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Structural Studies on the Rare Earth Carboxylates

22. The Crystal Structure of Tetra-aquo-thiodiacetatoneodymium(III) Chloride

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In order to determine the coordination geometry around the neodymium ion the crystal structure of $Nd(C_4H_4O_4S)(H_2O)_4Cl$ has been determined from three-dimensional X-ray intensity data. The compound crystallizes in the orthorhombic space group *Pnnm* with $Z=4$. The unit cell dimensions are $a=6.922$, $b=17.69$, and $c=10.226$ Å. The structure has been refined to $R=0.127$. The neodymium ion is surrounded by four carboxylate oxygen atoms, four water molecules, and one sulfur atom, which form a distorted tricapped trigonal prism. The Nd – O distances are in the range 2.31 – 2.53 Å. The thiodiacetate ion forms two five membered rings with the metal ion, with the sulfur atom located in the equatorial plane of the prism. The Nd – S distance is 3.15 Å. The coordination polyhedra are connected by the carboxylate groups forming layers stacked in the *b*-direction. The chloride ion is situated between the layers and accepts two hydrogen bonds from each layer, thus holding the structure together in the *b*-direction.

The structures of a number of rare earth complexes in the solid state with ligands of the composition OCORCOO with $R=CH_2OCH_2$,[1] CH_2NHCH_2,[2] and C_5H_5N [3] have been described in previous communications in this series. These studies have now been extended to the ligand thiodiacetate ($R=CH_2SCH_2$). The formation constants in aqueous solution of the lanthanoid-thiodiacetate complexes have been reported by Dellien, Grenthe and Hessler.[4] The complexes found are comparatively weak, making it difficult to decide if a chelate is formed. Thus, it is of interest to study a complex in the solid state in order to obtain information of the coordination geometry around the lanthanoid ion.

The tri-aquo-iminodiacetate-lanthanoid(III) chlorides form an isostructural series of compounds for the elements Pr – Lu,[5] and a similar series can be prepared with the ligand thiodiacetate. In this paper the crystal structure of tetra-aquo-thiodiacetato-neodymium(III) chloride is described, and it is referred to below as THIDAC.

EXPERIMENTAL

Preparation. Equimolar aqueous solutions of neodymium chloride and thiodiacetic acid were mixed and the pH of the resulting solution was adjusted to 2.5 with dilute sodium hydroxide. Slow evaporation at room temperature gave a crystalline compound. The composition $Nd(C_4H_4O_4S)(H_2O)_4Cl$ was determined by chemical analysis. If the pH was kept higher than 4 in the resulting solution, a microcrystalline compound of the composition $Nd_2(C_4H_4O_4S)_3(H_2O)_6$ was formed.

Single crystal work. The method of preparation resulted in crystals which were tabular (010). It was found that they slowly decomposed when exposed to X-rays. However, the rate of decomposition could be decreased by coating the crystals with Apiezon oil. A single crystal of the dimensions $0.22 \times 0.05 \times 0.16$ mm^3 was mounted along the b-axis. The intensities of 416 reflections of the layers $h0l-h10l$ were recorded using the integrated Weissenberg multifilm technique and Ni-filtered Cu-radiation ($\lambda = 1.5418$ Å). The intensities were estimated visually using a calibrated scale. The intensity data were corrected for Lorentz, polarization, and absorption effects. The linear absorption coefficient is 343 cm^{-1}. The transmission factor, evaluated by numerical integration, varied in the interval 0.010 – 0.188.

UNIT CELL AND SPACE GROUP

The diffraction symmetry mmm and the systematic absences $0kl$: $k+l \neq 2n$ and $h0l$: $h+l \neq 2n$ indicate $Pnnm$ (No. 58) or $Pnn2$ (No. 34)[6] as possible space groups. Using Ni-filtered Cu-radiation the a and c parameters were determined from a zero layer Weissenberg photograph, and the b parameter was determined from an oscillation photograph. Both photographs were calibrated with a single crystal of quartz ($a = 4.9126$ and $c = 5.4043$ Å). The measured θ-values were used for a least squares refinement of the unit cell dimensions. The following crystal data were obtained.

$a = 6.922(3)$ Å*	$D_m = 2.2$ g/cm^3
$b = 17.69(3)$ Å	$D_x = 2.12$ g/cm^3
$c = 10.226(4)$ Å	$Z = 4$
$V = 1251(2)$ Å^3	

The density D_m was determined by the displacement method using benzene.

STRUCTURE DETERMINATION AND REFINEMENT

The position of the neodymium ion was determined from a three-dimensional vector map. Assuming the centrosymmetric space group, the positional parameters and an isotropic temperature factor together with the interlayer scale factors, were improved by a full matrix least squares refinement. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$, with weights w chosen according

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* Numbers within parenthesis represent estimated standard deviations in the last significant digit.

to Cruickshank.[7] Due to the location of the neodymium ion close to $y=1/4$, a three-dimensional difference electron density map showed two images of the structure related by a mirror plane at $y=1/4$. Since the highest peak was at a possible coordination distance from the neodymium ion, the sulfur atom was placed at this position. The remaining ligand atoms were found from geometrical considerations. It was also possible to chose the position of the chloride ion belonging to the same image, since one of the two possible positions gave an improbable chloride carbon distance of 2.0 Å. A difference electron density map calculated after refining the parameters of the image chosen, revealed the positions of the four water molecules.

The preliminary positional coordinates, isotropic temperature factors and interlayer scale factors were improved by a series of least squares refinements. The convergency was followed by the agreement index R defined by $R=\sum||F_o|-|F_c||/\sum|F_o|$. All observed reflections were included in the calculations of R. The weights $w=1/(40+|F_o|+0.0025|F_o|^2)$ in the last cycle of refinement gave a smooth weighting scheme. The shifts in the parameters were less than 1 % of the estimated standard deviations. The final agreement index obtained was $R=0.127$. The interlayer scale factors increased from 0.5 for the zero layer to 3.2 for the tenth layer showing the decomposition of the crystal during the collection of the intensity data. The poor agreement between observed and calculated structure factors could mainly be ascribed to this circumstance. Since the main aim of this investigation was to determine the coordination geometry, no attempts were made to improve the results by collecting data from different crystals.

A final difference electron density map was featureless. The positional and thermal parameters are given in Table 1. Observed and calculated structure factors are compared in Table 2. The atomic scattering factors used in the calculations were taken from Ref. 8 (Cl, O, S, and C) and from Cromer *et al.*[9] (Nd).

An attempt to refine the structure in the non centrosymmetric space group *Pnn*2 was unsuccessful. All computations were made on the UNIVAC 1108 computor in Lund and the programs used are given in Ref. 10.

Table 1. Atomic parameters with estimated standard deviations. B denotes the isotropic temperature factor.

Atom	Group	$x\times10^4$	$y\times10^4$	$z\times10^4$	$B/\text{Å}^2$
Nd		2123(5)	2467(5)	0	1.3(1)
Cl		0	5000	2725(27)	5.4(7)
O(1)	$-COO^-$	6447(64)	3268(32)	3015(40)	3.7(10)
O(2)	$-COO^-$	4806(61)	2731(30)	1471(41)	4.0(10)
O(3)	H_2O	4103(81)	1332(48)	0	3.4(14)
O(4)	H_2O	515(48)	3386(26)	1544(31)	1.9(7)
O(5)	H_2O	−1162(90)	2227(39)	0	3.3(13)
C(1)	$-COO^-$	5616(74)	3325(42)	2071(48)	1.9(10)
C(2)	$-CH_2-$	5554(104)	4069(61)	1440(75)	4.9(17)
S	$-C-S-C-$	3865(26)	4111(18)	0	1.9(4)

Table 2. Observed and calculated structure factors. The columns are k, $|F_o|$ and $|F_c|$.

k	$\|F_o\|$	$\|F_c\|$
L= 0 H= 1		
3	82	101
4	57	60
7	154	147
L= 0 H= 2		
1	80	115
2	134	170
3	110	103
4	147	147
6	163	191
8	102	108
9	76	75
10	153	137
L= 0 H= 3		
1	71	66
5	53	42
6	34	37
L= 0 H= 4		
0	51	75
1	109	116
2	60	76
4	126	143
5	120	148
6	56	54
7	113	135
8	130	107
9	69	100
10	67	73
L= 0 H= 6		
1	134	135
3	62	80
5	84	96
7	99	105
9	72	79
L= 0 H= 8		
0	30	18
1	75	62
2	39	34
3	72	84
5	59	78
L= 1 H= 0		
5	95	77
L= 1 H= 1		
1	197	245
3	159	160
4	72	72
5	162	169
7	171	178
9	110	143
10	64	66
L= 1 H= 2		
1	42	28
3	52	52
4	25	37
5	35	24
7	49	42
8	44	42
L= 1 H= 3		
0	118	135
1	102	103
2	134	146
3	149	169
4	150	148
5	124	144
6	100	100
7	96	107
8	85	102
9	99	109
10	93	67
L= 1 H= 4		
2	23	34
3	27	22
5	34	30
L= 1 H= 5		
0	138	137
1	51	55
2	107	99
3	60	69
4	81	82
5	52	42
6	107	125
8	81	99
10	67	85
L= 1 H= 7		
0	117	93
2	94	90
3	34	33
4	81	92
6	70	90
8	81	81
10	63	74
L= 2 H= 0		
0	212	152
2	217	213
4	158	153
6	320	328
8	160	175
10	141	139
L= 2 H= 1		
1	86	50
2	64	46
3	89	88
9	47	55
10	57	60
L= 2 H= 2		
0	238	237
1	46	24
2	149	148
3	139	124
4	195	203
5	111	111
6	109	107
7	92	76
8	147	157
9	67	92
10	107	112
L= 2 H= 3		
2	21	38
5	33	34
7	65	67
L= 2 H= 4		
1	147	147
2	116	113
3	105	101
4	79	71
5	94	97
6	51	56
7	99	106
8	62	49
9	65	98
10	98	94
L= 2 H= 5		
2	31	22
L= 2 H= 6		
1	137	121
3	91	95
5	104	116
7	104	113
9	64	75
L= 2 H= 8		
1	62	69
2	30	21
3	67	78
4	29	36
5	52	63
L= 3 H= 0		
3	139	108
5	42	54
L= 3 H= 1		
1	197	172
2	64	64
3	150	124
4	161	145
5	214	169
6	60	78
7	169	200
8	57	65
9	144	130
L= 3 H= 2		
1	38	26
3	80	76
4	41	46
L= 3 H= 3		
0	60	42
1	140	131
2	110	106
3	174	185
4	97	95
5	115	110
6	76	83
7	69	73
8	60	87
9	110	121
10	94	102
L= 3 H= 4		
2	41	37
3	35	34
L= 3 H= 5		
0	167	153
1	52	45
2	111	103
3	46	47
4	95	101
6	119	120
8	106	105
10	66	77
L= 3 H= 6		
4	32	39
L= 3 H= 7		
2	78	85
4	63	77
6	66	85
8	76	67
10	45	67
L= 4 H= 0		
0	270	242
2	144	130
4	227	175
6	178	154
8	172	165
10	105	98
L= 4 H= 1		
3	60	57
4	47	51
9	70	47
L= 4 H= 2		
0	140	165
1	34	33
2	179	202
3	118	123
4	120	130
5	77	67
6	155	161
8	99	108
9	80	79
10	137	131
L= 4 H= 3		
1	45	41
L= 4 H= 4		
1	117	129
2	50	49
3	83	83
5	67	89
7	95	101
8	71	78
9	81	86
10	64	64
L= 4 H= 5		
2	29	22
L= 4 H= 6		
1	104	110
2	26	26
3	73	93
5	87	111
7	88	106
L= 4 H= 8		
1	58	61
2	34	30
3	57	70
5	49	60
L= 5 H= 0		
5	91	74
L= 5 H= 1		
1	246	186
2	108	83
3	160	124
4	60	54
5	168	135
6	42	36
7	165	140
10	57	46
L= 5 H= 2		
3	37	40
L= 5 H= 3		
0	108	116
1	74	96
2	96	102
3	125	144
4	59	108
5	95	103
6	51	43
7	75	76
8	73	79
9	92	101
10	67	74
L= 5 H= 4		
4	37	35
L= 5 H= 5		
0	94	117
2	60	96
3	46	48
4	75	72
5	47	50
6	92	113
8	66	82
10	62	78
L= 5 H= 7		
0	66	75
2	60	68
4	64	84
6	64	86
8	66	77
10	38	58
L= 6 H= 0		
0	285	255
2	245	196
4	139	101
6	227	166
8	124	115
10	149	120
L= 6 H= 1		
1	46	30
3	27	22
4	27	21
L= 6 H= 2		
0	79	95
1	48	50
2	95	94
3	91	80
4	146	142
5	41	36
6	98	103
8	121	113
9	77	66
10	106	84
L= 6 H= 3		
3	27	29
L= 6 H= 4		
1	80	95
2	73	86
3	77	95
4	72	74
5	96	102
6	65	54
7	88	97
9	88	77
10	63	74
L= 6 H= 6		
1	87	105
3	56	69
5	70	82
7	76	86
L= 7 H= 0		
1	70	50
L= 7 H= 1		
0	33	23
1	163	138
2	23	28
3	133	107
4	61	48
6	45	.31
7	174	125
9	114	102
L= 7 H= 2		
1	31	26
4	33	26
L= 7 H= 3		
0	47	50
1	53	64
2	89	96
3	107	108
4	93	92
5	98	101
6	93	99
7	87	82
8	77	73
9	95	78
10	63	67
L= 7 H= 5		
0	87	104
1	41	57
2	60	64
3	43	50
4	71	72
6	67	68
8	74	80
10	65	57
L= 7 H= 7		
2	78	80
3	24	23
4	64	61
6	52	60
L= 8 H= 0		
0	191	162
2	136	108
4	155	116
6	190	150
8	161	121
10	94	76
L= 8 H= 2		
0	86	84
1	23	19
2	107	105
3	77	66
4	114	96
5	69	52
6	101	91
8	91	82
10	89	88
L= 8 H= 4		
0	41	46
1	74	86
2	67	63
3	72	75
4	81	68
5	75	75
7	75	75
9	76	67
10	55	55
L= 8 H= 6		
1	86	85
3	64	62
5	79	76
7	77	77
L= 9 H= 0		
5	67	43
L= 9 H= 1		
1	110	107
2	56	42
3	106	85
4	52	42
5	118	103
6	49	38
7	129	105
9	92	77
L= 9 H= 3		
0	66	69
1	73	77
2	70	63
3	98	93
4	82	70
5	76	60
7	68	48
8	72	59
9	82	73
10	54	56
L= 9 H= 4		
1	22	19
L= 9 H= 5		
0	96	85
2	81	72
3	33	34
4	55	56
5	34	36
6	91	81
8	54	60
10	55	57
L= 10 H= 0		
0	119	115
2	100	92
4	80	79
6	.108	97
8	100	75
10	84	63
L= 10 H= 1		
3	23	13
4	31	27
L= 10 H= 2		
0	89	93
1	44	32
2	94	83
3	67	61
4	93	83
5	40	32
6	93	74
8	101	73
10	83	69
L= 10 H= 4		
1	76	72
2	47	43
3	65	54
4	67	52
5	66	59
6	41	34
7	77	63
9	61	53
10	55	45
L= 11 H= 0		
3	24	23
L= 11 H= 1		
1	91	89
2	27	24
3	76	57
4	43	33
5	94	73
9	77	62
L= 11 H= 3		
0	42	38
1	46	53
2	68	58
3	85	74
4	48	47
5	69	55
6	44	40
7	68	45
8	47	40
9	61	59
L= 12 H= 0		
0	81	83
2	72	73
4	68	66
6	102	87
8	85	69
L= 12 H= 2		
1	20	19
2	64	63
3	47	43
4	72	64
5	35	33
6	63	58

DESCRIPTION OF THE STRUCTURE

The structure is composed of layers of cross-linked neodymium ligand chains. These layers are stacked in the b-direction, and they are connected by hydrogen bonds *via* the chloride ion. A stereoscopic drawing of the contents of the unit cell is shown in Fig. 1. The superscripts $(i)-(x)$ are used to indicate the following equivalent sites in the structure:

(i)	$x,y,-z$	(ii)	$-1/2+x,1/2-y,1/2-z$
(iii)	$1/2+x,1/2-y,-1/2+z$	(iv)	$-1+x,y,z$
(v)	$-1+x,y,-z$	(vi)	$1/2-x,1/2+y,1/2+z$
(vii)	$-1/2+x,1/2-y,1/2-z$	$(viii)$	$-x,1-y,1-z$
(ix)	$-x,1-y,z$	(x)	$x,y,1-z$

where x,y,z are the atomic coordinates given in Table 1.

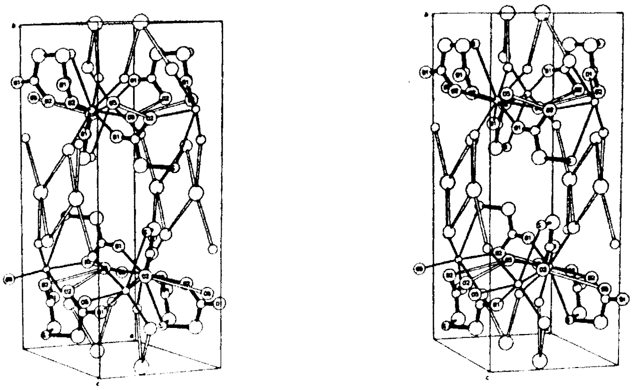

Fig. 1. A stereoscopic pair of drawings showing the contents of one unit cell. Figs. 1 – 3 were drawn by the program ORTEP.

The neodymium ion is coordinated by four water molecules, four carboxylate oxygen atoms, and one sulfur atom. The coordination polyhedron might be described as a distorted tricapped trigonal prism as is seen in Fig. 2. The thiodiacetate ligand is bent and has the oxygen atoms O(2) and O(2') on the same edge of the prism, and has the sulfur atom located outside the mid-

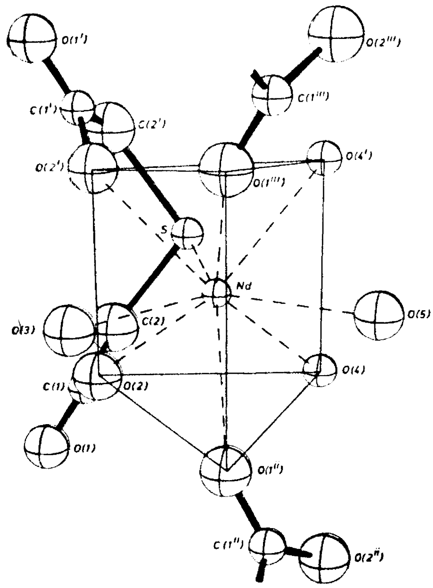

Fig. 2. The coordination polyhedron around the neodymium ion.

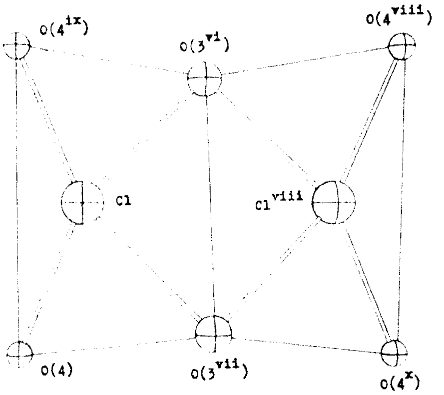

Fig. 3. The arrangement of the hydrogen bonded atoms around the chloride ions.

Table 3. Selected interatomic distances (Å) and angles (°) with estimated standard deviations.

A. The coordination polyhedron.

Distance		Distance	
Nd – O(1^{ii})	2.45(5)	O(3) – O(2)	2.94(9)
Nd – O(2)	2.44(4)	O(3) – O(1^{ii})	2.83(6)
Nd – O(3)	2.43(8)	O(5) – O(1^{ii})	2.85(6)
Nd – O(4)	2.53(4)	O(5) – O(4)	2.83(7)
Nd – O(5)	2.31(6)	O(1^{ii}) – O(2)	2.97(7)
Nd – S	3.15(3)	O(1^{ii}) – O(4)	3.19(6)
S – O(2)	2.94(6)	O(1^{ii}) – O(1^{iii})	4.06(10)
S – O(4)	3.09(4)	O(2) – O(2^{i})	3.01(9)
		O(4) – O(4^{i})	3.16(6)

B. The ligand.

Distance		Angle	
S – C(2)	1.88(8)	C(2) – S – C(2)	103(5)
C(2) – C(1)	1.46(12)	S – C(2) – C(1)	114(6)
C(1) – O(1)	1.13(7)	C(2) – C(1) – O(1)	118(7)
C(1) – O(2)	1.34(8)	C(2) – C(1) – O(2)	119(5)
		O(1) – C(1) – O(2)	122(7)

C. Possible hydrogen bonds.

Distance		Distance	
O(5) – O(2^{iv})	3.30(7)	Cl – O(3^{vi})	3.37(6)
O(4) – O(2^{ii})	2.87(6)	Cl – O(4)	3.12(5)

point of a "rectangular" face. A similar situation is found in $Nd(C_4H_5O_4N)(H_2O)_3Cl$.[2] Selected interatomic distances and angles within the coordination polyhedron are given in Table 3A. The large Nd – S distance, 3.15 Å, indicates only weak interaction between these two atoms. This supports the reported interpretation of the thermodynamic data for the rare earth thiodiacetate complexes, where a rather weak interaction has been assumed.[4] Of the 21 contact distances within the coordination polyhedron, four sulfur-oxygen and twelve oxygen-oxygen distances indicate van der Waals contacts.

The coordination polyhedra are connected by the carboxylate groups. This results in the formation of cross-linked chains aligned in the [101] and $[10\bar{1}]$ directions, and the Nd – Nd distances within the chains are 6.175 Å.

In THIDAC the thiodiacetate ion exhibits the symmetry *m*, and the structure contains only one half independent ligand ion. The ligand forms two five-membered rings with the metal ion. The carboxylate oxygen atoms O(1) participate in the coordination of neighbouring metal ions. Bond distances and angles within the thiodiacetate ion are given in Table 3B and they are not significantly different from those found in thiodiacetic acid.[11]

Judging from the oxygen-oxygen and oxygen-chloride distances, all water molecules are involved in hydrogen bonding (Table 3C). The water oxygen O(5) might be hydrogen bonded to O(2^{iv}) and O(2^{v}), thus connecting the coordination polyhedra in the *a*-direction. The chloride ion is situated between the metal-ligand layers and probably accepts hydrogen bonds from both layers, thus holding the structure together in the *b*-direction. The arrangement of the hydrogen bonded atoms around the chloride ion might be described as a distorted rectangle. Two rectangles are connected in pairs by sharing the edge O(3^{vi}) – O(3^{vii}) as is seen in Fig. 3. The hydrogen atom at O(4) not involved in hydrogen bonding with the chloride ion is probably attracted by O(2^{ii}).

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