Ion Tech FAB gun operating at 8 keV with a current of 30–40 μA. The magnet was typically scanned at a rate of 30–100 s/decade. All matrices were vacuum distilled before use.

Bis(phosphonium) Salts. All bis(phosphonium) salts (**14–18**) were prepared and purified as described in the literature.[22]

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Registry No. 8, 59-43-8; **14**, 106835-92-1; **15**, 40817-03-6; **16**, 7333-67-7; **17**, 22884-31-7; **18**, 22884-33-9; **21**, 106820-85-3; **22**, 106820-86-4; **23**, 106820-87-5; **24**, 106835-93-2; **25**, 106820-88-6; d(ApCpGpT), 106835-94-3; Xe, 7440-63-3; vancomycin hydrochloride, 1404-93-9; glycerol, 56-81-5.

Olation and Structure

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Abstract: The ability of cis hydroxoaqua–metal complexes to undergo olation and form the corresponding diols is correlated with their dimeric structure, having two μ-(H_3O_2) bridging ligands between the two metal atoms. A hypothesis is put forward that olation may take place only if the cis complex has this dimeric structure. The hypothesis is tested by means of the only cis hydroxoaqua complex that does not have a dimeric structure, $[Cr(pico)_2(H_2O)OH]S_2O_6$, compound **1** (pico = 2-picolylamine). This complex does not olate. Replacement of the dithionate counter ion by iodide yielded the complex $[(pico)_2Cr(H_3O_2)_2Cr(pico)_2]I_4 \cdot 2H_2O$, compound **2**. The structure of **2** was determined by a single-crystal X-ray study, which established that it had the normal dimeric structure. Compound **2** olates, as predicted by the hypothesis, and produces the diol $[(pico)_2Cr(OH)_2Cr(pico)_2]^{4+}$. The structure of this ion was determined by X-ray study of $[(pico)_2Cr(OH)_2Cr(pico)_2](S_2O_6)_2 \cdot 2^1/_2H_2O$, compound **3**. A two-step mechanism of olation, in the solid state, is proposed. A mono-ol is produced in the first step, followed by the formation of the diol. This mechanism predicts retention of the racemic $\Lambda\Lambda,\Delta\Delta$ configuration of compound **2** in the product **3** and was confirmed by the structures of **2** and **3**. The well-known fundamental feature of olation, namely that only cis isomers olate and trans isomers do not, is explained, for the first time, by the proposed mechanism and is correlated with the structure of the reagents and products.

Formation of μ-(OH) bridging between metal ions, also known as "olation" (reaction 1), is the first step in the processes of polymerization of metal aqua ions in solution and "aging" of metal hydroxides in the solid state.[3] Therefore, the mechanism of reaction 1 is a key to the understanding of these important processes.

$$M(OH_2)^{n+} + (HO)M^{(n-1)+} \rightarrow M(OH)M^{(2n-1)+} + H_2O \qquad (1)$$

Although olation was investigated and discussed since the beginning of this century,[2-4] no firm experimental evidence has yet been furnished for the mechanism of reaction 1 in the solid state. Pfeiffer, Werner, Dubski, and their contemporaries[2] who investigated olation reactions of hydroxoaqua–metal complexes such as

$$2\,cis\text{-}[Cr(en)_2(H_2O)(OH)]X_2 \xrightarrow{100\ °C} [(en)_2Cr(OH)_2Cr(en)_2]X_4 + 2H_2O \qquad (2)$$

noted that only cis hydroxoaqua ions olate to form diols, while their trans isomers do not. This notable difference was used in their classical structure determinations to distinguish between cis and trans configurations. However, no satisfactory explanation was given, to date, for the reactivity of the cis and inertness of the trans isomers, i.e., for the fact that cis isomers form di-μ-OH binuclear ions while trans isomers do not form μ-OH bridged polynuclear chains. The present investigation was undertaken in order to explain this fundamental difference in reactivity. Investigations conducted since the late fifties, and especially in the last decade,[3c,d,4] furnished some valuable insight into the mechanism of olation in aqueous solution. In his studies on the reverse of reaction 2, Springborg[4] proved that olation in solution proceeds by two consecutive steps

$$2[L_4M(H_2O)(OH)]^{2+} \rightleftharpoons [(HO)L_4M(OH)ML_4(H_2O)]^{4+} + H_2O \qquad (3)$$

$$[(OH)L_4M(OH)ML_4(H_2O)]^{4+} \rightleftharpoons [L_4M(OH)_2ML_4]^{4+} + H_2O \qquad (4)$$

The intermediate (product of reaction 3) was isolated, and its structure was determined.[4b]

Recent investigations of hydroxoaqua metal ions by single crystal X-ray studies revealed that these ions are not mononuclear, as their classical formulation implies, but *binuclear* or *polynuclear*.[5] A distinction between hydroxo and aqua ligands is usually impossible in these ions because they merge into a symmetrical $H_3O_2^-$ bridging ligand by means of a very short (<2.5 Å), strong, and centered hydrogen bond. As a result of this bridging, cis isomers have a dimeric structure with two $H_3O_2^-$ bridges between the metal atoms (form a), and trans isomers consist of infinite

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[2] (a) Werner, A. *Chem. Ber.* **1907**, *40*, 4434–4441. (b) Pfeiffer, P. *Z. Anorg. Chem.* **1908**, *58*, 272–296. (c) Dubski, J. V. *J. Prakt. Chem.* **1914**, *90*, 61.

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[4] (a) Springborg, J.; Toftlund, H. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 171–181. (b) Galsbol, F.; Larsen, S.; Rasmussen, B.; Springborg, J. *Inorg. Chem.* **1986**, *25*, 290 and references therein.

[5] (a) Ardon, M.; Bino, A. *J. Am. Chem. Soc.* **1983**, 105, 7748–7750. (b) Ardon, M.; Bino, A. *Inorg. Chem.* **1985**, *24*, 1343–1347. (c) Ardon, M.; Bino, A.; Jackson, W. G. *Polyhedron*, in press. (d) Ardon, M.; Bino, A., unpublished results.

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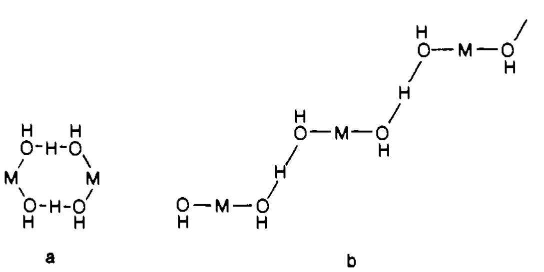
chains of metal atoms linked by single $H_3O_2^-$ bridges (form b).



On the basis of these structures, the olation reaction was reformulated as an elimination of two water molecules from the two $H_3O_2^-$ bridges of the cis dimer, accompanied by a contraction of the distance between the two metal atoms from ~5 Å [as it is in the dimers of Cr(III) and CO(III)] to ~3 Å [as it is in the corresponding diols].[5b] It was proposed that double-bridged dimers of form a may react in this way; hence, cis isomers, having such a structure, may olate.[5]

This assumption received some unexpected support, when the authors noticed that the only cis hydroxoaqua-metal complex, reported so far, which does not have the dimeric structure of form a, does *not* olate despite its cis configuration. This compound, the dithionate salt of bis(2-picolylamine)aqua(hydroxo)chromium(III) does not lose water even at 200 °C.[6,7] The fact that *cis*-α-$[Cr(pico)_2(H_2O)OH]S_2O_6$, compound **1**, is not a dimer and is also unable to olate supports a hypothesis that *a double-bridged dimeric structure is a necessary condition for olation* but does not prove it. It may well be that these two unusual features are not correlated at all but are a mere coincidence. Alternatively, the two properties may depend on some specific structural features of the *cis*-α-$[Cr(pico)_2(H_2O)OH]^{2+}$ ion. In order to explore these alternative interpretations, we prepared the compound *cis*-α-$[(pico)_2Cr(H_3O_2)_2Cr(pico)_2]I_4 \cdot 2H_2O$, **2**, which contains the same complex but with a different counter ion—iodide instead of dithionate. The structure and relevant properties of compound **2** were determined and are reported here. The results shed new light on the mechanism of olation reactions in the solid state and their steric course.

Experimental Section

Preparations. ***cis*-α-$[Cr(pico)_2(OH)(H_2O)]Cl_2 \cdot H_2O$, 1a**, was prepared as described in an earlier publication.[6]

***cis*-α-$[(pico)_2Cr(H_3O_2)_2Cr(pico)_2]I_4 \cdot 2H_2O$, 2**, was prepared by addition of NaI (1 g) to an ice-cooled solution containing 0.35 g (0.89 mmol) of **1a** in 5 mL of water. The violet precipitate was filtered and washed with ethanol, yield 0.43 g (84%). Violet crystals suitable for X-ray study were obtained by recrystallization from hot water (60 °C). Anal. Calcd for $(CrC_{12}H_{21}N_4O_3I_2)_2$: Cr, 9.04; C, 25.06; N, 9.74; H, 3.68; I, 44.13. Found: Cr, 8.97; C, 25.05; N, 9.74; H, 3.55; I, 43.04.

***cis*-α-$[(pico)_2Cr(H_3O_2)_2Cr(pico)_2](ClO_4)_4 \cdot 2H_2O$, 2a**, was prepared by addition of $NaClO_4 \cdot H_2O$ (1 g) to an ice-cooled solution containing 0.56 g (1.43 mmol) of **1a** in 5 mL of water. The red crystals were filtered and rinsed with ethanol, yield 0.62 g (83%). The product was recrystallized from hot water (60 °C). Anal. Calcd for $(CrC_{12}H_{21}N_4O_{11}C_2)_2$: Cr, 10.00; C, 27.71; N, 10.77; H, 4.07; Cl, 13.63. Found: Cr, 9.92; C, 27.43; N, 10.77; H, 4.57; Cl, 13.32.

***cis*-α-$[(pico)_2Cr(OH)_2Cr(pico)_2](S_2O_4)_2 \cdot 2^1/_2H_2O$, 3.** **2** (20 mg) was heated to 140 °C for 3 h. The reddish violet product was dissolved at room temperature in 1 mL of H_2O, and 1 mL of a saturated solution of $Na_2S_2O_6$ was added. Red-violet crystals of **3** were obtained.

Thermogravimetry. Measurements were performed on an instrument which has been described earlier.[8]

X-ray Crystallography. Crystallographic data and other pertinent information are given in Table I. For each crystal, Lorentz and polarization corrections were applied. Intensity data for **2** were corrected for absorption by the empirical ψ-scan method. The heavy-atom positions in **2** and **3** were obtained by direct methods by using the MULTAN program. Structure **2** was refined[9] in space group *C*2/*c* to convergence. All the hydrogen atoms of the complex were located from the difference Fourier map (with bond distances in the range of 0.9–1.15 Å), and they were included in the final refinement cycles by using the riding model with $U = 0.05$. Anisotropic thermal parameters were used for all nonhydrogen atoms. Structure **3** was refined in space group *Pbca* to convergence by using two blocks: one that included all the atoms in the dimer, and a second block that included all the dithionate and water atoms. One of the water oxygen atoms in the crystal, OW(3), was introduced with a half occupancy. All the hydrogen atoms in the structure except those of OW(3) were located from the difference Fourier map and were included in the refinement by using the riding model with $U = 0.05$. Anisotropic thermal parameters were used for all non-hydrogen atoms. The discrepancy indices, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, are listed in Table I. X-ray powder photographs were obtained on a camera of the Guinier type with Cu Kα radiation. Silicon was used as standard.

Table I. Crystallographic Data for **2** and **3**

compd	2	3
formula	$C_{24}H_{42}Cr_2I_4N_8O_6$	$C_{24}H_{39}Cr_2N_8O_{16.5}S_4$
fw	1150.25	935.85
space group	*C*2/*c*	*Pbca*
a, Å	24.759 (3)	21.082 (2)
b, Å	9.522 (1)	18.998 (2)
c, Å	17.673 (2)	18.563 (2)
β, deg	116.34 (3)	
V, Å^3	3734 (1)	7435 (1)
Z	4	8
d_{calcd}, g cm^{-3}	2.046	1.672
cryst size, mm	0.5 × 0.3 × 0.2	0.5 × 0.4 × 0.3
μ (Mo Kα), cm^{-1}	36.84	8.19
data collect instrmnt	Philips PW 1100	Philips PW 1100
radiatn (monochromtd in incidnt beam)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
orientatn reflcns, no., range 2θ	20 (24–32)	20 (24–32)
temp, °C	21	21
scan method	ω–2θ	ω–2θ
data col range, 2θ, deg	4–45	4–46
no. unique data	3619	5006
data with $F_o^2 > 3\sigma(F_o)^2$	2129	2974
R	0.055	0.048
R_w	0.065	0.049

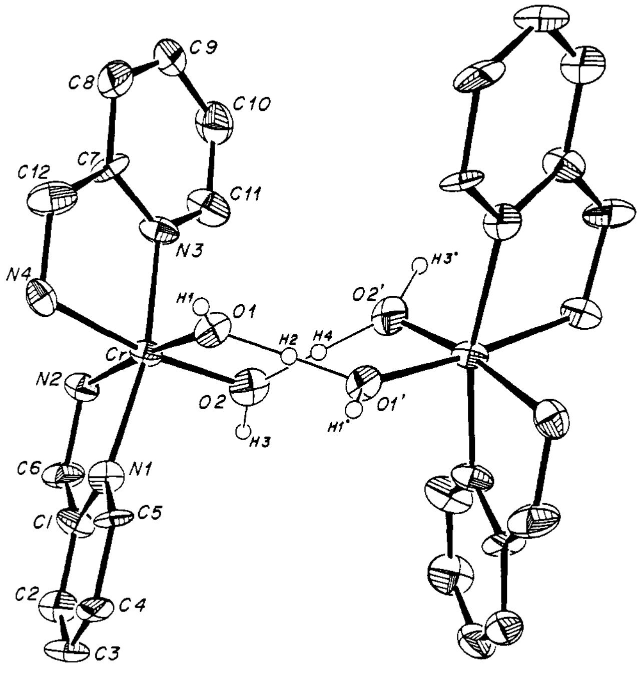


Figure 1. Structure of *cis*-α-$[(pico)_2Cr(H_3O_2)_2Cr(pico)_2]^{4+}$ as found in **2**. The thermal ellipsoids are of 50% probability. The hydrogen atoms were given an arbitrary thermal parameter.

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(9) All crystallorgraphic computing was done on a CYBER 855 computer at the Hebrew University of Jerusalem, with the SHELX 1977 structure determination package.

Table II. Positional Parameters and Estimated Standard Deviations for **2**[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
I(1)	0.69635 (4)	0.04967 (9)	0.22604 (6)	C(3)	0.2863 (6)	0.330 (1)	0.4402 (8)
I(2)	0.40131 (5)	0.1189 (1)	0.09186 (8)	C(4)	0.3277 (5)	0.238 (1)	0.4946 (8)
Cr	0.39203 (8)	0.4579 (2)	0.7340 (1)	C(5)	0.3558 (5)	0.267 (1)	0.5802 (7)
O(1)	0.4557 (4)	0.3202 (8)	0.7662 (5)	C(6)	0.2877 (6)	0.603 (1)	0.5957 (8)
O(2)	0.4444 (4)	0.5784 (8)	0.7079 (5)	C(7)	0.4058 (5)	0.464 (1)	0.9061 (8)
N(1)	0.3447 (4)	0.389 (1)	0.6120 (6)	C(8)	0.4238 (5)	0.507 (2)	0.9896 (8)
N(2)	0.3211 (4)	0.603 (1)	0.6872 (6)	C(9)	0.4535 (6)	0.636 (2)	1.0164 (9)
N(3)	0.4184 (4)	0.542 (1)	0.8514 (6)	C(10)	0.4632 (6)	0.716 (2)	0.959 (1)
N(4)	0.3465 (4)	0.325 (1)	0.7790 (6)	C(11)	0.4456 (6)	0.667 (1)	0.8783 (8)
C(1)	0.3016 (5)	0.477 (1)	0.5561 (7)	C(12)	0.3759 (6)	0.325 (1)	0.8728 (8)
C(2)	0.2736 (6)	0.449 (1)	0.4720 (8)	OW	0.5409 (5)	0.060 (1)	0.6640 (9)

[a] esd's in the least significant digits are shown in parentheses.

Table III. Important Bond Lengths (Å) and Angles (deg) for **2**

Cr-O(1)	1.932 (7)	N(4)-C(12)	1.49 (1)
Cr-O(2)	1.934 (9)	C(1)-C(2)	1.36 (1)
Cr-N(1)	2.053 (9)	C(1)-C(6)	1.51 (1)
Cr-N(2)	2.097 (9)	C(2)-C(3)	1.36 (2)
Cr-N(3)	2.040 (9)	C(3)-C(4)	1.37 (1)
Cr-N(4)	2.07 (1)	C(4)-C(5)	1.39 (1)
N(1)-C(1)	1.37 (1)	C(7)-C(8)	1.40 (1)
N(1)-C(5)	1.36 (1)	C(7)—C(12)	1.50 (1)
N(2)-C(6)	1.45 (1)	C(8)-C(9)	1.41 (2)
N(3)-C(7)	1.36 (1)	C(9)-C(10)	1.37 (2)
N(3)-C(11)	1.35 (1)	C(10)-C(11)	1.38 (2)
O(1)-O(1)′	2.50 (1)	O(2)-O(2)′	2.48 (1)
O(1)-Cr-O(2)	85.8 (4)	Cr-N(3)-C(11)	126.0 (9)
O(1)-Cr-N(1)	95.9 (4)	C(7)-N(3)-C(11)	118 (1)
O(1)-Cr-N(2)	174.6 (5)	Cr-N(4)-C(12)	110.4 (8)
O(1)-Cr-N(3)	96.6 (5)	N(1)-C(1)-C(2)	122 (1)
O(1)-Cr-N(4)	89.1 (4)	N(1)-C(1)-C(6)	115 (1)
O(2)-Cr-N(1)	94.1 (4)	C(2)-C(1)-C(6)	124 (1)
O(2)-Cr-N(2)	92.7 (4)	C(1)-C(2)-C(3)	121 (2)
O(2)-Cr-N(3)	93.7 (4)	C(2)-C(3)-C(4)	119 (2)
O(2)-Cr-N(4)	171.6 (5)	C(3)-C(4)-C(5)	119 (1)
N(1)-Cr-N(2)	79.1 (5)	N(1)-C(5)-C(4)	122 (1)
N(1)-Cr-N(3)	165.8 (4)	N(2)-C(6)-C(1)	112 (1)
N(1)-Cr-N(4)	93.0 (4)	N(3)-C(7)-C(8)	122 (1)
N(2)-Cr-N(3)	88.7 (5)	N(3)-C(7)-C(12)	115 (1)
N(2)-Cr-N(4)	92.9 (4)	C(8)-C(7)-C(12)	123 (1)
N(3)-Cr-N(4)	80.3 (4)	C(7)-C(8)-C(9)	119 (1)
Cr-N(1)-C(1)	117.3 (8)	C(8)-C(9)-C(10)	119 (2)
Cr-N(1)-C(5)	125 (1)	C(9)-C(10)-C(11)	120 (1)
C(1)-N(1)-C(5)	117 (1)	N(3)-C(11)-C(10)	123 (1)
Cr-N(2)-C(6)	113.7 (7)	N(4)-C(12)-C(7)	110 (1)
Cr-N(3)-C(7)	116.1 (9)		
Cr-O(1)-O(1)′	117.9 (3)	Cr-O(2)-O(2)′	130.9 (6)

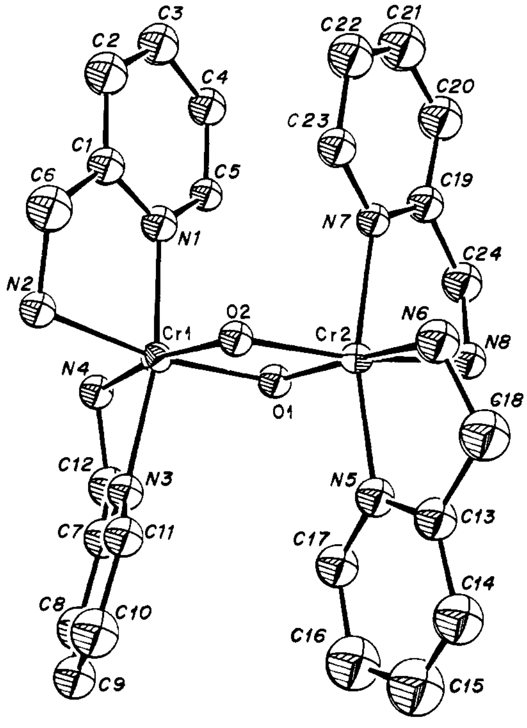


Figure 2. Structure of *cis*-α-$[(\text{pico})_2\text{Cr(OH)}_2\text{Cr(pico)}_2]^{4+}$ as found in **3**. The thermal ellipsoids are of 50% probability.

Results

Compound 2, *cis*-α-$[(\text{pico})_2\text{Cr}(\text{H}_3\text{O}_2)_2\text{Cr(pico)}_2]\text{I}_4{\cdot}2\text{H}_2\text{O}$. The atomic positional parameters are listed in Table II, and Table III gives the important bond lengths and angles. The thermal parameters and the positional parameters of the hydrogen atoms are included in the Supplementary Material. Figure 1 shows the numbering scheme in **2**.

With $Z = 4$ in the cell of space group $C2/c$ there is only half a *cis*-α-$[(\text{pico})_2\text{Cr}(\text{H}_3\text{O}_2)_2\text{Cr(pico)}_2]^{4+}$ ion in the asymmetric unit, with the other half related to it by a crystallographic twofold axis [the C_2 axis passes through H(2) and H(4), the central hydrogen atoms of the H_3O_2 ligands].

Each of the four dimers in the cell consists of two *cis*-α-$[(\text{Cr(pico)}_2(\text{H}_3\text{O}_2)]$ units having the same chirality (Λ,Λ or Δ,Δ). The two $H_3O_2^-$ groups are not symmetry related, but each one of them resides on the C_2 axis and is therefore symmetrical. The O···O separation in the $H_3O_2^-$ units, the Cr-O(H_3O_2) distances, and the M-O···O-M torsional angles are given in Table IV along with the corresponding parameters of other typical compounds containing $H_3O_2^-$ bridges.

The 4+ charge of the dimer $[(\text{pico})_2\text{Cr}(\text{H}_3\text{O}_2)_2\text{Cr(pico)}_2]_2^{4+}$ is balanced by four iodide anions in the crystal. The anions are hydrogen bonded to the NH_2 groups, the water molecule, and the $H_3O_2^-$ oxygen atoms with I-N(NH_2) distances in the range of 3.61-3.71 Å and a I(2)-O(2)(H_3O_2) distance of 3.42 Å. The water molecule in the crystal is hydrogen bonded to the second H_3O_2 oxygen atom, O(1) with a bond distance of 2.76 Å.

Olation of Compound 2. A preliminary test conducted on compound **2** by thermogravimetric analysis indicated that, when heated to 140 °C on a thermobalance, it lost weight corresponding to 2 mol of water per mol of chromium. This result was confirmed on a larger scale when 229.8 mg of compound **2** were heated in an oven at 140 °C for 3 h. The weight of this sample decreased

Table IV. Structural Data for **2** and Other Compounds Containing H_3O_2 Bridges

compound	O-O(H_3O_2), Å	M-O(H_3O_2), Å	M-M, Å	M-O···O-M torsional angle, deg
cis-α-$[\text{Cr(pico)}_2(\text{H}_3\text{O}_2)]_2\text{I}_4{\cdot}2\text{H}_2\text{O}$, **2**	2.50 (1) 2.48 (1)	1.932 (7) 1.934 (9)	5.12	60.4 90.1
cis-$[\text{Cr(bpy)}_2(\text{H}_3\text{O}_2)]_2\text{I}_4{\cdot}2\text{H}_2\text{O}$[5b]	2.446 (5)	1.925 (3) 1.928 (3)	5.03	64.9
trans-$[\text{Co(en)}_2(\text{H}_3\text{O}_2)](\text{ClO}_4)_2$[5b]	2.441 (2)	1.916 (1)	5.72	180.0

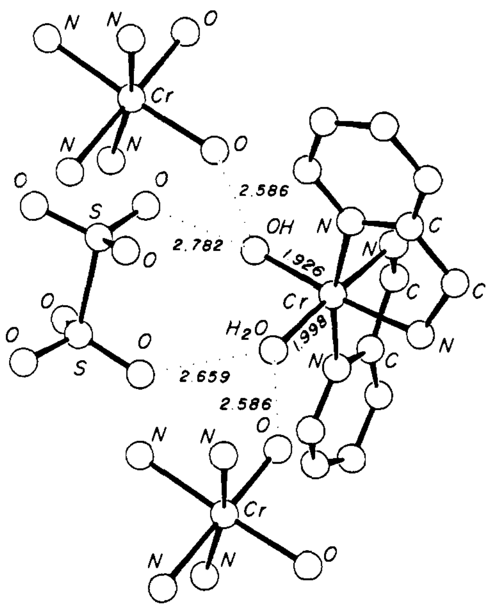


Figure 3. A section of the infinite chain of *cis*-α-[(pico)$_2$Cr(H$_2$O)(OH)]$^{2+}$ in **1** (ref 7) describing the interactions of the OH and H$_2$O ligands with neighboring complexes and with the S$_2$O$_6^{2-}$ counter ion. Hydrogen bonds are represented by the dotted lines. Only the central complex is drawn with a complete coordination sphere for the sake of clarity.

to 215.2 mg which compared well with the calculated weight of 215.5 mg corresponding to a loss of 2 mol of water per mol of chromium (one "crystal water" and one "complex-bound" water). The reddish violet product was dissolved in a minimum volume of water at room temperature, and the crystalline dithionate of the diol, compound **3**, was obtained by addition of a saturated solution of Na$_2$S$_2$O$_6$. A single crystal obtained in this way was used for the X-ray study of **3**. The results presented in Figure 2 show clearly that **3** is a diol with a $\Lambda\Lambda,\Delta\Delta$ configuration, just as that of the parent compound **2** (Figure 1).

Compound 3, *cis*-α-[Cr(pico)$_2$(OH)]$_2$(S$_2$O$_6$)$_2\cdot 2{}^1/{}_2$H$_2$O. The structure and dimensions of this complex are similar to those found in many other di-μ-OH–Cr(III) complexes.[5b] Therefore, all the positional and thermal parameters and the bond distances and angles are included in the Supplementary Material. Figure 2 shows the structure of the complex. With $Z = 8$ in the cell of space group *Pbca*, there is no crystallographic symmetry imposed upon the dinuclear ion. Each of the eight dimers in the cell consists of two *cis*-α-[Cr(pico)$_2$(OH)] units having the same chirality (Λ,Λ or Δ,Δ).

The 4+ charge of the dimer in the asymmetric unit is balanced by two S$_2$O$_6^{2-}$ anions which are involved in an extensive network of hydrogen bonds in the crystal that includes the bridging OH groups, the NH$_2$ groups, and the water molecules in the crystal.

The Cr(1)–Cr(2) separation in the complex is 3.024 (2) Å, the average Cr–O(H) distance is 1.948 (4) Å, and the average Cr–O(H)–Cr angle is 101.7 (2)°.

Olation of Compound 2a. Our attempts to prepare single crystals of compound **2a** suitable for an X-ray study, were unsuccessful. The microcrystalline product lost 2 mol of water per mol of chromium when heated in an oven at 140 °C for 3 h. The product was recrystallized from water. The violet product was identified by X-ray powder diagrams and absorption spectrum as the diol [(pico)$_2$Cr(OH)$_2$Cr(pico)$_2$](ClO$_4$)$_4$, which had been prepared earlier by a different procedure.[10]

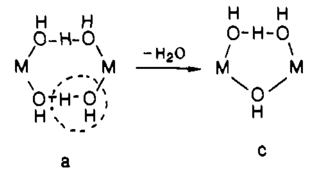
Discussion

All the cis hydroxoaqua–metal complexes, investigated so far, except compound **1** are dimers with two H$_3$O$_2$ bridging ligands between the metal atoms and undergo olation in a solid-state reaction to form the corresponding diols.

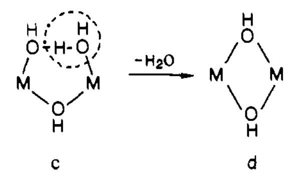
The existence of the same, so-called cis hydroxoaqua complex ion in two different configurations in compounds **1** and **2** (Figure 3 and 1) presents a unique opportunity to test the hypothesis, put forward in the introduction to this work, that *olation of a hydroxoaqua–metal complex in the solid state may take place if and only if it is a dimer.*

This hypothesis explains why compound **1**, a cis hydroxoaqua complex, does not olate (it is not a dimer) and *predicts* that compound **2** should olate if it has the "normal" dimeric structure. The results prove that it has and that it does. These conclusions, following directly from the structure of **2** (Figure 1), the occurrence of a reaction at 140 °C, and the structure of its product **3** (Figure 2), illustrate the predictive power of the hypothesis.

The Mechanism of Olation. The following mechanism of olation reactions in the solid state is proposed



(5)



(6)

This mechanism assumes an elimination of the first water molecule in reaction 5 by the breakdown of one H$_3$O$_2$ bridge and formation of a stable intermediate c, followed by a much faster second step of breaking the remaining H$_3$O$_2$ bridge and formation of the diol (reaction 6). This mechanism is similar to that of olation in solution which was established by Springborg.[4] An intermediate with the structure c, [en$_2$Ir(OH)(H$_3$O$_2$)Iren$_2$]$^{4+}$, was isolated from the inverse reaction 6 in aqueous solution.[4b] However, it does not necessarily follow that the detailed mechanisms of reaction 5 and 6 are the same in solution and in the solid state. It is assumed that reaction 5 is much slower than 6 (as it was shown to be in solution)[4] and that this is the reason why no accumulation of a detectable quantity of the intermediate c occurs in the olation process.

Each step of the proposed mechanism involves the breaking of one M–O bond and one strong hydrogen bond—hence the requirement of a considerable activation energy. A somewhat lower activation energy of reaction 6 may be expected due to the strained configuration of c. This strain is caused by a distortion of the H$_3$O$_2$ ligand from a skew configuration, with a torsional M–O$\cdots$O–M angle of $\sim$60°, which it has in cis dimers, to an almost planar configuration in c (torsional angle of 7.4°).[4b] This distortion is caused by the short M$\cdots$M separation of $\sim$3.8 Å[4b] which is imposed by the μ-(OH) bridge, compared to $\sim$5 Å in the dimers.[5] This mechanism dictates a steric course of olation in the solid state: if the dimer has a racemic $\Lambda\Lambda,\Delta\Delta$ configuration this configuration should be retained by the diol, and if it has a meso $\Lambda\Delta$ configuration—so should the diol derived from it. This prediction is corroborated in the case of compound **3** which retains the $\Lambda\Lambda,\Delta\Delta$ racemic configuration of **2** and may be verified, following additional experimental work, in other olation reactions by comparing the configuration of the dimers (reagents) with their diol products.

Finally, the proposed mechanism furnishes an answer to the key question of olation—why do cis isomers olate and trans isomers do not. An inspection of the chain structure b, characteristic of trans isomers, reveals that in order to convert a single μ-(H$_3$O$_2$) bridge to a single μ-(OH) bridge the separation between the two metal atoms of this bridge must be decreased from $\sim$5.7 to $\sim$3.8 Å. Such an operation may be carried out only if a second strong hydrogen bond is broken, in addition to the first strong hydrogen bond and the metal–oxygen bond which have to be broken in the case of the cis dimer. This requirement may substantially increase the total activation energy (bearing in mind that the very strong

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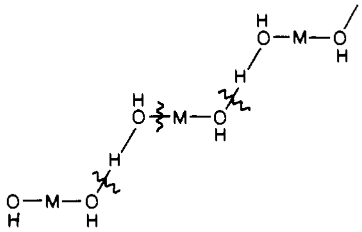
(10) Michelsen, K. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 429.



H bond has a bond energy of ~100 KJ).[5] Such an increase will prevent the olation of trans isomers at a temperature lower than the temperature at which total decomposition occurs (~250 °C).

Comparison and Correlation of Structure. The main difference between compounds **1** and **2** is in the way that the mononuclear hydroxoaqua species interact with each other. Structure **1** consists of chains of hydroxoaqua ions linked by a weaker, long [2.586 (6) Å], and asymmetric hydrogen bond between aqua and hydroxo ligands of neighboring chromium atoms (Figure 3).[7] The aqua and hydroxo ligands in this compound do *not* lose their identity and may be easily recognized by their very different Cr–O bond length [1.998 (5) and 1.926 (4) Å, respectively]. The two oxygen atoms of the hydroxo and aqua ligands of each chromium atom are also hydrogen bonded to two oxygen atoms of the dithionate counter ion as can be seen from Figure 3. This feature may account for the stabilization of this unusual hydroxoaqua structure in the crystalline state. Compound **1** provides the only example out of over 20 structures reported so far,[5] in which the hydroxo and aqua ligands of neighboring metal atoms do not merge into a symmetrical H_3O_2 ligand.

The replacement of the dithionate counter ion by iodide as in **2** is sufficient to change this unusual mode of interaction of $[Cr(pico)_2(H_2O)(OH)]^{2+}$ and convert it to a normal binuclear configuration with two $H_3O_2^-$ bridges.

The structure of the di-μ-$H_3O_2^-$ bridged dimer in **2** is similar to the one found in the iodide salt of *cis*-$[(bpy)_2Cr(H_3O_2)_2Cr(bpy)_2]^{4+}$.[5a,b] In both complexes the M–O···O–M bridges have torsional angles of an approximately gauche configuration as a result of the rigid double bridging system. From Table IV it can be seen that in **2** the two $H_3O_2^-$ bridges are not identical as in the bpy complex. The O···O separations are 2.50 (1) and 2.48 (1) Å and the torsional angles are 60.4° and 90.1°, respectively. In the bpy complex the O···O separation is shorter, 2.446 (5) Å, and the torsional angle is 64.9°. The distortion in **2** is probably the result of the difference in the hydrogen bonding to the $H_3O_2^-$ units or due to other lattice forces.

Acknowledgment. We are grateful to the Fund for Basic Research administered by the Israel Academy of Sciences and Humanities for financial support.

Supplementary Material Available: Tables of thermal parameters and positional parameters of hydrogen atoms of **2**, positional and thermal parameters and bond lengths and angles for **3** (9 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of the Reaction of the Bis(1,10-phenanthroline)copper(I) Ion with Hydrogen Peroxide in Aqueous Solution

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Abstract: Investigations of the reaction of the bis(1,10-phenanthroline)copper(I) ion, $Cu(phen)_2^+$, with hydrogen peroxide in the presence of a scavenger (RH = methanol, ethanol, 2-propanol, or formate ion) and of the reactions initiated by radiation-produced hydroxyl free radical, $OH^•$, in similar systems in the absence of H_2O_2 show that $OH^•$ is not formed by the $Cu(phen)_2^+ + H_2O_2$ reaction. The observed kinetics and stoichiometry of this reaction are interpreted in terms of a mechanism involving an intermediate, possibly a Cu–H_2O_2 complex, formed by reaction of $Cu(phen)_2^+$ with H_2O_2. The rate constant for the reaction of this intermediate with RH is smaller, by a factor of at least 10^4, than that for the reaction of $OH^•$ with RH.

The observation that cleavage of DNA is efficiently induced by treatment with 1,10-phenanthroline (phen), in the presence of H_2O_2, copper(II) ions, and various reducing agents[1-5] has stimulated interest in the mechanism of the reaction of $Cu(phen)_2^+$ with H_2O_2. It has usually been assumed[5-8] that the reactive intermediate is the hydroxyl free radical ($OH^•$), produced according to eq 1

$$Cu(phen)_2^+ + H_2O_2 \rightarrow Cu(phen)_2^{2+} + OH^• + OH^- \quad (1)$$

If $OH^•$ is involved, this should be apparent from the kinetics of the $Cu(phen)_2^+ + H_2O_2$ reaction, in the presence of an $OH^•$ scavenger, RH (e.g., an alcohol). Under these circumstances, generation of $OH^•$ by reaction 1 would be expected to lead to a chain reaction, because the free radical, $R^•$, produced by the scavenging reaction 2, is capable of reducing $Cu(phen)_2^{2+}$ by reaction 3 (where P is the oxidation product from $R^•$).

$$OH^• + RH \rightarrow R^• + H_2O \quad (2)$$

$$R^• + Cu(phen)_2^{2+} \rightarrow Cu(phen)_2^+ + P + H^+ \quad (3)$$

We recently investigated[9] the reaction of the aquacopper(I) ion with H_2O_2 with methanol as scavenger. In this case, reactions

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