A Very Short O–H···O Hydrogen Bond in the Crystal Structure of *trans*-(1,3-Diamino-2-propanolato-*N,N',O*)(1,3-diamino-2-propanol-*N,N',O*)cobalt(III) Dichloride Dihydrate

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The structure of $[Co(C_3H_9N_2O)(C_3H_{10}N_2O)]Cl_2 \cdot 2H_2O$ has been determined from single-crystal X-ray diffraction data and refined to a final R value of 0.022 for 1684 reflections. The compound forms monoclinic crystals, space group $C2/c$, and its unit cell has the following dimensions: a = 15.936(3), b = 8.071(1) and c = 10.727(1) Å, with β = 105.48(1)° and Z = 4. Two crystallographically equivalent, statistically halfdeprotonated ligands coordinate to the central atom in a tridentate fashion, with the six-membered chelate rings in nearly symmetrical boat conformation. Chemically the two ligands are non-equivalent, one being anionic and the other neutral. The complex units are bonded into infinite chains by very short, partly disordered hydrogen bonds, in which the O···O separation is only 2.422(1) Å. The IR spectrum exhibits an exceptionally broad band between about 1300 and 600 cm^{-1}, typical for very strong O–H···O hydrogen bonds.

Because of its three donor atoms, 1,3-diamino-2-propanol (denoted hereafter 2-tmOH) can coordinate to a metal ion in several different ways, and the chelate rings formed may adopt different conformations. Six-membered chelate rings with boat conformation are fairly uncommon and have not yet been found in solid copper(II) complexes of 2-tmOH.[1] However, Okamoto and Barefield[2] have reported a variety of equilibria involving hydroxyl groups in monomeric cobalt(III) complexes of 2-tmOH in solution, and in some of these complexes the aminoalcohol ligands are tridentate with the six-membered chelate rings in boat conformation. According to spectroscopic and other data, a complex of apparent formula *trans*-$[Co(2\text{-tmO})(2\text{-tmOH})]Cl_2$ is formed in 0.1 M HCl solution. The boat conformation of the chelate ring and the extraordinary formula of this complex prompted us to crystallize a (2-tmOH) Co(III) complex from 0.1 M HCl solution. Preliminary information about the complex formed, $[Co(2\text{-tmO})(2\text{-tmOH})]Cl_2 \cdot 2H_2O$, has been communicated elsewhere.[3] Also, preliminary X-ray results have recently been reported for $[Co(2\text{-tmO})_2]Cl \cdot 2H_2O$,[4] in which both of the tridentately coordinated ligands are deprotonated, and the crystal structure has been published for a cobalt complex with tridentate 2-tmO^- as one of the ligands.[5]

Experimental

The title compound was prepared applying the procedure of Okamoto and Barefield[2] and crystallized from 0.1 M HCl solution.

The unit cell parameters were determined by least-squares refinement from 25 centered reflections ($20° < 2\theta < 30°$) measured at ambient temperature on a Nicolet $P3$ diffractometer. The compound crystallizes in the monoclinic crystal system and systematic absences indicated space group $C2/c$ or Cc. Statistics of the intensities indicated centrosymmetry, and refinements in the two space groups gave identical R values and no significant differences in the resulting two structures. Therefore, the space group $C2/c$, which has

Table 1. Crystal data and details of data collection.

Mol. formula	$C_6H_{23}Cl_2CoN_4O_4$
Mol. weight	345.1
Crystal system	Monoclinic
a/Å	15.936(3)
b/Å	8.071(1)
c/Å	10.727(1)
β/°	105.48(1)
Space group	*C2/c*
V/Å^3	1329.7(3)
D_c/g cm^{-3}	1.72
Z	4
Crystal dimensions/mm	0.2×0.2×0.4
Diffractometer	Nicolet *P*3
Radiation	Mo*K*α(λ=0.71069 Å)
Absorption coefficient/cm^{-1}	17.5
Scan type	ω
2θ limits	5°<2θ<60°
Scan rate/° min^{-1}	1.5–20
No. of collected reflections	1945
No. of observed reflections	1684 (F_o>6σ$\|F_o\|$)
R (R=Σ$\|\|F_o\|-\|F_c\|\|$/Σ$\|F_o\|$)	0.022
R_w (R_w=[Σw($\|F_o\|-\|F_c\|$)^2/ Σ$w\|F_o\|^2$]$^{1/2}$)	0.023

higher symmetry, was selected for final calculations. Crystal data and details of the data collection are presented in Table 1. The data were corrected for Lp effects, and for absorption and dispersion. Intensity variation of the standard reflections was negligible.

The structure was solved by direct methods[6] and refined using the XRAY 76 system programs.[7] Refinements for all non-hydrogen atoms with anisotropic temperature factors gave an R value of 0.039, and approximate positions of all hydrogen atoms except the alcoholic hydrogen were picked from a subsequent difference Fourier map. After inclusion of all atoms, with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms except the alcoholic hydrogen, a new ΔF-map was calculated. Because of the symmetry and oxidation state of the central atom, the hydrogen atom of the coordinated hydroxy group must be situated at the two-fold axis (1/2,y,1/2) between oxygen atoms of neighbouring complex units, or it must be disordered. ΔF-synthesis revealed two maxima (0.35 e Å^{-3}) near the two-fold axis and less significant electron den-

Table 2. Positional and thermal parameters. U_{eq}=1/3(U_{11}+U_{22}+U_{33}).

Atom	*x*	*y*	*z*	U_{eq} or U_{iso}/Å^2
Co	0.50000	0.50000	0.50000	0.0135(1)
Cl	0.69955(3)	0.14049(6)	0.64415(4)	0.0325(2)
O1	0.54688(7)	0.55016(13)	0.35934(10)	0.0195(5)
O2	0.38275(10)	0.15044(24)	0.22033(16)	0.0406(8)
N1	0.49323(9)	0.73936(16)	0.52421(13)	0.0202(6)
N2	0.62104(8)	0.52096(17)	0.60361(12)	0.0193(5)
C1	0.54563(11)	0.82086(19)	0.44536(16)	0.0240(7)
C2	0.60236(10)	0.68823(20)	0.40974(14)	0.0218(7)
C3	0.66929(10)	0.61908(23)	0.52704(16)	0.0247(7)
H1(N1)	0.4421(14)	0.770(3)	0.506(2)	0.035(6)
H2(N1)	0.5126(13)	0.760(3)	0.607(2)	0.030(5)
H3(C1)	0.5094(13)	0.867(3)	0.367(2)	0.030(5)
H4(C1)	0.5778(14)	0.913(3)	0.490(2)	0.034(6)
H5(C2)	0.6280(11)	0.726(2)	0.344(2)	0.018(4)
H6[a](O1)	0.5155(24)	0.561(4)	0.286(3)	0.015(9)
H7(C3)	0.7029(13)	0.708(3)	0.581(2)	0.035(6)
H8(C3)	0.7082(13)	0.546(3)	0.503(2)	0.030(5)
H9(N2)	0.6229(13)	0.570(3)	0.674(2)	0.029(5)
H10(N2)	0.6467(13)	0.429(3)	0.622(2)	0.031(5)
H11(O2)	0.3422(21)	0.186(4)	0.182(3)	0.070(11)
H12(O2)	0.3604(18)	0.071(4)	0.254(3)	0.063(9)

[a]Population parameter 0.5.

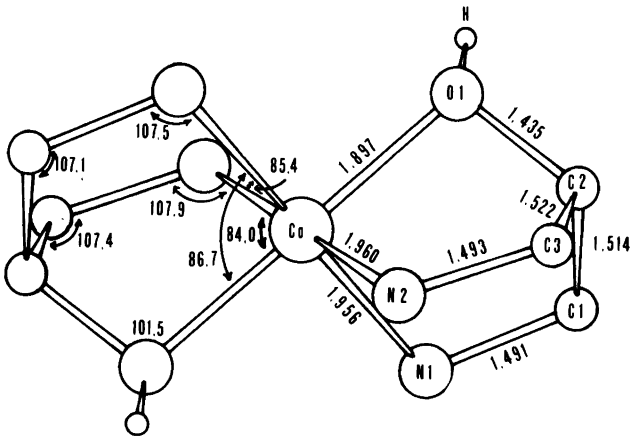

Fig. 1. Perspective view of the complex unit of *trans*- (1,3-diamino-2-propanolato-*N,N',O*)(1,3-diamino-2-propanol-*N,N',O*) cobalt(III) dichloride dihydrate together with the numbering system, selected bond lengths (Å) and angles (°). The hydrogen atoms, except the hydroxy hydrogen, are omitted for clarity.

sity (0.10 e $Å^{-3}$) at the axis. Since refinements made also for all atoms with the alcoholic hydrogen at the two-fold axis were unsuccessful, the data clearly indicated disordering of the alcoholic hydrogen atom. Refinements of the positions of all atoms reduced the R value to 0.022. The function minimized was $\Sigma w(\Delta F)^2$, where $w = 1/\sigma_F^2$. The largest maximum in the final difference map was 0.24 e $Å^{-3}$. Atomic scattering factors employed were those included in the program and f' and f'' components for Co and Cl were taken from Ref. 8. Lists of observed and calculated structure factors as well as anisotropic temperature factors are available from the author on request.

The IR spectrum (KBr) disc was recorded on a Perkin-Elmer 577 grating infrared spectrophotometer in the range 4000–200 cm^{-1}. A polystyrene film was used for calibration.

Discussion

Atomic coordinates are listed in Table 2 and the numbering system for the complex unit with selected bond lengths and angles is shown in Fig. 1. The bond lengths and angles are listed in full in Table 3.

The structure consists of strongly hydrogen-bonded [Co(2-tmO)(2-tmOH)] units, chloride

Table 3. Bond lengths (Å) and angles (°).

Co–O1	1.898(1)	C1–H3	0.96(2)
Co–N1	1.956(1)	C1–H4	0.95(2)
Co–N2	1.960(1)	C2–H5	0.95(2)
O1–C2	1.436(2)	O1–H6[a]	0.82(3)
N1–C1	1.491(2)	C3–H7	0.99(2)
N2–C3	1.493(2)	C3–H8	0.94(2)
C1–C2	1.515(2)	N2–H9	0.85(2)
C2–C3	1.522(2)	N2–H10	0.85(2)
N1–H1	0.82(2)	O2–H11	0.73(3)
N1–H2	0.88(2)	O2–H12	0.85(3)
O1–Co–N1	86.69(6)	N1–C1–C2	107.1(1)
O1–Co–N2	84.01(5)	O1–C2–C1	107.1(1)
N1–Co–N2	85.43(6)	O1–C2–C3	104.6(1)
Co–O1–C2	101.5(1)	C1–C2–C3	112.6(1)
Co–N1–C1	107.5(1)	N2–C3–C2	107.4(1)
Co–N2–C3	107.9(1)		

[a]See footnote to Table 2.

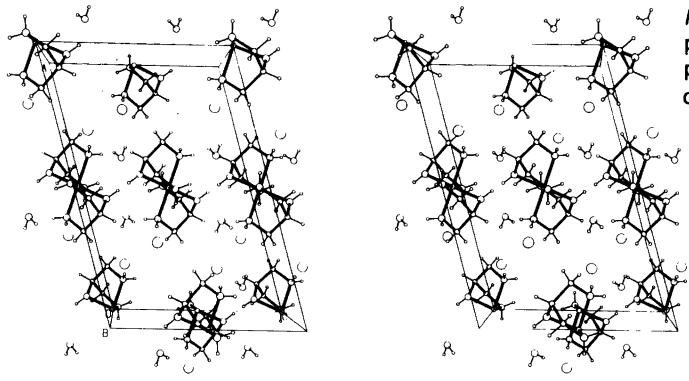

Fig. 2. Stereo view of *trans*-(1,3-diamino-2-propanolato-*N,N',O*)(1,3-diamino-2-propanol-*N,N',O*)cobalt(III) dichloride dihydrate.

ions and water molecules (Fig. 2). The cobalt(III) atom occupies the centre of symmetry and two statistically half-deprotonated 2-tmOH ligands coordinate to the central atom in a tridentate fashion, with the six-membered rings in nearly symmetrical boat conformation. The coordination around Co is slightly distorted octahedral, the Co-O bond being about 0.06 Å shorter than the Co-N bonds, and the angles between adjacent atoms ranging from 84.01(5) to 95.99(5)°.

As expected, the chelate ring-strain of the boat conformation is reflected most prominently in the bond angles. Comparison of the bond angles for the boat conformation of the chelate ring in the present compound with those for the chair conformation in $[Co(2\text{-tmOH})_2Cl_2]Cl$[9] reveals considerable differences. The values of the N1-Co-N2 and N-C-C angles are 3–5° smaller than those in $[Co(2\text{-tmOH})_2Cl_2]Cl$, and the values of flexible Co-N-C angles are as much as 14° smaller.

Comparison of the bond parameters for $[Co(2\text{-tmO})(2\text{-tmOH})]Cl_2 \cdot 2H_2O$ and $[Co(2\text{-tmO})_2]Cl \cdot 2H_2O$[4] shows that the different charges of the ligands have little effect on the bond parameters of the complex units, but they do cause different hydrogen-bonding systems. The most significant difference in the bond parameters of the two complex units is in the N-Co-O angle values. The greater difference in the N1-Co-O1 and N2-Co-O1 angles in the title complex [86.69(6) and 84.01(5)°, respectively] is more likely to arise from the very strong intermolecular O–H···O hydrogen bonds formed by the coordinated oxygen atoms than from different charges on the ligands.

The bond lengths in the 2-tmOH metal chelate ring in the present complex are also similar to those in ΔΛ-*abc,def*-(1,5-diamino-3-azapentane-*N,N',N'*)(1,3-diamino-2-propanolato-*N,N',O*)-cobalt(III) chloride tetrachlorozincate(II)[5] except for the Co-O bond lengths, which are 1.898(1) and 1.942(3) Å, respectively, in the two compounds. Although there are also significant differences in some bond angles, the tridentate cap of 2-tmOH in the tetrachloro zincate salt dis-

Table 4. Distances (Å) and angles (°) in the hydrogen bonds.

D–H···A	D···A	D–H	H···A	∠D–H···A
O1–H6[a]···O^{I}	2.422(1)	0.82(3)	1.61(3)	170(3)
N1–H1···Cl^{II}	3.268(2)	0.82(2)	2.51(2)	154(2)
N2–H10···Cl	3.301(2)	0.85(2)	2.46(2)	170(2)
O2–H11···Cl^{III}	3.281(2)	0.73(3)	2.61(3)	155(3)
O2–H12···Cl^{IV}	3.220(2)	0.85(3)	2.37(3)	177(3)

[a]See footnote to Table 2. Equivalent positions: I=1−*x*,*y*,1/2−*z*; II=1−*x*,1−*y*,1−*z*; III=−1/2+*x*,1/2−*y*,−1/2+*z*; IV=1−*x*,−*y*,1−*z*.

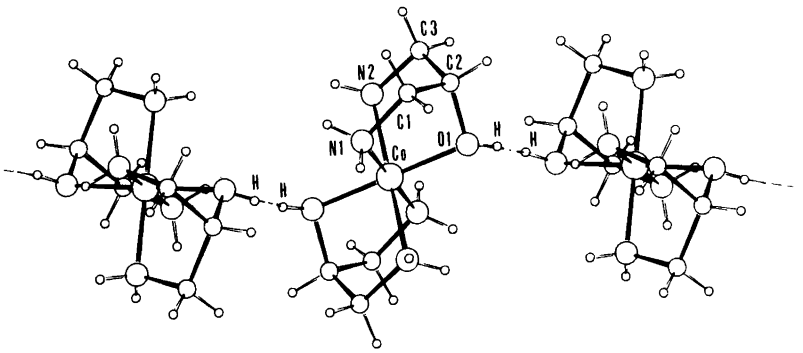

Fig. 3. Strongly hydrogen-bonded complex unit chain in the crystal structure of *trans*-(1,3-diamino-2-propanolato-*N,N',O*)(1,3-diamino-2-propanol-*N,N',O*) cobalt(III) dichloride dihydrate.

plays the tendency found also in the title compound and in $[Co(2\text{-}tmO)_2]Cl \cdot 2H_2O$[4] to decrease the bond angles of the six-membered chelate ring with respect to the bond angles for the chair conformation in $[Co(2\text{-}tmOH)_2Cl_2]Cl$.[9]

The nitrogen atoms, oxygen atoms and chloride ions all participate in hydrogen bonding (Table 4). One hydrogen atom of each amino group and both hydrogen atoms of the water molecule form weak hydrogen bonds to chloride ions. Very short disordered hydrogen bonds between oxygen atoms of neighbouring [Co(2-tmO)(2-tmOH)] units link the units into an infinite chain in the direction of the *z*-axis (Fig. 3).

The two halves of the disordered O–H···H–O type hydrogen bond, with statistically half-occupied hydrogen atom positions, are crystallographically equivalent owing to the two-fold axis between the oxygens. The O···O separation of 2.422(1) Å is in the very strong hydrogen bond range,[10] and the bond is nearly linear [∠ O–H···O = 170(3)°]. Non-inclusion of the alco holic hydrogen atom resulted in an O···O distance about 0.03 Å too short. Similar results have been reported in an earlier study.[11] The observed apparent H···H separation is 0.79(4) Å and the two H atom positions must therefore be mutually exclusive.

The present results indicate that this very short hydrogen bond is clearly asymmetric. However, the apparent half-hydrogen positions, as commonly observed in X-ray studies, are very much shifted towards oxygens [distance 0.82(3) Å]. The true internuclear O–H distance is expected to be around 1.10–1.20 Å for an asymmetric hydrogen bond of 2.50–2.55 Å.[12]

The averaging of hydrogen-bonded infinite chains –Co–O–H···O–Co–O–H···O–Co– and –Co–O···H–O–Co–O···H–O–Co– provides an explanation for the observed atomic arrangement O–H···H–O. This means that the coordinated ligands of the complex unit are chemically non-equivalent, one being neutral and the other deprotonated. On the other hand, the short apparent H···H separation and evidence of equilibria between the different complexes formed by cobalt(III) ion and 2-tmOH in solution[2] make it impossible to rule out dynamic equilibrium in the chains.

Above 1500 cm^{-1} the IR spectrum recorded for the title dihydrate is similar to that of $[Co(2\text{-}tmO)(2\text{-}tmOH)]Cl_2$.[2] The spectrum of the anhydrous form was not recorded below 1500 cm^{-1}, and the sharp absorptions at 3479 and 3391 cm^{-1} were attributed by the authors to OH vibrations. According to Bellamy's characterization, the spectrum recorded here for the dihydrate form is typical for compounds having a very strong O–H···O hydrogen bond, with the bond giving rise to an exceptionally broad band between about 1300 and 600 cm^{-1} upon which the normal fingerprint bands of the remainder of the spectrum are superimposed.[13] Compounds with no absorption due to OH stretching above 1700 cm^{-1} have essentially symmetric or near symmetric hydrogen bonds of very short length, and the OH stretching bands are then attributable to the asymmetric OHO stretching mode.

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