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Heteronuclear Trinuclear Complex Ions of the Types $[Cu^{II}\{Cr(A)_4(OH)_2\}_2]^{4+}$ and $[Cu^{II}\{Co(A)_4(OH)_2\}_2]^{4+}$

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The syntheses and characterization of a series of trinuclear complex ions of the types $[Cu^{II}\{Cr(A)_4(OH)_2\}_2]^{4+}$ and $[Cu^{II}\{Co(A)_4(OH)_2\}_2]^{4+}$, where $(A)_4$ represents the nitrogen donors from one tetradentate, two bidentate, or four monodentate ligands, are described. The complex $[Cu\{(OH)_2Cr(bispictn)\}_2](ClO_4)_4\cdot 2H_2O$ (**1a**), where bispictn is *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine, $C_{15}H_{20}N_4$, crystallizes in space group $P2_1/c$ of the monoclinic system with four trinuclear species in a cell of dimensions $a = 14.650$ (11) Å, $b = 14.226$ (8) Å, $c = 22.754$ (14) Å, and $\beta = 108.32$ (6)°. The structure has been refined to a final *R*-factor of 0.0534 based on 4825 observed independent reflections. The central copper(II) atom is bonded to the oxygen atoms of four bridging hydroxo groups and exhibits axial coordination to a perchlorate anion leading to approximate square pyramidal geometry. The hydroxo groups bridge, in pairs, to two chromium atoms. The complex $[Cu\{(OH)_2Cr(cyclam)\}_2](ClO_4)_4\cdot 4H_2O$ (**7a**), where cyclam is 1,4,8,11-tetraazacyclotetradecane, crystallizes in space group $P2_1/c$ of the monoclinic system with four trinuclear species in a cell of dimensions $a = 8.770$ (1) Å, $b = 20.791$ (3) Å, $c = 11.833$ (2) Å, and $\beta = 99.47$ (1)°. The structure has been refined to a final *R*-factor of 0.0593 based on 3415 observed independent reflections. The copper atom exhibits (4 + 2) axially elongated octahedral geometry, the in-plane ligands being the four oxygen atoms of the hydroxo bridges while the axial sites are occupied (at much longer distances) by the oxygen atoms of perchlorate anions. The hydroxo groups bridge, in pairs, to the two chromium atoms. Magnetic susceptibility data for both complexes indicate the presence of a ferromagnetic interaction between the central copper(II) ions and the chromium(III) centers, leading to an $S = {}^7/_2$ ground state.

Introduction

In a series of recent papers,[2–5] we have described briefly the ability of cations of the type *cis*-$[Cr(A)_4(OH)_2]^+$ and its cobalt(III) analogue (where $(A)_4$ represents four ligating nitrogen atoms from an appropriate number of tetradentate, bidentate, or monodentate ligands) to act as ligands to a variety of metal ions. This has allowed us to synthesize and characterize series of tetranuclear,[2,5] pentanuclear,[3] and trinuclear[4] complexes. Subsequently, other workers have characterized additional tetranuclear species,[6] and very recently an additional trinuclear species has been synthesized using this same methodology.[7]

The magnetic interactions in systems of those types are clearly of great interest. In those complexes where the ligands $(A)_4$ are very bulky, it can be expected that the heteronuclear complexes are magnetically isolated from each other, which might permit a detailed study of the intranuclear interactions in the absence of any significant interion interactions. In this paper we report the syntheses, structures, and magnetic properties of a variety of trinuclear species of the general formula $[Cu\{Cr(A)_4(OH)_2\}_2]^{4+}$.

Experimental Section

Absorption spectra were obtained on a Perkin-Elmer Lambda 17 spectrophotometer. The spectra are characterized by their absorption maxima (λ, ϵ), where λ is in nm and ϵ is in units of L mol^{-1} cm^{-1}. Diffuse reflectance spectra were obtained on a Perkin-Elmer Lambda 7 spectrophotometer. Magnetic susceptibility measurements were performed by the Faraday method in the temperature range 2–300 K at a field strength of 1.3 T using instrumentation described elsewhere.[8,9] The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants. The susceptibility measurements of compounds mixed with grease were performed in the following way: A weighed amount of the compound was mixed with exactly 10% (by weight) silicone grease (Dow Corning high-vacuum grease) dissolved in ether. When the ether had evaporated, the sample was weighed out. The susceptibility was corrected for the susceptibility of the grease; this minor correction is almost diamagnetic except at very low temperatures, where there is a small paramagnetic contribution. X-ray powder photographs were obtained on a Guinier camera using Cu Kα radiation and with a silicon standard. Copper, chromium, and cobalt analyses were performed on a Perkin-Elmer 403 atomic absorption spectrophotometer. Carbon, nitrogen, hydrogen, halogen, and sulfur analyses were performed at the microanalytical laboratory of the H. C. Ørsted Institute using standard procedures.

Syntheses of the Complexes. Reagents. The following starting materials were prepared according to literature methods: *cis*-β-$[Cr(bispictn)(OH)(H_2O)](ClO_4)_2\cdot 2H_2O$;[5] *cis*-$\beta$-$[Co(bispictn)(OH)(H_2O)](ClO_4)_2\cdot 2H_2O$;[5] *cis*-$[Cr(NH_3)_4(OH)(H_2O)](ClO_4)_2$;[5] *cis*-$[Cr(NH_3)_4(OH)(H_2O)]S_2O_6\cdot H_2O$;[10] *cis*-$[Cr(en)_2(OH)(H_2O)]S_2O_6\cdot 2H_2O$;[10] *cis*-$[Co(en)_2(OH)(H_2O)]S_2O_6\cdot 2H_2O$;[11] *cis*-$\alpha$-$[Cr(pico)_2(OH)(H_2O)]S_2O_6\cdot 2H_2O$[12] (pico = 2-picolylamine); *cis*-$[Cr(cyclam)(OH)(H_2O)]S_2O_6\cdot 3H_2O$.[13] *cis*-$[Cr(cyclam)(OH)(H_2O)](ClO_4)_2$ was obtained in a yield of 78% by starting from *cis*-$[Cr(cyclam)Cl_2]Cl$[13] and following the same procedure as described for *cis*-β-$[Cr(bispictn)(OH)(H_2O)](ClO_4)_2\cdot 2H_2O$.[5]

Warning! Several of the new complexes described here are perchlorate salts, all of which should be considered as potentially explosive.

In some cases, we have synthesized both perchlorate and dithionate salts of the same complex. Consequently, for convenience, in numbering

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[2] Hodgson, D. J.; Michelsen, K.; Pedersen, E.; Towle, D. K. *J. Chem. Soc., Chem. Commun.* **1988**, 426–428.

[3] Hodgson, D. J.; Michelsen, K.; Pedersen, E. *J. Chem. Soc., Chem. Commun.* **1988**, 1558–1559.

[4] Corbin, K. M.; Hodgson, D. J.; Lynn, M. H.; Michelsen, K.; Nielsen, K. M.; Pedersen, E. *Inorg. Chim. Acta* **1989**, *159*, 129–131.

[5] Hodgson, D. J.; Michelsen, K.; Pedersen, E.; Towle, D. K. *Inorg. Chem.* **1991**, *30*, 815–822.

[6] Müller, S.; Thewalt, U. *Z. Naturforsch* **1989**, *446*, 257–260.

[7] Zhong, Z. J.; Matsumoto, N.; Okawa, H.; Kida, S. *Inorg. Chem.* **1991**, *30*, 436–439.

[8] Pedersen, E. *Acta Chem. Scand.* **1972**, *26*, 333–342.

[9] Josephsen, J.; Pedersen, E. *Inorg. Chem.* **1977**, *16*, 2534–2538.

[10] Springborg, J.; Schäffer, C. *Inorg. Synth.* **1978**, *18*, 84.

[11] Springborg, J.; Schäffer, C. *Inorg. Synth.* **1973**, *14*, 74.

[12] Michelsen, K. *Acta Chem. Scand.* **1972**, *26*, 1517.

[13] Ferguson, J.; Tobe, M. L. *Inorg. Chim. Acta* **1970**, *4*, 109.

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Table I. Analytical Data for New Complexes of Cu^{II} with Bidentate Ligands of the Type $[Cr(A)_4(OH)_2]^+$ and $[Co(A)_4(OH)_2]^+$, Where $(A)_4$ Represents bispictn ($C_{15}H_{20}N_4$), Cyclam ($C_{10}H_{24}N_4$), 2 × pico ($C_6H_8N_2$), 2 × en, and 4 × Ammonia

		anal. (%): found (calcd)							
no.	compd	Cu	Cr/Co	C	H	N	Cl	S	% yield
1a	$[Cu\{(OH)_2Cr(C_{15}H_{20}N_4)\}_2](ClO_4)_4 \cdot 2H_2O$	5.50 (5.38)	8.76 (8.79)	30.21 (30.48)	3.71 (4.09)	9.42 (9.48)	11.08 (12.00)		52
2a	$[Cu\{(OH)_2Co(C_{15}H_{20}N_4)\}_2](ClO_4)_4 \cdot 3H_2O$	5.47 (5.23)	9.63 (9.71)	29.83 (29.68)	3.72 (4.15)	9.22 (9.23)	12.26 (11.68)		52
3b	$[Cu\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2 \cdot 2H_2O^a$	8.31 (8.73)	14.26 (14.28)			15.43 (15.39)		17.79 (17.61)	78
3a	$[Cu\{(OH)_2Cr(NH_3)_4\}_2](ClO_4)_4 \cdot 3H_2O^a$	8.63 (7.71)	12.66 (12.63)		3.69 (4.16)	13.64 (13.60)	16.78 (17.21)		53
4b	$[Cu\{(OH)_2Cr(C_2H_8N_2)_2\}_2](S_2O_6)_2 \cdot 2H_2O^a$	7.93 (7.64)	12.58 (12.50)	11.59 (11.55)	4.38 (4.84)	13.42 (13.46)		16.10 (15.41)	73
5b	$[Cu\{(OH)_2Co(C_2H_8N_2)_2\}_2](S_2O_6)_2 \cdot 3H_2O^a$	7.26 (7.35)	13.65 (13.64)	10.99 (11.12)	4.80 (4.90)	13.09 (12.97)		15.25 (14.84)	96
6b	$[Cu\{(OH)_2Cr(C_6H_8N_2)_2\}_2](S_2O_6)_2 \cdot 5H_2O^a$	6.03 (5.89)	9.65 (9.64)	27.04 (26.73)	4.32 (4.30)	10.16 (10.39)		12.20 (11.89)	50
7b	$[Cu\{(OH)_2Cr(C_{10}H_{24}N_4)\}_2](S_2O_6)_2 \cdot 4H_2O$	6.21 (6.18)	9.88 (10.11)	23.57 (23.35)	5.39 (5.88)	11.00 (10.39)		12.35 (12.47)	92
7a	$[Cu\{(OH)_2Cr(C_{10}H_{24}N_4)\}_2](ClO_4)_4 \cdot 4H_2O$	5.74 (5.74)	9.38 (9.40)	22.05 (21.72)	5.38 (5.49)	10.07 (10.13)	12.30 (12.82)		17

[a] In these compounds 1 or 2 mol of water may be complex-bound.

the complexes we designate all perchlorate complexes as "**a**" and all dithionate complexes as "**b**".

1. **$[Cu\{(OH)_2Cr(bispictn)\}_2](ClO_4)_4 \cdot 2H_2O$ (1a).** *cis*-*β*-$[Cr(bispictn)(OH)(H_2O)](ClO_4)_2 \cdot 2H_2O$ (174 mg, 0.300 mmol) was stirred with a solution of sodium hydroxide (3 mL, 0.1 M). The solution was filtered, and finely divided $CuSO_4 \cdot 5H_2O$ (25 mg, 0.10 mmol) was added. Two hours later, the blue-violet crystalline precipitate was filtered out and washed with sodium perchlorate solution (1 M) and ethanol (96%). Yield: 61 mg (52%). Analytical data for this and all other new compounds are presented in Table I.

2. **$[Cu\{(OH)_2Co(bispictn)\}_2](ClO_4)_4 \cdot 3H_2O$ (2a).** The complex was prepared exactly as above but from *cis*-*β*-$[Co(bispictn)(OH)(H_2O)](ClO_4)_2 \cdot 2H_2O$ (176 mg, 0.30 mmol). Yield: 63 mg (52%). The complex is isomorphous with **1a**.

3. **$[Cu\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2 \cdot 2H_2O$ (3b) and $[Cu\{(OH)_2Cr(NH_3)_4\}_2](ClO_4)_4 \cdot 3H_2O$ (3a).** *cis*-$[Cr(NH_3)_4(OH)(H_2O)]S_2O_6 \cdot H_2O$ (134 mg, 0.40 mmol) was stirred with a solution of sodium hydroxide (4 mL, 0.1 M). The solution was filtered, and finely divided $CuSO_4 \cdot 5H_2O$ (50 mg, 0.20 mmol) was added. The pink precipitate that separated after a few minutes was filtered out and washed with ethanol (50% and 96%). Yield: 114 mg (78%). The corresponding perchlorate was made analogously but from *cis*-$[Cr(NH_3)_4(OH)(H_2O)](ClO_4)_2$ (142 mg, 0.40 mmol). It was necessary to add sodium perchlorate to initiate the precipitation of the violet compound. Washing was performed as in **1**. Yield: 87 mg (53%).

4. **$[Cu\{(OH)_2Cr(en)_2\}_2](S_2O_6)_2 \cdot 2H_2O$ (4b).** The pink compound was prepared exactly as compound **3b** but from *cis*-$[Cr(en)_2(OH)(H_2O)]S_2O_6 \cdot 2H_2O$ (147 mg, 0.40 mmol). Yield: 121 mg (73%).

5. **$[Cu\{(OH)_2Co(en)_2\}_2](S_2O_6)_2 \cdot 3H_2O$ (5b).** The brownish red compound was prepared exactly as compound **3b** but from *cis*-$[Co(en)_2(OH)(H_2O)]S_2O_6$ (150 mg, 0.40 mmol). Yield: 166 mg (96%).

6. **$[Cu\{(OH)_2Cr(pico)_2\}_2](S_2O_6)_2 \cdot 5H_2O$ (6b).** The violet compound was prepared exactly as compound **3b** but from *cis*-*α*-$[Cr(pico)_2(OH)(H_2O)]S_2O_6 \cdot 2H_2O$ (200 mg, 0.40 mmol). Yield: 108 mg (50%).

7. **$[Cu\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2 \cdot 4H_2O$ (7b) and $[Cu\{(OH)_2Cr(cyclam)\}_2](ClO_4)_4 \cdot 4H_2O$ (7a).** The dithionate was prepared exactly as compound **3b** but from *cis*-$[Cr(cyclam)(OH)(H_2O)]S_2O_6 \cdot 3H_2O$ (200 mg, 0.40 mmol) and $CuCl_2 \cdot 2H_2O$ (34 mg, 0.20 mmol). Yield: 189 mg (92%). The corresponding perchlorate was made analogously but from *cis*-$[Cr(cyclam)(OH)(H_2O)](ClO_4)_2$ (194 mg, 0.40 mmol) and copper acetate hydrate (10 mg, 0.20 mmol). Large crystals separated after 2 days. Yield: 38 mg (17%). When $CuCl_2 \cdot 2H_2O$ was used as starting material, large blue-violet crystals of a corresponding mixed chloride–perchlorate separated out.

X-ray Structure Determinations. The structures were determined at room temperature (295 K) or at −100 °C on a Nicolet R3m/V diffractometer using Mo K*α* radiation and a graphite monochromator. Crystal data and experimental parameters are listed in Table II. The structures were solved by Patterson techniques and refined by full-matrix least-squares methods. All programs used were from the SHELXTL-PLUS system.[14]

$[Cu\{(OH)_2Cr(bispictn)\}_2](ClO_4)_4 \cdot 2H_2O$ (1a). The complex crystallizes as red-violet prisms in the space group $P2_1/c$ of the monoclinic system, with four trinuclear species in the unit cell.

Positions of the central copper atom and the two chromium atoms were determined from a Patterson map, and the remaining non-hydrogen atoms were located in successive difference Fourier maps. The hydrogen atoms belonging to the four bridging hydroxo groups were also located in difference Fourier maps; their positions were not refined. Hydrogen atoms in the ligand were observed in the Fourier maps, but their locations were calculated on the basis of reasonable geometry and assigned. Hydrogen atoms in the water molecules were not located. The structure was refined by least-squares methods to give final values of $R = 0.0534$, $R_w = 0.0696$, and $S = 1.0921$. The positional parameters of the non-hydrogen atoms, along with their standard deviations as estimated from the inverse matrix, are presented in Table III.

Table II. Crystallographic and Data Collection Parameters

	complex	
param	**1a**	**7a**
formula	$CuCr_2C_{30}H_{48}N_8O_{22}Cl_4$	$CuCr_2C_{20}H_{60}N_8O_{24}Cl_4$
system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	14.650 (11)	8.770 (1)
b (Å)	14.226 (8)	20.791 (3)
c (Å)	22.754 (14)	11.833 (2)
β (deg)	108.32 (6)	99.47 (1)
V (Å^3)	4502 (5)	2128 (5)
Z	4	2
T (°C)	22	−100
λ (Å)	0.710 73	0.710 73
μ (mm^{-1})	1.210	1.327
index ranges	$-16 \leq h \leq 16$	$0 \leq h \leq 11$
	$0 \leq k \leq 12$	$0 \leq k \leq 27$
	$0 \leq l \leq 25$	$-15 \leq l \leq 15$
no. of reflcns	10 134	4918
no. of obs reflcns	4825	3415
R^a	0.0534	0.0593
$R_w{}^b$	0.0696	0.0849

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

$[Cu\{(OH)_2Cr(cyclam)\}_2](ClO_4)_4 \cdot 4H_2O$ (7a). The complex crystallizes as prisms in the space group $P2_1/c$ of the monoclinic system, with two trinuclear species in the unit cell.

Positions of the central copper atom, the one independent chromium atom, the bridging oxygen atoms, and all the ligand C and N atoms were determined from a Patterson map, and the remaining non-hydrogen atoms were located in successive difference Fourier maps. Hydrogen atoms in the ligand were placed in calculated positions on the basis of reasonable geometry (C–H = 0.96 Å). Hydrogen atoms in the water molecules and on the hydroxyl bridges were not located. The structure was refined by least-squares methods to give final values of $R = 0.0596$, $R_w = 0.0849$, and $S = 1.8423$. The final difference Fourier map showed a peak of approximately 1.16 e Å^{-3}, which was located 0.84 Å from the chlorine atom of one of the perchlorate anions. It is possible that this peak is the result of some partial occupancy of this site by chloride ion, i.e. that the salt is a mixed chloride–perchlorate, but the successful refinement of all perchlorate groups suggests that this partial occupancy must be very low. The positional parameters of the non-hydrogen atoms, along with their standard deviations as estimated from the inverse matrix, are presented in Table IV. Hydrogen atom positional parameters and anisotropic thermal parameters for both structures are available as supplementary material.

Results and Discussion

Synthesis. As was noted above, when the divalent metal ions Mg(II), Mn(II), Co(II), Ni(II), and Zn(II) react with the dithionates or perchlorates of *cis*-$[Cr(A)_4(OH)(H_2O)]^{2+}$ in a

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[14] Sheldrick, G. M. *SHELXTL-PLUS Crystallographic System*, version 2; Nicolet XRD Corp.: Madison, WI, 1987.

Table III. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **1a**

	x	*y*	*z*	*U*(eq)[a]
Cu	6984 (1)	8221 (1)	1103 (1)	32 (1)
Cr(1)	8981 (1)	8707 (1)	1700 (1)	31 (1)
Cr(2)	4980 (1)	7663 (1)	776 (1)	28 (1)
O(1)	7764 (3)	9315 (3)	1368 (2)	33 (1)
O(2)	8211 (3)	7635 (3)	1412 (2)	40 (2)
O(3)	6213 (3)	7111 (3)	889 (2)	38 (2)
O(4)	5732 (3)	8789 (3)	874 (2)	34 (1)
Cl(1)	7143 (1)	8120 (2)	−473 (1)	55 (1)
O(11)	7033 (4)	8610 (4)	40 (2)	70 (2)
O(12)	7942 (6)	7550 (8)	−258 (4)	135 (5)
O(13)	7232 (7)	8727 (6)	−910 (3)	122 (4)
O(14)	6348 (5)	7511 (5)	−715 (3)	90 (3)
Cl(2)	3713 (1)	5179 (1)	2759 (1)	47 (1)
O(21)	3009 (4)	5607 (5)	2977 (3)	69 (2)
O(22)	4590 (4)	5156 (5)	3253 (3)	75 (2)
O(23)	3803 (5)	5654 (6)	2252 (3)	96 (3)
O(24)	3408 (5)	4241 (6)	2624 (4)	98 (3)
Cl(3)	2451 (2)	−26 (2)	2934 (1)	70 (1)
O(31)	1640 (6)	−267 (8)	3105 (5)	128 (5)
O(32)	2258 (8)	−213 (9)	2335 (4)	153 (5)
O(33)	3146 (7)	−696 (10)	3233 (4)	166 (6)
O(34)	2822 (10)	757 (8)	3189 (6)	184 (8)
Cl(4)	1316 (2)	7183 (3)	−316 (1)	97 (1)
O(41)	2172 (6)	6952 (8)	94 (5)	147 (5)
O(42)	563 (6)	6855 (11)	−197 (5)	187 (8)
O(43)	1346 (11)	7248 (13)	−893 (5)	229 (9)
O(44)	1302 (15)	8163 (12)	−110 (10)	265 (14)
N(1A)	8856 (4)	8616 (4)	2559 (2)	40 (2)
N(1B)	10280 (4)	8030 (4)	1908 (3)	44 (2)
N(1C)	4997 (4)	7663 (4)	1673 (2)	36 (2)
N(1D)	4308 (3)	6398 (4)	570 (2)	36 (2)
N(2A)	9718 (4)	9891 (4)	2094 (3)	43 (2)
N(2B)	9205 (4)	8842 (5)	861 (2)	45 (2)
N(2C)	3726 (4)	8376 (4)	673 (3)	40 (2)
N(2D)	4751 (4)	7669 (4)	−158 (2)	41 (2)
C(2A)	9072 (5)	9398 (6)	2893 (3)	48 (3)
C(3A)	8975 (6)	9440 (8)	3474 (4)	73 (4)
C(4A)	8654 (7)	8672 (9)	3700 (4)	81 (4)
C(5A)	8437 (6)	7905 (8)	3352 (4)	70 (4)
C(6A)	8529 (5)	7884 (6)	2786 (3)	51 (3)
C(7A)	9361 (5)	10214 (6)	2587 (3)	54 (3)
C(8A)	9777 (6)	10670 (6)	1680 (4)	62 (3)
C(9A)	10119 (6)	10337 (7)	1158 (4)	75 (4)
C(2B)	10575 (5)	7862 (5)	1429 (4)	49 (3)
C(3B)	11418 (5)	7441 (6)	1477 (5)	62 (4)
C(4B)	12005 (5)	7210 (6)	2060 (5)	66 (4)
C(5B)	11730 (5)	7418 (6)	2560 (4)	60 (3)
C(6B)	10845 (4)	7812 (5)	2473 (3)	46 (3)
C(7B)	9897 (6)	8152 (7)	812 (4)	70 (4)
C(8B)	9375 (6)	9784 (7)	666 (4)	66 (3)
C(2C)	4339 (5)	8182 (6)	1795 (3)	45 (3)
C(3C)	4284 (7)	8267 (7)	2381 (4)	71 (4)
C(4C)	4941 (8)	7801 (8)	2853 (4)	84 (4)
C(5C)	5615 (7)	7242 (7)	2728 (3)	69 (3)
C(6C)	5622 (5)	7206 (6)	2131 (3)	49 (3)
C(7C)	3689 (5)	8720 (5)	1277 (3)	48 (3)
C(8C)	3499 (6)	9164 (6)	227 (4)	63 (3)
C(9C)	3463 (6)	8857 (7)	−417 (4)	70 (4)
C(2D)	4065 (5)	6136 (5)	−22 (3)	46 (3)
C(3D)	3688 (7)	5278 (6)	−223 (4)	68 (4)
C(4D)	3516 (7)	4686 (7)	195 (4)	78 (4)
C(5D)	3755 (7)	4934 (6)	809 (5)	71 (4)
C(6D)	4128 (5)	5790 (5)	967 (3)	50 (3)
C(7D)	4208 (6)	6838 (6)	−463 (3)	62 (3)
C(8D)	4386 (6)	8534 (6)	−482 (3)	62 (3)
O(1W)	1191 (6)	962 (5)	3977 (4)	108 (4)
O(2W)	645 (15)	291 (13)	4916 (7)	266 (12)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

slightly alkaline medium, trinuclear[4] or tetranuclear[2,5] complexes are formed. In the case of Cu(II), however, only trinuclear species have been obtained.

Table IV. Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **7a**

	x	*y*	*z*	*U*(eq)[a]
Cu(1)	0	0	0	23 (1)
Cr(1)	2003 (1)	794 (1)	1713 (1)	29 (1)
O(1)	−6 (4)	819 (2)	750 (3)	31 (1)
O(2)	2005 (4)	−45 (2)	972 (3)	34 (1)
N(1)	3119 (5)	1238 (2)	502 (4)	44 (2)
N(2)	1799 (6)	1735 (3)	2266 (4)	55 (2)
N(8)	1148 (5)	433 (3)	3132 (3)	45 (2)
N(11)	4118 (5)	583 (3)	2719 (4)	66 (2)
C(2)	3302 (9)	1931 (3)	745 (6)	71 (3)
C(3)	1958 (10)	2159 (3)	1262 (7)	73 (3)
C(5)	366 (8)	1884 (3)	2764 (7)	72 (3)
C(6)	278 (8)	1485 (4)	3814 (6)	67 (3)
C(7)	−110 (7)	801 (3)	3550 (5)	56 (2)
C(9)	2463 (8)	271 (5)	4072 (5)	82 (3)
C(10)	3800 (8)	65 (5)	3543 (6)	86 (3)
C(12)	5404 (6)	364 (5)	2129 (5)	73 (3)
C(13)	5798 (7)	858 (5)	1265 (6)	80 (3)
C(14)	4562 (7)	936 (4)	233 (5)	60 (2)
Cl(1)	8594 (3)	−1003 (1)	2576 (1)	66 (1)
O(3)	8532 (5)	−468 (2)	1803 (3)	60 (2)
O(4)	10058 (11)	−1012 (5)	3292 (6)	168 (5)
O(5)	8374 (11)	−1555 (3)	1910 (5)	137 (4)
O(6)	7528 (12)	−945 (4)	3271 (6)	161 (5)
Cl(2)	5899 (2)	1810 (1)	4660 (2)	80 (1)
O(7)	6628 (6)	1221 (4)	4528 (6)	107 (3)
O(8)	6660 (14)	2122 (6)	5575 (8)	70 (4)
O(9)	6109 (31)	2129 (7)	3618 (12)	174 (11)
O(10)	4299 (10)	1717 (8)	4497 (16)	124 (10)
O(11)	4849 (20)	2076 (8)	3862 (14)	58 (6)
O(12)	4884 (36)	1633 (15)	5608 (20)	162 (14)
O(13)	6694 (33)	2444 (17)	5133 (30)	148 (14)
O(3W)	1689 (12)	8190 (5)	279 (10)	181 (6)
O(2W)	3094 (26)	8796 (8)	2331 (11)	92 (8)
O(1W)	2057 (25)	8580 (7)	1751 (36)	272 (19)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Spectra. The electronic spectra of the complexes are presented in Table V. As is shown in Figure 1 for the perchlorate salt of $[Cu\{(OH)_2Cr(cyclam)\}_2]^{4+}$, the spectra are dominated by the two spin-allowed chromium(III) bands in the regions 505–550 and 365–375 nm. The difference observed between the spectra of the dithionates and those of the corresponding perchlorates are presumably the result of coordination of the perchlorate ligand to the copper(II) center in the latter cases.

Description of the Structures. $[Cu\{(OH)_2Cr(bispictn)\}_2](ClO_4)_4 \cdot 2H_2O$ (1a). The central copper atom is bonded to the oxygen atoms of four bridging hydroxo groups and exhibits axial coordination to a perchlorate anion leading to approximate square pyramidal geometry. The axial Cu–O bond of 2.503 Å indicates tight anion coordination and can be compared with values of 2.52–2.68 Å normally associated with tight perchlorate binding in axially elongated d^9 copper(II) complexes;[15,16] weakly bound perchlorate ions are found to have Cu–O bond lengths in excess of 2.7 Å.[15,17] The hydroxo groups bridge, in pairs, to two chromium atoms, so the complex can be viewed as consisting of two *cis*-$[Cr(bispictn)(OH)_2]^+$ units which act as bidentate ligands to the central copper atom. Each chromium atom is in a roughly octahedral environment, being bonded to two oxygen atoms from the bridging hydroxo groups and four nitrogen atoms from the ligands. A view of the complex is presented as Figure 2. The bond lengths and angles are listed in Tables VI and VII, respectively.

As is the case with other bis(μ-hydroxo)dicopper(II) complexes,[18] the bond angles O–Cu–O corresponding to oxygen atoms which bridge to the same chromium atom are acute, while those

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(15) Lewis, D. L.; Hodgson, D. J. *Inorg. Chem.* **1974**, *13*, 143–147 and references therein.

(16) Lewis, D. L.; McGregor, K. T.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1974**, *13*, 1013–1019.

(17) Lewis, D. L.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1974**, *13*, 147–152.

(18) Hodgson, D. J. *J. Mol. Catal.* **1984**, *23*, 219–233 and references therein.

Table V. Absorption Spectra (Vis Region) and Diffuse Reflectance Spectral Data (in nm) for Complexes of Cu^{II} with Bidentate Ligands of the Type $[(Cr(A)_4(OH)_2]^+$, Where $(A)_4$ Represents bispictn ($C_{15}H_{20}N_4$), Cyclam ($C_{10}H_{24}N_4$), 2 × pico ($C_6H_8N_2$), 2 × en, and 4 × Ammonia

		N-methylformamide		diff refl spectrum	
no.	compd	λ_1 (ϵ_1)	λ_2 (ϵ_2)	λ_1	λ_2
1a	$[Cu\{(OH)_2Cr(C_{15}H_{20}N_4)\}_2](ClO_4)_4\cdot 2H_2O$	512.5 (165)	374 (175)	505	370
3a	$[Cu\{(OH)_2Cr(NH_3)_4\}_2](ClO_4)_4\cdot 3H_2O^a$	512 (107)	376 (101)	516	376
7a	$[Cu\{(OH)_2Cr(C_{10}H_{24}N_4)\}_2](ClO_4)_4\cdot 4H_2O$	522 (241)	371 (149)	524	374
3b	$[Cu\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2\cdot 2H_2O^a$			505	375
4b	$[Cu\{(OH)_2Cr(C_2H_8N_2)_2\}_2](S_2O_6)_2\cdot 2H_2O^a$			520	368
6b	$[Cu\{(OH)_2Cr(C_6H_8N_2)_2\}_2](S_2O_6)_2\cdot 5H_2O^a$			548	368
7b	$[Cu\{(OH)_2Cr(C_{10}H_{24}N_4)\}_2](S_2O_6)_2\cdot 4H_2O$			512	367

[a] In these compounds 1 or 2 mol of water may be complex-bound.

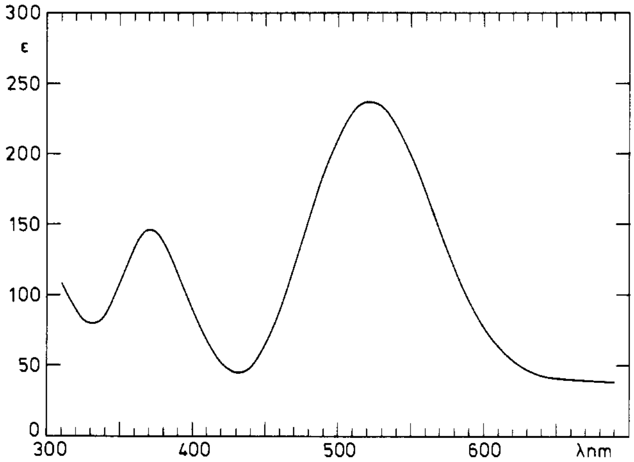

Figure 1. Electronic absorption spectrum of $[Cu\{(OH)_2Cr(cyclam)\}_2](ClO_4)_4\cdot 4H_2O$ in *N*-methylformamide. The spectra of complexes with other ligands are substantially similar, although in some cases the high-energy band is less well resolved than in the spectrum presented here.

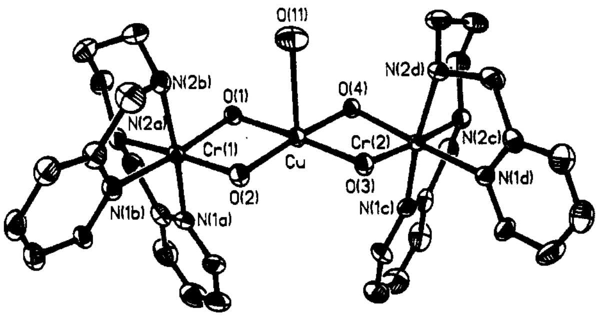

Figure 2. View of the cation in the structure of $[Cu\{(OH)_2Cr(bispictn)\}_2](ClO_4)_4\cdot 2H_2O$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids here and in other figures are at the 30% probability level.

Table VI. Selected Bond Lengths (Å) in **1a**

Cu–Cr(1)	2.895 (2)	Cu–Cr(2)	2.903 (2)
Cu–O(1)	1.912 (4)	Cu–O(2)	1.903 (4)
Cu–O(3)	1.912 (4)	Cu–O(4)	1.921 (4)
Cr(1)–O(1)	1.911 (4)	Cr(1)–O(2)	1.887 (4)
Cr(1)–N(1A)	2.024 (5)	Cr(1)–N(1B)	2.051 (5)
Cr(1)–N(2A)	2.050 (5)	Cr(1)–N(2B)	2.045 (5)
Cr(2)–O(3)	1.912 (4)	Cr(2)–O(4)	1.916 (4)
Cr(2)–N(1C)	2.033 (5)	Cr(2)–N(1D)	2.036 (5)
Cr(2)–N(2C)	2.046 (5)	Cr(2)–N(2D)	2.044 (5)

Table VII. Selected Bond Angles (deg) in **1a**

Cr(2)–Cu–Cr(1)	167.6 (1)	O(2)–Cu–O(1)	80.7 (2)
O(3)–Cu–O(1)	176.6 (2)	O(3)–Cu–O(2)	98.4 (2)
O(4)–Cu–O(1)	99.6 (2)	O(4)–Cu–O(2)	174.0 (2)
O(4)–Cu–O(3)	80.9 (2)	O(2)–Cr(1)–O(1)	81.2 (2)
N(1A)–Cr(1)–O(2)	93.4 (2)	N(1A)–Cr(1)–O(1)	93.2 (2)
N(1B)–Cr(1)–O(1)	170.6 (2)	N(1B)–Cr(1)–O(2)	96.4 (2)
N(1B)–Cr(1)–N(1A)	96.1 (2)	N(2A)–Cr(1)–O(2)	172.5 (2)
N(2A)–Cr(1)–O(1)	95.7 (2)	N(2A)–Cr(1)–N(1B)	87.8 (2)
N(2A)–Cr(1)–N(1A)	79.9 (2)	N(2B)–Cr(1)–O(1)	89.5 (2)
N(2B)–Cr(1)–O(2)	90.3 (2)	N(2B)–Cr(1)–N(1A)	175.7 (2)
N(2B)–Cr(1)–N(1B)	81.4 (2)	N(2B)–Cr(1)–N(2A)	96.5 (2)
O(4)–Cr(2)–O(3)	81.0 (2)	N(1C)–Cr(2)–O(4)	93.3 (2)
N(1C)–Cr(2)–O(3)	98.8 (2)	N(1D)–Cr(2)–O(3)	92.1 (2)
N(1D)–Cr(2)–O(4)	170.1 (2)	N(1D)–Cr(2)–N(1C)	94.8 (2)
N(2C)–Cr(2)–O(4)	93.5 (2)	N(2C)–Cr(2)–O(3)	174.5 (2)
N(2C)–Cr(2)–N(1D)	93.4 (2)	N(2C)–Cr(2)–N(1C)	80.9 (2)
N(2D)–Cr(2)–O(3)	88.9 (2)	N(2D)–Cr(2)–O(4)	91.1 (2)
N(2D)–Cr(2)–N(1C)	171.7 (2)	N(2D)–Cr(2)–N(1D)	81.6 (2)
N(2D)–Cr(2)–N(2C)	91.8 (2)	Cr(1)–O(1)–Cu	98.4 (2)
Cr(1)–O(2)–Cu	99.6 (2)	Cr(2)–O(3)–Cu	98.8 (2)
Cr(2)–O(4)–Cu	98.3 (2)		

which correspond to oxygen atoms bridging to different chromium atoms are obtuse. The angles are as follows: O(1)–Cu–O(2) = 80.7 (2)°; O(2)–Cu–O(3) = 98.4 (2)°; O(3)–Cu–O(4) = 80.9 (2)°; O(4)–Cu–O(1) = 99.6 (2)°. The bridging Cu–O–Cr angles are in the range 98.3 (2)–99.6 (2)°, with an average value of 98.8 (6)°. In the only bis(μ-hydroxo)copper(II)chromium(III) complex whose structure has been reported,[7] the Cu–O–Cr bridging angles are 100.2 (2) and 100.4 (2)°. The present angles are within the broad ranges of 97.6–104.1° and 95.6–104.1° found in bis(μ-hydroxo) complexes of chromium(III)[19] and copper(II),[18] respectively, but must be considered to be smaller than the majority of such angles. This result would be expected to have a major impact on the magnetic properties of the complex (vide infra).

The copper–chromium separations are 2.895 (1) and 2.913 (1) Å; these values are considerably smaller than the Cr–Cr separations of 3.02–3.06 Å normally found in bis(μ-hydroxo)dichromium(III) complexes[19] and are slightly shorter than the value of 2.989 (2) Å recently reported[7] for a bis(μ-hydroxo)copper(II)chromium(III) complex. The Cu–O bond lengths are in the range 1.903 (4)–1.921 (4) Å, with an average of 1.912 (7) Å, again comparable to those in copper(II) dimers.[18] The Cr–O bonds are apparently nearly symmetric, falling in the range of 1.887 (4)–1.916 (4) Å, with an average of 1.906 (13) Å; three of these four bonds are virtually equal, with values of 1.911 (4)–1.916 (4) Å [average, 1.913 (3) Å], but the fourth is apparently significantly shorter; these average values are all at the lower extreme of the range 1.91–1.980 Å reported for bis(μ-hydroxo)dichromium(III) complexes.[19] It is certainly surprising that the Cr–O distances in the present trinuclear species are very different from those in purely chromium(III) analogues, while the Cu–O distances appear to be normal for copper(II) dimers. Similarly, the Cu–Cr separation is not an averaged value of the related Cu–Cu and Cr–Cr distances but is similar to Cu–Cu distances in dimeric copper(II) systems.

The perchlorate anions are remarkably free from disorder; all were treated as ordered species, although there is some evidence in a final difference Fourier for the presence of slight disorder associated with Cl(4). Cl–O bond lengths range from 1.294 (8)

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(19) Hodgson, D. J. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., et al., Eds.; Reidel: Dordrecht, The Netherlands, 1985; pp 497–522 and references therein.

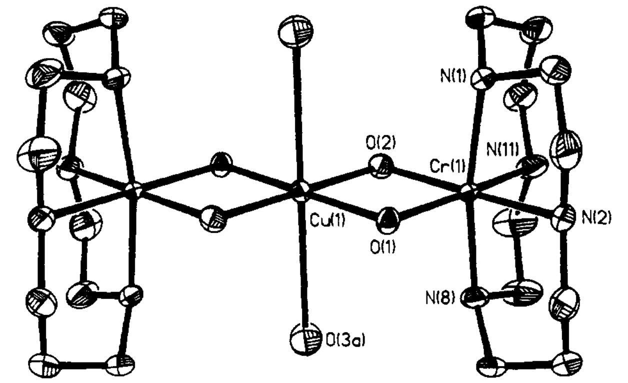

Figure 3. View of the cation in the structure of $[Cu\{(OH)_2Cr(cyclam)\}_2](ClO_4)_4{\cdot}4H_2O$. Hydrogen atoms are omitted for clarity.

Table VIII. Bond Lengths (Å) in **7a**

Cu(1)–Cr(1)	2.958 (1)	Cu(1)–O(1)	1.921 (3)
Cu(1)–O(2)	1.939 (3)	Cr(1)–O(1)	1.936 (3)
Cr(1)–O(2)	1.954 (4)	Cr(1)–N(1)	2.080 (5)
Cr(1)–N(2)	2.079 (5)	Cr(1)–N(8)	2.088 (5)
Cr(1)–N(11)	2.080 (4)	N(1)–C(2)	1.472 (9)
N(1)–C(14)	1.494 (8)	N(2)–C(3)	1.504 (9)
N(2)–C(5)	1.506 (10)	N(8)–C(7)	1.492 (8)
N(8)–C(9)	1.503 (7)	N(11)–C(10)	1.509 (11)
N(11)–C(12)	1.492 (8)	C(2)–C(3)	1.492 (12)
C(5)–C(6)	1.507 (11)	C(6)–C(7)	1.483 (10)
C(9)–C(10)	1.480 (11)	C(12)–C(13)	1.528 (12)
C(13)–C(14)	1.502 (8)	Cl(1)–O(3)	1.437 (5)
Cl(1)–O(4)	1.417 (9)	Cl(1)–O(5)	1.387 (6)
Cl(1)–O(6)	1.349 (10)	Cl(2)–O(7)	1.403 (7)
Cl(2)–O(8)	1.341 (10)	Cl(2)–O(9)	1.438 (16)
Cl(2)–O(10)	1.398 (9)	Cl(2)–O(11)	1.326 (16)
Cl(2)–O(12)	1.585 (30)	Cl(2)–O(13)	1.552 (34)

Table IX. Selected Bond Angles (deg) in **7a**

O(1)–Cu(1)–O(2)	80.8 (1)	O(1)–Cu(1)–O(2A)	99.2 (1)
O(1)–Cr(1)–O(2)	80.1 (1)	O(1)–Cr(1)–N(1)	93.9 (2)
O(2)–Cr(1)–N(1)	93.0 (2)	O(1)–Cr(1)–N(2)	92.5 (2)
O(2)–Cr(1)–N(2)	171.2 (2)	N(1)–Cr(1)–N(2)	82.7 (2)
O(2)–Cr(1)–N(8)	94.0 (2)	O(2)–Cr(1)–N(8)	93.8 (2)
N(1)–Cr(1)–N(8)	170.3 (2)	N(2)–Cr(1)–N(8)	91.4 (2)
O(1)–Cr(1)–N(11)	169.3 (2)	O(2)–Cr(1)–N(11)	90.1 (2)
N(1)–Cr(1)–N(11)	90.7 (2)	N(2)–Cr(1)–N(11)	97.7 (2)
N(8)–Cr(1)–N(11)	82.4 (2)	Cu(1)–O(1)–Cr(1)	100.2 (1)
Cu(1)–O(2)–Cr(1)	98.9 (1)		

to 1.473 (17) Å. These values are entirely consistent with those in other recent determinations.[20–22]

$[Cu\{(OH)_2Cr(cyclam)\}_2](ClO_4)_4{\cdot}4H_2O$ (7a). The central copper atom sits on a crystallographic inversion center which relates half of the molecule to the other. The copper atom exhibits (4 + 2) axially elongated octahedral geometry, the in-plane ligands being the four oxygen atoms of the hydroxo bridges while the axial sites are occupied (at much longer distances) by the oxygen atoms of perchlorate anions. In the present case, these axial distances are 2.838 (3) Å, which is in the range that has sometimes been referred to as "semicoordination".[15,17] As in the structure of **1a** above, the hydroxo groups bridge, in pairs, to the two chromium atoms. Each chromium atom is in a roughly octahedral environment, again being bonded to two oxygen atoms from the bridging hydroxo groups and four nitrogen atoms from the ligands. A view of the complex is presented as Figure 3. The bond lengths and angles are listed in Tables VIII and IX, respectively.

As was noted above for **1a**, the internal O–Cu–O angles are acute, the value of 80.8 (1)° falling within the range found in complex **1a**. The Cu–O–Cr angles of 98.9 (1) and 100.2 (1)° are slightly larger than those in **1a** and are closer to the values reported for the bis(μ-hydroxo)copper(II)chromium(III) complex reported earlier.[7] The Cu–Cr separation of 2.958 (1) Å is again longer than the values in **1a** and more nearly approximates the value of 2.989 (2) Å in the copper–chromium dimer.[7] The Cu–O bond lengths of 1.921 (3) and 1.939 (3) Å and the Cr–O distances 1.936 (3) and 1.954 (4) Å are unremarkable; the Cr–O bonds here are significantly longer than those in **1** and fall more nearly in the middle of the range observed for bis(μ-hydroxo)dichromium(III) complexes.[19]

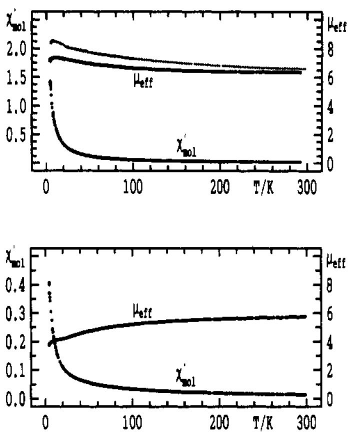

Figure 4. (a) Top: Magnetic susceptibility (left scale) and effective magnetic moment (right scale) of the cyclam complex **7a**. The dashed line represents the data obtained in the absence of silicone grease (see text). The data are consistent with a ferromagnetic interaction between Cu and Cr. (b) Bottom: Magnetic susceptibility (left scale) and effective magnetic moment (right scale) of the perchlorate salt of the ammine complex **3a**. The observed data may also be accounted for by invoking a ferromagnetic interction between Cu and Cr (see text).

The coordinated perchlorate anion is ordered in the structure, but the other [centered on Cl(2)] exhibits rotational disorder around the Cl(2)–O(7) bond; this kind of disorder around a *pseudo*-3-fold axis is relatively common in structural studies of perchlorate ions.[21,22]

Magnetic Properties. The temperature dependence of the magnetic susceptibility and the effective magnetic moment for the cyclam complex **7a** are shown in Figure 4a. The effective magnetic moment of **7a** at room temperature is approximately 6.4 μ_B, increasing monotonically to a value of approximately 7.2 μ_B at 4.5 K. This latter value is slightly lower than that of $\sqrt{63}$ μ_B anticipated (assuming $g = 2$) for the spin-only moment of a complex with an octet ground state ($S = {}^7/_2$) but is much higher than that of $\sqrt{35}$ μB calculated for a sextet ($S = {}^5/_2$) ground state. Hence, we can deduce that the ground state in the present complex has $S = {}^7/_2$, which is the maximum possible value for a complex containing one Cu(II) ($S = {}^1/_2$) and two Cr(III) ($S = {}^3/_2$) ions. Consequently, the magnetic interaction between the chromium(III) and copper(II) centers is ferromagnetic. A similar result was obtained by other workers for a related system.[7]

It is noteworthy that the present results were obtained by fixing the sample in silicone grease, which hardens at low temperatures. The dashed line in figure 4 represents the data obtained in the absence of such treatment and appears to show a higher effective magnetic moment. The reason for this anomaly is that at low temperatures ferromagnetic interactions will cause the individual crystallites within the sample to reorient in the magnetic field if they are not rigidly fixed. A similar result was noted in our recent study of manganese(III) complexes of cyclam,[23] another system with significant zero-field splitting. It may be that the higher effective magnetic moment reported by Zhong et al.[7] in their related complex results from such a reorientation effect.

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(20) Goodson, P. A.; Glerup, J.; Hodgson, D. J.; Michelsen, K.; Pedersen, E. *Inorg. Chem.* **1990**, *29*, 503–508.

(21) Oki, A. R.; Glerup, J.; Hodgson, D. J. *Inorg. Chem.* **1990**, *29*, 2435–2441.

(22) Hodgson, D. J.; Zeitlow, M. H.; Pedersen, E.; Toftlund, H. *Inorg. Chim. Acta* **1988**, *149*, 111–117.

(23) Daugherty, P. A.; Glerup, J.; Goodson, P. A.; Hodgson, D. J.; Michelsen, K. *Acta Chem. Scand.* **1991**, *45*, 244–253.

The temperature dependence of the magnetic susceptibility was approximated by the expression

$$\chi_{\mathrm{mol(exp)}} \simeq \chi_{\mathrm{mol(calc)}} = -\frac{N}{H}\,\frac{\sum_i \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K + C/T$$

by minimization of the function

$$\sum_T \frac{[\chi'_{\mathrm{mol(exp)}}(T) - \chi'_{\mathrm{mol(calc)}}(T)]^2}{\sigma^2(\chi') + \left(\frac{\partial\chi}{\partial T}\right)^2\sigma^2(T)}$$

within the framework of regression analysis. The term C/T accounts for the presence of small quantities of (presumably monomeric) paramagnetic impurities, while K accounts for temperature independent paramagnetism (TIP) and for any minor deviations in the corrections for the diamagnetism of the atoms. The energies E_i of the various components of the ground-state manifold were obtained using the Hamiltonian operator

$$H = J(\hat{S}_a\cdot\hat{S}_b + \hat{S}_b\cdot\hat{S}_c) + J'\hat{S}_a\cdot\hat{S}_c$$

where atoms a and c are the exterior Cr(III) atoms and b is the central Cu(II) ion. Hence, the first term corresponds to the interactions between Cu(II) and Cr(III), assumed by symmetry to be identical, while the second term accounts for the interaction between the two Cr(III) centers. Note that with the present choice of signs in the Hamiltonian, *positive* values of J and/or J' imply *antiferromagnetic* interactions, while *negative* values result from *ferromagnetic* interactions.

Attempts to fit the data using this model and allowing J, J', and g to all vary lead to instability. In principle, of course, each state has a different g value corresponding to a different linear combination of g_{Cr} and g_{Cu}, but we have forced a single, isotropic g value on the system. The best fit leads to a value of -50 cm^{-1} (ferromagnetic) for the Cu–Cr interaction J with a small antiferromagnetic (positive) value for the Cr–Cr interaction J'.

The magnetic properties of the bispictn and en complexes (**1a** and **5b**) and the dithionate salt of the ammine complex (**3b**) are qualitatively similar to those of **7a**, also exhibiting ferromagnetic interactions and $S = {}^7/_2$ ground states. As is shown in Figure 4b, however, the perchlorate salt of the ammine complex **3a** exhibits different magnetic properties. The effective magnetic moment of this salt at room temperature is 5.7 μ_B, as expected for three (noninteracting) metal centers with $S = {}^3/_2, {}^3/_2$, and ${}^1/_2$; the theoretical value is $\sqrt{33}$, or 5.74 μ_B. The effective magnetic moment declines with decreasing temperature to a value of 3.8 μ_B at 4.5 K; this value is very similar to that of $\sqrt{15}$, or 3.87 μ_B, expected for an $S = {}^3/_2$ ground state.

The energies of the available states can be described by the parameters $E(S,S')$, where S is the total spin of the trinuclear system and S' represents the spin state of the contribution from the two chromium(III) centers. Thus, S' can have values of 3, 2, 1, and 0 and S is $S' \pm {}^1/_2$. The energies of these seven terms are readily calculated from the Hamiltonian expression above, using the formula

$$E(S,S') = {}^1/_2J[S(S+1) - S_b(S_b+1) - S'(S'+1)] + {}^1/_2J'[S'(S'+1) - S_a(S_a+1) - S_c(S_c+1)]$$

leading to relative energies of

$$E({}^7/_2,3) = {}^7/_2J + 6J'$$

$$E({}^5/_2,2) = 3J + 3J'$$

$$E({}^3/_2,1) = {}^5/_2J + J'$$

$$E({}^1/_2,0) = 2J + 0$$

$$E({}^1/_2,1) = J + J'$$

$$E({}^3/_2,2) = J/2 + 3J'$$

$$E({}^5/_2,3) = 0 + 6J'$$

For the perchlorate salt of the ammine complex **3a**, we observe an $S = {}^3/_2$ ground state whose energy must correspond to either $E({}^3/_2,2)$ or $E({}^3/_2,1)$. If J' is assumed to be positive, i.e. the interaction between the two external chromium centers is assumed to be antiferromagnetic, the state $({}^3/_2,2)$ will be the ground state if $4J' > J > 6J'$; this implies, of course, that J is the same sign (positive) as J' and, hence, that the interaction between the copper(II) and chromium(III) centers must also be antiferromagnetic. The state $({}^3/_2,1)$ will be the ground state if $-4J' < J < -2J'$; i.e. the sign of J is negative and the interaction between the copper(II) and chromium(III) centers must be ferromagnetic. Hence, the apparently markedly different magnetic properties for **3a** may simply arise from an accidental set of values of the magnitudes of J and J' that lead to an $S = {}^3/_2$ ground state despite the continued presence of a ferromagnetic interaction between the copper and chromium centers and a smaller antiferromagnetic interaction between the two chromium centers in all cases.

If we look at the magnetic interactions on the basis of the structures as seen in the Figures 2 and 3, it is seen that the cations can be described as consisting of two halves each of which is a bis(μ-hydroxo) complex (a "diol"). The magnetic interactions in copper(II) diols,[24,25] chromium(III) diols,[26] and in mixed copper(II)/vanadium(IV) diols[27] have been discussed before; in the chromium(III) case, this has led to the development of the GHP model.[26]

In the GHP model, two kinds of interaction are discussed, i.e. a π–π and a σ–π interaction. In the d^3–d^3 case, the π–π interaction gives rise to an antiferromagnetic coupling because it is an interaction between two half-filled π orbitals, while the σ–π interaction gives rise to a ferromagnetic coupling because it is an interaction between an empty σ orbital and a half-filled π orbital. However, in the present chromium(III)/copper(II) cases the π–π interaction is between the half-filled π orbitals on chromium(III) and the *filled* π orbitals on copper(II). The result is a *ferromagnetic* interaction because the charge-transfer levels which mix with the ground levels all have the same spin multiplicity. The σ–π interaction between the filled d_{z^2} orbital on copper(II) and the half-filled d_{xy} orbital on chromium(III) also gives rise to a ferromagnetic coupling. There is no possible magnetic interaction between the chromium d_{yz} orbital and the half-filled $d_{x^2-y^2}$ on copper because these orbitals have different symmetries.[24] The interaction between the two chromium atoms, even though they are far apart, can have a significant interaction as we have

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(24) Charlot, M. F.; Jeannin, S.; Jeannin, Y.; Kahn, O.; Lucrece-Abaul, J. *Inorg. Chem.* **1979**, *18*, 1675–1681.

(25) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884–4899.

(26) Glerup, J.; Hodgson, D. J.; Pedersen, E. *Acta Chem. Scand.* **1983**, *A37*, 161–164.

(27) Kahn, O.; Galy, J.; Journaux, Y.; Jaud, J.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 2165–2176.

shown elsewhere.[28] To conclude, we anticipate that the chromium–copper interactions in these diol structures will be ferromagnetic, which is also what we observe. For the complex **3a**, which in Figure 4 is shown to exhibit an overall antiferromagnetic interaction, we have shown above that this is possible within certain limits of the two coupling constants.

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Supplementary Material Available: Tables S1 and S2 (hydrogen atom parameters for **1a** and **7a**) and Tables S3 and S4 (anisotropic thermal parameters for **1a** and **7a**) (8 pages). Ordering information is given on any current masthead page.

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(28) Glerup, J.; Hazell, A.; Michelsen, K. *Acta Chem. Scand.* **1991**, *45*, 1025–1031.