February, 1986] © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 59, 669—670 (1986)* 669

The Structure of Bis(dibenzyl sulfoxide)tris(*O,O′*-diethyl dithiophosphato)lanthanum(III), $La\{(C_2H_5O)_2PS_2\}_3\{(C_6H_5CH_2)_2SO\}_2$

Takashi Imai, Mamoru Shimoi, and Akira Ouchi*

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

(Received August 21, 1985)

Synopsis. The crystal and molecular structure of the title complex has been determined by the use of the single-crystal X-ray diffraction method. The crystal of $LaC_{40}H_{58}O_8P_3S_8$, F.W.=1155.20, is triclinic; space group $P\bar{1}$, a=13.300(5), b=19.816(8), c=11.257(4) Å, α=92.79(4), β=114.92(3), γ=75.40(4)°, U=2598(2) Å^3, Z=2, D_m=1.48(3), D_x=1.48 g cm^{-3}, and $\mu(\text{Mo}\,K\alpha)$=1.29 mm^{-1}. Each lanthanum(III) atom is octa-coordinated and is in a dodecahedral geometry. The oxygen atoms of dibenzyl sulfoxide molecules are ligated at both ends of the base of a trapezia, and the chelating *O,O′*-diethyl dithiophosphates span two m edges and one a edge.

Some stable *O,O′*-dialkyl dithiophosphate (R_2dtp)-Lewis base mixed complexes of lanthanoids(III), where the former ligands are ligated to the hard-metal atom through the soft sulfur atoms, have already been synthesized, and some of their structures have been elucidated.[1—6] In such mixed complexes, the same kind of the ligated atoms are apt to take contiguous positions;[3,7] the M(iPr$_2$dtp)$_3$L$_2$ complexes in the octa-coordinated dodecahedral geometry, where M=lanthanoid(III) metal, iPr=$(CH_3)_2CH$–, and L=dimethyl sulfoxide (dmso)[4] or *N,N*-dimethylacetamide (dma),[2] have the Lewis-base oxygen atoms at both ends of one m-edge; tentatively we have named these complexes the "mmm-type" after their chelating positions. However, even in the same type of complexes, when the Lewis-base ligands are relatively large in size, for example, in the cases of the triphenylphosphine oxide (Ph_3PO) and benzamide (bza) adducts, the base oxygen atoms ligate at both ends of the base of a trapezia; [1,3] tentatively we name these complexes the "mma-type." Although the steric hindrance of the ligands may be the main cause of this structure, the polarity of the Lewis base may affect the ligating position, too. Consequently, it is interesting to study the structures of some dialkyl sulfoxide adduct, where the base is more polar than acid amide, but is large. Therefore, we have investigated the structure of the title complex by means of the single-crystal X-ray diffraction method.

Experimental

Preparation of Bis(dibenzyl sulfoxide)tris(*O,O′*-diethyl dithiophosphato)lanthanum(III), and the Neodymium(III) Complex. Lanthanum(III) chloride heptahydrate (1.00 g, 2.7 mmol), Na(Et$_2$dtp) (Et=C_2H_5–) (2.24 g, 10.8 mmol), and dibenzyl sulfoxide (bzso) (1.36 g, 5.9 mmol) were dissolved in about 10 cm^3 of warm ethanol. After the residue has been filtered off, the solution was evaporated using a rotary vacuum evaporator at about 80 °C, and the resinous residue thus obtained was redissolved into warm benzene (about 10 cm^3). After the residue has then been cooled, it was allowed to stand in contact with the vapor of petroleum ether at the ambient temperature for several days. Crystals came out (about 2.2 g; 1.90 mmol; yield=90%). The isomorphous neodymium(III) complex was obtained by almost the same process. Anal. ($MC_{40}H_{58}O_8P_3S_8$) M=La or Nd, C, H. Neither mmm-type complexes, such as [Nd(iPr$_2$dtp)$_3$(dmso)$_2$],[4] nor ionic ones, such as [Nd(iPr$_2$dtp)$_2$(dbso)$_3$][Nd(iPr$_2$dtp)$_4$] (where dbso=dibutyl sulfoxide),[6] were obtained by this process.

Single-Crystal X-Ray Analysis. A crystal with dimensions of 0.35×0.32×0.30 mm^3 was used for the measurement. All edges were ground off. The reflections within the range of $3° < 2\theta < 56°$ were collected on a Rigaku AFC-6A four-circle automated X-ray diffractometer with Mo$K\alpha$ radiation, employing the ω—2θ scan technique. Of the 12632 independent reflections, 9764 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the refinement. The intensities were corrected for the Lorentz and polarization factors, but no correction was made for the absorption and extinction. All the calculations were carried out on a HITAC M-280H computer at the Computer Center of The University of Tokyo, using the local version of UNICS.[8] The scattering factors were taken from the tables.[9]

Structure Determination. The structure was solved by the heavy-atom method. All non-hydrogen atoms were found, and the positions of the phenyl hydrogen atoms were calculated from those of the neighboring carbon atoms, assuming that C–H=1.08 Å and that their B_{iso}=10.0. The final R value was 0.044,[10] applying anisotropic temperature factors for all non-hydrogen atoms.

Results and Discussion

Some selected bond lengths and angles are shown in Table 1.[11] A perspective drawing of the complex, with the numbering scheme, is shown in Fig. 1; the crystal packing diagram, in Fig. 2, and a schematic presentation of the bonding mode of the ligating atoms around the metal atom, in Fig. 3.

As is shown in the figures, the central metal atom is octa-coordinated and is in a dodecahedral geometry. Three Et$_2$dtp ligands are chelated through two corresponding sulfur atoms; two of them span m-edges, while the other one spans a-edge. Two bzso oxygen atoms ligate at both ends of the base of a trapezia. Therefore, this complex is of the mma-type; it was found that, even in the case of the adduct of polar dialkyl sulfoxides, the mma-type structure is more stable than the mmm-type structure when the steric effect is dominant.

The bond lengths of La–S are 2.992—3.091 Å (3.024 Å on the average); they are about the same as the sum of their ionic radii as presented by Shannon (3.00 Å).[12] On the other hand, the La–O bond lengths are 2.415 and 2.413 Å, shorter than the sum of the Shannon radii (2.51 Å); the phenomenon has previously been found in the other [La(R$_2$dtp)$_3$L$_2$]-type complexes, too.[1—4]

Respective complex molecules are independent in the crystal; no bridgings by the coordinated ligands or

Table 1. Bond Lengths and Bond Angles, with Estimated Standard Deviations in Parentheses

Bond length	(l/Å)	Bond length	(l/Å)	Bond length	(l/Å)
La-S(1)	3.023(2)	La-S(2)	2.992(2)	La-S(3)	3.018(3)
La-S(4)	3.008(2)	La-S(5)	3.013(2)	La-S(6)	3.091(2)
La-O(11)	2.415(3)	La-O(12)	2.413(3)	S(1)-P(1)	1.969(2)
S(2)-P(1)	1.959(2)	S(3)-P(2)	1.964(2)	S(4)-P(2)	1.961(2)
S(5)-P(3)	1.969(2)	S(6)-P(3)	1.955(2)	O(11)-S(11)	1.518(3)
O(12)-S(12)	1.504(3)				
Bond angle	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**	**Bond angle**	**(ϕ/°)**
S(1)-La-S(2)	66.81(4)	S(3)-La-S(4)	65.71(3)	S(5)-La-S(6)	65.65(4)
S(1)-La-S(3)	124.76(3)	S(1)-La-S(5)	138.61(4)	S(2)-La-S(3)	88.38(4)
S(2)-La-S(5)	154.11(4)	S(3)-La-S(5)	78.97(4)	S(4)-La-S(5)	81.79(4)
O(11)-La-O(12)	151.27(10)	S(3)-La-O(11)	69.96(7)	S(4)-La-O(12)	72.53(7)
La-S(1)-P(1)	88.12(5)	La-S(2)-P(1)	89.20(6)	La-S(3)-P(2)	90.55(5)
La-S(4)-P(2)	90.90(5)	La-S(5)-P(3)	90.57(6)	La-S(6)-P(3)	88.58(5)
La-O(11)-S(11)	141.9(2)	La-O(12)-S(12)	158.6(2)		

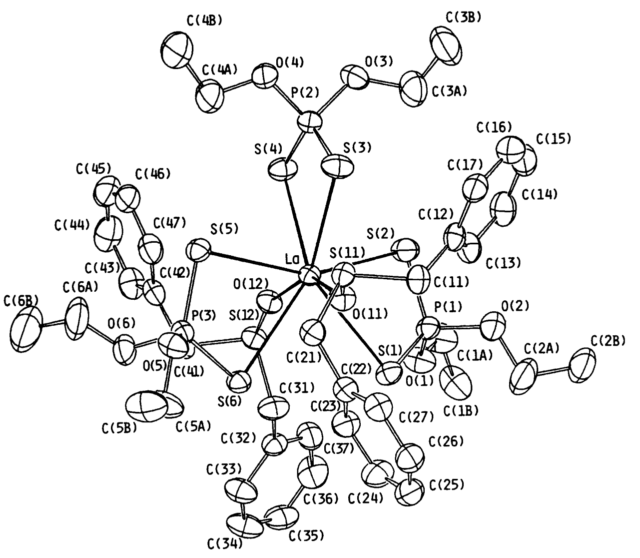

Fig. 1. A perspective drawing of the titled complex with the numbering scheme.

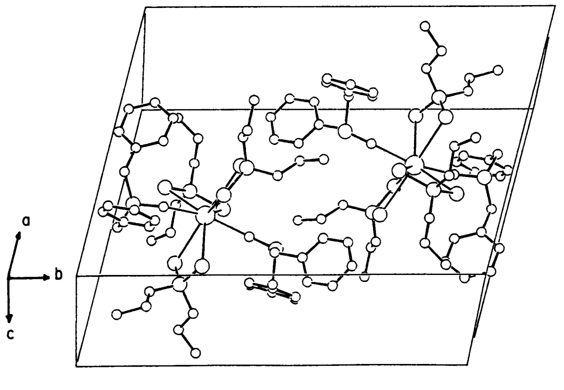

Fig. 2. The crystal packing diagram of the titled complex.

through the hydrogen bondings were found between them.

In the cases of the other Lewis-base adducts of lanthanoid *O,O′*-dialkyl dithiophosphates, it was found that the thermal parameters of some atoms, especially those of isopropyl carbon atoms, are very large.[3–6] In this complex, too, the temperature factors of the ethyl carbon atoms are large.

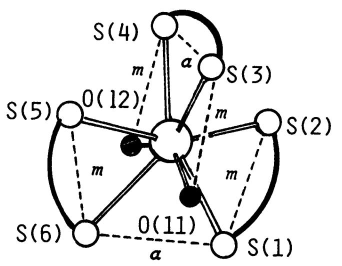

Fig. 3. A schematic presentation of the comprex around the central metal atom.

The authors are greatly obliged to the Shin-Etsu Chemical Ind. Co., Ltd., for presenting highly pure lanthanoid oxides.

References

1) A. A. Pinkerton and D. Schwarzenbach, *J. Chem Soc., Dalton Trans.*, **1976**, 2466.

2) K. Nagai, Y. Sato, S. Kondo, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **56**, 2605 (1983).

3) R. Nakamura, K. Nagai, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 2919 (1984).

4) M. Nakamura, K. Nagai, Y. Ohki, Y. Suzuki, M. Shimoi, and A. Ouchi, unpublished data.

5) K. Nagai, R. Nakamura, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 2725 (1984).

6) Y. Ohki, M. Nakamura, Y. Suzuki, K. Nagai, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **58**, 1593 (1985).

7) M. E. Silver, H. K. Chun, and R. C. Fay, *Inorg. Chem.*, **21**, 3765 (1982).

8) "The Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).

9) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72, 150.

10) $R=\sum||F_o|-|F_c||/\sum|F_o|$

11) The final positional and thermal parameters and the final F_o—F_c table are deposited as Document No. 8610 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

12) R. D. Shannon, *Acta Crystallogr., Sect A*, **32**, 751 (1976).