(3) A. J. Carty, C. R. Jablonski and V. Snieckus, unpublished results.
(4) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England 1962, pp 202–211.
(5) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(6) N. J. Taylor, Y. S. Wong, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Dalton Trans.*, 438 (1975).
(7) S. N. Vinogradov and R. H. Linnell, "Hydrogen Bonding", Van Nostrand, New York, N.Y., 1971.
(8) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968.
(9) P. Sartori and M. Weidenbruch, *Chem. Ber.*, **100**, 2049 (1967).
(10) D. W. J. Cruickshank, D. W. Jones, and E. Walker, *J. Chem. Soc.*, 1303 (1964).
(11) M. R. Churchill and R. Mason, *Adv. Organomet. Chem.*, **5**, 93 (1967).
(12) Δ_{C-C} is defined as the difference in bond length between the average of the two "outer" carbon–carbon bonds of the coordinated diene and the "inner" carbon–carbon bond length. Likewise Δ_{Fe-C} is defined as the difference between the mean Fe–C (inner) and Fe–C (outer) bond lengths.
(13) D. I. Woodhouse, G. A. Sim, and J. G. Sime, *J. Chem. Soc., Dalton Trans.*, 1331 (1974).
(14) A. Von Gieren and W. Hoppe, *Acta Crystallogr., Sect. B*, **28**, 2766 (1972).
(15) A. de Cian, P. M. L'Huillier, and R. Weiss, *Bull Soc. Chim. Fr.*, 457 (1973).
(16) F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Am. Chem. Soc.*, **95**, 4522 (1973).
(17) M. R. Churchill and S. W. Y. Chang, *Inorg. Chem.*, **14**, 1680 (1975).
(18) M. R. Churchill and P. R. Bird, *Inorg. Chem.*, **8**, 1941 (1969).
(19) A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).
(20) P. Dodman and T. A. Harmor, *J. Chem. Soc., Dalton Trans.*, 1010 (1974).
(21) M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Organomet. Chem.*, **39**, C9 (1972).
(22) M. R. Churchill and R. Mason, *Proc. R. Soc. London, Ser. A*, **292**, 61 (1966).
(23) A. Immirzi and G. Allegra, *Acta Crystallogr., Sect. B*, **25**, 120 (1969).
(24) M. R. Churchill and R. Mason, *Proc. R. Soc., A* **301**, 433 (1967).
(25) G. I. Birnbaum, *J. Am. Chem. Soc.*, **94**, 2455 (1972).
(26) See for example ref 13–18 and 21.
(27) N. A. Bailey and R. Mason, *Acta Crystallogr.*, **21**, 652 (1966).
(28) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975).
(29) R. Allman, *Angew. Chem., Int. Ed. Engl.*, **9**, 958 (1970).
(30) S. M. Johnson and I. C. Paul, *J. Chem. Soc. B*, 1783 (1970).
(31) M. G. Waite and G. A. Sim, *J. Chem. Soc. A*, 1009 (1971).
(32) R. L. Collin and W. N. Lipscomb, *Acta Crystallogr.*, **4**, 10 (1951).
(33) K. Sakurai and Y. Tomiie, *Acta Crystallogr.*, **5**, 289 (1952).
(34) K. Sakurai and Y. Tomiie, *Acta Crystallogr.*, **5**, 293 (1952).
(35) J. Donahue and W. N. Lipscomb, *J. Chem. Phys.*, **15**, 115 (1947).
(36) M. L. Kronberg and K. Harker, *J. Chem. Phys.*, **10**, 309 (1952).

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The Hydrated Proton $H^+(H_2O)_n$. IV. A High-Precision Neutron Diffraction Study of the Diaquohydrogen Ion, $(H_2O{\cdot}H{\cdot}OH_2)^+$, in *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride Hydrochloride Dihydrate[1]

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The crystal structure of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride hydrochloride dihydrate has been determined from three-dimensional single-crystal neutron diffraction data. The crystals are monoclinic, space group $P2_1/c$, with two formula units in the unit cell of dimensions $a = 10.682$ (7) Å, $b = 7.883$ (5) Å, $c = 9.075$ (6) Å, and $\beta = 110.59$ (4)°. A total of 5488 reflections were averaged yielding 2183 independent data and a full-matrix least-squares refinement based on F_o^2 gave a final $R(F_o^2)$ value of 0.077. The structure consists of *trans*-$[Co(en)_2Cl_2]^+$, Cl^-, and $H_5O_2^+$ ions. The diaquohydrogen ion, $(H_2O{\cdot}H{\cdot}OH_2)^+$, has the trans configuration. Analysis of the thermal motion of the bridging hydrogen atom of $H_5O_2^+$ indicates that it moves in a broad, flat, anharmonic, single-minimum potential energy well.

Introduction

Crystals of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride hydrochloride dihydrate, *trans*-$[Co(en)_2Cl_2]^+Cl^-(H_5O_2)^+Cl^-$, and related compounds were thought to be the first to contain the diaquohydrogen ion, $(H_2O{\cdot}H{\cdot}OH_2)^+$, in the solid state.[2–5] However no definitive information regarding the geometry of the $H_5O_2^+$ ion could be obtained from the previous x-ray diffraction studies of these adducts.[3] Two possible limiting structures may be considered for $H_5O_2^+$: (i) the diaquohydrogen ion, $(H_2O{\cdot}H{\cdot}OH_2)^+$, and (ii) the monoaquooxonium ion, $H_3O^+{\cdot}OH_2$. In the diaquohydrogen ion the bridging hydrogen ion is shared equally by two water molecules and this is the main feature that differentiates the two $H_5O_2^+$ species.[2] In a preliminary neutron diffraction investigation[5] of the structure of *trans*-$[Co(en)_2Cl_2]^+Cl^-(H_5O_2)^+Cl^-$ the existence of the $(H_2O{\cdot}H{\cdot}OH_2)^+$ ion was conclusively demonstrated for the first time. However, sample decomposition during data collection had limited the accuracy of the results. In addition to the geometry and atomic motion of $H_5O_2^+$ in this compound, the hydrogen atom positions and hydrogen bonding around the $[Co(en)_2Cl_2]^+$ complex cation are of interest in relation to its configurational stability in the solid state.[6]

Experimental Section

Crystal Preparation. Large crystals were grown by slow evaporation at room temperature of a concentrated hydrochloric acid solution of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride prepared following the method of Bailar.[7] The crystals were harvested and to avoid decomposition were kept in a sealed tube in a refrigerator before using.

Unit Cell and Space Group. Earlier studies[3,5] established the space group as $P2_1/c$, with two formula units per unit cell, and furnished preliminary monoclinic unit cell dimensions. These parameters were used with two reflections to calculate an orientation matrix from which 28 intense reflections (2θ ranging from 40 to 60°) were automatically centered. The precise unit cell parameters (at 22 ± 2 °C with λ 1.142 (1) Å) determined by a least-squares fit of the angles 2θ, χ, and ϕ were $a = 10.682$ (7) Å, $b = 7.883$ (5) Å, $c = 9.075$ (6) Å, $\beta = 110.59$ (4)°, and $V_c = 715.36$ Å^3. These values agree well with those given previously.[5] The density determined from the neutron data is 1.66 (1) g cm^{-3} which agrees well with the experimental value[3] of 1.65 (1) g cm^{-3}.

Data Collection. The crystal selected was a rectangular plate with {100} well developed. Approximate dimensions were 0.66 × 0.51 × 0.18 cm and the crystal weighed 90 mg. To prevent loss of H_2O and HCl, the crystal was coated with a fluorocarbon grease, fixed in place with epoxy, and sealed in a lead glass tube. The crystal was mounted with the c crystal axis displaced a few degrees from the instrument ϕ axis to avoid multiple diffraction effects. Full three-dimensional data were collected using an Electronics and Alloys four-circle diffractometer at the CP-5 reactor at Argonne National Laboratory. The neutron wavelength was 1.142 (1) Å.[8a] The fully automated diffractometer operates under remote Sigma 5 computer control. A θ–2θ step-scan technique was employed in data collection, using 0.1° step intervals, with background counts taken on each side of the peak with both crystal and counter being simultaneously stationary. A total

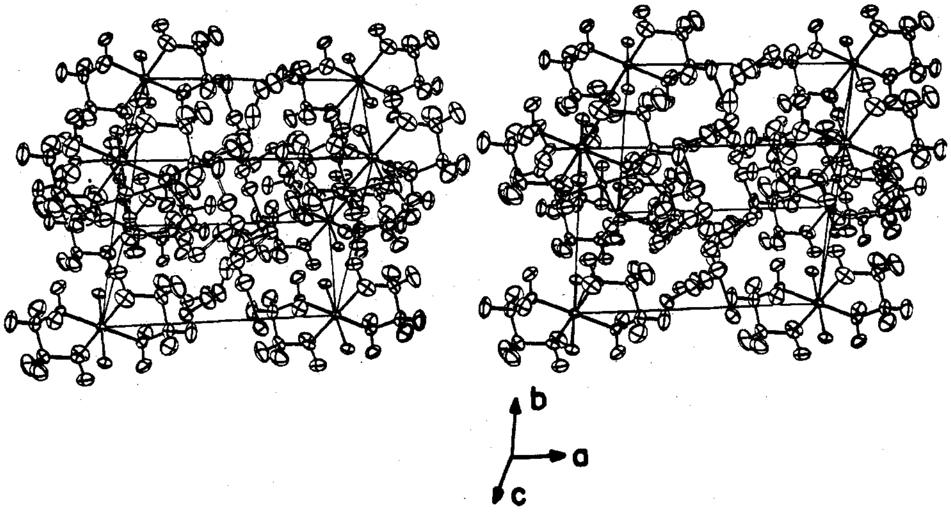

Figure 1. Stereoscopic drawing of the unit cell of *trans*-$[Co(en)_2Cl_2](H_5O_2)Cl_2$. Covalent bonds and the short hydrogen bond of $H_5O_2^+$ are filled; OH· · ·Cl bonds are open. Thermal ellipsoids of atomic motion are scaled to enclose 50% probability.

of 5488 reflections were collected to $2\theta = 110°$. Two reference reflections were repeated after every 30 regular reflections and their integrated intensities were observed to have a maximum random variation of 2% during data collection. No loss of intensity due to sample decomposition was observed as had been the case in the previous study.[5] The observed integrated intensity of each reflection was corrected for absorption using a linear absorption coefficient (μ = 2.88 cm^{-1}) determined experimentally. This agrees well with a value of 2.88 cm^{-1} calculated using 37 barns for the incoherent scattering cross section of hydrogen. The corresponding transmission factors ranged from 0.26 to 0.59; all symmetry-equivalent and duplicate reflections were averaged to yield a set of 2202 independent reflections. The "agreement factor" between averaged reflections was 7%.[8b] All data were placed on an absolute scale by calibration with a well-characterized NaCl crystal using a previously described method.[9]

Structure Refinement.[10] The previously derived neutron parameters[5] (atomic positions and isotropic temperature factors) were used initially in a full-matrix least-squares refinement after Fourier maps had indicated they were well determined. The function minimized was $\sum w_i(F_o^2 - F_c^2)^2$ with $w_i^{-1} = \sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0.02F_o^2)^2$ where σ_c is determined by counting statistics. The constant 0.02 used in the weighting scheme represents the 2% maximum variation observed in the integrated intensities of the two reference reflections used during data collection. This value is probably understated and would have resulted in a lower value of $\sum_1$ than 1.90 if a less conservative value had been used (vide infra). Three initial cycles where the scale factor, atomic positions, and isotropic temperature factors were allowed to vary converged and led to the values of the agreement indices

$$R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.21$$

$$R(F_o^2) = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2 = 0.28$$

$$R_w(F_o^2) = [\Sigma w_i|F_o^2 - F_c^2|^2/\Sigma w_i F_o^4]^{1/2} = 0.34$$

for all of the data. At this point an isotropic secondary extinction parameter was introduced, and after two further cycles, the agreement factors were reduced to $R(F_o) = 0.13$, $R(F_o^2) = 0.16$, and $R_w(F_o^2) = 0.17$. The final refinement with anisotropic thermal parameters converged quickly yielding the agreement factors given in Table I. The final change-to-esd ratio was less than 0.005 for all the parameters. In the final three cycles of refinement 19 reflections with $Q > 100$ ($Q = F_o^2/\sin 2\theta$) suffering from extreme extinction (extinction correction factors ranging from 6.3 to 2.3) were given zero weight. The final scale factor S was 0.859 (4) which may be compared with 0.778 (2)[9] also derived from a least-squares refinement using the same NaCl crystal. The most likely reason that S is less than the ideal value of 1.0 is that there is difficulty in selecting extinction-free reflections (in NaCl) for calibration purposes. Finally, the often large correlations between S and g in least-squares refinements may lead to values of S other than unity. The final isotropic extinction coefficient (g)[11] derived in this study was 3.4 (1) and for the reflections included in the refinement the highest correction factor was 3.5. Fewer than 2% of the reflections needed corrections factors greater than 2.0.

Table I. Final Agreement Factors

Data selection	No. of reflec-tions[a]	$R(F_o)$	$R(F_o^2)$	R_w-(F_o^2)	Σ_1
All data	2183	0.076	0.077	0.086	1.90
Reflections with $(F_o^2) > 1.0\sigma(F_o^2)$	1795	0.056	0.074	0.086	2.09

[a] A total of 19 intense reflections with severe extinction were removed from the refinement.

The standard deviation of an observation of unit weight

$$\Sigma_1 = [w_i(F_o - F_c)^2/(n - p)]^{1/2}$$

where n is the number of observations and p the number of parameters varied (viz., 167) in the least-squares refinement, was 1.90 for all of the data.

The final positional and thermal parameters are given in Table II. For the least-squares refinement the coherent neutron scattering amplitudes which were used for Co, N, C, O, Cl, and H were respectively 0.250, 0.940, 0.665, 0.580, 0.960, and −0.374 all in units of 10^{-12} cm.[12]

Discussion

The structure consists of $[Co(en)_2Cl_2]^+$, $H_5O_2^+$, and Cl^- ions as illustrated stereoscopically in Figure 1. The crystal is bound together via a three-dimensional network of hydrogen bonds involving the complex cation, the diaquohydrogen ion, and the chloride ions. The atomic coordinates of Table II agree reasonably well with the less precise values derived in the x-ray study (no hydrogen atom coordinates were given in the latter). The hydrogen atom positional parameters determined in this study are in excellent agreement with those determined in the previous neutron diffraction study.[5] Significant interatomic distances and angles are presented in Tables III–VI.

The $[Co(en)_2Cl_2]^+$ ion. The geometry and the bond distances and angles of the complex cation are presented in Figure 2 and Table III. As previously observed in the x-ray study the ethylenediamine molecules have the "gauche" configuration. There is a slight but significant difference between the two crystallographically nonequivalent Co–N distances (1.959 (1) and 1.951 (1) Å) which amounts to a bond length difference of 5.7σ; a similar difference of Co–N distances (maximum difference 4.1σ) was observed in the high-precision study of $(+)_D$-$[Co(en)_3]Cl_3 \cdot H_2O$.[13a] The maximum differences in the

Table II. Positional and Thermal Parameters for $[Co(en)_2Cl_2]ClH_5O_2Cl$ and Root-Mean-Square Thermal Displacements (in Å) of Atoms along Their Principal Ellipsoid Axes[a,b]

Atoms	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\mu(1)$	$\mu(2)$	$\mu(3)$
Co	0	0	0	42 (4)	47 (5)	47 (5)	4 (4)	23 (4)	2 (4)	116 (8)	121 (8)	151 (7)
O	4834 (3)	6431 (4)	395 (4)	109 (3)	212 (5)	131 (4)	47 (3)	65 (3)	41 (4)	190 (3)	206 (3)	290 (4)
Cl(1)	458 (1)	−302 (1)	2611 (1)	72 (1)	81 (1)	50 (1)	−4 (1)	27 (1)	1 (1)	129 (2)	159 (1)	192 (1)
Cl(2)	3435 (1)	−3859 (2)	2729 (2)	90 (1)	129 (2)	101 (2)	20 (1)	46 (1)	10 (2)	176 (2)	189 (2)	228 (2)
N(1)	874 (1)	2224 (1)	324 (1)	70 (1)	62 (1)	68 (1)	−6 (1)	33 (1)	−6 (1)	137 (2)	148 (2)	191 (1)
N(2)	1760 (1)	−925 (1)	264 (1)	50 (1)	87 (2)	72 (1)	15 (1)	24 (1)	0 (1)	139 (2)	162 (2)	180 (2)
C(1)	2267 (2)	2045 (2)	356 (2)	68 (2)	114 (3)	117 (3)	−28 (2)	39 (2)	−11 (2)	152 (2)	200 (2)	219 (2)
C(2)	2790 (2)	349 (2)	1071 (2)	47 (1)	135 (3)	101 (2)	−5 (2)	16 (1)	−11 (2)	152 (2)	194 (2)	212 (2)
H(1)	5000	5000	0	92 (6)	347 (19)	140 (10)	33 (9)	48 (6)	90 (11)	194 (8)	210 (7)	350 (10)
H(2)	4344 (5)	6406 (6)	1148 (6)	130 (5)	210 (8)	140 (7)	44 (5)	68 (5)	20 (6)	204 (5)	226 (5)	290 (6)
H(3)	4363 (5)	7199 (6)	−485 (6)	124 (5)	208 (8)	159 (7)	43 (5)	64 (5)	46 (6)	213 (5)	225 (5)	292 (6)
H(4)	372 (4)	3032 (5)	−556 (5)	113 (4)	121 (5)	129 (6)	23 (4)	44 (4)	34 (4)	173 (5)	226 (5)	247 (5)
H(5)	847 (5)	2742 (5)	1337 (5)	137 (5)	137 (6)	107 (5)	−32 (4)	67 (4)	−42 (4)	158 (5)	206 (5)	276 (5)
H(6)	1814 (4)	−1204 (5)	−814 (5)	90 (4)	172 (6)	107 (5)	14 (4)	47 (4)	−23 (4)	167 (5)	217 (4)	244 (4)
H(7)	1981 (4)	−2013 (5)	924 (5)	83 (3)	136 (6)	149 (6)	42 (4)	34 (4)	35 (5)	158 (5)	232 (5)	251 (5)
H(8)	2895 (5)	3088 (6)	991 (7)	112 (5)	196 (8)	254 (11)	−75 (5)	61 (6)	−61 (8)	171 (5)	279 (6)	322 (6)
H(9)	2237 (5)	2078 (6)	−858 (6)	137 (5)	210 (8)	176 (8)	−4 (6)	101 (6)	25 (6)	184 (5)	260 (5)	289 (6)
H(10)	3743 (4)	60 (6)	943 (7)	50 (3)	241 (9)	226 (9)	−1 (4)	36 (4)	−15 (7)	157 (9)	271 (5)	297 (6)
H(11)	2917 (5)	333 (6)	2326 (5)	111 (4)	230 (8)	100 (5)	−1 (5)	6 (4)	−10 (6)	181 (5)	264 (5)	272 (5)

[a] The estimated standard deviations in parentheses in this table and all subsequent tables refer to the least significant figure. Parameters are multiplied by 10^4. [b] The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Their values are multiplied by 10^4 and the rms displacement values are multiplied by 10^3.

Table III. Bond Distances (Å) and Angles (deg) in the $[Co(en)_2Cl_2]^+$ Cation

Distances[a]			
Co-Cl(1)	2.257 (1) [2.33][b]	N(1)-C(1)	1.486 (2) [1.48]
Co-N(1)	1.959 (1) [1.98]	N(2)-C(2)	1.480 (2) [1.47]
Co-N(2)	1.951 (1) [2.00]	C(1)-C(2)	1.505 (3) [1.55]

Angles			
N(2)-Co-N(1)	85.90 (5)	N(1)-C(1)-C(2)	108.10 (13) [110]
N(1)-Co-N(2)	94.10 (5)		
N(2)-Co-Cl(1)	89.30 (4)	N(2)-C(2)-C(1)	107.03 (13) [108]
Cl(1)-Co-N(2)	90.70 (4)		
N(1)-Co-Cl(1)	91.17 (4)	Co-N(1)-C(1)	109.90 (9) [104]
Cl(1)-Co-N(1)	88.83 (4)		
		Co-N(2)-C(2)	108.99 (9) [106]

[a] Distances in this table and all subsequent tables are uncorrected for thermal motion. [b] The second values in brackets are from the x-ray study.[3]

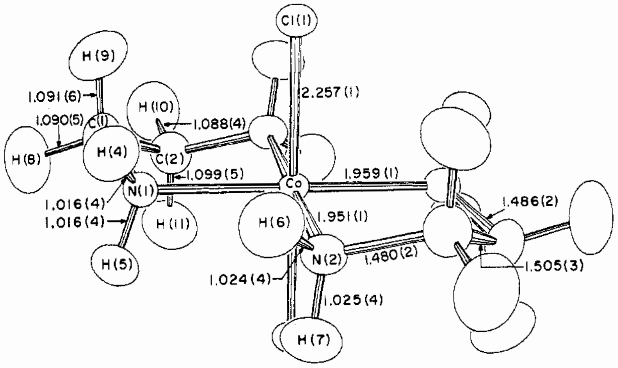

Figure 2. Configuration of the complex ion $[Co(en)_2Cl_2]^+$. The cobalt atom resides at a center of symmetry which also relates one ethylenediamine ring with the other.

Co–N distances in $[Co(en)_3]_2[HPO_4]_3 \cdot 9H_2O$[13b] and $[Co(en)_3]_2[CdCl_6]Cl_2 \cdot 2H_2O$[13c] amount to 2.8$\sigma$ and 2.3σ, respectively, which may also be considered as significant indications that these distances need not be equal. The two N–C distances (1.486 (2) and 1.480 (2) Å) are, within the significance limits given, essentially equal in this neutron diffraction study.

Table IV. Bond Distances (Å) and Angles (deg) Involving Hydrogen Atoms

(A) In the $[Co(en)_2Cl_2]^+$ Cation

Distances			
N(1)-H(4)	1.016 (4)	C(1)-H(8)	1.090 (5)
N(1)-H(5)	1.016 (4)	C(1)-H(9)	1.091 (6)
N(2)-H(6)	1.024 (4)	C(2)-H(10)	1.088 (4)
N(2)-H(7)	1.025 (4)	C(2)-H(11)	1.099 (5)

Angles			
H(4)-N(1)-H(5)	106.5 (4)	H(8)-C(1)-H(9)	108.1 (4)
H(4)-N(1)-Co	110.6 (2)	H(8)-C(1)-N(1)	111.4 (3)
H(4)-N(1)-C(1)	108.9 (3)	H(8)-C(1)-C(2)	112.1 (4)
H(5)-N(1)-Co	109.4 (2)	H(9)-C(1)-N(1)	107.7 (3)
H(5)-N(1)-C(1)	111.6 (3)	H(9)-C(1)-C(2)	109.4 (3)
H(6)-N(2)-H(7)	107.4 (3)	H(10)-C(2)-H(11)	109.3 (4)
H(6)-N(2)-Co	109.8 (2)	H(10)-C(2)-N(2)	111.5 (3)
H(6)-N(2)-C(2)	109.7 (2)	H(10)-C(2)-C(1)	111.0 (3)
H(7)-N(2)-Co	113.5 (2)	H(11)-C(2)-N(2)	107.7 (3)
H(7)-N(2)-C(2)	107.4 (3)	H(11)-C(2)-C(1)	110.4 (3)

(B) In the $H_5O_2^+$ Cation

Distances			
O-H(1)-O	2.431 (6)	O-H(2)	0.995 (6)
O-H(1)	1.216 (3)	O-H(3)	0.988 (6)

Angles			
H(2)-O-H(1)	110.5 (4)	H(2)-O-H(3)	109.1 (4)
H(3)-O-H(1)	114.5 (4)		

Table V. Short C-H···Cl Contacts with $d_{H\cdots Cl} < 3.0$ Å

C-H···Cl	C···Cl, Å	H···Cl, Å	C-H, Å	CHCl angle, deg
C(1)-H(8)···Cl(2)	3.839 (2)	2.824 (3)	1.090 (5)	155.0 (4)
C(2)-H(10)···Cl(2)	3.538 (2)	2.951 (4)	1.088 (4)	139.0 (3)
C(2)-H(10)···Cl(2)	3.607 (2)	2.972 (6)	1.088 (4)	112.8 (3)
C(2)-H(11)···Cl(1)	3.297 (2)	2.773 (5)	1.099 (5)	108.9 (3)

The Methylene Groups. The C–H bond lengths (uncorrected for thermal motion) are the same around the C(1) atom (1.090 (5) and 1.091 (6) Å); more asymmetry is observed around C(2) (1.088 (6) and 1.099 (5) Å, i.e., $\Delta = 1.4\sigma$), but it cannot be considered significant even though there is a slight difference in environment around the atoms H(10) and H(11) (Table V). The principal axis lengths of the thermal ellipsoids are not significantly different for any of the hydrogen atoms and the largest principal axis components make angles of 84–123° with the C–H direction.

Table VI. Hydrogen Bonds and Short Nonbonded Interatomic Distances and Angles

X-H···Y	X···Y, Å	X-H, Å	H···Y, Å	XHY angle, deg
N(1)-H(4)···Cl(1)	3.374 (2)	1.016 (4)	2.467 (4)	148.4 (3)
N(1)-H(4)···Cl(1)[a]	2.958 (2)	1.016 (4)	2.781 (4)	89.8 (2)
N(1)-H(5)···Cl(1)	3.349 (2)	1.016 (4)	2.484 (4)	142.8 (3)
N(1)-H(5)···Cl(1)[a]	3.018 (2)	1.016 (4)	2.757 (4)	94.9 (2)
N(2)-H(6)···Cl(2)	3.379 (2)	1.024 (4)	2.521 (4)	140.9 (3)
N(2)-H(6)···Cl(1)[a]	3.001 (2)	1.024 (4)	2.679 (4)	98.2 (2)
N(2)-H(7)···Cl(2)	3.277 (2)	1.025 (4)	2.329 (4)	153.3 (3)
N(2)-H(7)···Cl(1)[a]	2.965 (2)	1.025 (4)	2.926 (4)	82.2 (2)
O···H(1)···O	2.431 (6)	1.216 (3)	1.216 (3)	180
O-H(2)···Cl(2)	2.999 (3)	0.995 (6)	2.007 (5)	174.6 (4)
O-H(3)···Cl(2)	3.034 (3)	0.988 (6)	2.047 (5)	177.9 (5)

[a] Non-hydrogen-bonded atoms.

We can estimate the amplitude of the motion of the hydrogen atoms along the C–H bond by calculating the difference of the mean-square amplitude $\langle\langle R^2{}_H - R^2{}_C\rangle\rangle$. The average value is 0.0074 Å^2 around C(1) and 0.0045 Å^2 around C(2). If we assume harmonic motion for the hydrogen atoms, these amplitudes lead to C–H stretching frequencies of 2270 and 3720 cm^{-1} using the relationship[14] $\nu = 16.8/m\langle r^2\rangle$ where ν is in cm^{-1}, m in amu, and $\langle r^2\rangle$ in Å^2. These values may be compared with the accepted spectroscopic value of ~2900 cm^{-1} which indicates that they are of the right order of magnitude.

The Amino Groups. The N–H bond lengths range between 1.015 (4) and 1.025 (4) Å. These N–H distances are in good agreement with those which have been determined in other high-precision neutron diffraction studies of compounds containing similar chelate rings.[15] The N–H bond lengths within each NH_2 group, even though unconstrained by symmetry, are not different. This is obviously due to the fact that the N–H bonds of the NH_2 groups are in the same type of chemical environment in the crystal. The bond angles in the two amino groups are significantly different from the tetrahedral values [106.5 (4)–111.6 (3)° around N(1) and 107.4 (3)–113.5 (2)° around N(2)], and the highest value for the H(2)–N(2)–Co angle may be related to the ethylenediamine ring puckering. It is well worth pointing out that none of the hydrogen positions could have been inferred from their closest chlorine contact distances. The NH_2 groups are involved in considerably bent interionic hydrogen bonds. The N–H···Cl angles range from 140.9 (3) to 153.3 (3)° with either the coordinated Cl atom [Cl(1)] or the "free" chloride ion Cl(2). The nonlinear NH···Cl bond angles may be accounted for by semirigidity of the surroundings of the nitrogen atoms. Notice, for example, the slight departure of the angles around the nitrogen atoms from the tetrahedral values (see Table IV). In addition, it should be noted in each case that another close intraionic chlorine contact exists at about 90° from the N–H direction. In all of the cases, the shortest principal axes of the thermal ellipsoids of the hydrogen atom of the NH_2 groups are roughly directed along the N–H bond and the largest ones are approximately normal to the bond.

The Diaquohydrogen Ion $(H_2O{\cdot}H{\cdot}OH_2)^+$. Although the presence of an entity $(H_2O{\cdot}H{\cdot}OH_2)^+$ was suggested in the x-ray study,[3] the limited precision of this study prevented any definitive conclusions. In particular, the relatively long O–O distance (2.66 Å) between the two water molecules would not allow a distinction between $H_3O^+{\cdots}OH_2$ and $(H_2O{\cdot}H{\cdot}OH_2)^+$. The x-ray determined distance was corrected in the previous preliminary neutron diffraction study[5] [2.50 (3) Å] but was found to be still longer than the average O···O distances obtained in more recent structure determinations of $H_5O_2{}^+$ salts.[16] The symmetry of the diaquohydrogen ion as required by the space group is $\bar{1}$. The O···O distance of 2.431 (6) Å is shorter than previously reported[5] but is well within the error limits of the previous neutron diffraction study. The bridging proton O–H distance is 1.216 (3) Å. The terminal protons of the diaquohydrogen ion, H(2) and H(3), have O–H distances of 0.995 (6) and 0.988 (6) Å, respectively, and are involved in slightly bent hydrogen bonds with the chloride ion Cl(2), 174.6 (4) and 177.9 (5)°, respectively. The O···Cl distances are 2.999 (3) and 3.036 (3) Å. The geometry and environment of the *trans*-$H_5O_2{}^+$ ion are illustrated in Figure 3. This geometry is identical with that recently obtained in the neutron diffraction study of $Y(C_2O_4)_2H_5O_2H_2O$[17] where, as in the cobalt complex, the bridging proton of the $(H_2O{\cdot}H{\cdot}OH_2)^+$ ion resides on a crystal symmetry element (2 and $\bar{1}$, respectively). The *trans*-$H_5O_2{}^+$ has also been observed very recently as the central or "core" species in the largest hydrated proton cluster yet reported,[23] viz., $H_{13}O_6{}^+$. The O···O distance in the $H_5O_2{}^+$ entity is 2.39 (2) Å, and it is gratifying to note, as was earlier predicted,[2] that the *trans*-diaquohydrogen ion, $(H_2O{\cdot}H{\cdot}OH_2)^+$, may occur more frequently in crystalline solids than H_3O^+.

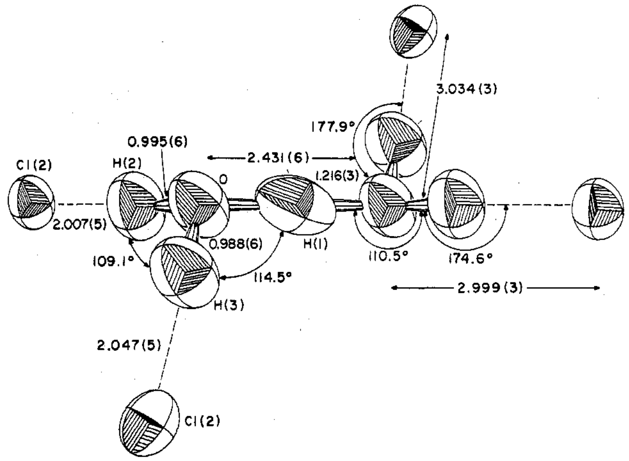

Figure 3. The diaquohydrogen ion $(H_2O{\cdot}H{\cdot}OH_2)^+$, having the trans configuration with $\bar{1}$ symmetry.

Table VII. Total Mean-Square Components in $H_5O_2{}^+$

Hydrogen $\langle\mu^2\rangle$, Å^2	Oxygen $\langle\mu^2\rangle$, Å^2	Rms $[\langle\mu^2{}_H\rangle - \langle\mu^2{}_O\rangle]^{1/2}$, Å
∥ 0.1147	0.0647	0.22
$\perp_1$ 0.0516	0.0611	No real root
$\perp_2$ 0.0378	0.0386	No real root

Atomic Motions in $(H_2O{\cdot}H{\cdot}OH_2)^+$. In previous neutron diffraction studies of very short hydrogen bonds, it has been shown that the proton often vibrates anisotropically with the largest mean-square amplitudes being along the bond or nearly so and this anisotropy has been related to the broadness of the potential well along the hydrogen bond.[18,19] As can be seen from Figure 3 the largest principal axis of the thermal ellipsoid of the central hydrogen atom of $H_5O_2{}^+$ is directed approximately along a line joining the two oxygen atoms (the angle between this axis and the O–O direction is 14°). It should be noted that for longer hydrogen bonds (see for instance the terminal hydrogen atoms of $H_5O_2{}^+$) the direction of the anisotropy is reversed and the largest principal axis lies in a direction perpendicular to the bond. A good approximation of the net motion of the bridging hydrogen atom of $H_5O_2{}^+$ should be obtained by solving for the difference tensor $U_{ij}{}^H - U_{ij}{}^O$.[14,18] Usually such a calculation leads to the largest axis of the difference thermal ellipsoid being along the O–O direction. Our attempt to obtain this difference tensor failed because we could only obtain one real root corresponding to the largest axis.[18] That axis makes an angle of 4° with the O–O direction and the rms component along the bond is 0.22

Å. These results can be easily understood: see Table VII in which the mean-square components of both hydrogen and oxygen atoms along the bond, and in a direction perpendicular to it, are given. These axes are chosen as closely as possible to be the principal inertial axes of the $H_5O_2^+$ unit, and in both cases of the perpendicular motion, the mean-square amplitudes of the oxygen atoms are greater than those for the bridging hydrogen. These results suggest that $H_5O_2^+$ undergoes large-amplitude librational motion in which the central hydrogen atom acts as the pivot point and in which the axes are perpendicular to the O–H–O bond.

No very close correlation can be found between the frequency of the asymmetric stretching (ν_{O-H}) as derived from these neutron results ($\simeq$350 cm^{-1}) and the spectroscopic data. Values of about 1000 cm^{-1} have been suggested in previous vibrational studies[20,21] of $H_5O_2^+$. We propose from our ir investigation[22] of the present compound the value 980 cm^{-1}.

Similar discrepancies have been found in like treatments of the hydrogen motion in very short O–H–O bonds and we agree with the suggestion that the difference could be accounted for by a slight amount of static disorder resulting from random shifts of the hydrogen atom equilibrium position due to local packing constraints.[15] The alternative model with half hydrogen atoms in two closely spaced sites (in this case the apparent rms displacement from the center of the bond should be $\simeq$0.17 Å) with an rms amplitude of vibration of $\sim$0.13 Å has been previously shown to be unrealistic.[18,19] Therefore we can conclude that, in the short hydrogen bond of $H_5O_2^+$, the proton moves in a broad, flat, anharmonic, single-minimum potential energy well. When a similar treatment is applied to the terminal OH_2 groups, which are expected to show much less anharmonic motion, this leads to more satisfactory values. The average quantity $\langle\langle U^2_H - U^2_O\rangle\rangle$ along the O–H bond is 0.0097 Å and the derived frequency of 2950 cm^{-1} is relatively close to the spectroscopic result[4] of 3100 cm^{-1}.

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Registry No. $(H_2O{\cdot}H{\cdot}OH_2)^+$, 22206-74-2; *trans*-$[Co(en)_2Cl_2]^+Cl^-(H_5O_2)^+Cl^-$, 58298-19-4.

Supplementary Material Available: listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Work performed under the auspices of the U.S. Energy Research and Development Administration.

(2) J. M. Williams, *Natl. Bur. Stand. (U.S.)*, *Spec. Publ.*, **No. 301**, 237 (1969).

(3) A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **25**, 331 (1952).

(4) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1640 (1964).

(5) J. M. Williams, *Inorg. Nucl. Chem. Lett.*, **3**, 297 (1967).

(6) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(7) J. C. Bailar, *Inorg. Synth.*, **2**, 222 (1946).

(8) (a) The monochromatic neutron beam is produced by reflection from the (110) plane of a Be single crystal at a monochromator angle of θ_m = 30°. In integrated θ–2θ step scans of the nonallowed (100) reflection from the NaCl standard crystal no reflection could be detected under conditions which yielded an integrated intensity of $\sim 10^5$ counts for the (200). Therefore, any $^1/_2\lambda$ contribution from the very intense (200), to produce a (100) reflection, was negligible and no corrections for harmonic contributions to the neutron beam were required. Calibration of the neutron wavelength of 1.142 (1) Å was made with two standard cubic crystals: NaCl (a = 5.6397 Å) and Si (a = 5.4308 Å) at 22 ± 2 °C. Measurements of the neutron flux at the sample position with calibrated Au foils yielded an intensity of 2.9×10^6 N cm^{-2} s^{-1}, which is comparable to that available at even the highest flux U.S. research reactors. (b) The agreement factor after averaging equivalent data and on the basis of F^2 is defined as $R(F^2) = \sum(F_{av}{}^2 - F^2)/\sum F^2$.

(9) J. L. Petersen, L. F. Dahl, and J. M. Williams, *J. Am. Chem. Soc.*, **96**, 6610 (1974).

(10) The computer programs which were used in performing the necessary calculations, with their accession names in the "World List of Crystallographic Computer Programs", 3d ed, are as follows: data reduction and absorption correction, DATALIB; data averaging and sort, DATASORT; Fourier summation, FORDAP; least-squares refinement, OR XLFS3; error analysis of distances and angles, OR FFE3; structural drawings, OR TEPII.

(11) P. Coppens and W. C. Hamilton, *Acta Crystallogr., Sect. A*, **26**, 71 (1970).

(12) G. E. Bacon, *Acta Crystallogr., Sect. A*, **28**, 357 (1972).

(13) (a) M. Iwata, K. Nakatzu, and Y. Saito, *Acta Crystallogr., Sect. B*, **25**, 2562 (1969); (b) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971); (c) J. T. Veal and D. J. Hodgson, *ibid.*, **11**, 597 (1972).

(14) W. C. Hamilton, *Natl. Bur. Stand. (U.S.)*, *Spec. Publ.*, **No. 301**, 193 (1969).

(15) E. O. Schlemper, W. C. Hamilton, and S. J. La Placa, *J. Chem. Phys.*, **56**, 3990 (1971).

(16) J. M. Williams and S. W. Peterson, *Spectrosc. Inorg. Chem.*, **2**, 1 (1971).

(17) G. D. Brunton and C. K. Johnson, *J. Chem. Phys.*, **62**, 3797 (1975).

(18) (a) A. Sequeira, C. A. Berkebile, and W. C. Hamilton, *J. Mol. Struct.*, **1**, 283 (1967–1968). (b) When obtaining the difference tensor it is *assumed* in the model that this tensor "should closely approximate the motion of the hydrogen atom in a static field of two motionless oxygen atoms".[18a] In the study reported herein the $H_5O_2^+$ moiety is undergoing large-amplitude librational motion and the model used is clearly inadequate for obtaining the "net" motion of the bridging hydrogen atom in the O···H···O bond.

(19) A. L. MacDonald, J. C. Speakman, and D. Hadzi, *J. Chem. Soc., Perkin Trans. 2*, 825 (1972).

(20) G. Picotin and J. Roziere, *J. Chim. Phys. Phys.-Chim. Biol.*, **69**, 372 (1972).

(21) J. B. Bates and L. M. Toth, *J. Chem. Phys.*, **61**, 129 (1974).

(22) J. Roziere and J. M. Williams, work in progress.

(23) R. A. Bell, G. G. Christoph, F. R. Fronczek, and R. E. Marsh, *Science*, **190**, 151 (1975).