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# Dichlorobis(2-amino-2-methyl-3-butanone oximato)cobalt(III), [Co(2AO–H)$Cl_2$]

BY E. O. SCHLEMPER

*Department of Chemistry, University of Missouri, Columbia, MO* 65201, *USA*

S. J. LAPLACA

*IBM Research Division, Yorktown Heights, NY* 10598, *USA*

B. R. DAVIS

*Suffolk County Community College, Selden, NY* 11784, *USA*

AND W. C. HAMILTON*

*Department of Chemistry, Brookhaven National Laboratory, Upton, Long Island, NY* 11973, *USA*

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**Abstract.** $CoCl_2(C_5H_{11}N_2O)_2H$, orthorhombic, *Pnma*, $a$ = 10·912 (4), $b$ = 11·435 (4), $c$ = 12·119 (4) Å, $V$ = 1512 Å$^3$, $M_r$ = 361·2, $Z$ = 4, $\rho_{calc}$ = 1·587 (2), $\rho_{obs}$ = 1·59 g cm$^{-3}$. Three-dimensional counter X-ray data were used to solve and refine the structure to a final $R(F^2)$ of 0·045. The structure consists of discrete monomeric, octahedral Co complex molecules. The complex has $C_s$ symmetry with the mirror including the Co atom, both Cl atoms and the H atom of the short intramolecular hydrogen bond. The O···O distance for the intramolecular hydrogen bond is 2·422 (3) Å, the average Co–Cl distance is 2·259 (4) Å, Co–N(amine) is 1·947 (2) Å, and Co–N(oxime) is 1·891 (2) Å.

**Introduction.** The deep-green crystals (Murmann, 1957) crystallize with primarily {100}, {101}, and {011} facial development. A crystal volume of 0·0458 mm$^3$ was chosen for the X-ray study. The space group and cell dimensions were first determined by precision methods, and the final cell dimensions were obtained from manually centered reflections on the General Electric–Datex programmed diffractometer used to collect the intensity data. Intensity data were collected for one octant by the $\theta$–$2\theta$ scan method using Mo $K\alpha$ radiation filtered with Nb. The data were corrected for background, Lp, and absorption ($\mu$ = 15·3 cm$^{-1}$). The transmission factor ranged from 0·55 to 0·68. Standards monitored about every fifty reflections showed no significant variation.

The structure was solved by conventional Patterson and Fourier methods. All H atoms were evident on difference Fourier maps. Full-matrix least-squares refinement on $F^2$ using 1902 independent reflections [sin $\theta/\lambda$(max) = 0·704 Å$^{-1}$], extinction correction (0·91–0·99) and anomalous-scattering effects for Co and Cl gave $R(F^2)$ = 0·045 and $R(wF^2)$ = 0·094 with the standard deviation of an observation of unit weight equal to 1·30. In the last least-squares cycles, the H

Table 1. *Positional parameters of the heavy atoms*

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| Co | 0·22596 (4) | 0·25 | 0·17917 (3) |
| Cl(1) | 0·32185 (9) | 0·25 | 0·34474 (6) |
| Cl(2) | 0·13503 (8) | 0·25 | 0·01213 (6) |
| O | 0·4326 (1) | 0·1441 (1) | 0·0802 (1) |
| N(1) | 0·3249 (2) | 0·1242 (1) | 0·1309 (1) |
| N(2) | 0·1175 (2) | 0·1236 (2) | 0·2245 (2) |
| C(1) | 0·2868 (2) | 0·0191 (2) | 0·1417 (2) |
| C(2) | 0·3525 (3) | −0·0842 (2) | 0·0976 (2) |
| C(3) | 0·1697 (2) | 0·0045 (2) | 0·2048 (2) |
| C(4) | 0·0779 (4) | −0·0671 (3) | 0·1383 (3) |
| C(5) | 0·1972 (4) | −0·0527 (3) | 0·3167 (2) |

Table 2. *Positional and thermal parameters of the hydrogen atoms*

H2,1, H2,2, and H2,3 are attached to methyl carbon C(2), *etc.* H1 and H2 are attached to N(2). H is the bridging hydrogen atom.

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| H2,1 | 0·437 (5) | −0·053 (5) | 0·073 (4) | 10·8 (1·5) |
| H2,2 | 0·374 (3) | −0·134 (4) | 0·154 (3) | 6·3 (0·9) |
| H2,3 | 0·307 (4) | −0·125 (4) | 0·043 (4) | 7·1 (1·0) |
| H4,1 | 0·112 (4) | −0·148 (5) | 0·128 (4) | 9·0 (1·2) |
| H4,2 | 0·067 (3) | −0·032 (4) | 0·067 (3) | 6·2 (0·9) |
| H4,3 | −0·002 (4) | −0·068 (4) | 0·179 (3) | 6·7 (1·1) |
| H5,1 | 0·229 (4) | −0·136 (5) | 0·309 (4) | 8·1 (1·2) |
| H5,2 | 0·257 (4) | −0·005 (4) | 0·362 (4) | 6·3 (1·0) |
| H5,3 | 0·123 (4) | −0·056 (3) | 0·356 (3) | 5·8 (0·9) |
| H1 | 0·038 (3) | 0·129 (3) | 0·184 (3) | 5·0 (0·8) |
| H2 | 0·084 (3) | 0·124 (3) | 0·292 (3) | 5·4 (0·8) |
| H | 0·445 (6) | 0·25 | 0·082 (5) | 8·6 (1·7) |

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* Deceased.

atoms were refined with isotropic thermal motion and the other atoms anisotropically to give a total of 138 variables. The weighting in the least squares was based on $\sigma^2(F_o^2) = \sigma^2(\text{counting}) + (0{\cdot}05F_o^2)^2$. The shifts on the last cycle were all less than 10% of the corresponding standard deviations.

The coordinates and, for H, the isotropic thermal parameters are in Tables 1 and 2.*

**Discussion.** The primary interest in the structure was to compare the short intramolecular hydrogen bond with that in the previously reported neutron study of the square-planar Ni$^{\rm II}$ complex of the same amine oxime ligand (Schlemper, Hamilton & LaPlaca, 1971). In that study the O···O distance in the short hydrogen bond was 2·420 (3) compared with 2·422 (3) Å in the present complex. These distances are remarkably similar despite the observed increase in $M$–N distances of about 0·035 Å in going from the Ni to the Co complex.

The structure consists of discrete mononuclear neutral Co complex molecules with the Co$^{\rm III}$ atom in a distorted octahedral configuration (Fig. 1). The crystal packing of the neutral molecules is shown in Fig. 2. The Co octahedron consists of *trans* chloro groups and four N atoms from the two bidentate amine oxime ligands. The Co is 0·04 Å out of the plane defined by the four N atoms toward Cl(1). There is a small, but significant, difference (0·008 Å) in Co–Cl distances (Table 3). This difference may simply be due to the steric effect of the slight puckering of the bidentate amine oxime ligands. This is a much smaller difference than that observed in Co–N distances for the *trans* nitro groups (0·047 Å) in *trans*-dinitro-2,2′-(1,3-diaminopropane)-bis(2-methyl-3-butanone oximato)cobalt(III) (Murmann & Schlemper, 1973). The Co–N(amine) distance of 1·891 (2) Å is comparable with that [1·900 (4) Å] in the previous study, but the present Co–N(oxime) distance [1·947 (4) Å] is quite significantly shorter [1·977 (2) Å]. This difference may be related to the quite different steric requirements of the tetradentate ligand in the previous study. The ligand distances (Table 3) and angles (Table 4) are very similar to those found for the Ni$^{\rm II}$ complex.

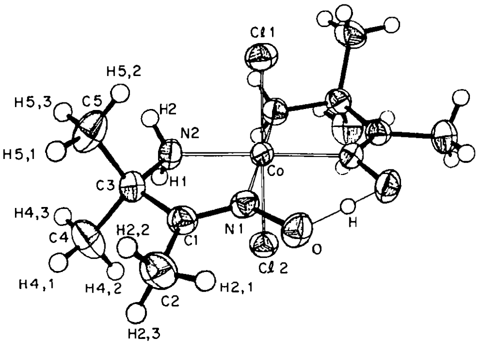

Fig. 1. The molecular structure of $[\mathrm{Co(2AO{-}H)Cl_2}]$ with the atom labeling scheme.

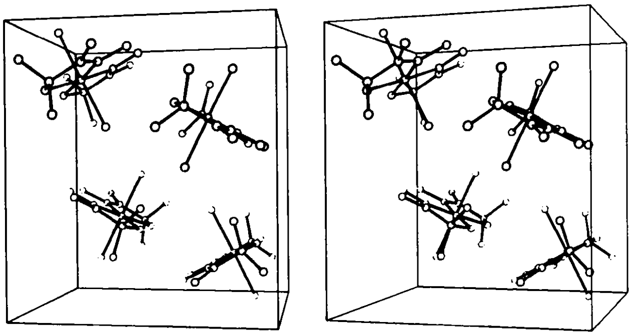

Fig. 2. A stereoscopic view of the unit-cell contents.

Table 3. *Bond distances* (Å) *in* $[\mathrm{Co(2AO{-}H)Cl_2}]$

| | | | |
|---|---|---|---|
| Co–Cl(1) | 2·2630 (8) | O–H | 1·22 (7) |
| Co–Cl(2) | 2·2545 (8) | C(2)–H2,1 | 1·03 (6) |
| Co–N(1) | 1·891 (2) | C(2)–H2,2 | 0·93 (4) |
| Co–N(2) | 1·947 (2) | C(2)–H2,3 | 0·95 (5) |
| N(1)–O | 1·345 (3) | C(4)–H4,1 | 1·02 (5) |
| N(1)–C(1) | 1·279 (3) | C(4)–H4,2 | 0·96 (4) |
| C(1)–C(2) | 1·482 (3) | C(4)–H4,3 | 1·00 (4) |
| C(1)–C(3) | 1·499 (4) | C(5)–H5,1 | 1·02 (6) |
| C)3)–C(4) | 1·525 (4) | C(5)–H5,2 | 1·01 (4) |
| C(3)–C(5) | 1·535 (3) | C(5)–H5,3 | 0·94 (4) |
| C(3)–N(2) | 1·495 (3) | N(2)–H1 | 1·00 (3) |
| O–O′ | 2·422 (3) | N(2)–H2 | 0·89 (4) |

Table 4. *Bond angles* (°) *in* $[\mathrm{Co(2AO{-}H)Cl_2}]$

| | | | |
|---|---|---|---|
| Cl(1)–Co–N(1) | 90·59 (6) | C(3)–N(2)–Co | 113·6 (2) |
| Cl(1)–Co–N(2) | 91·76 (6) | O–H–O′ | 166·9 (5·6) |
| Cl(2)–Co–N(1) | 88·48 (5) | C(1)–C(2)–H2,1 | 105 (3) |
| Cl(2)–Co–N(2) | 89·20 (6) | C(1)–C(2)–H2,2 | 110 (2) |
| N(1)–Co–N(2) | 82·53 (8) | C(1)–C(2)–H3,2 | 113 (3) |
| N(1)–Co–N(1′) | 99·0 (1) | H2,1–C(2)–H2,2 | 101 (4) |
| N(1)–Co–N(2′) | 117·17 (9) | H2,1–O(2)–H2,3 | 115 (4) |
| N(2)–Co–N(2′) | 95·8 (1) | H2,2–C(2)–H2,3 | 110 (4) |
| O–N(1)–Co | 120·7 (1) | C(3)–C(4)–H4,1 | 108 (2) |
| O–N(1)–C(1) | 119·3 (2) | C(3)–C(4)–H4,2 | 109 (2) |
| Co–N(1)–C(1) | 119·9 (2) | C(3)–C(4)–H4,3 | 108 (2) |
| N(1)–C(1)–C(2) | 123·8 (2) | H4,1–C(4)–H4,2 | 109 (3) |
| N(1)–C(1)–C(3) | 115·7 (2) | H4,1–C(4)–H4,3 | 112 (4) |
| C(2)–C(1)–C(3) | 120·5 (2) | H4,2–C(4)–H4,3 | 110 (3) |
| C(1)–C(3)–C(4) | 110·5 (2) | C(3)–C(5)–H5,1 | 113 (2) |
| C(1)–C(3)–C(5) | 109·4 (2) | C(3)–C(5)–H5,2 | 112 (2) |
| C(1)–C(3)–N(2) | 107·7 (2) | C(3)–C(5)–H5,3 | 107 (2) |
| C(4)–C(3)–C(5) | 111·5 (2) | H5,1–C(5)–H5,2 | 109 (3) |
| C(4)–C(3)–N(2) | 108·9 (2) | H5,1–C(5)–H5,3 | 107 (3) |
| C(5)–C(3)–N(2) | 108·7 (2) | H5,2–C(5)–H5,3 | 108 (3) |
| C(3)–N(2)–H1 | 108 (2) | | |
| C(3)–N(2)–H2 | 108 (2) | | |
| Co–N(2)–H1 | 110 (2) | | |
| Co–N(2)–H2 | 120 (2) | | |
| H1–N(2)–H2 | 95 (3) | | |

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33096 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

H atom positions were all refineable and resulted in the following average values: C—H 0·984 Å, C—C—H 109·4°, and H—C—H 109·0°. The H in the short intramolecular hydrogen bond must be either on the mirror or disordered across the mirror. Difference-Fourier-map examination of the electron density revealed considerable variation in the appearance of the H atom. Using a cut-off of $\sin\theta/\lambda = 0{\cdot}4$ Å$^{-1}$ (which gave excellent resolution and a clean three-peak map for the methyl H atoms), the H atom appears to be on the mirror but to be somewhat elongated in the bonding direction (O—H = 1·219 Å from least squares).

An interesting feature of the structure in comparison with the Ni$^{II}$ complex (Schlemper, Hamilton & LaPlaca, 1971) is the nearly planar nature of the five-membered chelate rings. The maximum deviation from the plane defined by the N atoms is only 0·07 Å [for C(1)] whereas in the Ni complex all the C atoms are well to one side of the metal–N plane (maximum 0·56 Å for the $sp^3$ C atoms). In this structure the methyl groups [C(4) and C(5)] are essentially equidistant from the plane of the four N atoms, whereas in the Ni complex one of these methyl groups is nearly in the plane while the other is about 2·00 Å out of the plane. This difference in conformation is probably due to the *trans* chloro groups [Cl(2)–C(4) 3·62 Å, and Cl(1)–C(5) 3·74 Å]. This change in the chelate ring geometry allows the O···O distance to be nearly identical to that in the Ni complex without an increase in the N(amine)–Co–N(amine) angle [it actually decreases from 96·5 (1) to 95·8 (1)°]. This change in conformation is then sufficient to balance the lengthening in O···O distance which might have been anticipated as a result of the longer *M*—N distances in this Co complex. The hydrogen bond then remains among the shorter observed O···O hydrogen bonds.

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# δ-Bis(*n*-Propylammonium) Tetrachloromanganate(II): A Neutron Refinement

By W. Depmeier

*Universität Konstanz, FB Chemie, Postfach* 7733, *D*7750 *Konstanz, Federal Republic of Germany*

and S. A. Mason

*Institut Laue–Langevin,* 156*X, F* 38042 *Grenoble CEDEX, France*

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**Abstract.** δ-$(C_3H_7NH_3)_2MnCl_4$, orthorhombic, *Abma* (No. 64), $T = 182$ K, $a = 7{\cdot}458\ (9)$, $b = 7{\cdot}169\ (9)$, $c = 25{\cdot}61\ (5)$ Å, $Z = 4$, $\lambda = 0{\cdot}745$ Å. The $MnCl_6$ octahedra layer takes the $a^-a^-c^0$ tilt system, the *n*-propylammonium group is disordered, and the hydrogen-bonding scheme is a superposition of two symmetry-related schemes.

**Introduction.** Crystals suitable for neutron work were obtained by slow evaporation of a solution of $MnCl_2$ and $C_3H_7NH_3Cl$ (molar ratio 1:1) in a mixture of water and ethanol. A crystal, 2·4 × 2·7 × 1·4 mm, was chosen and cooled to a set temperature of 182 K (17 K above the $\varepsilon \rightarrow \delta$ phase transition). A Displex cryo-refrigerator was used and the temperature was constant throughout the experiment. The cell dimensions and intensities were measured at the D9 diffractometer at the HFR of the Institut Laue–Langevin (Grenoble) with neutrons of wavelength 0·745 Å from a Cu(200) monochromator. Cell dimensions were obtained by least squares from the setting values of 11 reflexions. Data were collected by the $\omega/2\theta$-scan technique in the range $\theta < 30°$ yielding 910 unique reflexions of which about two-thirds had intensities $>3\sigma$. Transmission factors were estimated for two different crystal plates by their attenuation of a monochromatic beam. The