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The Syntheses, Properties, and Crystal and Molecular Structures of Bis(benzamide)tris(*O,O'*-diisopropyl dithiophosphato)neodymium(III), [Nd{$(C_3H_7O)_2PS_2$}$_3$($C_6H_5CONH_2$)$_2$], and Its Isomorphous Complexes of La, Ce, Pr, Sm, Eu, and Gd

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The new complexes indicated in the title have been synthesized, and the crystal and molecular structure of the neodymium(III) complex has been determined by the X-ray diffraction method. The crystal is monoclinic, with the space group C2/c, $Z=16$, $a=28.887(4)$, $b=28.913(5)$, $c=24.814(5)$ Å, $\beta=106.72(1)^\circ$. The final R value for 7761 reflections is 0.066. The central neodymium(III) atom of the complex is octa-coordinated and is in a dodecahedron geometry; three *O,O'*-diisopropyl dithiophosphato ligands, chelating by both of the sulfur atoms, span the two *m* edges of a trapezium as well as one *a* edge of the other trapezium, and two oxygen atoms of both the benzamide ligate at both tips of the base edge of the latter trapezium. The solid and the acetonitrile solution of the europium(III) complex are orange in color, and they show a charge-transfer band in their near-ultraviolet absorption spectra.

The lanthanoid metal complexes of sulfur-ligating ligands, such as *O,O'*-dialkyl dithiophosphate,[1–3] dialkyl dithiophosphinates,[4] and dialkyldithiocarbamates,[5] are very interesting compounds, because they are stable enough in spite of the fact that lanthanoid elements are known as "hard acids" according to the HSAB theory.[6] The structure of some complexes of the type have already been determined by means of X-ray analysis.[1,2,4,5,7]

Our group has already reported about the mixed complexes of lanthanoid(III) containing the *O,O'*-diisopropyl dithiophosphato (iPr$_2$dtp) ligand, as well as *N,N*-dimethylacetamide (dma).[1] Although we could obtain La, Ce, and Nd complexes of the type, all of which are isomorphous with each other, those of Sm and of the heavier members of lanthanoid were not synthesized in a stable crystalline state. Therefore, we tried to find more stable mixed complexes of the type. The adducts obtained this time, which are isomorphous with each other, were those of all members from La to Gd, except for Pm. All of them are stable, and all can be kept in air for several months at room temperature without decomposition.

Another interesting problem about the type of complexes is the coordination position of the oxygen atoms. As has been shown in the previous paper,[1] the two oxygen atoms take side-by-side positions in [La(iPr$_2$dtp)$_3$(dma)$_2$], while in the case of [La(Et$_2$dtp)$_3${$(C_6H_5)_3PO$}$_2$] the two oxygen atoms are apart.[2c] We assumed that the difference is due mainly to the size of the ligand molecule;[1] consequently, the titled complexes, where the benzamide (bza) ligand is larger than dma, are expected to have different oxygen-atom positions around the central metal atom.

Among the series of titled complexes, the best crystals were obtained for Nd(III) complex. Therefore, its structure was determined by the single-crystal X-ray diffraction method.

Attempts to obtain similar complexes of lanthanoid heavier than gadolinium has not been successful until now; in these cases, other isomorphous complexes with the formula of [M(iPr$_2$dtp)$_2$(bza)$_3$]$^+$(iPr$_2$dtp)$^-$ (where M=Gd, Tb, Dy, Er, and Yb) were obtained. The details about them will be shown in a separate paper.[8]

Experimental

Synthesis of Bis(benzamide)tris(O,O'-diisopropyl dithiophosphato)neodymium(III). Neodymium(III) chloride hexahydrate (0.5 g, 1.4 mmol) and sodium *O,O'*-diisopropyl dithiophosphate (1.5 g, 6.3 mmol)[1] were dissolved in 25 cm^3 of 2-propanol, and the mixture was refluxed for about 20 min at 80 °C to complete the reaction. The solution was then filtered off, and about 0.5 g (4.1 mmol) of benzamide was added to the filtrate. It was warmed and kept at about 65 °C for 5 min to terminate the reaction. The solution was then evaporated almost to dryness by the use of a rotary vacuum evaporator at 65 °C. The residue was dissolved in 5 cm^3 of 2-propanol, the turbid materials were filtered off, and the clear filtrate was kept in a silica-gel desiccator for several days. The deposited crystals were filtered off, washed with small portions of 2-propanol and diisopropyl ether, in that order, and dried in a vacuum desiccator. The yield was about 0.7 g (0.7 mmol, 49%).

The isomorphous complexes of La, Ce, and Pr(III) were obtained in almost the same way. In the cases of the Sm and Eu(III) complexes, the crude product was obtained by adding 10 cm^3 of diisopropyl ether to the evaporating residue. Their crystals were obtained when they were dissolved in 5 cm^3 of 2-propanol; then were subsequently kept in the diisopropyl ether-vapor moiety. In all cases, the yield was about 50% calculated from the starting metal salt.

In the case of the Gd(III) complex, 0.49 g (1.3 mmol) of gadolinium chloride hexahydrate and 1.29 g (5.5 mmol) of sodium *O,O'*-diisopropyl dithiophosphate were used as the starting materials. The added benzamide should be less than 0.33 g (2.7 mmol). About 10 cm^3 of diisopropyl ether was added to the solution before it was placed in a desiccator to obtain the crystals. The yield was 0.63 g (0.6 mmol, 47%). (If the mol ratio of benzamide to the metal salt was higher, the [Gd(iPr$_2$dtp)$_2$(bza)$_3$]$^+$(iPr$_2$dtp)$^-$-type complex was mainly deposited).

The results of the elemental analyses, their average yields, and their magnetic moments as measured by a Gouy balance at the ambient temperature are shown in Table 1.

Intensity-data Collection. A crystal with dimensions of 0.4×0.4×0.25 mm^3 was used for the measurement without shaping. The crystallographic data are $NdC_{32}H_{56}N_2O_8P_3S_6$, *F.W.*=1026.36, monoclinic, space group C2/c, $Z=16$, $a=28.887(4)$, $b=28.913(5)$, $c=24.814(5)$ Å $\beta=106.72(1)^\circ$, $U=$

Table 1. Analyses, yields of the syntheses, and magnetic moments of the $[M\{((CH_3)_2CHO)_2PS_2\}_3(H_2NCOC_6H_5)_2]$ complexes

M		M(%)	C(%)	H(%)	N(%)	Yield/%	μ_{eff}/BM[a]
La	Found	13.60	37.54	5.49	2.69	62.0	(diamag.)
	Calcd	13.61	37.65	5.53	2.74		
Ce	Found	13.72	37.63	5.52	2.83	54.0	2.4_7
	Calcd	13.71	37.60	5.49	2.73		
Pr	Found	13.74	37.69	5.50	2.86	56.0	3.5_3
	Calcd	13.77	37.55	5.51	2.74		
Nd	Found	14.22	37.15	5.49	2.64	55.7	3.5_6
	Calcd	14.05	37.45	5.50	2.73		
Sm	Found	14.68	37.12	5.46	2.72	41.3	1.5_6
	Calcd	14.56	37.23	5.47	2.71		
Eu	Found	14.81	37.20	5.44	2.72	55.5	3.3_2
	Calcd	14.70	37.17	5.46	2.71		
Gd	Found	15.01	37.00	5.41	2.74	46.6	7.4_3
	Calcd	15.13	36.98	5.43	2.70		

a) 1 BM=9.274078(36)×10^{-24} J T^{-1}

19, 848(6) Å^3, D_x=1.37, D_m=1.36(3) Mg m^{-3}, μ(Mo $K\alpha$)=1.47 mm^{-1}. The reflections whithin the range of $3° < 2\theta < 48°$ 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}; scan width: 1.40+0.5tanθ°). The crystal was stable during the exposure to X-rays. From the 10017 independent reflections thus measured, 7761 with $|F_o| > 3\sigma(|F_o|)$ were selected and used for the structure determination. 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 Nd, P, and S atoms were deduced from a three-dimensional Patterson map; the other non-hydrogen atoms were located by means of successive Fourier syntheses. Their positional, isotropic, and then anisotropic thermal parameters were refined by the block-diagonal least-squares method. All the calculations were carried out on a HITAC M-200H computer at the Computer Center of the University of Tokyo, using the local version of the UNICS program system.[9] The atomic-scattering factors were taken from the tables.[10]

Although the positional and thermal parameters of the central Nd(III) atoms, as well as those of the other atoms near them, were exactly determined, those of some isopropyl groups and of some phenyl rings were found to have relatively large standard deviations; this may be due to the fact that they are not fixed tightly in the crystal. As is shown in Table 2, the thermal parameters of some isopropyl carbon atoms are very large; therefore, we can know only the probable domains, not the exact positions, of some atoms, even after the repeated-refinement process, although they converged to the respective values. The position of C(226) was not decided. The seven carbon atoms of the phenyl groups, C(11C), C(11D), C(11E), C(11F), C(31D), C(31E), and C(31F), were fixed at the positions calculated from those of the vicinal atoms; their isotropic temperature factors were assumed to be 16.0 Å^2. In the final cycle of the refinement, the parameter shifts of the atoms were less than one-third of the corresponding standard deviations.

The final R value was 0.066.[11]

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 40° in 2θ. The infrared spectra of the samples were obtained by means of a JASCO A202 grating infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mull. The near-ultraviolet absorption spectra of the complexes were measured with a Hitachi 124 spectrophotometer.

Results and Discussion

The final atomic parameters of the title complex are listed in Table 2.[12] The sixteen neodymium(III) atoms in one unit cell are divided into three groups. The Nd(1) atom is at a general equivalent position, while the Nd(2) as well as Nd(3) atoms and P(21) as well as P(31) atoms take special equivalent positions on the two-fold axes (Wyckoff notation: e). Some bond lengths and bond angles of the complex are shown in Table 3.[13] The general features of the three types of complex molecules are almost the same; their corresponding bond lengths and bond angles are compared in the table.

A perspective drawing of the complex around the central metal Nd(1) atom is shown in Fig. 1. The numbering scheme of the ligand atoms is shown in Fig. 2, and the configuration of the ligating atoms around the Nd(1) atom, in Fig. 3.

Each complex molecule is isolated, and no bridgings are found between them. However, as is shown in Table 2, some interatomic distances between S and N atoms are shorter than 3.5 Å; these may be the hydrogen bonds, since the S···H–N hydrogen bond length has been reported to be about 3.42 Å between S and N atoms.[14] As is shown in Fig. 3, the central Nd(III) atom is octa-coordinated and is in a distorted dodecahedron geometry, where three iPr$_2$dtp ligands span at two m edges of a trapezium and one a edge of the other trapezium, chelating by both of the sulfur atoms. Two oxygen atoms of bza ligands take the two tip positions of the base edge of the latter trapezium. Five atoms, including the central metal atom, of each trapezium of each complex are almost on one plane (the deviation of each atom's position from the plane was 0.267 Å in the maximum and 0.12 Å on the average), and the dihedral angle between the two planes of each complex is almost right-angled (88.7—90.2°).[13]

Table 2. Final atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($B/\text{Å}^2$) of non-hydrogen atoms with estimated standard deviations in parentheses

Atom	x	y	z	$B_{eq}/\text{Å}^{2\,a)}$
Nd(1)	2921.0(2)	4377.2(2)	2571.2(2)	4.9
S(111)	2137(1)	3842(1)	2853(2)	6.4
S(112)	1979(1)	4880(1)	2273(2)	6.9
P(11)	1693(1)	4360(1)	2580(2)	6.2
S(121)	2959(2)	4754(2)	3666(2)	9.1
S(122)	3928(2)	4530(2)	3286(2)	9.0
P(12)	3661(2)	4712(2)	3910(2)	9.0
S(131)	2459(2)	4006(2)	1463(2)	9.7
S(132)	3600(2)	4276(2)	1883(2)	9.1
P(13)	3070(2)	4039(2)	1275(3)	10
O(111)	1482(4)	4572(4)	3029(6)	9.9
O(112)	1242(3)	4147(4)	2135(5)	8.0
C(111)	1391(8)	4292(7)	3518(10)	12
C(112)	842(9)	4392(9)	3466(12)	15
C(113)	1731(11)	4425(14)	4045(9)	20
C(114)	892(7)	4413(7)	1743(8)	9.9
C(115)	395(7)	4313(9)	1742(14)	16
C(116)	975(11)	4304(12)	1199(13)	18
O(121)	3876(8)	5204(6)	4179(9)	19
O(122)	3851(5)	4393(5)	4432(5)	11
C(121)	4083(14)	5462(11)	4356(13)	19
C(122)	3983(15)	5927(9)	4115(15)	22
C(123)	4431(17)	5347(14)	4948(13)	24
C(124)	3703(9)	3892(7)	4360(8)	11
C(125)	3392(12)	3783(10)	4717(12)	17
C(126)	4222(14)	3669(11)	4533(12)	20
O(131)	3276(7)	3541(7)	1088(10)	20
O(132)	2996(6)	4308(6)	699(5)	13
C(131)	2931(13)	3286(18)	737(18)	25
C(132)	3221(18)	2811(16)	949(21)	30
C(133)	3096(28)	3237(20)	292(25)	40
C(134)	2853(9)	4792(9)	679(10)	14
C(135)	2442(15)	4843(15)	233(16)	24
C(136)	3218(13)	5027(13)	497(14)	22
O(11)	3188(3)	3619(3)	2861(4)	7.1
N(11)	3810(6)	3282(6)	2656(9)	15
C(11A)	3458(6)	3284(5)	2885(7)	7.3
C(11B)	3414(8)	2880(7)	3215(15)	19
C(11G)	3770(11)	2515(7)	3357(14)	19
O(12)	3010(3)	5143(3)	2281(4)	6.5
N(12)	3722(4)	5528(5)	2563(6)	8.8
C(12A)	3274(6)	5464(5)	2225(7)	6.9
C(12B)	3079(6)	5812(7)	1764(9)	9.7
C(12C)	3377(7)	6132(7)	1625(8)	10
C(12D)	3197(8)	6432(9)	1183(11)	14
C(12E)	2702(9)	6370(11)	817(15)	20
C(12F)	2419(9)	6028(11)	1007(14)	18
C(12G)	2606(7)	5731(8)	1431(10)	13
Nd(2)	0	2286.3(3)	2500	4.7
S(211)	442(1)	1428(1)	2198(2)	6.2
P(21)	0	1059(2)	2500	5.5
S(221)	643(2)	2083(2)	3605(2)	8.4
S(222)	295(2)	3130(1)	3198(2)	8.3
P(22)	672(2)	2739(2)	3807(2)	8.8
O(211)	327(4)	731(4)	2950(5)	8.9
C(211)	168(8)	477(7)	3361(10)	12
C(212)	274(11)	−24(7)	3310(12)	16
C(213)	468(12)	701(11)	3924(12)	17
O(221)	550(5)	2827(5)	4378(5)	12
O(222)	1233(7)	2964(7)	3954(8)	17
C(221)	50(9)	2738(9)	4398(9)	13
C(222)	66(16)	2345(15)	4845(14)	26
C(223)	−119(15)	3169(12)	4613(13)	24
C(224)	1706(13)	2757(10)	4185(15)	21
C(225)	1976(13)	3086(16)	4283(17)	25
O(21)	693(3)	2469(3)	2204(4)	6.2
N(21)	1118(6)	3098(5)	2441(7)	11
C(21A)	1006(5)	2739(5)	2155(7)	6.7
C(21B)	1246(5)	2660(5)	1724(7)	7.7
C(21C)	1118(8)	2280(7)	1388(10)	12
C(21D)	1323(13)	2200(9)	953(15)	22
C(21E)	1615(10)	2532(8)	815(14)	18
C(21F)	1735(9)	2907(7)	1200(11)	14
C(21G)	1535(7)	3000(7)	1591(8)	10
Nd(3)	5000	1477.0(3)	2500	5.4
S(311)	4407(1)	2340(1)	2222(2)	7.4
P(31)	5000	2709(2)	2500	6.9
S(321)	5094(2)	1694(2)	1396(3)	11
S(322)	4963(2)	647(2)	1793(3)	10
P(32)	4994(2)	1055(2)	1169(3)	10
O(311)	5084(4)	3035(4)	2027(5)	9.7
C(311)	4704(7)	3268(6)	1582(8)	9.6
C(312)	4693(13)	3099(11)	1041(11)	18
C(313)	4812(9)	3776(7)	1572(12)	15
O(321)	4544(5)	995(5)	644(5)	11
O(322)	5426(6)	920(9)	888(8)	20
C(321)	4075(7)	1098(9)	660(9)	13
C(322)	3799(12)	652(14)	441(16)	23
C(323)	3877(11)	1521(12)	305(15)	20
C(324)	5650(11)	718(14)	698(14)	20
C(325)	5424(14)	630(15)	56(16)	23
C(326)	6159(10)	702(15)	962(16)	22
O(31)	4161(3)	1291(3)	2209(5)	7.4
N(31)	3863(6)	631(5)	2396(10)	14
C(31A)	3814(5)	1029(5)	2170(7)	7.4
C(31B)	3329(7)	1148(7)	1883(12)	15
C(31C)	2958(6)	847(8)	1749(10)	13
C(31G)	3291(10)	1553(12)	1741(27)	36
C(11C)	2860	2676	2939	16
C(11D)	2750	2233	3102	16
C(11E)	3121	1931	3376	16
C(11F)	3603	2071	3488	16
C(31D)	2517	929	1413	16
C(31E)	2403	1403	1290	16
C(31F)	2770	1742	1421	16

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

As is shown in Table 3, all the Nd–S bond lengths are in the range from 2.888(6) to 2.988(5) Å; they are almost equal. Taking the difference in the ionic radii of La^{III} and Nd^{III} (1.160 and 1.109 Å respectively)[15] into consideration, they are comparable with the La–S bond lengths of $La(iPr_2dtp)_3(bza)_2$, which range from 2.998(3) to 3.046(7) Å[1] All the P–S bond lengths are not very different, either; they are in the range of 1.943(8)—1.961(7) Å, except for S(122)–P(12) (1.982(8) Å); it is likely that the P=S double bond of the ligand is almost completely delocalized. Although in some cases the respective lengths of the pair of Nd–S and of P–S of each ligand are different from each other, there is probably no general rule such as that the sulfur

TABLE 3. SELECTED BOND LENGTHS AND BOND ANGLES OF THE COMPLEX, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond length	l/Å $n=1$ a)	Bond length	l/Å $n=2$ a)	$n=3$ a)
Nd(1)-S(111)	2.898(4)	Nd(n)-S(n11)	2.984(4)	2.933(4)
Nd(1)-S(112)	2.985(4)			
Nd(1)-S(121)	2.900(7)	Nd(n)-S(n21)	2.895(5)	2.898(8)
Nd(1)-S(131)	2.896(6)			
Nd(1)-S(122)	2.972(4)	Nd(n)-S(n22)	2.971(5)	2.956(6)
Nd(1)-S(132)	2.962(7)			
Nd(1)-O(11)	2.366(9)	Nd(n)-O(n1)	2.380(11)	2.381(9)
Nd(1)-O(12)	2.364(9)			
S(111)-P(11)	1.963(5)	S(n11)-P(n1)	1.970(6)	1.967(5)
S(112)-P(11)	1.970(6)			
S(121)-P(12)	1.945(7)	S(n21)-P(n2)	1.960(7)	1.929(9)
S(131)-P(13)	1.953(10)			
S(122)-P(12)	1.988(10)	S(n22)-P(n2)	1.950(8)	1.966(11)
S(132)-P(13)	1.940(8)			
P(11)-O(111)	1.542(17)	P(n1)-O(n11)	1.559(12)	1.579(16)
P(1.1)-O(112)	1.572(11)			
P(12)-O(121)	1.617(20)	P(n2)-O(n21)	1.576(21)	1.564(15)
P(13)-O(131)	1.671(23)			
P(12)-O(122)	1.556(16)	P(n2)-O(n22)	1.687(19)	1.641(27)
P(13)-O(132)	1.588(20)			
O(11)-C(11A)	1.233(18)	O(n1)-C(n1A)	1.228(18)	1.238(17)
O(12)-C(12A)	1.234(18)			
S(122)···N(12)	3.362(17)	S(n22)···N(n1)	3.428(22)	
S(132)···N(11)	3.412(21)			
S(322)···N(31^{ii})	3.409(18)	N(31)···S(112^{iii})	3.529(21)	
S(211)···N(12^{iii})	3.482(14)			
Bond angle	ϕ/° $n=1$ a)	**Bond angle**	ϕ/° $n=2$ a)	$n=3$ a)
S(111)-Nd(1)-S(112)	67.15(11)	S(n11)-Nd-S(n12)	67.41(11)	67.01(10)
S(111)-Nd(1)-S(121)	78.61(16)	S(n11)-Nd(n)-S(n21[b])	78.32(13)	78.72(18)
S(111)-Nd(1)-S(131)	81.75(15)	S(n11)-Nd(n)-S(n21[c])	82.18(13)	80.48(18)
S(121)-Nd(1)-S(122)	67.54(16)	S(n21)-Nd(n)-S(n22)	67.49(14)	67.13(20)
S(131)-Nd(1)-S(132)	67.46(18)			
S(111)-Nd(1)-O(11)	69.64(23)	S(n11)-Nd(n)-O(n1)	69.41(27)	69.73(22)
S(111)-Nd(1)-O(12)	135.46(24)	S(n11)-Nd(n)-O(n1[d])	136.05(27)	136.28(23)
Nd(1)-S(111)-P(11)	89.26(18)	Nd(n)-S(n11)-P(n1)	89.09(19)	89.34(15)
Nd(1)-S(112)-P(11)	89.22(19)			
S(111)-P(11)-S(112)	114.3(2)	S(n11)-Nd(n)-S(n12)	114.4(2)	114.3(2)
S(111)-P(11)-O(111)	114.0(6)	S(n11)-P(n1)-O(n11)	106.0(4)	111.6(5)
S(112)-P(11)-O(112)	112.5(4)			
Nd(1)-S(121)-P(12)	91.3(3)	Nd(n)-S(n21)-P(n2)	90.8(2)	91.2(3)
Nd(1)-S(131)-P(13)	90.4(2)			
Nd(1)-S(122)-P(12)	88.4(2)	Nd(n)-S(n22)-P(n2)	88.7(2)	88.8(2)
Nd(1)-S(132)-P(13)	88.8(2)			
S(121)-P(12)-S(122)	112.2(3)	S(n21)-P(n2)-S(n22)	113.0(3)	112.4(4)
S(131)-P(13)-O(131)	104.9(8)			
S(122)-P(12)-O(122)	111.6(6)	S(n22)-P(n2)-O(n22)	103.4(7)	113.9(9)
S(132)-P(13)-O(132)	113.5(7)			
Nd(1)-O(11)-C(11A)	152.7(9)	Nd(n)-O(21)-C(n1A)	151.6(10)	153.2(9)
Nd(1)-O(12)-C(12A)	149.7(9)			

a) $n=1$, 2 or 3 means the numbering of the central metal atom. Keys to the symmetry operations: i $-x, y, 0.5-z$; ii $1.0-x, y, 0.5-z$; iii $0.5-x, -0.5+y, 0.5-z$. "The symmetry operations for the atoms around Nd(n) ($n=2$ or 3) in the bond-angle columns are: b) i for $n=2$, and original for $n=3$; c) original for $n=2$, and ii for $n=3$; d) i for $n=2$, and ii for $n=3$.

atom of a longer P-S has the shorter Nd-S bond. The nitrogen atoms of bza ligands are not ligated to the central metal atom; the average Nd···N distance is 4.040 Å. The Nd-O bond lengths of this complex are about 0.047 Å shorter than those of the $\mathrm{La(iPr_2dtp)_3(dma)_2}$; this difference is also comparable to the difference in the ionic radii of $\mathrm{Nd^{III}}$ and $\mathrm{La^{III}}$.[15] Therefore, the Nd-O bond lengths are shorter than those of the common oxygen-atom-ligating lanthanoid complexes (2.5 Å),[16,17,18] as in the case of the dma adduct of lanthanum.[1]

The positions of the coordinating oxygen atoms

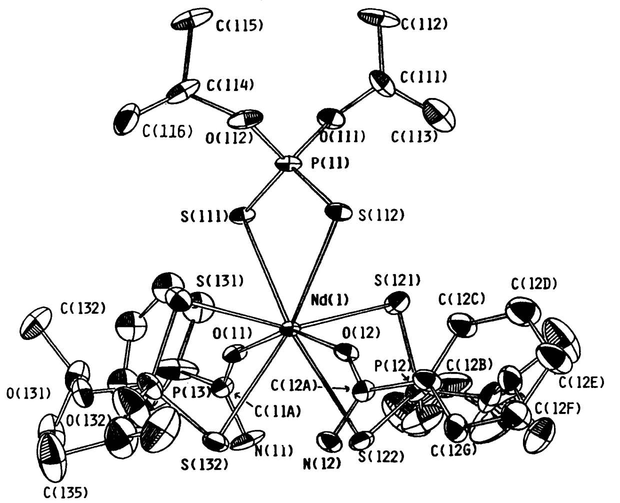

Fig. 1. A perspective drawing of the neodymium(III) complex around Nd(1) atom with numbering scheme.

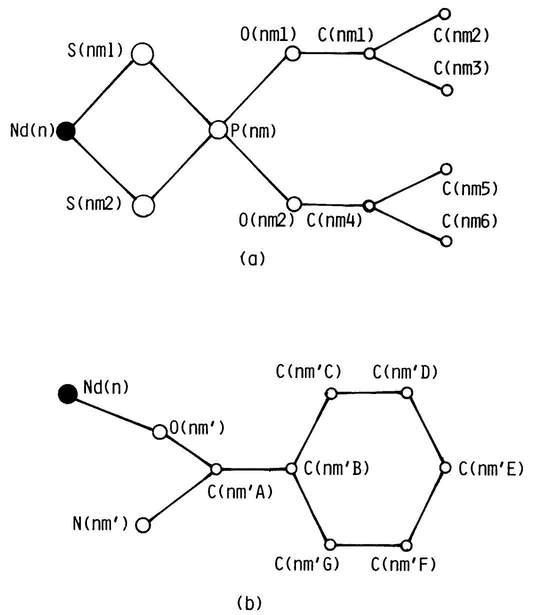

Fig. 2. Numbering scheme of the ligand atoms.
a) iPr_2dtp (where *n*: numbering of the central Nd(III) atom, 1—3; *m*: numbering of each iPr_2dtp ligand, 1—3). b) bza (where *n*: numbering of the central Nd(III) atom, 1—3; *m'*: numbering of each bza ligand, 1—2).

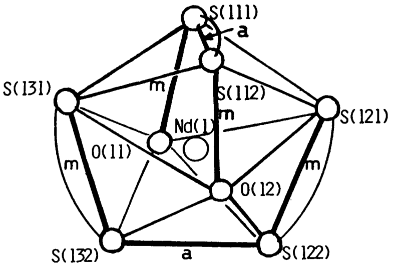

Fig. 3. Dodecahedron geometry around Nd(1) atom of the complex.

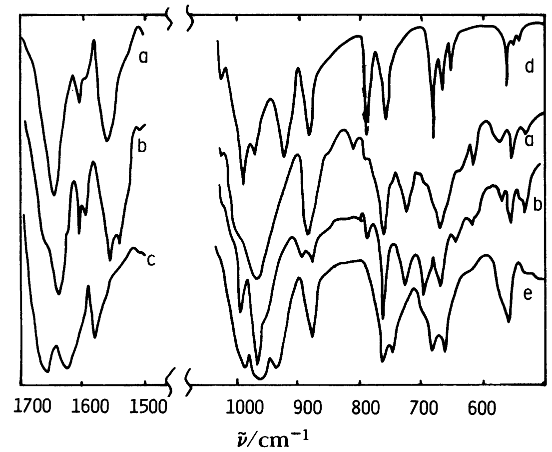

Fig. 4. Infrared spectra of the complex and some related compounds. a: $[Nd(iPr_2dtp)_3(bza)_2]$, b: $[Er(iPr_2dtp)_2(bza)_3](iPr_2dtp)$, c: bza, d: $Na[Nd(iPr_2dtp)_4]$, e: $Na(iPr_2dtp)$.

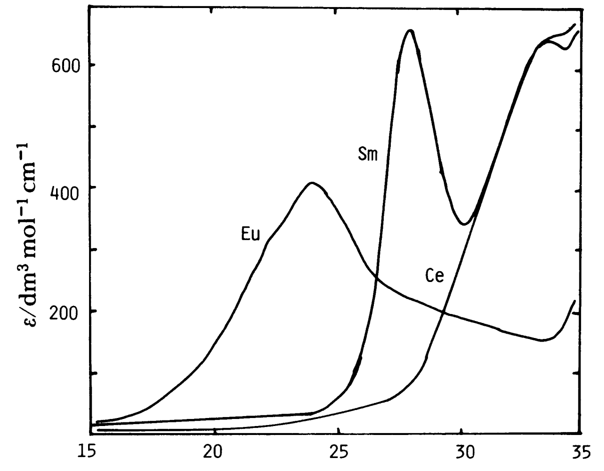

Fig. 5. Electronic spectra of $[M(iPr_2dtp)_3(bza)_2]$ type complexes (M=Ce, Sm, and Eu).

of the title complex are different from those of the $La(iPr_2dtp)_3(dma)_2$. This discrepancy is probably due to the bulkiness of the bza molecule. Although Pinkerton wrote that $La(Et_2dtp)_3\{(C_6H_5)_3PO\}_2$ is in a deformed square-antiprism geometry,[2c] it can also be regarded as in the deformed dodecahedron geometry. According to the latter aspect, two coordinating oxygen atoms of the complex take positions of the two tips of the base edge of a trapezium, like the titled complex.

The powder X-ray diffraction patterns of the $M(iPr_2dtp)_3(bza)_2$ (where M=La, Ce, Pr, Nd, Sm, Eu, and Gd) complexes show that they are all isomorphous.

The infrared-absorption spectral pattern of the title complex, benzamide, $Na[Nd(iPr_2dtp)_4]$, and $Na(iPr_2dtp)$ are shown in Fig. 4. As all of the isomorphous complexes show almost the same spectral pattern, only the spectra of the neodymium(III) complex are shown. The amide I and II bands of bza appear at about 1660, 1623, and 1578 cm^{-1}, the former one seeming to split into two peaks. In the spectra of the neodymium complex, the corresponding peaks appear in a wave-number region about 20 cm^{-1} lower. The bands characteristic of the iPr_2dtp ligand, $\nu_s(P-S)+\nu_s(P-O)$, $\nu_{as}(P-O)$, and $\nu_{as}(P-S)$, which were expected to be found near the

700-cm^{-1} region, appeared at 783, 748, and 676 cm^{-1} in the spectra of the title complex. Their wave numbers are a little lower than those of the corresponding peaks of Na[Nd(iPr$_2$dtp)$_4$].

The ultraviolet absorption spectra of the type of the cerium, samarium, and europium complexes in acetonitrile solutions (about 0.4—1.0×10^{-2} mol dm^{-3} in concentration) are shown in Fig. 5. The samarium and europium complexes show a very strong absorption in this region (Sm complex: ν_{max}=3.39×10^4 cm^{-1}, ε_{max}=6.4×10^2 dm^3 mol^{-1} cm^{-1}; Eu complex: ν_{max}=4.27×10^4 cm^{-1}, ε_{max}=4.2×10^2 dm^3 mol^{-1} cm^{-1}). This kind of band has already been found in the spectra of the lanthanoid complexes where sulfur atoms ligate the central metal atom, and it has been assigned as a charge-transfer band.[3,5,19] However, these iPr$_2$dtp–bza mixed complexes are found to be more stable than any other compounds ever reported which show the absorption band.

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13) Some additional data about bond lengths and bond angles, as well as the plane equations, the deviations of the atomic positions from the plane, and the dihedral angles between them of the trapezia of dodecahedrons, are also deposited as Document No. 8438 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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