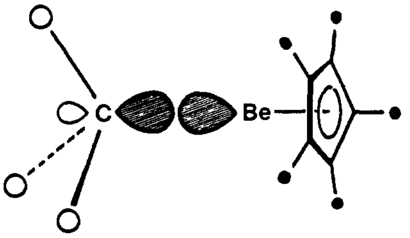
distance of 2.781 ± 0.006 Å in $(Me_5C_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$[9a] and is shorter than the average Yb—C(MeC≡CMe) distance of 2.85 ± 0.01 Å in $(Me_5C_5)_2Yb(MeC{\equiv}CMe)$.[9b] The hydrogen atoms on C(1), which were located and refined isotropically, are close to the ytterbium atom with an average Yb···H distance of 2.59 ± 0.08 Å which is identical with the closest Yb···H distance of 2.61 ± 0.02 Å found in $(Me_5C_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$.[9a] In addition the average YbCH angle is 69.6 ± 5.7°, the BeCH angle is 110.6 ± 4.7°, and the HCH angle is 108.3 ± 8.2°. The X-ray crystallographic data are consistent with the HOMO of $MeBe(C_5Me_5)$, shown below, acting as a σ-donor toward the Lewis acid $(Me_5C_5)_2Yb$. The geometry of the bridging methyl group is very similar to that found in $Li_4B_4(\mu\text{-}Me)_8(Me)_8$ by X-ray and neutron diffraction[11a] and perhaps in $(Me_5C_5)_4Lu_2(\mu\text{-}Me)(Me)$[11b] (though the hydrogen atoms were not located in the X-ray structure) though different from that found in $Cp_4Zr_2(\mu\text{-}Me)[OCH(CH_2CMe_3)]_2AlMe_2$ in which the Zr(μ-Me)Zr angle is ca. 148°.[11c]



In solution, the resonance in the ^1H NMR spectrum due to the briding methyl group is deshielded by 0.1 ppm relative to free $MeBe(C_5Me_5)$. The complex is undergoing rapid intermolecular chemical exchange to −70 °C.[10a]

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Supplementary Material Available: Tables of positional parameters, thermal parameters, and bond lengths and bond angles (8 pages). Ordering information is given on any current masthead page.

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Long-Distance Magnetic Exchange between Chromium(III) Atoms Bridged by $H_3O_2^-$ Ligands

Michael Ardon,*[1a] Avi Bino,*[1a] Kirsten Michelsen,*[1b] and Erik Pedersen*[1b]

Department of Inorganic and Analytical Chemistry
The Hebrew University of Jerusalem
91904 Jerusalem, Israel
Chemistry Department I, Inorganic Chemistry
H. C. Ørsted Institute, University of Copenhagen
DK-2100 Copenhagen, Denmark

Received March 26, 1987

We report an unexpected long distance antiferromagnetic coupling between chromium(III) atoms in hydroxoaqua complexes. It has recently[2,3] been established that the so-called hydroxoaqua complexes are not mononuclear in the solid state (and concentrated aqueous solution[2e,f]) as their classical formulation implies but binuclear or polynuclear: the hydroxo ligand of one metal atom merges with the aqua ligand of a neighboring metal atom to form an $H_3O_2^-$ bridging ligand, by means of a very strong hydrogen bond (2.4–2.5 Å).

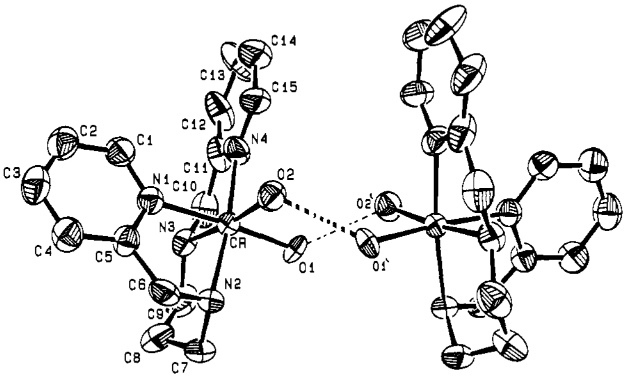

Figure 1. The structure of β-*cis*-$[(bispictn)Cr(H_3O_2)_2Cr(bispictn)]^{4+}$ as found in **2**. The O···H···O bonds in the $H_3O_2^-$ units are represented by the dashed lines.

Table I. Structural Data for **1** and **2**

compd	O–O($H_3O_2^-$), Å	M–O($H_3O_2^-$), Å	M–M, Å	M–O···O–M torsnl angle, deg
1[a]	2.50 (1)	1.932 (7)		60.4
	2.48 (1)	1.934 (7)	5.118 (2)	90.1
2[b]	2.472 (5)	1.906 (3)		
		1.961 (4)	4.797 (1)	

[a] Reference 3. [b] This work.

The present investigation was conducted on two chromium(III) "hydroxo–aqua" complexes whose structures were determined by single-crystal X-ray studies: **1**, α-*cis*-$[(pico)_2Cr(H_3O_2)_2Cr(pico)_2]I_4{\cdot}2H_2O$ [pico = (2-picolylamine), and **2**, β-*cis*-$[(bispictn)Cr(H_3O_2)_2Cr(bispictn)]I_4{\cdot}4H_2O$ [bispictn = *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine].[4a] Preparation and structure of **1** were reported elsewhere.[3] Structure **2** is presented in Figure 1.[4b] Some important distances and angles of **1** and **2** are listed in Table I. Both have a double-bridged dimeric structure with a Cr to Cr separation of 5.118 and 4.797 Å, respectively. This configuration is typical for most *cis*-hydroxoaqua complexes.[2d] The hydrogen bond of $H_3O_2^-$ in **1** and **2** is very short, as expected (Table I).

The magnetic susceptibilities of powdered samples of **1** and **2** in the temperature range 1.7–300 K were measured by the Faraday method at a field strength of 12 000 Oe. As an example, data for **2** are presented in Figure 2. The date exhibit a decreasing magnetic moment at low temperatures, which has been interpreted in terms of magnetic saturation at 13 kG combined with anti-

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(1) (a) The Hebrew University. (b) University of Copenhagen.

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(4) (a) Bispictn was prepared as reported earlier.[5b] Compound **2** was prepared by base hydrolysis of *cis*-β-$[Cr(bispictn)Cl_2]Cl{\cdot}2H_2O$ and precipitation with excess NaI. Recrystallization from water yielded orange-red crystals. *cis*-β-$[Cr(bispictn)Cl_2]Cl{\cdot}2H_2O$ was prepared by the same procedure employed for *cis*-α-$[Cr(bispictn)Cl_2]Cl{\cdot}3H_2O$.[5b] (b) Compound **2** is monoclinic, space group *P*2/*n* with a = 9.076 (1) Å, b = 10.714 (1) Å, c = 23.660 (3) Å, β = 96.03 (2)°, and Z = 2. The structure was refined by least-squares methods by using 2910 unique reflections with $I > 3\sigma(I)$ to a conventional R factor of 3.76%.

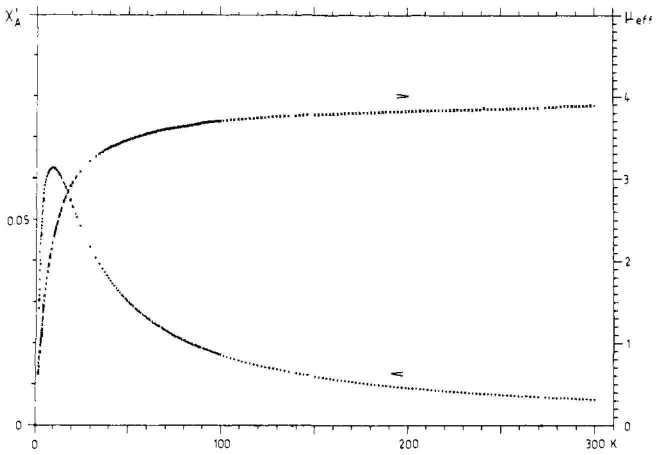

Figure 2. Magnetic susceptibilities in cgs units (left scale) and effective magnetic moments in Bohr magnetons (right scale) of **2**.

Table II. Results of Fitting Susceptibilities to Eq 1

	1	2	model
J, cm^{-1}	2.27 (1)	4.58 (1)	1
var/f	1.54	1.67	
f	237	227	
J, cm^{-1}	2.40 (2)	4.86 (3)	2
j, cm^{-1}	−0.036 (4)	−0.061 (5)	
var/f	1.13	1.01	
f	236	226	
E(1)	2.03 (3)	4.40 (3)	3
E(2)	6.86 (3)	13.84 (5)	
E(3)	13.6 (1)	28.3 (1)	
var/f	1.02	1.00	
f	235	225	

ferromagnetic coupling between the two nearest centers. The susceptibilities were fitted to the expression

$$\chi'_A(T) = -\frac{N}{2H}\,\frac{\sum_i \left[\frac{\partial E_i}{\partial H}\right]\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT} + K \qquad (1)$$

by minimization of

$$\sum_j \frac{[\chi^{\text{obsd}}(T_j) - \chi'_A(T_j)]^2}{\left[\sigma^2\{\chi(T_j)\} + \frac{\partial \chi^{\text{obsd}}}{\partial T}(T_j)\right]^2 \sigma^2(T_j)} \qquad (2)$$

In (1) E_i values are the energies of the sixteen components of the ground-state manifold obtained from an isotropic Zeeman term, $\beta g H{\cdot}S$, in the Hamiltonian by addition of exchange terms according to three different models. The Heisenberg-type Hamiltonian is

$$\hat{H} = J\hat{S}_1{\cdot}\hat{S}_2 - j(\hat{S}_1{\cdot}\hat{S}_2)^2 \qquad (3)$$

in which the triplet, quintet, and septet energies are $J + 6.5j$, $3J + 13.5j$, and $6J + 9j$, respectively. In the following (3) is referred to as model 2. If j is fixed to zero we call it model 1. A generalized Hamiltonian has the eigenvalues $E(S')$ at zero field where S' has the values 0–3 in this case with two spins of $^3/_2$. This is called model 3. The adjustable parameters in the fitting procedure are g, K, and J or J and j or $E(S')$ according to models 1–3, respectively. Other symbols in (1), (2), and (3) have their usual meaning.

The results of the data fittings are shown in Table II, apart from values of g and K which in both cases came out as slightly below 2.00 and as approximately zero, respectively. Also given in Table II, are the calculated variances per degree of freedom, var/f.

For both compounds models 2 and 3 fit the data well according to a V^2 test as seen from var/f and significantly better than model 1. But even model **1** with only one exchange parameter gives a fair description of the data.

In both **1** and **2** the exchange couplings are unexpectedly large in view of the Cr–Cr distances of 5.118 and 4.797 Å respectively, and the coupling constants are within the range observed for di-μ-hydroxo complexes of chromium.[6] There is no doubt that the O–H–O bridges act as exchange paths, although only weakly so. This is not surprising since for chromium(III) systems π-overlaps are known to be important for antiferromagnetic coupling, and hydrogen bonds are expected to be poor π-bond transmitters. To our knowledge these examples are the only ones known in which chromium(III) centers exhibit a fairly strong magnetic interaction via hydrogen bonds. Some related copper(II) systems having M–O–H–O–M structures[7] show fairly strong antiferromagnetic couplings due to σ-overlaps in which hydrogen bonds could be good σ-bond transmitters.

Structural and magnetic measurements will be conducted on other hydroxoaqua–chromium(III) complexes, in order to achieve a more precise location of the positions of the terminal hydrogen atoms of the $H_3O_2^-$ ligand. This will enable comparison of the coupling constants in terms of the Glerup–Hodgson–Pedersen model.[6]

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Registry No. 1, 106905-91-3; **2**, 109432-44-2.

Supplementary Material Available: Tables of atomic positional and thermal positional and thermal parameters for **2** (3 pages). Ordering information is given on any current masthead page.

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Asymmetric Hydrogenation of β-Keto Carboxylic Esters. A Practical, Purely Chemical Access to β-Hydroxy Esters in High Enantiomeric Purity

R. Noyori,* T. Ohkuma, and M. Kitamura

Department of Chemistry, Nagoya University
Chikusa, Nagoya 464, Japan

H. Takaya

Institute for Molecular Science
Myodaiji, Okazaki 444, Japan

N. Sayo, H. Kumobayashi, and S. Akutagawa*

R & D Institute, Takasago International Corporation
Kamata, Tokyo 144, Japan

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Optically active β-hydroxy carboxylic esters are an extremely important class of compounds for natural product synthesis. Access to such compounds has so far relied mainly on biological or biochemical transformations.[1] Asymmetric hydrogenation of the keto esters is an alternative complementary methodology, and the purely chemical means should allow even easier control of the chiral outcome at will, giving both antipodes with equal ease.