and activation energies (0.03 eV), although the interplanar spacing for the Ge material is ~0.3 Å shorter than that of the Ga analogue.

Acknowledgment. The author wrote this paper while a Visiting Scholar in the Department of Chemical Engineering, Stanford University, and a Visiting Scientist at the IBM Research Laboratory, San Jose, CA, and gratefully acknowledges the generous hospitality provided. The author thanks M. Kenney of Case Western Reserve University, J. M. Troup and M. W. Extine of Molecular Structure Corp., and D. Weber of the Naval Research Laboratory for stimulating discussions, R. Nohr for the preparation of samples of $[Ga(Pc)F]_n$ and $[Al(Pc)]_2O$, and the Office of Naval Research for financial support.

Registry No. $[Ga(Pc)F]_n$, 74018-73-8; $[Al(Pc)]_2O$, 12369-63-0.

Supplementary Material Available: Stereoscopic views of the $[Ga(Pc)F]_n$ and $[Al(Pc)]_2O$ unit cells (Figures 1-S and 2-S, respectively) and positional and thermal parameters and esd's (Tables I-S (Ga) and IX-S (Al)), general temperature factor expressions (Tables II-S and III-S (Ga) and X-S (Al)), bond distances and angles (Tables IV-S and V-S (Ga) and XI-S and XII-S (Al)), least-squares planes (Tables VI-S (Ga) and XIII-S (Al)), intermolecular contacts (Tables VII-S (Ga) and XIV-S (Al)), and observed and calculated structure factor amplitudes (Tables VIII-S (Ga) and XV-S (Al)) (55 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Inorganic and Analytical Chemistry,
The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Role of the H_3O_2 Bridging Ligand in Coordination Chemistry. 1. Structure of Hydroxoaquametal Ions

MICHAEL ARDON* and AVI BINO*

Received June 18, 1984

The structures of two classical, so-called hydroxo aqua complex ions of chromium(III) and cobalt(III) were investigated by single-crystal X-ray diffraction. These structures were shown not to be mononuclear hydroxo aqua ions, with distinct OH and H_2O ligands, but binuclear or polynuclear ions with symmetrical hydrogen oxide bridges (H_3O_2) between the metal atoms. Compound **1**, *cis*-$[Cr(bpy)_2(H_3O_2)]_2I_4 \cdot 2H_2O$, forms orthorhombic crystals, space group *Pbcn*, with $a = 15.511$ (2) Å, $b = 15.115$ (2) Å, $c = 20.955$ (3) Å, $V = 4913$ (1) Å^3, and $Z = 4$. Compound **2**, *trans*-$[Co(en)_2(H_3O_2)](ClO_4)_2$, forms monoclinic crystals, space group $P2_1/c$, with $a = 5.724$ (1) Å, $b = 8.146$ (1) Å, $c = 14.923$ (2) Å, $\beta = 99.17$ (2)°, $V = 687$ (1) Å^3, and $Z = 2$. The two structures were refined by full-matrix least-squares methods to residuals of $R = 0.037$, $R_w = 0.042$ and $R = 0.026$, $R_w = 0.039$, respectively. In structure **1** there are two H_3O_2 units that are symmetry related with an O···O distance of 2.446 (5) Å. In structure **2** the cobalt atom and the central hydrogen atom of the H_3O_2 group reside on crystallographic inversion centers, thus forming infinite chains of ···Co–H_3O_2–Co··· with an O···O distance of 2.441 (2) Å. It is concluded that hydroxo aqua ions do not exist in the crystalline state as such: the so-called cis hydroxo aqua ions are dimers bridged by two H_3O_2 bridges and the so-called trans hydroxo aqua ions are polynuclear chains of metal atoms bridged by single H_3O_2 ligands. The mechanism of olation reactions, in the solid state and in aqueous solutions, is formulated as an elimination of water molecules from H_3O_2 bridges, accompanied by formation of OH bridges between the metal ions.

Introduction

Coordinated hydrogen oxide, $H_3O_2^-$, was first reported and characterized as a bridging ligand between trinuclear, triangular cluster ions of molybdenum and tungsten.[1] In these clusters, generally formulated as $[M_3O_2(O_2CR)_6(H_2O)_3]^{2+}$, each metal atom is coordinated to one water ligand that may hydrolyze to a hydroxo ligand to give $[M_3O_2(O_2CR)_6(H_2O)_2(OH)]^+$. The H_3O_2 ligand is formed by means of a short and symmetrical hydrogen bond between a water ligand of one metal atom and a hydroxo ligand of another metal atom. The distance between the two oxygen atoms in the H_3O_2 unit varies between 2.44 and 2.52 Å in the six structures of cluster salts determined by X-ray crystallography.[1] Two classes of H_3O_2-bridged clusters were discovered: (a) "diclusters" in which two clusters are bridged by a single hydrogen oxide bridge, as in $\{[W_3O_2(O_2CC_2H_5)_6(H_2O)_2]_2(H_3O_2)\}(NCS)_3 \cdot H_2O$; (b) "polyclusters" in which two of the three metal atoms are linked with the atoms of neighboring clusters by hydrogen oxide bridges, thus forming an infinite cluster chain as in $[W_3O_2(O_2CC_2H_5)_6(H_2O)(H_3O_2)]_n(NCS)_n$. The dicluster and polycluster salts are crystallized by varying the pH of the mother liquor. Formation of the dicluster is favored at a 1:1 ratio of the triaqua cluster and the hydroxo–diaqua cluster, i.e. at pH = pK_1. The polycluster is precipitated at a higher pH in which the hydroxo–diaqua cluster is the predominant monocluster species.[1c]

The starting point of the present investigation was the realization that metal atoms in trinuclear clusters do not have any unique property that makes them more susceptible to hydrogen oxide bridging than ordinary, mononuclear metal ions. This conclusion led to a working hypothesis that hydrogen oxide bridging may be a fundamental, hitherto unrecognized, property of many, if not all, metal ions having H_2O and OH^- ligands.

The strategy employed in the search of evidence for this hypothesis was to grow single crystals of classical hydroxo aqua complexes of chromium(III) and cobalt(III) and to determine their structure by X-ray crystallography. The reason for the choice of Cr(III) and Co(III) was the following. Formation of hydrogen oxide bridged species (reaction 1) was expected to be intimately linked with the "olation" reaction (2) in which more stable

$$[L_5M(OH)]^{(n-1)+} + [(H_2O)ML_5]^{n+} \rightleftarrows [L_5M(H_3O_2)ML_5]^{(2n-1)+} \tag{1}$$

$$[L_5M(H_3O_2)ML_5]^{(2n-1)+} \rightarrow [L_5M(OH)ML_5]^{(2n-1)+} + H_2O \tag{2}$$

μ-hydroxo-bridged species were formed. The hydrogen oxide bridged product of reaction 1 was expected to have a transient existence and only a very low equilibrium concentration, *unless* reaction 2 was very slow. Reaction 1, the hydrogen bond formation, is very fast, probably diffusion controlled. Reaction 2, which involves the breaking of a metal-to-oxygen bond, is slow in trinuclear clusters and any other *inert* complexes. Therefore, the most abundant and common inert complexes, namely those of chromium(III) and low-spin cobalt(III), were investigated first.

---

[1] (a) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1981**, *103*, 6741–6742. (b) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1982**, *104*, 4383–4388. (c) Bino, A.; Gibson, D. *Inorg. Chem.* **1984**, *23*, 109–115.

Table I. Crystallographic Data

	1	2
formula	$C_{40}Cr_2H_{42}I_4N_8O_6$	$C_4Cl_2CoH_{19}N_4O_{10}$
fw	1342.43	413.05
space group	*Pbcn*	$P2_1/c$
a, Å	15.511 (2)	5.724 (1)
b, Å	15.115 (2)	8.146 (1)
c, Å	20.955 (3)	14.923 (2)
β, deg		99.17 (2)
V, $Å^3$	4913 (1)	687 (1)
Z	4	2
d(calcd), g cm^{-3}	1.815	1.997
d(exptl), g cm^{-3} [a]	1.81 ± 0.01	2.00 ± 0.01
μ, cm^{-1}	28.07	15.97
cryst color and habit	red prisms	red rectangular parallelepipeds
crystal size, mm	0.22 × 0.37 × 0.44	0.26 × 0.44 × 0.48
transmission factors	0.408-0.638	0.569-0.738
range of 2θ, deg	3-55	3-50
obsrvns	*hkl*	±*h*,*k*,*l*
systematic reflcn absences	$0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h + k = 2n + 1$	$h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$
check reflcns	10,2,4; 093; 408	$\bar{3}42$; $\bar{2}53$; $\bar{1}19$
no of unique data	5478	1202
no. of data with $F_o^2 > 3\sigma(F_o^2)$	3122	1079
R	0.037	0.026
R_w	0.042	0.039

[a] Measured by flotation in $CCl_4/CHBr_3$.

The structures of two complexes, representing two different modes of H_3O_2 bridging, were determined: *cis*-$[Cr(bpy)_2(H_3O_2)]_2I_4{\cdot}2H_2O$ (**1**);[2] *trans*-$[Co(en)_2(H_3O_2)](ClO_4)_2$ (**2**). Three additional structures with bridging H_3O_2 ligands have been determined and will be published separately. A preliminary report on the structure of compound **1** was published earlier.[2]

Experimental Section

Preparations. ***cis*-$[Cr(bpy)_2(H_3O_2)]_2I_4{\cdot}2H_2O$ (1).** *cis*-$[Cr(bpy)_2(H_2O)_2](NO_3)_3{\cdot}{}^1/_2H_2O$[4] (1 g) was dissolved in 10 mL of H_2O and titrated with 1 M NaOH to pH 5. KI (0.5 g) was added, and the solution was placed in an open beaker at room temperature. Red crystals were obtained within a few days.

***trans*-$[Co(en)_2(H_3O_2)](ClO_4)_2$ (2).** *cis*-$[Co(en)_2CO_3]ClO_4$ (2.67 g) was dissolved in 5 mL of H_2O and 2 mL of 70.7% $HClO_4$. The solution was heated on a steam bath, and 31.6 mL of 0.5 M NaOH was added. A heavy precipitate of red polycrystalline product was obtained. Single crystals suitable for X-ray analysis were grown from the filtrate of the product by adding $NaClO_4$ (0.5 g) and placing the solution in an open beaker for a few days.

X-ray Crystallography

Data were collected on a PW1100 Philips four-circle computer-controlled diffractometer. Mo Kα (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 25 reflections in the range 12° < θ < 16°. Data were measured by using an ω-2θ motion. The scan width, Δω, for each reflection was 1° with a scan time of 20 s. Background measurements were made for 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found. Crystallographic data and other pertinent information are given in Table I. For each crystal, Lorentz and polarization corrections were applied. Intensity data for **1** were corrected for absorption by the empirical ψ-scan method. For **2**, ψ scans of several reflections indicated no absorption correction was necessary. The heavy-atom positions in **1** were obtained by using the results of MULTAN direct-method analysis and in **2** from a three-dimensional Patterson function.[5a] Values of the atomic scattering factors and the anomalous terms were taken from the conventional sources.[5b,c]

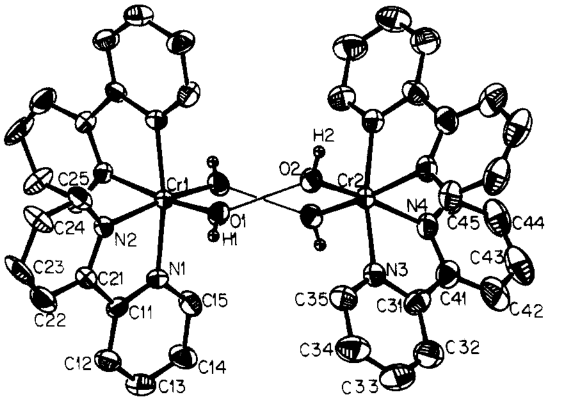


Figure 1. Structure of *cis*-$[(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2]^{4+}$ as found in **1**. The O···H···O bonds in the H_3O_2 units are represented by the dashed lines. The thermal ellipsoids are of 50% probability. The hydrogen atoms were given an arbitrary thermal parameter.

In **1**, anisotropic thermal parameters were used for all non-hydrogen atoms. The hydrogen atoms of the bipyridyl, the water molecule, and the H_3O_2 group were located from the difference Fourier map. The bipyridyl hydrogens were introduced as fixed contributions to *F*. The thermal parameters of the water and hydrogen oxide hydrogens were included in the least-squares refinement. The isotropic thermal vibration parameters (*U*) of the latter, H(1) and H(2), were refined to the reasonable values of 0.02 (2) and 0.03 (2) $Å^2$, respectively. Some electron density was located between O(1) and O(2), the H_3O_2 oxygen atoms. Introduction of a hydrogen atom at this location and refinement of its thermal parameter indicated a very low value of electron density. Therefore, this hydrogen atom was not included in the final refinement.

In **2**, anisotropic thermal parameters were used for all non-hydrogen atoms and isotropic ones for all hydrogen atoms. All hydrogen atoms were located from the difference Fourier map, and their positional and thermal parameters were included in the least-squares refinement [except the positional parameters of H(9), the terminal hydrogen in the H_3O_2 unit].

The discrepancy indices $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2|F|$) are listed in Table I.

Results

Compound 1, *cis*-$[Cr(bpy)_2(H_3O_2)]_2I_4{\cdot}2H_2O$. The atomic positional parameters are listed in Table II while Table III gives the important bond lengths and angles. Figure 1 shows the numbering scheme in **1**. With *Z* = 4 in space group *Pbcn* there is only half a $[Cr(bpy)_2(H_3O_2)]_2{}^{4+}$ ion in the asymmetric unit with the other half related to it by a crystallographic 2-fold axis [Cr(1) and Cr(2) reside on this axis].

Each of the four dimers in the cell consists of two *cis*-$[Cr(bpy)_2(H_3O_2)]$ units having the same chirality (Δ, Δ or Λ, Λ). The two hydrogen oxide ligands in the dimer relate to each othei by the 2-fold axis. The O···O separation in the H_3O_2 unit, the $Cr-O(H_3O_2)$ distance, and the M-O···O-M torsional angle are given in Table VI along with the corresponding dimensions in **2** and other structures containing $H_3O_2^-$ bridges. The 4+ charge of the dimeric unit $[Cr(bpy)_2(H_3O_2)]_2{}^{4+}$ is balanced by four iodide anions in the crystal. Each iodide is hydrogen bonded to the water molecule OL with I(1)-OL and I(2)-OL distances of 3.65 and 3.58 Å, respectively, and to one of the oxygen atoms of the H_3O_2 unit. The distances I(1)-O(1) and I(2)-O(2) are 3.49 and 3.44 Å, respectively, and the angles I(1)-H(1)-O(1) and I(2)-H(2)-O(2) are 177°.

Compound 2, *trans*-$[Co(en)_2(H_3O_2)](ClO_4)_2$. The atomic positional parameters are listed in Table IV. Table V presents the bond distances and angles, and Figure 2 shows the numbering scheme of **2**. The structure consists of infinite chains of *trans*-$Co(en)_2{}^{3+}$ units linked by $H_3O_2^-$ bridges. Both the cobalt and the central hydrogen atom of the H_3O_2 unit reside on crystallographic inversion centers at $^1/_2$, 0, 0 and 0, 0, 0, respectively. (However the possibility that the H atom is disordered across the inversion center rather than residing on it is not excluded.) The unit cell contains two $[Co(en)_2(H_3O_2)_{2/2}]^{2+}$ units, where $(H_3O_2)_{2/2}$

---

(2) Ardon, M.; Bino, A. *J. Am. Chem. Soc.* **1983**, *105*, 7748-7750.

(3) Inskeep, R. G.; Benson, M. *J. Inorg. Nucl. Chem.* **1961**, *20*, 290-291.

(4) Inskeep, R. G.; Bjerrum, J. *Acta Chem. Scand.* **1961**, *15*, 62-68.

(5) (a) All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem with the SHELX 1977 structure determination package. (b) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. (c) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175-3187.

Table II. Positional Parameters and Estimated Standard Deviations for **1**[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
I(1)	−0.19415 (4)	0.73791 (4)	0.08295 (3)	C(24)	−0.1872 (4)	1.0004 (4)	0.2078 (3)
I(2)	−0.21879 (3)	0.50138 (3)	0.38943 (2)	C(25)	−0.1439 (4)	0.9313 (4)	0.2367 (3)
Cr(1)	0.00000 (0)	0.79297 (8)	0.25000 (0)	C(31)	0.0099 (4)	0.3767 (4)	0.1257 (3)
Cr(2)	0.00000 (0)	0.46033 (8)	0.25000 (0)	C(32)	−0.0076 (5)	0.3587 (5)	0.0613 (3)
O(1)	−0.0803 (3)	0.7027 (2)	0.2242 (2)	C(33)	−0.0642 (5)	0.4110 (6)	0.0282 (4)
O(2)	−0.0868 (3)	0.5500 (2)	0.2624 (2)	C(34)	−0.1028 (5)	0.4829 (5)	0.0583 (3)
N(1)	0.0542 (3)	0.8046 (3)	0.1607 (2)	C(35)	−0.0812 (4)	0.4981 (5)	0.1216 (3)
N(2)	−0.0748 (3)	0.8925 (3)	0.2100 (2)	C(41)	0.0699 (4)	0.3263 (4)	0.1651 (3)
N(3)	−0.0279 (3)	0.4472 (3)	0.1553 (2)	C(42)	0.1107 (5)	0.2487 (5)	0.1455 (4)
N(4)	0.0833 (3)	0.3593 (3)	0.2244 (3)	C(43)	0.1680 (5)	0.2083 (5)	0.1853 (5)
C(11)	0.0242 (4)	0.8709 (4)	0.1237 (3)	C(44)	0.1841 (5)	0.2437 (5)	0.2444 (4)
C(12)	0.0577 (4)	0.8869 (4)	0.0638 (3)	C(45)	0.1409 (4)	0.3206 (4)	0.2629 (3)
C(13)	0.1225 (4)	0.8328 (4)	0.0409 (3)	OL	−0.1044 (4)	0.9012 (4)	−0.0267 (3)
C(14)	0.1512 (4)	0.7636 (4)	0.0771 (3)	H(1)	−0.1049 (3)	0.7116 (2)	0.1953 (2)
C(15)	0.1161 (4)	0.7513 (4)	0.1370 (3)	H(2)	−0.1191 (3)	0.5364 (2)	0.2929 (2)
C(21)	−0.0473 (4)	0.9213 (4)	0.1519 (3)	H(3)	−0.1559 (4)	0.9256 (4)	−0.0373 (3)
C(22)	−0.0875 (5)	0.9920 (4)	0.1220 (3)	H(4)	−0.1098 (4)	0.8617 (4)	−0.0042 (3)
C(23)	−0.1578 (5)	1.0314 (5)	0.1500 (4)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses in each table.

Table III

Important Bond Lengths (Å) for **1**

Cr(1)–O(1)	1.925 (3)	Cr(2)–N(4)	2.071 (4)
Cr(1)–N(1)	2.058 (4)	O(1)–O(2)	2.446 (5)
Cr(1)–N(2)	2.076 (4)	O(1)–H(1)	0.73
Cr(2)–O(2)	1.928 (3)	O(2)–H(2)	0.84
Cr(2)–N(3)	2.041 (4)		

Important Angles (deg) for **1**

O(1)–Cr(1)–O(1)′	89.7 (2)	O(2)–Cr(2)–N(3)′	94.9 (2)
O(1)–Cr(1)–N(1)	94.0 (2)	O(2)–Cr(2)–N(4)′	92.7 (2)
O(1)–Cr(1)–N(2)	92.2 (2)	N(3)–Cr(2)–N(4)	79.0 (2)
O(1)–Cr(1)–N(1)′	93.0 (2)	N(3)–Cr(2)–N(3)′	168.9 (2)
O(1)–Cr(1)–N(2)′	171.3 (2)	N(3)–Cr(2)–N(4)′	92.8 (2)
N(1)–Cr(1)–N(2)	78.4 (2)	N(4)–Cr(2)–N(4)′	85.0 (2)
N(1)–Cr(1)–N(1)′	170.2 (2)	Cr(1)–O(1)–H(1)	116.2 (5)
N(1)–Cr(1)–N(2)′	94.4 (2)	Cr(1)–O(1)–O(2)	127.1 (2)
N(2)–Cr(1)–N(2)′	87.1 (2)	H(1)–O(1)–O(2)	115.1 (5)
O(2)–Cr(2)–O(2)′	90.7 (2)	Cr(2)–O(2)–O(1)	126.2 (2)
O(2)–Cr(2)–N(3)	92.9 (2)	Cr(2)–O(2)–H(2)	110.3 (4)
O(2)–Cr(2)–N(4)	171.4 (2)	H(2)–O(2)–O(1)	120.4 (4)

denotes two doubly shared bridging hydrogen oxide ligands, and four perchlorate ions.

Discussion

In his definitive work on the hydrolysis of metal ions,[6] Alfred Werner described hydrolysis as a dissociation of a water ligand into a hydrogen ion and a hydroxo ligand. Accordingly, the product of hydrolysis of a diaquametal salt such as *trans*-$[Co(en)_2(H_2O)_2]Br_2$ was formulated as a *hydroxo aqua* complex, *trans*-$[Co(en)_2(H_2O)(OH)]Br_2$. This universally accepted formulation[7] requires the existence of two distinct oxygen ligands, OH and H_2O. One should be able, at least in principle, to distinguish between the OH ligand and the H_2O ligand in the structure of crystalline hydroxo aqua complexes.

The results of the present investigation call for some modification of this classical model of hydrolysis. In the structures reported here, one cannot distinguish between coordinated H_2O and coordinated OH. Instead of each pair of hypothetical OH and H_2O ligands, there exists *one* symmetrical hydrogen oxide bridge between neighboring metal atoms. The structures reported here represent two modes of hydrogen oxide bridging between mononuclear octahedral complexes. The cis "hydroxo aqua" ions of **1** are dimers bridged by two H_3O_2 ligands, and the trans "hydroxo aqua" ions of **2** are linear polymers in which infinite chains of metal atoms are bridged by single H_3O_2 ligands. These findings support our hypothesis that the, so called, mononuclear "hydroxo aqua" ions are, in fact, hydrogen oxide bridged dimers or polymers in the crystalline state.

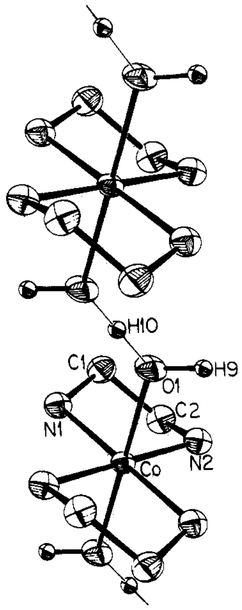


Figure 2. Section of the infinite chain of *trans*-$[Co(en)_2(H_3O_2)]_n^{2n+}$ in **2**. The thermal ellipsoids are of 50% probability. The hydrogen atoms were given an arbitrary thermal parameter.

A literature search for a similar general structural model of hydroxo aqua ions yielded negative results. A relevant crystallographic work dealing with a hydroxoaquaruthenium(III) complex is included in a paper by Hodgson, Meyer, and their coworkers,[8] who report the structure of *trans*-$[Ru(bpy)_2(H_2O)(OH)](ClO_4)_2$. This structure contains characteristic polynuclear ruthenium chains, similar to the cobalt chains of compound **2**, with an O–O separation of 2.538 Å. The authors characterize them explicitly as "infinite chains of *trans*-$Ru(bpy)_2(OH_2)(OH)^{2+}$ cations linked by symmetrical hydrogen bonds" but do not draw any general conclusion pertaining to the existence or structure of hydroxo aqua ions in the crystalline state.

Comparison and Correlation of Structure. The M–O···O–M bridge has the approximate anti structure (structure a) in compound **2** and some other structures containing a *single* H_3O_2 bridge between two metal atoms.[1,8] This configuration is favored because at $\phi = 180°$ the M–M separation attains a maximal value. In compound **1** the torsional angle ($\phi = 65°$) is near that of a gauche

---

(6) Werner, A. *Chem. Ber.* **1907**, *40*, 272–287.

(7) Burgess, J. "Metal Ions in Solution"; E. Harwood: Chichester, England, 1978; pp 259–304.

(8) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600–607.

Table IV. Positional Parameters and Estimated Standard Deviations for **2**

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	0.50000	0.00000	0.00000	H(1)	0.716 (4)	0.783 (3)	0.161 (2)
Cl	0.0295 (1)	0.46672 (8)	0.14066 (5)	H(2)	0.526 (5)	0.659 (4)	0.157 (2)
O(1)	0.1677 (3)	0.9661 (2)	−0.0379 (1)	H(3)	0.240 (6)	0.853 (4)	0.149 (2)
O(2)	0.2241 (4)	0.3637 (3)	0.1256 (2)	H(4)	0.413 (5)	0.897 (4)	0.232 (2)
O(3)	0.0221 (4)	0.6067 (2)	0.0823 (1)	H(5)	0.657 (5)	0.737 (4)	0.025 (2)
O(4)	0.0624 (4)	0.5194 (3)	0.2334 (1)	H(6)	0.432 (5)	0.718 (4)	0.016 (2)
O(5)	−0.1886 (4)	0.3779 (3)	0.1199 (1)	H(7)	0.344 (6)	0.113 (4)	0.130 (2)
N(1)	0.5403 (4)	0.7709 (3)	0.0396 (2)	H(8)	0.592 (6)	0.084 (4)	0.155 (2)
N(2)	0.4517 (4)	0.0450 (3)	0.1244 (1)	H(9)	0.1374	0.8591	−0.0628
C(1)	0.5597 (5)	0.7625 (4)	0.1392 (2)	H(10)	0.00000	0.00000	0.00000
C(2)	0.3943 (5)	0.8896 (4)	0.1677 (2)				

Table V

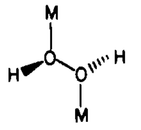
Important Bond Lengths (Å) for **2**

Co-O(1)	1.916 (1)	C(1)-C(2)	1.509 (4)
Co-N(1)	1.960 (2)	Cl-O(2)	1.440 (2)
Co-N(2)	1.955 (2)	Cl-O(3)	1.431 (2)
O(1)-H(9)	0.953 (2)	Cl-O(4)	1.433 (2)
O(1)-H(10)	1.221 (1)	Cl-O(5)	1.434 (2)
N(1)-C(1)	1.475 (3)	O(1)-O(1)′	2.441 (2)
N(2)-C(2)	1.481 (3)		

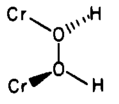
Important Angles (deg) for **2**

O(1)-Co-N(1)	90.91 (9)	N(1)-C(1)-C(2)	107.6 (2)
O(1)-Co-N(2)	91.33 (9)	N(2)-C(2)-C(1)	105.7 (2)
N(1)-Co-N(2)	85.40 (1)	O(2)-Cl-O(3)	108.5 (1)
N(1)-Co-N(2)′	94.60 (1)	O(2)-Cl-O(4)	109.8 (1)
Co-O(1)-H(9)	110.9 (2)	O(2)-Cl-O(5)	109.9 (1)
Co-O(1)-H(10)	130.4 (1)	O(3)-Cl-O(4)	109.6 (1)
H(9)-O(1)-H(10)	106.2 (2)	O(3)-Cl-O(5)	109.3 (1)
Co-N(1) -C(1)	109.6 (2)	O(4)-Cl-O(5)	109.6 (1)
Co-N(2)-C(2)	109.2 (2)		

configuration (structure b), which is imposed by the rigid *double* bridge in this stable dimer.



a



b

The O···O distances in the H_3O_2 bridges of **1** and **2** (2.446 and 2.442 Å, respectively) are similar to those found in other compounds with H_3O_2 bridges.[1]

The exact position of the central hydrogen atom of the H_3O_2 bridge in **1** could not be determined in this X-ray diffraction study. Therefore, one cannot conclude unequivocally that the HO···H···OH unit is symmetric. However, the fact that the two Cr–O(H_3O_2) distances [1.925 (3) and 1.928 (3) Å] are identical (within experimental error) implies that the H_3O_2 bridge is indeed symmetric. In structure **2** the M–O···H···O–M unit resides on a crystallographic inversion center and is therefore symmetric. The central hydrogen atom was located and refined on the inversion center, yielding reasonable thermal parameters. However, an alternative scheme of a disordered hydrogen atom about the inversion center cannot be ruled out due to the limitations of the X-ray technique. A more definite answer to the problem of symmetry of the H_3O_2 bridge may be furnished by a neutron study.

The Cr–O(H_3O_2) distances in **1** (1.927 Å) are shorter than the distance reported for the Cr–O(H_2O) bond (1.98–2.01 Å)[9] and slightly longer than that reported for Cr–O(OH) (1.90–1.91 Å)[10] as expected. A similar phenomenon is found in the Co(III) compound **2** where the Co–O(H_3O_2) distance (1.916 Å) is shorter than the average Co–O(H_2O) distance (1.94 Å)[11] but slightly longer than the Co–O(OH) distance (1.89 Å).[12]

H_3O_2 Bridging in Solution and Its Significance in Olation and Redox Reactions. The bridging of hydroxo aqua ions in the solid state raises the question whether similar hydrogen oxide bridged species exist in *aqueous solution*. The bond energy of the short and symmetrical hydrogen bond in H_3O_2 (>100 kJ/mol[13]) favors dimerization, since it is much higher than the energy of ordinary, long, and unsymmetrical hydrogen bonds between OH ligands or H_2O ligands and solvent water molecules (~20 kJ/mol[14]). On the other hand, the relatively high concentration of solvent water molecules in dilute solutions of hydroxo aqua ions would favor dissociation of such dimers into monomeric hydroxo aqua ions. Therefore, it is to be expected that dimers exist, if at all, in concentrated solutions. Preliminary results, obtained by three-phase vapor tensiometry (TPVT) confirm this expectation.[15] In a 0.12 M solution of $[(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2](NO_3)_4$, most chromium species are dimers. On the other hand in a dilute solution ($<5 \times 10^{-4}$ M), most chromium ions were shown to be dipositive rather than tetrapositive, i.e. true hydroxo aqua ions.[16]

The structural features of polynuclear hydrolytic species were described by Werner in 1907.[17] In all these species, the metal atoms are bridged by an oxygen atom that is coordinated *directly* to two (or three) metal atoms. This oxygen atom may be protonated, forming a *hydroxo* bridge M–O(H)–M. If it is not protonated, the bridge M–O–M, is known as an *oxo* bridge. One, two, or three oxygen bridges may exist between two metal atoms. All the polynuclear hydrolytic species proposed or investigated between 1907 and 1981[1] possessed this direct M–O–M bridge.

The hydrolytic polymers described here are of an entirely different kind: their metal atoms are *not* bridged by an oxygen atom but by a strong hydrogen bond between two oxygen ligands. The two main differences between oxygen bridges and hydrogen oxide bridges are as follows: (1) *Structural*: the separation between metal atoms is much longer in H_3O_2-bridged species, ~5 Å in $M(H_3O_2)_2M$ compared to a separation of ~3 Å in $M(OH)_2M$.[18] (2) *Kinetic*: formation of M–O–M bridges between mononuclear hydroxo aqua ions involves breaking of metal to oxygen bonds and may be quite sluggish, especially in inert complexes, whereas formation of hydrogen oxide bridges involves only the formation of a hydrogen bond and is therefore much faster, probably diffusion controlled.

Most crystalline *cis*-hydroxoaquametal salts undergo an *olation* reaction at 100 °C. In this reaction, two water molecules are

---

(9) (a) Chesick, J. P.; Doany, F. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1076–1079. (b) Cline, S. J.; Kallesøe, S.; Pedersen, E.; Hodgson, D. J. *Inorg. Chem.* **1979**, *18*, 796–801.

(10) (a) Kaas, K. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1603–1607. (b) Hodgson, D. J.; Pedersen, E. *Inorg. Chem.* **1980**, *19*, 3116–3121.

(11) Kanazawa, Y.; Matsumoto, T. *Acta Crystallogr., Sect. B* **1976**, *B32*, 282–284.

(12) Kucharski, E. S.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 47–51.

(13) (a) Rohlfing, C. L.; Allen, L. C.; Cook, M. C. *J. Chem. Phys.* **1983**, *78*, 2498–2503. (b) Roos, B. O.; Kraemer, W. P.; Diercksen, G. H. F. *Theor. Chim. Acta* **1976**, *42*, 77–82.

(14) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 221.

(15) Ardon, M.; Magyar, B. *J. Am. Chem. Soc.* **1984**, *106*, 3359–3360.

(16) Ardon, M., unpublished results.

(17) (a) Werner, A. *Chem. Ber.* **1907**, *40*, 2103–2125. (b) Werner, A. *Chem. Ber.* **1907**, *40*, 4434–4441. (c) Werner, A. *Chem. Ber.* **1907**, *40*, 4834–4844.

(18) (a) Kaas, K. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2021. (b) Michelsen, K.; Pedersen, E.; Wilson, S. R.; Hodgson, D. J. *Inorg. Chim. Acta* **1982**, *63*, 141–150. (c) Cline, S. J.; Hodgson, D. J.; Kallesøe, S.; Larsen, S.; Pedersen, E. *Inorg. Chem.* **1983**, *22*, 637–642.

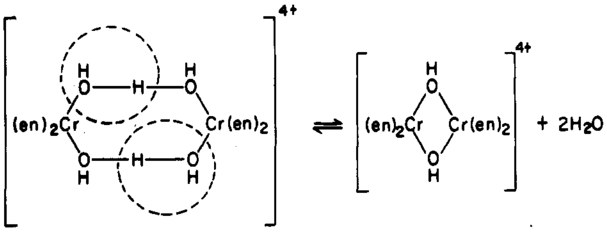
Table VI. Structural Data for **1**, **2**, and Other Compounds Containing H_3O_2 Bridges

compd	O–O(H_3O_2), Å	M–O(H_3O_2), Å	M–M, Å	M–O···O–M, torsional angle, deg
cis-$[Cr(bpy)_2(H_3O_2)]_2I_4\cdot 2H_2O$ (**1**)	2.446 (5)	1.925 (3) 1.928 (3)	5.03	64.9
trans-$[Co(en)_2(H_3O_2)](ClO_4)_2$ (**2**)	2.441 (2)	1.916 (1)	5.72	180.0
trans-$[Ru(bpy)_2(H_3O_2)](ClO_4)_2$[8]	2.538 (6)	2.007 (3)	5.79	137.7
$\{[Mo_3O_2(pr)_6(H_2O)_2]_2(H_3O_2)\}Br_3\cdot 6H_2O$[1]	2.52 (1)	2.009 (7)	5.63	180.0

eliminated from two cis hydroxo aqua ions while the two remaining OH ligands form two μ-hydroxo bridges between the metal atoms as in reaction 3. This reaction was described by Pfeiffer[19] (1908)

$$\underset{\text{I}}{2\textit{cis-}[Cr(en)_2(H_2O)(OH)]X_2} \xrightarrow{100\ ^\circ C} \underset{\text{II}}{[(en)_2Cr(OH)_2Cr(en)_2]X_4} + 2H_2O \quad (3)$$

as the splitting of two water molecules from two hydroxo aqua ions and the relocation of the two (5-coordinated) hydroxo complexes in such a way that each substitutes the water molecule of the other complex ion. The steric course of this reaction is clarified if the correct structure of cis hydroxo aqua ions is considered. The mutual orientation of the octahedra in the *dimeric product* II (reaction 3) with an M–M distance in the range of 2.950–3.059 Å[18] is readily accessible from the *dimeric reagent*. As in compound **1**, the two octahedra of the reagent are held together by two μ-hydrogen oxide bridges. In the olation process these two bridges collapse and two water molecules are eliminated while two hydroxo bridges are being formed as in reaction 4. The olation of these "cis hydroxo aqua" ions involves only a decrease in the Cr–Cr distance from 5 to 3 Å accompanied by a 60° twist of the octahedra around the Cr–Cr axis (to make the two chromium and the two oxygen atoms coplanar). These features rationalize the fact that only cis hydroxo aqua salts undergo olation at 100 °C while trans isomers do not and, also, that only *doubly* bridged μ-hydroxo dimers are formed in this reaction and not *singly* bridged μ-hydroxo ions such as $[(en)_2(H_2O)Cr(\mu\text{-}OH)Cr(OH)(en)_2]^{4+}$ (the latter may be prepared, subsequently, from the doubly bridged complex in aqueous solution[20]).



(4)

Formation of polynuclear ions by olation reactions also takes place in *aqueous solution* of hydroxoaquametal ions.[21] Reaction 5 illustrates that in solution, just as in the solid phase, the doubly bridged μ-hydroxo product is preferred over the singly bridged ion.[22] Here too, the singly bridged species $[(H_2O)_5Cr(OH)Cr(H_2O)_5]^{5+}$ may be obtained by a slow decomposition of $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$ in acid solution.[23] Dimerization of the cis hydroxo aqua reagent (III) in concentrated solutions, just as in the solid state, may explain the similarity of the reactions in the two media.

$$\underset{\text{III}}{2[Cr(H_2O)_5OH]^{2+}} \rightarrow \underset{\text{IV}}{[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}} + 2H_2O \quad (5)$$

The mechanism of olation of hydroxo aqua ions in solution via a hydrogen oxide bridged dimer is further supported by kinetic data obtained by Hamm et al.[24] Their work on the kinetics of the reaction

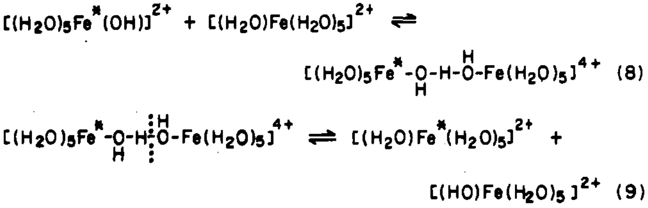
$$2\textit{cis-}[Cr(C_2O_4)_2(H_2O)(OH)]^{2-} \rightarrow [(C_2O_4)_2Cr(OH)_2Cr(C_2O_4)_2]^{4-} + 2H_2O \quad (6)$$

revealed that in dilute solutions the reaction had the *second-order* kinetics expected from reaction 6 but that at higher concentrations the order decreased until it became *first order* at chromium concentrations above 0.01 M. This behavior is to be expected if a monomer–dimer equilibrium exists in solution, in which most of the chromium is dimeric at 0.01 M and dissociates at lower concentrations.

Over 30 years ago an H atom transfer mechanism was proposed by Silverman and Dodson[25] for the Fe(III)/Fe(II) exchange reaction

$$[Fe^*(H_2O)_5(OH)]^{2+} + [Fe(H_2O)_6]^{2+} \rightleftharpoons [Fe^*(H_2O)_6]^{2+} + [Fe(H_2O)_5OH]^{2+} \quad (7)$$

Such H atom transfer may be carried out by cleavage of a hydrogen oxide ligand bridging the oxidizing and the reducing ion:



$$[(H_2O)_5Fe^*(OH)]^{2+} + [(H_2O)Fe(H_2O)_5]^{2+} \rightleftharpoons [(H_2O)_5Fe^*\text{-}\underset{H}{O}\text{-}H\text{-}\overset{H}{O}\text{-}Fe(H_2O)_5]^{4+} \quad (8)$$

$$[(H_2O)_5Fe^*\text{-}\underset{H}{O}\text{-}H\vdots\overset{H}{O}\text{-}Fe(H_2O)_5]^{4+} \rightleftharpoons [(H_2O)Fe^*(H_2O)_5]^{2+} + [(HO)Fe(H_2O)_5]^{2+} \quad (9)$$

Acknowledgment. A.B. is a "Bat-Sheva" fellow. We are grateful to the Bat-Sheva de Rothschild Foundation for financial support.

Registry No. **1**, 87764-12-3; **2**, 14099-22-0.

Supplementary Material Available: Tables of structure factors of **1** and **2**, thermal parameters of **1** and **2**, bond distances and angles in the bpy ligands in **1**, and positional parameters of hydrogen atoms in **1** (29 pages). Ordering information is given on any current masthead page.

---

(19) Pfeiffer, P. *Z. Anorg. Chem.* **1908**, *58*, 272–296.

(20) Springborg, J.; Toftlund, H. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 171–181.

(21) Stünzy, H.; Marty, W. *Inorg. Chem.* **1983**, *22*, 2145–2150.

(22) (a) Laswick, J. A.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3564–3567. (b) Ardon, M.; Plane, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 3197–3200.

(23) Thompson, M.; Connick, R. E. *Inorg. Chem.* **1981**, *20*, 2279–2285.

(24) Grant, D. M.; Hamm, R. E. *J. Am. Chem. Soc.* **1956**, *78*, 3006–3009.

(25) Silverman, J.; Dodson, R. W. *J. Phys. Chem.* **1952**, *56*, 846–842.