The Synthesis and the Crystal and Molecular Structure of [Tris(dibutyl sulfoxide)bis(*O,O'*-diisopropyl dithiophosphato)neodymium(III)] [Tetrakis(*O,O'*-diisopropyl dithiophosphato)neodymium(III)] $[Nd\{(C_3H_7O)_2PS_2\}_2\{(C_4H_9)_2SO\}_3][Nd\{(C_3H_7O)_2PS_2\}_4]$

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Synopsis. The title complex has been synthesized, and its crystals and molecular structure has been determined by the use of the single-crystal X-ray-diffraction method. The crystal of $Nd_2C_{60}H_{138}O_{15}P_6S_{15}$, F. W.=2055.03, was monoclinic, with a space group of An; a=23.696(4), b=23.466(4), c=20.208(4) Å, β=111.22(2)°, Z=4, V=10475(4) Å^3, D_m=1.30(3), D_x=1.30 Mg m^{-3}, and μ(Mo $K\alpha$)=1.41 mm^{-1}. The complex consists of cationic and anionic species, as is shown in the title. The metal atom of the cationic complex is hepta-coordinated and is in a pentagonal-bipyramidal geometry, while the anionic one is octa-coordinated and is in a dodecahedral geometry.

In previous papers, we reported the syntheses and the structure determination of several *O,O'*-diisopropyl dithiophosphate (iPr$_2$dtp)—Lewis base mixed complexes.[1—4] One of them, [Eu(iPr$_2$dtp)$_2$(dmso)$_3$][Eu(iPr$_2$dtp)$_4$] (**1**) (where dmso=dimethyl sulfoxide),[4] consists of a cationic complex and an anionic complex. We tried to obtain the same types of complexes from some other ligands, and found from its elemental analysis, that the title one could be expected to have that structure. However, as the ligand size of the title complex is much larger than that of **1**, it might have a structure different from that of **1**. Therefore, we determined its structure by the single-crystal X-ray-diffraction method.

Experimental

Synthesis of [Nd(iPr$_2$dtp)$_2$(dbso)$_3$][Nd(iPr$_2$dtp)$_4$] (where dbso=Dibutyl Sulfoxide). Neodymium(III) chloride hexahydrate (0.59 g, 1.6 mmol) and Na(iPr$_2$dtp) (1.7 g, 7.1 mmol) were added to 35 cm^3 of 2-propanol, and the mixture was refluxed for 20 min. After cooling, the residue was filtered off, and to the filtrate dbso (0.76 g, 5.0 mmol) was added. The solution was then refluxed for 10 min at about 65 °C and concentrated to about 7 cm^3 by the use of a vacuum rotary evaporator at about 60 °C, after which the solution was left standing in a refrigerator (about 5 °C) several days. Pure crystals appeared. Yield, 0.29 g (17%). The isomorphous europium(III) complex, [Eu(iPr$_2$dtp)$_2$(dbso)$_3$][Eu(iPr$_2$dtp)$_4$] (**2**), was also obtained in the same way. Anal. ($M_2C_{60}H_{138}O_{15}P_6S_{15}$) M, C, H, S. (where M=Nd or Eu)

From lanthanum(III) chloride another type of complex, one with the formula of La(iPr$_2$dtp)$_3$(dbso)$_2$, was obtained. Anal. ($LaC_{34}H_{78}O_8P_3S_8$) La, C, H.

Single-crystal X-Ray Analysis. A crystal 0.3×0.3×0.25 mm^3 in size (all the edges were cut off, and it was shaped almost into a sphere) was used. The reflections within the range of $3° < 2\theta < 55°$ were collected on a Rigaku AFC-6A four-circle automated X-ray diffractometer, with graphite-monochromated Mo $K\alpha$ radiation (scan speed, 4° min^{-1}) by means of the ω-scan technique. Of the 9536 reflections measured, 4674 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 the UNICS.[5] The scattering factors were taken from the tables.[6]

The structure was solved by the heavy-atom method. Although those of the central metal atoms and the neighboring atoms were exactly determined, those of the butyl and isopropyl carbon atoms were found to have relatively large standard deviations, even after repeated refinements, probably because they are not fixed tightly in the crystal, as in cases of the other adducts of the lanthanoid *O,O'*-dialkyl dithiophosphates.[1—4,7] The positions of six carbon atoms, C(9), C(11), C(103), C(123), C(124), and C(128), were fixed to the respective most probable positions. The position of a dbso sulfur atom, S(10), was divided into two; the occupancy factors of S(10A) and S(10B) are 53 and 47% respectively. The final R value was 0.055[8] reached by applying anisotropic temperature factors for all the atoms except the fixed ones.

The Measurement of the Visible Absorption Spectra. The visible absorption spectra were measured with a Hitachi 124 spectrophotometer, using an acetonitrile solution of the complexes (1.0×10^{-3}—10^{-2} mol dm^{-3} in concentration).

Results and Discussion

Selected bond lengths and bond angles are given in Table 1.[9] Perspective drawings of the cationic (**3**) and the anionic (**4**) complexes, along with the num-

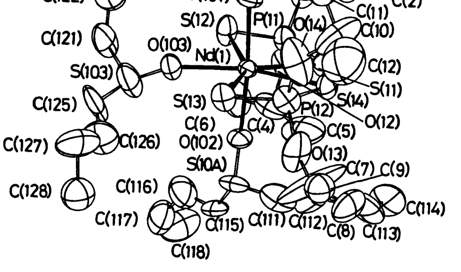

Fig. 1. A perspective drawing of [Nd(iPr$_2$dtp)$_2$(dbso)$_3$]$^+$ and the numbering scheme. (S(10B) is not shown in the figure)

Table 1. Selected bond lengths and bond angles of the complex, with estimated standard deviations in parentheses

Bond length	l/Å	Bond length	l/Å	Bond length	l/Å
Nd(1)-S(11)	2.889(8)	Nd(1)-S(12)	2.895(7)	Nd(1)-S(13)	2.916(8)
Nd(1)-S(14)	2.908(6)	Nd(1)-O(101)	2.284(18)	Nd(1)-O(102)	2.317(16)
Nd(1)-O(103)	2.356(17)	Nd(2)-S(21)	2.938(7)	Nd(2)-S(22)	2.911(8)
Nd(2)-S(23)	2.904(9)	Nd(2)-S(24)	2.939(6)	Nd(2)-S(25)	2.928(5)
Nd(2)-S(26)	2.933(5)	Nd(2)-S(27)	2.882(5)	Nd(2)-S(28)	2.950(5)
Bond angle	ϕ/°	Bond angle	ϕ/°	Bond angle	ϕ/°
O(101)-Nd(1)-O(103)	89.2(6)	O(102)-Nd(1)-O(103)	85.6(6)	O(101)-Nd(1)-S(11)	98.9(5)
O(102)-Nd(1)-S(11)	86.7(4)	O(101)-Nd(1)-S(12)	84.9(5)	O(102)-Nd(1)-S(12)	96.2(4)
O(101)-Nd(1)-S(13)	88.1(5)	O(102)-Nd(1)-S(13)	88.3(4)	O(101)-Nd(1)-S(14)	88.8(5)
O(102)-Nd(1)-S(14)	94.0(4)	O(103)-Nd(1)-S(11)	142.5(4)	O(103)-Nd(1)-S(12)	76.0(4)
O(103)-Nd(1)-S(13)	76.0(4)	O(103)-Nd(1)-S(14)	144.6(4)	S(11)-Nd(1)-S(12)	68.5(2)
S(13)-Nd(1)-S(14)	68.6(2)	S(11)-Nd(1)-S(14)	72.6(2)	O(101)-Nd(1)-O(102)	174.3(6)
S(21)-Nd(2)-S(22)	68.0(2)	S(23)-Nd(2)-S(24)	67.7(2)	S(25)-Nd(2)-S(26)	67.49(14)
S(27)-Nd(2)-S(28)	68.50(15)	S(21)-Nd(2)-S(24)	68.53(18)	S(25)-Nd(2)-S(28)	68.63(15)
S(22)-Nd(2)-S(23)	155.7(2)	S(26)-Nd(2)-S(27)	155.25(15)		

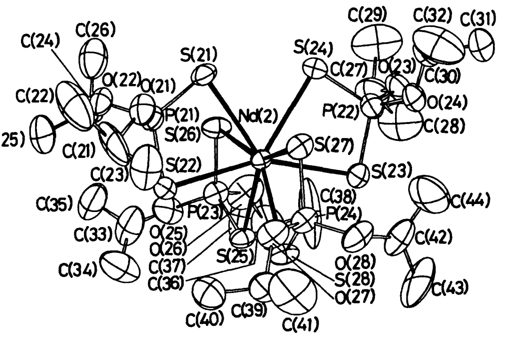

Fig. 2. A perspective drawing of $[Nd(iPr_2dtp)_4]^-$ and the numbering scheme.

bering scheme, are shown in Figs. 1 (for **3**) and 2 (for **4**),[9]

In **3**, $[Nd(iPr_2dtp)_2(dbso)_3]^+$, the neodymium(III) atom is hepta-coordinated and is in a pentagonal-bipyramidal configuration. Four sulfur atoms of two iPr_2dtp ligands, as well as one oxygen atom of a dbso ligand, bond equatorially, and two oxygen atoms of the dbso ligands are coordinated from the two ends of the axis. The average positional deviation of the central metal and the ligating four sulfur and one oxygen atoms from the average pentagon plane is 0.156 Å (the maximum deviation is 0.283 Å for S(14)). The angles between the average pentagon plane and the axis, O(101)–Nd(1) and O(102)–Nd(1), are 84.5 and 87.3 ° respectively.

In **4**, $[Nd(iPr_2dtp)_4]^-$, the central metal atom is octa-coordinated and is in a dodecahedral geometry. Each iPr_2dtp ligand spans an *m*-edge coordinated through both sulfur atoms.[9] The atomic positional deviations of the central metal and ligated sulfur atoms from their average trapezium plane are 0.055 Å on the average (0.097 Å at the maximum for S(28)). The dihedral angle between the two trapezia is 88.0 °.

Therefore, both **3** and **4** are in about the same type of configuration as those of **1**, although **3** and **4** are a little more deviated from the ideal forms than the respective ions of **1**.

The acetonitrile solution of **2** shows a charge-transfer band. The wavelength and the absorption coefficient of the absorption maximum are 410 nm and 1.8×10^2 dm^3 mol(Eu)$^{-1}$ cm^{-1}. These values are almost the same as those of **1**; the absorption coefficient is about one-half of the value of a neutral complex such as $Eu(iPr_2dtp)_3(bza)_2$ (bza=benzamide, $\varepsilon_{max}=4.2\times10^2$ dm^3 mol(Eu)$^{-1}$ cm^{-1}.[1])

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8) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

9) The final atomic coordinates and thermal parameters, the final F_o—F_c table, and some additional data about the bond lengths and bond angles, as well as the crystal packing diagram and a schematic drawing of **3** and **4**, are deposited as Document No. 8521 at the Office of the Editor of *Bull. Chem. Soc. Jpn.*