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# The Synthesis, Properties, and Structure of Bis(*N*,*N*-dimethylacetamide)tris(*O*,*O*′-diisopropyl dithiophosphato)lanthanum(III)

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The new complex indicated in the title has been synthesized, and its crystal and molecular structure has been determined by the X-ray diffraction method. The crystal was triclinic; space group $P\bar{1}$, $Z=2$, $a=23.071(9)$, $b=11.060(11)$, $c=10.793(13)$ Å, $\alpha=120.0(1)$, $\beta=97.2(2)$, $\gamma=88.9(2)°$. The final $R$ value for 5969 reflections is 0.047. The central lanthanum(III) atom is an octa-coordination and in a dodecahedron geometry, being coordinated with six sulfur atoms of three *O*,*O*′-diisopropyl dithiophosphate ligands ($iPr_2dtp$), which span at three *m* edges, and with two oxygen atoms of both the *N*,*N*-dimethylacetamide ligands (dma) at both ends of the remaining *m* edge. The other [Ln($iPr_2dtp$)$_3$L$_2$]-type complexes, where Ln=La or Nd; L=dma or *N*,*N*-dimethylformamide, have also been obtained. The P=S double bond of the $iPr_2dtp$ ligand in the title complex is almost completely delocalized.

Some lanthanoid metal compexes, where sulfur atoms are coordinated to metal, such as their dialkyldithiocarbamates,$^{1-6)}$ dialkyldithiophosphinates,$^{7-10)}$ and *O*,*O*′-dialkyl dithiophosphates($R_2dtp$),$^{8,11,12)}$ had previously been synthesized and investigated, though the lanthanoid elements are known as "hard acid" according to the HSAB theory.$^{13)}$ The structures of a number of these complexes were also clarified; the octa-coordination of the central metal is common for the complexes of light lanthanoid elements,$^{5,6,11,12)}$ except for those where voluminous ligands are coordinated.$^{7,10)}$

The authors had previously found that some amine adducts of cobalt(II) *O*,*O*′-dialkyl dithiophosphates are more stable than the original complexes.$^{14,15)}$ Although triphenylphosphine oxide–*O*,*O*′-diethyl dithiophosphate($Et_2dtp$) mixed complexes of lanthanoid (III) elements had already been investigated,$^{11b)}$ almost no other such type of mixed complex was known yet. Therefore, the syntheses and the structure determination of the adducts of lanthanoid(III) *O*,*O*′-dialkyl dithiophosphates was started in our laboratory. Thus far, the title complex and some related ones have been obtained; their structure and properties will be shown below.

## Experimental

*Synthesis of Bis(*N,N*-dimethylacetamide)tris(*O,O′*-diisopropyldithiophosphato)lanthanum(III).* Sodium *O*,*O*′-diisopropyl dithiophosphate (Na($iPr_2dtp$)) was obtained from diphosphorus pentasulfide and 2-propanol (sodium carbonate was used for the neutralization of the free acid), by applying the method used for synthesizing the sodium *O*,*O*′-diethyl dithiophosphate (Na($Et_2dtp$)).$^{16)}$ Sodium tetrakis(*O*,*O*′-diisopropyl dithiophosphato)lanthanate(III) (Na[La($iPr_2dtp$)$_4$]) was obtained by a reaction between lanthanum(III) chloride and Na($iPr_2dtp$) in a 2-propanol medium, using the method of synthesizing Na[La($Et_2dtp$)$_4$], written by Pinkerton.$^{8)}$

The sodium salt (0.83 g, 0.82 mmol) and *N*,*N*-dimethylacetamide (dma) (0.14 g, 2.2 mmol) were refluxed in 20 cm$^3$ of diisopropyl ether for 20 minutes; then it was filtered off to remove a turbid white mass and the residue while warm, and the filtrate was left standing for several hours. The product was precipitated as white crystals. The crude product was dissolved in 20 cm$^3$ of diisopropyl ether (60—65 °C), a turbid white mass was filtered off, the solution was left standing in a silica-gel desiccator overnight, and the complex was precipitated. Yield: 0.63 g (81%). The crystals thus obtained were submitted to X-ray diffraction after having been checked by means of Weissenberg photography. Found: La, 14.45; C, 32.68; H, 6.35; N, 2.89%. Calcd for $LaC_{26}H_{60}N_2O_8S_6P_3$: La, 14.58; C, 32.77; H, 6.35; N, 2.94%.

*Syntheses of Other Ln($iPr_2dtp$)$_3$L$_2$-type Complexes, Where Ln=La, Nd; L=Amides.* These mixed complexes were obtained by almost the same technique as that used for the title complex. The neodymium(III) complexes were obtained via sodium tetrakis(*O*,*O*′-diisopropyl dithiophosphato)neodymate(III), which has been synthesized similarly. To synthesize the *N*,*N*-dimethylformamide (dmf) adducts, the optimum ratio of the starting materials was: the sodium salt:dmf=1:3 (in mol/mol).

Nd($iPr_2dtp$)$_3$(dma)$_2$: Found, Nd, 15.68; C, 32.08; H, 6.26; N, 2.63%. Calcd for $NdC_{26}H_{60}N_2O_8S_6P_3$: Nd, 15.05; C, 32.59; H, 6.13; N, 2.92%. Yield, 73%. Magnetic moment of the solid, $3.4_2$ BM† (22 °C). La($iPr_2dtp$)$_3$(dmf)$_2$: Found, La, 14.82; C, 30.54; H, 6.12; N, 2.99%. Calcd for $CaC_{24}H_{56}N_2O_8S_6P_3$: La, 15.03; C, 31.18; H, 6.11; N, 3.03%. Yield, 62%. Nd($iPr_2dtp$)$_3$(dmf)$_2$: Found, Nd, 15.77; C, 30.55; H, 6.07; N, 2.93%. Calcd for $NdC_{24}H_{56}N_2O_8S_6P_3$: Nd, 15.51; C, 31.00; H, 6.07; N, 3.01%. Yield, 76%. Magnetic moment of the solid, $3.4_1$BM (22 °C).

*Single-crystal X-Ray Analysis.* A crystal with dimensions of $0.3\times0.3\times0.2$ mm$^3$ was used for the measurement. All its edges were ground off, but it was not shaped into a sphere.

The crystallographic data are: $LaC_{26}H_{60}N_2O_8S_6P_3$: F.W. =952.91, triclinic, space group $P\bar{1}$, $Z=2$, $a=23.071(9)$, $b=11.060(11)$, $c=10.793(13)$ Å, $\alpha=120.00(11)$, $\beta=97.17(16)$, $\gamma=88.92(24)°$, $D_x=1.34$, $D_m=1.37(3)$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$)= 1.08 mm$^{-1}$. The reflections within the range of $2\theta<50°$ were collected on a Philips PW 1100 automated four-circle diffractometer with Mo $K\alpha$ radiation, the $\theta-2\theta$ scan technique being employed. Due to the limitation of our computation program (upper limit of the numbers of reflections=6000), 5969 $|F_o|>5.5\sigma(|F_o|)$ reflections from the 6753 independent ones measured were used for the calculation. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption or extinction.

All the calculations were carried out on a HITAC M-

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† 1 BM=$9.274078(36)\times10^{-24}$ J T$^{-1}$.

TABLE 1. FINAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

| Atom | $x$ | $y$ | $y$ | $B_{eq}$/Å$^2$ a) | Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ a) |
|---|---|---|---|---|---|---|---|---|---|
| La | 2320.8(1) | 1148.5(3) | 99.7(4) | 4.8 | S(5) | 2415(1) | 1348(2) | 3021(2) | 7.1 |
| S(1) | 3616(1) | 827(2) | 530(2) | 7.5 | S(6) | 2531(1) | 4091(2) | 2608(2) | 6.8 |
| S(2) | 3040(1) | 2377(2) | -1227(2) | 7.1 | P(3) | 2625(1) | 3373(2) | 3964(2) | 6.2 |
| P(1) | 3763(1) | 1834(2) | -503(2) | 6.8 | O(5) | 2275(2) | 4253(5) | 5304(4) | 7.1 |
| O(1) | 4225(2) | 3099(5) | 474(6) | 9.3 | O(6) | 3277(2) | 3756(5) | 4776(5) | 7.8 |
| O(2) | 4107(2) | 956(5) | -1844(6) | 9.0 | C(51) | 1629(3) | 4203(8) | 5084(8) | 8.4 |
| C(11) | 4095(4) | 4327(8) | 1865(10) | 10.1 | C(52) | 1462(4) | 5689(9) | 5581(11) | 11.3 |
| C(12) | 4272(7) | 5580(11) | 1746(16) | 19.5 | C(53) | 1419(4) | 3595(10) | 5973(11) | 12.3 |
| C(13) | 4448(6) | 4337(12) | 3125(12) | 15.4 | C(61) | 3472(4) | 3258(9) | 5791(8) | 10.0 |
| C(21) | 4680(3) | 442(9) | -1669(10) | 10.6 | C(62) | 3935(5) | 2287(14) | 5209(13) | 16.6 |
| C(22) | 5135(4) | 1223(13) | -1875(16) | 17.8 | C(63) | 3695(6) | 4563(13) | 7184(11) | 14.7 |
| C(23) | 4663(5) | -1065(13) | -2658(16) | 17.2 | O(100) | 2303(2) | -1144(4) | -106(4) | 7.6 |
| S(3) | 1544(1) | 2748(2) | -968(2) | 7.6 | C(101) | 2239(5) | -2136(7) | 61(8) | 10.8 |
| S(4) | 1066(1) | 979(2) | 452(2) | 8.4 | C(102) | 1525(4) | -2586(10) | -21(11) | 12.0 |
| P(2) | 857(1) | 1969(2) | -638(2) | 6.9 | N(100) | 2494(5) | -2839(6) | 308(8) | 14.7 |
| O(3) | 399(2) | 3123(5) | 138(5) | 7.7 | C(103) | 3187(4) | -2255(10) | 558(13) | 13.3 |
| O(4) | 483(2) | 1004(5) | -2173(5) | 8.2 | C(104) | 2421(5) | -4124(9) | 381(12) | 14.0 |
| C(31) | 527(3) | 4198(8) | 1670(8) | 8.3 | O(200) | 2173(2) | -568(4) | -2440(4) | 7.1 |
| C(32) | -19(5) | 4371(13) | 2317(14) | 16.8 | C(201) | 2275(4) | -829(8) | -3668(10) | 10.6 |
| C(33) | 732(6) | 5554(9) | 1776(12) | 13.0 | C(202) | 1867(5) | -181(11) | -4491(10) | 13.5 |
| C(41) | 16(3) | 19(8) | -2411(9) | 9.2 | N(200) | 2656(4) | -1522(8) | -4276(9) | 13.9 |
| C(42) | 221(6) | -1420(10) | -3422(15) | 15.8 | C(203) | 3023(5) | -2231(10) | -3497(10) | 11.6 |
| C(43) | -529(4) | 357(10) | -3043(11) | 12.1 | C(204) | 2842(8) | -1759(14) | -5676(13) | 19.8 |

a) The equivalent isotropic temperature factors were computed using the following expressing: $B_{eq}=(4/3)(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$. The $B_{ij}$'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

200H computer at the Computer Center of The University of Tokyo, using the local version of the UNICS program.[17] The atomic-scattering factors were taken from the tables.[19]

*Structure Determination.* The structure was solved by the heavy-atom method. The positions of the lanthanum, phosphorus, and sulfur atoms were deduced from a three-dimensional Patterson map, while all the other non-hydrogen atoms were located by means of successive Fourier syntheses. Their positional and thermal parameters were refined by the block-diagonal least-squares method. All attempts to determine hydrogen-atom positions were unsuccessful, and so they were not included in the calculation. In the last cycle of the refinement with anisotropic temperature factors for all atoms, almost all the parameter shifts were less than one-third of the corresponding standard deviations; the exceptions were only slightly higher than one-third of the corresponding standard deviations. The final $R$ value obtained was 0.047.[19]

*Other Measurements.* The X-ray powder patterns of these complexes were obtained by the use of a diffractometer, Model DX-GO-F JEOL, using Cu $K\alpha$ radiation, in the range from 6° to 50° in $2\theta$. The magnetic moments of the solid samples were measured using a Gouy balance at an ambient temperature. The infrared absorption spectra of the samples were obtained by means of a JASCO A-202 grating infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mull. The visible absorption spectra of the solutions, as well as the diffuse reflectance spectra of the solid samples, were measured by means of a Hitachi 124 spectrophotometer. The $^1$H-NMR spectra were measured by means of a Varian EM-390 NMR-spectrometer, using tetramethylsilane (TMS) as the internal standard.

## Results and Discussion

The final atomic parameters of the title complex are listed in Table 1,[20] while the bond lengths as well as the bond angles are tabulated in Table 2. The perspective drawing of the complex around the central lanthanum atom, together with the numbering scheme, is shown in Fig. 1, and the crystal packing diagram, in Fig. 2.

The complex molecules in the crystal are discrete, and neither bridges nor hydrogen bonds are recognized between different molecules. As is shown in Fig. 3, the central lanthanum(III) atom is in an octa-coordination and in a distorted dodecahedron geometry, coordinated to six sulfur atoms of three iPr$_2$dtp ligands, which span at $m$ edges of the dodecahedron, and to two oxygen atoms of two dma ligands, which bond at both the ends of its remaining $m$ edge. The plane equations of the two trapezia of the dodecahedron are shown as follows.

($x$, $y$, and $z$ in the equations are taken in the $a$, $b$, and $c$ directions of the unit cell respectively, and are shown in Å units):

TABLE 2. BOND LENGTHS AND BOND ANGLES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

| Bond length | $l$/Å | Bond length | $l$/Å |
|---|---|---|---|
| La-S(1) | 3.009(3) | La-S(2) | 3.046(7) |
| La-S(3) | 3.012(9) | La-S(4) | 2.988(3) |
| La-S(5) | 3.029(4) | La-S(6) | 3.013(10) |
| La-O(100) | 2.432(5) | La-O(200) | 2.413(10) |
| S(1)-P(1) | 1.986(6) | S(2)-P(1) | 1.964(6) |
| P(1)-O(1) | 1.583(10) | P(1)-O(2) | 1.588(10) |
| O(1)-C(11) | 1.499(13) | O(2)-C(21) | 1.458(12) |
| C(11)-C(12) | 1.522(22) | C(11)-C(13) | 1.490(23) |
| C(21)-C(22) | 1.477(23) | C(21)-C(23) | 1.460(16) |
| S(3)-P(2) | 1.971(7) | S(4)-P(2) | 1.986(6) |
| P(2)-O(3) | 1.595(9) | P(2)-O(4) | 1.593(9) |
| O(3)-C(31) | 1.470(12) | O(4)-C(41) | 1.452(14) |
| C(31)-C(32) | 1.478(19) | C(31)-C(33) | 1.526(18) |
| C(41)-C(42) | 1.478(19) | C(41)-C(43) | 1.485(17) |
| S(5)-P(3) | 1.981(7) | S(6)-P(3) | 1.973(5) |
| P(3)-O(5) | 1.594(9) | P(3)-O(6) | 1.593(7) |
| O(5)-C(51) | 1.477(8) | O(6)-C(61) | 1.475(17) |
| C(51)-C(52) | 1.512(15) | C(51)-C(53) | 1.543(22) |
| C(61)-C(62) | 1.463(19) | C(61)-C(63) | 1.508(17) |
| O(100)-C(101) | 1.212(13) | C(101)-C(102) | 1.707(18) |
| C(101)-N(100) | 1.083(17) | N(100)-C(103) | 1.675(17) |
| N(100)-C(104) | 1.476(17) | O(200)-C(201) | 1.260(16) |
| C(201)-C(202) | 1.610(22) | C(201)-N(200) | 1.187(16) |
| N(200)-C(203) | 1.579(21) | N(200)-C(104) | 1.516(26) |

| Bond angle | $\theta$/° | Bond angle | $\theta$/° |
|---|---|---|---|
| S(1)-La-S(2) | 65.88(5) | S(1)-La-S(3) | 135.74(5) |
| S(1)-La-S(4) | 156.80(5) | S(1)-La-S(5) | 81.37(5) |
| S(1)-La-S(6) | 87.26(4) | S(1)-La-O(100) | 80.79(12) |
| S(1)-La-O(200) | 95.74(9) | S(2)-La-S(3) | 70.54(6) |
| S(2)-La-S(4) | 137.16(6) | S(2)-La-S(5) | 134.29(6) |
| S(2)-La-S(6) | 81.95(5) | S(2)-La-O(100) | 131.39(13) |
| S(2)-La-)(200) | 76.43(10) | S(3)-La-S(4) | 66.75(5) |
| S(3)-La-S(5) | 127.54(6) | S(3)-La-S(6) | 79.38(5) |
| S(3)-La-O(100) | 137.39(12) | S(3)-La-O(200) | 81.02(9) |
| S(4)-La-S(5) | 77.89(5) | S(4)-La-S(6) | 93.20(4) |
| S(4)-La-O(100) | 81.87(12) | S(4)-La-O(200) | 93.70(9) |
| S(5)-La-S(6) | 64.81(5) | S(5)-La-O(100) | 67.96(12) |
| S(5)-La-O(200) | 140.55(9) | S(6)-La-O(100) | 132.47(12) |
| S(6)-La-O(200) | 154.64(9) | O(100)-La-O(200) | 72.73(14) |
| La-S(1)-P(1) | 90.91(10) | La-S(2)-P(1) | 90.26(10) |

| Bond angle | $\theta$/° | Bond angle | $\theta$/° |
|---|---|---|---|
| S(1)-P(1)-S(2) | 112.9(2) | S(1)-P(1)-O(1) | 109.9(2) |
| S(1)-P(1)-O(2) | 113.3(3) | S(2)-P(1)-O(2) | 106.8(3) |
| O(1)-P(1)-O(2) | 99.7(3) | P(1)-O(1)-C(11) | 122.0(5) |
| O(1)-C(11)-C(12) | 103.5(1) | O(1)-C(11)-C(13) | 111.0(9) |
| C(12)-C(11)-C(13) | 110.7(11) | P(1)-O(2)-C(21) | 121.1(6) |
| O(2)-C(21)-C(22) | 109.9(11) | O(2)-C(21)-C(23) | 108.7(7) |
| C(22)-C(21)-C(23) | 113.6(11) | La-S(3)-P(2) | 89.26(11) |
| La-S(4)-P(2) | 89.70(13) | S(3)-P(2)-S(4) | 113.1(1) |
| S(3)-P(2)-O(3) | 112.4(2) | S(3)-P(2)-O(4) | 107.2(3) |
| S(4)-P(2)-O(3) | 109.9(2) | S(4)-P(2)-O(4) | 113.1(2) |
| O(3)-P(2)-O(4) | 100.5(3) | P(2)-O(3)-C(31) | 121.0(5) |
| O(3)-C(31)-C(32) | 107.3(8) | O(3)-C(31)-C(33) | 108.7(10) |
| C(22)-C(31)-C(33) | 111.4(9) | P(2)-O(4)-C(41) | 123.2(6) |
| O(4)-C(41)-C(42) | 105.7(7) | O(4)-C(41)-C(43) | 108.4(9) |
| C(42)-C(41)-C(43) | 112.8(8) | La-S(5)-P(3) | 89.58(10) |
| La-S(6)-P(3) | 90.20(9) | S(5)-P(3)-S(6) | 113.1(1) |
| S(5)-P(3)-O(5) | 111.1(2) | S(5)-P(3)-O(6) | 112.2(2) |
| S(6)-P(3)-O(5) | 111.6(2) | S(6)-P(3)-O(6) | 108.4(2) |
| O(5)-P(3)-O(6) | 99.8(3) | P(3)-O(5)-C(51) | 120.1(4) |
| O(5)-C(51)-C(52) | 105.8(6) | O(5)-C(51)-C(53) | 106.9(9) |
| C(52)-C(51)-C(53) | 113.9(9) | P(3)-O(6)-C(61) | 119.2(7) |
| O(6)-C(61)-C(62) | 108.1(10) | O(6)-C(61)-C(63) | 104.6(8) |
| C(62)-C(61)-C(63) | 111.9(9) | La-O(100)-C(101) | 165.9(6) |
| O(100)-C(101)-C(102) | 114.1(9) | O(100)-C(101)-N(100) | 140.4(12) |
| C(102)-C(101)-N(100) | 105.5(10) | C(101)-N(100)-C(103) | 104.0(10) |
| C(101)-N(100)-C(104) | 140.5(12) | C(103)-N(100)-C(104) | 115.2(9) |
| La-O(200)-C(201) | 144.21(7) | O(200)-C(201)-C(202) | 118.7(9) |
| O(200)-C(201)-N(200) | 124.7(12) | C(202)-C(201)-N(200) | 116.6(13) |
| C(201)-N(200)-C(203) | 115.6(12) | C(201)-N(200)-C(204) | 127.5(14) |
| C(203)-N(200)-C(204) | 116.8(11) | | |

a) La, S(1), S(2), S(3), and S(4) plane:

$$-0.040x-0.480y-0.876z+0.960=0.0.$$

Deviations (in Å): La, 0.080; S(1), −0.105; S(2), 0.088; S(3), −0.113; S(4), 0.093.

b) La, S(5), S(6), 0(100), and 0(200) plane:

$$-0.997x+0.076y-0.008z+5.288=0.0.$$

Deviations (in Å): La, 0.030; S(5), 0.077; S(6), −0.053; 0(100), −0.092; 0(200), 0.043 Å.

The dihedral angle of both the planes is 89.4 °.

As is shown in Table 2, all the La–S bond lengths are in the range of 3.046(7)—2.988(3) Å; they are almost equal. All the P–S bond lengths are also almost the same; 1.986(6)—1.964(6) Å. Therefore, it is likely that the P=S double bond of the ligand is almost completely delocalized in the complex. The oxygen atom of $iPr_2dtp$, and the nitrogen atom of the dma ligand are not coordinated to the central metal atom.

The La–S bond length of this complex is comparable with those of $La(Et_2dtp)_3\{(C_6H_5)_3PO\}_2$ (2.98—3.07

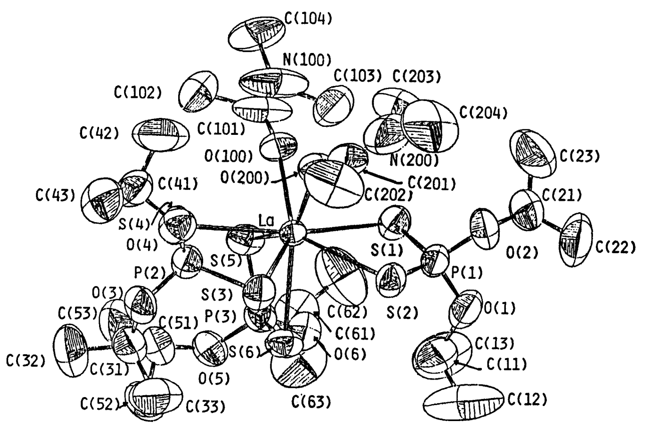

Fig. 1. A perspective drawing of the title complex with the numbering scheme.

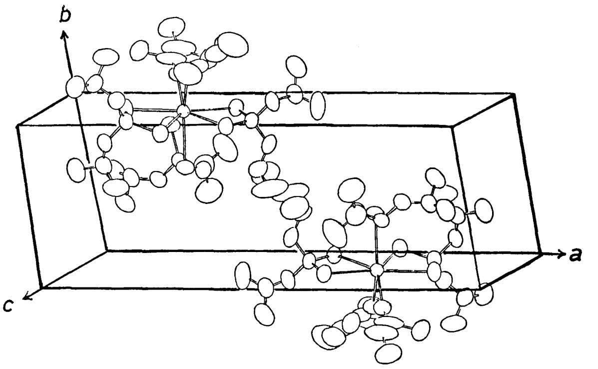

Fig. 2. Crystal packing diagram of the title complex.

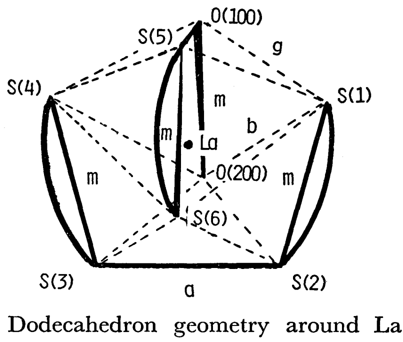

Fig. 3. Dodecahedron geometry around La$^{III}$.

Å),11a) and $[As(C_6H_5)_4][La(Et_2dtp)_4]$ (2.96—3.01 Å).12) The La–O bond lengths of this complex(2.41, 2.43 Å) are also almost equal to those of $La(Et_2dtp)_3\{(C_6H_5)_3PO\}_2$(2.42, 2.46 Å).11a) The bond lengths are slightly shorter than those of the common lanthanum(III) complexes in which the oxygen atoms of the ligands are coordinated(about 2.5 Å).21–24) Consequently, the bond between La$^{III}$ and dma in this complex can be expected to be very strong.

The configuration of the central metal of the title complex is different from that of $La(Et_2dtp)_3\{(C_6H_5)_3PO\}_2$, which is in the square-antiprism geometry, and the two triphenylphosphine oxide ligands are located on opposite sides of the molecule.11a) The discrepancy between them is probably due to the bulkiness of the triphenylphosphine oxide ligands in the latter complex, for the ligands cannot be located side by side on the coordination sphere due to the steric hindrance.

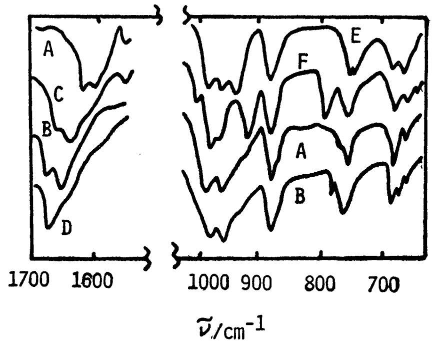

Fig. 4. Infrared absorption spectra of the title complex and the related compounds. A: $La(iPr_2dtp)_3(dma)_2$; B: $La(iPr_2dtp)_3(dmf)_2$; C: dma; D: dmf; E: Na(iPr$_2$dtp); F: $Na[La(iPr_2dtp)_4]$.

In tetrakis(4-thioxo-2-pentanonato)zirconium(IV), where the central metal is in a square-antiprism geometry, four sulfur atoms and four oxygen atoms of the ligands are located side by side.25) Similarly, it is expected that, in the comlpexes with high-coordination-number geometry, if two kinds of ligating atoms exist, the same kind of atoms may be apt to be located side by side on the coordination polyhedron if their "hardness" (in the HSAB concept) is different from that of the others, unless no steric interference exists.

Although the positions and thermal parameters of the lanthanum(III) atom and the atoms near it are exactly determined, those of the isopropyl carbon atoms have relatively large standard deviations; the hydrocarbon chains are not tightly fixed.

From the powder X-ray diffraction patterns of $Ln(iPr_2dtp)_3L_2$, where Ln=La or Nd; L=dma or dmf, both of the dma complexes, as well as both of the dmf complexes, may be said to be isostructural with each other.

The infrared absorption spectral patterns of the dma adducts of the lanthanum(III) and neodymium(III) complexes, as well as of their dmf adducts, resemble each other. The infrared spectra of the title complex and of some related compounds are shown in Fig. 4. The $\nu$(CO) of dma shifts to the lower-wave number side when it is coordinated with the lanthanoid metal; *i.e.* 1657, 1640→1620, 1597 cm$^{-1}$. On the other hand, the $\nu$(CO) of dmf makes only a small shift, but splits into two peaks, 1668→1680, 1643 cm$^{-1}$, when it is coordinated to La$^{III}$ or Nd$^{III}$ in this type of complex.

In the infrared spectra of these metal R$_2$dtp complexes, the characteristic strong peak, which is probably to be assigned as a mixed band of $\nu$(P–S) and $\nu$(P–O), appears near 750 cm$^{-1}$.26) In the case of $Na[La(iPr_2dtp)_4]$, the band is split into two peaks; 760 and 741 cm$^{-1}$. On the other hand, in the case of the title adduct, the peak appears as a single one at 760 cm$^{-1}$. The X-ray diffraction data shows that, in the $[La(Et_2dtp)_4]^-$ ion, the La–S pair as well as the P–S bond lengths of a Et$_2$dtp ligand are a little different from each other,11a) probably because of the partial localization of the P=S double bond of the ligand. In the title complex, as was shown above, the P=S double bond is delocalized almost completely. There-

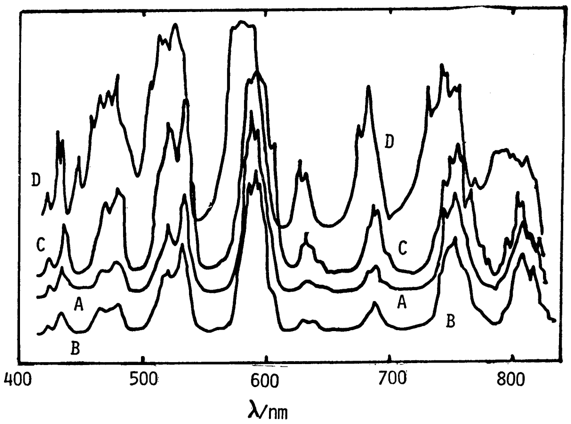

Fig. 5. Diffuse reflectance spectra of the neodymium(III) complexes and its chloride hexahydrate. A: $Nd(iPr_2dtp)_3(dma)_2$; B: $Nd(iPr_2dtp)_2(dmf)_2$; C: $Na[(iPr_2dtp)_4]$; D: $NdCl_3 \cdot 6H_2O$.

fore, some relation between the splitting of the peak and the delocalization degree of the P=S double bond of the ligand is to be expected. In the infrared spectra of the dmf adduct, the main, strong peak is found at 766 $cm^{-1}$, although a small additional one appears at 788 $cm^{-1}$.

The diffuse reflectance spectra of $Nd(iPr_2dtp)_3(dma)_2$ and of the related compounds are shown in Fig. 5. The general features of the spectra resemble each other; however, all the bands of the $R_2$dtp-containing complexes, $Na[Nd(iPr_2dtp)_4]$ and $Nd(iPr_2dtp)_3L_2$(where L=dma or dmf), make red shift compared with the corresponding peaks of $NdCl_3 \cdot 6H_2O$. The $Nd(iPr_2dtp)_3(dma)_2$ complex is soluble in chloroform, and the visible absorption spectra of the solution show the maxima which are also found in the reflection spectra of its solid. The absorption maxima are as follows:

808(1.2); 754($0.9_5$); 590(1.5); 532, 518($0.9_5$, $0.8_2$) (concentration of the samples: $8 \times 10^{-3}$ mol $dm^{-3}$; figures are shown by λ/nm; log ε in parentheses).

When dma is added to the solution, these peaks make a blue shift; their intensities decrease a little at the same time, and its spectral pattern tends to become the same as that of the $NdCl_3$ dissolved in chloroform containing dma. Although the quantitative study has not yet been completed, the change in the spectra is likely to be due to the displacement of the $iPr_2$dtp ligand with dma in the solution when the concentration of dma increases.

The $^1H$-NMR spectra of the title complex and some related compounds are shown in Table 3. The samples were dissolved in chloroform-*d*(about 5 wt%). As is shown in the table, the methyl proton signals of dma or dmf in the complexes appeared in a lower-magnetic-field region compared with those of the respective free amides. This shows that such amide ligands are coordinated to the lanthanoid metal, acting as donors even in a solution.

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TABLE 3. $^1H$-NMR SPECTRA OF THE TITLE COMPLEX AND SOME RELATED COMPOUNDS

| | $-N(CH_3)_2$ (2 singlets) | $CH_3CO-$ | $CH_3$ in $iPr_2$dtp (doublet) |
|---|---|---|---|
| $La(iPr_2dtp)_3(dma)_2$ | 3.12, 3.05 | 2.30 | 1.30($J$=6) |
| $La(iPr_2dtp)_3(dmf)_2$ | 3.05, 3.00 | | 1.30($J$=6) |
| dma | 3.05, 2.94 | 2.11 | |
| dmf | 2.99, 2.87 | | |

Chemical shift, δ ppm, TMS=0; $J$ in Hz.

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