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Syntheses, and Crystal and Molecular Structures of Tris(benzamide)-bis(*O,O'*-diisopropyl dithiophosphato)lanthanoid(III) *O,O'*-Diisopropyl Dithiophosphate (M=Gd, Tb, Dy, Er, and Yb)

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Five isomorphous lanthanoid(III) complexes were synthesized, and the structure of the terbium (**1**) and erbium (**2**) complexes were determined by the use of the single-crystal X-ray diffraction method. Crystals of **1** and **2** are monoclinic, with the space group $P2_1/n$, and the cell constants are: (**1**) a=25.076(8), b=15.446(3), c=14.579(8) Å, β=100.77(4)°; (**2**) a=25.036(20), b=15.228(4), c=14.805(19) Å, β=99.50(12)°. The structures were solved by the heavy-atom method and refined by the block-diagonal least-squares method. The final R values of **1** and **2** are 0.061 and 0.055 respectively. They consist of discrete complex cations and dithiophosphate anions. The central metal atom of the cationic complex is hepta-coordinated, and it is in a pentagonal bipyramidal geometry, where four sulfur atoms of two dithiophosphate ions and one oxygen atom of a benzamide ligand take the equatorial positions, while two benzamide oxygen atoms are in the axial positions.

Although lanthanoid elements are "hard" acid according to the HSAB theory,[1] their complexes of *O,O'*-dialkyl dithiophosphate (R_2dtp),[2-4] *N,N*-dialkyldithiocarbamates,[5] and dialkyl dithiophosphinates[6] have already been reported. Pinkerton obtained two kinds of *O,O'*-diethyl dithiophosphate-triphenylphosphine oxide lanthanoid(III) mixed complexes, $[M(Et_2dtp)_3\{(C_6H_5)_3PO\}_2]$ (where M=La—Pr, and Et=C_2H_5) and $[M(Et_2dtp)_2\{(C_6H_5)_3PO\}_3](Et_2dtp)$ (where M=Nd—Lu), and established their structures by means of the X-ray diffraction technique.[3] The present authors previously tried to obtain such types of mixed complexes of the *O,O'*-diisopropyl dithiophosphate, using *N,N*-dimethylacetamide (dma) as the additional ligand, but only $[M(iPr_2dtp)_3(dma)_2]$[where M=La or Nd; iPr=$(CH_3)_2CH$}-type complexes of light lanthanoids were obtained, as was reported in a previous paper.[7] Furthermore, we obtained a series of mixed complexes of the heavy lanthanoid elements with the formula $[M(iPr_2dtp)_2(bza)_3](iPr_2dtp)$ (where M=Gd, Tb, Dy, Er, and Yb; bza=benzamide). The present paper reports on the structures of the terbium(III) (**1**) and erbium(III) (**2**) complexes as determined by the X-ray diffraction technique.

Experimental

Preparation of $[Er(iPr_2dtp)_2(bza)_3](iPr_2dtp)$, and the Tb, Dy, and Yb Complexes. Erbium (III) chloride hexahydrate ($ErCl_3\cdot6H_2O$)(0.61 g, 1.6 mmol) and sodium *O,O'*-diisopropyl dithiophosphate (2.0 g, 8.6 mmol) were dissolved in 25 cm^3 of 2-propanol, and the solution was refluxed for 20 min at about 80 °C. After the residue had then been filtered off, 0.57 g (4.7 mmol) of benzamide was added to the filtrate and the mixture was allowed to stand for 5 min at about 65 °C to terminate the reaction. The solution was then evaporated to dryness using the vacuum rotary evaporator at about 65 °C. The residue was dissolved in 5 cm^3 of 2-propanol, the insoluble matter was filtered off, and the filtrate was left in a silica-gel desiccator for several days. The crystalline product was then filtered off, washed with diisopropyl ether, and dried in a vacuum desiccator at the ambient temperature. The yield was about 0.83 g (0.71 mmol, 45%). The Tb, Dy, and Yb complexes were obtained in almost the same way.

Preparation of $[Gd(iPr_2dtp)_2(bza)_3](iPr_2dtp)$. The added benzamide should be more than three times the metal salt in mole units. After the 2-propanol solution of the crude product has been concentrated by a vacuum rotary evaporator, it was left in diisopropyl ether vapor at the ambient temperature for several days. The $[Gd(iPr_2dtp)_2(bza)_3](iPr_2dtp)$ complex was thus precipitated. The yield of the complex was 0.80 g (0.69 mmol, 31%) from 0.83 g of $GdCl_3\cdot6H_2O$ (2.2 mmol).

$[Gd(iPr_2dtp)_3(bza)_2]$ was obtained if the added benzamide was less than 2.1 times the starting metal salt in mole units.

All the complexes thus obtained are stable in air for several months. The elemental analyses and their magnetic moments, as measured by means of a Gouy balance at the ambient temperature, are shown in Table 1.

TABLE 1. ANALYSES, YIELDS OF THE SYNTHESES, AND MAGNETIC MOMENTS OF THE COMPLEXES, $[Ln\{[(CH_3)_2CHO]_2PS_2\}_2(H_2NCOC_6H_5)_3][\{((CH_3)_2CHO)_2PS_2\}]$

Ln		Ln(%)	C(%)	H(%)	N(%)	Yield/%	μ_{eff}/BM[a]
Gd	Found	13.56	40.22	5.47	3.60	31	7.7_1
	Calcd	13.55	40.36	5.47	3.64		
Tb	Found	13.50	40.18	5.46	3.58	41	10.0_1
	Calcd	13.67	40.30	5.46	3.63		
Dy	Found	13.92	40.06	5.49	3.52	56	10.8_7
	Calcd	13.94	40.19	5.45	3.60		
Er	Found	14.61	39.92	5.48	3.47	45	9.5_8
	Calcd	14.29	40.00	5.43	3.59		
Yb	Found	14.74	39.31	5.28	3.56	67	4.3_9
	Calcd	14.71	39.83	5.40	3.57		

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

TABLE 2. FINAL ATOMIC COORDINATES (×10⁵ for M and 10⁴ for the other atoms) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS (B_{eq}/Å²) OF NON-HYDROGEN ATOMS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

	M=Tb				M=Er			
Atom	x	y	z	B_{eq}/Å²[a]	x	y	z	B_{eq}/Å²[a]
M	66953(2)	30631(2)	46182(3)	4.7	66847(2)	29933(3)	46826(4)	4.1
S(1)	6135(2)	1933(2)	3267(3)	9.3	6128(2)	1845(2)	3400(3)	7.9
S(2)	6762(1)	3689(2)	2829(2)	7.3	6801(1)	3573(2)	2938(2)	5.8
P(1)	6357(1)	2646(2)	2286(2)	7.9	6383(2)	2532(2)	2424(3)	6.3
S(3)	7368(1)	4560(2)	4783(2)	5.1	7372(1)	4470(2)	4815(2)	4.5
S(4)	7029(1)	3495(2)	6541(2)	5.8	6999(1)	3433(2)	6541(2)	5.5
P(2)	7486(1)	4423(2)	6160(2)	5.0	7471(1)	4357(2)	6169(2)	4.5
S(5)	9221(1)	2466(2)	1114(2)	7.3	9177(1)	2454(2)	1080(3)	6.9
S(6)	9192(1)	1428(2)	3131(3)	8.9	9120(2)	1391(2)	3048(3)	8.8
P(3)	9289(1)	2509(2)	2477(2)	7.2	9202(1)	2495(2)	2400(3)	6.8
O(100)	7439(2)	2250(4)	4677(5)	7.4	7402(3)	2146(5)	4764(5)	6.2
O(200)	5954(2)	3914(3)	4569(4)	5.2	5960(3)	3861(4)	4607(5)	4.8
O(300)	6267(2)	2052(3)	5407(5)	5.7	6267(3)	2010(5)	5477(5)	5.7
C(101)	7841(4)	1833(5)	4517(7)	6.0	7813(4)	1766(7)	4569(8)	5.9
C(102)	7947(4)	957(6)	4923(7)	6.3	7967(5)	914(8)	4988(9)	6.8
C(103)	7647(4)	667(7)	5537(9)	8.4	7679(6)	567(8)	5593(10)	7.9
C(104)	7739(5)	−133(8)	5943(10)	9.8	7811(7)	−221(10)	6021(10)	9.4
C(105)	8120(6)	−633(8)	5757(11)	11.4	8215(8)	−673(12)	5869(14)	13.9
C(106)	8393(8)	−390(11)	5092(17)	22.1	8509(12)	−340(17)	5289(23)	31.9
C(107)	8327(7)	415(9)	4693(14)	17.9	8392(10)	461(15)	4844(21)	27.2
N(1)	8170(3)	2191(5)	4009(7)	7.3	8091(4)	2133(7)	3986(7)	7.9
C(201)	5735(3)	4597(5)	4202(6)	4.9	5749(4)	4554(7)	4209(7)	4.4
C(202)	5133(3)	4619(5)	3863(6)	5.1	5152(4)	4592(7)	3897(7)	4.2
C(203)	4845(3)	3900(6)	4017(8)	6.2	4848(4)	3872(8)	4042(9)	5.9
C(204)	4274(4)	3892(7)	3724(9)	7.8	4293(4)	3862(8)	3760(11)	7.6
C(205)	4022(4)	4602(7)	3259(9)	7.6	4055(4)	4592(8)	3320(10)	6.8
C(206)	4319(4)	5303(7)	3101(9)	7.7	4365(5)	5297(8)	3158(10)	7.3
C(207)	4876(3)	5328(6)	3393(8)	6.6	4914(4)	5310(7)	3430(9)	6.0
N(2)	6028(3)	5279(4)	4102(7)	6.8	6065(3)	5241(5)	4131(7)	5.9
C(301)	5870(3)	1840(5)	5719(7)	5.0	5841(4)	1811(7)	5766(7)	4.7
C(302)	5745(3)	919(5)	5831(6)	4.6	5712(4)	861(6)	5880(7)	4.3
C(303)	5343(4)	647(6)	6293(7)	6.2	5295(5)	613(7)	6315(8)	6.0
C(304)	5230(4)	−206(7)	6377(9)	7.8	5184(5)	−270(8)	6396(9)	7.5
C(305)	5515(4)	−812(7)	5985(9)	8.4	5465(6)	−882(8)	6033(10)	7.9
C(306)	5914(5)	−562(7)	5532(10)	9.0	5893(6)	−628(8)	5613(11)	8.1
C(307)	6036(4)	322(6)	5452(7)	6.3	6025(5)	247(7)	5541(9)	6.0
N(3)	5542(3)	2458(5)	5939(6)	6.9	5514(4)	2446(6)	5957(7)	6.7
O(1)	5865(3)	2894(5)	1512(5)	7.9	5914(3)	2794(5)	1636(5)	6.7
C(11)	5410(5)	3424(9)	1709(8)	9.3	5462(5)	3363(10)	1829(9)	7.7
C(12)	4903(5)	2864(12)	1557(12)	14.0	4938(6)	2834(14)	1649(14)	13.0
C(13)	5337(6)	4214(9)	1091(12)	11.8	5439(8)	4180(11)	1216(13)	11.3
O(2)	6676(3)	2126(6)	1621(7)	11.3	6719(4)	1918(6)	1871(7)	9.4
C(21)	7240(6)	2048(8)	1700(11)	11.4	7176(9)	2080(12)	1536(15)	16.6
C(22)	7381(8)	1093(10)	2073(16)	16.4	7554(7)	1472(23)	1586(27)	32.0
C(23)	7462(8)	2207(15)	932(13)	17.8	6971(24)	2096(27)	570(23)	44.8
O(3)	7377(2)	5282(4)	6672(4)	6.0	7359(3)	5242(5)	6655(5)	5.5
C(31)	7655(4)	6098(6)	6514(8)	6.8	7660(5)	6052(8)	6506(9)	6.5
C(32)	7205(5)	6787(7)	6320(10)	9.1	7222(6)	6763(8)	6300(11)	8.2
C(33)	8104(5)	6264(8)	7365(9)	9.0	8102(6)	6208(10)	7353(10)	8.8
O(4)	8114(2)	4290(4)	6557(5)	6.2	8092(3)	4214(5)	6575(5)	5.8
C(41)	8441(4)	3632(7)	6189(8)	7.4	8433(5)	3560(9)	6212(10)	7.4
C(42)	8554(5)	2898(9)	6891(12)	11.3	8548(6)	2819(10)	6898(13)	10.6
C(43)	8942(4)	4105(10)	6015(10)	11.1	8929(6)	4049(12)	6016(13)	12.1
O(5)	8867(3)	3185(4)	2778(6)	9.1	8761(4)	3147(5)	2685(7)	8.7
O(51)	8819(6)	4078(7)	2423(10)	10.9	8709(7)	4071(8)	2373(11)	9.4
C(52)	8292(6)	4180(9)	1772(13)	12.6	8215(7)	4168(11)	1636(14)	12.2
C(53)	8900(8)	4670(8)	3327(12)	13.8	8711(11)	4616(10)	3234(14)	15.9
O(6)	9882(3)	2912(4)	2838(6)	8.7	9775(4)	2952(6)	2781(6)	7.9
C(61)	10194(6)	2856(9)	3802(10)	10.3	10069(7)	2906(12)	3722(10)	10.7
C(62)	10379(8)	3770(12)	4074(15)	16.9	10267(10)	3844(15)	4013(17)	17.0
C(63)	10642(7)	2230(13)	3768(13)	15.5	10519(8)	2284(16)	3750(16)	16.5

a) The equivalent isotropic temperature factors for non-hydrogen atoms 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: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

Single-crystal X-ray Analysis. **1** and **2** are isomorphous and monoclinic, the space group being $P2_1/n$. Their crystallographic data are as follows:

1. $TbC_{39}H_{63}N_3O_9P_3S_6$, F. W.=1162.3, a=25.076(8), b=15.446(3), c=14.579(8) Å, β=100.77(4)°, U=5547(3) Å^3, D_m=1.41(3), D_x=1.39 Mg m^{-3}, μ(Mo $K\alpha$)=1.67 mm^{-1}, Z=4.

2. $ErC_{39}H_{63}N_3O_9P_3S_6$, F. W.=1170.4, a=25.036(20), b=15.228(4), c=14.805(19) Å, β=99.50(12)°, U=5567(8) Å^3, D_m=1.41(3), D_x=1.39 Mg m^{-3}, μ(Mo $K\alpha$)=1.94 mm^{-1}, Z=4.

The crystals of **1** and **2** used for the structure determination were about 0.3×0.3×0.4 mm^3 in size. All their edges were ground off, but they were not shaped into spheres.

The reflections in the range of $3°<2\theta<50°$ were collected on a Rigaku AFC-6A automated four-circle diffractometer, with graphite monochromated Mo $K\alpha$ radiation (the scan speed and scan width for **1** and **2** were 2° min^{-1} and 1.40+0.5tanθ°, and 4° min^{-1} and 1.50+0.5tanθ°, respectively), the ω-scan technique being employed. The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction. Among the 10196 and 10222 independent reflections collected for **1** and **2**, 6538 and 5220 with $|F_o|>3\sigma(|F_o|)$ were respectively used for the structure determination.

Structure Determination. The structure of **2** was solved by the heavy-atom method. The positional and thermal parameters were refined by the block-diagonal least-squares method. Although all the non-hydrogen atoms were found, we could not determine the positions of any hydrogen atoms from the Fourier map.[8] At the first stage of the refinement of **1**, the positional and thermal parameters of **2** were tentatively applied; they were then refined by the block-diagonal least-squares method in the same way as that of **2**.

The final R values obtained for **1** and **2** are 0.061 and 0.055 respectively,[9] applying the anisotropic temperature factors for non-hydrogen atoms. In each calculation, twenty-one hydrogen atoms obtained by the calculation[8] were included, with their positional and thermal parameters fixed and assuming B_{iso}=10.0.

There is a large void near a isopropyl group (C(22), C(23)) and a phenyl group (C(106), C(107)), and the thermal parameters of these four atoms are abnormally large, although no significant peaks remained in the difference Fourier synthesis map.

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.[10] The atomic-scattering factors were taken from Ref. 11.

Other Measurements. The visible absorption spectra were measured with a Hitachi 124 spectrophotometer. The X-ray powder patterns of these complexes were obtained by the use of Model DX-GO-F JEOL, using Cu $K\alpha$ radiation in the range from 4° to 40° in 2θ.

Results and Discussion

The final atomic parameters of **1** and **2** are listed in Table 2, while the bond lengths and angles and short intermolecular distances are tabulated in Table 3.[12] The perspective drawing of **1** around the central

TABLE 3. SELECTED BOND LENGTHS AND BOND ANGLES OF THE Tb AND Er COMPLEXES, $[M\{[(CH_3)_2CHO]_2PS_2\}_2(H_2NCOC_6H_5)_3]\{(CH_3)_2CHO\}_2PS_2$ (where M=Tb, Er), WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond length	l/Å		Bond length	l/Å	
	M=Tb	M=Er		M=Tb	M=Er
M-S(1)	2.806(4)	2.781(5)	M-S(2)	2.816(4)	2.790(6)
M-S(3)	2.845(2)	2.818(3)	M-S(4)	2.850(4)	2.814(6)
M-O(100)	2.236(6)	2.198(7)	M-O(200)	2.267(5)	2.232(7)
M-O(300)	2.296(7)	2.264(9)	S(1)-P(1)	1.967(6)	1.973(7)
S(2)-P(1)	1.988(4)	1.981(5)	P(1)-O(1)	1.556(8)	1.564(10)
P(1)-O(2)	1.586(12)	1.575(12)	S(3)-P(2)	1.985(5)	1.986(6)
S(4)-P(2)	1.978(4)	1.973(5)	P(2)-O(3)	1.572(7)	1.575(9)
P(2)-O(4)	1.587(6)	1.586(8)	S(5)-P(3)	1.964(6)	1.946(8)
S(6)-P(3)	1.961(4)	1.964(6)	P(3)-O(5)	1.605(8)	1.593(10)
P(3)-O(6)	1.605(8)	1.610(9)	O(100)-C(101)	1.255(12)	1.255(15)
O(200)-C(201)	1.261(10)	1.279(13)	O(300)-C(301)	1.252(12)	1.251(14)
S(6)···N(1)	3.290(10)	3.319(14)	N(3)···S(5^{i})	3.371(9)	3.386(11)
S(5)···N(2^{ii})	3.439(7)	3.429(9)			
Bond angle	**ϕ/°**		**Bond angle**	**ϕ/°**	
	M=Tb	M=Er		M=Tb	M=Er
S(1)-M-S(2)	70.85(11)	71.57(13)	S(1)-M-S(3)	140.93(9)	141.31(11)
S(1)-M-S(4)	148.50(10)	147.67(12)	S(1)-M-O(100)	88.98(18)	88.9(2)
S(1)-M-O(200)	92.18(15)	91.53(19)	S(1)-M-O(300)	73.47(19)	73.5(2)
S(3)-M-S(4)	70.50(8)	70.91(11)	O(100)-M-O(200)	179.7(2)	179.7(2)
O(100)-M-O(300)	92.8(2)	91.5(3)	M-S(1)-P(1)	88.36(17)	88.89(19)
M-S(2)-P(1)	88.65(16)	88.46(17)	S(1)-P(1)-S(2)	111.0(2)	110.9(2)
S(1)-P(1)-O(1)	111.8(3)	112.7(4)	S(2)-P(1)-O(2)	112.1(4)	112.4(4)
M-S(3)-P(2)	88.45(14)	88.52(17)	M-S(4)-P(2)	88.44(15)	88.91(18)
S(3)-P(2)-S(4)	112.10(17)	111.2(2)	S(3)-P(2)-O(3)	112.6(3)	112.6(3)
S(4)-P(2)-O(4)	113.1(2)	113.0(3)	S(5)-P(3)-S(6)	117.9(2)	118.4(2)
S(5)-P(3)-O(5)	111.2(3)	112.2(4)	S(6)-P(3)-O(6)	111.2(3)	111.0(4)
M-O(100)-C(101)	167.1(6)	162.1(7)	M-O(200)-C(201)	141.9(5)	141.4(7)
M-O(300)-C(301)	147.2(6)	146.3(7)	O(100)-C(101)-N(1)	119.7(8)	119.8(11)

Keys to the symmetric opertions: i: −0.5+x, 0.5−y, 0.5+z; ii: 1.5−x, −0.5+y, 0.5−z.

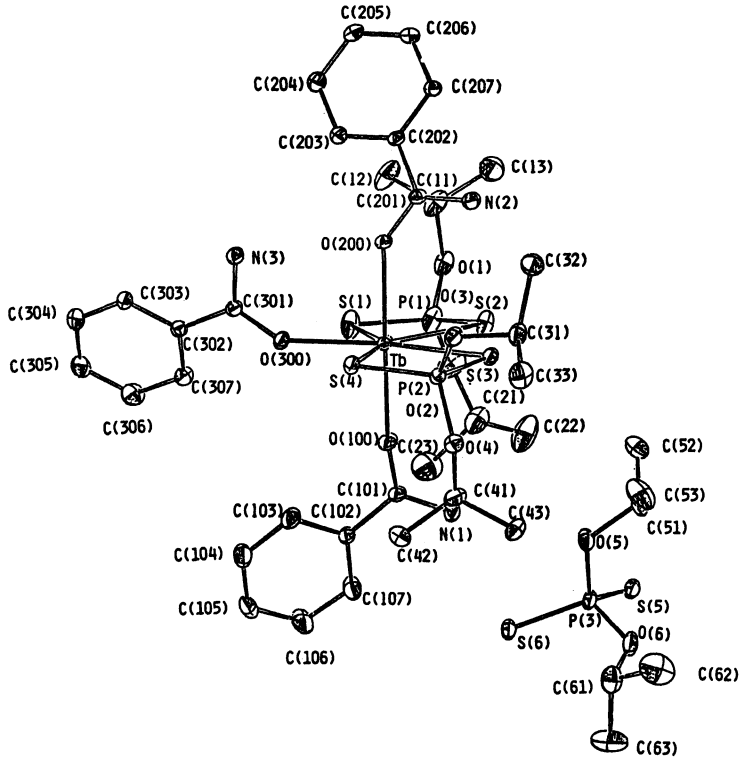

Fig. 1. A perspective drawing of the terbium(III) complex with the numbering scheme.

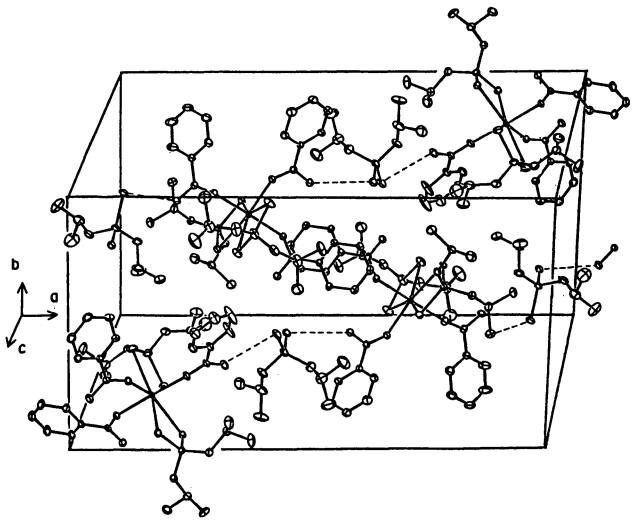

Fig. 2. Crystal packing diagram of the terbium(III) complex.

metal atom, together with the numbering scheme, is shown in Fig. 1, and the crystal packing diagram, in Fig. 2. The general features of **2** are the same as those of **1**, and the numbering scheme of **2** is the same as that of **1**. The metal atoms in the crystals have no mutual magnetic interaction with each other, judging from the magnetic-moment data shown in Table 1. The complex molecule is mono-cationic, and its electric charge is balanced by the $(iPr_2dtp)^-$ anion existing separately. Some interatomic distances, such as S(6)···N(1), N(3)···S(5^{i}), S(5)···N(2^{ii}) (where the keys to the symmetry operations are: i: $-0.5+x$, $0.5-y$, $0.5+z$; ii: $1.5-x$, $-0.5+y$, $0.5-z$), are shorter than 3.5 Å; they may be hydrogen bonds, since the S···H–N hydrogen bond has been reported to be about 3.42 Å in length between S and N.[13]

The central metal atom of the complex is heptacoordinated and is in a pentagonal-bipyramidal geometry, where four sulfur atoms of two iPr_2dtp ligands and one oxygen atom of a bza ligand take the equatorial position, while two bza oxygen atoms from the two ends of the axis. The positional deviations of the coordinated sulfur and oxygen atoms, as well as of the central metal atom, from the average pentagon plane are: **1**. 0.095 Å at the maximum (0.055 Å in the average); **2**. 0.070 Å at the maximum (0.041 Å in average).

As is shown in Table 3, the bond lengths of the M–S pair of each coordinated ligand are approximately the same; however, M–S(1) and M–S(2) are significantly shorter than M–S(3) and M–S(4). The difference in the average M–S bond lengths of Complexes **1** and **2** is 0.029 Å, which is comparable with the difference in their ionic radii, Tb=1.040 and Er=1.004 Å.[14]

The bond lengths of the P–S pair of each ligand are approximately the same, too. Therefore, it is likely that the P=S double bonds of the ligands in both complexes are delocalized. Each Er–O bond length is shorter than that of the corresponding Tb–O by about 0.035 Å; this is also approximately the same as the difference in the ionic radii. The metal–oxygen bond length of the equatorial ligand (Er of Tb–O(300)) is slightly longer than those of the axial ligands in each complex, probably because of the steric effect of the vicinal sulfur atoms on the plane. The other bond lengths, as well as the bond angles of **2** are in good agreement with the corresponding values of **1**. The unit-cell volume of **2** is

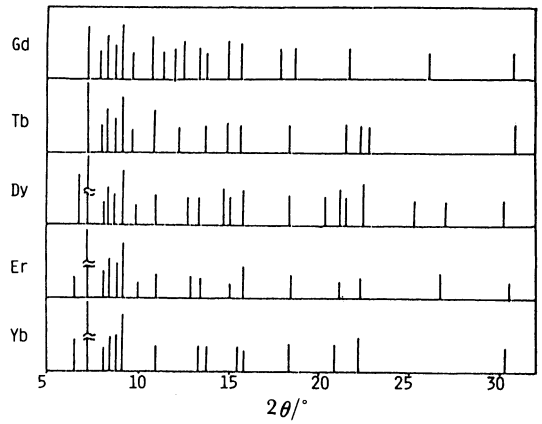

Fig. 3. X-Ray powder patterns of the five lanthanoid(III) complexes.

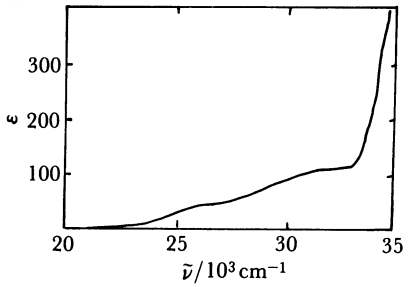

Fig. 4. Absorption spectra of the Yb(III) complex in an acetonitrile solution. (1.88 mmol dm^{-3})

larger than that of **1**, although the unit-cell volume of the series of isomorphous lanthanoid(III) complexes commonly decreases when the metal atomic number increases.[15-18]

The X-ray powder patterns of the gadolinium(III), terbium(III), dysprosium(III), erbium(III), and ytterbium(III) complexes, which have the same chemical formula, judging from the results of elemental analysis, are shown in Fig. 3. They can likely be divided into two groups on the base of their features; Gd(III) and Tb(III) make one group, and the others, another one. This is why we have analysed the two isomorphous structures of **1** and **2**.

In some lanthanoid complexes, extraordinary charge-transfer bands in the near-ultraviolet region have been reported.[2,5,19] The absorption spectra of the Yb complex in an acetonitrile solution are shown in Fig. 4. Although the solid is colorless, the solution is yellow in color, and a charge-transfer band is found at about 33000 cm^{-1}.

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