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CRYSTAL STRUCTURE OF BIS(*r*-1,*c*-3,*c*-5-CYCLOHEXANETRIAMINE)COBALT(III) IODIDE

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The molecular structure of the title compound was determined by X-ray diffraction. Six six-membered chelate rings formed by the *r*-1, *c*-3,*c*-5-cyclohexanetriamine were found to take chair-conformations. The complex ion had an approximate D_3 symmetry. The presence of the six-membered chelate rings did not introduce much distortion on the octahedral geometry of the complex ion.

r-1,*c*-3,*c*-5-Cyclohexanetriamine(Fig. 1, abbreviated chta) acts as a terdentate ligand and forms a triplet of six-membered chelate rings with the cobalt(III).1)2) There is no geometrical and optical isomer for the $[Co(chta)_2]^{3+}$ complex ion, because the coordination of the chta always takes a *facial* configuration. In the CoN_6 chromophores, the d-d absorption bands shift to the lower energy side as the number of ring members of the ligands increases. A similar shift was observed for complexes of the type, $[Co(triamine)_2]^{3+}$ In the case of the chta complex, however, such a shift has not been observed in this region, and the band maxima (20900, 29200 cm^{-1} for $[Co(chta)_2]Cl_3$) are close to that observed in the hexaammine complex (20960, 29400 cm^{-1} for $[Co(NH_3)_6]Cl_3$). A study of scaled models suggested that the chta ligand can build up a robust structure with the central atom. But no report has been made on the molecular structure of the chat cobalt(III) complexes. This letter deals with the molecular structure of the bis(*r*-1,*c*-3, *c*-5-cyclohexanetriamine)cobalt(III) iodide, $[Co(chta)_2]I_3$.

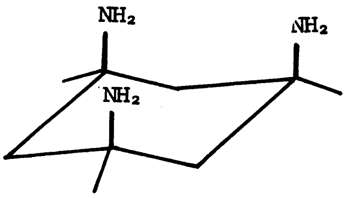

Fig. 1
r-1,*c*-3,*c*-5-cyclohexanetriamine

The title complex was prepared by the method in the literature.1) The orange-red crystals are monoclinic with space group $A2/a$3); a=10.437(2), b=16.131(2) c=12.486(2) Å and β=94.36(3)°, V=2096.0(5) Å^3, D_x=2.21, D_m=2.20 g cm^{-3} and Z=4. A crystal having dimensions of about 0.5x0.5x0.5x mm^3 was used for the intensity measurements. Intensities were collected on a Rigaku AFC-5 four-circle diffractometer (Josai University) with graphite-monochromated Mo Kα radiation (λ=0.710 Å) up to 60°, θ-2θ scan technique being employed. Independent 2974 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for structure determination. The usual corrections were made for Lorentz, polarization, absorption and extinction. The structure was solved by Patterson-Fourier methods with a local version of UNICS.4) The final refinement was carried out using the full-matrix least squares program LINUS5)# with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. The final R and R_2 values were 0.048 and 0.055, respectively. The positions of all hydrogen atoms were determined from the difference-Fourier map. A projection of the crystal structure along *b*, and a perspective drawing of the complex cation are shown in Figs. 2 and 3, respectively.

The cobalt atom lies on a center of symmetry of the monoclinic unit cell. Two molecules of the chta ligand coordinate with six nitrogen atoms from above and below the cobalt atom to form an octahedral complex. Each one of these ligands is spanned on a face of an octahedron, that is, coordinates in the *facial* positions as expected. The chelate rings in the triplet have stable chair-conformations.

Bond distances and angles within a complex ion are listed in Table 1. The Co-N distances agree with the results observed for the $(-)_{589}$-$[Co(tn)_3]Cl_3\cdot H_2O$,6) $(-)_{546}$-$[Co(R,R\text{-ptn})_3]Cl_3\cdot 2H_2O$7) and $(+)_{589}$-*fac*-[Co(*meso*-2,4-ptn)$_3$][Co(CN)$_6$]8) having six-membered chelate rings. The C-N and C-C distances are also normal for the single bond. The N-Co-N angles in the chelate rings are close to 90°. The Co-N-C angles are much larger than the normal tetrahedral angle. The chair-conformations of the six-membered chelate rings are significantly flattened out. However, the octahedron formed by the six nitrogen atoms is compressed or elongated along the quasithreefold axis of D_3 symmetry only very little, in contrast to the $[Co(diamine)_3]^{3+}$ complex ion with the six-membered rings:6∿8) the distances between the upper and lower triangles (2.292∿2.297 Å) agree with that estimated for a regular octahedron (2.294 Å). These facts suggest that the distortion of the octahedron is fairly much alleviated owing to the presence of the triplet six-membered chelate rings, the CoN_6 group retaining approximate O_h symmetry. The strucure of the complex ion as determined in this work is in good accordance with the speculation based on the absorption spectra.

The 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.

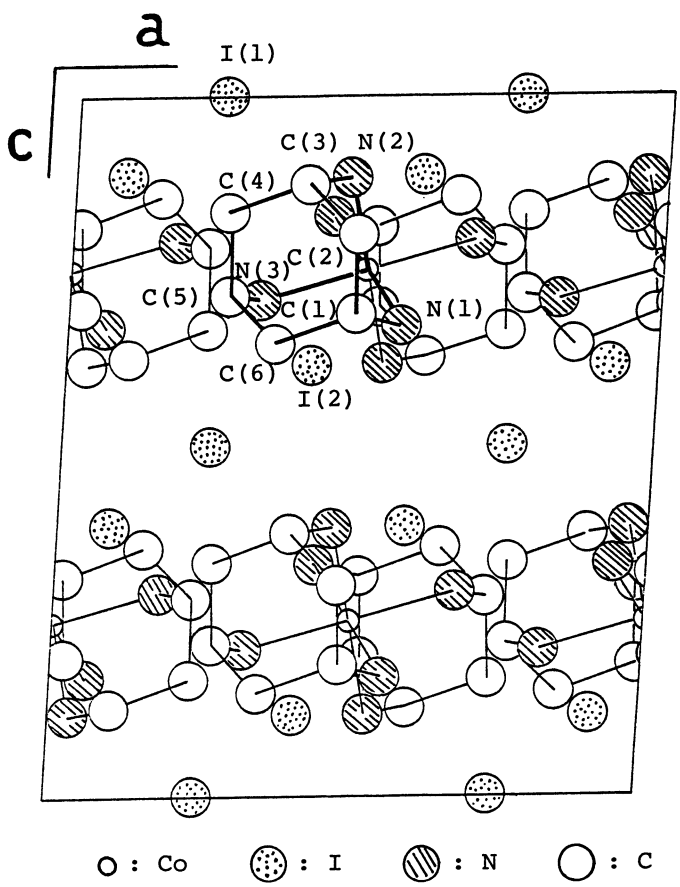

Fig. 2. A projection of the crystal structure along *b*

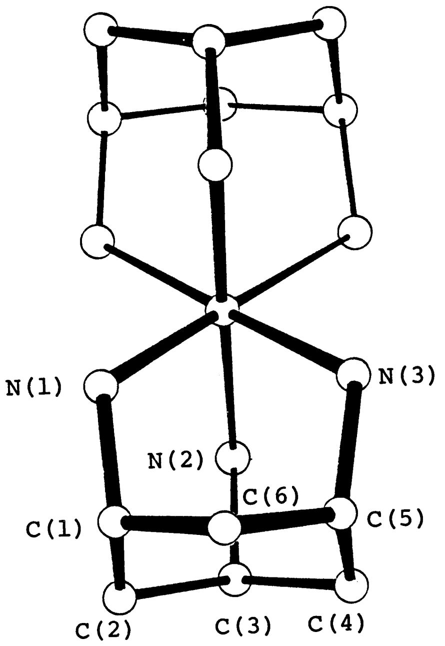

Fig. 3. Perspective drawing of the $[Co(chta)_2]^{3+}$ cation.

Bond distances		Bond angles			
Co-N(1)	1.984[6] Å	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 1. Bond distances and angles within the complex cation, $[Co(chta)_2]^{3+}$ with their estimated standard deviations in brackets

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