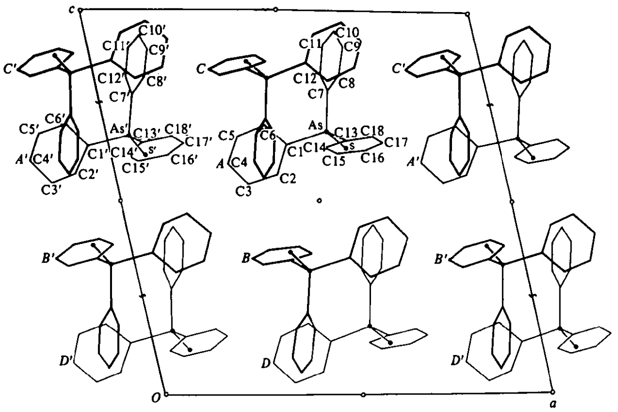

Fig. 2. Crystal packing of triphenylarsine sulfide as viewed down the short b axis.

disregards small deviations. Therefore, a pseudo glide plane is present at $y = 0{\cdot}379$, but only in the range $z = \frac{1}{2}$–1. Similarly D, B, D' and B' are related across a pseudo center at ($\frac{1}{4}$,0·3704,$\frac{1}{4}$) with a pseudo glide plane at $y = 0{\cdot}1201$ in the range $z = 0$–$\frac{1}{2}$. The distances between the alternating pseudo glide planes are thus about 0·241 (*ca* 2·35 Å) and 0·259 (*ca* 2·53 Å).

The structure is therefore built up from two non-identical layers of molecules stacked in alternate planes of the set (200). The interlayer distance is 8·87 Å. In these planes the stacking is through the screw axes and centers of symmetry. Because of the different positions of the molecules in the non-identical layers with respect to the center of symmetry the contacts between molecules A and B are not identical to those between A' and B'. There are no short (<3·0 Å) intermolecular contacts and the packing of the molecules involves mainly van der Waals forces.

We are grateful to Dr A. Datta for supplying the triphenylarsine sulfide and to Dr J. K. Suri for helping with the computation on the EC-1030 computer in IIT, Bombay. One of the authors (SVLN) is indebted to IIT, Bombay, for providing a scholarship.

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The Structure of *trans*-Dichlorobis[(+)-(S,S)-*trans*-1,2-diaminocyclopentane]cobalt(III) Chloride Hydrochloride Dihydrate, *trans*-$[CoCl_2\{(+)\text{-cptn}\}_2]Cl.HCl.2H_2O$

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Abstract

Crystals of the title compound, $[Co(C_5H_{12}N_2)_2Cl_2]Cl.$-$HCl.2H_2O$, $M_r = 438{\cdot}11$, are orthorhombic, space group $P22_12_1$, with $a = 9{\cdot}571$ (2), $b = 24{\cdot}541$ (3), $c = 8{\cdot}412$ (2) Å, $U = 1975{\cdot}9$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}47$, $D_m = 1{\cdot}47$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·446 mm^{-1}. The crystal structure has been refined to give an R value of 0·044 for 2666 observed reflections collected by X-ray diffractometry. The complex cation has approximate D_2 symmetry, the Co atom being surrounded pseudo-octahedrally by the four N atoms of two (+)-cptn

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ligands in an approximate plane with an average Co—N distance of 1·979 (3) Å, and by two Cl atoms occupying axial positions with an average separation from the Co of 2·257 (2) Å. The previously reported anomalous solution CD behavior of the title complex arises from the strain present at the bridgehead C atoms of the (+)-cptn chelate rings.

Introduction

Solution CD spectra of the *trans*-dianionobis[(*R*,*R*)-1,2-diaminocyclopentane]cobalt(III) ion, *trans*-$[CoX_2\{(-)\text{-cptn}\}_2]^+$ ($X = Cl^-$ and CN^-), have been reported to exhibit CD components with the opposite signs for the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition compared with analogous chelates of (*R*)-1,2-diaminopropane [(−)-pn] and (*R*,*R*)-1,2-diaminocyclohexane [(−)-chxn] in spite of the fact that the five-membered chelate rings formed with all of these diamines invariably take the preferred λ conformation (Goto, Takeshita & Sakai, 1979). A similarly anomalous CD spectrum has also been reported for the tris-lel_3-chelate of $[Co\{(+)\text{-cptn}\}_3]^{3+}$ and the crystal structure of $(-)_{589}[Co\{(+)\text{-cptn}\}_3]Cl_3.4H_2O$ has been determined by Ito, Marumo & Saito (1971). In the present study, the molecular and crystal structure of *trans*-dichlorobis[(+)-*trans*-1,2-diaminocyclopentane]cobalt(III) chloride hydrochloride dihydrate, *trans*-$[CoCl_2\{(+)\text{-cptn}\}_2]Cl.HCl.2H_2O$, has been determined. A main feature of interest is the relationship between the molecular structure and the anomalous CD behavior.

Experimental

The title complex was synthesized by dissolving the parent *trans*-$[CoCl_2\{(+)\text{-cptn}\}_2]Cl$ (Goto, Takeshita & Sakai, 1979) in dilute hydrochloric acid, followed by the addition of concentrated hydrochloric acid to the solution. The green plate crystals thus obtained were found to lose hydrogen chloride and water of crystallization easily when exposed to air at room temperature. A crystal of dimensions 0·32 × 0·32 × 0·25 mm was therefore coated with a thin layer of paraffin and used for the intensity measurements. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Within the range $2\theta \leq 70°$, 2666 independent reflexions with $|F_o| > 3\sigma(|F_o|)$ were obtained and used in the structure analysis. The intensities were corrected for Lorentz and polarization factors. The intensities for three standard reflexions measured after every 50 measurements decreased by about 6% during the data collection. No corrections for the intensity decrease or for absorption were applied.

Preliminary Weissenberg photographs were taken around the b and c axes with Cu $K\alpha$ radiation. The intensity distribution showed the following characteristic features: $hk0$ very weak when h or k is odd; $h0l$ very weak when $h + l$ is odd. Because systematic absences due to the presence of twofold axes were obscured, it was impossible to determine the space group uniquely from Weissenberg photographs on the basis of the extinction rule.

Determination of the structure

The Weissenberg photographs suggest eight possible space groups ($P222$, $P2_122$, $P22_12$, $P222_1$, $P2_12_12$, $P2_122_1$, $P22_12_1$, $P2_12_12_1$). The space group was determined from an examination of the peak distribution in three-dimensional Patterson maps. Patterson maps were exclusively interpreted with space group $P22_12_1$.

The position of the Co atom was derived from the Patterson maps. Nevertheless, an attempt to locate the remaining non-hydrogen atoms from successive Fourier syntheses was unsuccessful. Taking into account the Patterson maps and crystal packing, the positions of the non-hydrogen atoms (except for those of the water molecules) could be determined. Block-diagonal least-squares calculations were carried out with anisotropic thermal parameters and converged to an R value of 0·10. At this stage, a difference synthesis revealed one ordered $[H_2O(1)]$ and one disordered water molecule $[H_2O(2)]$. The disordered $H_2O(2)$ was located at three positions [$H_2O(2a)$, $H_2O(2b)$, and $H_2O(2c)$]. Further refinements including water molecules were made and the positions of all the H atoms except those of water were determined in subsequent difference Fourier maps. At the final stage, full-matrix least-squares calculations with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for H atoms were carried out in order to determine the population of the disordered water, under the restricted conditions $P_{O(2b)} = P_{O(2c)}$ and $P_{O(2a)} + 2P_{O(2b)} = 1$. The scattering factors and the anomalous-scattering corrections for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974). For H atoms, the values given by Stewart, Davidson & Simpson (1965) were used. The weighting scheme employed was $w = [\sigma^2_{\text{count}} + (0{\cdot}015|F_o|)^2]^{-1}$. Final R and R_w values were 0·044 and 0·048, respectively, for 2666 independent reflections. Atomic parameters are given in Table 1.*

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* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35956 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters* ($\times 10^5$, *for* H $\times 10^3$) *and thermal parameters*

For the non-hydrogen atoms, equivalent isotropic thermal parameters were calculated from the refined anisotropic thermal parameters (Hamilton, 1959).

	x	*y*	*z*	*B* (Å^2)
Co	25124 (8)	25065 (2)	77859 (5)	2·08
Cl(1)	1518 (13)	25053 (12)	77845 (18)	2·81
Cl(2)	48689 (14)	25046 (12)	77837 (17)	2·79
Cl(3)	56 (20)	39239 (6)	52773 (26)	4·60
Cl(4)	50167 (20)	39363 (6)	53006 (28)	5·06
N(1)	24772 (74)	23025 (14)	55141 (40)	2·63
N(2)	25170 (70)	17210 (13)	82862 (39)	2·60
N(3)	24533 (69)	27085 (15)	100656 (39)	2·48
N(4)	25655 (67)	32962 (14)	72898 (40)	2·71
C(1)	21173 (45)	17175 (20)	54543 (53)	2·67
C(2)	29074 (51)	14387 (20)	67646 (59)	3·12
C(3)	25214 (142)	8420 (20)	65372 (62)	4·58
C(4)	24735 (180)	7902 (24)	47060 (69)	6·11
C(5)	23927 (102)	13718 (24)	40039 (63)	3·79
C(6)	21205 (48)	32944 (21)	101138 (60)	3·16
C(7)	29004 (48)	35747 (20)	87968 (62)	3·10
C(8)	25637 (135)	41736 (21)	90315 (74)	4·89
C(9)	24832 (175)	42230 (24)	108513 (79)	6·65
C(10)	25146 (117)	36411 (21)	115672 (66)	4·47
O(1)	24536 (72)	3816 (14)	109238 (42)	4·86
O(2*a*)	74909 (260)	4378 (51)	94058 (149)	4·11
O(2*b*)	62846 (110)	539 (66)	93026 (227)	6·91
O(2*c*)	86706 (122)	154 (83)	92575 (215)	6·89
H(1)	193 (4)	248 (2)	498 (6)	1·6 (1·0)
H(2)	329 (6)	239 (3)	522 (9)	4·6 (1·8)
H(3)	186 (8)	149 (4)	962 (11)	11·0 (3·2)
H(4)	317 (4)	164 (2)	879 (5)	0·2 (0·7)
H(5)	338 (7)	254 (5)	1061 (12)	10·6 (2·9)
H(6)	185 (4)	256 (2)	1054 (6)	1·4 (1·0)
H(7)	172 (4)	337 (2)	672 (5)	0·4 (0·7)
H(8)	294 (8)	341 (3)	595 (8)	8·7 (2·2)
H(9)	116 (4)	171 (2)	561 (5)	1·0 (0·8)
H(10)	402 (5)	155 (2)	647 (6)	2·6 (1·0)
H(11)	295 (9)	56 (3)	720 (10)	9·3 (2·7)
H(12)	165 (6)	70 (3)	697 (8)	4·4 (1·5)
H(13)	356 (7)	67 (4)	456 (11)	8·9 (2·6)
H(14)	196 (7)	55 (3)	418 (9)	7·7 (2·4)
H(15)	172 (7)	144 (3)	316 (8)	4·5 (1·6)
H(16)	324 (6)	144 (3)	367 (9)	4·8 (1·8)
H(17)	114 (4)	331 (2)	992 (6)	2·8 (1·0)
H(18)	391 (4)	353 (2)	902 (5)	1·6 (0·8)
H(19)	305 (8)	446 (3)	823 (10)	8·4 (2·3)
H(20)	157 (6)	427 (3)	869 (9)	6·2 (1·9)
H(21)	224 (6)	454 (2)	1200 (6)	6·1 (1·3)
H(22)	337 (6)	442 (2)	1124 (7)	4·4 (1·3)
H(23)	363 (7)	348 (3)	1222 (9)	7·2 (2·1)
H(24)	194 (5)	361 (2)	1229 (6)	2·9 (1·3)
H(25)	232 (15)	0	1000	7·6 (2·3)
H(26)	755 (18)	0	1000	8·3 (2·5)

In order to confirm the absolute configuration, the enantiomeric structure was also refined. The R and R_w values were 0·047 and 0·052 respectively. The enantiomeric structure can be rejected at the 0·005 significance level by the R-factor ratio test (Hamilton, 1965). The absolute configuration of (+)-cptn shown in Fig. 1 is in agreement with the results of Ito, Marumo & Saito (1971).

Description of the molecular structure and discussion

Fig. 1 shows a perspective drawing of the complex cation. Two Cl atoms coordinate to the Co atom in axial positions and four N atoms lie in an approximate plane, from which displacements of the four N and Co atoms are within 0·04 (1) Å. The complex ion has pseudo D_2 symmetry. Bond lengths and bond angles, averaged by assuming D_2 symmetry, within the complex cation are shown in Fig. 2.* The five-membered rings take *δ-gauche* conformations as shown in Fig. 1. The two C atoms C(*a*) and C(*a*′) lie 0·36 (3) Å above and below the plane defined by Co, N(*a*), and N(*a*′). The dihedral angles N(*a*)—C(*a*)—C(*a*′)—N(*a*′) and C(*b*)—C(*a*)—C(*a*′)—C(*b*′) are 55·2 (11) and 46·8 (9)° respectively. These values are smaller than those, 61·5 and 49·2°, for the tris-chelate, $(-)_{589}$-*lel*$_3$-[Co{(+)-cptn}$_3$]$^{3+}$ (Ito, Marumo & Saito, 1971). This indicates that the five-membered chelate rings in the present *trans*-dichloro complex are flattened compared with those in the tris-chelate.

In order to examine the relationship between the molecular structure and the anomalous CD behavior, the structural dimensions of the present complex ion were compared with those of related compounds. The reference compounds are *trans*-[$CoCl_2(en)_2$]Cl.-HCl.2H_2O (Nakahara, Saito & Kuroya, 1952; Roziere & Williams, 1976), *trans*-[$CoCl_2${(−)-pn}$_2$]-Cl.HCl.2H_2O (Saito & Iwasaki, 1962), $(-)_{589}$-*lel*$_3$-[Co{(+)-cptn}$_3$]Cl_3.4H_2O (Ito, Marumo & Saito, 1971), $(+)_{589}$-*ob*$_3$-[Co{(−)-chxn}$_3$]Cl_3.H_2O (Kobayashi, Marumo & Saito, 1972), and $(-)_{589}$-*lel*$_3$-[Co{(+)-chxn}$_3$]Cl_3.5H_2O (Marumo, Utsumi & Saito, 1970), where en and chxn denote 1,2-diaminoethane and

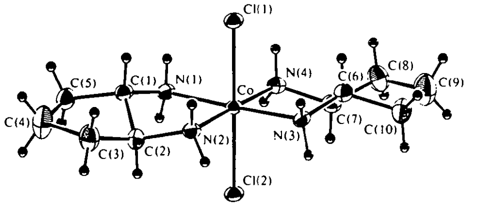

Fig. 1. A perspective drawing of the complex cation *trans*-[$CoCl_2${(+)-cptn}$_2$]$^+$.

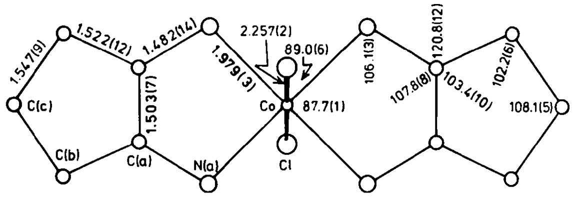

Fig. 2. Mean bond lengths (Å) and angles (°) within the complex cation. The labeling scheme in this figure is used for representing mean molecular dimensions.

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* Throughout this paper, the e.s.d. of a mean value for chemically equivalent bond lengths or angles is taken to be the largest of the following values: the e.s.d. for each parameter (q_i) or $\{[\sum(q_i - \bar{q})^2]/(N-1)\}^{1/2}$. In the case of $N = 2$, the e.s.d. is taken to be the largest of three values: q_1, q_2 or $|q_1 - q_2|/2$.

1,2-diaminocyclohexane respectively. All of these complexes have 1,2-diamines as ligands and thereby form five-membered chelate rings. Of these complexes, those containing cptn, the present complex and $(-)_{589}[Co\{(+)\text{-cptn}\}_3]^{3+}$ show anomalous CD behavior.

Except for the angles around C(*a*) and the C(*a*)—C(*a*′) distance, bond lengths and bond angles are within the normal ranges. The C(*a*)—C(*a*′) distances of the complexes containing cptn are 1·503 (7) Å for the present complex and 1·514 (25) Å for $[Co\{(+)\text{-cptn}\}_3]^{3+}$ and are slightly shorter than the corresponding values for other reference compounds. The most relevant difference in the structural dimensions between the complexes showing normal CD behavior and the complexes which show anomalous CD behavior involves the angles around the bridgehead carbon C(*a*). Specifically, the angle N(*a*)—C(*a*)—C(*b*) of 120·8 (12)° for *trans*-$[CoCl_2\{(+)\text{-cptn}\}_3]^+$ deviates significantly from the normal tetrahedral angle. A very similar distortion has been reported for $(-)_{589}$-$[Co\{(+)\text{-cptn}\}_3]^{3+}$ (Ito, Marumo & Saito, 1971). These distortions arise from the presence of the fused cyclopentane rings. The strain present at the bridgehead carbon C(*a*) is reflected also in the dihedral angles Co—N(*a*)—C(*a*)—C(*b*) and Co—N(*a*)—C(*a*)—C(*a*′), which are given in Table 2 along with the corresponding values for the reference *trans*-dichloro complexes and tris-chelates. As shown in Table 2, the angles Co—N(*a*)—C(*a*)—C(*b*) for the (+)-cptn chelates are the smallest in each series, whereas the angles Co—N(*a*)—C(*a*)—C(*a*′) for the (+)-cptn chelates are the largest in each series.

The optical activity of a *d–d* transition for these Co^{III} complexes arises from the perturbed *d* orbitals with ligands. Liehr (1964) reported that the rotatory strength of a *d–d* transition is affected by the direction of the lone-pair orbital of the ligating atom toward the metal orbital. Furthermore, the signs, as well as the magnitudes, of the CD component of the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition of *trans*-dichlorobis(diamine) chelates have been reported by Hawkins, Lawrance & Peachey (1977) to depend on the solvents. One of the plausible mechanisms of this dependency is the change in the orientation of N—H bonds upon formation of hydrogen bonds with solvents. This is supported by the experimental facts that the chemical shifts of the N—H protons in the NMR spectrum change with different solvents. As far as the molecular structure of the present complex is concerned, the anomalous CD behavior seems to correlate with the strain present at the bridgehead carbon, C(*a*), of cptn. Possibly, this distortion causes the misalignment of the lone-pair orbital of the N atom toward the Co atom.

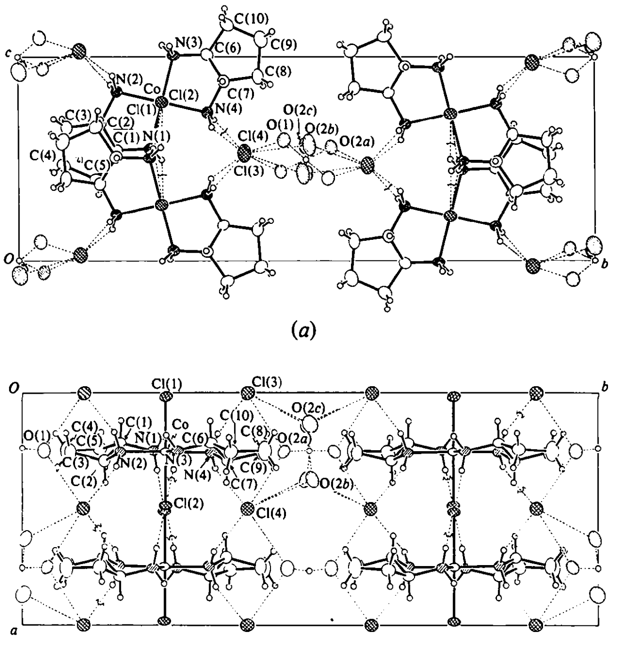
Table 2. *Dihedral angles* (°) Co—N(*a*)—C(*a*)—C(*a*′) *and* Co—N(*a*)—C(*a*)—C(*b*) *of trans*-$[CoCl_2\{(+)\text{-cptn}\}_2]^+$ *and the reference compounds*

Compounds	Co—N(*a*)—C(*a*)—C(*a*′)	Co—N(*a*)—C(*a*)—C(*b*)	Reference
trans-$[CoCl_2(en)_2]^+$	37·9	–	(*a*)
trans-$[CoCl_2\{(-)\text{-pn}\}_2]^+$	39·1	165·4	(*b*)
trans-$[CoCl_2\{(+)\text{-cptn}\}_2]^+$	40·7 (13)	159·1 (21)	(*c*)
tris-*ob*$_3$-$[Co\{(-)\text{-chxn}\}_3]^{3+}$	40·7	162·8	(*d*)
tris-*lel*$_3$-$[Co\{(+)\text{-chxn}\}_3]^{3+}$	44·2	162·8	(*e*)
tris-*lel*$_3$-$[Co\{(+)\text{-cptn}\}_3]^{3+}$	45·3	157·6	(*f*)

References: (*a*) Nakahara, Saito & Kuroya (1952). (*b*) Saito & Iwasaki (1962). (*c*) Present study. (*d*) Kobayashi, Marumo & Saito (1972). (*e*) Marumo, Utsumi & Saito (1970). (*f*) Ito, Marumo & Saito (1971).

Description of the crystal structure

Projections of the crystal structure along the *a* and *c* axes are shown in Fig. 3(*a*) and (*b*), where hydrogen bonds are indicated with broken lines. The structure consists of complex cations, Cl^- ions, and diaquahydrogen ions $[H_2O\cdots H\cdots OH_2]^+$ (Lundgren & Olovsson, 1976), which are held together *via* a three-dimensional network of hydrogen bonds. All the N atoms, chloride ions, and water molecules participate in the hydrogen bonds. The hydrogen-bond parameters are listed in Table 3. The structural features closely resemble those found in *trans*-$[CoCl_2(en)_2]$-$Cl.HCl.2H_2O$ (Nakahara, Saito & Kuroya, 1952; Roziere & Williams, 1976) and *trans*-$[CoCl_2\{(-)\text{-pn}\}_2]Cl.HCl.2H_2O$ (Saito & Iwasaki, 1962).



(*a*)

(*b*)

Fig. 3. Projections of the crystal structure (*a*) along **a**, and (*b*) along **c**.

The complex cations are arranged parallel to the (010) plane with the Co—Cl bond almost parallel to the *a* axis. The complex cations are held together by hydrogen bonds of the $N—H\cdots Cl^-$ type, forming a layer structure. The cyclopentane rings, however, are parallel to the (100) plane and appear superimposed when viewed along the *a* axis, although there is no interaction between the neighboring cyclopentane rings. The Co atom is located at (0·250, 0·250, 0·778), which is close to the position $(\frac{1}{4},\frac{1}{4},\frac{3}{4})$. These structural features resulted in the failure to solve the structure in the routine application of the heavy-atom method.

There are two crystallographically independent water molecules. Each water molecule forms a diaquahydrogen ion $[H_2O\cdots H\cdots OH_2]^+$. The central H atoms in the diaquahydrogen ions were clearly found on the twofold axis in the difference map. One of the two crystallographically independent waters $[H_2O(2)]$ is disordered and located at three positions with populations of 0·252 (9) for $H_2O(2a)$ and 0·374 for $H_2O(2b)$ and $H_2O(2c)$. The disordered water molecules of the diaquahydrogen ion share the single H atom as a central H atom. The two water molecules in $[H_2O(2a)\cdots H\cdots O(2a')H_2]^+$ are related by a twofold axis, while $[H_2O(2b)\cdots H\cdots O(2c')H_2]^+$ is related to $[H_2O(2b')\cdots H\cdots O(2c)H_2]^+$ by the twofold axis. The diaquahydrogen ions and Cl^- ions are linked *via* hydrogen bonds and form a chain structure along the *a* axis. This structural feature may be related to the fact that the crystals easily lose hydrogen chloride and water of crystallization.

Table 3. *Hydrogen-bond distances* (Å) *with their estimated standard deviations*

Key to symmetry operations

(i) $x, \quad y, \quad z$
(ii) $1\cdot0-x, \quad -0\cdot5+y, \quad 1\cdot5-z$
(iii) $1\cdot0-x, \quad 0\cdot5-y, \quad -0\cdot5-z$
(iv) $1\cdot0-x, \quad 0\cdot5-y, \quad 0\cdot5+z$
(v) $-x, \quad 0\cdot5-y, \quad -0\cdot5+z$
(vi) $-x, \quad 0\cdot5-y, \quad 0\cdot5+z$
(vii) $x, \quad -y, \quad 2\cdot0-z$

$Y—H\cdots X$	$Y\cdots X$	$H\cdots X$
$N(1)—H(1)\cdots Cl(1^{v})$	3·439 (6)	2·72 (5)
$N(1)—H(2)\cdots Cl(2^{iii})$	3·457 (6)	2·72 (6)
$N(2)—H(3)\cdots Cl(3^{vi})$	3·338 (6)	2·22 (8)
$N(2)—H(4)\cdots Cl(4^{iv})$	3·323 (6)	2·57 (4)
$N(3)—H(5)\cdots Cl(2^{iv})$	3·474 (6)	2·48 (9)
$N(3)—H(6)\cdots Cl(1^{vi})$	3·424 (6)	2·69 (5)
$N(4)—H(7)\cdots Cl(3^{i})$	3·353 (6)	2·46 (4)
$N(4)—H(8)\cdots Cl(4^{i})$	3·282 (5)	2·43 (7)
$O(1)\cdots Cl(3^{vi})$	2·956 (6)	
$O(1)\cdots Cl(4^{iv})$	2·990 (6)	
$O(2a)\cdots Cl(3^{iv})$	2·96 (2)	
$O(2a)\cdots Cl(4^{iv})$	2·95 (2)	
$O(2b)\cdots Cl(4^{iv})$	2·90 (2)	
$O(2b)\cdots Cl(4^{ii})$	3·03 (2)	
$O(2c)\cdots Cl(3^{ii})$	2·99 (2)	
$O(2c)\cdots Cl(3^{iv})$	3·02 (2)	
$O(1)\cdots O(1^{vii})$	2·434 (7)	
$O(2a)\cdots O(2a^{vii})$	2·37 (3)	
$O(2b)\cdots O(2c^{vii})$	2·59 (2)	

The $O\cdots O$ distances in the diaquahydrogen ions are 2·434 (7) Å for $O(1)\cdots O(1')$ and 2·48 (11) Å as an average for $O(2a)\cdots O(2a')$ and $O(2b)\cdots O(2c')$. These values are significantly shorter than the average value of 2·60 Å found in the crystal structures of *trans*-$[CoCl_2(en)_2]Cl_2.HCl.2H_2O$ (Nakahara, Saito & Kuroya, 1952) and *trans*-$[CoCl_2\{(-)\text{-pn}\}_2]Cl.HCl.2H_2O$ (Saito & Iwasaki, 1962). However, the values are in fair agreement with the $O\cdots O$ distance [2·431 (6) Å] found recently on the basis of high-precision neutron diffraction data for $[H_2O\cdots H\cdots OH_2]^+$ in *trans*-$[CoCl_2(en)_2]Cl_2.HCl.2H_2O$ (Roziere & Williams, 1976). The short $O\cdots O$ distances found in the present study are also comparable to the strong hydrogen-bond distance of 2·436 (2) Å found for the $O\cdots O$ interaction of diaquahydrogen ions in the crystal of picrylsulfonic acid tetrahydrate (Lundgren & Tellgren, 1974).

Other intermolecular contacts appear to be normal. The closest approach is the $C(9)\cdots O(2a)$ contact of 3·10 (1) Å.

The calculations were carried out on the HITAC M-180 computer at the Computer Center of the Institute for Molecular Science with the *Universal Crystallographic Computation Program System – UNICS* III (Sakurai & Kobayashi, 1979).

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