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Chain-Structured *cis*-Hydroxoaquachromium(III) Complexes and Their Magnetic Properties

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Antiferromagnetic coupling between chromium(III) atoms was found to exist in two *cis*-hydroxoaquachromium(III) complexes, having a chain structure with μ-$H_3O_2^-$ bridges. Compound **1**, *trans*-$[Cr(Py)_2(H_3O_2)_2]Cl$ (Py = pyridine), consists of infinite chains of Cr(III) ions bridged by two $H_3O_2^-$ units with Cr···Cr and O···O separations of 5.2073(5) and 2.422(2) Å, respectively. Compound **2**, α-*cis*-$[Cr(bispicen)(H_3O_2)]I_2$ [bispicen = N,N′-bis(2-pyridylmethyl)-1,2-ethanediamine], consists of infinite chains of Cr(III) ions bridged by one $H_3O_2^-$ unit with Cr···Cr and O···O separations of 5.6328(6) and 2.428(5) Å, respectively. The exchange coupling constants, $J = -1.31$ cm^{-1} in **1** and $J = -0.47$ cm^{-1} in **2**, were obtained by magnetic susceptibility measurements between 2 and 81 K. These values indicate intrachain antiferromagnetic interactions, mediated by hydrogen bonding through μ-H_3O_2 bridges. Compound **1** crystallizes in the monoclinic space group $C2/c$ with $a = 9.967(1)$ Å, $b = 15.020(3)$ Å, $c = 9.909(2)$ Å, $\beta = 116.81(3)$°, and $Z = 4$. Compound **2** crystallizes in the monoclinic space group $C2/c$ with $a = 21.380(4)$ Å, $b = 9.793(1)$ Å, $c = 10.220(2)$ Å, $\beta = 116.69(2)$° and $Z = 4$.

Introduction

The hydroxo and aqua ligands of classical hydroxoaquametal complexes have been shown to lose their distinct identity by merging into an $H_3O_2^-$ bridging ligand. The OH^- and H_2O ligands of two neighboring metal atoms form this ligand by means of a very strong hydrogen bond (>100 kJ) which is both short (<2.5 Å) and symmetric.[2] *trans*-hydroxoaquametal complexes form infinite linear chains in which the metal atoms are linked to each other by single $H_3O_2^-$ ligands,[2b,c] while the *cis*-isomers form "dimers" in which two metal atoms are linked by *two* $H_3O_2^-$ ligands.[2a,c] The dimeric structure of the *cis*-isomers was shown to be essential for "olation" reactions in which the diols are formed by elimination of two water molecules from the corresponding hydroxoaquametal complexes at elevated temperatures (100−150 °C).[3] The dimeric structure of the *cis*-isomers was shown to persist in concentrated aqueous solutions.[4] The existence of an antiferromagnetic coupling between the pair of chromium(III) atoms in *cis*-isomers was first reported for α-*cis*-$[(pico)_2Cr(H_3O_2)_2Cr(pico)_2]I_4{\cdot}2H_2O$ and β-*cis*-$[(bispictn)Cr(H_3O_2)_2Cr(bispictn)]I_4{\cdot}4H_2O$[5] [pico = (2-picolylamine), bispictn = *N*,*N*′-bis(2-pyridylmethyl)-1,3-propanediamine]. This magnetic interaction was later shown to exist in other *cis*-dimers.[6] The existence of this interaction, despite the separation of about 5 Å between the Cr(III) centers,

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(1) (a) Erik Pedersen took part in the initial stage of the work reported here. This paper is dedicated to the memory of Erik Pedersen (1943−1992), whose important contributions to magnetochemistry were interrupted by his untimely death. (b) The Hebrew University of Jerusalem. (c) University of Copenhagen. (d) University of British Columbia.

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was ascribed to an H_3O_2- mediated coupling of the pair of chromium atoms.[5,6] Is a dinuclear structure necessary for antiferromagnetic coupling, or could there be an intrachain interaction in long chains of *cis*-hydroxoaquachromium(III) complexes? This was, until now, a hypothetical question because no chain structured *cis*-hydroxoaquametal complexes were ever reported.[7] We now report the existence of chain structures in two *cis*-hydroxoaquachromium Cr(III) complexes, in which the metal atoms are linked to each other by $H_3O_2^-$ ligands. Both compounds show antiferromagnetic coupling. This interaction suggests an intrachain rather than a "dimeric" interaction and is treated as such. We describe here the preparation, structure and magnetic properties of *trans*-[Cr(Py)$_2$H$_3$O$_2$)$_2$]Cl, **1**, and of α-*cis*-[Cr(bispicen)(H_3O_2)]I_2, **2** [Py = pyridine, bispicen = *N,N′*-bis(2-pyridylmethyl)-1,2-ethanediamine].

Experimental Section

Preparation of *trans*-[Cr(py)$_2$(H$_3$O$_2$)$_2$]Cl, 1. A powdered sample of *trans*-[Cr(py)$_2$(H_2O)$_2$(OH)$_2$]Cl was prepared by a literature procedure.[8] The grayish green dried precipitate was dissolved in dilute HCl to yield a solution of *trans*-[Cr(py)$_2$(H_2O)$_4$]$^{3+}$. Single crystals of **1** were formed in this solution by allowing pyridine vapor to diffuse into it. This was done by placing an aqueous solution of pyridine near this solution in a desiccator. Anal. Calcd for $C_{10}H_{16}ClCrN_2O_4$: C, 38.04; H, 5.11; N, 8.87. Found: C, 37.74; H, 5.19; N, 8.73.

Preparation of α-*cis*-[Cr(bispicen)(H$_3$O$_2$)]I$_2$, 2. α-*cis*-[Cr(bispicen)-Cl$_2$]Cl·3H_2O, prepared by a literature method[9] (0.30 g, 0.66 mmol), was suspended in water (3 mL), and a solution of sodium hydroxide (1 mL, 2 M) was added. The solution was slightly heated and then filtered. After cooling of the solution on ice, sodium iodide (0.7 g) was added and 1 M hydrochloric acid was added dropwise to ensure weak acid reaction. The red precipitate that separated was filtered off and washed with ethanol (96%). Yield: 0.34 g (88%). The compound was recrystallized from boiling water with a recovery of 53%. Anal. Calcd for $C_{14}H_{21}CrI_2N_4O_2$: C, 28.84; H, 3.63; Cr, 8.92; I, 43.52; N, 9.61. Found: C, 28.50; H, 3.70; Cr, 8.86; I, 43.10; N, 9.53. Electronic spectrum in 1 M NaCl (λ_{max}, nm; ϵ, M^{-1} cm^{-1}): 522, 84.6; 398, 59.2.

X-ray Crystallography. Intensity data for **1** and **2** were collected at 22 °C on a PW1100 Philips diffractometer. Mo Kα ($\lambda = 0.710\,69$ 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 24 reflections in the range of $12° < \theta < 16°$. Data were measured by using an $\omega-2\theta$ motion. Crystallographic data and other pertinent information are given in Table 1. Data were corrected for Lorentz and polarization effects. Intensity data of **2** were corrected for absorption using the empirical absorption program DIFABS, incorporated into TEXSAN. The heavy atom positions in **1** and **2** were obtained from a three-dimensional Patterson function. Structure refinement was carried out with the full-matrix least-squares program of TEXSAN.[10a] Structure **1** was refined in space group *C*2/*c* to convergence, using anisotropic thermal parameters for all non-hydrogen atoms.[10b] All the hydrogen atoms of the pyridine ligand were introduced in calculated positions using the riding model. The hydrogen atoms of the bridging H_3O_2 unit were located from the difference map and introduced in fixed positions, and their thermal parameters were refined. Structure **2** was refined in space group *C*2/*c* to convergence using anisotropic thermal parameters for all non-hydrogen atoms and isotropic ones for hydrogen atoms, all of which were located from the difference map.

Table 1. Crystallographic Data for *trans*-[Cr(Py)$_2$(H$_3$O$_2$)$_2$]Cl, **1**, and *β-cis*-[Cr(bispicen)(H$_3$O$_2$)]I$_2$, **2**

	compound	
	1	**2**
chem formula	$C_{10}H_{16}ClCrN_2O_4$	$C_{14}H_{21}CrI_2N_4O_2$
fw	315.70	583.14
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a, Å	9.967(1)	21.380(4)
b, Å	15.020(3)	9.793(1)
c, Å	9.909(2)	10.220(2)
β, deg	116.81(3)	116.69(2)
V, Å^3	1324(1)	1911.8(7)
Z	4	4
T, °C	22	22
λ, Å	0.710 69	0.710 69
ρ_{calcd}, g cm^{-3}	1.584	2.026
linear abs coeff, cm^{-1}	10.53	37.94
R[a]	0.033	0.032
*R*w[b]	0.048	0.046

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

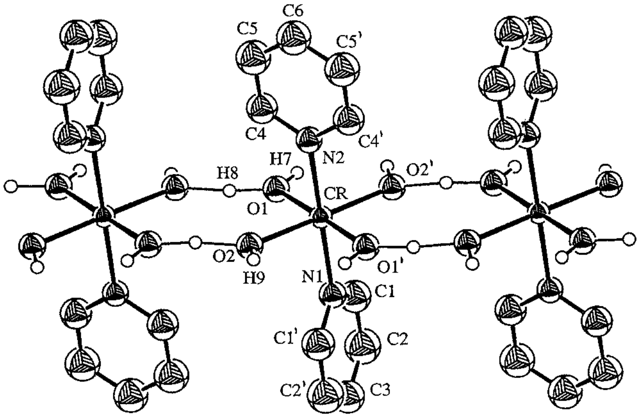

Figure 1. ORTEP drawing showing 50% probability ellipsoids and labeling scheme for a section of the infinite chain in *trans*-[Cr(Py)$_2$-(H$_3$O$_2$)$_2$]Cl, **1**.

Magnetic Susceptibilities. Magnetic susceptibilities of powdered samples were measured over the temperature range ~2 to ~82 K at an applied field of 9225 Oe using a PAR Model 155 vibrating-sample magnetometer as previously described.[11] Corrections were made for the background signal of the Kel-F sample holder over the entire temperature range studied. Magnetic susceptibilities were corrected for diamagnetism of all atoms (-183×10^{-6} cm^3 mol^{-1} for **1** and -300×10^{-6} cm^3 mol^{-1} for **2**).

Results and Discussion

Description of Structures. The positional parameters of the significant atoms in **1** are given in Table 2. Table 3 gives some important bond distances and angles in **1**, and Figure 1 shows a section of the polymeric chain and the numbering scheme. The structure of **1** consists of infinite chains of chromium(III) ions bridged by two $H_3O_2^-$ units and coordinated to two pyridine ligands. The chains propagate in the lattice parallel to the [1,0,1] vector. With $Z = 4$ in the cell of space group *C*2/*c*, there is only a half [Cr(py)$_2$(H$_3$O$_2$)$_2$]$^+$ unit in the asymmetric unit with Cr(1), N(1), N(2), C(3), and C(6) residing on a crystallographic 2-fold axis at 0, *y*, $^1/_4$. A crystallographic center of symmetry exists midway between the chromium atoms in the chain, and the Cr···Cr separation is 5.2073(5) Å. This distance is slightly longer than that found in discrete dinuclear *cis*-Cr(III) complexes with two $H_3O_2^-$ bridges.[2c] The O···O ($H_3O_2^-$) distance, 2.422(2) Å, falls within the range of 2.4−2.5 Å, found in other compounds containing bridging $H_3O_2^-$ ligands.[2c] The two crystallographically independent Cr−O($H_3O_2^-$) distances,

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(7) α-*cis*-[Cr(bispicen)(OH)(H_2O)]ClO$_4$·0.5H_2O was reported, by mistake, to have a chain structure (cf. ref 6b).

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Table 2. Positional Parameters of Significant Atoms in **1**

atom	*x*	*y*	*z*
Cr(1)	0	0.74746(6)	$^1/_4$
Cl(1)	$^1/_4$	$^1/_4$	$^1/_2$
O(1)	0.0515(2)	0.7459(2)	0.4647(2)
O(2)	0.2147(2)	0.7487(2)	0.3041(2)
N(1)	0	0.6069(3)	$^1/_4$
N(2)	0	0.8873(3)	$^1/_4$
C(1)	−0.0835(5)	0.5603(3)	0.2986(6)
C(2)	−0.0858(6)	0.4686(3)	0.3008(7)
C(3)	0	0.4213(4)	$^1/_4$
C(4)	0.0892(5)	0.9342(3)	0.3731(5)
C(5)	0.0910(6)	1.0259(3)	0.3767(6)
C(6)	0	1.0724(5)	$^1/_4$
H1(O1)	−0.0256	0.7459	0.4781
H2(O1)	0.1607	0.7442	0.5715
H1(O2)	0.2352	0.7552	0.2278

Table 3. Important Bond Distances (Å) and Angles (deg) in **1**[a]

	Distances		
Cr(1)−O(1)	1.951(2)	O(2)−H1(O2)	0.874(2)
Cr(1)−O(2)	1.958(2)	Cr(1)−Cr(1)′	5.2073(5)
Cr(1)−N(1)	2.112(5)	O(1)−O(2)′	2.422(3)
Cr(1)−N(2)	2.100(5)	Cl(1)−O(1)	3.179(2)
O(1)−H1(O1)	0.836(2)	Cl(1)−O(2)	3.188(2)
O(1)−H2(O1)	1.125(2)		
	Angles		
O(1)−Cr(1)−O(1)′	178.7(2)	O(2)−Cr(1)−N(1)	90.54(9)
O(1)−Cr(1)−O(2)	89.08(8)	O(2)−Cr(1)−N(2)	89.46(9)
O(1)−Cr(1)−O(2)′	90.93(8)	Cr(1)−O(1)−H1(O1)	111.3(2)
O(1)−Cr(1)−N(1)	89.3(1)	Cr(1)−O(1)−H2(O1)	133.9(2)
O(1)−Cr(1)−N(2)	90.7(1)	H(1O1)−O(1)−H2(O1)	114.8(2)
O(2)−Cr(1)−O(2)′	178.9(2)	Cr(1)−O(2)−H1(O2)	114.7(2)

Table 4. Positional Parameters of Significant Atoms in **2**

atom	*x*	*y*	*z*
I	0.11800(1)	0.20936(3)	0.26093(3)
Cr	0	0.62100(7)	$^1/_4$
O	−0.0041(1)	0.4796(2)	0.1130(3)
N(1)	0.1067(1)	0.6322(3)	0.3288(3)
N(2)	0.0048(2)	0.7787(3)	0.1179(3)
C(1)	0.1531(2)	0.5566(4)	0.4391(4)
C(2)	0.2224(2)	0.5463(5)	0.4693(6)
C(3)	0.2446(2)	0.6144(5)	0.3793(6)
C(4)	0.1981(2)	0.6947(5)	0.2664(6)
C(5)	0.1285(2)	0.7037(4)	0.2433(4)
C(6)	0.0757(2)	0.7879(4)	0.1237(4)
C(7)	−0.0166(2)	0.9068(4)	0.1671(4)
H1(O)	0.021(2)	0.412(5)	0.166(5)
H2(O)	0	$^1/_2$	0

Cr(1)−O(1) 1.951(2) Å and Cr(1)−O(2) 1.958(2) Å, are similar, indicating a nearly symmetric M−O···H···O−M system. The M−O···O−M ($H_3O_2^-$) torsional angle in the polymeric chain in **1** is 0° compared with an angle of ~60° in discrete *cis*-dinuclear complexes which adopt an unconstrained configuration.[2c] The 1+ charge of the $[Cr(py)_2(H_3O_2)]^+$ unit is balanced by a chloride anion residing on a crystallographic center of symmetry at $^1/_4$, $^1/_4$, $^1/_2$. The chloride ion which is coplanar with the CrO_4 system is hydrogen bonded to two H_3O_2 oxygen atoms of one complex and to an additional two H_3O_2 oxygen atoms from a neighboring chain with Cl(1)−O(1) and Cl(1)−O(2) distances of 3.179(2) and 3.188(2) Å, respectively.

Table 4 presents the atomic positional parameters of the significant atoms in **2**. Table 5 presents the essential bond distances and angles in **2**, and Figure 2 shows a section of the chain and the numbering scheme. The structure of **2** consists of infinite chains of chromium(III) ions bridged by one $H_3O_2^-$ unit and coordinated to the tetradentate bispicen ligand. The chains propagate in the lattice parallel to the [0,0,1] vector. With $Z = 4$ in the cell of space group *C*2/*c*, there is only a half $[Cr(bispicen)(H_3O_2)]^{2+}$ unit in the asymmetric unit with the chromium atom residing on a crystrallographic 2-fold axis at 0, *y*, $^1/_4$. A crystallographic center of symmetry exists midway between the two oxygen atoms of the $H_3O_2^-$ bridge with the central hydrogen atom residing on the center at 0, $^1/_2$, 0. The O···O ($H_3O_2^-$) distance, 2.428(5) Å, is very similar to that found in **1** and in other μ-H_3O_2-containing compounds.[2c] The Cr−O···H···O−Cr system in **2** is symmetrical with Cr−O($H_3O_2^-$) distance of 1.943(2) Å, M-O···O-M torsional angle of 180.0°, and Cr···Cr separation of 5.6328(6) Å. The torsional angle and M···M separation in **2** are very similar to those found in the inifite chain of *trans*-$[Co(en)_2(H_3O_2)](ClO_4)_2$ in which the two $H_3O_2^-$ bridges are in *trans* positions.[2b] The 2+ charge of the $[Cr(bispicen)(H_3O_2)]^{2+}$ unit is balanced by two iodide anions in the lattice which are hydrogen bonded to the $H_3O_2^-$ unit and NH groups of the bispicen ligand with I···O($H_3O_2^-$) and I···N-(H) distances of 3.544(2) and 3.573(3) Å, respectively.

Table 5. Important Bond Distances (Å) and Angles (deg) in **2**[a]

	Distances		
Cr−O	1.943(3)	O−H2(O)	1.214(2)
Cr−N(1)	2.053(3)	Cr−Cr′	5.6328(6)
Cr−N(2)	2.084(3)	O−O′	2.428(6)
O−H1(O)	0.87(5)		
	Angles		
O−Cr−O′	89.1(2)	N(1)−Cr−N(2)	81.1(1)
O−Cr−N(1)	90.2(1)	N(1)−Cr−N(2)′	94.3(1)
O−Cr−N(1)′	94.2(1)	N(2)−Cr−N(2)′	84.3(2)
O−Cr−N(2)	93.5(1)	Cr−O−H1(O)	106(3)
O−Cr−N(2)′	174.6(1)	Cr−O−H2(O)	124.7(2)
N(1)−Cr−N(1)′	173.9(2)	H1(O)−O−H2(O)	116(3)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

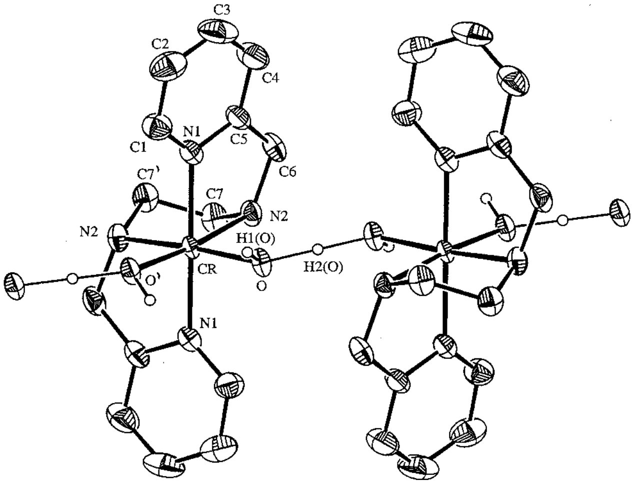

Figure 2. ORTEP drawing showing 50% probability ellipsoids and labeling scheme for a section of the infinite chain in α-*cis*-$[Cr(bispicen)_2(H_3O_2)]I_2$, **2**.

Magnetic Behavior of *trans*-$[Cr(py)_2(H_3O_2)_2]Cl_2$, 1, and α-*cis*-$[Cr(bispicen)(H_3O_2)]I_2$, 2. The magnetic properties of **1** and **2** between ~2 and ~81 K are shown in Figure 3. The magnetic moments range from 3.56 and 3.76 μ_B, respectively, at ~81 K to 1.16 and 1.93 μ_B, respectively, at ~2 K. Since temperature-independent moments are expected for octahedral chromium(III) ($^4A_{2g}$ ground state in O_h symmetry), these results suggest intrachain antiferromagnetic coupling between metal centers mediated by the bridging H_3O_2 groups in both compounds. The magnetic susceptibility versus temperature data for **1** (Figure 3) clearly show the presence of a susceptibility maximum at about 5 K. A susceptibility maximum is not seen for **2**, consistent with weaker exchange in this material. The susceptibility−temperature behavior of **1** below 5 K indicates

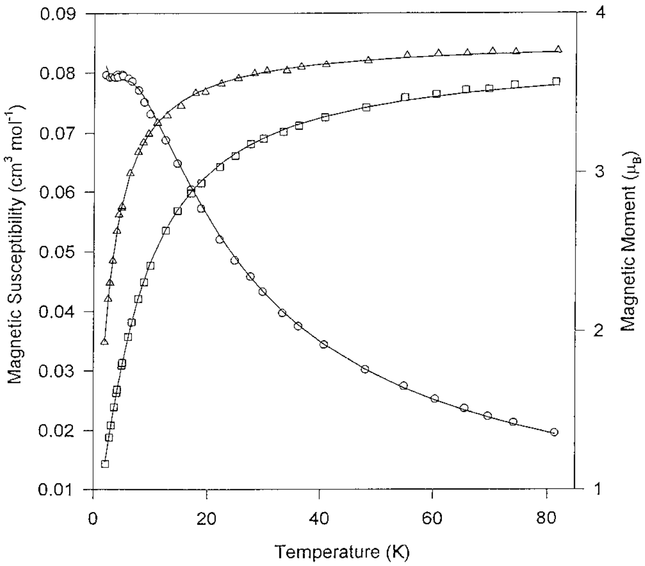

Figure 3. Magnetic susceptibility (circles) for **1** and magnetic moment (squares for **1** and triangles for **2**) versus temperature plots. Lines are calculated from theory as described in the text.

the presence of a small amount of paramagnetic impurity. The susceptibility data for both compounds were analyzed according to the scaling model for linear chains of Wagner and Friedberg.[12] The Hamiltonian is $H = -2J\sum_i s_j$,and the susceptibility is given by eq 1, where $U = \coth K - 1/K$, $K = 2JS(S + 1)kT$, $S = {}^3/_2$,

$$\chi_M = Ng^2\beta^2 S(S + 1)/3k[(1 + U)/(1 - U)] \qquad (1)$$

J is the exchange coupling constant, and the other terms have their usual meanings. To allow for the paramagnetic component, the calculated susceptibility, χ_{calc}, is obtained by combining the theoretical expression for the susceptibility (eq 1) with the Weiss term, $\chi_{para} = Ng^2\beta^2 S(S + 1)/3kT$, in the following way:

$$\chi_{calc} = (1 - P)\chi_M + P\chi_{para} \qquad (2)$$

The magnetic susceptibilities were fitted to [2] by allowing g, *J*, and *P* to vary. This gave the best-fit values of g, *J*, and *P* listed in Table 6. The function *F*, defined by eq 3 is minimized in the fitting procedure and provides a measure of agreement between the experimental data and the model. In eq 3 *n* is the number of data points and χ^i_{calc} and χ^i_{obs} are the calculated and observed molar magnetic susceptibilities. Values of *F* obtained

$$F = \left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\chi^i_{calc} - \chi^i_{obs}}{\chi^i_{obs}}\right)^2\right]^{1/2} \qquad (3)$$

for the best-fits for each compound are given in Table 6. Theoretical curves obtained with these best-fit parameter values are shown as solid lines in Figure 3.

Table 6. Magnetic Parameters for **1** and **2**

compd	*g*	*J* (cm⁻¹)	*P*	*F*
1	1.94	−1.31	0.018	0.0090
2	1.98	−0.47	0.027	0.0010

Significant magnetic exchange interactions between chromium(III) atoms bridged via H_3O_2 groups is of current interest,[5,6] particularly in view of the fact that the exchange is mediated by hydrogen-bonding interactions. Several binuclear chromium(III) complex cations which contain double H_3O_2 bridges have been studied structurally and magnetically.[6b] The O···O distances in five compounds listed in Table 8 of ref 6b are similar (range from 2.446 to 2.5 Å) and slightly longer compared to the distance of 2.422(2) Å in **1** and 2.428(5) Å in **2**. In comparing *J* values, it is necessary to take account of the differences in the Hamiltonian operators ($-2Js_is_j$ term in the model used here versus $+ Js_1s_2$ term in ref 6b). In both studies the observed sign of *J* reflects antiferromagnetic coupling. To use the magnitude of *J* values as a measure of relative strengths of exchange coupling, the values reported here should be doubled when compared with the *J* values in Table 8 of ref 6b (range from ~0 to 6.67 cm⁻¹). When this is done we see that the strength of exchange coupling in **1** and **2** is in the middle of the range found for the binuclear species. The weaker coupling observed in **2** compared with **1** is probably a consequence of the fact that in **2** the metal centers are bridged by single $H_3O_2^-$ group, whereas, in **1**, as in all other related Cr(III) complexes reported so far, the Cr centers are double bridged.[2] Furthermore, the Cr···Cr separation in **2** is much longer than in any of these complexes.[5,6]

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal parameters, intermolecular distances, and least-squares planes and a stereoview of the chains in **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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