Analytical data and physical properties for $[NiL_3(ClO_4)_2]$ complexes [a]

Crystal and Molecular Structure of Tris(dimethyl sulphoxide)trinitratoytterbium

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The title complex crystallises in the monoclinic space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 10{\cdot}08(2)$, $b = 12{\cdot}74(2)$, $c = 16{\cdot}02(2)$ Å, and $\beta = 100{\cdot}5(3)°$. The structure was solved by the heavy-atom method and refined by three-dimensional least-squares procedures, from 2172 visually estimated independent reflections, to R 0·078. The ytterbium is co-ordinated by nine oxygen atoms which form a tricapped trigonal prism. The three dmso oxygen atoms occupy a triangular face of the trigonal prism while the six oxygen atoms from the three nitrate groups occupy the remaining sites. The Yb–O distances are 2·23—2·48 Å. All three nitrate groups are bidentate. The sulphur atom of one dmso group is disordered.

We are carrying out systematic X-ray investigations of rare-earth metal complexes in order to study the effect of the lanthanide contraction on the co-ordination number and geometry of the co-ordination polyhedron around the metal ion. We have chosen a series of complexes of rare-earth nitrates with dimethyl sulphoxide (dmso), of general formula $[Ln(NO_3)_3(dmso)_n]$ [1] where $n = 4$ for Ln = La to Gd, and $n = 3$ for Ln = Tb to Yb. The crystal structure of $[La(NO_3)_3(dmso)_4]$ has already been reported.[2] The Yb^{3+} ion has an ionic radius of 0·858 Å which is considerably smaller than that of the La^{3+} ion (1·061 Å).[3] This decrease was expected to have an influence on its co-ordination and consequently on the crystal structure. It was therefore considered worthwhile to analyse the crystal structure of the $[Yb(NO_3)_3(dmso)_3]$ complex.

EXPERIMENTAL

The complex was prepared as described in ref. 1 and recrystallised from acetonitrile. Crystals were tabular and elongated along c. Cell constants were obtained from single-crystal rotation and Weissenberg techniques by use of Cu-K_α radiation.

Crystal Data.—$C_6H_{18}N_3O_{12}S_3Yb$, $M = 593{\cdot}5$, Monoclinic, $a = 10{\cdot}08(2)$, $b = 12{\cdot}74(2)$, $c = 16{\cdot}02(2)$ Å, $\beta = 100{\cdot}5(3)°$, $U = 2023$ Å^3, D_m (by flotation) = 1·968, $Z = 4$, $D_c = 1{\cdot}949$ g cm^{-3}, $F(000) = 289$. Space group $P2_1/c$. Cu-K_α radiation, $\lambda = 1{\cdot}542$ Å; $\mu(\text{Cu-}K_\alpha) = 123{\cdot}5$ cm^{-1}.

Intensity Data Collection.—Three-dimensional intensity data were collected about the a and c axes by the multiple-film equi-inclination Weissenberg techniques for reflections 0—6kl and hk0—10 by use of Cu-K_α radiation. The crystals used for data collection were cut from the tabular crystal and ground to cylinders of radii 0·088 and 0·125 mm. They were sealed in Lindemann capillaries. The intensities of 2172 independent reflections were measured visually and estimated by use of a calibrated strip. Intensities were corrected for Lorentz and polarisation factors, and for absorption effects (μr 1·1 for the a and 1·55 for the c axis). The intensities were first placed on a relative scale by

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[1] S. K. Ramalingam and S. Soundararajan, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1763.

[2] K. Krishna Bhandary and H. Manohar, *Acta Cryst.*, 1973, **B29**, 1093.

[3] T. Moeller, in 'The Chemistry of Lanthanides,' ed. H. H. Sisler and C. A. Vander Werf, Wiley, 1963.

correlating the data about the two axes and then on an absolute scale by Wilson's method.[4]

Structure Determination and Refinement.—The ytterbium positional parameters were obtained from a three-dimensional Patterson synthesis and refined. *R* was 0·30 at this stage. The positions of the other atoms were identified from a difference Fourier map. *R* was reduced to 0·25 when all atoms were included in the structure-factor calculation. After a few cycles of block-diagonal least-squares refinement *R* was 0·13. It was then found that S(1) had a temperature factor of 14 Å^2 while S(2) and S(3) had lower values of *ca.* 7 Å^2. A difference-Fourier map was computed and showed sulphur S(1) to be disordered, the two positions being symmetrical with respect to the plane through the three other atoms of the dmso group. Final refinement with anisotropic temperature factors for all the atoms converged at *R* 0·078, the two positions of S(1) being allocated equal occupancy.

TABLE 1

Final fractional atomic co-ordinates, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Yb	0·2218(2)	0·2528(1)	0·4379(1)
S(1)	0·2144(21)	0·0872(15)	0·6097(11)
S(1′)	0·1650(24)	0·0390(16)	0·5591(15)
S(2)	0·1706(12)	0·3957(9)	0·6117(7)
S(3)	0·5139(11)	0·2256(9)	0·5843(9)
O(1)	0·1784(38)	0·1321(21)	0·5300(22)
O(2)	0·1274(28)	0·3638(20)	0·5202(18)
O(3)	0·4035(32)	0·2872(27)	0·5374(20)
O(4)	−0·0170(29)	0·2135(31)	0·4042(24)
O(5)	0·0552(34)	0·3115(30)	0·3179(22)
O(6)	−0·1458(31)	0·2530(20)	0·2832(29)
O(7)	0·2792(35)	0·4325(23)	0·4039(23)
O(8)	0·3622(37)	0·3118(31)	0·3407(25)
O(9)	0·4026(47)	0·4693(35)	0·3169(27)
O(10)	0·3772(33)	0·1071(25)	0·4191(22)
O(11)	0·1907(30)	0·1122(23)	0·3387(21)
O(12)	0·3426(38)	−0·0021(31)	0·3210(28)
N(1)	−0·0396(32)	0·2537(21)	0·3328(28)
N(2)	0·3482(36)	0·4092(24)	0·3584(23)
N(3)	0·3036(36)	0·0697(24)	0·3591(24)
C(1)	0·0658(77)	0·0626(43)	0·6425(43)
C(2)	0·3041(62)	−0·0370(43)	0·6078(47)
C(3)	0·0230(49)	0·4279(44)	0·6444(32)
C(4)	0·2373(67)	0·5204(47)	0·6033(37)
C(5)	0·5329(52)	0·2630(32)	0·6939(29)
C(6)	0·6708(52)	0·2654(37)	0·5638(50)

TABLE 2

Bond distances (Å) and angles (°)

(*a*) In the dmso groups			
S(1)–O(1)	1·39(4)	O(1)–S(1)–C(1)	105(3)
S(1)–C(1)	1·71(7)	O(1)–S(1)–C(2)	113(3)
S(1)–C(2)	1·83(6)	C(1)–S(1)–C(2)	108(3)
S(1′)–O(1)	1·29(4)	O(1)–S(1′)–C(1)	103(3)
S(1′)–C(1)	1·84(7)	O(1)–S(1′)–C(2)	123(3)
S(1′)–C(2)	1·76(6)	C(1)–S(1′)–C(2)	105(3)
S(2)–O(2)	1·51(3)	O(2)–S(2)–C(3)	104(2)
S(2)–C(3)	1·71(4)	O(2)–S(2)–C(4)	103(2)
S(2)–C(4)	1·74(6)	C(3)–S(2)–C(4)	100(3)
S(3)–O(3)	1·45(3)	O(3)–S(3)–C(5)	107(2)
S(3)–C(5)	1·80(3)	O(3)–S(3)–C(6)	112(2)
S(3)–C(6)	1·75(4)	C(5)–S(3)–C(6)	100(2)
(*b*) NO_3 groups			
N(1)–O(4)	1·24(6)	O(4)–N(1)–O(5)	113(3)
N(1)–O(5)	1·26(4)	O(4)–N(1)–O(6)	127(4)
N(1)–O(6)	1·21(5)	O(5)–N(1)–O(6)	119(3)
N(2)–O(7)	1·13(5)	O(7)–N(2)–O(8)	120(4)
N(2)–O(8)	1·29(5)	O(7)–N(2)–O(9)	126(4)
N(2)–O(9)	1·21(5)	O(8)–N(2)–O(9)	114(4)
N(3)–O(10)	1·20(5)	O(10)–N(3)–O(11)	116(3)
N(3)–O(11)	1·25(4)	O(10)–N(3)–O(12)	124(4)
N(3)–O(12)	1·21(5)	O(11)–N(3)–O(12)	124(4)

Scattering factors were taken from ref. 5, the effects of anomalous dispersion being taken into account for Yb^{3+} ($\Delta f', \Delta f''$). The quantity minimised in the least-squares calculation was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/(a + F_o + cF_o^2)$, with $a = 10{\cdot}0$ and $c = 0{\cdot}0088$.[6]

Final fractional co-ordinates are given in Table 1, and bond length and angles found in Table 2. Final observed and calculated structure factors and anisotropic thermal parameters are given in Supplementary Publication No. SUP 21171 (5 pp., 1 microfiche).*

DISCUSSION

The structure as viewed down the *a* axis is shown in Figure 1. The packing in the crystal appears to be decided by the co-ordination and orientation of the groups around the metal ion. The Yb^{3+} ion is surrounded by nine oxygen atoms, three from the three dmso groups and six from the three nitrate groups. All the nitrate groups are bidentate as in the structure of $[La(NO_3)_3(dmso)_4]$ and other complexes of 4*f* and 5*f* transition metals.[7] I.r. and other physicochemical studies [1] had suggested that only one nitrate group is likely to be bidentate.

The co-ordination polyhedron around the Yb^{3+} ion can be described as a slightly distorted tricapped trigonal prism (Figure 2). The idealised symmetry of this polyhedron is D_{3h}. Besides this geometry, the only other idealised geometry for nine-co-ordination is the monocapped square antiprism of C_{4v} symmetry. The tricapped trigonal prism appears to be the most common polyhedron for nine-co-ordination and has been found in many molecular complexes and ionic lattices of lanthanides and actinides.[8] The Yb–O co-ordinating distances (Table 3) vary between 2·23 and 2·48 Å. The mean Yb–O(dmso) and Yb–O(NO_3) distances are 2·24 ± 0·03 and 2·43 ± 0·035 Å respectively; similar differences in the co-ordinating distances were also found in $[La(NO_3)_3(dmso)_4]$.[2] The shorter distance to the dmso oxygen may be due to strong interaction with the metal since dmso is a powerful complexing ligand with a wide variety of acceptors.[9] Another reason might be that dmso being a unidentate ligand, can make a closer approach to the metal atom than can the bidentate nitrate group.

The three oxygen atoms O(1)—(3) of the three dmso groups form one triangular face while the nitrate oxygen atoms O(5), O(8), and O(11) are at the corners

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[4] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[5] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[6] D. W. J. Cruickshank, A. Bujosa, D. M. Lovell, and M. R. Truter, in ' Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis,' eds. R. Prepinsky, J. M. Robertson, and J. C. Speakman, London, Pergamon Press, Oxford, 1961.

[7] C. N. Caughlan, Mazhar-ul Hague, F. A. Hart, and R. Van Nice, *Inorg. Chem.*, 1971, **10**, 115.

[8] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109.

[9] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, 1960, **82**, 2986.

of the other triangular face, and O(4), O(7), and O(10) at the centres of the rectangular faces. Distances and angles in the co-ordination polyhedron are given in Table 3, which also shows that the triangles O(1), O(2), O(3) [plane (1)], O(5), O(8), O(11) [plane (2)], and O(4), O(7), O(10) [plane (3)] are approximately equilateral, the angles between the edges of the triangles agreeing well with the ideal value of 60°. These planes are also nearly parallel to each other, the angles between them being: (1)–(3) 2° 24′, (1)–(2) 2° 30′, and (2)–(3) 4° 27′. The Yb^{3+} ion is 0·45 Å out of plane (3) through the capping atoms. The slight distortion found in the tricapped trigonal prism around Yb^{3+} ion can be attributed to the presence of mixed and multidentate ligands around the metal ion.

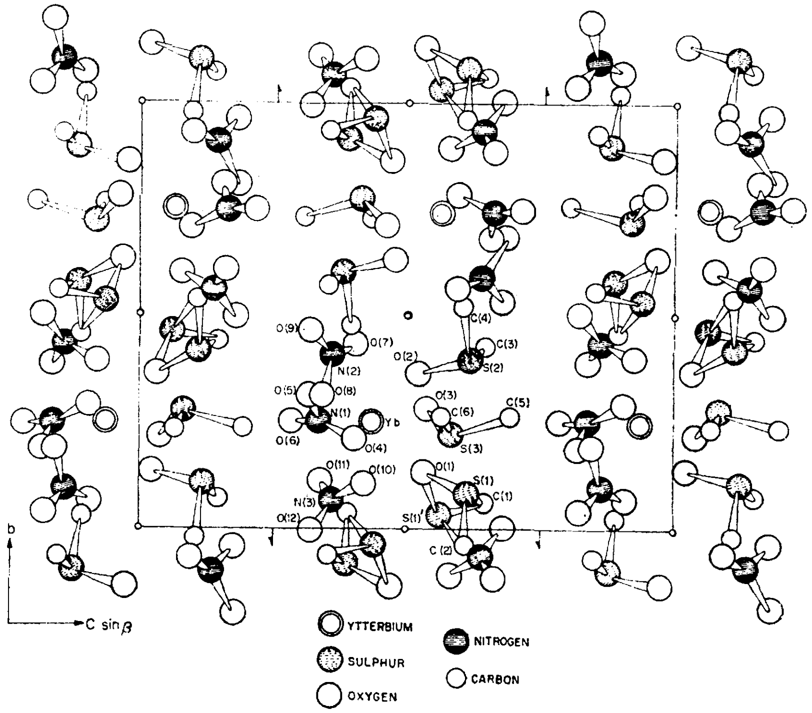

FIGURE 1 View of the structure projected down the *a* axis

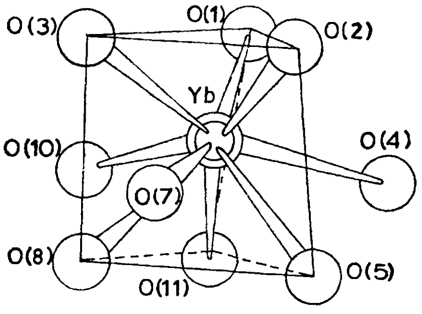

FIGURE 2 Co-ordination polyhedron around Yb^{3+}

In the structure of $[La(NO_3)_3(dmso)_4]$ the co-ordination number was shown to be ten, four oxygen atoms being contributed by the four dmso groups and six by the three nitrate groups. However, in the present structure the co-ordination number is nine. The contact distances between the oxygen atoms of the different groups in the polyhedron are 2·75—3·07 Å, which correspond to normal van der Waals contacts.

It is therefore evident that the atom packing around the Yb is very tight thus preventing co-ordination of any additional atom. Thus the changes observed in the co-ordination of the metal ions in the two complexes may be attributed to the decrease in the size of the metal ion at the centre of the co-ordination polyhedron. It is also of interest to compare the co-ordinating

TABLE 3

Distances (Å) and angles (°) in the co-ordination polyhedron

(*a*) Metal–oxygen distances

Yb–O(1)	2·23(03)	Yb–O(7)	2·45(03)
Yb–O(2)	2·26(03)	Yb–O(8)	2·41(04)
Yb–O(3)	2·24(03)	Yb–O(10)	2·48(03)
Yb–O(4)	2·42(02)	Yb–O(11)	2·38(03)
Yb–O(5)	2·43(03)		

(*b*) Tricapped trigonal prism

O(1)–O(2)	3·00	O(1)–O(2)–O(3)	60·9
O(2)–O(3)	2·92	O(2)–O(3)–O(1)	60·9
O(3)–O(1)	3·00	O(3)–O(1)–O(2)	58·2
O(5)–O(8)	3·05	O(5)–O(8)–O(11)	56·0
O(8)–O(11)	3·07	O(8)–O(11)–O(5)	61·6
O(11)–O(5)	2·87	O(11)–O(5)–O(8)	62·4
O(4)–O(7)	4·08	O(4)–O(7)–O(10)	59·8
O(7)–O(10)	4·26	O(7)–O(10)–O(4)	58·1
O(10)–O(4)	4·16	O(10)–O(4)–O(7)	62·1
O(8)–O(3)	3·12		
O(5)–O(2)	3·26		
O(11)–O(1)	3·10		
O(4)–O(5)	2·09		
O(7)–O(8)	2·10		
O(10)–O(11)	2·08		

distances in the two complexes. In the lanthanum complex, mean La–O(dmso) was 2·48 ± 0·03 Å and La–O(NO_3) 2·67 ± 0·03 Å. The decrease of 0·24 Å in the metal–oxygen distances in the present structure corresponds very nearly to the decrease in the ionic radius of the metal (0·203 Å).

In the disordered dmso group [S(1),O(1),C(1),C(2)] sulphur atoms S(1) and S(1′) are 0·56 and 0·50 Å out of the plane through C(1),C(2),O(1), and the S–O bond distances are unusually short. However, the nature of the intermolecular packing in the region of this dmso group shows that even with the disordered sulphur split into two, there are no intermolecular contacts <3·5 Å. Thus the intermolecular packing in this region is loose, a situation favouring disorder.

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