standard deviations.**a. The coordination polyhedron**

Distance	Distance
$\text{Pr}-\text{O}(1)^a$	$2.43(2)$
$\text{Pr}-\text{O}(2^{ii})$	$2.40(2)$
$\text{Pr}-\text{O}(3^{iii})$	$2.45(2)$
$\text{Pr}-\text{O}(4)$	$2.53(2)$
$\text{Pr}-\text{O}(5)$	$2.75(2)$
$\text{Pr}-\text{O}(5^{iii})$	$2.34(2)$
$\text{Pr}-\text{O}(6)$	$2.58(2)$
$\text{Pr}-\text{O}(7)$	$2.58(2)$
$\text{Pr}-\text{O}(8)$	$2.54(2)$
$\text{O}(1)-\text{O}(4)$	$2.94(2)$
$\text{O}(1)-\text{O}(5^{iii})$	$3.19(2)$
$\text{O}(1)-\text{O}(7)$	$3.10(3)$
$\text{O}(1)-\text{O}(8)$	$2.96(3)$
	$\text{O}(2^{ii})-\text{O}(3^{iii})$
	$3.17(2)$
	$\text{O}(2^{ii})-\text{O}(6)$
	$3.05(2)$
	$\text{O}(2^{ii})-\text{O}(7)$
	$2.73(3)$
	$\text{O}(2^{ii})-\text{O}(8)$
	$2.94(2)$
	$\text{O}(3^{iii})-\text{O}(5)$
	$2.92(3)$
	$\text{O}(3^{iii})-\text{O}(5^{iii})$
	$2.87(2)$
	$\text{O}(3^{iii})-\text{O}(6)$
	$3.09(3)$
	$\text{O}(3^{iii})-\text{O}(8)$
	$2.78(2)$
	$\text{O}(4)-\text{O}(5)$
	$2.95(2)$
	$\text{O}(4)-\text{O}(5^{iii})$
	$2.96(3)$
	$\text{O}(4)-\text{O}(7)$
	$2.99(3)$
	$\text{O}(5)-\text{O}(5^{iii})$
	$2.93(3)$
	$\text{O}(5^{iii})-\text{O}(8)$
	$3.02(3)$
	$\text{O}(6)-\text{O}(7)$
	$2.93(3)$

^a The superscripts (i)–(vii) indicate the following equivalent sites in the structure

(i)	$1-x$,	$-y$,	$1-z$	(v)	$-x$,	$-y$,	$1-z$
(ii)	$-1+x$,	y ,	z	(vi)	$-1+x$,	y ,	$-1+z$
(iii)	$-x$,	$-y$,	z	(vii)	$-1-x$,	$-y$,	$-z$
(iv)	x ,	$\frac{1}{2}-y$,	z				

b. Ligand 1

Distance	Angle
$\text{C}(1)-\text{O}(1)$	$1.29(3)$
$\text{C}(1)-\text{O}(2)$	$1.27(3)$
$\text{C}(4)-\text{O}(3)$	$1.27(3)$
$\text{C}(4)-\text{O}(4)$	$1.22(3)$
$\text{C}(1)-\text{C}(2)$	$1.51(4)$
$\text{C}(3)-\text{C}(4)$	$1.55(4)$
$\text{N}(1)-\text{C}(2)$	$1.52(3)$
$\text{N}(1)-\text{C}(3)$	$1.51(3)$
	$\text{O}(1)-\text{C}(1)-\text{O}(2)$
	$124(2)$
	$\text{O}(1)-\text{C}(1)-\text{C}(2)$
	$115(2)$
	$\text{O}(2)-\text{C}(1)-\text{C}(2)$
	$120(2)$
	$\text{O}(3)-\text{C}(4)-\text{O}(4)$
	$129(3)$
	$\text{C}(3)-\text{C}(4)-\text{O}(3)$
	$113(2)$
	$\text{C}(3)-\text{C}(4)-\text{O}(4)$
	$117(2)$
	$\text{C}(1)-\text{C}(2)-\text{N}(1)$
	$112(2)$
	$\text{C}(2)-\text{N}(1)-\text{C}(3)$
	$114(2)$
	$\text{N}(1)-\text{C}(3)-\text{C}(4)$
	$110(2)$

c. Ligand 2

Distance	Angle
$\text{C}(6)-\text{O}(5)$	$1.29(3)$
$\text{C}(6)-\text{O}(6)$	$1.29(3)$
$\text{C}(5)-\text{C}(6)$	$1.54(4)$
$\text{N}(2)-\text{C}(5)$	$1.54(4)$
	$\text{O}(5)-\text{C}(6)-\text{O}(6)$
	$125(2)$
	$\text{O}(5)-\text{C}(6)-\text{C}(5)$
	$117(2)$
	$\text{O}(6)-\text{C}(6)-\text{C}(5)$
	$119(2)$
	$\text{N}(2)-\text{C}(5)-\text{C}(6)$
	$105(2)$
	$\text{C}(5)-\text{N}(2)-\text{C}(5^{iv})$
	$109(3)$

d. Possible hydrogen bonds

Distance	Distance
$\text{O}(7)-\text{Cl}(2^{ii})$	$3.11(2)$
$\text{O}(7)-\text{Cl}(1)$	$3.16(2)$
$\text{N}(1)-\text{Cl}(1)$	$3.23(2)$
$\text{N}(1)-\text{Cl}(2)$	$3.22(2)$
	$\text{O}(8)-\text{O}(2^i)$
	$2.94(2)$
	$\text{O}(8)-\text{O}(7^{iv})$
	$2.90(2)$
	$\text{N}(2)-\text{O}(9^{vi})$
	$3.12(6)$
	$\text{O}(9^{vi})-\text{O}(10^{iii})$
	$3.14(4)$
	$\text{O}(10^{iii})-\text{O}(8^{vii})$
	$2.77(5)$

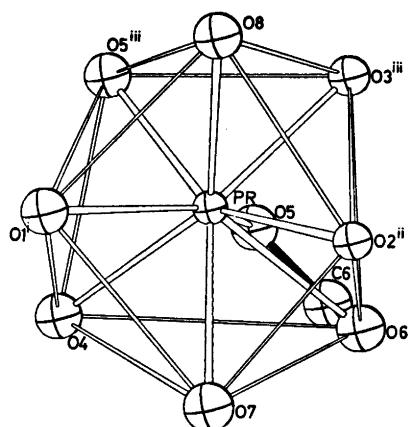


Fig. 4. The coordination polyhedron around the praseodymium ion.

oxygen distances within the coordination polyhedron, which are less than 3.0 Å, thus indicating van der Waals contacts.

The ligands. The atoms in ligand 1 are crystallographically independent, while ligand 2 has the symmetry m . From the stoichiometry of the compound, there must be two protons balancing the charge of the chloride ions. These protons are most probably bonded to the nitrogen atoms N(1). Thus, the structure should contain both $-\text{NH}_2^+$ (ligand 1) and $-\text{NH}-$ groups (ligand 2). In contrast to the situation in $\text{Nd}(\text{C}_4\text{H}_9\text{NO}_4)_2(\text{H}_2\text{O})_3\text{Cl}$,⁹ the $-\text{NH}-$ group in ligand 2 is not coordinated to the metal ion. Bond distances and angles for the ligands are given in Tables 3b and 3c. They are compatible with those found for the iminodiacetic acid group in other structures.⁸⁻¹¹

Possible hydrogen bonds. Judging from the chloride-oxygen and chloride-nitrogen distances (Table 3d), each chloride ion might accept four hydrogen bonds. The arrangement of the hydrogen bonded atoms around the chloride ions may be described as distorted rectangles. These rectangles are connected by sharing the edges N(1)-N(1) and O(7)-O(7), and infinite chains running in the a -direction are formed (Fig. 3). The water oxygen O(8) may donate hydrogen bonds to O(7) and O(2) in the neighbouring coordination polyhedron. It is also possible that there is a hydrogen bonded chain N(2)-O(9)-O(10)-O(8) in the structure. Since N(2) and

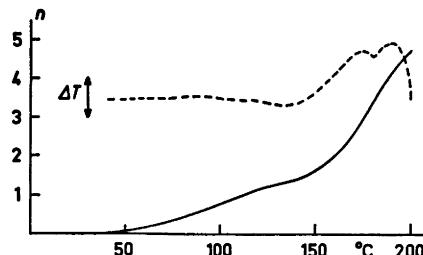


Fig. 5. TGA (solid line) and DTA (dashed line) curves for PRIMIN. n is the number of moles of water lost per two moles of praseodymium. In the DTA curve ΔT is on an arbitrary scale.

O(9) are located in a mirror plane, there would be two O(9)-O(10)-O(8) branches.

The water oxygen O(10) could not be located by using the data collected at room temperature.¹ In this analysis it was found to be situated at interstices of the structure. It will probably have a high mobility in these interstices at room temperature. This dynamic disorder will decrease at low temperature to form the above mentioned hydrogen bonded chain. At -50 °C there might still be some disorder since the occupancy number refines to 0.81 for O(10). The large value of the temperature factor supports this view. In Fig. 5 the TGA and DTA curves for PRIMIN are shown. The compound starts losing weight at about 40 °C. A weight loss equivalent to 1.5 mol of water is achieved at about 145 °C, and up to this temperature no change in the DTA curve is observed. There is one maximum in the DTA curve at 175 °C, and the weight loss at this temperature is equivalent to the loss of 3 mol of water. Thus, the DTA curve indicates that half of the hydrated water is very loosely bonded, and can therefore be expected to have a high thermal mobility at room temperature. Similar dynamic disorder of water molecules is found in $\text{Nd}_2(\text{C}_2\text{O}_4)_{10}\cdot 5 \text{ H}_2\text{O}$,^{12,13} where at room temperature one third of the water molecules are disordered.

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