

Références

- AHRENS, L. H. (1952). *Geochim. Cosmochim. Acta*, **2**, 155–169.
- BORGEN, G. & DALE, J. (1969). *Chem. Commun.* pp. 447–448.
- CORFIELD, W. R., DOEDENS, R. J. & IBERS, J. A. (1967). *Inorg. Chem.* **6**, 197–204.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–105.
- CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, p. 114. Oxford: Pergamon Press.
- GROTH, P. (1971). *Acta Chem. Scand.* **25**, 3189–3190.
- HAGIHARA, H., YOSHIDA, N. & WATANABE, Y. (1969). *Acta Cryst.* **B25**, 1775–1784.
- HERCEG, M. & WEISS, R. (1972). *Bull. Soc. Chim. Fr.* pp. 549–551.
- HERCEG, M. & WEISS, R. (1973). *Acta Cryst.* **B29**, 542–547.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 213–216. Birmingham: Kynoch Press.
- LAWTON, S. L. & KOKOTAILO, G. T. (1972). *Inorg. Chem.* **11**, 363–368.
- MOORE, W. T. & PAULING, L. (1941). *J. Amer. Chem. Soc.* **63**, 1392–1394.
- MORAS, D., METZ, B., HERCEG, M. & WEISS, R. (1972). *Bull. Soc. Chim. Fr.* pp. 551–555.
- MORAS, D., METZ, B. & WEISS, R. (1973). *Acta Cryst.* **B29**, 383–388.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. p. 221–264, 538. Ithaca: Cornell Univ. Press.
- PEDERSEN, C. J. (1967). *J. Amer. Chem. Soc.* **89**, 7017–7036.
- PREWITT, C. T. (1966). ORNL-TM 305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- SPIRO, T. G., TEMPLETON, D. H. & ZALKIN, A. (1969). *Inorg. Chem.* **8**, 856–861.
- WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). Adaptation du programme Fortran 'Single Crystal Orienter Absorption Corrections'. Report ORNL-TM-299, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Acta Cryst. (1973). **B29**, 1093

Crystal and Molecular Structure of a Dimethyl Sulphoxide Complex with Lanthanum Nitrate, $\text{La}(\text{NO}_3)_3 \cdot 4(\text{CH}_3)_2\text{SO}$

BY K. KRISHNA BHANDARY AND H. MANOHAR

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

(Received 2 January 1973; accepted 31 January 1973)

The crystal structure of the complex $\text{La}(\text{NO}_3)_3 \cdot 4(\text{CH}_3)_2\text{SO}$ has been solved by the heavy-atom method. The complex crystallizes in the monoclinic space group $C2/c$ with four formula units in a unit cell of dimensions $a = 14.94$, $b = 11.04$, $c = 15.54$ Å and $\beta = 109^\circ 10'$. The parameters have been refined by three-dimensional least-squares procedures with anisotropic thermal parameters for all atoms except hydrogen. The final R index for 1257 observed reflexions is 0.094. The La^{3+} ion is coordinated by ten oxygen atoms with La–O distances varying from 2.47 to 2.71 Å. The geometry of the coordination polyhedron is described.

Introduction

Recently there has been an increasing interest in the crystal chemistry of lanthanide ions. To date many complexes of lanthanides having different ligands have been prepared and characterized by various physico-chemical methods. The bonding of the ligands to the lanthanide ions is essentially electrostatic with little interaction between the $4f$ orbitals and ligand orbitals (Karraker, 1970). However, recent n.m.r. and electron spectroscopic studies appear to provide evidence for covalent bonding in some organometallic complexes of heavier lanthanides (Gysling & Tsutsui, 1970).

Because of their comparatively large size, the lanthanide ions exhibit a high coordination number, usually between six and ten (Karraker, 1970). The lanthanide contraction plays an important role in the coordination chemistry of lanthanides. As the size of the lanthanide ion decreases, the repulsion between the ligands in the coordination sphere increases and becomes large

enough to make the structure energetically unstable. At this point, the coordination number of the lanthanide ion decreases and the crystal structure changes.

With a view to correlating the effect of lanthanide contraction with the changes in coordination number and crystal structure, a programme to elucidate the crystal structures of lanthanide complexes having different ligands has been taken up in this laboratory. This, we hoped, would also add to our understanding of the coordination geometry and crystal chemistry of lanthanons. As part of the programme, a series of complexes of dimethyl sulphoxide with lanthanide nitrates, prepared and characterized earlier in this laboratory (Ramalingam & Soundararajan, 1967), has been taken up for X-ray structural studies. These complexes have the general formula $\text{Ln}(\text{NO}_3)_3 \cdot n(\text{DMSO})$, where $n = 4$ for $\text{Ln} = \text{La}$ to Gd , $n = 3$ for $\text{Ln} = \text{Y}$, Ho and Yb and DMSO is $(\text{CH}_3)_2\text{SO}$. The structure of $\text{La}(\text{NO}_3)_3 \cdot 4(\text{CH}_3)_2\text{SO}$ has been solved and is reported herein.

Experimental

Well developed crystals were grown by slow evaporation of a solution of an authenticated sample of the complex in acetonitrile. The crystals were tabular in form and elongated along the c axis. The crystals were examined by single-crystal rotation and Weissenberg techniques using $\text{Cu } K\alpha$ ($\lambda = 1.542 \text{ \AA}$) radiation. The crystal data for the complex are

Crystal system	Monoclinic
Cell dimensions	$a = 14.94(2) \text{ \AA}$ $b = 11.04(2)$ $c = 15.54(2)$ $\beta = 109^\circ 10'(33')$
Space group	Cc or $C2/c$ (hkl , $h+k$ odd and $h0l$, l odd are absent)
Unit-cell volume	$V = 2421 \text{ \AA}^3$
Measured density by flotation method	$D_{\text{obs}} = 1.740 \text{ g cm}^{-3}$
Calculated density	$D_{\text{calc}} = 1.749 \text{ g cm}^{-3}$
Formula weight	637.5
Number of formula units per unit cell	$Z = 4$
$F(0,0,0)$	318
Linear absorption coefficient for $\text{Cu } K\alpha$ radiation	171.0 cm^{-1}

A cylindrical crystal, cut along the length of the tabular crystal and ground to a radius of 0.1 mm was sealed in a Lindemann capillary of 0.15 mm radius and used to collect intensities on the reciprocal levels hkl ($l=0$ to 10) using the multiple-film Weissenberg equi-inclination technique and $\text{Cu } K\alpha$ radiation. The intensities of 1257 independent reflexions, which were in the observable range, were measured visually with the help of a calibrated intensity strip prepared from the same crystal. The intensities were corrected for Lorentz and polarization factors. Absorption corrections ($\mu r = 1.71$) were also applied. The intensities were placed on a common relative scale by correlating them with the intensities collected about the $[110]$ direction. They were then placed on an absolute scale by a Wilson plot (1942).

Structure determination and refinement

As there are four formula units per unit cell, there are four lanthanum ions and hence the La^{3+} ion should occupy one of the special fourfold positions if the space group were $C2/c$ or a general position if the space group were Cc (*International Tables for X-ray Crystallography*, 1962). The y coordinate of the lanthanum ion was obtained from a three-dimensional Patterson synthesis. The value, $y = 0.117$, obtained suggested that in the space group $C2/c$ only the fourfold position $4(e)$ ($0, y, \frac{1}{4}; 0, \bar{y}, \frac{3}{4}$) is possible. In the space group Cc the x and z coordinates may be chosen arbitrarily. Hence the position would serve equally well for Cc with $x = 0$ and $z = \frac{1}{4}$ arbitrarily chosen for La^{3+} to fix the origin. An

electron-density map was computed using the observed amplitudes with the phases calculated from the lanthanum atom alone. Since the lanthanum arrangement was centrosymmetric the resulting map was also centrosymmetric. If the structure were non-centric then one should observe twice the number of expected peaks owing to the additional centre of symmetry. However, only twenty-nine important peaks, which correspond to the actual number of atoms present in one formula unit, were observed in one fourth of the unit cell, indicating the structure to be centrosymmetric. Moreover, the effects of anomalous scattering of $\text{Cu } K\alpha$ radiation by lanthanum are considerable ($\Delta f' = -2.1$; $\Delta f'' = 8.9$). If the crystal belongs to the non-centrosymmetric space group Cc we should then expect intensity differences between pairs of reflexions such as $hk0$ and $\bar{h}k0$ (Peerdeman, van Bommel & Bijvoet, 1949). However, careful examination of the intensities did not show any Bijvoet differences. Further evidence for the centrosymmetric space group came from the morphological examination of the crystals under the microscope

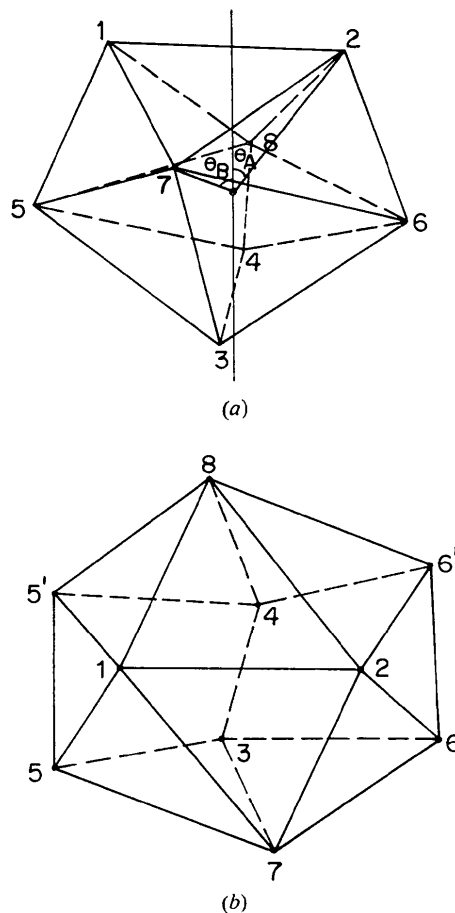


Fig. 1. (a) Idealized dodecahedron. (b) The coordination polyhedron around the lanthanum ion. The vertices 1, 2, 3 and 4 denote $\text{O}(1)$, $\text{O}(1')$, $\text{O}(2)$ and $\text{O}(2')$ respectively and vertices 5, 5', 6, 6', 7 and 8 denote $\text{O}(3)$, $\text{O}(4)$, $\text{O}(4')$, $\text{O}(3')$, $\text{O}(6)$ and $\text{O}(6')$ respectively.

which clearly indicated the presence of a twofold axis. Hence the space group $C2/c$ was chosen. The choice was confirmed by the successful refinement of the structure in this space group.

The contribution of La^{3+} to the structure factor was computed. The residual index, defined as $||F_o| - |F_c||/|F_o|$, was 36%. A three-dimensional Fourier synthesis was computed using the signs of those reflexions for which $|F_c| \geq 0.60|F_o|$. The positions of sulphur atoms were easily identified from this map. Using the positions of sulphur atoms and the chemical information available regarding the geometry of dimethyl sulphoxide and the nitrate ions the positions of all the atoms were located. Structure factor calculations with the positional parameters and isotropic thermal parameters of all the atoms gave an R index of 25%. Four cycles of structure factor least-squares refinement using the block-diagonal matrix approximation reduced the discrepancy index to 16%. At this stage it was found that the thermal parameters of two atoms were abnormally high, suggesting that these atoms were wrongly placed. A difference Fourier map was computed and this indicated considerable shifts in the positions of these atoms. Introduction of the new positions of these atoms and three cycles of isotropic refinement reduced the R index to 13%. Individual anisotropic temperature factors of the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$ were introduced and the structure was refined to an R index of 10.9% in three cycles. The scattering factors used in the refinement were taken from Cromer & Waber (1965) for all the atoms. At this stage the corrections for anomalous dispersion for La^{3+} ($\Delta f' = -2.1$, $\Delta f'' = 8.9$) were introduced in the scattering factors of La^{3+} [$f = \sqrt{(f_o + \Delta f')^2 + (\Delta f'')^2}$]. Three further cycles of refinement reduced the residual index to 0.094. The shifts in the positional parameters were one-tenth of the standard deviations and hence the refinement was stopped at this stage. The quantity minimized in the program used was $\sum w(F_o - F_c)^2$. In the earlier stages of the refinement the weighting scheme $w = 1/[1 + (kF_o - b)^2/a^2]$, where $a = 40$ ($8F_{\min}$) and $b = 25(5F_{\min})$, was used. However, in the final stages the weighting scheme of the form $w = 1/[a + bkF_o + c(kF_o)^2]$ (Cruickshank, Bujosa, Lovell & Truter, 1961), where $a = 12.0$, $b = 1.0$ and $c = 0.0118$, was found appropriate.

Table 1 lists the final positional parameters with standard deviations and Table 2 the thermal parameters. In Table 3 are listed the final observed and calculated structure factors for all the observed reflexions. The bond lengths and valency angles are given in Table 4. The average standard deviations in bond lengths for La-O, S-O, S-C and N-O are 0.03, 0.03, 0.058 and 0.049 Å respectively.

Description of the structure

(a) Coordination around La^{3+}

The lanthanum ion is found to be coordinated to ten oxygen atoms, six from the three nitrate groups which

Table 1. Final fractional atomic coordinates of the non-hydrogen atoms

Standard deviations in the last digits are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
La	0.0	0.1141 (02)	0.2500
S(1)	0.0343 (07)	0.1741 (10)	0.0260 (08)
S(2)	0.1683 (09)	0.3671 (10)	0.2727 (10)
O(1)	0.0646 (22)	0.1597 (29)	0.1263 (20)
O(2)	0.0996 (21)	0.2955 (26)	0.3082 (24)
O(3)	0.1331 (21)	0.0718 (30)	0.4144 (22)
O(4)	0.1748 (20)	0.0313 (30)	0.2970 (20)
O(5)	0.2755 (21)	0.0169 (33)	0.4369 (23)
O(6)	-0.0059 (20)	-0.1092 (25)	0.3060 (24)
O(7)	0.0000	-0.2803 (36)	0.2500
N(1)	0.1955 (22)	0.0416 (30)	0.3852 (29)
N(2)	0.0000	-0.1758 (48)	0.2500
C(1)	0.1375 (31)	0.2149 (41)	0.0030 (38)
C(2)	-0.0196 (44)	0.3232 (54)	0.0028 (45)
C(3)	0.2827 (39)	0.3332 (69)	0.3536 (76)
C(4)	0.1626 (61)	0.5164 (50)	0.3121 (54)

Table 2. Anisotropic thermal parameters* and the equivalent isotropic temperature factor

$$B = (4/3) \sum \sum B_{ij} \cdot a_i \cdot a_j$$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	B
La	326	573	310	0	133	0	2.76
S(1)	483	904	394	-107	179	-13	4.00
S(2)	732	999	516	-282	238	-26	5.23
O(1)	75	121	39	7	39	3	5.07
O(2)	62	104	64	-24	21	-14	5.38
O(3)	45	131	68	16	24	-4	5.40
O(4)	53	125	58	12	9	-19	5.39
O(5)	45	181	51	19	6	17	5.86
O(6)	59	93	73	-17	-1	51	5.66
O(7)	162	52	124	0	62	0	9.03
N(1)	41	101	75	18	12	12	5.16
N(2)	112	86	146	0	95	0	8.44
C(1)	54	112	59	-8	36	-10	4.98
C(2)	98	124	97	53	6	18	8.02
C(3)	50	203	228	26	47	95	11.67
C(4)	158	102	125	-20	84	-17	9.55

* The values for La, S(1) and S(2) are multiplied by 10^5 and for other atoms by 10^4 .

are bidentates and four from the four DMSO groups. It is interesting to note that all the three nitrate groups are bidentates in contradiction to the earlier suggestion (Ramalingam & Soundararajan, 1967) that only one nitrate ion is likely to be bidentate. The coordination polyhedron formed by the ten oxygen atoms is shown in Fig. 1(b). The pairs of corners 55', 66' and 78 are occupied by the three bidentate nitrate groups while the atoms at the vertices 1, 2, 3 and 4 are the DMSO oxygens. The lanthanum to oxygen coordinating distances are given in Table 5. The distances vary from 2.47 to 2.71 Å. The average La-O(DMSO) and La-O(NO_3) distances are 2.475 ± 0.027 Å and 2.665 ± 0.027 Å respectively, but the difference could be considered to be significant. The La-O(NO_3) distance is consistent with the reported La-O(NO_3) distance of 2.605 ± 0.011 Å in bis(bipyridyl)lanthanum nitrate (Al-Karaghoulis & Wood, 1968).

Table 3. Observed and calculated structure factors

h	k	l	F_o	F_c	R	h	k	l	F_o	F_c	R
1	0	0	100	100	0	1	0	0	100	100	0
2	0	0	100	100	0	2	0	0	100	100	0
3	0	0	100	100	0	3	0	0	100	100	0
4	0	0	100	100	0	4	0	0	100	100	0
5	0	0	100	100	0	5	0	0	100	100	0
6	0	0	100	100	0	6	0	0	100	100	0
7	0	0	100	100	0	7	0	0	100	100	0
8	0	0	100	100	0	8	0	0	100	100	0
9	0	0	100	100	0	9	0	0	100	100	0
10	0	0	100	100	0	10	0	0	100	100	0
11	0	0	100	100	0	11	0	0	100	100	0
12	0	0	100	100	0	12	0	0	100	100	0
13	0	0	100	100	0	13	0	0	100	100	0
14	0	0	100	100	0	14	0	0	100	100	0
15	0	0	100	100	0	15	0	0	100	100	0
16	0	0	100	100	0	16	0	0	100	100	0
17	0	0	100	100	0	17	0	0	100	100	0
18	0	0	100	100	0	18	0	0	100	100	0
19	0	0	100	100	0	19	0	0	100	100	0
20	0	0	100	100	0	20	0	0	100	100	0
21	0	0	100	100	0	21	0	0	100	100	0
22	0	0	100	100	0	22	0	0	100	100	0
23	0	0	100	100	0	23	0	0	100	100	0
24	0	0	100	100	0	24	0	0	100	100	0
25	0	0	100	100	0	25	0	0	100	100	0
26	0	0	100	100	0	26	0	0	100	100	0
27	0	0	100	100	0	27	0	0	100	100	0
28	0	0	100	100	0	28	0	0	100	100	0
29	0	0	100	100	0	29	0	0	100	100	0
30	0	0	100	100	0	30	0	0	100	100	0
31	0	0	100	100	0	31	0	0	100	100	0
32	0	0	100	100	0	32	0	0	100	100	0
33	0	0	100	100	0	33	0	0	100	100	0
34	0	0	100	100	0	34	0	0	100	100	0
35	0	0	100	100	0	35	0	0	100	100	0
36	0	0	100	100	0	36	0	0	100	100	0
37	0	0	100	100	0	37	0	0	100	100	0
38	0	0	100	100	0	38	0	0	100	100	0
39	0	0	100	100	0	39	0	0	100	100	0
40	0	0	100	100	0	40	0	0	100	100	0
41	0	0	100	100	0	41	0	0	100	100	0
42	0	0	100	100	0	42	0	0	100	100	0
43	0	0	100	100	0	43	0	0	100	100	0
44	0	0	100	100	0	44	0	0	100	100	0
45	0	0	100	100	0	45	0	0	100	100	0
46	0	0	100	100	0	46	0	0	100	100	0
47	0	0	100	100	0	47	0	0	100	100	0
48	0	0	100	100	0	48	0	0	100	100	0
49	0	0	100	100	0	49	0	0	100	100	0
50	0	0	100	100	0	50	0	0	100	100	0
51	0	0	100	100	0	51	0	0	100	100	0
52	0	0	100	100	0	52	0	0	100	100	0
53	0	0	100	100	0	53	0	0	100	100	0
54	0	0	100	100	0	54	0	0	100	100	0
55	0	0	100	100	0	55	0	0	100	100	0
56	0	0	100	100	0	56	0	0	100	100	0
57	0	0	100	100	0	57	0	0	100	100	0
58	0	0	100	100	0	58	0	0	100	100	0
59	0	0	100	100	0	59	0	0	100	100	0
60	0	0	100	100	0	60	0	0	100	100	0
61	0	0	100	100	0	61	0	0	100	100	0
62	0	0	100	100	0	62	0	0	100	100	0
63	0	0	100	100	0	63	0	0	100	100	0
64	0	0	100	100	0	64	0	0	100	100	0
65	0	0	100	100	0	65	0	0	100	100	0
66	0	0	100	100	0	66	0	0	100	100	0
67	0	0	100	100	0	67	0	0	100	100	0
68	0	0	100	100	0	68	0	0	100	100	0
69	0	0	100	100	0	69	0	0	100	100	0
70	0	0	100	100	0	70	0	0	100	100	0
71	0	0	100	100	0	71	0	0	100	100	0
72	0	0	100	100	0	72	0	0	100	100	0
73	0	0	100	100	0	73	0	0	100	100	0
74	0	0	100	100	0	74	0	0	100	100	0
75	0	0	100	100	0	75	0	0	100	100	0
76	0	0	100	100	0	76	0	0	100	100	0
77	0	0	100	100	0	77	0	0	100	100	0
78	0	0	100	100	0	78	0	0	100	100	0
79	0	0	100	100	0	79	0	0	100	100	0
80	0	0	100	100	0	80	0	0	100	100	0
81	0	0	100	100	0	81	0	0	100	100	0
82	0	0	100	100	0	82	0	0	100	100	0
83	0	0	100	100	0	83	0	0	100	100	0
84	0	0	100	100	0	84	0	0	100	100	0
85	0	0	100	100	0	85	0	0	100	100	0
86	0	0	100	100	0	86	0	0	100	100	0
87	0	0	100	100	0	87	0	0	100	100	0
88	0	0	100	100	0	88	0	0	100	100	0
89	0	0	100	100	0	89	0	0	100	100	0
90	0	0	100	100	0	90	0	0	100	100	0
91	0	0	100	100	0	91	0	0	100	100	0
92	0	0	100	100	0	92	0	0	100	100	0
93	0	0	100	100	0	93	0	0	100	100	0
94	0	0	100	100	0	94	0	0	100	100	0
95	0	0	100	100	0	95	0	0	100	100	0
96	0	0	100	100	0	96	0	0	100	100	0
97	0	0	100	100	0	97	0	0	100	100	0
98	0	0	100	100	0	98	0	0	100	100	0
99	0	0	100	100	0	99	0	0	100	100	0
100	0	0	100	100	0	100	0	0	100	100	0

Table 4. Bond lengths and angles with their standard deviations in parentheses

DMSO			
S(1)–O(1)	1.48 (3) Å	O(1)–S(1)–C(1)	105 (2)°
S(1)–C(1)	1.75 (3)	O(1)–S(1)–C(2)	106 (2)
S(1)–C(2)	1.82 (6)	C(1)–S(1)–C(2)	95 (2)
S(2)–O(2)	1.53 (3)	O(2)–S(2)–C(3)	104 (3)
S(2)–C(3)	1.80 (8)	O(2)–S(2)–C(4)	104 (3)
S(2)–C(4)	1.77 (6)	C(3)–S(2)–C(4)	95 (3)
Nitrate			
N(1)–O(3)	1.21 (3) Å	O(3)–N(1)–O(4)	118 (3)°
N(1)–O(4)	1.31 (5)	O(3)–N(1)–O(5)	121 (3)
N(1)–O(5)	1.23 (4)	O(4)–N(1)–O(5)	121 (3)
N(2)–O(6)	1.16 (5)	O(6)–N(2)–O(7)	102 (3)
N(2)–O(6')	1.16 (5)	O(6)–N(2)–O(7)	129 (3)
N(2)–O(7)	1.15 (7)	O(6)–N(2)–O(7)	129 (3)

Table 5. Coordinating distance La–O in the coordination polyhedron

La–O(1)	2.47 (3) Å
La–O(2)	2.48 (3)
La–O(3)	2.71 (3)
La–O(4)	2.63 (2)
La–O(6)	2.62 (3)

Decoordination has been structurally established in a few cases (Shinn & Eick, 1968). Muetterties & Wright (1967) have suggested two types of coordination polyhedra which have appropriate symmetry for an sp^3d^5f hybrid model. These are the bi-capped square antiprism and the bi-capped dodecahedron. In the present case the absence of even approximately planar square faces rules out the earlier model. The polyhedron can best be explained in terms of the idealized symmetry D_{2d} ($42m$) as follows: Adopting the nomenclature of Muetterties & Wright, sites 5 and 6 are each occupied by two oxygen atoms of the bidentate nitrates, thereby splitting the sites. The sites 7 and 8 are also

occupied by the two oxygens of the third nitrate group. As a result of the doubling of the sites 5 and 6 the idealized symmetry of the polyhedron is reduced to $C_{2v}(mm2)$. However in the present case the polyhedron has a lower symmetry C_2 since the orientation of the DMSO ligands prohibits the presence of any mirror plane in the coordination polyhedron.

An ideal dodecahedron may be visualized as two interpenetrating trapezoids which are orthogonal to each other. The trapezoids in the present case are defined by atoms O(1), O(1'), O(6), O(6') and O(2), O(2'), N(1), N(1'), where N(1) and N(1') replace the oxygens of the two bidentate nitrate groups. The best least-squares planes passing through these trapezoids have been calculated and their equations are given in Table 6. The angle between the trapezoids is found to be $89^\circ 42'$. A dodecahedron is normally described by two angles θ_A and θ_B as shown in Fig. (1a). For a hard sphere dodecahedral model the predicted values are 36.9 and 69.5° respectively. The values calculated by Hoard & Silverton (1963) on the basis of energy considerations are 35.2 and 73.5° . The corresponding values in the present case are 36.2 and 78.5° , if only the unidentate ligands are considered. Hence the polyhedron though distorted from the C_{2v} symmetry approximates the suggested model. A similar coordination polyhedron has been found in the structure of lanthanum carbonate octahydrate (Shinn & Eick, 1968).

(b) Dimethyl sulphoxide molecule

The dimethyl sulphoxide is found to coordinate through the oxygen atom as suggested from infrared studies (Ramalingam & Soundararajan, 1967). These groups are found to be pyramidal. The average S–O distance observed is 1.50 ± 0.03 Å. This can be compared with the S–O distances found in the free DMSO

Table 6. *Least-squares planes*

The equation to the plane is $AX+BY+CZ=D$ with respect to the crystallographic axes a , b and c^* where X , Y , Z are in Å.

Trapezoid I:

$$-0.6489X + 0.0022Y + 0.7609Z = 3.6262$$

La	-0.0032
O(2)	-0.1215
N(1)	0.0576
O(2)'	0.1241
N(1)'	-0.0675

Trapezoid II:

$$0.7573X + 0.0045Y + 0.6531Z = 1.4506$$

La	-0.0146
O(1)	0.0081
O(6)	0.2279
O(1)'	-0.0355
O(6)'	-0.2793

Nitrate ion I:

$$0.2927X + 0.9558Y - 0.0292Z = 0.5457$$

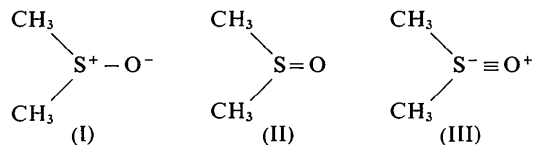
O(3)	-0.0026
O(4)	-0.0029
O(5)	-0.0024
N(1)	0.0078

Nitrate ion II:

$$0.9103X - 0.0000Y + 0.4141Z = 0.3582$$

O(6)	0.0000
O(6)'	0.0000
O(7)	0.0000
N(2)	0.0000

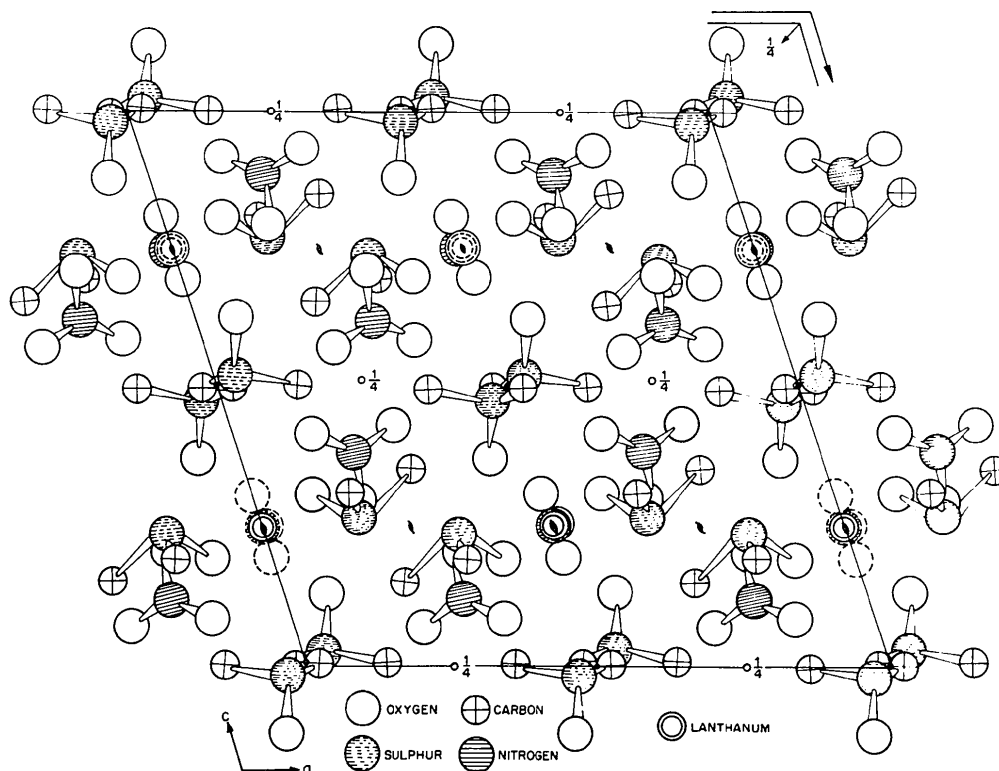
molecule. The values obtained by Viswamitra & Kannan (1966) at -60°C and Thomas, Shoemaker & Eriks (1966) at 5°C are 1.475 \AA and $1.531 \pm 0.005 \text{ \AA}$ respectively. There appears to be no clear evidence regarding the increase in the S-O distance which has been observed in some complexes (Bennett, Cotton & Weaver, 1967), where the DMSO coordinates through the oxygen atom. The three resonating structures proposed for DMSO are



with structure (II) making a significant contribution to the structure of the DMSO molecule. From the observed differences in the S-O distances, in the present case, the contributions from structures (I) and (III) appear to be negligible.

(c) Nitrate ion

The nitrate ion is known to be planar in a regular environment with all O-N-O interbond angles equal to 120° and the N-O distances equal to $1.245 \pm 0.01 \text{ \AA}$ (Addison, Logan, Wallwork & Garner, 1971). In this structure all the three nitrates are found to be bidentate. Two nitrate groups are unsymmetrically bidentate.

Fig. 2. View of the structure projected down b .

tate with bond lengths 1.22 ± 0.03 and 1.31 ± 0.05 Å. The M–O distances are 2.71 ± 0.03 and 2.63 ± 0.02 Å respectively. The third nitrate group is symmetrically bidentate with N–O distance 1.16 ± 0.05 and M–O distance of 2.62 ± 0.03 Å. The O–N–O valency angles are quite normal. The N–O distances of the symmetrically bidentate group are rather small (1.16 ± 0.05 Å). The nitrate groups are found to be planar within experimental errors. The equations for the mean plane and the deviations are given in Table 6.

(d) *Crystal packing*

The packing down the *b* axis is shown in Fig. 2. The crystal packing is apparently decided by the geometry of the coordination polyhedron around the four La^{3+} ions in the unit cell. The intermolecular contact distances in this structure are quite normal.

(e) *Thermal parameters*

The anisotropic temperature factors for all the non-hydrogen atoms are given in Table 2. It must be emphasized that any extensive discussion of anisotropic thermal motion is not warranted in view of the large absorption effects. However, the variations in the values of the equivalent isotropic temperature factors calculated for all the atoms using Hamilton's (1959) equation appear to be meaningful (Table 2) and call for some comments.

It can be seen that the lanthanum ion which is surrounded by ten oxygen atoms has the lowest temperature factor, as expected. Both the sulphur atoms, all the coordinated oxygen atoms and one nitrogen atom have almost the same thermal parameter. The end atoms of the groups are generally expected to have high temperature factor compared to the rest of the atoms. However, of the non-coordinated oxygen atoms, O(5) and O(7) at the ends of the nitrate groups, O(5) has a lower temperature factor, perhaps due to the larger number of close intermolecular contacts. O(5) has six contacts less than 4 Å whereas O(7) has only three. The nitrogen atom N(1) bonded to O(5) likewise has a lower temperature factor.

All the carbon atoms except C(1) have almost the same high temperature factor, which could be due to the hindered rotation of these terminal atoms of the

sulphoxide groups about the S–O bond. The lower temperature factor of C(1) is possibly due to the larger number of intermolecular contacts it makes.

The authors thank Professor A. R. Vasudeva Murthy for his keen interest in this investigation. They are also grateful to Dr K. Venkatesan of the Organic Chemistry Department for useful discussions. The award of a Junior Research Fellowship to one of us (K.K.B.) by the C.S.I.R., India is gratefully acknowledged.

References

- ADDISON, C. C., LOGAN, N., WALLWORK, S. C. & GARNER, C. D. (1971). *Quart. Rev.* **25**, 289–322.
- AL-KARAGHOULI, A. R. & WOOD, J. S. (1968). *J. Amer. Chem. Soc.* **90**, 6548–6549.
- BENNETT, M. J., COTTON, F. A. & WEAVER, D. L. (1967). *Acta Cryst.* **23**, 581–586.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- CRUICKSHANK, D. W. J., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. Edited by R. PEPINSKY, J. M. ROBERTSON & J. C. SPEAKMAN. London: Pergamon Press.
- GYSLING, H. & TSUTSUI, M. (1970). *Advanc. Organometal. Chem.* **9**, 361–395.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HOARD, J. L. & SILVERTON, J. V. (1963). *Inorg. Chem.* **2**, 235–243.
- International Tables for X-ray Crystallography* (1962). Vol. I. Birmingham: Kynoch Press.
- KARRAKER, D. G. (1970). *J. Chem. Ed.* **47**, 424–430.
- MUETTERTIES, E. L. & WRIGHT, C. M. (1967). *Quart. Rev.* **21**, 109–194.
- PEERDEMAN, A. F., VAN BOMMEL, A. J. & BIJVOET, J. M. (1951). *Koninkl. Ned. Akad. Wetenschap. Proc.* **B54**, 16–19.
- RAMALINGAM, S. K. & SOUNDARARAJAN, S. (1967). *J. Inorg. Nucl. Chem.* **29**, 1763–1768.
- SHINN, D. B. & EICK, H. A. (1968). *Inorg. Chem.* **7**, 1340–1345.
- THOMAS, R., SHOEMAKER, C. B. & ERIKS, K. (1966). *Acta Cryst.* **21**, 12–20.
- VISWAMITRA, M. A. & KANNAN, K. K. (1966). *Nature, Lond.* **209**, 1016–1017.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151–152.