The Crystal and Molecular Structure of Tetrakis(μ-1-hydroxy-2-naphthoato)-bis{aqua(ethanol)(1-hydroxy-2-naphthoato)neodymium(III)}-Water–Ethanol (1/2/2), $[\{Nd[C_{10}H_6(OH)(COO)]_3(H_2O)(C_2H_6O)\}_2]\cdot 2H_2O\cdot 2C_2H_6O$

Yoshiyuki Ohki,† Yasuo Suzuki,† Toshio Takeuchi,†† 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
††Department of Natural Sciences, Faculty of Science and Technology, Sophia University, Kioi, Chiyoda-ku, Tokyo 102

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The structure of the title complex was determined by the single-crystal X-ray-diffraction method. It is triclinic, with the space group $P\bar{1}$; the cell constants were a=12.529(2), b=15.044(4), c=10.063(1) Å, α=104.15(2), β=98.73(1), and γ=87.16(2)°; Z=1, and the final R value was 0.053. The central metal atom is in a tricapped trigonal-prism geometry and is ennea-coordinated with seven oxygen atoms of the carboxylate ligands and with each oxygen atom of one water and one ethanol molecule. The complex is dimeric and the metal atoms are bridged with four carboxylate ions; two of them act as bidentates, and the other two, as tridentates, where one oxygen atom is coordinated to both metal atoms. The other carboxylate ion makes a chelate ring with each metal atom. The dimer is connected through hydrogen bondings to the atoms on both sides along the c-axis.

It has already been reported by several authors that carboxylate complexes of lanthanoids(III) take many kinds of geometries.[1–5] In cases of the aromatic carboxylates,[1,3] as well as of some nicotinates and isonicotinates,[4,6] the central metal is in a square-antiprism geometry and is octa-coordinated, where the squares of the complex molecules are parallel and are lined up along one axis. They are dimeric or linear polymeric bridged by the carboxylate ligands. On the other hand, acetates of some heavy lanthanoids[5] and cerium(III) *m*-hydroxybenzoate,[7] for example, take the tricapped trigonal prism geometry, and the central metal atoms are ennea-coordinated. The geometries of the complexes are thought to depend on the size of the ligand compared with that of the metal atom, as well as on the substituted groups of the carboxylate ions, which affect the mutual interaction of the ligand molecules. In a previous paper, we have reported about the interesting structures of some lanthanoid 2-naphthalenesulfonates, where the hydrophobic layer of the naphthalene rings makes a sheet between the hydrophilic metal complex cores, which form network layers bridged by hydrogen bondings via water molecules.[8] Along this line of research, we have tried to determine the structure of the title complex, where the ligand molecule has a naphthalene ring as well as a carboxyl group, using the single-crystal X-ray-diffraction method.

Experimental

Synthesis of Tetrakis(μ-1-hydroxy-2-naphthoato)-bis{aqua(ethanol)(1-hydroxy-2-naphthoato)neodymium(III)}-water–ethanol (1/2/2) (1). Neodymium(III) chloride hexahydrate (0.72 g, 2.0 mmol) was dissolved in water, and an excess of sodium hydroxide (in an aqueous solution) was added. The hydroxide thus precipitated was filtered off, washed with water, and warmed (60 °C) in 20 cm^3 of an ethanol-water mixture (2:1=v/v), together with 1-hydroxy-2-naphthoic acid (1.13 g, 6.0 mmol), for 30 min: The solution obtained was then filtered off. The filtrate was left standing for several days at ambient temperature, thus precipitating the crystals. The crystals thus obtained effloresced in a few min when they were separated from their mother liquor; however, they are stable for several weeks if they are not dried. By the same way of synthesis, praseodymium, samarium, dysprosium, and erbium complexes were obtained in a crystalline state, but all of them effloresce rapidly, too. Especially the crystals of the erbium complex cleave even when they are left in pure ethanol, water, or a mixture of them. The elemental analysis of the complex after it has dried for 24 h on a vacuum silica-gel desiccator shows it to be the dihydrate; all the ethanol is removed. Found: Nd, 19.80: C, 53.58: H, 3.29%. Calcd for $NdC_{33}H_{25}O_{11}$: Nd, 19.44: C, 53.43: H, 3.40%. The mass-loss of the rapidly washed and dried sample after it has been left standing on the vacuum silica-gel desiccator for 24 h: Found: 11.11%. Calcd for the difference between $NdC_{37}H_{37}O_{13}$ and $NdC_{33}H_{25}O_{11}$ (corresponding to two ethanols per neodymium) : 11.05%.

Thermal Analysis. Simultaneous thermogravimetric (TG) and differential thermal analyses (DTA) were carried out with a Rigaku-Denki "Thermoflex" M-8075, using a sample of about 10 mg in each run, with reference to Al_2O_3, at the heating rate of 10 K min^{-1}.

Single-Crystal X-Ray Analysis. A crystal 0.45×0.30×0.20 mm^3 in size was used as the sample. It was sealed in a glass capillary immediately after having been picked out from the mother liquor. Crystallographic data: $Nd_2C_{74}H_{74}O_{26}$, F.W. 1667.86, triclinic, space group $P\bar{1}$, a=12.529(2), b=15.044(4), c=10.063(1) Å, α=104.15(2), β=98.73(1), γ=87.16(2)°, U=1817.7(6) Å^3, Z=1, D_x=1.52, D_m=1.52(3) Mg m^{-3} by floatation in a CH_2BrCH_2Br-CCl_4 mixture, μ(Mo $K\alpha$)=1.51 mm^{-1}. The reflections were collected on a Rigaku AFC-6A automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (0.7107 Å), in the range of $3° < 2\theta < 65°$, the ω—2θ scan technique being employed (scan speed: 4° min^{-1} (θ): scan width: $(1.25+0.5\tan\theta)°$). Of the 13315 independent reflections observed, 10370 $|F_o| > 3\sigma(|F_o|)$ reflections were used for the refinement. The intensities were corrected for the Lorentz and polarization factors, but no correction was made for absorption or extinction.

Structure Determination. The structure was solved by the heavy-atom method. The positions of the metal and some oxygen atoms were deduced from the three-dimensional Patterson map. The positional and thermal parameters were refined successively by the repeated block-diagonal least-squares method and by Fourier syntheses. At the end, all the non-hydrogen atoms were found. An uncoordinated water molecule was found to be disordered and to have been divided into two: The occupancy factors of O(W2A) and O(W2B) were determined to be 0.66 and 0.34, respectively. The atoms of one ethanol molecule, O(E2), C(E3), and C(E4), are fixed assuming their isotropic temperature parameters to be 8.0. The positions of the naphthalene hydrogen atoms were calculated by assuming the C–H bond length to be 1.08 Å; their B_{iso}'s were assumed to be 6.0. The parameters of the hydrogen atoms were also fixed in the refinement. The final R value was 0.053, R_w=0.065, and S=4.07.[9]

All the calculations were carried out on a HITAC M-280H apparatus 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.

Infrared-Absorption-Spectrum Measurement. The infrared-absorption spectra were obtained by means of a JASCO A202 grating infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mull.

Results and Discussion

The final atomic parameters are listed in Table 1, while some bond lengths and bond angles, as well as some interatomic distances which are thought to be the hydrogen-bonding ones, are tabulated in Table 2. The projection of the unit-cell along the a-axis, the perspective drawing along the metal–metal axis, and the schematic presentation of the coordination geometry around the central metal atom are shown in Figs. 1, 2, and 3.[12]

The complex is dimeric, with a center of inversion between the metal atoms, bridged by four carboxylate ligands. As is depicted in Fig. 3, the metal atom is ennea-coordinated and is in a deformed tricapped trigonal prism geometry, where seven oxygen atoms of five carboxylate ligands and two oxygen atoms of ethanol and water molecules are bound to the metal atom.

A pair of carboxylates span two neodymium atoms through both oxygen atoms of each carboxyl group. As is shown in Table 1, the C–O and Nd–O bond lengths of two oxygen atoms of this type of ligand are not equal. The longer C–O bonding has the longer Nd–O bond; therefore, the double-bonding oxygen atom, not the single-bonding oxygen atom, of the carboxyl group bonds with the metal atom more strongly. The other pair of carboxylate ligands act as a "tridentate" bridge: one of the oxygen atoms is bridging two metal atoms, and the other oxygen atom is coordinating to one of the metal atoms to form a chelate ring at the same time.

Table 1. Final Atomic Coordinates (×10⁴), with Estimated Standard Deviations in Parentheses, and Their Equivalent Isotropic Temperature Factors ($B_{eq}/\text{Å}^2$)

Atom	x	y	z	$B_{eq}/\text{Å}^{2\,a)}$	Atom	x	y	z	$B_{eq}/\text{Å}^{2\,a)}$
Nd	4586.5(2)	4543.3(2)	2906.3(3)	2.3_8	C(12)	6257(4)	2508(3)	122(5)	3.0_4
O(1)	6755(3)	4361(2)	6076(4)	3.4_8	C(13)	7128(5)	2725(4)	−471(7)	4.8_8
O(2)	6319(3)	3997(3)	3775(4)	3.9_2	C(14)	7881(6)	2089(5)	−883(8)	5.8_6
O(3)	4764(3)	3024(3)	1314(4)	3.5_5	C(15)	7815(5)	1182(4)	−732(6)	4.0_5
O(4)	5688(3)	4066(2)	833(4)	3.8_0	C(16)	8640(6)	510(5)	−1071(8)	5.6_6
O(5)	5411(3)	5966(2)	2793(4)	3.6_1	C(17)	8577(6)	−344(5)	−885(8)	5.9_6
O(6)	5530(3)	5896(2)	4947(4)	3.4_3	C(18)	7674(6)	−588(4)	−377(7)	5.2_4
O(W1)	3521(3)	5011(3)	870(4)	3.7_4	C(19)	6866(5)	30(4)	−56(6)	4.1_3
O(E1)	2843(3)	3696(3)	2326(4)	3.9_8	C(20)	6940(4)	937(3)	−201(5)	3.1_6
O(C1)	8398(3)	3610(3)	7184(4)	4.1_3	C(21)	5965(4)	7827(3)	3526(5)	2.9_6
O(C11)	5324(4)	1354(3)	741(5)	4.5_1	C(22)	5795(4)	7347(3)	4492(5)	2.9_4
O(C21)	5932(4)	7410(3)	2173(4)	4.0_4	C(23)	5831(5)	7832(4)	5905(5)	4.0_1
C(C1)	6883(4)	3893(4)	4854(5)	3.0_6	C(24)	6034(5)	8735(4)	6319(5)	4.0_6
C(C2)	5531(4)	3237(3)	747(5)	3.0_0	C(25)	6223(4)	9231(3)	5363(5)	3.2_4
C(C3)	5574(4)	6356(3)	4066(5)	2.8_9	C(26)	6455(5)	10179(4)	5779(6)	4.0_0
C(1)	8455(4)	3071(3)	5899(5)	3.0_5	C(27)	6623(5)	10649(4)	4837(7)	4.3_6
C(2)	7755(4)	3187(3)	4754(5)	3.0_1	C(28)	6558(6)	10208(4)	3434(7)	4.7_3
C(3)	7858(5)	2599(4)	3445(6)	4.1_4	C(29)	6334(5)	9284(4)	2978(6)	4.0_3
C(4)	8630(5)	1934(4)	3294(7)	4.8_1	C(30)	6178(4)	8778(3)	3940(5)	2.9_8
C(5)	9358(4)	1814(4)	4452(6)	3.8_3	C(E1)	1894(7)	3786(6)	2990(11)	7.9_1
C(6)	10166(5)	1119(4)	4316(8)	5.1_8	C(E2)	1288(9)	2965(8)	2673(15)	11.2_8
C(7)	10871(5)	1018(5)	5442(9)	5.7_7	O(W2A)	7594(7)	7151(6)	404(8)	6.2_9
C(8)	10800(5)	1581(5)	6755(8)	5.6_8	O(W2B)	7698(12)	6636(10)	524(15)	5.6_2
C(9)	10022(5)	2259(4)	6919(7)	4.5_1	O(E2)	8309	5499	1001	(8.0)
C(10)	9278(4)	2387(4)	5764(6)	3.4_0	C(E3)	8002	5207	2194	(8.0)
C(11)	6150(4)	1614(3)	214(5)	3.0_1	C(E4)	8901	5205	3296	(8.0)

a) The equivalent isotropic temperature factors were computed using the following equation:

$$B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha).$$

The B_{ij}'s are defined by:

$$T=\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})].$$

Table 2. Selected Interatomic Distances and Bond Angles of the Complex

Bond length	(l/Å)	Bond length	(l/Å)	Bond length	(l/Å)
Nd-O(1^{i})	2.452(4)	Nd-O(2)	2.398(4)	Nd-O(3)	2.471(4)
Nd-O(4)	2.611(4)	Nd-O(5)	2.457(4)	Nd-O(6)	2.685(3)
Nd-O(W1)	2.501(4)	Nd-O(E1)	2.503(4)	Nd-O(6^{i})	2.435(5)
O(1)-C(C1)	1.288(7)	O(2)-C(C1)	1.241(7)	C(C1)-C(2)	1.482(7)
O(3)-C(C2)	1.280(7)	O(4)-C(C2)	1.252(6)	C(C2)-C(12)	1.471(7)
O(5)-C(C3)	1.262(6)	O(6)-C(C3)	1.261(8)	C(C3)-C(22)	1.474(7)
O(W1)···O(4^{ii})	2.769(7)	O(W1)···O($\mathrm{E2}^{\mathrm{ii}}$)	2.747(4)	O(E2)···O(W2A)	2.773(9)
O(W2A)···O(C21)	2.893(11)	Nd···Nd^{i}	4.087(1)	Nd···$\mathrm{Nd}^{\mathrm{ii}}$	6.564(1)
Bond angle	(ϕ/°)	Bond angle	(ϕ/°)	Bond angle	(ϕ/°)
O(1^{i})-Nd-O(6)	68.61(11)	O(1^{i})-Nd-O(6^{i})	77.62(14)	O(1^{i})-Nd-O(E1)	74.47(12)
O(1^{i})-Nd-O(5)	81.37(13)	O(6)-Nd-O(6^{i})	74.18(13)	O(6)-Nd-O(2)	71.88(12)
O(6)-Nd-O(5)	49.89(12)	O(6^{i})-Nd-O(2)	70.66(14)	O(6^{i})-Nd-O(E1)	78.05(14)
O(E1)-Nd-O(5)	142.71(13)	O(2)-Nd-O(5)	90.10(13)	O(2)-Nd-O(E1)	127.03(13)
O(W1)-Nd-O(3)	86.16(13)	O(W1)-Nd-O(4)	71.91(14)	O(W1)-Nd-O(5)	74.48(14)
O(W1)-Nd-O(E1)	72.43(13)	O(3)-Nd-O(4)	50.70(13)	O(3)-Nd-O(E1)	68.56(12)
O(3)-Nd-O(2)	76.64(12)	O(4)-Nd-O(2)	72.66(13)	O(4)-Nd-O(5)	75.02(14)
O(1^{i})-Nd-O(W1)	76.11(13)	O(6)-Nd-O(4)	112.43(12)	O(6^{i})-Nd-O(3)	100.89(14)
C(C1)-O(1)-Nd^{i}	136.4(3)	C(C1)-O(2)-Nd	142.6(4)	O(1)-C(C1)-O(2)	123.9(5)
C(C2)-O(3)-Nd	96.4(3)	C(C2)-O(4)-Nd	90.5(3)	O(3)-C(C2)-O(4)	118.9(5)
C(C3)-O(5)-Nd	99.7(3)	C(C3)-O(6)-Nd^{i}	163.0(4)	C(C3)-O(6)-Nd	88.9(3)
O(5)-C(C3)-O(6)	119.4(5)	Nd-O(6)-Nd^{i}	105.82(14)		

Keys to the symmetric operations: i, $1-x$, $1-y$, $1-z$, ii, $1-x$, $1-y$, $-z$.

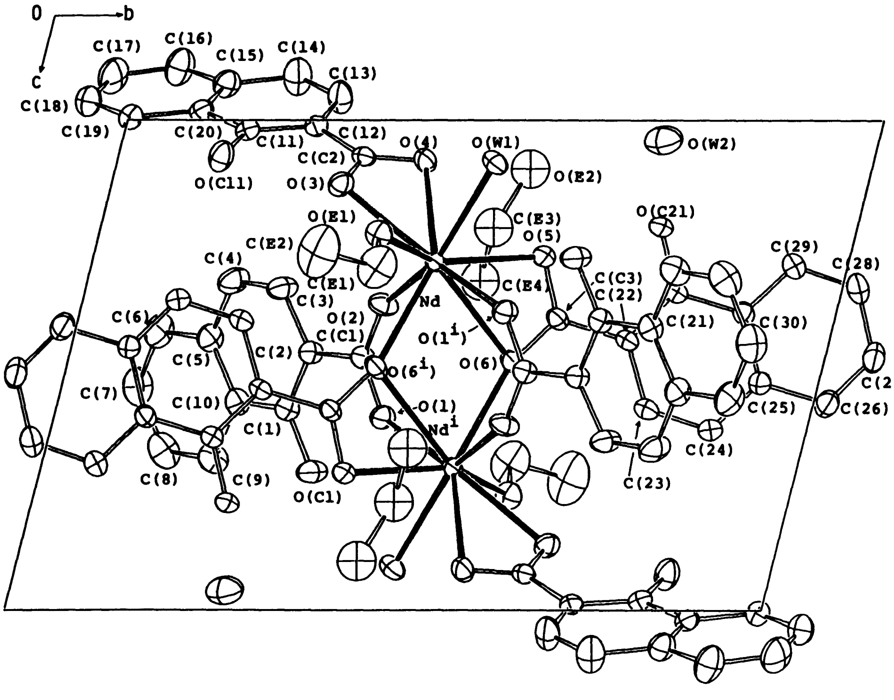

Fig. 1. The projection of the unit cell along a-axis with the numbering scheme. (O(W2B) is neglected. Key to the symmetry operation: i, $1-x$, $1-y$, $1-z$).

Its C-O bond lengths, as well as the bridging Nd-O lengths of the respective oxygen atoms, are almost the same; however, the third Nd-O bond, Nd-O(6), is longer than the other two.

The other carboxylate ligand chelates to the metal atom, forming a four-membered ring. The two C-O bond lengths of the ligand are not equal, and the oxygen atom of the longer C-O bond has the shorter Nd-O bond; this shows that its C=O double bond is localized. The chelate spans one edge of the bottom triangle of the prism; although the structures of some lanthanoid carboxylates taking the tricapped trigonal prism geometry have been reported, the chelating carboxylate is apt to span an apex of the prism and the cap position; therefore, the spanning position of this complex is exceptional.

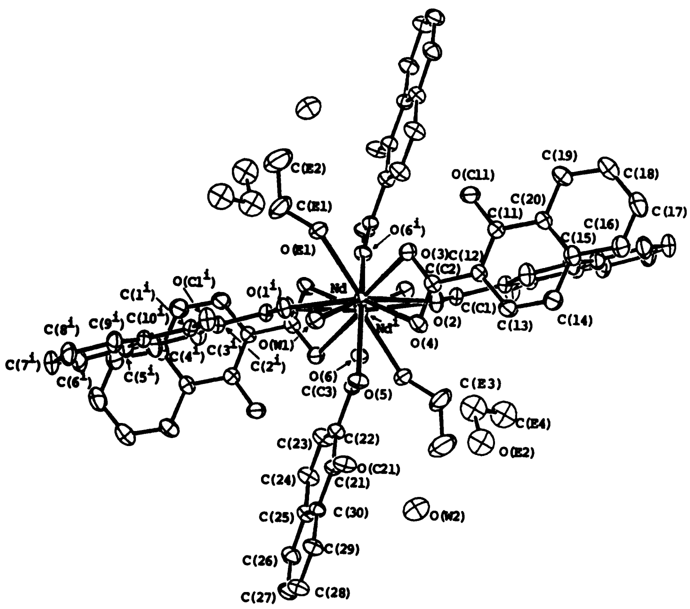

Fig. 2. The perspective of the complex along Nd–Ndⁱ axis.

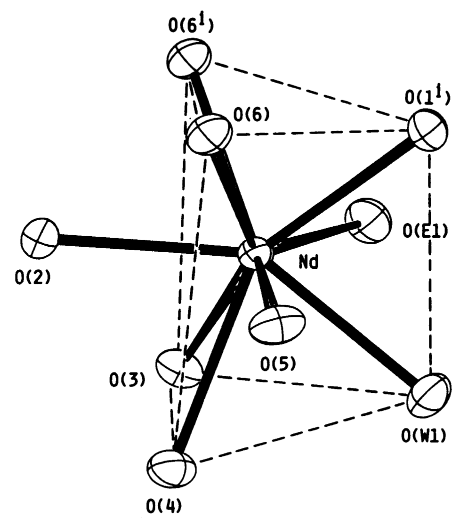

Fig. 3. The schematic presentation of the coordination geometry of the central metal atom.

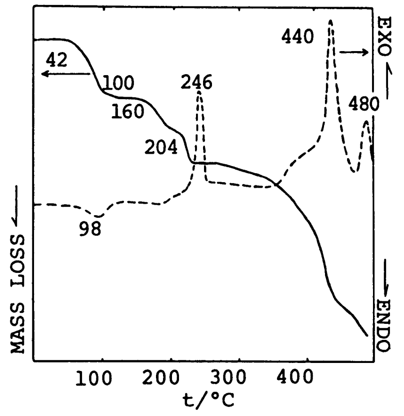

Fig. 4. TG(——) and DTA(---) curves of the complex. Mass loss of TG was taken downwards, and the exothermal change of DTA was taken upwards.

As is depicted in Fig. 2, the naphthylene group of the bridging carboxylates are arrayed radially from the line of the metal atoms. The dihedral angle between the planes of C(1)···C(10) and C(21ⁱ)···C(30ⁱ) is 62.6° The C(11)···C(20) naphthalene ring is lying over the C(1)···C(10) ring, with a dihedral angle of 81.6°.

The Nd–O bond length to the water oxygen atom is almost the same as that to the ethanol oxygen atom; 2.501(4) and 2.503(4) Å, respectively. The distances are almost the same as the average Nd–O bond length to the seven carboxyl oxygen atoms (2.501 Å). Generally, the water molecules are bound more strongly to lanthanoid metal atoms than are those of ethanol; therefore, it is necessary to use an anhydrous medium to synthesize their alcohol complexes. This is the first case in which water and alcohol are coordinated at the same time to one lanthanoid atom, although the ethanol is quite easily removed in open air. As is shown in Fig. 2, the ethanol ligands are surrounded by the naphthalene rings. Probably the large naphthylene group of the carboxylates around the core of the complex makes the moiety more feasible for the ethanol molecule to be kept between them.

As is shown in Table 2, the coordinating water molecule forms a hydrogen bond with the carboxyl oxygen atom of the neighboring complex along the c-axis. The crystals contain uncoordinated ethanol and water molecules. These are bound to the complex through hydrogen bonds with the coordinated water molecule and the hydroxyl group of the naphthalene ring, as is shown in Table 2. The water molecule was found to be disordered, and the position of ethanol is nebulous. Furthermore, the interatomic distance of

O(E2)···O(W2B) is too short (1.976(15) Å). This phenomenon may be due to the only partial occupancy of ethanol, a result of the efflorescence of the crystal.

The results of thermogravimetric (TG), and differential thermal analyses (DTA) simultaneous measurements are depicted in Fig. 4. The TG curve shows that, when the complex is heated, the ethanol and also all of the water molecules seem to be removed in the first step, from 42 °C to about 100 °C. The anhydrous salt thus formed is stable up to about 160 °C; then the decomposition of the ligand starts to occur.

The ν_{as}(COO) band as well as the ν_s(COO) band in the infrared spectrum of the title complex is split. The former is split into three peaks: 1632(m), 1580(s), and 1550(sh) cm^{-1}. The relatively low-wavenumber bands may correspond to the bridging carboxyl groups. The latter band is also split into three peaks: 1470(m), 1440(s), and 1412(s) cm^{-1}.

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9) $R=\sum||F_o|-|F_c||/\sum|F_o|$; $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o{}^2]^{1/2}$ where $w=1/[\{\sigma(|F_o|)\}^2+(F_{wt}\times F_o)^2]$, $F_{wt}=0.015$; $S=[\sum w(|F_o|-|F_c|)^2/(N_o-N_p)]^{1/2}$, where N_o=number of reflections and N_p number of parameters.

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12) Some additional bond-length and bond-angle data, the positions of the hydrogen atoms, the final anisotropic thermal parameters, and the F_o-F_c tables are deposited as Document No. 8623 at the Office of the Editor of the *Bull. Chem. Soc. Jpn.*