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Isomerism of the Metal Complexes Containing Multidentate Ligands. IX. Structure of the *meso* Isomer of $[Co(hexaen)]^{3+}$ (hexaen = 1,4,7,10,13,16-Hexaazacyclooctadecane)

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The crystal and molecular structure of *meso*-$[Co(hexaen)]Cl_3$ has been determined by single crystal X-ray diffractometry. The crystals are rhombohedral with space group $R\bar{3}$, $a=9.2976(10)$, $c=16.851(2)$ Å, and $Z=3$. The structure has been refined by least-squares calculations to an R value of 0.021 for 952 observed reflections. The complex ion has S_6 symmetry. The Co–N distance is 1.9966(8) Å and the N–Co–N angle in the chelate ring is 83.62(3)°. The molecular dimensions are in good agreement with those obtained from the conformational analysis.

An octahedral complex of a cyclic hexadentate ligand takes either *meso* or racemic form. Curry and Busch prepared an iron(III) complex with such kind of ligand, 2,16-dimethyl-3,6,9,12,15,21-hexaazabicyclo[15.3.1]heneicosa-1(21),2,15,17,19-pentaene.[1] However, the complex of the *meso* form was not obtained on account of the rigidity of the ligand. Groth carried out an X-ray analysis on the complex between potassium *p*-toluenesulfonate and 1,4,7,10,13,16-hexaoxacyclooctadecane(18-crown-6).[2] The 18-crown-6 molecule in this compound, as well as those in most complexes of this crown and its derivatives,[3] have roughly S_6 symmetry (*meso* form). However, the crown complexes are labile in solution. It is stereochemically more interesting to investigate inert metal chelates with cyclic hexadentate ligands.

Recently we succeeded in isolating the *meso* isomer of $[Co(hexaen)]^{3+}$ as a minor reaction product, as well as a major product of the racemic one.[4] The conformational analysis of $[Co(hexaen)]^{3+}$ suggested that the *meso* isomer was much more unstable than the racemic one; that is, the calculated energy difference amounts to 15 kJ mol^{-1}. Searle *et al.* prepared the cobalt(III) complex of a very similar hexadentate ligand, 1,4,8,11,15,18-hexaazacycloheneicosane, but did not obtain the *meso* isomer.[5] Thus the title compound is the first example of the *meso* isomer of the inert complex with a cyclic hexadentate ligand.

In this study, the crystal structure of the title compound has been determined.

Experimental

Preparation of the Complex. To half a gram of hexaen·$3H_2SO_4$ suspended in 10 cm^3 of water, 1 cm^3 of concentrated aqueous ammonia was added. The mixture was diluted with water until the total volume of solution was about 500 cm^3. To the mixture was added a solution of 0.3 g of $[Co(H_2O)(NH_3)_5]_2(SO_4)_3\cdot 3H_2O$ in 500 cm^3 of water. The solution was heated and kept at 77 °C for 4 h. After standing overnight, the resulting orange-red solution was allowed to pass through a small column of SP-Sephadex C-25, which adsorbed cationic species. A portion of the mixture was subjected to the chromatographic separation described in a previous paper.[4] The effluents containing the *meso* isomer, which were obtained from several separations, were diluted with water and were adsorbed again by a small column of SP-Sephadex. The column was washed with a large amount of 10^{-2} mol dm^{-3} HCl, and then the complex was eluted with 1.0 mol dm^{-3} HCl. The effluent was evaporated to dryness in a vacuum desiccator over NaOH and P_2O_5. The resulting orange-red crystals were recrystallized from water. Crystals are orange-red square-plates. Found: C, 33.61; H, 7.21; N, 19.90%. Calcd for $C_{12}H_{30}N_6CoCl_3$: C, 34.02; H, 7.14; N, 19.83%. Absorption spectrum; $\tilde{\nu}_{max}$/cm^{-1} (log ε), 20830 (2.33).

TABLE 1. CRYSTAL DATA

Molecular formula	$C_{12}H_{30}N_6CoCl_3$
Formula weight	423.70
Crystal system	Rhombohedral
Cell dimensions (Hexagonal setting)	
	$a=9.2976(10)$ Å
	$c=16.851(2)$ Å
	$U=1261.6(3)$ Å^3
Space group	$R\bar{3}$
Z	3
Density	$D_m=1.67_7$ g cm^{-3}
	$D_x=1.67_3$ g cm^{-3}
μ(Mo $K\alpha$)	15.38 cm^{-1}

Physical Measurements. Electronic absorption and ^{13}C NMR spectra were recorded on a UNION SM-401 spectrophotometer and a JEOL JNM-FX60 spectrometer operating at 15.04 MHz, respectively.

X-Ray Structure Determination. A spherically shaped crystal of 0.43 mm in diameter was used for the X-ray experiment. Intensity data were collected up to $2\theta=65°$ on a Rigaku automated four-circle diffractometer AFC-5 with graphite-monochromatized Mo $K\alpha$ radiation, the θ-2θ scan technique being employed. 961 independent reflections with $|F_o|>3\sigma(|F_o|)$ were observed, and used in the structure analysis. No correction was made for absorption and extinction effect. The accurate cell dimensions were determined by a least-squares method from the θ values for 21 reflections in the range of $26°<2\theta<30°$ measured on the diffractometer. The crystallographic data are listed in Table 1.

The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method with anisotropic temperature factors for non-hydrogen atoms. The scattering factors and the anomalous scattering corrections for non-hydrogen atoms were taken from International Tables for X-Ray Crystallography.[6] For hydrogen atoms, the values given by Stewart, Davidson, and Simpson

Table 2. Fractional coordinates, with their estimated standard deviations, multiplied by 10^5 for the non-hydrogen atoms and 10^3 for the hydrogen atoms

Atom	*x*	*y*	*z*	*B* or B_{eq}/Å^2 a)
Co	0	0	0	1.0
Cl(1)	0	0	50000	2.5
Cl(2)	0	0	22293(3)	2.0
N	21287(10)	11952(10)	6033(5)	1.4
C(1)	29154(12)	1391(13)	5946(6)	1.8
C(2)	32874(12)	28799(12)	2559(6)	1.8
H(1)	196(2)	125(2)	109(1)	1.7(0.2)
H(2)	229(2)	−75(2)	93(1)	2.0(0.3)
H(3)	409(2)	84(2)	76(1)	3.2(0.4)
H(4)	434(2)	307(2)	30(1)	2.1(0.3)
H(5)	318(2)	372(2)	56(1)	1.4(0.2)

a) The equivalent isotropic temperature factors as defined by W. C. Hamilton (*Acta Crystallogr.*, **12**, 609 (1959)).

were used.[7] The weighting scheme in the least-squares calculation was taken as $w=[\sigma_{\text{count}}^2+(0.015|F_o|)^2]^{-1}$. The R and R_w values were 0.024 and 0.040 for 961 independent reflections. The results at this stage revealed that nine strong, low-angle reflections (110, 300, 330, 011, 102, 003, 204, 014, $\bar{3}44$) were seriously affected by secondary extinction effect. The least-squares calculation for 952 intensities except for these nine reflections gave R=0.021 and R_w= 0.038.

The final atomic parameters are listed in Table 2.[8] All the calculations were performed on a HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with Universal Crystallographic Computational Program System UNICS III.[9]

Results and Discussion

Figure 1 shows a perspective drawing of *meso*-[Co(hexaen)]$^{3+}$ along the threefold axis. The bond lengths and angles are listed in Table 3. The cobalt atom lies at a crystallographic special position $\bar{3}$ and the complex ion has S_6 symmetry. The macrocyclic ligand, hexaen, is composed of six equivalent –NHCH$_2$-CH$_2$– units. Six five-membered chelate rings are equivalent. This compound has very interesting structure containing both Δ- and Λ-[Co(en)$_3$]$^{3+}$ type chelate rings and was named "Cobalt Spinner" in a previous paper,[4] as it is suggestive of an old-fashioned spinning wheel which rotates about its threefold axis. The two methylene groups in each chelate ring are crystallographically independent. The five-membered ring adopts the unsymmetrical gauche conformation. The differences in the structural parameters of the two methylene carbon atoms are given in Table 3.

Table 3. Molecular geometries obtained from the X-ray and conformational analyses

Bond distances (l/Å) and angles (ϕ/°) with their e.s.d.'s.

	X-Ray	Conformational analysis
Co-N	1.9966(8)	1.9925
N-C(1)	1.489(2)	1.489
N-C(2)	1.507(1)	1.503
C(1)-C(2)	1.515(2)	1.515
N-Co-N	83.62(4)	85.01
Co-N-C(1)	107.76(6)	106.88
Co-N-C(2)	110.49(8)	110.99
N-C(1)-C(2)	107.16(8)	108.22
N-C(2)-C(1)	108.73(7)	109.70
C(1)-N-C(2)	110.49(7)	109.38

Torsional angles (ϕ/°) with their e.s.d.'s.

	X-Ray	Conformational analysis
Co-N-C(1)-C(2)	−48.1(1)	−46.3
Co-N-C(2)-C(1)	−20.1(1)	−18.9
C(2)-N-C(1)-C(2)	74.6(1)	73.7
C(1)-N-C(2)-C(1)	100.1(1)	98.6
N-C(2)-C(1)-N	44.0(1)	42.8

Distances (l/Å) from the plane defined by Co, N, and N′ atoms.

	X-Ray	Conformational analysis
C(1)	0.704(1)	0.689
C(2)	0.127(1)	0.136

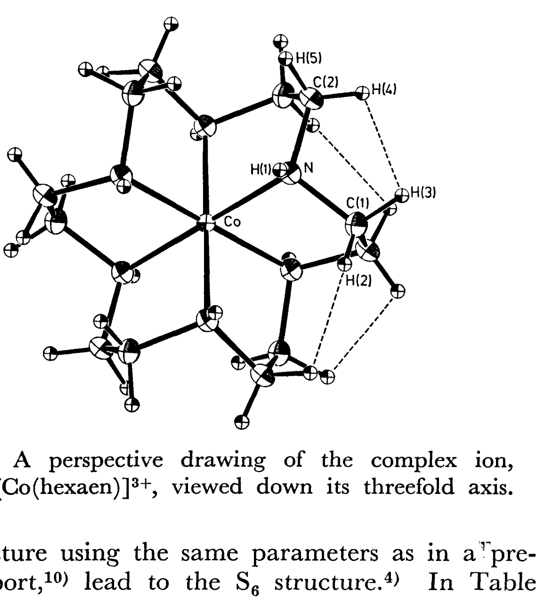

Fig. 1. A perspective drawing of the complex ion, *meso*-[Co(hexaen)]$^{3+}$, viewed down its threefold axis.

A Dreiding molecular model shows that the *meso* isomer may have a highly symmetrical and rigid D_{3d} structure with twelve equivalent methylene carbons. The D_{3d} structure, however, contains non-bonded hydrogen-hydrogen pairs which may have significantly large repulsive interactions. The conformational analysis of this compound, which was initiated from the D_{3d} structure using the same parameters as in a previous report,[10] lead to the S_6 structure.[4] In Table 3, the molecular dimensions obtained from the conformational analysis are compared with those found in the X-ray crystal structure analysis. The agreement between them is excellent. In the energy minimized structure, the Co–N bond distance (1.993 Å) is longer than the initial one (1.970 Å) and almost the same as that found in the crystal (1.997(1) Å). The elongated coordination-bond distances are reflected on the red-shift of the absorption maximum as compared with that of [Co(en)$_3$]$^{3+}$. The two N–C

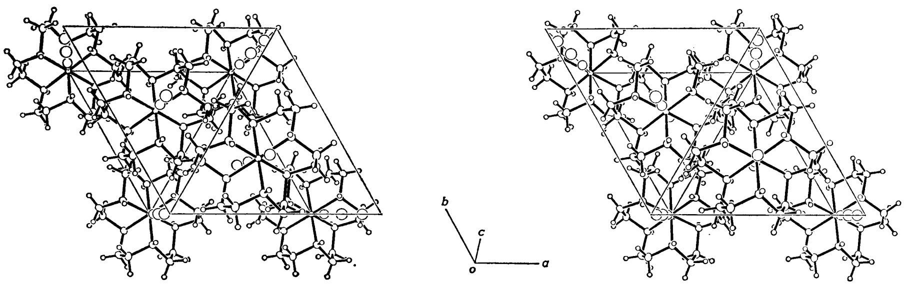

Fig. 2. Stereoscopic view of the crystal structure along the c axis.

Table 4. Relevant interatomic distances (l/Å) outside the complex ion with their e.s.d.'s

Cl(2)···N	3.234(1)
Cl(2)···H(1)	2.49(2)
Cl(2)···H(5)	2.82(2)
Cl(1)···H(3)	2.81(2)

bond distances in each chelate ring differ in such a way that large hydrogen-hydrogen repulsions inherent in the initial D_{3d} structure can be avoided. The relaxed hydrogen-hydrogen interactions are depicted as dotted lines in Fig. 1 (H(3)···H(4), 2.11(3) Å; H(2)···H(5), 2.11(2) Å). Although the two methylene carbons are crystallographically independent, they are equivalent in solution. The ^{13}C NMR spectrum of this compound shows only one resonance signal in an aqueous solution.4) It is highly probable that the *meso* isomer undergoes a rapid interconversion between the two equivalent S_6 structures, resulting in an average structure of D_{3d} symmetry.

Figure 2 shows a stereoscopic view of the crystal structure. Close contact pairs in the crystal are listed in Table 4. All the chloride ions and the cobalt atoms are aligned on the same crystallographic threefold axis; Co and Cl(1) sit on the $\bar{3}$ special positions and Cl(2) on 3. The Cl(2) ion approaches a complex cation and makes hydrogen-bonds with three equivalent NH groups (N–H···Cl(2), 3.235(1) Å).

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