January, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 125—129 (1987) 125

Crystal Structures of Bis(*r*-1,*c*-3,*c*-5-cyclohexanetriamine)cobalt(III) Iodide and Tricyano(*r*-1,*c*-3,*c*-5-cyclohexanetriamine)-cobalt(III) Monohydrate

Minoru Ishii,* Michiko Umehara, and Masayoshi Nakahara
Department of Chemistry, Faculty of Science, Rikkyo (St. Paul's) University,
Nishiikebukuro 3, Toshima-ku, Tokyo 171

(Received June 13, 1986)

The crystal structures of bis(*r*-1,*c*-3,*c*-5-cyclohexanetriamine)cobalt(III) iodide (**1**) and tricyano(*r*-1,*c*-3*c*-5-cyclohexanetriamine)cobalt(III) monohydrate (**2**) were determined by the X-ray diffraction technique. **1** is monoclinic with space group *A*2/*a*,[1] a=10.437(2), b=16.131(2), c=12.486(2) Å, and β=94.36(3)°, and **2** is orthorhombic with space group *Pbca*, a=12.599(1), b=16.818(2), and c=11.659(1) Å, the final R values for **1** and **2** were 0.048 and 0.045, respectively. In both the complexes, all six-membered chelate rings formed by the *r*-1,*c*-3,*c*-5-cyclohexanetriamine ligand and central cobalt atom assume chair conformations. The presence of the six-membered chelate rings does not introduce much distortion on the octahedral geometry of the chromophores. These findings are in fair agreement with spectroscopic data on these complexes.

r-1,*c*-3,*c*-5-Cyclohexanetriamine (Fig. 1; abbreviated as chta) can act as a terdentate ligand and coordinate to the central metal in only one topological way (facial). Two kinds of complexes containing chta ligand, $[Co(chta)_2]^{3+}$[2] and $[CoX_3(chta)]$[3] (X=CN^-, Cl^-, and CH_3COO^-), have been prepared. It is expected that a chta ligand coordinates to form a triplet six-membered ring, leading to existence of three six-membered chelate rings in $[CoX_3(chta)]$ (X=CN^-, Cl^-, and CH_3COO^-) and that of six in $[Co(chta)_2]^{3+}$. The d-d absorption bands of cobalt(III) complexes shift to the lower energy side as the number of chelate rings increases.[4] Rather large shifts were observed also for complexes of the type $[Co(triamine)_2]^{3+}$: for example, 19400 and 27200 cm^{-1} for $[Co(dpt)_2]^{3+}$ (dpt=bis(3-aminopropyl)amine)[5] and 21800 and 30000 cm^{-1} for *s*-*fac*-$[Co(dien)_2]^{3+}$ (dien= diethylenetriamine).[6] Although their band maxima are in lower energy sides than those of five-membered chelate polyamine complexes, they are located quite close to those of the corresponding ammine complexes: $[Co(chta)_2]Cl_3$, 20900 and 29200 cm^{-1},[2] $[Co(NH_3)_6]Cl_3$, 20960 and 29400 cm^{-1},[7] $[Co(CN)_3(chta)]$, 26300 and 33000 cm^{-1},[3] *fac*-$[Co(CN)_3(NH_3)_3]$, 26300 and 33000 cm^{-1}.[8] These facts suggest that the chta chelate assumes a undistorted structure in the complex. A study with scaled models has suggested that the chta ligand can build up a robust structure with the central atom. This work deals with the molecular structures of bis(*r*-1,*c*-3,*c*-5-cyclohexanetriamine)cobalt(III) iodide, $[Co(chta)_2]I_3$,[9] and tricyano(*r*-1,*c*-3,*c*-5-cyclohexanetriamine)cobalt(III) monohydrate, $[Co(CN)_3(chta)]\cdot H_2O$.

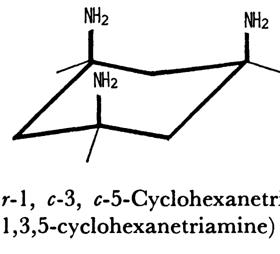

Fig. 1. *r*-1, *c*-3, *c*-5-Cyclohexanetriamine. (*cis*,*cis*-1,3,5-cyclohexanetriamine)

Experimental

Both the complexes were prepared according to the literatures.[2,3] The crystal of $[Co(chta)_2]I_3$ is of orange-red hexagonal prism and that of $[Co(CN)_3(chta)]\cdot H_2O$ is of yellow cube. Anal. for $[Co(chta)_2]I_3$. Found: C, 20.45; H, 4.32; N, 11.88; I, 54.54%. Calcd for $CoC_{12}H_{30}N_6I_3$: C, 20.65; H, 4.34; N, 12.04; I, 54.54%. Anal. for $[Co(CN)_3(chta)]\cdot H_2O$. Found: C, 37.44; H, 6.03; N, 28.95%. Calcd for $CoC_9H_{17}N_6O$: C, 38.04; H, 6.03; N, 29.57%. Specific gravities were determined by the floating method. Lattice constants were first approximately determined from Weissenberg photographs obtained with Cu *Kα* radiation and then refined. Crystal data of both the complexes are listed in Table 1. Intensities were collected on a Rigaku AFC-5 four-circle diffractometer (Josai University) with graphite-monochromated Mo *Kα* radiation (λ=0.7107 Å) up to 2θ=60°, the θ—2θ scan technique being employed. The usual corrections for Lorentz and polarization effects were made with both the crystals, and further corrections for absorption and

Table 1. Crystal Data

Compound	$[Co(chta)_2]I_3$	$[Co(CN)_3(chta)]\cdot H_2O$
Formula	$CoC_{12}N_{12}H_{60}I_3$	$CoC_9N_9H_{32}O$
Formula weight	698.11	284.25
Crystal system	Monoclinic	Orthorhombic
Space group	*A*2/*a*	*Pbca*
a/Å	10.437(2)	12.599(1)
b/Å	16.131(2)	16.818(2)
c/Å	12.486(2)	11.659(1)
β/°	94.36(3)	
V/Å^3	2096.05(5)	2470.2(5)
D_m/Mg m^{-3}	2.20	1.53
D_x/Mg m^{-3}	2.21	1.53
Z	4	8
μ(Mo *Kα*)/mm^{-1}	5.187	

extinction were made with [Co(chta)$_2$]I$_3$. Calculations were carried out on a Univac 1100 computer at the Rikkyo University Computer Center and partially on a HITAC 200 H computer at the Computer Center of the University of Tokyo.

Crystal Structure Determination. a) **[Co(chta)$_2$]I$_3$**: The observed systematic absence of $h\ k\ l$ for $k+l=2n+1$ and $h\ 0\ l$ for $h=2n+1$ indicated that possible space groups would be $A2/a$ or Aa. Then, two refinements were carried out independently by assuming the two space groups.[10] In the case of Aa, some C–C and C–N bond lengths were abnormal and the coordinates and temperature factors had unusually high values, whereas no anomalies were found in the case of $A2/a$. Independent 2794 reflections with $|F_o|>3\sigma(|F_o|)$ were used for structure determination. The structure was solved by the heavy-atom method with a local version of UNICS.[11] The final refinement was carried out by using the full-matrix least squares program LINUS[12] with anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen atoms. The final R and R_2 values were 0.048 and 0.055,[13] respectively. The positions of all hydrogen atoms were determined from the difference-Fourier map.

Table 2. Final Atomic Coordinates/10^{-4} with Estimated Standard Deviations in Parentheses, and Their Equivalent Isotropic Temperature Factors

Atom	x	y	z	B_{eq}/Å^2 a)
I (1)	2500	1169(<1)	0	3.5_3
I (2)	4142(<1)	6649(<1)	8855(<1)	3.1_8
Co	5000	7500	2500	1.8_2
N (1)	4387(6)	6489(3)	1716(5)	2.6_0
N (2)	5362(6)	6835(3)	3827(5)	2.5_5
N (3)	6777(5)	7283(3)	2089(5)	2.5_3
C (1)	5140(7)	5704(4)	1860(6)	2.7_9
C (2)	5219(7)	5428(4)	3013(7)	3.0_3
C (3)	6041(7)	6009(4)	3742(6)	2.9_3
C (4)	7351(7)	6133(5)	3334(7)	3.2_3
C (5)	7293(6)	6409(4)	2166(7)	3.0_6
C (6)	6469(7)	5834(5)	1442(7)	3.3_9

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

Table 3. Final Atomic Coordinates/10^{-4} with Estimated Standard Deviations in Parentheses, and Their Equivalent Isotropic Temperature Factors

Atom	x	y	z	B_{eq}/Å^2 a)
Co	2358(<1)	2275(<1)	609(<1)	1.4_1
N1A	1292(2)	1862(2)	1745(2)	2.1_5
N2A	1940(2)	1428(2)	−501(2)	2.1_5
N3A	3463(2)	1575(2)	1309(2)	1.7_4
C1C	3344(3)	2686(2)	−456(3)	1.9_9
C2C	1335(3)	2976(2)	−8(3)	2.1_3
C3C	2774(3)	3103(2)	1600(3)	1.9_4
N4C	3936(3)	2942(2)	−1108(3)	2.7_7
N5C	698(3)	3399(2)	−360(3)	3.2_0
N6C	3050(3)	3602(2)	2193(3)	2.7_2
C4A	1242(3)	982(2)	1935(3)	1.9_6
C5A	949(3)	561(2)	823(3)	2.3_4
C6A	1831(3)	599(2)	−66(3)	2.1_1
C7A	2889(3)	314(2)	404(3)	2.6_3
C8A	3182(3)	724(2)	1534(3)	2.6_1
C9A	2292(3)	672(2)	2397(3)	2.2_4
O	352(3)	3774(3)	2548(4)	7.3_8

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

b) **[Co(CN)$_3$(chta)]·H$_2$O**: From the observed systematic absence of $0\,k\,l$ for $k=2n+1$, $h\,0\,l$ for $l=2n+1$, and $h\,k\,0$ for $h=2n+1$, the space group was uniquely determined to be $Pbca$. Independent 2674 reflections with $|F_o|>3\sigma(|F_o|)$ were used. The structure was solved by the Patterson–Fourier method with UNICS.[11] The refinement was carried out by using the block-diagonal least squares program HBLS IV. With anisotropic temperature factors for non-hydrogen atoms and isotropic ones for hydrogen atoms, the final R and R_2 values were 0.045 and 0.049, respectively. Fourteen of fifteen hydrogen atoms, except those of the water molecule, were located from the difference-Fourier map. The position of the remaining hydrogen atom was determined theoretically.

The final atomic parameters and temperature factors of both the complexes are given in Tables 2 and 3.[14]

Results and Discussion

Projections of the crystal structures of [Co(chta)$_2$]I$_3$ along the b axis and of [Co(CN)$_3$(chta)]·H$_2$O along the c axis are shown in Figs. 2 and 3. Perspective drawings of the complexes are shown in Figs. 4 and 5.

In both the complexes, the chta ligands are spanned on a face of an octahedron, that is, they coordinate in the facial positions, as expected.

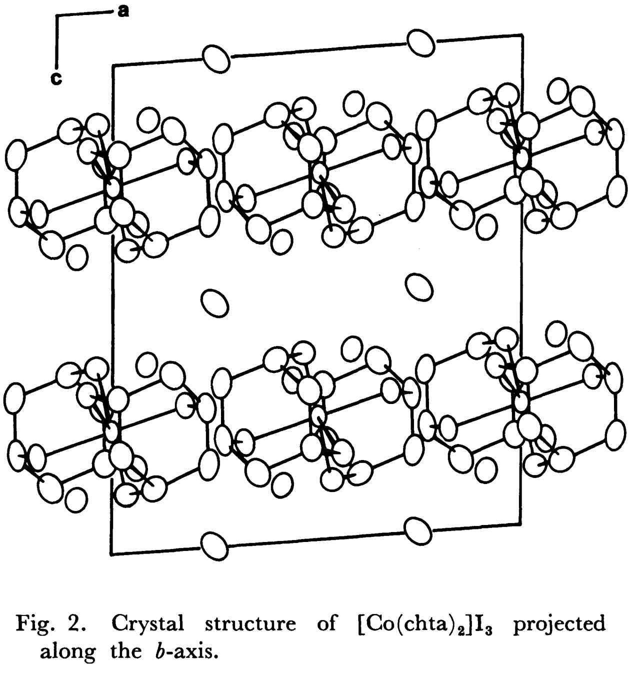

Fig. 2. Crystal structure of [Co(chta)$_2$]I$_3$ projected along the b-axis.

Bond distances and angles within the complex ion and molecule are listed in Tables 4 and 5, together with estimated standard deviations. Between both the complexes there are no remarkable differences with respect to the chta chelate. The Co–N(amine) bond distances which range from 1.948(6) to 2.010(3) Å are similar to those of some CoN_6 complexes with six-membered chelate rings.[15,16] These values are also in good agreement with the $Co–N(NH_3)$ bond lengths of the corresponding ammine complexes (2.01 Å for *fac*-$[Co(CN)_3(NH_3)_3]$[8] and 1.979(1) Å for $[Co(NH_3)_6][Cr(CN)_6]$). The angles N(amine)–Co–N(amine) in the

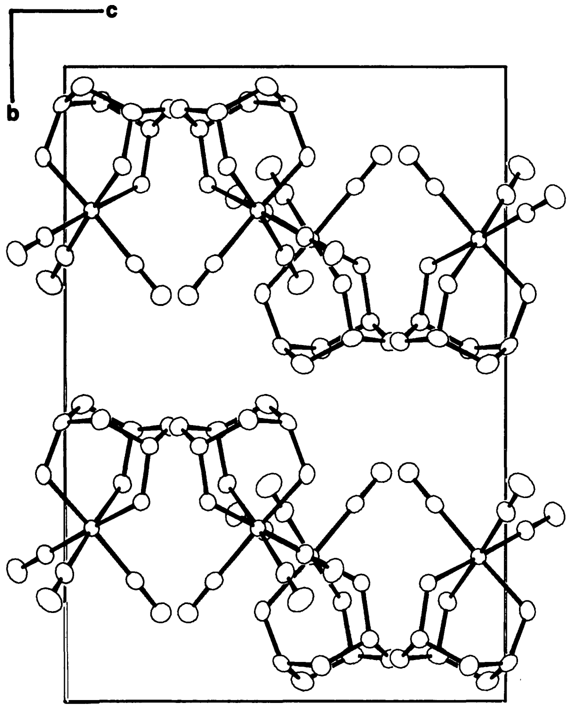

Fig. 3. Crystal structure of $[Co(CN)_3(chta)]$ projected along the *a*-axis.

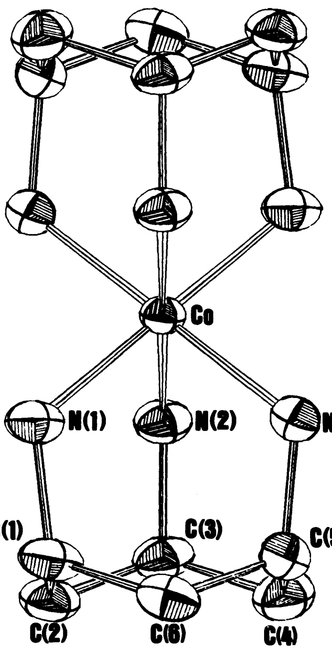

Fig. 4. Perspective drawing of the $[Co(chta)_2]^{3+}$.

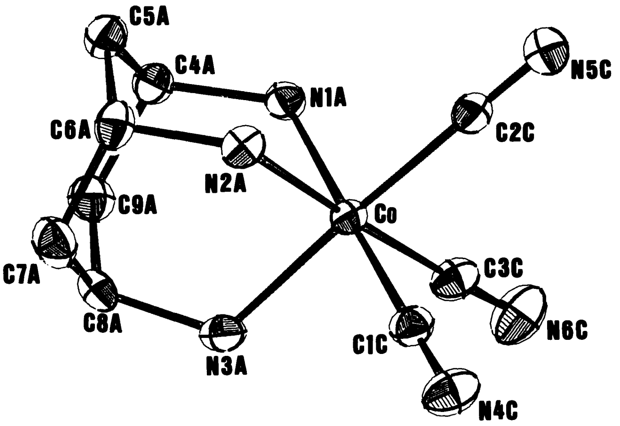

Fig. 5. Perspective drawing of the $[Co(CN)_3(chta)]$.

Table 4. Bond Distances and Angles within Cation $[Co(chta)_2]^{3+}$ with Estimated Standard Deviations in Parentheses

Bond distances l/Å		Bond angles ϕ/°			
Co-N(1)	1.984(6)	N(1)-Co-N(2)	90.1(3)	C(1)-C(2)-C(3)	112.2(7)
Co-N(2)	1.986(6)	N(1)-Co-N(3)	90.0(3)	C(2)-C(3)-C(4)	111.3(7)
Co-N(3)	1.992(7)	N(2)-Co-N(3)	89.9(3)	C(3)-C(4)-C(5)	113.0(7)
				C(4)-C(5)-C(6)	111.8(7)
N(1)-C(1)	1.494(10)	Co-N(1)-C(1)	119.3(5)	C(5)-C(6)-C(1)	111.6(7)
N(2)-C(3)	1.517(10)	Co-N(2)-C(3)	118.4(5)	C(6)-C(1)-C(2)	112.4(7)
N(3)-C(5)	1.510(10)	Co-N(3)-C(5)	118.9(5)		
C(1)-C(2)	1.502(11)	N(1)-C(1)-C(2)	110.9(6)		
C(2)-C(3)	1.524(11)	N(1)-C(1)-C(6)	108.9(6)		
C(3)-C(4)	1.508(12)	N(2)-C(3)-C(2)	109.7(6)		
C(4)-C(5)	1.522(12)	N(2)-C(3)-C(4)	110.4(6)		
C(5)-C(6)	1.516(12)	N(3)-C(5)-C(4)	108.8(7)		
C(6)-C(1)	1.534(12)	N(3)-C(5)-C(6)	110.4(7)		

Table 5. Bond Distances and Angles within Complex $[\mathrm{Co(CN)_3(chta)}]$ with Estimated Standard Deviations in Parentheses

Bond distances l/Å		Bond angles ϕ/°			
Co-N1A	2.010(3)	N1A-Co-N2A	90.3(1)	C4A-C5A-C6A	112.5(3)
Co-N2A	1.996(3)	N2A-Co-N3A	91.7(1)	C5A-C6A-C7A	112.5(3)
Co-N3A	1.997(3)	N3A-Co-N1A	89.6(1)	C6A-C7A-C8A	112.3(3)
				C7A-C8A-C9A	111.7(3)
Co-C1C	1.888(3)	C1C-Co-C2C	88.3(1)	C8A-C9A-C4A	112.9(3)
Co-C2C	1.890(3)	C2C-Co-C3C	87.8(1)	C9A-C4A-C5A	110.7(3)
Co-C3C	1.884(3)	C3C-Co-C1C	87.1(1)		
N1A-C4A	1.498(4)	Co-N1A-C4A	117.8(2)		
N2A-C6A	1.490(4)	Co-N2A-C6A	118.1(2)		
N3A-C8A	1.498(5)	Co-N3A-C8A	118.0(2)		
C4A-C5A	1.523(5)	Co-C1C-N4C	179.3(3)		
C5A-C6A	1.522(5)	Co-C2C-N5C	178.3(3)		
C6A-C7A	1.519(5)	Co-C3C-N6C	178.3(3)		
C7A-C8A	1.532(5)				
C8A-C9A	1.509(5)	N1A-C4A-C5A	110.1(3)		
C9A-C4A	1.521(5)	N1A-C4A-C9A	110.8(3)		
		N2A-C6A-C5A	109.8(3)		
C1C-N4C	1.148(5)	N2A-C6A-C7A	109.7(3)		
C2C-N5C	1.148(5)	N3A-C8A-C7A	109.6(3)		
C3C-N6C	1.142(5)	N3A-C8A-C9A	110.4(3)		

chta chelate, close to 90°, are in agreement with those of analogous complexes.[15] Between both the complexes there is few difference in bond length and angle with respect to the triplet six-membered chelate rings, in contrast to the case of $[\mathrm{Co(diamine)_3}]^{3+}$ complexes containing six-membered chelate rings.[15,16] The C–N(amine) and C–C bond distances are normal as such single bonds. The N(amine)–C–C angles are also normal as regular tetrahedral angles, but the Co–N(amine)–C ones are larger than those angles. Thus, these six-membered chelate rings are significantly flattened out. Absolute values of deviations from the plane Co–N–N(in chelate) are 0.91—0.96 Å (C(1)) and 0.56—0.62 Å (C(2)) for $[\mathrm{Co(chta)_2}]^{3+}$ and 0.90—0.97 Å (C4A) and 0.53—0.67 Å (C5A) for $[\mathrm{Co(CN)_3(chta)}]$. These six-membered rings assume more stable and less undistorted chair conformations than $[\mathrm{Co(tn)_3}]^{3+}$[17] (Fig. 6). In complex $[\mathrm{Co(CN)_3(chta)}]$, the Co–C(cyano) and C–N(cyano) bond lengths agree with those of $[\mathrm{Co(CN)_3(NH_3)_3}]$.[8] The C(cyano)–Co–C(cyano) angles are smaller than 90°. The dihedral angle between the opposite N–N–N planes in $[\mathrm{Co(chta)_2}]^{3+}$ is 0° as deduced necessarily from this symmetry, and that between the N–N–N and C–C–C planes in $[\mathrm{Co(CN)_3(chta)}]$ is smaller than 1°. The octahedra of the $\mathrm{CoN_6}$ and $\mathrm{CoN_3C_3}$ chromophores are compressed or elongated along the quasi-threefold axes only slightly; the distance between the upper and lower triangles (2.292—2.297 Å) agrees with that estimated for a regular octahedron (2.294 Å).

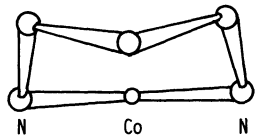

Fig. 6. Conformation of chta chelate ring.

These facts suggest that the distortion of the chromphores, although six-membered rings are formed by the chta ligands, is fairly alleviated by to the presence of the chta itself and that the octahedra retain approximately the O_h symmetry. The structures of the complex and ion, as determined in this work, are in good agreement with the speculations based on the absorption spectra.

References

1) Standard space group is $C2/c$ (No. 15).

2) R. A. D. Wentworth and J. J. Felton, *J. Am. Chem. Soc.*, **90**, 621 (1968).

3) M. Umehara, M. Ishii, T. Nomura, I. Muramatsu, and M. Nakahara, *Nippon Kagaku Kaishi*, **1980**, 657.

4) M. Kojima, H. Yamada, H. Ogino, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 2325 (1977).

5) S. Yamada, M. Umehara, M. Ishii, and M. Nakahara, *Nippon Kagaku Kaishi*, **1983**, 1733.

6) Y. Yoshikawa and K. Yamasaki, *Bull. Chem. Soc. Jpn.*, **45**, 179 (1972).

7) J. Fujita and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **36**, 1281 (1963).

8) Y. Yamamoto, *Nippon Kagaku Kaishi,* **1974**, 259.

9) M. Ishii, M. Umehara, T. Nomura, and M. Nakahara, *Chem. Lett.,* **1983**, 541.

10) The reliability indices were 0.060 for *A*2/*a* (the number of reflections 2794 and that of parameteres 110) and 0.063 for *Aa* (the number of reflections 2933 and that of parameters 200). The positions of the non-hydrogen atoms (I, Co, C, N) were determined by using anisotropic temperature factors.

11) T. Sakurai, UNICS, the Universal Crystallographic Computing System, Tokyo: The Crystallographic Society of Japan (1967).

12) P. Coppens and W. C. Hamilton, *Acta. Crystallogr., Sect. A,* **26**, 71 (1970).

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

14) The complete F_o—F_c data are deposited as Document No. 8701 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

15) S. Sato and Y. Saito, *Acta. Crystallogr., Sect. B,* **31**, 1378 (1975).

16) S. Sato and Y. Saito, *Acta. Crystallogr., Sect. B,* **34**, 420 (1978).

17) R. Nagao, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B,* **29**, 2438 (1973).