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The Crystal and Molecular Structure of Di-μ-oxo-bis(pentaammineruthenium)bis(ethylenediamine)ruthenium Hexachloride. The Ethylenediamine Analog of "Ruthenium Red"

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Di-μ-oxo-bis(pentaammineruthenium)bis(ethylenediamine)ruthenium) hexachloride, $Ru_3O_2(en)_2(NH_3)_{10}Cl_6$, formed by exhaustive reaction of "ruthenium red" with ethylenediamine, crystallizes in the space group $P2_1/c$, C_{2h}^5, of the monoclinic system with unit cell dimensions $a = 8.788$ (1) Å, $b = 11.740$ (1) Å, $c = 14.689$ (1) Å, $\beta = 106.29$ (10)°, and $Z = 2$. The calculated and observed densities are 1.91 and 1.93 (2) g cm^{-3}, respectively. The structure has been determined from 2559 independent reflections (measured by counter methods out to $(\sin\theta)/\lambda = 0.6$) and refined by full-matrix least squares to a conventional R factor of 0.054. The cation is a centrosymmetric linear trimeric ion containing three ruthenium atoms linked by oxygen bridges. Ru–N distances lie between 2.12 and 2.21 Å. The central ruthenium atom is coordinated to two ethylenediamine molecules. The conformation of the ethylenediamine is similar to that in other complexes. The Ru–O bond distances are 1.850 (4) and 1.891 (4) Å to the central and terminal ruthenium atoms, respectively. This difference is statistically significant but is not taken as an indication of localized (III, IV, III) oxidation states for the ruthenium atoms.

Introduction

A well-defined compound "ruthenium red" can be isolated from the intensely colored solutions which result from the reaction of low-valent ruthenium chloro compounds with oxygen in aqueous ammonia. Following an extensive study, Fletcher[1] proposed that the cation of ruthenium red is $(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5^{6+}$. Jørgensen and Orgel[2] devised a molecular orbital scheme which accounts for the stability of this ion in which the average oxidation state of the ruthenium atoms is $^{10}/_3$.

An X-ray structural study on a compound referred to as "ruthenium red" had a discrepancy of 18% and disorder was postulated.[3] Preliminary results of another X-ray study of "ruthenium red" have been reported.[4] The principal support for the trimeric formulation is the observation that oxidation of the red cation to a related brown species requires 0.33 equiv of oxidant per ruthenium atom. Since ruthenium ammines,[5] especially those involving mixed oxidation states,[6] are importantly concerned in areas of current structural[7] and dynamic[8] interest, we have determined the structure of a compound closely related to ruthenium red.

Experimental Section

Preparation.—Ruthenium red chloride (0.3 g), prepared by Fletcher's method,[1] was dissolved in water and the solution was filtered. Fifteen milliliters of 20% aqueous ethylenediamine (hereafter en) was added and the mixture was stirred at room temperature for 1 day. The solution was then heated to 40–45° until no further odor of ammonia gas could be detected (6 hr). Addition of a few drops of concentrated NaCl solution induced the formation of a green precipitate which was collected by filtration and washed with cold dilute NH_4Cl solution. The well-formed crystals are highly reflective and iridescent. Thin crystals were red in transmitted light.

TABLE I

ANALYTICAL DATA FOR $Ru_3O_2(en)_2(NH_3)_{10}Cl_6$

% C[a]		% N[a]		% Cl[a]		% H[a]		% Ru	
Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
5.73	5.86	23.38	23.01	25.37	25.21	5.53	5.62	36.17	34.40
	5.91		22.80		24.93		5.40		33.82

[a] Analyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] Ruthenium analyses performed in this laboratory using the method of J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961).

Analyses are reported in Table I. Ir spectra (KBr pellets) showed no water bands.

An Ru:en:NH_3:Cl ratio of 3:2:10:6 is indicated by the analytical results and suggests a structure containing three or a multiple of three ruthenium atoms per cation.

The crystal used for the preliminary photographic work and data collection was a rhombic prism. It exhibited the forms $\{100\}$, $\{011\}$, and $\{01\bar{1}\}$ and measured 0.12, 0.27, and 0.21 mm in the a, $b + c$, and $b - c$ directions, respectively. Precession photographs showed absences of $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The space group is therefore $P2_1/c$ (C_{2h}^5). Using the approximate unit cell dimensions determined from the photographs and the crystal density measured by flotation in a mixture of tetrabromoethane and dichloroethylene, a value of *ca.* 1730 amu was calculated for the mass in the unit cell. This mass, in conjunction with the analytical data, suggested that there are two trimeric units in the unit cell. Thus the space group required that the center of each presumed trimeric cation lie at a special position with symmetry $\bar{1}$, and therefore a linear structure with three ruthenium atoms in each cation was predicted.

Accurate cell parameters were obtained using a Picker four-circle diffractometer (Mo Kα X radiation, Zr filter, λ 0.7107 Å). The 2θ values for 20 high-angle general reflections were measured and a least-squares refinement using these values gave the cell dimensions reported in Table II, standard deviations being shown parenthetically and referring to the last decimal place.

TABLE II

CRYSTAL DATA

$a = 8.788$ (1) Å $d_m = 1.93$ (2) g/cc
$b = 11.740$ (1) Å $Z = 2$
$c = 14.689$ (1) Å $d_x = 1.91$ g/cc
$\beta = 106.29$ (10)° $\mu = 15.9$ cm^{-1}
$V = 1454.4$ (1) Å^3 $T = 24 \pm 2°$

The crystal was mounted along its a^* reciprocal axis and goniostat coordinates were computed using a program written by J. V. Silverton. A total of 2559 reflections out to $(\sin\theta)/\lambda = 0.595$ were recorded using Mo Kα X radiation (Zr filter). The peak height method was utilized for measuring intensities with an X-ray tube takeoff angle of 6°. The intensities of reflection of

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(1) J. M. Fletcher, B. F. Greenfield, C. J. Hardy, D. Scargill, and J. L. Woodhead, *J. Chem. Soc. A*, 2000 (1960).

(2) C. K. Jørgensen and L. E. Orgel, *Mol. Phys.*, **4**, 215 (1961).

(3) C. Sterling, *Amer. J. Bot.*, **57** (2), 172 (1970).

(4) M. T. Flood, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1969.

(5) F. M. Lever, *Platinum Metals Rev.*, **13** (4), 115 (1969).

(6) (a) C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, **91**, 3988 (1969); (b) C. Creutz, Ph.D. Thesis, Stanford University, Stanford, Calif., 1970.

(7) B. Jezowska-Trzebiatowska and W. Wojciechowski, *Transition Metal Chem.*, **6**, 1 (1970).

(8) D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968); J. L. Woodhead and J. M. Fletcher, *J. Chem. Soc.*, 5039 (1961).

TABLE III

FINAL PARAMETERS FOR NONHYDROGEN ATOMS AS OBTAINED FROM THE LEAST-SQUARES REFINEMENT[a]

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	527 (10)	−2522 (7)	136 (6)	73 (12)	45 (6)	32 (4)	2 (7)	7 (6)	−3 (4)
C(2)	2097 (10)	−2020 (7)	112 (5)	63 (11)	45 (6)	24 (4)	6 (6)	1 (5)	−0 (4)
O(1)	1450 (5)	380 (4)	1138 (3)	43 (7)	35 (3)	14 (2)	0 (4)	0 (3)	2 (2)
N(1)	1790 (7)	−916 (5)	−391 (4)	46 (9)	32 (4)	17 (3)	0 (5)	8 (4)	−5 (3)
N(2)	−344 (7)	−1634 (5)	546 (4)	59 (9)	34 (5)	20 (3)	−7 (5)	9 (4)	6 (3)
N(3)	1501 (8)	267 (6)	3110 (5)	83 (11)	62 (5)	22 (4)	3 (6)	25 (5)	4 (4)
N(4)	4764 (8)	1286 (6)	3546 (5)	74 (10)	49 (5)	22 (4)	−2 (6)	−16 (5)	−7 (3)
N(5)	32 (8)	1353 (5)	1470 (5)	56 (9)	45 (5)	26 (3)	−12 (5)	19 (5)	−4 (3)
N(6)	2066 (7)	2496 (5)	2201 (4)	56 (9)	41 (5)	16 (3)	13 (5)	−4 (4)	0 (3)
N(7)	4096 (8)	−805 (5)	2461 (5)	70 (9)	26 (5)	24 (3)	3 (5)	5 (5)	−3 (3)
Ru(1)	0	0	0	34 (1)	32 (1)	12 (1)	−3 (1)	2 (1)	0 (1)
Ru(2)	2988 (1)	813 (1)	2267 (1)	40 (1)	33 (1)	14 (1)	−1 (1)	0 (1)	3 (1)
Cl^-(1)	1588 (2)	−2797 (2)	2590 (2)	59 (3)	74 (2)	28 (1)	−14 (2)	4 (1)	20 (1)
Cl^-(2)	3130 (3)	3980 (2)	452 (2)	117 (4)	65 (2)	24 (1)	−27 (2)	1 (2)	3 (1)
Cl^-(3)	3940 (2)	3884 (2)	4119 (2)	77 (3)	41 (1)	28 (1)	−4 (2)	22 (1)	−9 (1)

[a] All parameters quoted are multiplied by 10^4 and estimated standard deviations are given parenthetically, referring to the last one or two figures as appropriate. The temperature factor used was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

14 planes at different 2θ angles were measured by both the peak height and θ–2θ scan methods. The ratio between the two measurements (normalized to 1.00 at low 2θ angles) was 1.08 at the limiting angle used. Peak heights and backgrounds on either side of a reflection were measured for 10 sec. The stability of the crystal was monitored periodically by measuring three standard reflections. A variation of less than 3% was observed in the intensities of these standards throughout the data collection.

Correction of the data for Lorentz and polarization factors, the coding of a reflection as observed or unobserved, and the calculation of weighting factors (ω) for the least-squares refinement was carried out using a program primarily designed for absorption corrections, described by Wuensch and Prewitt.[9] This program was modified by P. M. Smith for our data collection methods. No absorption corrections were applied to the data. The ratio of maximum to minimum transmission factors is 1.22 and thus the average error due to absorption should be *ca.* 10% on intensity. This was confirmed empirically by checking the variation in intensity for a reflection at $\chi = 90.0°$ with rotation about ϕ. The variation in intensity was found to be less than 7%. Of the reflections measured, 2311 were observed and 248 were unobserved. The criterion for deciding whether a reflection was observed required that the difference between the peak height and average background be more than twice its standard deviation based on counting statistics.

Structure Determination

The programs used in solving the structure were those of the "X-ray 67" system.[10] All atomic scattering factors were taken from ref 11. Normalized structure factors, E values, were computed by program DATFIX[10] and a sharpened, origin-removed three-dimensional Patterson map was calculated. Since it was assumed that there are two trimeric cations in the unit cell, the centers of these cations should be at centers of symmetry at 0, 0, 0, and 0, $^1/_2$, $^1/_2$. A large peak at 0, $^1/_2$, $^1/_2$ confirmed that there are two ruthenium atoms at these positions. The remaining four ruthenium atoms are in general positions and their coordinates were deduced from the Patterson map. The interatomic distances were consistent with two linear trimers in the unit cell. A structure factor calculation using only the ruthenium atoms with temperature factors as given by DATFIX gave an agreement factor, $R = 0.475$

$$R = \frac{\sum||F_o| - |F_c||}{\sum|F_o|}$$

Two cycles of full-matrix least-squares refinement of the ruthenium atom positions using isotropic temperature factors, scattering factors for ruthenium(0), and a Peterson and Levy[12] weighting scheme reduced R to 0.348. Isotropic temperature factors were in the form $e^{-(\beta \sin^2\theta)/\lambda^2}$ and the function minimized was $\Sigma\omega(\Delta F)^2$. The weighting factor ω for a reflection was given by

$$\omega = \frac{(Lp)^2(4F_o^2)}{I + {}^3/_4(B_1 + B_2) + (0.04I)^2}$$

where L and p are the Lorentz and polarization factors, respectively; F_o is the observed structure factor and is equal to $\sqrt{ILp}$. I is equal to the peak height with the average background subtracted. B_1 and B_2 are the low and high 2θ backgrounds, respectively, measured on either side of the peak. At this stage a three-dimensional difference map clearly showed the positions of the chlorine atoms. A structure factor calculation with these chlorine atoms included gave a residual of 0.262. The rest of the light atoms in the structure were found by calculating three-dimensional difference maps and refining the positions of the atoms as they were found. An agreement factor of 0.056 was obtained using isotropic temperature factors for the carbon, nitrogen, and oxygen atoms and anisotropic temperature factors for the ruthenium and chlorine atoms. On introducing anisotropic temperature factors for the light atoms, a final factor of 0.054 resulted. This reduction is significant according to Hamilton's criterion.[13] A final difference map indicated two peaks with values of *ca.* 0.7 e^- Å^{-3} which could be correlated with hydrogen atoms bonded to the carbons of the ethylenediamine ring. The rest of the map was essentially featureless, containing peaks which were less than 0.4 e^- Å^{-3}. Negative areas associated with the ruthenium atom positions were not greater than 0.3 e^- Å^{-3}. The final structure parameters for the nonhydrogen atoms are listed in Table III. The observed and calculated structure factors (multiplied by 10) are listed on microfilm.[14] The magnitudes of the root-

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(9) B. J. Wuensch and C. T. Prewitt, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **122**, 24 (1965).

(10) J. M. Stewart, *et al.*, "X-ray 67," The University of Maryland Computer Science Center.

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

(12) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957).

(13) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964.

(14) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

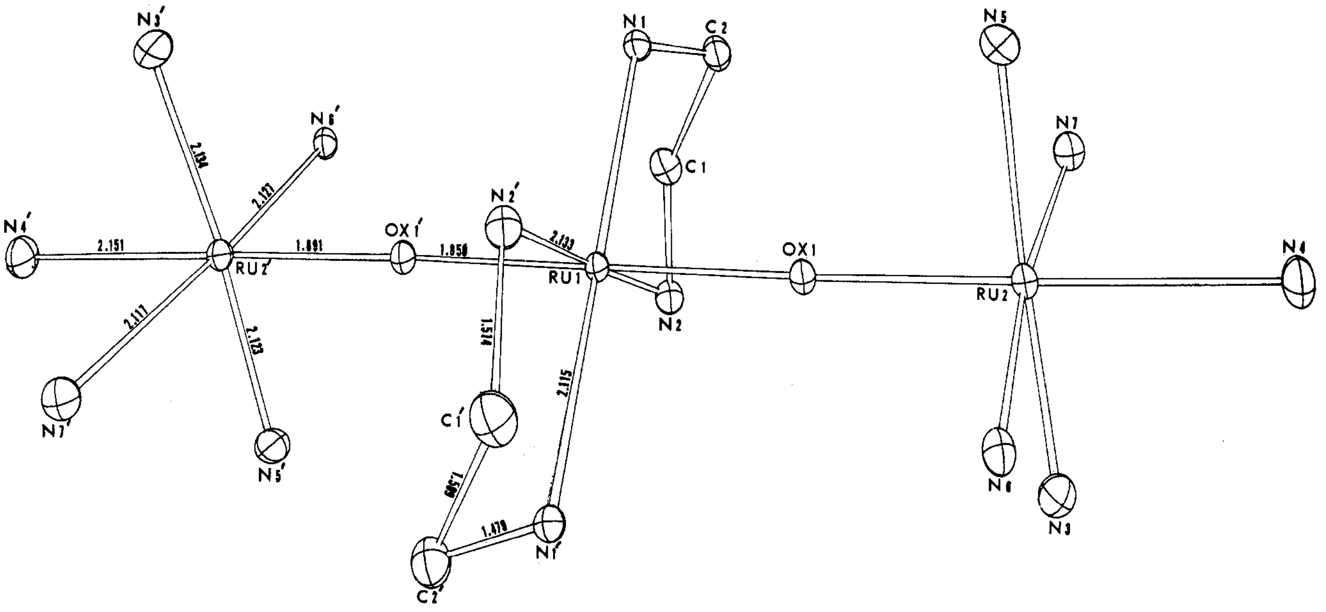

Figure 1.—A view of the $Ru_3O_2(en)_2(NH_3)_{10}{}^{6+}$ cation. The atoms are represented by ellipsoids whose principal axes were derived from the final values of the anisotropic temperature factors. Primed atoms are related to the corresponding atoms in the asymmetric unit by a center of symmetry.

mean-square displacements of all atoms are given in Table IV.

TABLE IV

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å) ALONG THE PRINCIPAL AXES, $R_i{}^n$

Atom	R_1	R_2	R_3
C(1)	0.155	0.177	0.197
C(2)	0.135	0.174	0.181
O(1)	0.107	0.144	0.157
N(1)	0.121	0.139	0.153
N(2)	0.135	0.145	0.168
N(3)	0.147	0.173	0.209
N(4)	0.121	0.184	0.202
N(5)	0.140	0.163	0.180
N(6)	0.113	0.159	0.176
N(7)	0.134	0.143	0.180
Ru(1)	0.099	0.126	0.150
Ru(2)	0.104	0.140	0.153
$Cl^-(1)$	0.138	0.169	0.237
$Cl^-(2)$	0.157	0.169	0.180
$Cl^-(3)$	0.150	0.199	0.235

Description of the Structure

The trimeric cation is shown in Figure 1.[15] The central ruthenium atom (Ru(1)) is linked to the terminal ruthenium atoms (Ru(2)) *via* single oxygen bridges. The ruthenium–oxygen–ruthenium bridges are very nearly linear, the Ru(1)–O–Ru(2) bond angle being 177.2° (estimated standard deviation = 0.4°). The two bridging oxygens are displaced toward the central ruthenium atom. The Ru(1)–O bond distance is 1.850 Å and the terminal ruthenium to oxygen bond distance is 1.891 Å. Since the estimated standard deviations of both bond lengths are 0.004 Å, this shortening is significant.

Scattering factors used for ruthenium atoms were for those of the zerovalent species. In the final difference map the electron density at the ruthenium atomic positions was negative and it is possible that scattering factors for ionized ruthenium atoms might have been more appropriate although other factors such as extinction may account for the negative areas. The numerical values of the difference density at the central and terminal ruthenium atom positions were essentially the same to within the estimated accuracy of the map.

The coordination geometry about each ruthenium atom is octahedral. The angle of twist between the central and terminal octahedra is about 44°. The terminal ruthenium atoms are coordinated to five ammonia molecules and one oxygen atom. These ruthenium–nitrogen bond distances all lie within the range of 2.21–2.15 Å. The longest ruthenium–nitrogen bond is to N(4) which indicates that the oxygen may be exerting a small trans effect. Both the terminal and central ruthenium–oxygen bonds are much shorter than those found in ruthenium dioxide[16] where the Ru–O bond lengths vary from 1.94 to 1.98 Å. Principal intramolecular bond distances and angles are given in Table V.

The central ruthenium atom (Ru(1)) is bonded to two ethylenediamine molecules and two oxygen atoms. The carbon atoms of each ethylenediamine ring are in the gauche conformation as is the case for all other structures reported involving ethylenediamine as a ligand. C(1) is 0.35 Å from the plane passing through Ru(1), N(1), and N(2) while C(2) is on the other side and 0.34 Å from the plane. The average ruthenium–nitrogen bond distances are 2.115 and 2.113 Å to Ru(1) and Ru(2), respectively. The C(1)–C(2) bond length is 1.509 Å and the carbon–nitrogen bond lengths C(1)–N(2) and C(2)–N(1) are 1.479 and 1.514 Å, respectively. The nitrogen–nitrogen bite distance for the chelating ligand is 2.752 Å. These latter lengths all lie within the range of distance previously found for the ethylenediamine ligands in other compounds.[17]

The arrangement in which the polynuclear ions and the chloride ions pack together in the structure is shown for a perspective projection down the *b* axis in Figure 2.

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[15] C. K. Johnson ORTEP, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965, graphical illustrations.

[16] C. Boman, *Acta Chem. Scand.*, **24** (1), 116 (1970).

[17] J. R. Wiesner and E. C. Lingafelter, *Inorg. Chem.*, **5**, 1770 (1966).

TABLE V

INTERATOMIC DISTANCES AND ANGLES WITHIN THE $Ru_3O_2(en)_2(NH_3)_{10}^{6+}$ ION

Distances, Å		Angles, deg			
Ru(1)-O(1)	1.850 (4)	O(1)-Ru(1)-N(1)	90.5 (2)	N(7)-Ru(2)-O(1)	93.8 (2)
Ru(1)-N(1)	2.115 (7)	O(1)-Ru(1)-N(2)	90.7 (2)	N(4)-Ru(2)-N(3)	89.0 (3)
Ru(1)-N(2)	2.133 (6)	N(2)-Ru(1)-N(1)	99.2 (3)	N(5)-Ru(2)-N(3)	178.1 (3)
C(1)-N(2)	1.514 (11)	Ru(2)-O(1)-Ru(1)	177.2 (4)	N(6)-Ru(2)-N(3)	90.6 (4)
C(2)-N(1)	1.479 (10)	N(2)-C(1)-C(2)	107.9 (6)	N(7)-Ru(2)-N(3)	89.2 (3)
C(1)-C(2)	1.509 (12)	N(1)-C(2)-C(1)	108.7 (9)	N(5)-Ru(2)-N(4)	89.2 (3)
Ru(2)-O(1)	1.891 (4)	Ru(1)-N(1)-C(2)	110.8 (8)	N(6)-Ru(2)-N(4)	88.5 (2)
Ru(2)-N(3)	2.134 (8)	Ru(1)-N(2)-C(1)	109.2 (7)	N(7)-Ru(2)-N(4)	85.4 (2)
Ru(2)-N(4)	2.151 (6)	N(3)-Ru(2)-O(1)	91.5 (2)	N(6)-Ru(2)-N(5)	89.7 (4)
Ru(2)-N(5)	2.123 (7)	N(4)-Ru(2)-O(1)	179.1 (9)	N(7)-Ru(2)-N(5)	90.2 (4)
Ru(2)-N(6)	2.127 (6)	N(5)-Ru(2)-O(1)	90.4 (2)	N(7)-Ru(2)-N(6)	173.9 (2)
Ru(2)-N(7)	2.117 (6)	N(6)-Ru(2)-O(1)	92.3 (2)		

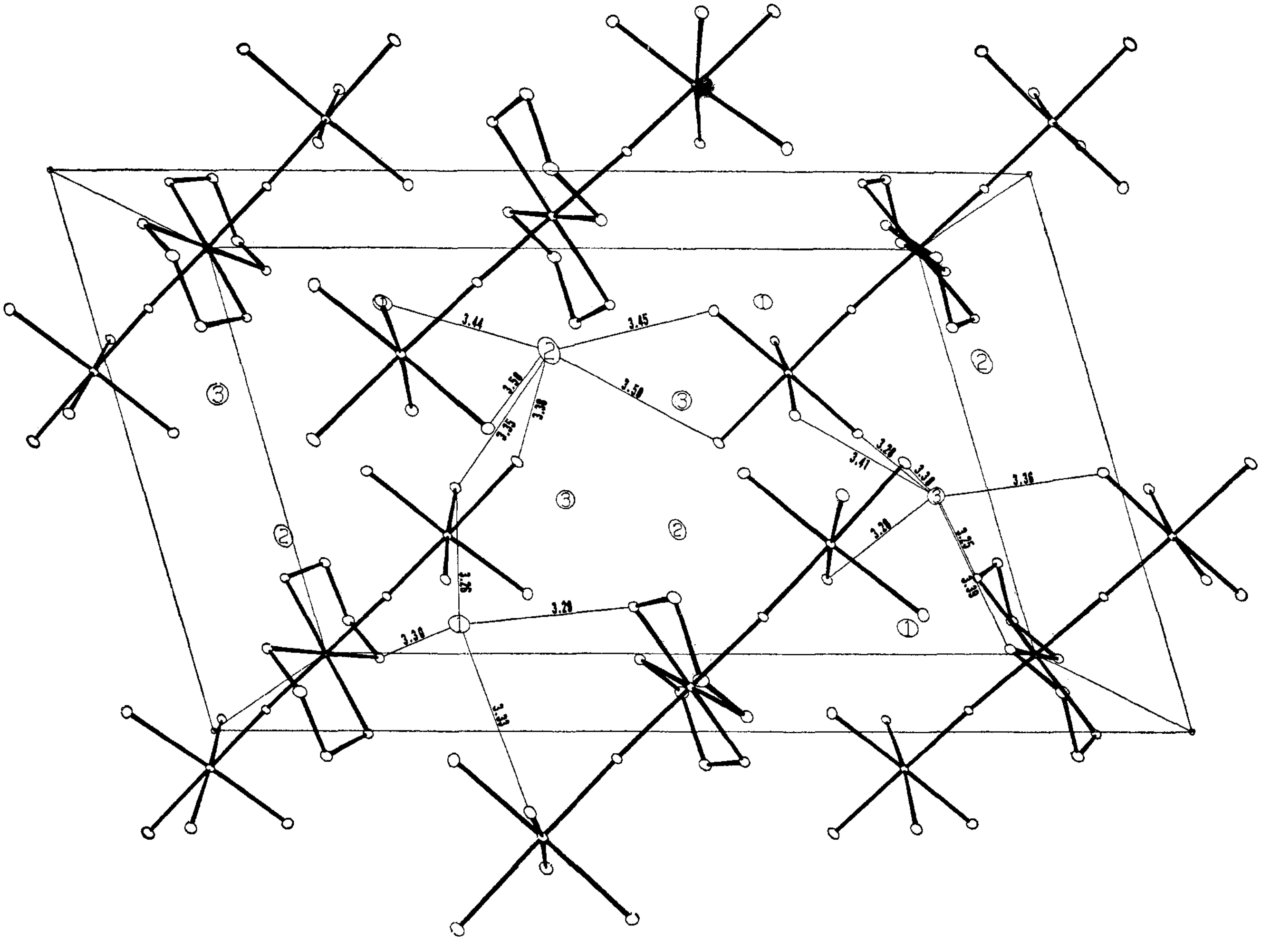

Figure 2.—Packing diagram. Perspective projection down the *b* axis of the unit cell. The labeled positions 1, 2, and 3 represent the chloride anions.

The cations are held together by chloride ions Cl(1)–Cl(3). Some interesting Cl–N contact distances are also shown in Figure 2. Cl(1) and Cl(2) appear to link the cations related by the screw axis while Cl(2), in addition, joins cations related by the diagonal translation vector $\vec{c}-\vec{a}$. Similarly Cl(3) holds together units repeated by the twofold screw axis and units repeated by the lattice translation along the *a* axis. The closest cation–anion approach distances are those between the chloride ions and the ammine nitrogens. A number of Cl–N contact distances are below 3.30 Å indicating that there is a possibility of hydrogen bonding of the form Cl· · ·H–N as found for $[Pt(en)_2Cl_2]Cl_2$.[18]

Discussion

The linear structure suggested by Fletcher[1] for ruthenium red is confirmed for the ethylenediamine analog.

Recent Mössbauer results[19] have been interpreted as implying localized valences (III, IV, III) in ruthenium red. The small but significant displacement of the oxygens toward the central ruthenium atom might seem to confirm this assignment. On this basis, the preferential substitution of en for NH_3 on the central metal atom might be taken to be a consequence of greater lability of the central Ru(IV) as compared with the terminal Ru(III) atoms.

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[18] C. F. Liu and J. A. Ibers, *Inorg. Chem.*, **9**, 773 (1970).

[19] C. A. Clausen, R. A. Prados, and M. L. Good, *Inorg. Nucl. Chem. Lett.*, **7**, 485 (1971); private communication.

On the other hand, the shortening of both Ru–O bond distances relative to those in RuO_2 and the diamagnetism of ruthenium red clearly indicate metal–metal interaction requiring either a molecular orbital or a superexchange interpretation.

Optical spectra of solutions of the ethylenediamine compound of interest here closely resemble corresponding spectra of solutions of ruthenium red and can be interpreted on the basis of a molecular orbital scheme.[20] Fully occupied bonding molecular orbitals involve d_{xz}, d_{yz} orbitals of the terminal ruthenium atoms and p_x, p_y orbitals of the bridging oxygens. Antibonding orbitals principally composed of d_{xz}, d_{yz} orbitals of Ru(1) remain unoccupied.

Shielding of s electrons by different configurations of d electrons largely accounts for isomer shifts observed in Mössbauer spectroscopy of ruthenium compounds.[21] The molecular orbital scheme corresponds to a lower d-electron density on the central ruthenium atom than on the terminal ones and is consistent with the Mössbauer spectrum of ruthenium red.[19] This molecular orbital model is consistent with the low magnetic moment of ruthenium red and the observed 45° angle of twist between central and terminal ruthenium atoms: it is more difficult to accommodate this angle in a model in which low magnetic moment results from superexchange between metal atoms in localized (III, IV, III) oxidation states.

To translate the molecular orbital model to the vocabulary of localized oxidation states, the assignment (II, VI, II) should be considered. In view of the sensitivity of isomer shifts to covalency variations, this seems to be a possible assignment and it is one which more easily accommodates the 45° angle of twist reported here.

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(21) G. Kaindl, W. Potzel, F. Wagner, U. Zahn, and R. L. Mossbauer, *Z. Phys.*, **226**, 103 (1969).

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A Novel Iron Carbonyl Complex Containing Arsenic.

The Crystal Structure of $(As(CH_3)_2)C{=}CCF_2CF_2\{(As(CH_3)_2)Fe_3(CO)_9\}$

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The crystal structure of $ffarsFe_3(CO)_9$ where the ligand ffars is $(As(CH_3)_2)C{=}C(As(CH_3)_2)CF_2CF_2$ has been determined from three-dimensional X-ray data collected by scintillation counter methods. The structure has been refined by full-matrix least-squares techniques (iron and arsenic atoms with anisotropic thermal parameters) to a conventional R factor of 5.9% for the 1364 observed reflections. The compound crystallizes in the monoclinic space group $P2_1/n$ with four formula units in a cell of dimensions $a = 13.803$ (3), $b = 19.001$ (4), $c = 9.482$ (2) Å, and $\beta = 82.77$ (2)°. The compound may be viewed as formed by skeletal rearrangement of an $Fe_3(CO)_{12}$ molecule and coordination of an ffars ligand which has undergone cleavage of an $As(CH_3)_2$ group. The resulting structure may be described in terms of three $Fe(CO)_3$ groups and an $As(CH_3)_2$ group being linked together at the corners of a tetrahedrally distorted square-planar arrangement. The rearranged ligand, $(As(CH_3)_2)C{=}CCF_2CF_2$, is bonded to the first iron atom by an arsenic linkage, to the second iron atom by a π bond from the cyclobutene ring, and to the third iron atom by a σ bond from the cyclobutene ring. The long iron–iron bond of 2.917 (5) Å involves the iron atom bonded to the two arsenic atoms while the shorter contact 2.667 (5) Å involves one Fe–As bond.

Substitution reactions of polynuclear iron carbonyl complexes with phosphine derivatives which result in displacement of terminal carbonyl groups are relatively common. For example, the crystal structure determination of the compound $(P(C_6H_5)_3)Fe_3(CO)_{11}$[1] has revealed two different molecules in the asymmetric unit. In one molecule, the $P(C_6H_5)_3$ group has replaced a terminal carbonyl group from the unique iron atom of the parent compound $Fe_3(CO)_{12}$,[2] and, in the other, a terminal carbonyl group from one of the two equivalent iron atoms has been replaced. The compounds $Fe_3(CO)_{11}P(OCH_3)_3$, $Fe_3(CO)_{10}\{P(OCH_3)_3\}_2$, and $Fe_3(CO)_9\{P(OCH_3)_3\}_3$[3] have been reported to retain the iron triangle and bridging carbonyl groups of $Fe_3(CO)_{12}$. An X-ray crystal structure study of $\{(\pi\text{-}C_5H_5)_2Fe_2(CO)_3\}_2$DPPA[4,5] [DPPA = bis(diphenylphosphino)acetylene] showed that DPPA reacted with the parent compound $\{(\pi\text{-}C_5H_5)Fe(CO)_2\}_2$ by substitution of a terminal carbonyl group, leaving the bridging-carbonyl groups intact.

Replacement of both terminal and bridging car-

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