conductivity behavior to be similar throughout the series. Conductivity measurements on this system[6,10,15–17] are inconsistent but favor the latter mechanism.

A new family of compounds may be proposed in which the link atom is replaced by a metal, A, of appropriate valency and size. Some materials of this type have already been prepared, *e.g.*, $NaCrSe_2$[18] and $FeCr_2Se_4$.[19] Examples of other possibilities are $GaCr_3Se_6$ or VCr_4Se_8. The substitution of other transition metals, B, for chromium, and chalcogens, Y, for selenium adds two further variables to this series, with the general formula $[BY_2]_n^{n-}\ (1/v)A^{v+}$.

The scheme of $Cd(OH)_2$-type layers with ionic cross-links may probably be extended to most NiAs-vacancy structures, in which the metal vacancies are located in alternate sheets. It also explains why many of the compounds with nominal metal to chalcogenide ratios of 1:1 are, in fact, always metal deficient.

Acknowledgments.—It is a pleasure to thank Miss S. M. Vincent for the X-ray fluorescence analysis, J. W. Shiever for dta measurements, D. J. Nitti for Guinier powder photographs, and Miss B. E. Prescott for transmission spectra.

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The Crystal Structure of a Dimeric Cobalt Compound Containing a Chloro Bridge

BY ROBERT BARRO, RICHARD E. MARSH, AND WILLIAM P. SCHAEFER

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The compound μ-chloro-μ-amido-octaamminedicobalt tetrachloride tetrahydrate, $(NH_3)_4Co{<}^{Cl}_{NH_2}{>}Co(NH_3)_4Cl_4\cdot 4H_2O$, forms triclinic crystals with cell dimensions $a = 7.812\ (1)$ Å, $b = 6.666\ (2)$ Å, $c = 20.577\ (4)$ Å, $\alpha = 107.02\ (2)°$, $\beta = 90.52\ (2)°$, $\gamma = 107.14\ (2)°$. The observed density is 1.77 (2) g cm^{-3}, and that calculated for two formula units in the cell is 1.771 (1) g cm^{-3}. All reflections with l odd are absent or extremely weak, indicating a pseudo structure with $c = 10.288$ Å. The pseudo structure has been solved and refined in space group $P\bar{1}$ by least-squares methods using 1018 reflections measured by counter diffractometry, to a final R index of 0.040. The two cobalt octahedra share an edge with the cobalt atoms 3.2 Å apart; the average cobalt–bridge chlorine distance is 2.325 (9) Å and the average cobalt–bridge nitrogen distance is 1.88 (2) Å. In this pseudo structure the bridging atoms are disordered, the cation lying on a center of symmetry. It is probable that the weak reflections with l odd are due to a partial ordering of the cation. The structure is approximately the same as that reported by Vannerberg and by Prout for $(NH_3)_4Co{<}^{OH}_{OH}{>}Co(NH_3)_4Cl_4\cdot 4H_2O$.

Introduction

The mixture of cobalt compounds knows as Vortmann's sulfate[1] produces, upon treatment with nitric acid, two compounds, referred to by Werner as a red nitrate and a green nitrate.[2] The green compound has the formula $(NH_3)_4Co(O_2)(NH_2)Co(NH_3)_4(NO_3)_4$; its structure has been reported.[3] Werner named the red compound μ-sulfato-μ-amino-octaamminedicobalt nitrate; it can be transformed into many other dibridged compounds. We wish to report here the structure of one of these compounds; it is the first dicobalt species shown to contain a chloro bridge.

Experimental Section

Vortmann's sulfate was prepared and transformed to the nitrate according to Werner's directions.[2] The green nitrate was removed by extraction with water; the red nitrate which remained was mixed with a small amount of concentrated hydrochloric acid and left for several hours. The liquid was then sucked off and the solid residue was dissolved in warm, dilute hydrochloric acid; upon standing, a few large, red, triclinic crystals formed. Many of these crystals were obviously twinned, but some appeared to be single. They were all covered with a fine pink powder, and there was more of this powder in the beaker. Because only a few of the large crystals were formed, no chemical analyses were performed on the material. As will become clear, it is unfortunate that we do not have highly accurate chemical analyses, especially for nitrogen, of this compound, but none of our preparations ever gave crystals of only one variety, so no analyses were attempted.

Crystal data for the compound are collected in Table I; the tabulated cell dimensions and their errors were derived from a least-squares fit of 2θ values measured on the diffractometer for 21 reflections with 2θ between 72 and 146° and including both the Fe Kα_1 and Kα_2 peaks for each reflection. The density was measured both by flotation and by displacement of ethanol.

After the structure determination had been completed, Dr. A. W. Chester sent us a compound formulated as a monobridged

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[1] G. Vortmann, *Monatsh. Chem.*, **6**, 404 (1885).

[2] A. Werner, *Ber. Deut. Chem. Ges.*, **40**, 4605 (1907).

[3] G. G. Christoph, R. E. Marsh, and W. P. Schaefer, *Inorg. Chem.*, **8**, 291 (1969).

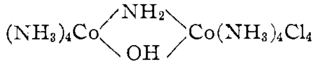
TABLE I

CRYSTAL DATA FOR μ-CHLORO-μ-AMIDO-OCTAAMMINEDICOBALT TETRACHLORIDE TETRAHYDRATE

$a = 7.812$ (2) Å	$\alpha = 107.02$ (2)°	
$b = 6.666$ (2) Å	$\beta = 90.52$ (2)°	
$c = 20.577$ (4) Å	$\gamma = 107.14$ (1)°	
λ(Fe Kα_1) 1.93597 Å	λ(Fe Kα_2) 1.93991 Å	
Space group P$\bar{1}$ (no. 2), determined by structure analysis		
$Co_2Cl_5O_4N_9H_{34}$	$F(000) = 536$	mol wt 519.6
$D_m = 1.77$ (2) g/cm³	$D_x = 1.771$ (1) g/cm³	($Z = 2$)

species, $(NH_3)_4ClCoNH_2Co(H_2O)(NH_3)_4Cl_4 \cdot 4H_2O$. Rotation and zero-layer Weissenberg photographs of a crystal of this compound showed it to be identical with our compound. Chester[4] had analyzed his preparation and his results are given here, compared with those calculated for our formulation of the compound. *Anal.* Calcd for $(NH_3)_4Co(Cl)(NH_2)Co(NH_3)_4Cl_4 \cdot 4H_2O$: Co, 22.7; N, 24.3; H, 6.60; H_2O, 13.9. Found: Co, 22.5; N, 23.7; H, 6.84; H_2O, 13.4.

Werner had originally[5] written this compound as



$$(NH_3)_4Co\langle{}^{NH_2}_{OH}\rangle Co(NH_3)_4Cl_4$$

and commented[6] that the chloride content was high, namely, 34.3% instead of 28%. (In a different paper,[2] Werner presented a method of preparation which yielded the OH- and NH_2-bridged compound and there reported the confirming analytical results.) The high chloride content that Werner mentioned implies that he had at that time prepared the same compound as we have but he never recognized it as having a chloro bridging group. *Anal.* Calcd for the Cl- and NH_2-bridged compound: Cl, 34.1. Found by Werner: Cl, 34.3. Although we could not get analytical data for our crystals, these two independent analytical results, together with our X-ray results, substantiate our formulation.

Sykes and Taylor[7] have recently identified a μ-amido-μ-chloro-dicobalt species by spectroscopic studies and have examined the equilibria involving the two compounds μ-amido-aquochloro $[(NH_3)_4H_2OCo{-}NH_2{-}CoCl(NH_3)_4{}^{4+}]$ and μ-amido-μ-chloro $[(NH_3)_4Co(Cl)(NH_2)Co(NH_3)_4{}^{4+}]$. Their sample of the μ-amido-μ-chloro compound had cell dimensions and intensity distributions (*hk*0 reflections) the same as the material we had prepared. Sykes measured the visible spectrum of our material in 0.1 *M* perchloric acid and found it agreed with the spectrum of the authentic μ-amido-μ-chloro-dicobalt ion.[8]

Photographic data were collected and analyzed by R. B., but because of the difficulties to be explained later, it was not possible to derive a satisfactory ordered structure. In hopes that an ordered structure could be found, a new batch of the material was prepared and a new set of data was collected on an automated diffractometer; these data were used for the refinement of the structure. The crystal was cut from a large chunk and ground to a prolate spheroid, with average diameter 0.22 mm. It was mounted in a random orientation and carefully centered on a G.E. diffractometer and cell dimensions were measured. Intensity data were collected using MnO_2-filtered iron radiation. A θ–2θ scan technique was used with a scanning speed of 1°/min; the scan range was varied from 3° at $2\theta = 21.50°$ to 4.5° at $2\theta = 139.0°$ to include both the α_1 and the α_2 peaks of each reflection. Background was counted for 100 sec at each end of the scan. The intensity of the 226 reflection was measured periodically during the entire data collection process; it showed no changes in intensity greater than those predicted by counting statistics. The data were corrected for Lorentz and polarization factors and a spherical absorption correction was applied. The value of μ for this compound is 162.8 cm^{-1} and thus μr was about 1.79 for the sphere used. Because the crystal was not exactly spherical, we estimate that the maximum error caused by the use of a spherical absorption correction was 10% in *F*. A standard deviation was assigned to each intensity from the formula

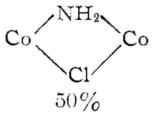
$$\sigma(I) = \left\{S + (B_1 + B_2)\left(\frac{t}{200}\right)^2 + (0.02S)^2\right\}^{1/2}$$

where *S* is counts in scan, B_1 and B_2 are background counts, *t* is time for scan in seconds, and the term $(0.02S)^2$ is included to account for errors not due to counting statistics.[9] A total of 2080 reflections were measured. Those with *l* odd were very weak; of the 1038 reflections with *l* even, 1018 were measured greater than background and were used in the final refinement of the structure.

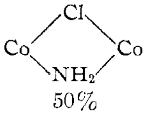
Determination and Refinement of the Structure

The original photographic data were used to prepare a three-dimensional Patterson map, from which the positions of the cobalt atoms were easily found. The extreme weakness of the odd-layer lines about *c* indicated a subunit half as big as the true unit cell. Working in this half-unit cell (ignoring the odd-layer data) and assuming the space group to be P$\bar{1}$ we were able to locate the coordinated ammonia ligands, the chloride ions, and the water molecules by successive structure factor and electron density calculations, adding new atoms as their positions became obvious. The electron density at the positions of the bridging atoms was too great to be explained by OH or NH_2 bridges but too small for chlorine atoms; however, both its size and shape could be explained by a combination of half a nitrogen or oxygen atom and half a chlorine atom, at slightly different positions. The space group P$\bar{1}$ would require the single molecule in the subcell to be centrosymmetric; hence, if the two bridging groups are different, they must be disordered.

It was at this point that we collected the diffractometer data. The new data were comparable with the original photographic data, but the odd-layer reflections about *c* were even weaker (relatively) than they had appeared on the photographs. This was not an artifact of the diffractometer; photographs of the new crystals showed the odd-layer lines were substantially weaker than they were on the earlier photographs. We decided that the varying intensities were caused by varying amounts of disorder in the two bridging groups. If the disorder is confined to the bridging groups, then a completely disordered structure, as



and



would give zero intensity to all the odd-layer lines; that is, the unit cell would be exactly halved along *c*. Such a crystal could form if there were a zero free energy difference between the two orientations of the cation or if the energy difference was small and the crystals were formed rapidly. Slow crystallization will aid in ordering the ions; presumably the crystal used for the origi-

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(4) A. W. Chester, Ph.D. Dissertation, Michigan State University, 1966.

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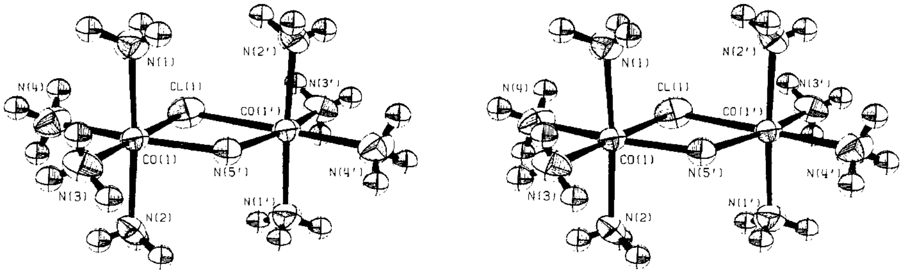

Figure 1.—A stereoscopic drawing of the cation prepared with ORTEP. Thermal ellipsoids are drawn at the 50% probability level; for clarity, all hydrogen atoms were assigned isotropic thermal parameters, B, of 2.0 Å^2.

nal photographs was more completely ordered than the one used to obtain the diffractometer data.

With these considerations in mind, we first assumed a completely disordered structure with one NH_2 bridge and one Cl bridge and, working in the small pseudounit cell, began refinement by least squares. All calculations were done with programs working under the CRYRM crystallographic computing system.[10] Atomic form factors for Co (reduced by 1.74 electrons to correct for the real part of the anomalous dispersion), Cl and Cl^- (increased by 0.36 electron for the same reason), N, and O were taken from ref 11; those for H are from Stewart, Davidson, and Simpson.[12] The quantity minimized in the least-squares calculations was $\Sigma w \cdot (F_o^2 - F_c^2)^2$; all reflections with $F > 0$ were treated as observed. Various weighting functions were used, with the weights during the final cycles being based on the standard deviations of the measured intensities. After the heavy-atom positions and isotropic temperature factors had been refined, the hydrogen atoms were introduced at positions near the ammine nitrogen atoms and the water oxygen atoms on the basis of difference maps; both their coordinates and isotropic temperature factors were refined by least-squares calculations. We chose to refine the positions and temperature factors of the hydrogen atoms, rather than merely including them as constant contributions to the structure factor calculations, because they appeared to be very clearly defined in difference maps and because they cannot be introduced at "calculated" positions; their rotational orientation must first be obtained from a difference map. The heavy atoms (with the exception of the bridging nitrogen atom) were given anisotropic temperature factors because of their appearance in difference maps; the disordered bridging chlorine atom obscures the amide bridge and that nitrogen atom was kept isotropic.

Many cycles of refinement were run using various matrix arrangements in a number of attempts to obtain a satisfactory final structure; the last four cycles of refinement leading to the atomic parameters reported here included in a single matrix a scale factor and all the positional and thermal parameters of all of the atoms—a total of 159 parameters. These cycles used only data with l even and converged with a conventional R index of 0.040; the goodness of fit was 2.92, indicating that perhaps our estimate of the instrumental errors was a bit too small. There is no doubt, however, that our model accounts very satisfactorily for the data with l even.

At this point we were left with the problem of explaining the weak reflections with l odd. A structure factor calculation using all the data and assuming the bridging groups were partially ordered was not helpful; it led to an R index of 0.081, but R for the weak reflections alone was 0.58—essentially random agreement. The chloride ion Cl(2) is very near the bridging atoms and probably has a disorder that is coupled to that of the cation; the major axis of its thermal ellipsoid, for example, is nearly parallel to the Cl(1)–N(5) vector and the value of B along this axis is 9.17 Å^2. Therefore we split this chloride ion into two isotropic chloride ions, each of which was 0.2 Å from the original position of the atom along the axis of principal vibration. A structure factor calculation using this model was in no way better than any previous one. We concluded at this point that the disorder probably involved more than just the bridging groups and one chloride ion—for example, the water molecules must surely change positions if a chloride ion moves—and that our data for the weak reflections were not numerous or accurate enough to define a satisfactory model. [We measured 1042 reflections with l odd, of which 656 (or only 135 more than random) were greater than zero.] Thus we report here a structure based on a cell with c = 10.289 Å only, but because we know that the true length of c is twice that value, the indices and atomic parameters are all given in terms of that larger cell.

The observed structure factors, their standard deviations, and the calculated structure factors for all reflections with l even are listed in Table II. The final atomic parameters are given in Table III. The $\bar{4}11$ reflection had the largest value of F_o of all the reflections with l odd; the value observed for the first crystal (on the same scale as Table II) was 4.7 electrons, and for the second crystal, 3.2 electrons.

Description of the Structure

The cation of this compound is composed of two cobalt octahedra sharing an edge; the octahedra are distorted from regularity principally by the necessarily long Co–Cl distances, 2.316 (4) and 2.334 (4) Å. The cobalt–bridging nitrogen atom distances (1.865 (9) and

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(10) D. J. Duchamp, Paper B-14, American Crystallographic Association Meeting, Bozeman, Mont., 1964.

(11) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202–205.

(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, J. Chem. Phys., **42**, 3175 (1965).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

[illegible]

[a] The columns contain, in order, l, $10F_o$, $10\sigma(F_o)$, and $10F_c$.

TABLE III

FINAL ATOMIC PARAMETERS[a]

Atom	x	y	z	b_{11} or B	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Co(1)	72(.9)	57(1)	3273(.4)	92(2)	210(5)	15(.3)	26(5)	0(.9)	[illegible]
Cl(1)	340(4)	[illegible]	2747(2)	187(6)	212(10)	34(1)	100(11)	5(4)	[illegible]
Cl(2)	6299(2)	3695(3)	2833(.9)	[illegible]	291(5)	40(.6)	-77(7)	-9(2)	[illegible]
Cl(3)	5118(2)	1390(2)	139(.7)	163(3)	412(8)	26(.4)	209(8)	[illegible]	[illegible]
N(1)	2674(6)	871(11)	3300(3)	136(10)	279(19)	20(2)	16(25)	[illegible]	[illegible]
N(2)	-2527(6)	-460(9)	3264(3)	131(10)	309(20)	21(2)	49(21)	[illegible]	[illegible]
N(3)	-177(8)	-2104(9)	3729(4)	140(12)	266(18)	31(2)	[illegible]	55(9)	[illegible]
N(4)	437(8)	2479(8)	-128(3)	162(11)	228(16)	30(2)	94(22)	-6(7)	17(6)
N(5)	280(12)	1638(17)	2636(4)	2.6(2)					
C(1)	7031(8)	3394(10)	4020(5)	302(13)	409(18)	41(2)	314(2[illegible])	102(9)	124(10)
C(2)	6731(7)	3649(9)	1223(5)	171(10)	436(17)	35(2)	61(21)	7(7)	69(8)
H(1)	517(10)	54(11)	376(4)	6.4(18)					
H(2)	512(7)	155(9)	327(3)	2.5(14)					
H(3)	300(9)	-58(11)	310(3)	4.7(16)					
H(4)	-273(6)	-63(7)	358(3)	.6(11)					
H(5)	-304(11)	41(13)	320(4)	7.2(25)					
H(6)	-314(8)	-184(10)	298(3)	4.2(15)					
H(7)	71(10)	-246(10)	377(3)	4.0(16)					
H(8)	[illegible]	-163(9)	403(3)	2.6(16)					
H(9)	-89(10)	-305(13)	346(4)	6.0(18)					
H(10)	124(11)	370(13)	410(4)	6.7(19)					
H(11)	96(11)	236(13)	448(4)	7.6(23)					
H(12)	-50(8)	278(9)	429(3)	3.3(12)					
H(13)	662(12)	466(14)	464(4)	8.3(24)					
H(14)	648(14)	284(17)	476(5)	9.0(30)					
H(15)	636(11)	390(13)	161(5)	7.3(23)					
H(16)	590(11)	305(12)	97(4)	5.9(21)					

[a] The x, y, z, and b_{ij} values of the heavy atoms have been multiplied by 10^4. The x, y, and z values of the hydrogen atoms have been multiplied by 10^3. The anisotropic thermal parameters are of the form $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

1.903 (10) Å) are shorter than the other four Co–N distances, which average 1.952 Å with an rms deviation of 0.006 Å. The overall configuration of the cation is shown in Figure 1. The distances and angles involved in the ammine groups are collected in Table IV. The average N–H distance we found was 0.83 Å, with the esd of this average being 0.09 Å. The distortions of these groups from a tetrahedral geometry are within the standard deviations of our determination.

No hydrogen atoms were positioned near the bridging nitrogen atom. The region in which these hydrogen atoms are expected to lie is obscured by the presence of the disordered bridging chlorine atom, and difference maps gave no clear indication of hydrogen atoms (actually, half-atoms) in this region. This fact is somewhat unsettling for another reason. Although we have been assuming that this compound has chloro and amido bridges, there is a possibility that the amino bridge is actually a hydroxo bridge. Because of the orientational disorder, the total electron density at this point cannot be used to distinguish the two possibilities, and chemical analyses—even if we had been able to obtain them—would probably have been equivocal. Our choice of an amide bridge was made on the basis of chemical reactivities: The amide bridge is a very stable group in dicobalt complexes, surviving even very vigorous attempts to hydrolyze it, whereas the hydroxo

TABLE IV

DISTANCES AND ANGLES[a]

Atoms	Distance, Å	Atoms	Angle, deg
Co(1)–Co(1′)	3.151 (1)	N(2)–Co(1)–N(5′)	89.9 (4)
Co(1)–Cl(1)	2.316 (4)	N(3)–Co(1)–N(4)	93.6 (3)
Co(1)–Cl(1′)	2.334 (4)	N(3)–Co(1)–N(5′)	99.6 (4)
Co(1)–N(1)	1.959 (6)	N(4)–Co(1)–N(5′)	166.7 (4)
Co(1)–N(2)	1.953 (5)	Cl(1′)–Co(1)–N(1)	91.3 (2)
Co(1)–N(3)	1.949 (7)	Cl(1′)–Co(1)–N(2)	90.8 (2)
Co(1)–N(4)	1.949 (6)	Cl(1′)–Co(1)–N(3)	86.2 (2)
Co(1)–N(5)	1.903 (10)	Cl(1′)–Co(1)–N(4)	179.5 (2)
Co(1)–N(5′)	1.865 (9)	Cl(1′)–Co(1)–N(5)	80.0 (3)
N(1)–H(1)	0.92 (8)	Co(1)–N(1)–H(1)	116 (5)
N(1)–H(2)	0.71 (6)	Co(1)–N(1)–H(2)	109 (5)
N(1)–H(3)	0.90 (7)	Co(1)–N(1)–H(3)	114 (5)
N(2)–H(4)	0.67 (5)	H(1)–N(1)–H(2)	112 (7)
N(2)–H(5)	0.83 (9)	H(1)–N(1)–H(3)	93 (7)
N(2)–H(6)	0.94 (7)	H(2)–N(1)–H(3)	112 (7)
N(3)–H(7)	0.79 (8)	Co(1)–N(2)–H(4)	106 (4)
N(3)–H(8)	0.68 (6)	Co(1)–N(2)–H(5)	124 (6)
N(3)–H(9)	0.93 (9)	Co(1)–N(2)–H(6)	110 (4)
N(4)–H(10)	0.89 (9)	H(4)–N(2)–H(5)	104 (7)
N(4)–H(11)	0.86 (9)	H 4)–N(2)–H(6)	107 (6)
N(4)–H(12)	0.86 (7)	H(5)–N(2)–H(6)	106 (6)
O(1)–H(13)	0.92 (10)	Co(1)–N(5)–Co(1′)	113.5 (2)
O(1)–H(14)	0.76 (11)	Co(1)–Cl(1)–Co(1′)	85.3 (2)
O(2)–H(15)	0.84 (9)	Co(1)–N(3)–H(7)	114 (5)
O(2)–H(16)	0.76 (8)	Co(1)–N(3)–H(8)	110 (6)
Atoms	Angle, deg	Co(1)–N(3)–H(9)	113 (5)
Cl(1)–Co(1)–N(1)	92.8 (2)	H(7)–N(3)–H(8)	111 (7)
Cl(1)–Co(1)–N(2)	91.1 (2)	H(7)–N(3)–H(9)	97 (7)
Cl(1)–Co(1)–N(3)	178.9 (2)	H(8)–N(3)–H(9)	112 (7)
Cl(1)–Co(1)–N(4)	85.5 (2)	Co(1)–N(4)–H(10)	111 (5)
Cl(1)–Co(1)–N(5′)	81.2 (4)	Co(1)–N(4)–H(11)	117 (6)
N(1)–Co(1)–N(2)	175.5 (3)	Co(1)–N(4)–H(12)	117 (4)
N(1)–Co(1)–N(3)	87.8 (3)	H(10)–N(4)–H(11)	98 (8)
N(1)–Co(1)–N(4)	88.3 (3)	H(10)–N(4)–H(12)	110 (7)
N(1)–Co(1)–N(5′)	93.0 (4)	H(11)–N(4)–H(12)	102 (7)
N(2)–Co(1)–N(3)	88.3 (3)	H(13)–O(1)–H(14)	104 (10)
N(2)–Co(1)–N(4)	89.7 (3)	H(15)–O(2)–H(16)	106 (9)

[a] The primed atoms have coordinates which are related to those given in Table III by the transformation $\bar{x}$, $\bar{y}$, $\bar{z} + {}^1/_2$.

TABLE V

THE HYDROGEN-BONDING SYSTEM

From	To	At	Distance, Å
N(1)	Cl(2)	x, y, z	3.34
	Cl(2′)	$x + 1, y, z$	3.42
	Cl(3′)	$\bar{x}, \bar{y}, \bar{z} + 1$	3.56
N(2)	Cl(2′)	x, y, z	3.41
	Cl(2)	$x - 1, y, z$	3.43
	Cl(3′)	x, y, z	3.53
N(3)	Cl(3′)	x, y, z	3.32
	O(2′)	$x + 1, y, z$	3.14
	Cl(2)	$x - 1, y, z$	3.36
N(4)	O(1)	$x - 1, y, z$	2.97
	Cl(3′)	$\bar{x}, \bar{y}, \bar{z} + 1$	3.31
	O(2′)	$x + 1, y + 1, z$	3.14
O(1)	Cl(3′)	$\bar{x}, \bar{y}, \bar{z} + 1$	3.38
	Cl(3′)	$x + 1, y + 1, z$	3.38
O(2)	Cl(3)	x, y, z	3.26
	Cl(2)	x, y, z	3.34

bridge is usually a point of easy attack. We must admit, however, that we are not able to present any definitive evidence to support our choice of an NH_2 bridge.

The ions forming this structure are held together by electrostatic forces and by a well-developed system of hydrogen bonds. The hydrogen-bonding scheme is indicated in Table V and is depicted in Figure 2, which is a projection of a portion of the contents of the unit cell perpendicular to the *bc** plane. It is very satisfying to observe in this drawing that the hydrogen atoms are positioned so nearly along the lines joining the heavy atoms which we consider to be hydrogen bonded. The overall packing is represented in Figure 3, which also shows the disorder we found in the crystal.

Thermal Motion.—The atoms of the cation in general exhibit only moderately anisotropic thermal motions (Table VI). The cobalt atoms vibrate the least and

TABLE VI

RMS AMPLITUDES OF VIBRATION ALONG THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS

	Amplitude, Å		
Atom	Axis 1	Axis 2	Axis 3
Co(1)	0.214 (3)	0.180 (3)	0.156 (4)
Cl(1)	0.263 (8)	0.231 (8)	0.198 (9)
Cl(2)	0.323 (5)	0.282 (4)	0.199 (3)
Cl(3)	0.277 (4)	0.217 (4)	0.203 (4)
N(1)	0.26 (2)	0.21 (1)	0.18 (1)
N(2)	0.26 (2)	0.21 (2)	0.16 (1)
N(3)	0.25 (2)	0.21 (1)	0.19 (2)
N(4)	0.26 (2)	0.22 (2)	0.19 (1)
O(1)	0.34 (1)	0.26 (1)	0.24 (1)
O(2)	0.31 (1)	0.25 (1)	0.21 (1)

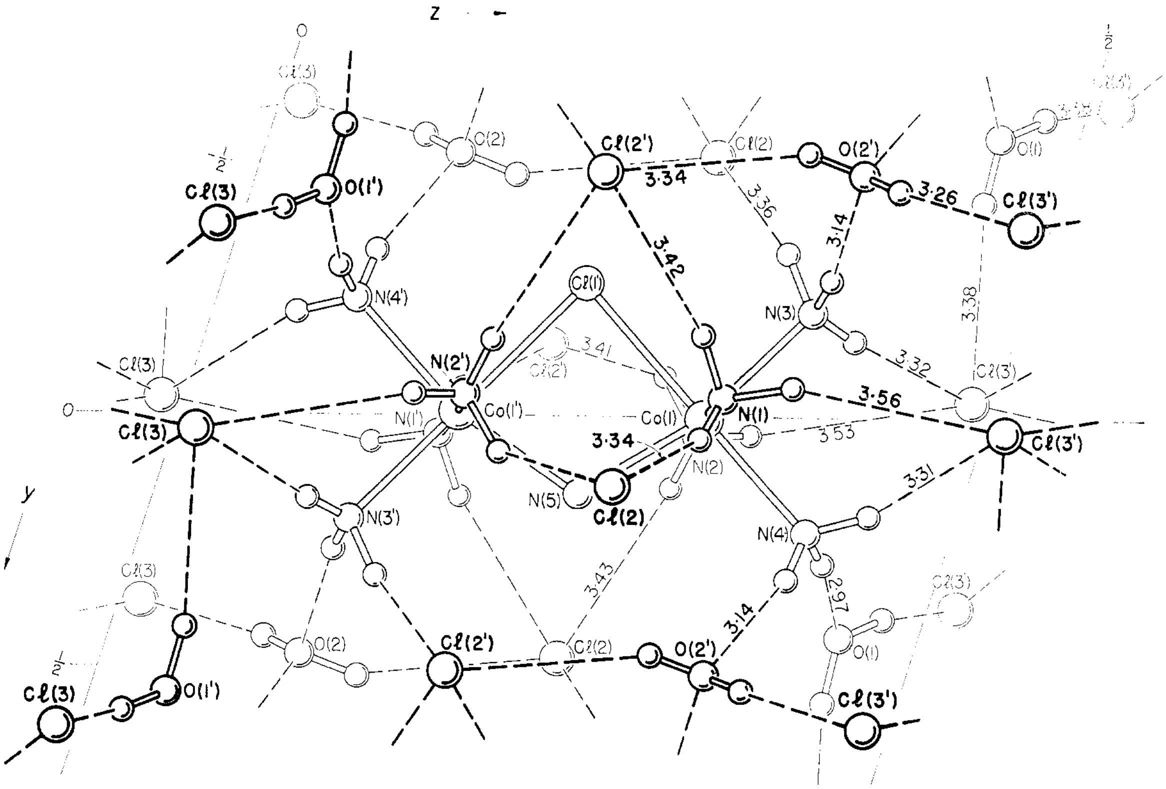

Figure 2.—A projection of a portion of the contents of a unit cell perpendicular to the *bc** plane. Hydrogen bonds are indicated by dashed lines; the distances given are between the heavy atoms involved in the hydrogen bond.

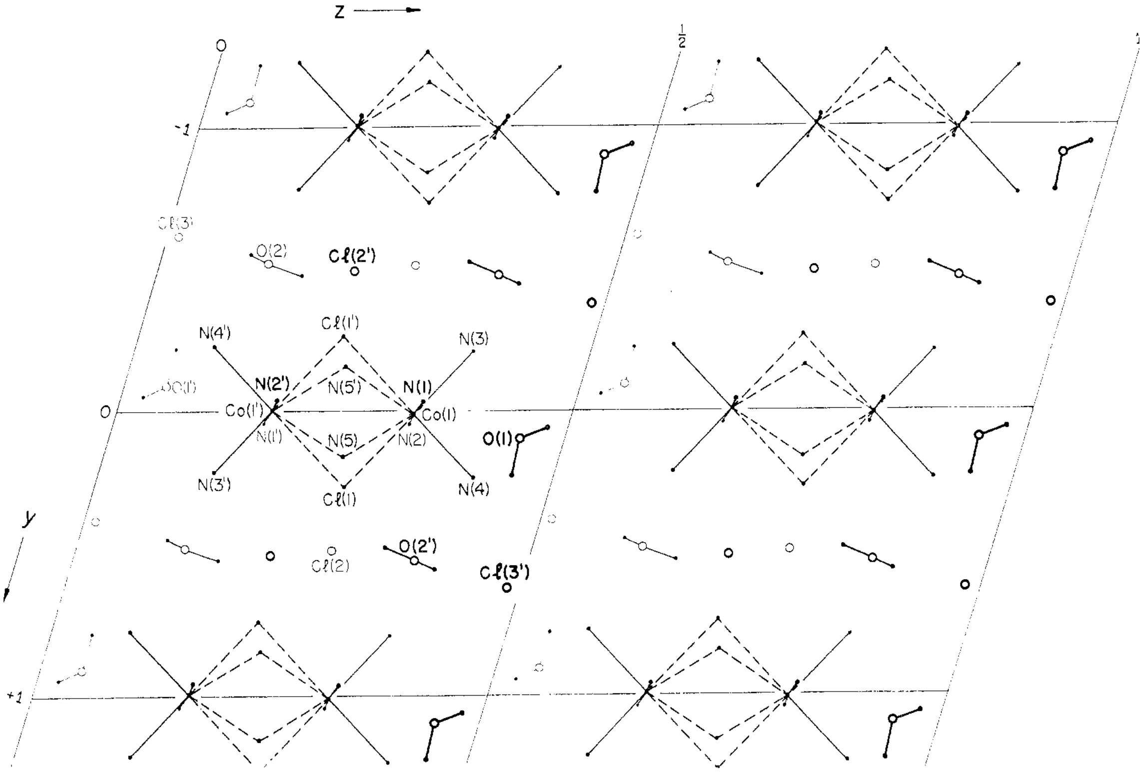

Figure 3.—A projection of the contents of two unit cells perpendicular to the *bc** plane showing the disorder in the cations. The atoms shown do not all have coordinates *x*, *y*, *z* as given in Table III.

the nitrogen ligand atoms only slightly more. The vibrations of these ligand atoms are in directions nearly perpendicular to the Co–N bonds, as can be seen from Figure 1. The bridging chlorine atom has a motion which is less easy to understand, but the derived thermal ellipsoids for this atom and the bridging nitrogen atom probably represent not only thermal vibration but also some positional disorder related to the overall disorder in the structure. The same thing is true of the oxygen atoms of the water molecules. The hydrogen atoms attached to the nitrogen ligands have (except for H(4)) reasonable *B* values, comparable to those of the nitrogen atoms to which they are attached; the same is true of the water hydrogen atoms.

This compound is nearly isostructural with $(NH_3)_4Co(OH)(OH)Co(NH_3)_4Cl_4 \cdot 4H_2O$, the structure of which has been reported by both Vannerberg[13] and Prout.[14] The two cations are of nearly the same size and shape, and therefore the crystal forces must be very similar in the two cases. Evidently, with ions this large, the exact charge distribution in the ion is not as important in determining the structure of the crystal as is the general shape of and overall charge on the ion. The comparison between these two compounds is striking. The two formulas are nearly identical as are the cell dimensions and the overall structure. Table VII lists the cell parameters for the two compounds; the length of our *c* axis has been halved to account for the disorder in our compound, and *a* and *b* of the di-μ-hydroxo compound have been interchanged to afford a direct comparison. The only significant difference between these dimensions is in the length of *c*, which reflects the different Co–Co distances in the two compounds. In the Cl- and NH_2-bridged cation, the Co–Co distance is 3.151 (1) Å, while it is approximately 2.97 (1) Å in the $(OH)_2$-bridged species.

TABLE VII

	μ-Cl-μ-NH_2	Di-μ-OH		μ-Cl-μ-NH_2	Di-μ-OH
a, Å	7.812	7.79	α, deg	107.02	106.5
b, Å	6.666	6.69	β, deg	90.52	92.5
c, Å	10.289	10.05	γ, deg	107.14	106.6

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The Crystal Structure of Tetrafluorocyclobutenebis(dimethylarsine)triiron Decacarbonyl, $(CH_3)_2As\overline{C{=}C(As(CH_3)_2)CF_2C}F_2 \cdot Fe_3(CO)_{10}$

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Tetrafluorocyclobutenebis(dimethylarsine)triiron decacarbonyl, $(CH_3)_2As\overline{C{=}C(As(CH_3)_2)CF_2C}F_2 \cdot Fe_3(CO)_{10}$, crystallizes in the monoclinic space group $P2_1/c$, with $a = 11.60$ (2) Å, $b = 20.04$ (2) Å, $c = 22.11$ (2) Å, $\beta = 93.7$ (2)°, and $Z = 8$ (two molecules per asymmetric unit). The structure was determined with Mo Kα diffractometer data by a combination of direct, Patterson, and electron density methods and was refined by least-squares procedures to a final *R* of 0.09 for 2524 observed (of a total of 3234) reflections. The molecule is best described as a derivative of $Fe_3(CO)_{12}$, in which one terminal carbonyl group on each of the two equivalent iron atoms is replaced by an arsenic atom of the diarsine ligand. The central Fe_3As_2 cluster is significantly folded in one of the molecules of the asymmetric unit but is more nearly planar in the other molecule. The Fe–Fe bond distances in the iron triangle (2.53, 2.65, 2.65 Å) do not different significantly from those in the parent compound.

Complexes of metal carbonyls with ditertiary arsines have been extensively studied.[2,3] The diarsine derivative[4] $LFe_3(CO)_{10}$, $L = (CH_3)_2As\overline{C{=}C(As(CH_3)_2)CF_2C}F_2$, is of particular structural interest both in terms of the manner of attachment of the ligand, L, and of possible distortions of the skeleton of the parent $Fe_3(CO)_{12}$, whose structure is known from X-ray studies on disordered crystals of $Fe_3(CO)_{12}$ itself[5] and on the derivatives $(C_2H_5)_3NH)(HFe_3(CO)_{11}$[6] and $(C_6H_5)_3PFe_3(CO)_{11}$.[7]

The infrared, nmr, and Mössbauer spectra of $LFe_3(CO)_{10}$ suggest a structure in which two terminal carbonyl groups of the two equivalent iron atoms of $Fe_3(CO)_{12}$ are replaced by the arsenic atoms of the diarsine ligand.[4] The presence of only one ^{19}F resonance in the nmr spectrum indicates that all the fluorine atoms are equivalent, so that the diarsine ligand would be expected to be planar, in contrast to the previously determined structure of $LFe_2(CO)_6$, in which the ligand is bent as a result of the formation of a π bond from the cyclobutene system to one of the iron atoms.[8]

An X-ray crystal analysis of $LFe_3(CO)_{10}$ has been

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