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## $\pi$ Complexes of Nitrogen Heterocycles. Molecular Structure of Tricarbonyl( $\eta^4$ -1(1*H*),2(2*H*)-diazepinium)iron Trifluoroacetate, a Fluxional Molecule from the Protonation of Tricarbonyl( $\eta^4$ -1(1*H*),2-diazepine)iron

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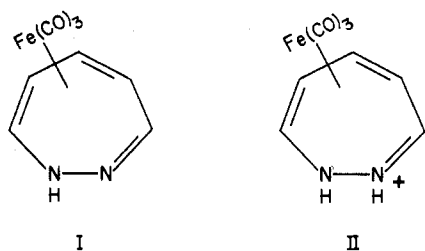
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The complex  $[(C_5H_7N_2)Fe(CO)_3]CF_3CO_2$ , synthesized by monoprotection of  $(\eta^4-C_5H_6N_2)Fe(CO)_3$  in trifluoroacetic acid, crystallizes in the centrosymmetric triclinic space group  $P\bar{1}$  ( $C_i^1$ ; No. 2) with  $a = 10.812$  (7) Å,  $b = 9.403$  (6) Å,  $c = 6.690$  (4) Å,  $\alpha = 94.72$  (7)°,  $\beta = 78.16$  (5)°, and  $\gamma = 103.59$  (5)°. The observed density of  $1.78$  g cm<sup>-3</sup> agrees with the value of  $1.770$  g cm<sup>-3</sup> calculated for mol wt 348.01 with  $Z = 2$ . X-ray intensity data were measured using Mo  $K\alpha$  radiation out to  $2\theta = 65^\circ$  on a General Electric XRD-6 Datex automated diffractometer. The structure was solved by a combination of Patterson, Fourier, and least-squares methods. All of the atoms in the molecule were located and refined. Refinement using anisotropic thermal parameters for nonhydrogen atoms gave convergence at  $R = 0.037$  and  $R_w = 0.043$ . The structure consists of discrete ion pairs in which the trifluoroacetate anions are hydrogen bonded via carboxylate oxygen atoms to the N-H groups of the heterocyclic cation. The structure determination confirms that protonation occurs at the imine nitrogen yielding a  $\eta^4$ -iminium ion. The iron atom is bonded to four carbon atoms of the heterocycle in typical diene fashion with iron-carbon distances being Fe-C(5) = 2.149 (2) Å, Fe-C(6) = 2.038 (2) Å, Fe-C(7) = 2.050 (2) Å, and Fe-C(8) = 2.179 (2) Å. The heterocycle is folded about a line joining the terminal carbon atoms C(5) and C(8) of the diene moiety with a dihedral angle of  $35.25^\circ$  between the planes defined by the diene carbon atoms and the atoms C(5), C(4), N(2), N(1), and C(8). The N(1)-N(2) distance in the heterocycle is 1.346 (3) Å, somewhat shorter than in unprotonated diazepine complexes. The structural results are discussed in the light of molecular parameters for other  $\eta^4$  complexes of azepines and diazepines as well as the dynamic nature of the molecule in solution.

### Introduction

The first synthesis of the unsubstituted molecule 1(1*H*),-2-diazepine trapped as the tricarbonyliron complex I has



recently been described.<sup>1</sup> This molecule is dynamic in solution at room temperature as a result of simultaneous N-H tautomerism and molecular fluxionality. Protonation of I by trifluoroacetic acid proceeds in two stages yielding initially a monoprotinated species formulated as the iminium ion complex II<sup>2</sup> and subsequently, with 2 mol of acid, a novel diprotinated complex in which the heterocycle is bound to iron as a  $\eta^5$ -diazacycloheptadienyl ligand.<sup>3</sup> In complex II the presence of adjacent N-H groups eliminates the need for hydrogen tautomerism as a prerequisite for fluxionality and the molecule remains dynamic even at low temperatures. To confirm the site of protonation in II as the imine nitrogen and to establish the stereochemistry of the  $\pi$ -complexed heterocyclic cation, an x-ray crystal structure analysis of II was performed. The present structure determination is one of the most precise yet reported for a  $\eta^4$ -dieneiron tricarbonyl complex and the first for the unsubstituted 1(1*H*),2-diazepine ring system.

### Experimental Section

**Unit Cell Data.** Crystals of the complex, prepared as described elsewhere,<sup>2</sup> were recrystallized from concentrated methylene chloride solutions at  $-20^\circ$  C. On the basis of Weissenberg and precession photography the crystals were assigned to the triclinic system. Least-squares refinement of  $2\theta$  values for 25 reflections measured on a General Electric XRD-6 Datex automated diffractometer yielded the following unit cell dimensions:  $a = 10.812$  (7),  $b = 9.403$  (6),  $c = 6.690$  (4) Å,  $\alpha = 94.72$  (7),  $\beta = 78.16$  (5),  $\gamma = 103.59$  (5)°. The

experimental density of  $1.78$  g cm<sup>-3</sup> measured by flotation is in agreement with the value of  $1.770$  g cm<sup>-3</sup> calculated on the basis of two empirical formula units  $[(C_5H_7N_2)Fe(CO)_3]CF_3CO_2$  of mol wt 348.01 per unit cell. With  $Z = 2$  and no systematic absences the choice of space groups was  $P1$  or  $P\bar{1}$  of which the latter proved to be correct by the successful refinement of the structure.

**Collection and Reduction of Intensity Data.** A rhombic prism of dimensions  $0.40 \times 0.30 \times 0.30$  mm was mounted on a glass fiber and aligned with  $a^*$  parallel to the  $\phi$  axis of the diffractometer. The intensity data were collected at room temperature using Zr-filtered Mo  $K\alpha$  radiation ( $\lambda$  0.7107 Å) and a takeoff angle of  $4^\circ$ . The integrated intensities were measured with a scintillation counter employing a pulse height analyzer. The diffracted x-ray beam passed through a collimator of 1-mm diameter placed 5 cm from the crystal and then to the counter via an aperture of 1-cm diameter, 18 cm from the crystal. Data were collected in the  $\theta$ - $2\theta$  scan mode with the scan width determined by the equation  $\Delta\theta = \pm(0.9 + 0.43 \tan \theta)^\circ$  and the scan rate  $2^\circ$ /min. Stationary-counter, stationary-crystal background counts of 10 s were taken before and after each scan. Three standard reflections (003, 03 $\bar{3}$ , 00 $\bar{3}$ ) were monitored after every 100 reflections measured. These declined in intensity by ca. 7% over the course of data collection and were used to scale the data to a common level. Standard deviations were estimated from counting statistics. Of 4670 independent reflections measured ( $2\theta \leq 65^\circ$ ), 3385 with intensities  $I \geq 3\sigma(I)$  were considered observed and used in the analysis. Lorentz and polarization corrections were applied to the derivation of structure amplitudes. The value of  $\mu$  for these atoms using Mo  $K\alpha$  radiation was  $12.5$  cm<sup>-1</sup> with a range of transmission coefficients of 0.188–0.250. No absorption correction was applied. A systematic check of the intensity of an axial reflection (at  $\chi = 90^\circ$ ) with  $\phi$  varying from 0 to  $360^\circ$  showed a variation of <10%.

**Solution and Refinement of Structure.** The coordinates of the iron atom were determined from a three-dimensional Patterson synthesis. A subsequent Fourier map phased by the iron atom revealed positions of all nonhydrogen atoms. With all atoms having isotropic temperature parameters, the structure was refined by full-matrix least-squares methods to an agreement value  $R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$  of 0.140. In all least-squares cycles the function minimized was  $\sum w(F_o - |F_c|)^2$ . Scattering factors used including anomalous scattering corrections for iron were taken from ref 4 with the exception of hydrogen values when the data of ref 5 were used. Refinement with anisotropic temperature factors reduced  $R$  to 0.059. A difference Fourier at this stage showed the positions of all seven hydrogen atoms. Furthermore, rotational disorder of the  $CF_3$  group was apparent with the second partially occupied sites being approximately  $60^\circ$  (rotated about the

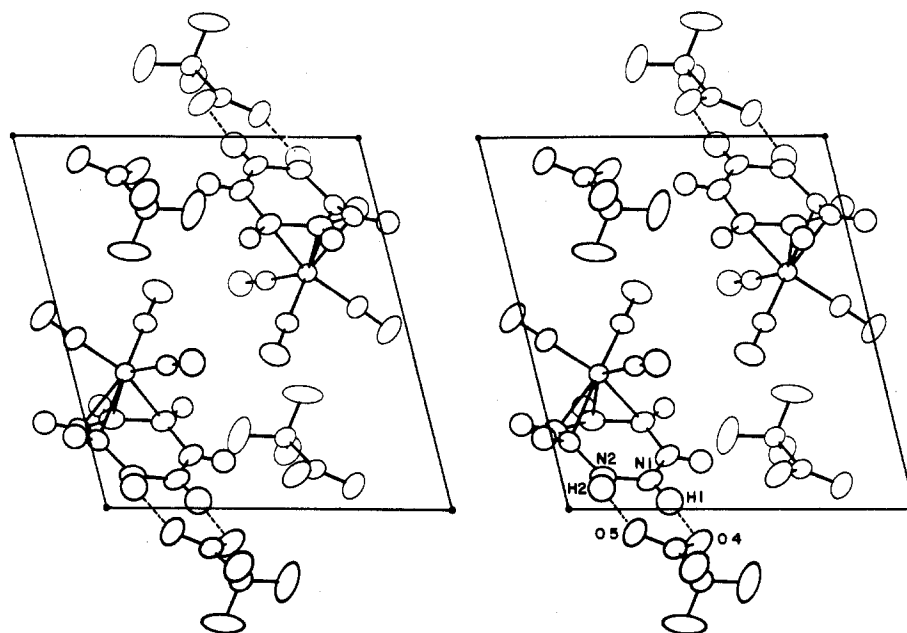


Figure 1. Stereoscopic packing diagram showing the arrangement of cations and anions in the unit cell. The cations shown in the outlined cell are hydrogen bonded to the trifluoroacetate ions outside the cell.

C(9)–C(10) bond) from the principally occupied positions. An occupancy ratio of 3:1 for the two sets of sites gave a best approximation to the intensity data. Incorporation of the partially occupied fluorine sites and the hydrogen atoms into the refinement reduced  $R$  to 0.045. A weighting scheme of the type  $w^{-1} = 1.8146 - 0.1327|F| + 0.0087|F|^2$  with coefficients derived from the program Ranger was then introduced and refined till convergence was achieved at  $R = 0.037$ , with a weighted residual  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  of 0.043. In the final cycle, no parameters except those of the disordered fluorine atoms were observed to shift by more than one-fourth of their standard deviations. A final difference Fourier revealed no peaks greater than  $0.25 \text{ e } \text{Å}^{-3}$  except in the region of the  $\text{CF}_3$  group (maximum  $0.5 \text{ e } \text{Å}^{-3}$ ). Computer programs used have been previously described.<sup>6</sup> All computations were carried out on an IBM 360-75 system in the University computing center.

The positional parameters for all atoms together with isotropic temperature coefficients for hydrogen are listed in Table I and thermal parameters for heavy atoms in Table II. A list of observed and calculated structure factors is available (supplementary material).

### Description and Discussion of the Structure

**Crystal Structure.** The crystal structure consists of an assembly of cations ( $(\eta^4\text{-C}_5\text{H}_7\text{N}_2)\text{Fe}(\text{CO})_3^+$ ) and anions  $\text{CF}_3\text{COO}^-$  strongly hydrogen bonded to one another in pairs via N(1)–H(1)---O(4)–C(9) hydrogen bonds. A stereoscopic packing diagram illustrating the arrangement of the two ion pairs in the unit cell is shown in Figure 1. A compilation of selected nonbonded inter- and intramolecular contacts is given in Table III. The distance between the iminium nitrogen atom N(1) and the carboxylate oxygen O(4) involved in the hydrogen bond is 2.615 (3) Å, considerably shorter than the average N---O separation (2.93 Å) in N–H---O hydrogen bonds.<sup>7,8</sup> The distance O(4)---H(1) (1.71 (3) Å) is also significantly less than the H---O separation of 1.93 Å used as a criterion of strong N–H---O hydrogen bonding.<sup>7,8</sup> The presence of strong cation–anion hydrogen-bonding interactions in  $[(\eta^4\text{-C}_5\text{H}_7\text{N}_2)\text{Fe}(\text{CO})_3](\text{CF}_3\text{CO}_2)$  is apparent in the solid-state infrared spectrum where a broad  $\nu(\text{N–H})$  band envelope with several maxima extends from 3500 to 2300  $\text{cm}^{-1}$  and a broad  $\nu(\text{CO}_2)_{\text{as}}$  of the anion ( $\Delta\nu_{1/2} = 115 \text{ cm}^{-1}$ ) is centered at 1650  $\text{cm}^{-1}$ . For comparison,  $\nu(\text{COO})_{\text{as}}$  of the trifluoroacetate ion appears as a strong, relatively sharp band at 1689  $\text{cm}^{-1}$  in sodium trifluoroacetate.<sup>9</sup> For each ion pair there is a second, weaker hydrogen-bonding interaction between the N(2)–H(2) moiety and the second carboxylate

Table I. Positional Parameters and Hydrogen Atom Temperature Factors

(a) Nonhydrogen Atom Positions (Fractional, $\times 10^4$ )				
	x	y	z	
Fe	3645.4 (3)	1903.6 (3)	3955.0 (4)	
F(1*) <sup>a</sup>	8436 (3)	3161 (3)	–2376 (3)	
F(2*)	8026 (4)	4683 (4)	–67 (5)	
F(3*)	6905 (2)	2536 (6)	47 (7)	
F(1**)	7524 (18)	2402 (11)	–1606 (27)	
F(2**)	8551 (10)	4564 (16)	–1095 (29)	
F(3**)	6995 (8)	3647 (13)	894 (12)	
O(1)	5837 (2)	3607 (3)	5718 (4)	
O(2)	5155 (2)	–233 (2)	2124 (3)	
O(3)	3931 (2)	3569 (2)	322 (3)	
O(4)	9069 (2)	3538 (3)	2439 (3)	
O(5)	9368 (2)	1748 (2)	127 (3)	
N(1)	772 (2)	2622 (2)	3968 (3)	
N(2)	868 (2)	1294 (2)	3122 (3)	
C(1)	4982 (2)	2952 (3)	5067 (4)	
C(2)	4552 (2)	591 (3)	2795 (3)	
C(3)	3852 (2)	2951 (2)	1743 (3)	
C(4)	1428 (2)	3329 (3)	5295 (4)	
C(5)	2341 (2)	2878 (3)	6214 (3)	
C(6)	2383 (2)	1445 (3)	6656 (3)	
C(7)	2117 (2)	301 (3)	5241 (4)	
C(8)	1811 (2)	566 (2)	3357 (4)	
C(9)	8933 (2)	2811 (2)	826 (4)	
C(10)	8061 (2)	3321 (3)	–383 (4)	
(b) Hydrogen Atom Positions (Fractional, $\times 10^3$ ) and Isotropic Temperature Factors				
	x	y	z	$B_{\text{iso}}, \text{Å}^2$
H(1)	21 (3)	305 (3)	350 (5)	6.7 (8)
H(2)	55 (3)	114 (3)	205 (5)	6.5 (8)
H(4)	127 (3)	426 (3)	559 (4)	5.1 (6)
H(5)	271 (2)	361 (3)	707 (4)	4.2 (5)
H(6)	274 (3)	131 (3)	787 (4)	5.1 (6)
H(7)	228 (3)	–67 (3)	545 (4)	5.2 (6)
H(8)	191 (3)	–18 (3)	225 (4)	5.5 (6)

<sup>a</sup> One asterisk indicates multiplicity 0.75; two asterisks indicate multiplicity 0.25.

oxygen atom O(5). The oxygen (O(5))–nitrogen (N(2)) separation in this case is 2.937 (3) Å. It is probable that the relative strengths of the N(1)–H(1)---O(4) and N(2)–H(2)---O(5) hydrogen bonds are a function of the acidities

Table II. Thermal Parameters<sup>a</sup> ( $\times 10^4$ ) for Nonhydrogen Atoms

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Fe	76.5 (3)	107.6 (3)	187.7 (6)	22.3 (2)	-32.7 (3)	1.5 (3)
F(1*)	203 (4)	255 (5)	247 (5)	111 (4)	-76 (4)	-36 (4)
F(2*)	355 (7)	207 (5)	526 (11)	183 (5)	-225 (7)	-124 (6)
F(3*)	79 (2)	500 (11)	635 (14)	-23 (4)	-82 (5)	203 (10)
F(1**)	501 (30)	194 (14)	1151 (71)	200 (18)	-658 (42)	-258 (26)
F(2**)	179 (13)	342 (26)	1340 (86)	-30 (16)	-71 (29)	543 (42)
F(3**)	123 (9)	357 (20)	406 (24)	128 (11)	-38 (11)	31 (17)
O(1)	125 (2)	235 (4)	440 (7)	-16 (2)	-118 (3)	1 (4)
O(2)	193 (3)	229 (3)	332 (6)	142 (3)	-46 (3)	-16 (3)
O(3)	163 (2)	196 (3)	300 (5)	36 (2)	-70 (3)	73 (3)
O(4)	170 (3)	251 (4)	377 (6)	123 (3)	-144 (3)	-147 (4)
O(5)	167 (2)	167 (3)	352 (5)	91 (2)	-114 (3)	-72 (3)
N(1)	93 (2)	189 (3)	291 (5)	59 (2)	-51 (3)	-31 (3)
N(2)	88 (2)	180 (3)	270 (5)	19 (2)	-65 (2)	-31 (3)
C(1)	88 (2)	150 (3)	259 (5)	11 (2)	-50 (3)	12 (3)
C(2)	114 (2)	153 (3)	220 (5)	60 (2)	-38 (3)	14 (3)
C(3)	88 (2)	123 (3)	237 (5)	23 (2)	-43 (2)	6 (3)
C(4)	106 (2)	175 (4)	283 (6)	63 (2)	-45 (3)	-57 (4)
C(5)	98 (2)	170 (3)	219 (5)	44 (2)	-47 (3)	-66 (3)
C(6)	94 (2)	189 (4)	189 (5)	27 (2)	-22 (2)	13 (3)
C(7)	96 (2)	130 (3)	286 (6)	4 (2)	-23 (3)	45 (3)
C(8)	96 (2)	117 (3)	261 (5)	7 (2)	-40 (3)	-24 (3)
C(9)	89 (2)	144 (3)	264 (5)	36 (2)	-51 (3)	-25 (3)
C(10)	100 (2)	142 (3)	284 (6)	43 (2)	-48 (3)	-16 (3)

<sup>a</sup> In the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$ .

Table III. Inter- and Intramolecular Nonbonded Contacts (Å)

(a) Intermolecular			
F(1*)-H(8)	2.74 (3)	O(4)-H(4)	2.42 (3)
F(2*)-H(5)	2.58 (2)	O(5)-H(2)	2.98 (3)
F(3*)-H(8)	2.98 (3)	O(5)-H(8)	2.48 (3)
F(1**)-H(7)	2.93 (3)	O(2)-O(2)	3.007 (3)
F(1**)-H(8)	2.30 (3)	O(3)-F(2*)	3.006 (5)
F(2**)-H(1)	2.78 (4)	N(1)-C(7)	3.622 (3)
F(3**)-H(5)	2.80 (3)	N(2)-N(2)	3.562 (3)
O(2)-H(6)	2.70 (3)	N(2)-C(7)	3.227 (3)
O(3)-H(5)	2.77 (2)	N(2)-C(8)	3.535 (3)
O(3)-H(6)	2.81 (3)		
(b) Intramolecular			
O(5)-N(2)	2.937 (3)	Fe-H(7)	2.67 (3)
O(4)-N(1)	2.615 (3)	Fe-H(8)	2.73 (3)
O(5)-H(1)	2.70 (3)	Fe-C(4)	2.963 (3)
O(5)-H(2)	2.18 (3)	Fe-N(1)	3.330 (2)
Fe-H(5)	2.70 (2)	Fe-N(2)	3.079 (2)
Fe-H(6)	2.66 (3)		

of the iminium and amine functions respectively in the  $\pi$ -complexed heterocycle. None of the other contacts listed in Table III are significantly less than the sums of van der Waals radii for the respective atoms.

### Molecular Structure

Figure 2 represents a perspective view of the molecular structure and includes the atomic numbering scheme. Bond distances and angles are listed in Table IV. The dimensions of the trifluoroacetate ion are basically similar to those measured by Cruickshank, Jones, and Walker for ammonium trifluoroacetate.<sup>10</sup> Thus the C-O bond lengths (average 1.234 Å) are somewhat shorter than in  $\text{NH}_4(\text{CF}_3\text{CO}_2)$  (average 1.269 Å); however, in the latter, each oxygen atom of the carboxylate is involved in two hydrogen bonds with adjacent ammonium ions. The C(9)-C(10) bond length in  $[(\eta^4\text{-C}_5\text{H}_7\text{N}_2)\text{Fe}(\text{CO})_3](\text{CF}_3\text{CO}_2)$  (1.536 (3) Å) is not significantly different from that in the ammonium salt (1.542 (9) Å). Although the fluorine atoms of the trifluoromethyl group were found to exhibit partial rotational disorder over six sites, with a "best fit" of the disorder suggesting a 75:25% occupancy of the two sets of threefold sites no attempt was made to correct C(10)-F bond lengths for rotational motion. The average C(10)-F distance (1.295 Å) is thus slightly shorter than the value corrected for rotational shortening (average 1.346 Å)

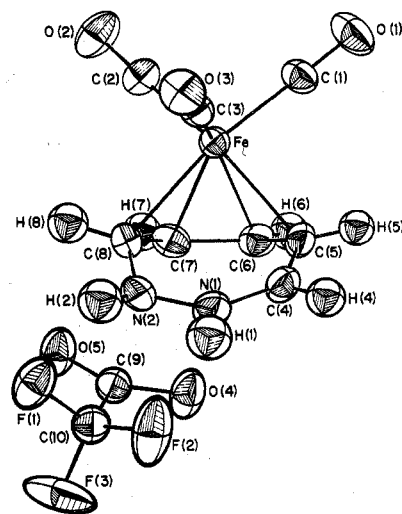


Figure 2. Perspective view of the molecular structure showing the atomic numbering.

in ammonium trifluoroacetate.<sup>10</sup>

In view of the dynamic behavior of  $[(\eta^4\text{-C}_5\text{H}_7\text{N}_2)\text{Fe}(\text{CO})_3](\text{CF}_3\text{CO}_2)$  in solution, the principal structural features of interest are the nature of the metal-ring bonding and the effects of protonation on the conformation and bond lengths of the 1(1H),2-diazepine ring system. The analysis unequivocally establishes the site of protonation as the imine nitrogen (N(1) of Figure 2) and confirms that the protonated heterocycle is bonded to the iron tricarbonyl moiety in  $\eta^4$  fashion via carbon atoms C(5)-C(8). The bond lengths within the coordinated diene portion of the diazepine follow the pattern initially established for other dieneiron tricarbonyls<sup>11</sup> with the central bond (C(6)-C(7) of 1.391 (3) Å) significantly shorter ( $\Delta/\sigma > 8$ ) than the outer (C(5)-C(6) of 1.416 (4) Å and C(7)-C(8) of 1.422 (3) Å) bonds which are of equal length to within experimental error. It is of some interest that while an almost identical difference ( $\Delta_{\text{C-C}} = 0.025$  Å)<sup>12</sup> between outer and inner carbon-carbon bond lengths was found recently in an accurate determination of the structure of (3-formyl-N-ethoxycarbonylazepine)tricarbonyliron,<sup>13</sup> results for (azepine)tricarbonyliron<sup>14</sup> and (N-ethoxy-

Table IV. Bond Lengths (Å) and Angles (deg)

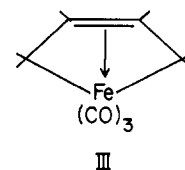
(a) Bond Lengths			
Fe-C(1)	1.807 (2)	N(1)-H(1)	0.92 (3)
Fe-C(2)	1.785 (2)	N(2)-H(2)	0.85 (3)
Fe-C(3)	1.792 (2)	C(4)-H(4)	0.93 (3)
Fe-C(5)	2.149 (2)	C(5)-H(5)	0.93 (3)
Fe-C(6)	2.038 (2)	C(6)-H(6)	1.00 (3)
Fe-C(7)	2.050 (2)	C(7)-H(7)	0.99 (3)
Fe-C(8)	2.179 (2)	C(8)-H(8)	0.99 (3)
C(1)-O(1)	1.130 (3)	C(9)-C(10)	1.536 (3)
C(2)-O(2)	1.134 (3)	C(9)-O(4)	1.246 (3)
C(3)-O(3)	1.133 (3)	C(9)-O(5)	1.222 (3)
N(1)-N(2)	1.346 (3)	C(10)-F(1*)	1.319 (3)
N(1)-C(4)	1.294 (3)	C(10)-F(2*)	1.289 (4)
C(4)-C(5)	1.422 (4)	C(10)-F(3*)	1.282 (4)
C(5)-C(6)	1.416 (4)	C(10)-F(1**)	1.26 (2)
C(6)-C(7)	1.391 (3)	C(10)-F(2**)	1.25 (2)
C(7)-C(8)	1.422 (3)	C(10)-F(3**)	1.37 (1)
C(8)-N(2)	1.394 (3)	O(4)-H(1)	1.71 (3)
(b) Bond Angles			
C(1)-Fe-C(2)	92.2 (1)	N(1)-C(4)-H(4)	112 (2)
C(1)-Fe-C(3)	99.6 (1)	C(5)-C(4)-H(4)	120 (2)
C(1)-Fe-C(5)	89.1 (1)	C(4)-C(5)-C(6)	128.7 (1)
C(1)-Fe-C(6)	96.0 (1)	C(4)-C(5)-H(5)	112 (1)
C(1)-Fe-C(7)	128.7 (1)	C(6)-C(5)-H(5)	114 (1)
C(1)-Fe-C(8)	166.6 (0)	C(5)-C(6)-C(7)	119.6 (1)
C(2)-Fe-C(3)	97.8 (1)	C(5)-C(6)-H(6)	119 (1)
C(2)-Fe-C(5)	158.4 (1)	C(7)-C(6)-H(6)	121 (1)
C(2)-Fe-C(6)	119.1 (1)	C(6)-C(7)-C(8)	120.4 (1)
C(2)-Fe-C(7)	92.1 (1)	C(6)-C(7)-H(7)	119 (2)
C(2)-Fe-C(8)	93.7 (0)	C(8)-C(7)-H(7)	120 (2)
C(3)-Fe-C(5)	103.3 (0)	C(7)-C(8)-N(2)	126.1 (1)
C(3)-Fe-C(6)	139.2 (0)	C(7)-C(8)-H(8)	117 (2)
C(3)-Fe-C(7)	130.3 (0)	N(2)-C(8)-H(8)	110 (2)
C(3)-Fe-C(8)	91.5 (0)	C(8)-N(2)-N(1)	124.3 (1)
C(5)-Fe-C(6)	39.4 (0)	C(8)-N(2)-H(2)	120 (2)
C(5)-Fe-C(7)	70.5 (0)	N(1)-N(2)-H(2)	111 (2)
C(5)-Fe-C(8)	80.9 (0)	Fe-C(1)-O(1)	178.4 (1)
C(6)-Fe-C(7)	39.8 (0)	Fe-C(2)-O(2)	177.2 (1)
C(6)-Fe-C(8)	70.6 (0)	Fe-C(3)-O(3)	176.7 (1)
C(7)-Fe-C(8)	39.2 (0)	O(4)-C(9)-O(5)	128.9 (1)
Fe-C(5)-C(4)	110.5 (1)	O(4)-C(9)-C(10)	114.0 (1)
Fe-C(5)-C(6)	66.1 (0)	O(5)-C(9)-C(10)	117.1 (1)
Fe-C(5)-H(5)	117 (1)	C(9)-C(10)-F(1*)	112.6 (1)
Fe-C(6)-C(5)	74.5 (1)	C(9)-C(10)-F(2*)	114.1 (1)
Fe-C(6)-C(7)	70.6 (1)	C(9)-C(10)-F(3*)	109.6 (2)
Fe-C(6)-H(6)	118 (1)	C(9)-C(10)-F(1**)	117.6 (7)
Fe-C(7)-C(6)	69.7 (1)	C(9)-C(10)-F(2**)	112.8 (7)
Fe-C(7)-C(8)	75.3 (0)	C(9)-C(10)-F(3**)	111.0 (4)
Fe-C(7)-H(7)	119 (2)	F(1*)-C(10)-F(2*)	105.1 (2)
Fe-C(8)-C(6)	65.5 (1)	F(1*)-C(10)-F(3*)	106.0 (2)
Fe-C(8)-N(2)	117.3 (0)	F(2*)-C(10)-F(3*)	109.1 (2)
Fe-C(8)-H(8)	114 (2)	F(1**)-C(10)-F(2**)	114 (1)
N(2)-N(1)-C(4)	125.3 (1)	F(1**)-C(10)-F(3**)	100.5 (8)
N(2)-N(1)-H(1)	115 (2)	F(2**)-C(10)-F(3**)	98.2 (8)
C(4)-N(1)-H(1)	120 (2)	N(1)-H(1)-O(4)	169.9 (1)
N(1)-C(4)-C(5)	128.6 (1)		

carbonyl-1(1*H*),2-diazepine)tricarbonyliron<sup>15</sup> did not reveal significant differences. A precise structural analysis of (C<sub>11</sub>H<sub>14</sub>)Fe(CO)<sub>3</sub><sup>16</sup> indicated an essential equality of "outer" and "inner" carbon-carbon bond lengths in the coordinated diene while statistically shorter "inner" carbon-carbon bond lengths were found in the recently determined structures of [C<sub>5</sub>H<sub>4</sub>C<sub>6</sub>H<sub>6</sub>CO]Fe<sub>2</sub>(CO)<sub>5</sub> ( $\Delta_{C-C} = 0.042$  (5) Å)<sup>17</sup> and (C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>Fe<sub>4</sub>(CO)<sub>10</sub>C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> ( $\Delta_{C-C} = 0.068$  (9) Å).<sup>18</sup>

Clearly the more accurate recent structural work on diene complexes suggests that  $\Delta_{C-C}$  is likely to be small (usually <0.04 Å) and, if present, will in many cases only be discernible when esd's on carbon-carbon lengths are better than 0.010 Å. As pointed out by Cotton and coworkers,<sup>16</sup> the significant observation is the shortening of the "inner" C-C bonds of the complexed dienes compared to the length of the same bond in the free ligands, emphasizing a distortion toward the stereochemistry in the first excited state of the diolefin. For the ion ( $\eta^4$ -C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>)Fe(CO)<sub>3</sub><sup>+</sup> the C(6)-C(7) bond length

(1.391 (3) Å) is 0.092 Å shorter than the central C-C bond in uncomplexed *trans*-butadiene.<sup>19</sup> Originally<sup>11</sup> it was thought that a greater perturbation toward the geometry of the first excited state was evident when the olefin had fluorine substituents or when a metal fragment inferior to Fe(CO)<sub>3</sub> in  $\pi$ -acceptor capability was present. This trend, as estimated from the magnitude of  $\Delta_{C-C}$ , has not been entirely substantiated by more recent work. Thus for tricarbonyl-(decafluorocyclohepta-1,3-diene)iron<sup>20</sup>  $\Delta_{C-C}$  (0.030 (7) Å) is smaller than the corresponding differences in several unfluorinated complexes<sup>17,18</sup> while  $\Delta_{C-C}$  values of essentially zero were found in ( $\eta^4$ -C<sub>4</sub>H<sub>4</sub>Cl<sub>2</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Rh and ( $\eta^4$ -C<sub>6</sub>H<sub>10</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Rh.<sup>21</sup> The latter values are particularly surprising in view of the large  $\Delta_{C-C}$  (0.09 (2) Å) found in ( $\eta^4$ -(CF<sub>3</sub>)<sub>6</sub>C<sub>6</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Rh<sup>22</sup> and the value  $\Delta_{C-C} = 0.07$  (2) Å in ( $\eta^4$ -C<sub>4</sub>H<sub>6</sub>)<sub>2</sub>RhCl.<sup>23</sup> Clearly, further accurate structural work on diene complexes of metal fragments isoelectronic with Fe(CO)<sub>3</sub> is required before any valid generalizations concerning the effects of the metal fragment on the electronic state and stereochemistry of the coordinated olefin can be made.

The inner carbon atoms of the diene are considerably closer (average Fe-C 2.044 Å) to the metal than the peripheral atoms (mean Fe-C = 2.164 Å). Although the same structural feature is apparent in many other diene complexes<sup>11,13-18</sup> for which  $\Delta_{Fe-C}$  generally lies between 0.05 and 0.15 Å, the opposite situation prevails for tricarbonyl(octafluorocyclohexa-1,3-diene)iron ( $\Delta_{Fe-C} = -0.067$  Å)<sup>24</sup> and tricarbonyl-(decafluorocycloheptadiene)iron ( $\Delta_{Fe-C} = -0.035$  Å).<sup>20</sup> For the perfluoroolefin complexes the Fe-C bond lengths emphasize a distortion toward a metallocyclopentene structure or alternatively a major contribution from a valence-bond structure III. Clearly for the imminium ion complex the



presence of a full positive charge and two electronegative nitrogen atoms adjacent to the coordinated diene moiety does not produce the same structural effect as fluorine substitution on the diene. Moreover from a survey of available structural parameters for diene complexes of iron, it is clear that there is no linear or simple relationship between  $\Delta_{Fe-C}$  and  $\Delta_{C-C}$ . A more valid comparison, that of  $\Delta_{Fe-C}$  vs. the change in "inner" C-C bond length on coordination, is precluded by lack of data for the free ligands.

The average Fe-C(diene) bond length in the ion ( $\eta^4$ -C<sub>5</sub>H<sub>7</sub>N<sub>2</sub>)Fe(CO)<sub>3</sub><sup>+</sup> (2.104 Å) is slightly longer than the mean values in ( $\eta^4$ -C<sub>10</sub>H<sub>11</sub>O<sub>3</sub>N)Fe(CO)<sub>3</sub> (2.088 Å),<sup>13</sup> ( $\eta^4$ -C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>)Fe(CO)<sub>3</sub> (2.089 Å), ( $\eta^4$ -C<sub>11</sub>H<sub>14</sub>)Fe(CO)<sub>3</sub> (2.094 Å),<sup>16</sup> ( $\eta^5$ , $\eta^4$ -C<sub>12</sub>H<sub>10</sub>O)Fe<sub>2</sub>(CO)<sub>5</sub> (2.073 Å),<sup>17</sup> (C<sub>10</sub>H<sub>8</sub>)<sub>2</sub>-Fe<sub>4</sub>(CO)<sub>10</sub>C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (2.093 Å),<sup>18</sup> and ( $\eta^4$ , $\eta^4$ -C<sub>12</sub>H<sub>12</sub>O)[Fe(CO)<sub>3</sub>]<sub>2</sub> (2.079 and 2.073 Å),<sup>25</sup> these being the most accurate of the structures reported to date for cyclic diene complexes. While these values may indicate weaker iron-diene bonding in the imminium ion complex, their significance is lessened by the fact that in ( $\eta^4$ -C<sub>6</sub>H<sub>7</sub>N)Fe(CO)<sub>3</sub><sup>14</sup> the Fe-C(diene) bonds are even longer (average 2.113 Å). It is interesting, however, that monoprotonation of ( $\eta^4$ -1(1*H*),2-diazepine)-Fe(CO)<sub>3</sub> to give the imminium ion results in an average increase in  $\nu$ (CO) frequency of 50 cm<sup>-1</sup>, consistent with less Fe-CO back-donation in the cation and hence, possibly, weaker forward  $\sigma$  donation from the coordinated heterocycle.

A view of the molecule along the pseudo-threefold axis of the iron tricarbonyl moiety and projected onto the C(5)-C(8) diene plane is shown in Figure 3. Although the carbonyl

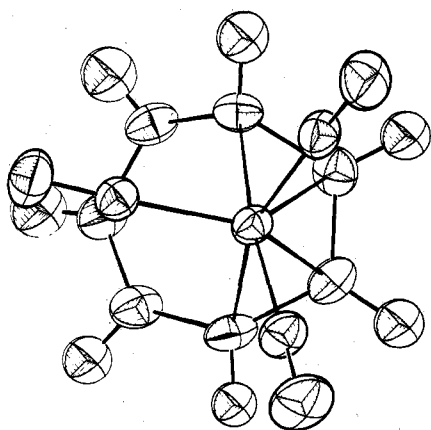


Figure 3. View of the molecule emphasizing the stereochemistry of the  $\text{Fe}(\text{CO})_3$  moiety relative to the coordinated diene fragment of the ring.

groups  $\text{C}(1)\text{--O}(1)$  and  $\text{C}(2)\text{--O}(2)$  eclipse the coordinated bonds  $\text{C}(5)\text{--C}(6)$  and  $\text{C}(7)\text{--C}(8)$ , respectively, the arrangement is somewhat more asymmetric than in other diene complexes. The iron atom is also slightly displaced toward  $\text{C}(5)$  and  $\text{C}(6)$ . A least-squares plane calculation (plane 4, Table V) shows that the iron atom is located 0.526 Å above the mean plane defined by  $\text{C}(1)$ ,  $\text{C}(2)$ , and the midpoints of the  $\text{C}(5)\text{--C}(6)$  and  $\text{C}(7)\text{--C}(8)$  bonds. This square-pyramidal stereochemistry for iron is considerably more distorted than in the compound (3-formyl-*N*-ethoxycarbonylazepine)tricarbonyliron<sup>13</sup> where the basal points of the pyramid are almost planar. The distortion of the local threefold symmetry of the  $\text{Fe}(\text{CO})_3$  moiety is demonstrated by the magnitudes of the three angles  $\text{C}(7)\text{--Fe--C}(2) = 92.2 (1)^\circ$ ,  $\text{C}(1)\text{--Fe--C}(3) = 99.6 (1)^\circ$ , and  $\text{C}(2)\text{--Fe--C}(3) = 97.8 (1)^\circ$ . The form of this distortion from three internal angles of  $90^\circ$  appears to be very similar for all nonfluorinated diene complexes of iron, with one angle lying close to  $90^\circ$  and two other angles near  $100^\circ$ .<sup>26</sup> In this sense the distortion is toward a square-pyramidal fragment. For the fluorodiene complexes investigated to date the distortion is of smaller magnitude but apparently in the same sense. Thus for  $(\eta^4\text{-C}_7\text{F}_{10})\text{Fe}(\text{CO})_3$ ,<sup>22</sup>  $(\eta^4\text{-C}_6\text{F}_8)\text{Fe}(\text{CO})_3$ ,<sup>22</sup> and  $[\eta^4\text{-(CF}_3)_4\text{C}_5\text{O}]\text{Fe}(\text{CO})_3$ ,<sup>27</sup> the  $\text{OC--Fe--CO}$  angles are  $90.4 (3)$ ,  $95.8 (3)$ , and  $95.8 (3)^\circ$ ;  $89.6 (4)$ ,  $97.8 (4)$ , and  $97.8 (4)^\circ$ ; and  $89.3 (1.1)$ ,  $94.7 (1.1)$ , and  $97.8 (1.1)^\circ$ , respectively. The extent of distortion may be related to the  $\sigma$ -donor- $\pi$ -acceptor character of the dienes, with strong  $\pi$ -acceptor properties facilitating withdrawal of a high-energy electron pair from iron and relieving the  $\text{Fe}(\text{CO})_3$  moiety of the requirement to distort.<sup>28</sup>

The seven-membered heterocyclic cation is folded about a line joining  $\text{C}(5)$  and  $\text{C}(8)$ , with the plane defined by atoms  $\text{C}(5)$ ,  $\text{C}(4)$ ,  $\text{N}(1)$ ,  $\text{N}(2)$ , and  $\text{C}(8)$  (Table V) inclined at a dihedral angle of  $35.35^\circ$  to the plane defined by the coordinated diene moiety. This dihedral angle is smaller than the corresponding angles in the diazepine complexes  $(\eta^4\text{-C}_8\text{H}_{10}\text{N}_2\text{O}_2)\text{Fe}(\text{CO})_3$ <sup>15</sup> (average  $39.4^\circ$  for the two molecules in the asymmetric unit) and  $(\eta^4\text{-C}_9\text{H}_{12}\text{N}_2\text{O}_2)\text{Fe}(\text{CO})_3$ <sup>29</sup> ( $40^\circ$ ). Larger dihedral angles have also been found for the various azepine complexes.<sup>13,14,30,31</sup> In the context of molecular fluxionality, these dihedral angles may be of some importance since the motion of the  $\text{Fe}(\text{CO})_3$  fragment in the dynamic process is over a five-carbon moiety ( $\text{C}(4)\text{--C}(8)$ ) in  $[(\eta^4\text{-C}_5\text{H}_7\text{N}_2)\text{Fe}(\text{CO})_3][\text{CF}_3\text{CO}_2]$ .

Greater planarity of the five-carbon unit might be expected to facilitate molecular motion by reducing the degree of angular rearrangement at the terminal atoms of the diene implied by the fluxional process. Of course there is no guarantee that the small dihedral angle in the present

Table V. Equations of Least-Squares Planes and Atomic Displacements from These Planes<sup>a</sup>

Plane 1: $0.8860x + 0.1893y - 0.4234z + 1.1844 = 0$			
<i>C</i> (5)	-0.0005	<i>H</i> (8)	0.2855
<i>C</i> (6)	0.0011	<i>N</i> (2)	-0.8811
<i>C</i> (7)	-0.0011	<i>N</i> (1)	-1.1392
<i>C</i> (8)	0.0005	<i>C</i> (4)	-0.7385
<i>H</i> (5)	0.2036	<i>H</i> (2)	-1.0070
<i>H</i> (6)	0.1522	<i>H</i> (1)	-1.1392
<i>H</i> (7)	0.1458	<i>H</i> (4)	-0.9582
Plane 2: $0.4679x + 0.5103y - 0.7215z - 0.3379 = 0$			
<i>C</i> (5)	-0.0427	<i>H</i> (5)	0.0513
<i>C</i> (4)	0.0449	<i>H</i> (4)	0.1790
<i>N</i> (1)	0.0133	<i>H</i> (1)	0.0806
<i>N</i> (2)	-0.0646	<i>H</i> (2)	0.1717
<i>C</i> (8)	0.0491	<i>H</i> (8)	0.2913
Plane 3: $0.5905x + 0.6312y - 0.5029z + 6.7317 = 0$			
<i>O</i> (4)	-0.0034	<i>C</i> (9)	0.0093
<i>O</i> (5)	-0.0036	<i>C</i> (10)	-0.0023
Plane 4: $-0.3742x + 0.6079y - 0.7003z - 2.8579 = 0$			
<i>C</i> (1)	0.0720	<i>C</i> (2)	-0.0711
Mid pt <i>C</i> (5)- <i>C</i> (6)	-0.0889	Mid pt <i>C</i> (7)- <i>C</i> (8)	0.0880
Fe	0.5262		

<sup>a</sup> Only italic atoms were included in the derivation.

solid-state structure has any bearing on the stereochemistry of the coordinated diazepine in solution. Nevertheless it is tempting to suggest that one structural consequence of the protonation of  $(\eta^4\text{-C}_5\text{H}_6\text{N}_2)\text{Fe}(\text{CO})_3$  consistent with a lowering of  $\Delta G^\ddagger$  is an increase in planarity of the five-carbon fragment ( $\text{C}(4)\text{--C}(8)$ ) of the heterocycle.

Plane 2 (Table V) illustrates that the stereochemistry at  $\text{N}(1)$  is more planar than at  $\text{N}(2)$  since  $\text{H}(2)$  protrudes 0.172 Å above the best plane defined by the uncoordinated portion of the ring. While this agrees with anticipated amine character for  $\text{N}(2)$  and imminium character for  $\text{N}(1)$ , the stereochemistry at  $\text{N}(2)$  is far from tetrahedral. Greater planarity about the nitrogen atoms in coordinated as opposed to free ligands has been noted previously for azepine complexes.<sup>13,14,30,31</sup> Although x-ray data are not available for  $(\eta^4\text{-C}_5\text{H}_6\text{N}_2)\text{Fe}(\text{CO})_3$ , the effects of protonating  $\text{N}(1)$  on the  $\text{N}(1)\text{--N}(2)$  bond length can be gauged approximately from a comparison with the  $\text{N--N}$  bond lengths in tricarbonyl(1-carboethoxy-1,1(*H*)-2-diazepine)iron<sup>15</sup> and tricarbonyl(1-isopropoxycarbonyl-1(*H*),2-diazepine)iron.<sup>29</sup> The latter bond lengths (1.381 (6) and 1.37 (1) Å) are quite significantly larger than in the present case. The relatively short  $\text{N}(1)\text{--N}(2)$  distance in the imminium ion complex can be attributed in large part to the absence of nitrogen lone pair-lone pair repulsions present in the unprotonated species. A similar decrease in  $\text{N--N}$  bond length accompanies protonation of hydrazine. The  $\text{N--N}$  distance in crystalline  $\text{N}_2\text{H}_4$  is 1.46 Å<sup>32</sup> whereas in the mono- and diprotonated cations  $\text{N}_2\text{H}_5^+$  and  $\text{N}_2\text{H}_6^{2+}$  bond lengths are 1.44–1.45<sup>33,34</sup> and 1.40–1.42 Å,<sup>35,36</sup> respectively.

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**Registry No.**  $[(\text{C}_5\text{H}_7\text{N}_2)\text{Fe}(\text{CO})_3]\text{CF}_3\text{CO}_2$ , 57535-35-0.

**Supplementary Material Available:** listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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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<sup>1</sup>

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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)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, Cl<sup>-</sup>, and H<sub>5</sub>O<sub>2</sub><sup>+</sup> 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<sub>5</sub>O<sub>2</sub><sup>+</sup> 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)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>Cl<sup>-</sup>(H<sub>5</sub>O<sub>2</sub>)<sup>+</sup>Cl<sup>-</sup>, 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.<sup>2-5</sup> However no definitive information regarding the geometry of the H<sub>5</sub>O<sub>2</sub><sup>+</sup> ion could be obtained from the previous x-ray diffraction studies of these adducts.<sup>3</sup> Two possible limiting structures may be considered for H<sub>5</sub>O<sub>2</sub><sup>+</sup>: (i) the diaquohydrogen ion,  $(H_2O \cdot H \cdot OH_2)^+$ , and (ii) the monoaquooxonium ion, H<sub>3</sub>O<sup>+</sup>·OH<sub>2</sub>. 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<sub>5</sub>O<sub>2</sub><sup>+</sup> species.<sup>2</sup> In a preliminary neutron diffraction investigation<sup>5</sup> of the structure of *trans*-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>Cl<sup>-</sup>(H<sub>5</sub>O<sub>2</sub>)<sup>+</sup>Cl<sup>-</sup> 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<sub>5</sub>O<sub>2</sub><sup>+</sup> in this compound, the hydrogen atom positions and hydrogen bonding around the [Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complex cation are of interest in relation to its configurational stability in the solid state.<sup>6</sup>

### 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.<sup>7</sup> The crystals were harvested and to avoid decomposition were kept in a sealed tube in a refrigerator before use.

**Unit Cell and Space Group.** Earlier studies<sup>3,5</sup> 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 ( $2\theta$  ranging from 40 to 60°) were automatically centered. The precise unit cell parameters (at  $22 \pm 2$  °C with  $\lambda$  1.142 (1) Å) determined by a least-squares fit of the angles  $2\theta$ ,  $\chi$ , and  $\phi$  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<sup>3</sup>. These values agree well with those given previously.<sup>5</sup> The density determined from the neutron data is 1.66 (1) g cm<sup>-3</sup> which agrees well with the experimental value<sup>3</sup> of 1.65 (1) g cm<sup>-3</sup>.

**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<sub>2</sub>O 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  $\phi$  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.<sup>8a</sup> The fully automated diffractometer operates under remote Sigma 5 computer control. A  $\theta$ - $2\theta$  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