  Bull. Chem. Soc. Jpn., 59, 2115—2122 (1986)

The Syntheses, Properties, and Crystal and Molecular Structures of the Lanthanoid Mixed-Complexes of *O,O'*-Diisopropyl Dithiophosphate and Dimethyl Sulfoxide: $[Ln\{(C_3H_7O)_2PS_2\}_3\{(CH_3)_2SO\}_2]$ (Ln=La or Nd), and $[Eu\{(C_3H_7O)_2PS_2\}_2\{(CH_3)_2SO\}_3][Eu\{(C_3H_7O)_2PS_2\}_4]$

Takashi IMAI, Masao NAKAMURA, Kiyofumi NAGAI, Yoshiyuki OHKI,†
Yasuo SUZUKI,† Mamoru SHIMOI, and Akira OUCHI*
Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153
†Department of Industrial Chemistry, Faculty of Engineering, Meiji University, Higashi-Mita, Tama-ku, Kawasaki, Kanagawa 214
(Received January 6, 1986)

Two types of the mixed complexes indicated in the title have been synthesized, and their crystal and molecular structures of the lanthanum (**1**) and the europium (**2**) complexes have been determined by the X-ray diffraction method. Both **1** and **2** are monoclinic, space group $P2_1/n$, and $Z=4$. **1**, $a=17.354(7)$, $b=23.336(4)$, $c=10.955(2)$ Å, $\beta=96.04(2)°$, final R value calculated from 4870 reflections is 0.069; **2**, $a=29.846(7)$, $b=20.070(3)$, $c=14.057(3)$ Å, $\beta=92.13(2)°$, final R value calculated from 7811 reflections is 0.077. In **1**, the central metal atom is octa-coordinated, and is in a dodecahedral geometry, where all *O,O'*-diisopropyl dithiophosphato ligands (iPr_2dtp) span m-edges of the dodecahedron, chelating through both of the respective sulfur atoms. Dimethyl sulfoxide (dmso) ligands occupy the apexes of the other m-edge. In **2**, the europium(III) metal atom of the cationic species is hepta-coordinated and is in a pentagonal-bipyramidal geometry where two oxygen atoms of dmso ligate from respective ends of the axis and one oxygen atom of the remaining dmso from the equatorial direction. The central metal atom of the anion is octa-coordinated and is in a dodecahedron; where all m-edges are spanned by iPr_2dtp ligands. The solid and the acetonitrile solution of **2** is orange in color due to the charge-transfer band ($\lambda_{max}=415$ nm; $\varepsilon_{max}=1.5\times10^2$ dm^3 mol(Eu)$^{-1}$ cm^{-1}).

In previous papers, some of the present authors have reported on the syntheses and the structures of some mixed complexes of *O,O'*-diisopropyl dithiophosphate (iPr_2dtp), and benzamide (bza),[1,2] *N,N*-dimethylacetamide (dma),[3] or dibutyl sulfoxide.[4] Pinkerton has also published a study about the mixed complexes of *O,O'*-diethyl dithiophosphate (Et_2dtp) and triphenylphosphine oxide (Ph_3PO).[5] It is an interesting fact that, in these complexes sulfur atoms ligate to the central lanthanoid atom tightly in spite of the "hard acid" character of the metal.[6]

Moreover, in a series of the dialkyl dithiophosphates mixed complexes of lanthanoid elements, the molecular structures of the lighter and heavier elements are not the same. For example, in the case of the iPr_2dtp–bza mixed complexes, lanthanum(III), through gadolinium(III), form the $[M(iPr_2dtp)_3(bza)_2]$ types and gadolinium(III), through ytterbium(III), the $[M(iPr_2dtp)_2(bza)_3](ipr_2dtp)$ types.[1,2] In cases of the Et_2dtp–Ph_3PO mixed complexes, the former types are formed for lanthanum(III), through praseodymium(III), and the latter types for the rest of lanthanoid elements.[5]

In order to add such examples, we have tried to synthesize a series of the lanthanoid mixed complexes of iPr_2dtp and dimethyl sulfoxide (dmso) and obtained the two types of the complexes indicated in the title: Type **1** complexes were obtained for lanthanum and neodymium, and Type **2** complexes for europium. As shown in the title formula, a Type 2 complex includes an anionic complex, $[M(iPr_2dtp)_4]^-$, like the dibutyl sulfoxide adduct[4] in place of the free $(R_2dtp)^-$ ion (where R=ethyl or isopropyl), which is found in the R_2dtp–bza or Ph_3PO mixed complexes of the heavier lanthanoids.[2,5]

Another problem regarding the type of complex is the coordination sites of the oxygen atoms. As shown in a dodecahedral iPr_2dtp–dma[3] mixed complex, two oxygen atoms take neighbouring positions on one m-edge of the dodecahedron, which is expected to be the preferable situation because the same kind of the ligating atoms are apt to locate nearer,[7] if no steric hindrance occurs.[3] However, as no other example of the type of complex has been found yet, other than the iPr_2dtp–dma type, this time we tried to synthesize the iPr_2dtp–dmso mixed complexes of lanthanoid elements since dmso is relatively small in size and is polar.

To clarify the above-mentioned problems, we determined the structures of the title complexes by the X-ray diffraction technique using single crystals.

Experimental

Synthesis of Tris(*O,O'*-diisopropyl dithiophosphato)bis(dimethyl sulfoxide)lanthanum(III) (1). The Na(iPr_2dtp) was obtained from phosphorus pentasulfide and 2-propanol by the Livingstone's method used to prepare Na(Et_2dtp).[8] Lanthanum(III) chloride heptahydrate (0.49 g, 1.3 mmol) and Na(iPr_2dtp) (1.27 g, 5.4 mmol) were mixed in 30 cm^3 of 2-propanol and refluxed for 30 min. After cooling, a deposited curdy matter was filtered off, and dmso (0.20 g, 2.6 mmol) was added to the filtrate. After being warmed to about 65 °C for 10 min, the solution was concentrated to about 10 cm^3 using a vacuum rotary

evaporator at about 60 °C. The solution, thus obtained, was left standing at about 5 °C overnight in a refrigerator; the crude product was precipitated. When more dmso was added in the process, no crystals were obtained by this method; even if the standing solution was more concentrated, the sirupy liquid did not become solidified. The crude product was dissolved in benzene (about 30 cm^3) and a little insoluble matter was filtered off. The filtrate was concentrated to about 5 cm^3 by a rotary vacuum evaporator at about 70 °C, and was left standing in a refrigerator (10 °C) for several days; pure crystals precipitated. They were washed with benzene, and dried in a vacuum desiccator on silica gel. Yield, 0.5 g (40%).

The neodymium(III) complex was obtained by the same way from its chloride. Yield from 0.45 g (1.3 mmol) of the metal chloride heptahydrate, 0.9 g (70%). Anal. ($MC_{22}H_{54}O_8P_3S_8$) M, C, H, S. (M=La or Nd).

The Synthesis of [Bis(*O,O'*-diisopropyl dithiophosphato)-tris(dimethyl sulfoxide)europium(III)][tetrakis(*O,O'*-diisopropyl dithiophosphato)europate(III)] (2). Europium(III) chloride hexahydrate (0.61 g, 1.7 mmol) and Na(iPr2dtp) (1.6 g, 6.7 mmol) were dissolved in 25 cm^3 of 2-propanol and refluxed for 20 min. After cooling, the residue was filtered off and was added to the filtrate 0.31 g (0.40 mmol) of dmso. The solution was warmed to 65 °C for about 10 min to complete the reaction and was concentrated to about 5 cm^3 using a rotary vacuum evaporator at about 60 °C. The obtained solution was left standing overnight and the deposited curdy matter was filtered off. When the filtrate was kept in a refrigerator for several days, pure crystals were precipitated. These were separated, washed with 2-propanol, and dried in a vacuum desiccator. Yield, 0.65 g(43%). Anal. ($EuC_{42}H_{102}O_{15}P_6S_{15}$), Eu, C, H, S.

Intensity-Data Collection. Crystals with the dimensions of 0.4×0.3×0.3 mm^3 (all apexes were cut off) (**1**), and of 0.4 mm ϕ in sphere (**2**) were used for the respective measurements. The crystallographic data, some experimental conditions to obtain the intensity data, and the final R values[9] obtained by applying the anisotropic temperature factors are tabulated in Table 1. The reflections were collected on a Rigaku AFC-6A automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation, the ω-scan technique being employed (scan speed 4° min^{-1}). The intensities were corrected for the Lorentz and polarization factors, but no correction was made for absorption and extinction.

Structure Determination. The structure was solved by the heavy-atom method. The positions of the metal, phosphorus, and sulfur atoms were deduced from a three-dimensional Patterson map; the other non-hydrogen atoms were located successively by the repeated Fourier syntheses. Their positional, isotropic and then anisotropic thermal parameters were refined by the block-diagonal least-squares method using the local version of the UNICS program.[10]

S(8), C(21), and C(22) of a dmso ligand of **1**, and S(17), C(17), C(18), and S(16) of the dmso ligand of **2** are found to be disordered, and are divided into two. Their positions and occupancy factors were refined with the fixed S–C bond length (1.799 Å). Most of the isopropyl groups of the both compounds showed quite large thermal parameters and gave some abnormal bond lengths if refined without any restrictions. We tried to divide them into disordered structures, but failed. Therefore, they were refined with a fixed geometry, assuming O–C, C–C, O···C, and C···C lengths to be 1.41, 1.53, 2.50, and 2.40 Å, respectively. These procedures were carried out by the blocked full-matrix least-squares method using the SHELX-76 program.[11]

Such ambiguity of positions of peripheral alkyl groups is often encountered in a structural determination of lanthanoid(III) *O,O'*-dialkyl dithiophosphato complexes.[1-5]

All the calculations were carried out on a HITAC M-280H computer at the Computer Center of the University of Tokyo. The atomic scattering factors were taken from the tables.[12]

Other Measurements. The infrared absorption spectra of the samples were obtained by means of a JASCO A202 grating infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mull. The visible absorption spectra of the complexes were measured with a Hitachi 124 spectrophotometer.

Table 1. The Crystallographic Data of the Complexes **1** and **2**, as well as Some Experimental Conditions to Obtain Their Intensity Data

1. $La(iPr_2dtp)_3(dmso)_2$	
$LaC_{22}H_{54}O_8P_3S_8$	F.W. = 934.98
Monoclinic	Space group: $P2_1/n$
$Z=4$	μ(Mo $K\alpha$) = 1.49 mm^{-1}
$a=17.354(7)$ Å	$\beta=96.04(2)°$
$b=23.336(4)$ Å	$U=4412.0(15)$ Å^3
$c=10.955(2)$ Å	$D_m=1.40(3)$, $D_x=1.41$ Mg m^{-3}
Number of reflections measured: 10476	
Reflections used for the calculation: 4870	
Measured range (2θ/°): 3—55	
Scan width (ϕ/°): $(1.40+0.5\tan\theta)$	
Final R value: 0.069	
2. $[Eu(iPr_2dtp)_2(dmso)_3][Eu(iPr_2dtp)_4]$	
$EuC_{42}H_{102}O_{15}P_6S_{15}$	F.W. = 1817.99
Monoclinic	Space group: P_{21}/n
$Z=4$	μ(Mo $K\alpha$) = 2.00 mm^{-1}
$a=29.846(7)$ Å	$\beta=92.13(2)°$
$b=20.070(3)$ Å	$U=8415(3)$ Å^3
$c=14.057(3)$ Å	$D_m=1.43(3)$, $D_x=1.44$ Mg m^{-3}
Number of reflections measured: 13413	
Reflections used for the calculation: 7811	
Measured range (2θ/°): 3—55	
Scan width (ϕ/°): $(1.30+0.5\tan\theta)$	
Final R value: 0.077	

Results and Discussion

The final atomic parameters of the title complexes are listed in Table 2 (for **1**), and Table 3 (for **2**).[13] Selected bond lengths and bond angles of the complexes are shown in Table 4 (for **1**), and 5 (for **2**). A perspective drawings of the complexes around the respective central metal atoms and the numbering

Table 2. Final Atomic Coordinates ($\times 10^4$) of La(iPr_2dtp)$_3$-(pmso)$_2$ Together with the Equivalent Isotropic Temperature Factors with the Equivalent Isotropic or with the Isotropic Temperature Factors; Estimated Standard Deviations of Them are Shown in Parentheses

Atom	x	y	z	B_{eq}/Å^2 [a]
La	2986.7(3)	7671.6(3)	3058.3(5)	5.5
S(1)	3374(2)	7603(2)	5791(3)	8.0
S(2)	1593(2)	7661(2)	4482(3)	8.9
S(3)	2761(2)	6394(1)	3105(3)	8.2
S(4)	4483(2)	7005(1)	3269(3)	7.0
S(5)	2548(2)	8908(2)	2917(4)	10.5
S(6)	4351(2)	8475(1)	3354(3)	7.8
S(7)	4165(2)	7719(2)	497(3)	9.1
S(8A)[b]	1128(3)	7509(3)	799(4)	9.8
S(8B)[b]	1337(10)	7025(8)	1269(23)	18.5
P(1)	2274(2)	7656(2)	6034(3)	7.0
P(2)	3888(2)	6284(1)	3116(3)	7.1
P(3)	3639(2)	9123(2)	3179(4)	9.3
O(1)	2027(4)	7169(3)	6933(6)	7.5
O(3)	4111(4)	5972(3)	1913(7)	8.3
O(4)	4215(5)	5826(3)	4124(7)	9.0
O(7)	3371(4)	7684(4)	966(6)	7.8
O(8)	1829(4)	7594(4)	1675(7)	8.4
C(1)	1961(7)	6578(5)	6491(12)	8.7
C(2)	1119(7)	6385(7)	6407(15)	11.5
C(3)	2507(8)	6236(6)	7465(13)	10.4
C(7)	3707(7)	5437(5)	1502(12)	8.9
C(8)	4297(10)	4974(6)	1674(14)	12.2
C(9)	3467(14)	5524(7)	198(16)	17.4
C(10)	4100(10)	5880(7)	5429(13)	12.6
C(11)	4812(12)	6139(7)	6152(14)	14.7
C(12)	3941(10)	5247(7)	5799(15)	13.3
C(19)	4224(10)	7115(6)	−431(14)	12.0
C(20)	4045(10)	8261(7)	−699(14)	12.8
Atom	**x**	**y**	**z**	**B_{iso}/Å^2**
O(2)	2238(5)	8210(4)	6885(7)	9.42(2)
O(5)	3936(6)	9456(4)	2044(10)	12.67(3)
O(6)	3924(8)	9605(6)	4151(12)	17.09(4)
C(4)	1518(10)	8410(7)	7195(15)	12.52(5)
C(5)	1602(12)	8613(9)	8531(19)	16.75(7)
C(6)	1246(10)	8910(8)	6353(16)	13.62(5)
C(13)	3539(12)	9948(9)	1570(19)	15.95(6)
C(14)	4098(12)	10457(9)	1645(19)	17.24(7)
C(15)	3228(11)	9843(9)	230(18)	15.19(6)
C(16)	3586(12)	9646(9)	5262(19)	16.17(7)
C(17)	4003(14)	9239(10)	6207(21)	19.18(8)
C(18)	3663(15)	10262(12)	5740(23)	22.22(10)
C(21A)[b]	504(14)	7022(11)	1505(22)	12.64(7)
C(21B)[b]	408(23)	7365(18)	1296(38)	7.86(9)
C(22A)[b]	1385(22)	7024(17)	−369(34)	21.89(13)
C(22B)[b]	1365(29)	6976(23)	−366(46)	11.10(14)

a) The equivalent isotropic temperature factors were computed using the following expression; $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\theta)$. The B_{ij}'s are defined by; $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$. b) The probability of the occupancy of each position was as follows: S(8A), C(21A), and C(22A), 70.4; S(8B), C(21B), and C(22B), 29.6%.

scheme of the atoms are shown in Figs. 1 (for **1**), 2, and 3 (for **2**). The schematic presentations to show the configurations of the ligating atoms around the respective metal atoms are shown in Figs. 4 (for **1**), and 5 (for **2**). The crystal packing diagrams of **1** and **2** are shown in Figs. 6 (for **1**), and 7 (for **2**).

Both of the crystals consist of discrete molecules or ions: No bridging is found between them.

In **1**, the lanthanum(III) atom is octa-coordinated and is in a dodecahedral geometry where each iPr_2dtp ligand spans m-edge forming a four-membered chelate ring. Two oxygen atoms of the dmso ligands occupy the apexes of the remaining m-edges. The average deviation of the central metal and the ligating atoms from the respective average trapezium planes is 0.063 Å (the maximum deviation (to O(8)) is 0.119 Å) and the dihedral angle between the two trapezia is 88.2°. The phosphorus atoms of the iPr_2dtp ligands as well as the sulfur atoms of the dmso ligands are also almost on the respective trapezium plane (average deviation of the six phosphorus and two sulfur atoms are 0.144 Å).

The average bond lengths of La–S and La–O of **1** are 3.01(1), and 2.42(3) Å, respectively. These values are comparable to those of La(iPr_2dtp)$_3$(dma)$_2$ (3.02(2), and 2.42(1) Å),[3] and to those of La(Et_2dtp)$_3$-(Ph_3PO)$_2$ (3.05(4), and 2.44(2) Å).[5] The expected bond lengths of La–S and LaO are 3.00 and 2.51 Å, respectively, according to Shannon's ionic radii ($r_{La(III)}$ (octa coordinated), $r_{O(2-)}$, and $r_{S(2-)}$ are 1.160, 1.35, and 1.84 Å, respectively).[14] Therefore, compared with the calculated values, the La–S length of **1** is about the same; however, its La–O length is much shorter as was found in La(iPr_2dtp)$_3$(dma)$_2$.[3]

Complex **2** consists of a cationic and anionic species. All the metal atoms are almost on the (101) plane.

In the cation, the central europium(III) atom is hepta-coordinated and is in a pentagonal-bipyramidal geometry where four sulfur atoms of two iPr_2dtp ligands and one oxygen atom of a dmso molecule take the equatorial positions. The dmso oxygen atoms occupy both ends of the axis. The average positional deviations of the central metal and the five equatorially ligated atoms (from their average plane) is 0.069 Å (the maximum deviation is 0.126 Å for O(17)). The respective angles between the axial Eu(1)–O(15) or Eu(1)–O(16) bondings to the average pentagone plane are 88.2 and 88.3°. The average bond lengths of Eu–S and Eu–O are 2.880(8) and 2.249(8) Å, respectively. Although the former value is comparable to the calculated bond length, 2.85 Å, the latter is shorter by 0.11 Å than the sum of Shannon's ionic radii, 2.36 Å ($r_{Eu(III)}$ (hepta-coordinated) is 1.01 Å). The same tendency was observed in the average M–S and M–O bond lengths of the cationic complexes of the same type of geometry, [M(iPr_2dtp)$_2$-(bza)$_3$](iPr_2dtp): 2.83(2) and 2.27(2) Å for M=Tb, and

Table 3. Final Atomic Coordinates ($\times 10^4$), and Equivalent Isotropic (above the Line) or Isotropic (below the Line) Temperature Factors of $[Eu(iPr_2dtp)_2(dmso)_3][Eu(ipr_2dtp)_4]$, with Their Estimated Standard Deviations in Parentheses[a)]

Atom	x	y	z	B_{eq}/Å^2 [b)]	Atom	x	y	z	B_{eq}/Å^2 [b)]
Eu(1)	4197.0(2)	3314.7(4)	6156.5(6)	5.9	O(25)	2848(3)	11129(5)	7243(7)	7.7
S(11)	3894(2)	4546(2)	5293(4)	8.9	O(26)	2594(3)	11200(5)	5647(7)	7.8
S(12)	3877(2)	3118(2)	4210(4)	9.8	O(27)	3125(4)	7041(5)	5048(9)	11.4
S(13)	4310(2)	4383(2)	7504(4)	10.1					
S(14)	4566(2)	2829(2)	7943(4)	9.0	C(1)	2918(8)	3992(13)	3777(18)	15.0
S(15)	5225(2)	4072(2)	5472(4)	10.3	C(2)	2756(9)	3536(13)	2962(18)	15.0
S(16A)[b)]	3072(2)	3255(3)	7114(4)	7.5	C(3)	2582(9)	4558(13)	3895(18)	15.0
S(16B)[b)]	3036(6)	3323(10)	6214(14)	7.9	C(4)	4155(9)	4241(13)	2404(18)	15.0
S(17A)[b)]	4640(4)	1654(6)	5949(10)	15.0	C(5)	4629(9)	3993(13)	2217(18)	15.0
S(17B)[b)]	4440(3)	1697(4)	5121(7)	7.8	C(6)	4047(8)	4846(13)	1773(18)	15.0
P(11)	3795(2)	4081(2)	4084(4)	8.9	C(11)	3807(8)	2917(13)	10148(18)	15.0
P(12)	4534(2)	3747(2)	8455(4)	8.2	C(12)	3482(9)	4007(13)	9606(18)	15.0
O(11)	3339(5)	4261(7)	3567(12)	13.8	C(13)	5724(9)	3828(13)	6140(18)	15.0
O(12)	4131(6)	4426(7)	3369(9)	14.1	C(14)	5439(8)	3921(13)	4310(18)	15.0
O(13)	5009(4)	4032(5)	8854(8)	9.1	O(21)	4373(5)	8481(8)	8109(11)	14.0
O(14)	4256(3)	3741(6)	9396(7)	8.7	O(23)	3580(5)	10023(8)	2546(11)	14.0
O(15)	4883(3)	3527(5)	5628(9)	8.7	O(24)	3600(5)	8868(8)	2596(11)	14.0
O(16)	3495(3)	3146(5)	6621(8)	8.4	O(28)	3543(5)	7069(8)	6559(11)	14.0
O(17)	4366(3)	2239(4)	5858(7)	7.6	C(21)	4804(9)	8192(13)	8161(18)	15.0
C(7)	5249(6)	3706(9)	9624(13)	9.7	C(22)	4782(8)	7491(13)	7734(18)	15.0
C(8)	5654(7)	3374(11)	9133(18)	13.5	C(23)	4968(9)	8152(13)	9203(18)	15.0
C(9)	5403(7)	4281(11)	10312(14)	11.4	C(24)	4417(8)	10351(13)	8557(18)	15.0
C(10)	3822(7)	3463(11)	9390(15)	12.5	C(25)	4232(8)	10446(13)	9488(18)	15.0
C(15)	2658(6)	2797(11)	6520(16)	12.1	C(26)	4839(9)	10642(13)	8424(18)	15.0
C(16)	2916(7)	4080(9)	6779(15)	11.0	C(27)	3622(9)	10712(13)	2726(18)	15.0
C(17A)[b)]	5216(16)	1924(24)	5996(46)	19.0	C(28)	4097(9)	10938(13)	2514(18)	15.0
C(18A)[b)]	4599(21)	1197(25)	4848(42)	24.4	C(29)	3283(8)	11092(13)	2087(18)	15.0
C(17B)[b)]	4694(9)	1072(13)	5745(29)	8.3	C(30)	3937(8)	8627(13)	2008(18)	15.0
C(18B)[b)]	4852(10)	2006(15)	4759(47)	15.5	C(31)	3766(9)	8648(13)	968(18)	15.0
Eu(2)	3511.9(2)	9275.8(3)	5761.0(5)	5.5	C(32)	4052(8)	7909(13)	2287(18)	15.0
S(21)	3594(2)	9132(3)	7799(4)	10.7	C(33)	3153(8)	10979(13)	8123(18)	15.0
S(22)	4429(2)	9469(3)	6453(4)	9.7	C(34)	2839(9)	10722(13)	8827(18)	15.0
S(23)	4096(2)	9563(2)	4202(4)	8.1	C(35)	3356(9)	11671(13)	8361(19)	15.0
S(24)	3022(2)	9339(2)	3966(3)	8.2	C(36)	2540(9)	11110(13)	4655(18)	15.0
S(25)	3525(1)	10707(2)	5863(3)	7.2	C(37)	2641(9)	11765(13)	4149(18)	15.0
S(26)	2663(1)	9811(2)	6328(3)	7.7	C(38)	2058(9)	10896(13)	4408(18)	15.0
S(27)	2878(2)	8209(2)	6114(4)	10.7	C(39)	2969(8)	7226(13)	4127(18)	15.0
S(28)	3877(2)	7980(2)	5362(4)	9.3	C(40)	2456(9)	7216(13)	4081(18)	15.0
P(21)	4251(3)	9195(3)	7710(4)	12.6	C(41)	3146(9)	6735(13)	3400(18)	15.0
P(22)	3584(2)	9480(2)	3326(3)	8.5	C(42)	3302(9)	6709(13)	7233(19)	15.0
P(23)	2903(1)	10724(2)	6278(3)	6.2	C(43)	3456(9)	6926(13)	8237(18)	15.0
P(24)	3327(2)	7557(2)	5766(4)	9.8	C(44)	3391(9)	5963(13)	7110(18)	15.0
O(22)	4490(5)	9615(7)	8522(10)	13.2					

a) The isotropic temperature factors of the atoms below the line were fixed. The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\theta)$. The B_{ij}'s are defined by: $T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$. b) The probability of the occupancy of each position was as follows: S(16A), 77.5; S(16B), 22.5; S(17A), C(17A), and C(18A), 54.4; S(17B), C(17B), and C(18B), 45.6%.

2.80(2) and 2.23(3) Å for M=Er,[2] whereas corresponding bond lengths calculated with Shannon's ionic radii are 2.82, 2.33, 2.78, and 2.29 Å, respectively ($r_{Tb(III)}$ and $r_{Er(III)}$ are 0.98 and 0.945 Å for hepta-coordination).

The equatorial Eu–O bond length (2.260(9) Å) is longer than both of the axial Eu–O ones (2.244(10) Å (both)) in this species, too, as in the case of the other same type of complexes above mentioned.[2]

In the anion, the central metal atom is octa-

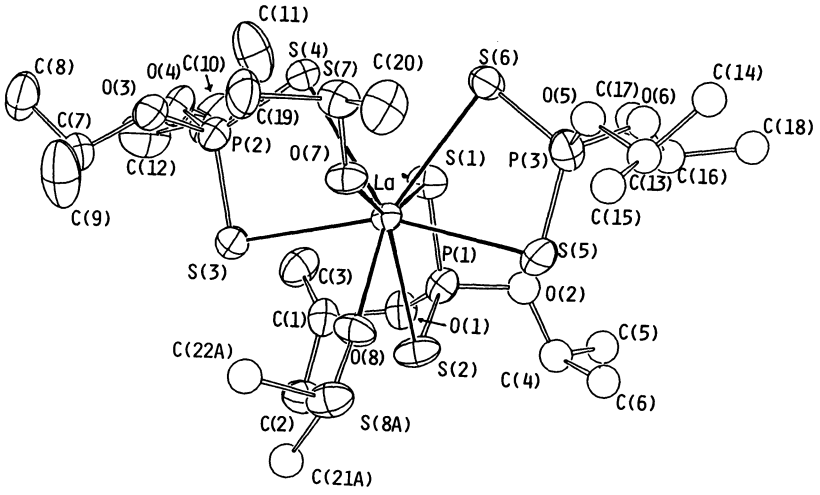

Fig. 1. A perspective drawing of $[La(iPr_2dtp)_3(dmso)_2]$ with the numbering scheme.

Table 4. Selected Bond Lengths and Bond Angles of $La(iPr_2dtp)_3(dmso)_2$ (**1**), with Estimated Standard Deviations in Parentheses

Bond length	l/Å	Bond length	l/Å
La-S(1)	3.002(3)	La-S(2)	3.014(4)
La-S(3)	3.008(3)	La-S(4)	3.014(3)
La-S(5)	2.984(4)	La-S(6)	3.011(3)
La-O(7)	2.454(8)	La-O(8)	2.392(7)
S(1)-P(1)	1.959(5)	S(2)-P(1)	1.966(5)
S(3)-P(2)	1.971(5)	S(4)-P(2)	1.973(5)
S(5)-P(3)	1.950(6)	S(6)-P(3)	1.948(5)
O(7)-S(7)	1.522(8)	O(8)-S(8A)	1.481(9)
O(8)-S(8B)	1.617(20)	P(1)-O(1)	1.592(8)
P(1)-O(2)	1.599(10)	P(2)-O(3)	1.589(9)
P(2)-O(4)	1.596(9)	P(3)-O(5)	1.597(12)
P(3)-O(6)	1.592(15)	S(7)-C(19)	1.747(16)
S(7)-C(20)	1.817(17)		
Bond angle	ϕ/°	**Bond angle**	ϕ/°
S(1)-La-S(2)	65.87(9)	S(1)-La-S(3)	86.91(9)
S(1)-La-S(4)	78.21(8)	S(1)-La-S(5)	97.61(10)
S(1)-La-S(6)	80.49(9)	S(1)-La-O(7)	151.4(2)
S(2)-La-S(3)	82.52(9)	S(2)-La-S(5)	79.67(10)
S(2)-La-O(8)	70.19(18)	S(3)-La-S(4)	66.43(8)
S(3)-La-S(5)	157.86(10)	S(3)-La-O(8)	80.40(18)
S(4)-La-S(6)	69.64(8)	S(5)-La-S(6)	66.20(9)
S(5)-La-O(7)	91.87(20)	S(5)-La-O(8)	81.25(19)
La-S(1)-P(1)	90.75(15)	La-S(2)-P(1)	90.29(14)
La-S(3)-P(2)	89.92(15)	La-S(4)-P(2)	89.70(14)
La-S(5)-P(3)	90.13(18)	La-S(6)-P(3)	89.38(16)
La-O(7)-S(7)	131.4(4)	La-O(8)-S(8A)	176.4(5)
S(1)-P(1)-S(2)	112.9(2)	La-O(8)-S(8B)	128.4(8)
S(3)-P(2)-S(4)	113.5(2)	S(5)-P(3)-S(6)	114.3(2)

coordinated, and is in a dodecahedral geometry, where four iPr_2dtp ligands span all m-edges. The positional deviation of the central metal and four

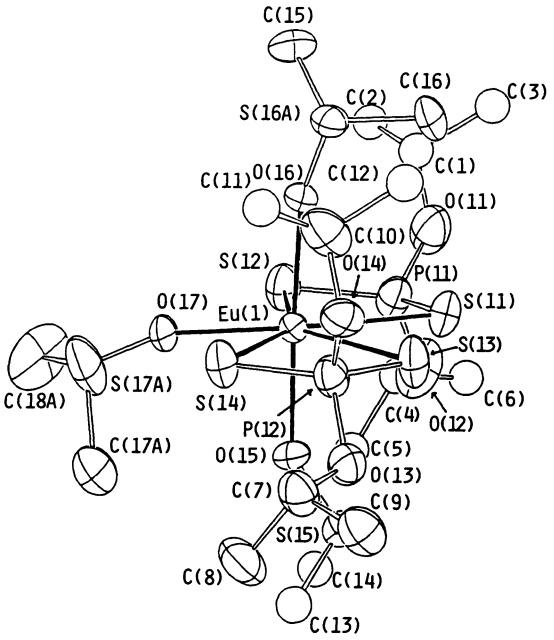

Fig. 2. A perspective drawing of $[Eu(iPr_2dtp)_2(dmso)_3]^+$ in **2** with numbering scheme.

ligating sulfur atoms from the respective plane is 0.025 Å on the average (maximum deviation is 0.045 Å, to S(26)). The dihedral angle between two trapezia is 89.4°. All phosphorus atoms of the iPr_2dtp ligands are also almost on the respective planes: The average deviation of the four phosphorus atom positions from the respective planes is 0.087 Å.

The average Eu-S bond length of this anionic complex is 2.888 Å, which is comparable to the sum of Shannon's ionic radii, 2.91 Å ($r_{Eu(III)}$ (octa-coordinated) is 1.066 Å).

As the pair of P-S bond lengths of each iPr_2dtp ligand are about the same in the anion, the P=S

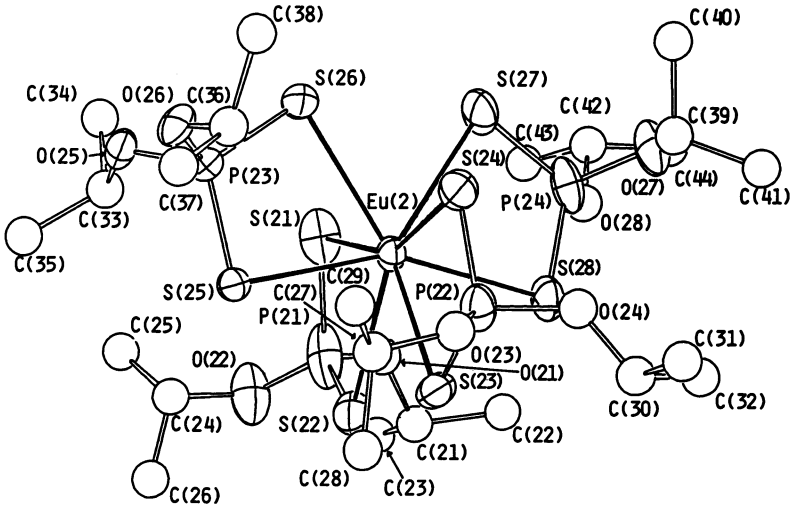

Fig. 3. A perspective drawing of $[Eu(iPr_2dtp_4)]^-$ in **2** with the numbering scheme.

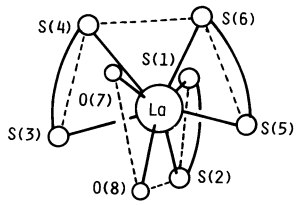

Fig. 4. The schematic presentation of the ligating atom positions around the central metal atom of **1**.

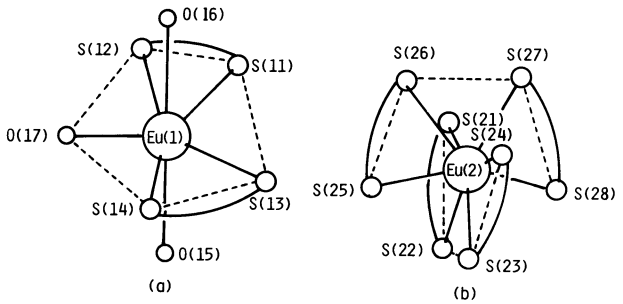

Fig. 5. The schematic presentation of the ligating atom positions around the central metal atoms of the cationic (a), and of anionic (b) complexes of **2**.

double bonds of the ligands are likely delocalized. The lengths of Eu–S of a pair of the sulfur atoms of each ligand are not much different from each other.

The infrared absorption spectral patterns of complexes **1** and **2**, together with those of some related compounds, are shown in Fig. 8. As shown in the figure, the ν(S–O) band of dmso in the 1000—1100 cm^{-1} region of the complex, which is red-shifted compared with that of the free ligand, splits into several peaks, probably due to the variety of the

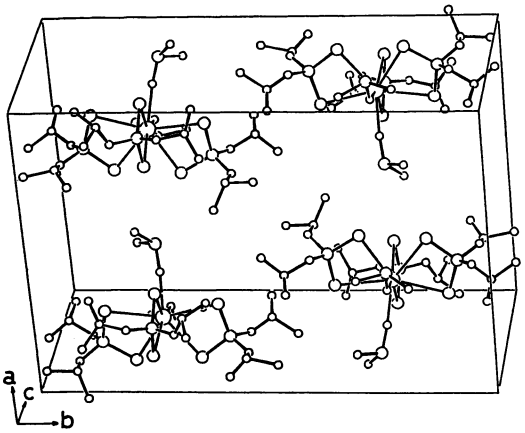

Fig. 6. The crystal packing diagram of **1**.

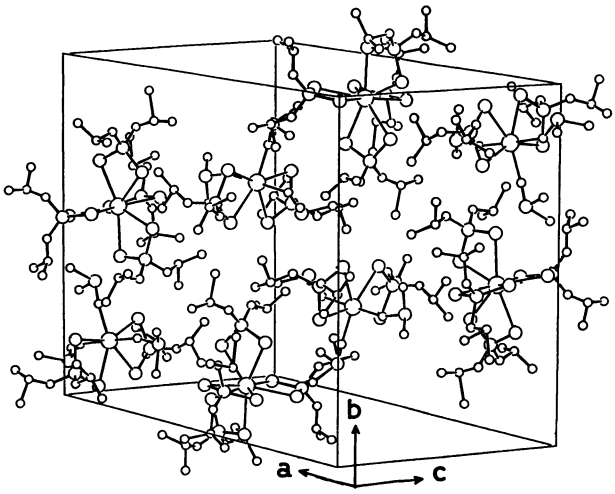

Fig. 7. The crystal packing diagram of **2**.

Table 5. Selected Bond Lengths and Bond Angles of $[Eu(iPr_2dtp)_2(dmso)_3][Eu(iPr_2dtp)_4]$ (**2**), with Estimated Standard Deviations in Parentheses

Bond length	l/Å	Bond length	l/Å
Eu(1)-S(11)	2.883(5)	Eu(1)-S(12)	2.891(6)
Eu(1)-S(13)	2.872(5)	Eu(1)-S(14)	2.874(6)
Eu(1)-O(15)	2.244(10)	Eu(1)-O(16)	2.244(10)
Eu(1)-O(17)	2.260(9)	S(11)-P(11)	1.952(8)
S(12)-P(11)	1.956(7)	S(13)-P(12)	1.948(8)
S(14)-P(12)	1.981(7)	S(15)-O(15)	1.520(11)
S(16A)-O(16)	1.478(12)	S(16B)-O(16)	1.51(2)
S(17A)-O(17)	1.433(15)	S(17B)-O(17)	1.523(15)
Eu(2)-S(21)	2.880(6)	Eu(2)-S(22)	2.898(5)
Eu(2)-S(23)	2.908(5)	Eu(2)-S(24)	2.872(5)
Eu(2)-S(25)	2.877(4)	Eu(2)-S(26)	2.890(4)
Eu(2)-S(27)	2.911(5)	Eu(2)-S(28)	2.882(5)
S(21)-P(21)	1.975(10)	S(22)-P(21)	1.942(10)
S(23)-P(22)	1.933(7)	S(24)-P(22)	1.955(8)
S(25)-P(23)	1.967(6)	S(26)-P(23)	1.968(6)
S(27)-P(24)	1.949(8)	S(28)-P(24)	1.949(8)
Bond angle	**ϕ/°**	**Bond angle**	**ϕ/°**
S(11)-Eu(1)-S(12)	68.37(15)	S(13)-Eu(1)-S(14)	69.21(15)
O(17)-Eu(1)-S(12)	76.2(3)	O(17)-Eu(1)-S(14)	76.0(3)
S(11)-Eu(1)-S(13)	70.44(14)	O(16)-Eu(1)-O(17)	97.3(3)
O(16)-Eu(1)-S(12)	88.6(3)	O(16)-Eu(1)-S(11)	88.3(3)
O(16)-Eu(1)-S(13)	90.5(3)	O(16)-Eu(1)-S(14)	91.5(3)
O(15)-Eu(1)-O(17)	84.7(4)	O(15)-Eu(1)-S(12)	89.2(3)
O(15)-Eu(1)-S(11)	88.5(3)	O(15)-Eu(1)-S(13)	89.5(3)
O(15)-Eu(1)-S(14)	91.7(3)	O(15)-Eu(1)-O(16)	176.6(4)
S(21)-Eu(2)-S(22)	68.60(16)	S(23)-Eu(2)-S(24)	68.22(15)
S(25)-Eu(2)-S(26)	67.98(11)	S(27)-Eu(2)-S(28)	67.81(14)
S(22)-Eu(2)-S(23)	68.98(14)	S(26)-Eu(2)-S(27)	69.21(14)
S(21)-Eu(2)-S(24)	154.13(17)	S(25)-Eu(2)-S(28)	154.99(12)
Eu(1)-S(11)-P(11)	89.6(2)	Eu(1)-S(12)-P(11)	89.3(2)
Eu(1)-S(13)-P(12)	89.6(2)	Eu(1)-S(14)-P(12)	88.9(2)
Eu(1)-O(15)-S(15)	144.3(7)	Eu(1)-O(16)-S(16A)	159.6(6)
Eu(1)-O(16)-S(16B)	134.4(10)	Eu(1)-O(17)-S(17A)	153.7(8)
Eu(1)-O(17)-S(17B)	147.9(7)	Eu(2)-S(21)-P(21)	88.8(3)
Eu(2)-S(22)P-(21)	88.9(3)	Eu(2)-S(23)-P(22)	89.0(2)
Eu(2)-S(24)-P(22)	89.6(2)	Eu(2)-S(25)-P(23)	91.20(18)
Eu(2)-S(26)-P(23)	90.78(19)	Eu(2)-S(27)-P(24)	89.6(3)
Eu(2)-S(28)-P(24)	90.5(3)		

coordination situations. The peak of **2** is broader than that of **1**. The ν_{as}(P-S) band appeared in 600—700 cm^{-1} region of **2**, splits into three peaks, while that of **1** into two peaks. The isostructural neodymium(III) complex shows almost the same infrared spectral pattern as that of **1**.

As in the case of $Eu(iPr_2dtp)_3(bza)_2$,[1] complex **2** is orange in color due to a charge-transfer band in both its solid and its acetonitrile-solution. The absorption spectra of the solution of **2**, as well as those of some other europium(III) complexes , are shown in Fig. 9. As shown in the figure, although the wavelength with maximum absorption of the band of **2** is about the same as that of $Na[Eu(iPr_2dtp)_4]$, or of $Eu(iPr_2dtp)_3(bza)_2$ (about 415 nm),[1] the absorpion coefficient of **2** at the wavelength, 1.5×10^2 dm^3 $mol(Eu)^{-1}$ cm^{-1}, is much smaller than those of the other europium complexes above mentioned.[1]

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

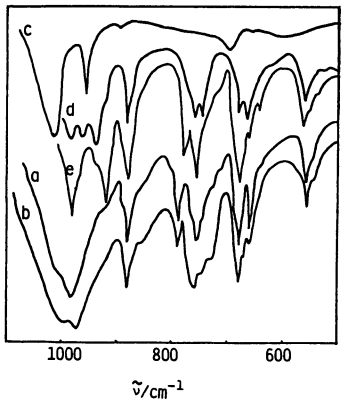

Fig. 8. Infrared absorption spectra of **1**, **2**, and some related compounds. (a), $[La(iPr_2dtp)_3(dmso)_2]$; (b), $[Eu(iPr_2dtp)_2(dmso)_3][Eu(iPr_2dtp)_4]$; (c), dmso; (d), $Na(iPr_2dtp)$; (e), $Na[La(iPr_2dtp)_4]$.

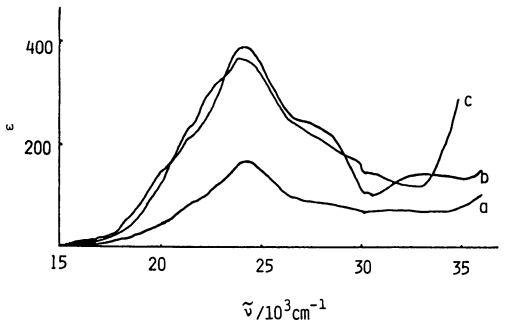

Fig. 9. The absorption spectra of **2** and some related complexes in acetonitrile solutions. (a), $[Eu(iPr_2dtp)_2(dmso)_3][Eu(iPr_2dtp)_4]$; (b), $Na[Eu(iPr_2dtp)_4]$; (c), $[Eu(iPr_2dtp)_3(bza)_2]$. The concentration of [Eu(III)] is 0.01—0.001 mol dm^{-3}.

present work was partially supported by a Grant-in-Aid for Scientific Research (No. 57430011) from the Ministry of Education, Sciences and Culture.

References

1) R. Nakamura, K. Nagai, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 2919 (1984).
2) K. Nagai, R. Nakamura, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **57**, 2725 (1984).
3) K. Nagai, Y. Sato, S. Kondo, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **56**, 2605 (1983).
4) Y. Ohki, M. Nakamura, Y. Suzuki, K. Nagai, M. Shimoi, and A. Ouchi, *Bull. Chem. Soc. Jpn.*, **58**, 1593 (1985).
5) A. A. Pinkerton and D. Schwarzenbach, *J. Chem. Soc., Dalton Trans.*, **1976**, 2466.
6) R. G. Pearson, *J. Chem. Educ.*, **45**, 581, 643 (1968).
7) M. E. Silver, H. K. Chun, and R. C. Fay, *Inorg. Chem.*, **21**, 3765 (1982).
8) S. E. Livingstone and A. E. Mihkelson, *Inorg. Chem.*, **9**, 2545 (1970).
9) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$
10) "Universal Crystallographic Computation Program System (UNICS)," ed by T.Sakurai, Crystallographic Society of Japan, Tokyo (1967).
11) G. M. Sheldrick, "SHELX-76. A program for crystal structure determination," University of Cambridge, Cambridge, England, U.K. (1976).
12) "International Tables for Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72, 150.
13) The final thermal parameters and the final F_o-F_c table are deposited as Document No. 8628 at the Office of the Editor of Bull. Chem. Soc. Jpn.
14) R. D. Shannon, *Acta Crystallogr., Sect. A*, **32**, 751 (1976).