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Heteronuclear Trinuclear Complex Ions of the Type $[M^{II}\{Cr(A)_4(OH)_2\}_2]^{4+}$

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The syntheses and characterization of a series of trinuclear complex ions of the types $[M^{II}\{Cr(A)_4(OH)_2\}_2]^{4+}$, where $(A)_4$ represents four ligating nitrogen atoms, are described. The zinc(II)/chromium(III) complex $[Zn\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2 \cdot 2.5H_2O$ (**5h**), 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 $a = 15.719$ (12) Å, $b = 16.805$ (15) Å, $c = 16.800$ (10) Å, and $\beta = 116.86$ (5)°. The structure has been refined to a final R factor of 0.065 based on 3472 observed independent reflections. The central zinc(II) atom is bonded to the oxygen atoms of four bridging hydroxo groups and exhibits axial coordination to a dithionate anion leading to approximate square pyramidal geometry. The axial Zn–O bond of 2.217 Å indicates strong anion coordination. The hydroxo groups bridge, in pairs, to two chromium atoms, so the complex can be viewed as consisting of two *cis*-$[Cr(cyclam)(OH)_2]^+$ units which act as bidentate ligands on the central zinc atom. Each chromium atom is in a roughly octahedral environment, bonded to two oxygen atoms from the bridging hydroxo groups and four nitrogen atoms from the ligands. The manganese(II)/chromium(III) complex $[Mn\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2 \cdot 0.5H_2O$ (**2g**), where pico is (2-pyridylmethyl)amine, crystallizes in space group $C2/c$ of the monoclinic system with four trinuclear species in a cell of dimensions $a = 16.969$ (3) Å, $b = 14.587$ (1) Å, $c = 17.014$ (1) Å, and $\beta = 99.13$ (1)°. The structure has been refined to a final R factor of 0.037 based on 1849 observed independent reflections. The cobalt analogue, $[Co\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2 \cdot 0.5H_2O$ (**3g**) is isomorphous with the manganese complex, with cell constants $a = 16.968$ (7) Å, $b = 14.490$ (3) Å, $c = 16.996$ (3) Å, and $\beta = 98.76$ (2)°, and has been refined to a final R factor of 0.069 based on 1183 observed independent reflections. The central metal atom sits on a crystallographic inversion center which relates one half of the molecule to the other. The central Mn or Co atom exhibits approximate octahedral geometry, being bonded to four terminal water molecules and two hydroxo bridges. Hence, in the present cases, each of the chromium complexes is linked to the central metal by only a single hydroxo bridge. The bridging Mn–O–Cr and Co–O–Cr angles are 134.3 (2) and 135.2 (5)°, respectively. The magnetic susceptibility data for the complexes demonstrate that the "open-form" μ-hydroxo complexes **2g** and **3g** and their analogues exhibit antiferromagnetic interactions while the "closed-form" bis(μ-hydroxo) cyclam complexes with paramagnetic central metal ions either are weakly ferromagnetic or exhibit no magnetic interaction. The zinc cyclam complex **5h** exhibits a weak antiferromagnetic interaction between the two chromium(III) centers.

Introduction

In recent papers,[2–6] we have described briefly the ability of cations of the type *cis*-$[Cr(A)_4(OH)_2]^+$ (where $(A)_4$ represents four ligating nitrogen atoms from an appropriate number of tetradentate, bidentate, or monodentate ligands) to act as ligands toward a variety of metal ions and have demonstrated the synthesis and isolation of series of trinuclear[4,6] complexes. Subsequently, other workers have characterized an additional, related trinuclear species using this same methodology.[7] We here report a new kind of trimeric complex of this type, in which the central metal is able to serve as a diamagnetic insulator between the two paramagnetic chromium centers.

While most of the polynuclear complexes isolated by this technique involve bis(μ-hydroxo) bridges from the central metal to the two (or more) exterior metals, in one previous communication[4] we described the existence of "open-form" μ-hydroxo species in which the *cis*-$[Cr(A)_4(OH)_2]^+$ complex acts as a monodentate rather than as a bidentate ligand. In the present paper, we provide additional information concerning the synthesis and properties of these "open-form" complexes.

Experimental Section

The diffuse reflectance spectra were obtained on a Perkin-Elmer Lambda 7 reflectance 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. X-ray powder photographs were obtained on a Guinier camera using Cu Kα radiation and with a silicon standard. Metal 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. The following compounds were prepared according to procedures described in the literature: *cis*-$[Cr(NH_3)_4(OH)(H_2O)](S_2O_6)$,[10] *cis*-$[Cr(en)_2(OH)(H_2O)](S_2O_6)$,[10] *cis*-$[Co(en)_2(OH)(H_2O)](S_2O_6)$,[11] *cis*-$\alpha$-$[Cr(pico)_2(OH)(H_2O)](S_2O_6) \cdot 2H_2O$,[12] and *cis*-$[Cr(cyclam)(OH)(H_2O)](S_2O_6) \cdot 3H_2O$.[13]

Stock Solutions. Solution C. Five solutions containing 0.9 mmol of *cis*-$[Cr(NH_3)_4(OH)_2]^+$ were prepared by the following procedure: *cis*-

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Table I. Analytical Data for Dithionate Salts of Complex Ions of M^{II} with the Ligand $[Cr(NH_3)_4(OH)_2]^+$ [a]

		anal. found (calcd), %				
no.	compound	M^{II}	M^{III}	N	S	yield, %
1c	$[Mg(H_2O)_2\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2\cdot H_2O$		14.58 (14.71)	15.77 (15.85)		33
2c	$[Mn(H_2O)_2\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2\cdot H_2O$	7.34 (7.45)	14.13 (14.10)	15.28 (15.19)	17.46 (17.39)	75
3c	$[Co(H_2O)_2\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2\cdot H_2O$	7.85 (7.95)	13.99 (14.02)	15.15 (15.11)	16.10 (17.29)	81
3c′	$[Co(H_2O)_2\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2\cdot 4H_2O$	7.41 (7.41)	13.33 (13.07)	14.06 (14.09)	15.45 (16.12)	67
4c	$[Ni(H_2O)_2\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2\cdot 2H_2O$	7.86 (7.73)	13.61 (13.70)	14.53 (14.76)		40
4c′	$[Ni(H_2O)_2\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2\cdot 4H_2O$	7.41 (7.38)	13.00 (13.08)	14.05 (14.09)		80
5c	$[Zn(H_2O)_2\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2\cdot H_2O$		13.95 (13.90)	15.15 (14.98)	16.92 (17.17)	76

[a] The ligand is assumed to behave as a bidentate ligand. M^{II} = Mg^{II}, Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II}. Compounds **1c**, **2c**, **3c**, and **5c** form an isomorphous series. Compounds **3c′** and **4c′** constitute another isomorphous series.

Table II. Analytical Data for Dithionate Salts of Complex Ions of M^{II} with the Ligands $[Cr(en)_2(OH)_2]^+$ and $[Co(en)_2(OH)_2]^+$ [a]

		anal. found (calcd), %						
no.	compound	M^{II}	Cr^{III}	C	H	N	S	yield, %
1e	$[Mg(H_2O)_2\{(OH)Cr(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 4H_2O$		12.07 (12.02)	10.77 (11.11)	5.35 (5.58)	12.96 (12.95)	14.92 14.82	46
2e	$[Mn(H_2O)_2\{(OH)Cr(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 4H_2O$	6.16 (6.13)	11.64 (11.61)	10.61 (10.73)	5.08 (5.40)	12.58 (12.51)	14.38 (14.32)	56
3e	$[Co(H_2O)_2\{(OH)Cr(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 3H_2O$	6.77 (6.68)	11.80 (11.80)	10.82 (10.90)	5.14 (5.26)	12.71 (12.71)	14.46 (14.55)	69
4e	$[Ni(H_2O)_2\{(OH)Cr(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 4H_2O$	6.64 (6.53)	11.77 (11.56)	10.55 (10.68)	5.24 (5.36)	12.29 (12.45)	14.11 (14.25)	62
5e	$[Zn(H_2O)_2\{(OH)Cr(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 4H_2O$	8.50 (7.22)	11.43 (11.48)	10.62 (10.60)	5.10 (5.34)	12.38 (12.37)	14.18 (14.15)	81
1f	$[Mg(H_2O)_2\{(OH)Co(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 4H_2O$		13.69 (13.69)	11.03 (11.16)	5.38 (5.39)	12.94 (13.02)	14.18 (14.90)	77
2f	$[Mn(H_2O)_2\{(OH)Co(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 3H_2O$	6.14 (6.16)	13.20 (13.22)	10.67 (10.78)	5.08 (5.20)	12.58 (12.57)	14.35 (14.38)	67
3f	$[Co(H_2O)_2\{(OH)Co(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 3H_2O$		19.71[b] (19.74)	10.75 (10.73)	5.14 (5.18)	12.42 (12.51)	14.05 (14.32)	74
4f	$[Ni(H_2O)_2\{(OH)Co(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 3H_2O$	6.73 (6.56)	13.08 (13.17)	10.49 (10.73)	5.12 (5.18)	12.52 (12.52)	13.20 (14.32)	71
5f	$[Zn(H_2O)_2\{(OH)Co(C_2H_8N_2)_2(OH)\}_2](S_2O_6)_2\cdot 3H_2O$	8.74 (7.11)	12.89 (12.81)	10.54 (10.44)	5.00 (5.26)	12.13 (12.18)	14.18 (13.94)	69

[a] The ligands are assumed to behave as bidentate ligands. M^{II} = Mg^{II}, Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II}; en = 1,2-ethanediamine. For most of the compounds, the content of crystal water could vary between 3 and 4 mol. All the compounds constitute one isomorphous series. [b] Total amount of cobalt.

$[Cr(NH_3)_4(OH)(H_2O)]S_2O_6\cdot H_2O$ (300 mg, ~0.9 mmol) was dissolved in water (6 mL). A solution of sodium hydroxide (2 M, 0.45 mL ~0.9 mmol) was added with stirring, and the resulting solution was filtered and used immediately.

Solution E. Five solutions each containing 0.3 mmol of *cis*-$[Cr(en)_2(OH)_2]^+$ were prepared by the following procedure: *cis*-$[Cr(en)_2(OH)(H_2O)]S_2O_6$ (110 mg, ~0.3 mmol) was suspended in water (2 mL). A solution of sodium hydroxide (2 M, 0.15 mL, ~0.3 mmol) was added with stirring, and the resulting solution was filtered and used immediately.

Solution F. Five solutions each containing 0.3 mmol of *cis*-$[Co(en)_2(OH)_2]^+$ were prepared exactly as solution E, but from *cis*-$[Co(en)_2(OH)(H_2O)]S_2O_6$ (112 mg, ~0.3 mmol).

Solution G. Five solutions each containing 0.4 mmol of *cis*-α-$[Cr(pico)_2(OH)_2]^+$ were prepared exactly as solution E, but from *cis*-α-$[Cr(pico)_2(OH)(H_2O)]S_2O_6\cdot 2H_2O$ (200 mg, ~0.4 mmol) and a solution of sodium hydroxide (2 M, 0.20 mL, ~0.4 mmol).

Solution H. Five solutions each containing 0.3 mmol of *cis*-$[Cr(cyclam)(OH)_2]^+$ were prepared exactly as solution E, but from *cis*-$[Cr(cyclam)(OH)(H_2O)]S_2O_6\cdot 3H_2O$ (150 mg, ~0.3 mmol) suspended in water (1 mL).

Heteronuclear Compounds. C. Dithionate Salts of Complex Ions of M^{II} with the Ligand $[Cr(NH_3)_4(OH)_2]^+$. Suggested formulation: $[M^{II}(H_2O)_2\{(OH)_2Cr(NH_3)_4\}_2](S_2O_6)_2\cdot XH_2O$; M^{II} = Mg, Mn, Co, Ni, and Zn. Each of the solid compounds $MgSO_4\cdot 7H_2O$ (73.8 mg, ~0.3 mmol), $MnCl_2\cdot 4H_2O$ (59.4 mg, ~0.3 mmol), $CoCl_2\cdot 6H_2O$ (71.4 mg, ~0.3 mmol), $NiCl_2\cdot 6H_2O$ (71.4 mg, ~0.3 mmol), and $(NH_4)_2ZnCl_4$ (72.9 mg, ~0.3 mmol) was dissolved in water (2 mL), and the solutions were added to solutions C with stirring. The pink needle-shaped crystals that separated immediately at room temperature were filtered out and washed with ethanol (50% and 96%). Analytical data are summarized in Table I.

E. Dithionate Salts of Complex Ions of M^{II} with the Ligand $[Cr(en)_2(OH)_2]^+$. Suggested formulation: $[M^{II}(H_2O)_2\{(OH)_2Cr(en)_2\}_2](S_2O_6)_2\cdot 3$–$4H_2O$; M^{II} = Mg, Mn, Co, Ni, and Zn. Each of the solid compounds $MgSO_4\cdot 7H_2O$ (24.6 mg, ~0.1 mmol), $MnCl_2\cdot 4H_2O$ (19.8 mg, ~0.1 mmol), $CoCl_2\cdot 6H_2O$ (23.8 mg, ~0.1 mmol), $NiCl_2\cdot 6H_2O$ (23.8 mg, ~0.1 mmol), and $(NH_4)_2ZnCl_4$ (24.3 mg, ~0.1 mmol) was added to solutions E with stirring. The rose-colored needle-shaped crystals that separated immediately at room temperature were filtered out and washed with ice-cold water and with ethanol (96%). Analytical data are summarized in Table II.

F. Dithionate Salts of Complex Ions of M^{II} with the Ligand $[Co(en)_2(OH)_2]^+$. Suggested formulation: $[M^{II}(H_2O)_2\{(OH)_2Co(en)_2\}_2](S_2O_6)_2\cdot 3$–$4H_2O$; M^{II} = Mg, Mn, Co, Ni, and Zn. The rose-red compounds were synthesized as the corresponding chromium complexes, but from stock solutions F. Analytical data are summarized in Table II.

G. Dithionate Salts of Complex Ions of M^{II} with the Ligand $[Cr(pico)_2(OH)_2]^+$. Formulation: $[M^{II}(H_2O)_4\{(OH)Cr(pico)_2(OH)\}_2\cdot H_2O$; M^{II} = Mg, Mn, Co, Ni, and Zn. The compounds were synthesized as the compounds E, but from stock solutions G and 0.2 mmol of each of the solid metal salts. The dark-violet crystals that separated slowly (24 h) at room temperature were washed with ethanol (50% and 96%). Analytical data are summarized in Table III.

H. Dithionate Salts of Complex Ions of M^{II} with the Ligand $[Cr(cyclam)(OH)_2]^+$. M^{II} = Mn, Co, Ni, and Zn. The compounds were synthesized as the compounds E, but from stock solutions H. The crystals that separated slowly (24 h) at room temperature were washed with

Table III. Analytical Data for Dithionate Salts of Complex Ions of M^{II} with the Ligand $[Cr(pico)_2(OH)_2]^+$ [a]

		anal. found (calcd), %						
no.	compound	M^{II}	Cr^{III}	C	H	N	S	yield, %
1g	$[Mg(H_2O)_4\{(OH)Cr(C_6H_8N_2)_2(OH)\}_2](S_2O_6)_2{\cdot}H_2O$		9.72	27.70	4.48	10.80	12.42	29
			(10.01)	(27.74)	(4.46)	(10.78)	(12.34)	
2g	$[Mn(H_2O)_4\{(OH)Cr(C_6H_8N_2)_2(OH)\}_2](S_2O_6)_2{\cdot}H_2O$	5.05	9.49	27.01	4.36	10.68	11.96	70
		(5.14)	(9.72)	(26.94)	(4.33)	(10.47)	(11.99)	
3g	$[Co(H_2O)_4\{(OH)Cr(C_6H_8N_2)_2(OH)\}_2](S_2O_6)_2{\cdot}H_2O$	5.52	9.81	26.59	4.41	10.38	11.75	67
		(5.49)	(9.68)	(26.84)	(4.32)	(10.43)	(11.94)	
4g	$[Ni(H_2O)_4\{(OH)Cr(C_6H_8N_2)_2(OH)\}_2](S_2O_6)_2{\cdot}H_2O$	5.41	9.60	26.53	4.41	10.35	11.90	22
		(5.47)	(9.69)	(26.85)	(4.32)	(10.44)	(11.94)	
5g	$[Zn(H_2O)_4\{(OH)Cr(C_6H_8N_2)_2(OH)\}_2](S_2O_6)_2{\cdot}H_2O$	7.09	9.31	26.52	4.36	10.41	11.88	60
		(6.05)	(9.63)	(26.68)	(4.29)	(10.37)	(11.87)	

[a] The ligand behaves as a monodentate ligand. M^{II} = Mg^{II}, Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II}; pico = 2-picolylamine.

Table IV. Analytical Data for Dithionate Salts of Complex Ions of M^{II} with the Ligand $[Cr(cyclam)(OH)_2]^+$ [a]

		anal. found (calcd), %						
no.	compound	M^{II}	Cr^{III}	C	H	N	S	yield, %
2h′	$[Mn(H_2O)_2\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2{\cdot}5H_2O$	5.12	9.67	22.45	5.27	10.53	11.84	26
		(5.12)	(9.68)	(22.37)	(6.19)	(10.43)	(11.94)	
3h	$[Co(H_2O)_2\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2{\cdot}2H_2O$	6.00	10.19	23.91	5.66	11.22	12.53	68
		(5.76)	(10.16)	(23.46)	(5.91)	(10.94)	(12.52)	
3h′	$[Co(H_2O)_2\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2{\cdot}6H_2O$	5.46	9.43	21.94	5.56	10.29	11.93	46
		(5.38)	(9.49)	(21.92)	(6.25)	(10.22)	(11.70)	
4h′	$[Ni(H_2O)_2\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2{\cdot}6H_2O$	5.36	9.14	21.64	6.07	10.34	11.70	93
		(5.36)	(9.49)	(21.92)	(6.25)	(10.23)	(11.70)	
5h	$[Zn(S_2O_6)\{(OH)_2Cr(cyclam)\}_2](S_2O_6){\cdot}6H_2O$	6.24	9.65	22.44	5.45	10.57	11.62	67
		(6.13)	(9.73)	(22.53)	(6.05)	(10.51)	(12.03)	

[a] M^{II} = Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II}; cyclam = 1,4,8,11-tetraazacyclotetradecane. Complexes **3h′** and **4h′** are isomorphous. Complex **3h** is isomorphous with an analogous copper complex.

Table V. Crystallographic and Data Collection Parameters

formula	$ZnCr_2C_{20}H_{50}N_8O_{14}S_4{\cdot}2.5H_2O$	$MnCr_2C_{24}H_{44}N_8O_{20}S_4{\cdot}0.5H_2O$	$CoCr_2C_{24}H_{44}N_8O_{20}S_4{\cdot}0.5H_2O$
system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$C2/c$
a, Å	15.719 (12)	16.969 (3)	16.968 (7)
b, Å	16.805 (15)	14.587 (1)	14.490 (3)
c, Å	16.800 (10)	17.014 (1)	16.996 (3)
β, deg	116.86 (5)	99.13 (1)	98.76 (2)
V, Å^3	3959 (5)	4158 (1)	4130 (2)
Z	4	4	4
T, °C	22	22	22
μ, mm^{-1}	1.63	10.317	11.46
index ranges	$-12 \le h \le 12$	$-21 \le h \le 21$	$-21 \le h \le 21$
	$0 \le k \le 21$	$0 \le k \le 17$	$0 \le k \le 17$
	$0 \le l \le 21$	$0 \le l \le 21$	$0 \le l \le 21$
no. of reflns	8160	3179	4773
no. of obs reflns	3472	1849	1183
R^a	0.065	0.037	0.069
$R_w{}^b$	0.078	0.042	0.046

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

ethanol (50% and 96%). In a single case [Co(II)], two different kinds of crystals (red and bluish-red) were obtained. They have different X-ray powder patterns and different contents of water. Analytical data are summarized in Table IV.

X-ray Structure Determinations. The structures were determined at room temperature (295 K) on a Nicolet R3m/V diffractometer using Mo Kα radiation [$\lambda(K\alpha_1)$ = 0.709 26 Å, $\lambda(K\alpha_2)$ = 0.713 54 Å] and a graphite monochromator. Crystal data and experimental parameters are listed in Table V. All programs used were from the SHELXTL-PLUS system.[14]

$[Zn\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2{\cdot}2.5H_2O$ (5h). The complex crystallizes as vivid magenta prisms in space group $P2_1/c$ of the monoclinic system with four trinuclear cations in the unit cell. Positions of the central zinc atom, the two chromium atoms, and the four bridging oxygen atoms were located in a Patterson map. The positions of the remaining non-hydrogen atoms were determined from successive difference Fourier maps. Hydrogen atoms on the bridging hydroxo groups were located in difference Fourier maps; the hydrogen atoms belonging to the ligands were observed, but their positions were calculated and assigned on the basis of reasonable geometry. Three of the six hydrogen atoms associated with water molecules were located in difference Fourier maps. The structure was refined by least-squares methods to give final values of R = 0.0649, R_w = 0.0782, and S (GOF) = 1.4606. The positional parameters of the non-hydrogen atoms, along with their standard deviations as estimated from the inverse matrix, are presented in Table VI. Hydrogen atom positions and anisotropic thermal parameters are available as supplementary material.

$[Mn\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2{\cdot}{}^1/_2H_2O$ (2g). The complex crystallizes as red-brown prisms in space group $C2/c$ of the monoclinic system with four trinuclear complexes in the unit cell. The structure was solved by Patterson methods, which revealed the locations of the Mn and Cr atoms. The remaining non-hydrogen atoms were located in difference Fourier summations. All hydrogen atoms were located in a difference Fourier map, but only their isotropic thermal parameters were varied, their positions being fixed at the locations indicated in the difference Fourier. Non-hydrogen atoms were refined anisotropically. In the final least-squares cycle, no parameter experienced a shift greater than 0.5σ, which is taken as evidence of convergence. Final residuals are R = 0.037 and R_w = 0.042, with S = 1.15. Positional parameters are given in Table VII, and supplementary material (as above) is available.

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(14) Sheldrick, G. M. *SHELXTL-PLUS Crystallographic System*, Version 2; Nicolet XRD Corp.: Madison, WI, 1987.

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Zn\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2 \cdot 2.5H_2O$

	x	*y*	*z*	*U*(eq)[a]
Cr(1)	2419 (1)	−947 (1)	4138 (1)	28 (1)
Cr(2)	2731 (1)	387 (1)	943 (1)	28 (1)
Zn	2438 (1)	−153 (1)	2525 (1)	38 (1)
O(1)	1788 (6)	−1019 (5)	2866 (5)	42 (4)
O(2)	3163 (5)	−137 (4)	3898 (5)	45 (3)
O(3)	3274 (7)	576 (5)	2217 (6)	37 (4)
O(4)	2047 (5)	−425 (4)	1252 (4)	36 (3)
N(1)	3146 (7)	−701 (5)	5497 (6)	49 (5)
C(2)	2768 (11)	69 (7)	5632 (8)	70 (8)
C(3)	1712 (12)	40 (7)	5138 (9)	68 (8)
N(4)	1430 (7)	−162 (5)	4203 (6)	50 (5)
C(5)	406 (11)	−360 (8)	3712 (11)	75 (9)
C(6)	142 (10)	−1139 (9)	3951 (10)	71 (7)
C(7)	580 (9)	−1862 (8)	3712 (9)	67 (7)
N(8)	1630 (7)	−1910 (5)	4266 (6)	44 (5)
C(9)	1995 (11)	−2629 (6)	4036 (9)	61 (8)
C(10)	3056 (11)	−2601 (7)	4503 (9)	68 (8)
N(11)	3390 (7)	−1839 (5)	4279 (6)	48 (5)
C(12)	4399 (10)	−1686 (9)	4831 (9)	78 (8)
C(13)	4643 (10)	−1444 (9)	5792 (9)	78 (7)
C(14)	4217 (10)	−681 (9)	5871 (8)	69 (6)
N(1A)	3473 (7)	1357 (5)	771 (6)	42 (4)
C(2A)	2967 (10)	2093 (6)	843 (8)	56 (7)
C(3A)	1942 (11)	1983 (6)	346 (10)	68 (9)
N(4A)	1656 (7)	1228 (5)	641 (6)	47 (5)
C(5A)	675 (10)	957 (9)	33 (10)	72 (8)
C(6A)	540 (9)	673 (8)	−835 (8)	63 (6)
C(7A)	1075 (9)	−80 (8)	−820 (7)	59 (6)
N(8A)	2104 (6)	29 (5)	−392 (5)	39 (4)
C(9A)	2615 (9)	−717 (6)	−432 (8)	55 (6)
C(10A)	3667 (10)	−573 (7)	118 (7)	57 (7)
N(11A)	3834 (6)	−358 (5)	1034 (5)	38 (4)
C(12A)	4821 (9)	−81 (8)	1580 (8)	67 (7)
C(13A)	5062 (10)	708 (8)	1310 (9)	70 (7)
C(14A)	4501 (10)	1385 (8)	1386 (8)	67 (7)
S(1)	1224 (2)	1575 (2)	2659 (2)	54 (2)
O(11)	1422 (6)	794 (4)	2449 (6)	59 (4)
O(12)	847 (8)	2038 (6)	1868 (7)	117 (7)
O(13)	752 (9)	1571 (7)	3199 (8)	113 (7)
S(2)	2584 (3)	2079 (2)	3475 (2)	53 (2)
O(21)	3067 (6)	2101 (4)	2928 (5)	59 (4)
O(22)	3013 (6)	1541 (5)	4224 (5)	67 (4)
O(23)	2408 (7)	2876 (5)	3722 (6)	74 (5)
S(3)	1252 (2)	7321 (2)	1175 (2)	42 (1)
O(31)	838 (5)	7642 (4)	1728 (5)	48 (4)
O(32)	1603 (6)	7919 (4)	775 (5)	56 (4)
O(33)	676 (6)	6719 (5)	552 (5)	64 (4)
S(4)	2500 (2)	6705 (2)	2065 (2)	49 (1)
O(41)	2225 (7)	6177 (5)	2566 (6)	78 (5)
O(42)	3138 (6)	7325 (5)	2610 (5)	62 (4)
O(43)	2853 (7)	6354 (5)	1498 (6)	74 (5)
O(1W)	4188 (9)	8095 (7)	1788 (10)	105 (8)
O(2W)	4168 (12)	3582 (8)	3522 (17)	238 (19)
O(3W)	2528 (28)	4565 (23)	2509 (29)	191 (16)

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

$[Co\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2 \cdot {}^1/_2H_2O$ (3g). The complex, which forms as red-purple prisms, is isomorphous with the manganese analogue, **2g**. The structure was solved as for **2g**. Hydrogen atoms on the ligands were placed in calculated positions (C–H = 0.96 Å), while other H atoms were located in a difference Fourier map. Hydrogen atom parameters were not refined. In the final least-squares cycle, no parameter shifted by more than 0.5σ. Final residuals are $R = 0.069$ $R_w = 0.046$ with $S = 1.35$. Positional parameters are listed in Table VIII, and supplementary material is available.

Results and Discussion

Synthesis. When the divalent metal ions Mg(II), Mn(II), Co(II), Ni(II), and Zn(II) react with $[Cr(A)_4(OH)(H_2O)](ClO_4)_2$ in slightly alkaline medium, tetranuclear complexes of the general formula $[M^{II}\{(OH)_2Cr(A)_4\}_3](ClO_4)_5$ are formed.[2,5] When the perchlorate salts are replaced as reactants by the corresponding dithionates, trinuclear dithionate salts are obtained. We have demonstrated by X-ray diffraction studies (vide infra) that the "ligand" $[Cr(pico)_2(OH)_2]^+$ acts as a monodentate ligand on the divalent metal ions and that $[Cr(cyclam)(OH)_2]^+$ acts as a bidentate ligand on zinc; we may assume that this complex ion behaves as a bidentate ligand on other metal centers also. Examination of the spectroscopic and magnetic properties of the Co(II), Ni(II), and Mn(II) complexes demonstrates that for some amines, specifically including cyclam and NH_3, two forms of each complex may occur. The magnetic data (vide infra) lead us to conclude that both of these involve bidentate coordination, but there is some spectroscopically and magnetically significant structural distinction between the two forms. For each metal ion, one form is more highly hydrated than the other, which also allows for an analytical distinction; the more highly hydrated form is the one that exhibits approximate Curie–Weiss magnetic behavior, while the less hydrated forms exhibit weak ferromagnetic interactions (vide infra).

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[Mn\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2$

	x	*y*	*z*	*U*(eq)[a]
Cr	2406 (1)	3 (1)	9526 (1)	22 (1)
Mn	2500	2500	10000	24 (1)
S(1)	3471 (1)	2343 (1)	7457 (1)	35 (1)
S(2)	2276 (1)	1972 (1)	6983 (1)	31 (1)
N(1A)	1192 (2)	176 (3)	9135 (2)	27 (2)
C(1A)	1132 (3)	−1388 (6)	9577 (4)	57 (3)
C(2A)	743 (3)	−578 (5)	9184 (3)	38 (2)
C(3A)	−67 (4)	−553 (7)	8859 (5)	68 (4)
C(4A)	−409 (3)	214 (8)	8537 (5)	79 (4)
C(5A)	49 (3)	977 (6)	8521 (4)	58 (3)
C(6A)	849 (3)	933 (5)	8808 (3)	42 (2)
N(2A)	2009 (2)	−1334 (4)	9671 (3)	32 (2)
N(1B)	3563 (2)	−498 (3)	9710 (2)	29 (2)
C(1B)	3402 (3)	−396 (5)	8280 (3)	39 (2)
C(2B)	3879 (3)	−681 (5)	9053 (3)	34 (2)
C(3B)	4608 (3)	−1115 (5)	9104 (4)	50 (3)
C(4B)	5025 (3)	−1338 (6)	9829 (5)	59 (3)
C(5B)	4709 (3)	−1170 (6)	10504 (4)	54 (3)
C(6B)	3971 (3)	−737 (5)	10421 (3)	39 (2)
N(2B)	2556 (2)	−267 (3)	8354 (2)	29 (1)
O(1)	2649 (2)	1281 (3)	9372 (2)	28 (1)
O(2)	2362 (2)	300 (3)	10624 (2)	32 (1)
O(3)	3291 (2)	1803 (3)	11032 (2)	37 (1)
O(4)	1497 (2)	1838 (3)	10468 (2)	36 (1)
O(11)	3619 (2)	1957 (3)	8246 (2)	42 (2)
O(12)	3466 (3)	3321 (4)	7452 (3)	80 (2)
O(13)	3933 (3)	1940 (5)	6923 (3)	79 (3)
O(21)	2140 (2)	2380 (3)	6201 (2)	44 (2)
O(22)	1781 (2)	2353 (4)	7510 (2)	58 (2)
O(23)	2275 (2)	982 (4)	6960 (3)	52 (2)
Ow	0	4679 (13)	2500	68 (7)

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

Reflectance Spectra. The data obtained from the reflectance spectra are presented in Table IX. The spectra are dominated by the two spin-allowed chromium(III) bands at approximately 495–540 and 350–375 nm and resemble those of the parent hydroxo aqua complexes. The spectra for the Co(II) and Ni(II) complexes that occur in two different modifications (**3c**, **3c′**; **4c**, **4c′**; **3h**, **3h′**) are sufficiently different to suggest the presence of two different isomers.

Description of the Structures. $[Zn\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2 \cdot 2.5H_2O$ (5h). A view of the entire cation is given in Figure 1, and the inner coordination spheres around the metals are depicted in Figure 2. As can be seen from these figures, the central zinc atom is five-coordinate, being bonded to an oxygen atom from one of the dithionate anions as well as to the oxygen atoms of the four bridging hydroxo groups. Although relatively uncommon, anion binding leading to pentacoordination in zinc-

Table VIII. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[Co\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2$

	x	*y*	*z*	*U*(eq)[a]
Cr	2396 (2)	26 (2)	9535 (2)	22 (1)
Co	2500	2500	10000	22 (1)
S(1)	3480 (3)	2363 (4)	7456 (3)	43 (2)
S(2)	2269 (3)	1978 (3)	6981 (3)	40 (2)
N(1A)	1184 (9)	175 (8)	9159 (7)	23 (5)
C(1A)	1125 (11)	−1388 (12)	9577 (11)	39 (5)
C(2A)	755 (13)	−564 (13)	9184 (11)	31 (5)
C(3A)	−49 (13)	−607 (15)	8875 (12)	65 (11)
C(4A)	−375 (14)	179 (15)	8556 (11)	62 (7)
C(5A)	13 (15)	982 (14)	8521 (11)	56 (9)
C(6A)	826 (13)	951 (14)	8832 (10)	45 (9)
N(2A)	2014 (8)	−1324 (9)	9685 (8)	27 (5)
N(1B)	3551 (9)	−477 (9)	9704 (8)	31 (6)
C(1B)	3392 (12)	−377 (12)	8292 (10)	42 (8)
C(2B)	3887 (11)	−665 (11)	9053 (11)	29 (7)
C(3B)	4593 (12)	−1097 (12)	9079 (11)	40 (6)
C(4B)	5012 (12)	−1346 (13)	9787 (13)	47 (9)
C(5B)	4710 (13)	−1163 (12)	10485 (14)	49 (10)
C(6B)	3973 (13)	−750 (12)	10397 (11)	37 (8)
N(2B)	2534 (9)	−240 (9)	8354 (7)	30 (6)
O(1)	2638 (7)	1314 (7)	9395 (6)	22 (5)
O(2)	2358 (8)	321 (7)	10634 (6)	31 (5)
O(3)	3233 (7)	1811 (7)	10986 (6)	32 (4)
O(4)	1533 (6)	1872 (7)	10468 (6)	32 (4)
O(11)	3617 (7)	1979 (8)	8240 (6)	46 (5)
O(12)	3474 (9)	3345 (8)	7471 (9)	75 (7)
O(13)	3940 (8)	1969 (11)	6930 (7)	88 (7)
O(21)	2144 (7)	2394 (8)	6201 (6)	45 (5)
O(22)	1775 (8)	2339 (10)	7509 (7)	66 (6)
O(23)	2286 (9)	1001 (7)	6956 (7)	59 (6)
Ow	0	4581 (19)	2500	30 (9)

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

Table IX. Diffuse Reflectance Data for Dithionate Salts of Complexes of M^{II} with the Ligand $[Cr(A)_4(OH)_2]^+$ [a]

no.	M	$(A)_4$	λ_1, nm	λ_2, nm	λ_3, nm
3c	Co	$(NH_3)_4$	514	373	249
3c′ [b]	Co	$(NH_3)_4$	508	359	253
4c	Ni	$(NH_3)_4$	505	373	234
4c′	Ni	$(NH_3)_4$	506	365	231
1e	Mg	$(en)_2$	505	367	214
2e	Mn	$(en)_2$	499	375	
3e	Co	$(en)_2$	503	363	218
4e	Ni	$(en)_2$	497	373	206
5e	Zn	$(en)_2$	499	373	204
1g	Mg	$(pico)_2$	582	374	263
2g	Mn	$(pico)_2$	576	375	259
3g	Co	$(pico)_2$	576	373	261
4g	Ni	$(pico)_2$	582	379	263
5g	Zn	$(pico)_2$	578	375	263
2h	Mn	cyclam	534	360	272
3h	Co	cyclam	529	352	285
3h′	Co	cyclam	540	366	272
4h	Ni	cyclam	~560	366	259
5h	Zn	cyclam	538	370	232

[a] M^{II} represents Mg^{II}, Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II}; A represents the amines NH_3, $C_2H_8N_2$ (en), $C_6H_8N_2$ (pico), and $C_{10}H_{24}N_4$ (cyclam). [b] Primed complexes (e.g., **3c′**) differ from unprimed complexes (e.g., **3c**) by having different water contents and different powder patterns.

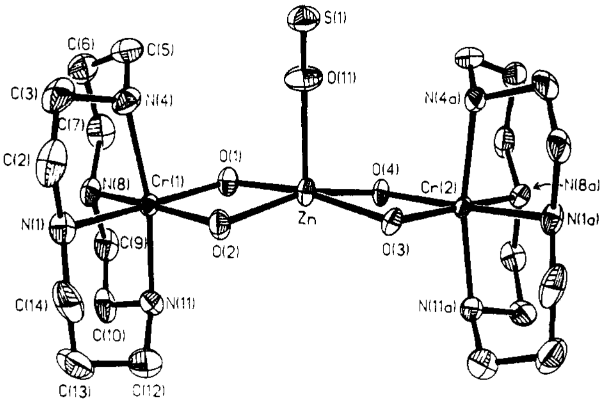

Figure 1. View of the cation in the structure of $[Zn\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2\cdot 2.5H_2O$. Hydrogen atoms are omitted for clarity. Thermal ellipsoids in this and in other figures are at the 30% probability level.

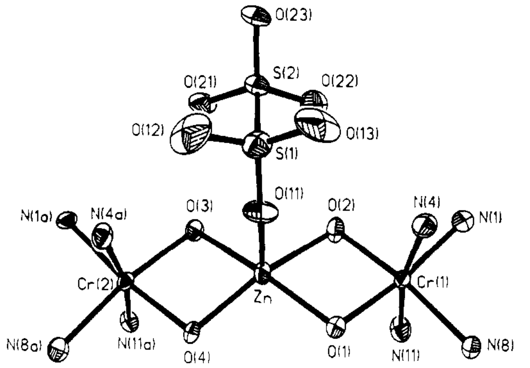

Figure 2. View of the inner sphere around Zn and Cr in $[Zn\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2\cdot 2.5H_2O$ showing the coordinated dithionate group.

(II) complexes has been the subject of a recent theoretical study.[15] As is most easily seen in Figure 2, the hydroxo groups bridge in pairs to two chromium atoms, each of which is also bonded to four nitrogen donors from the ligands.

The geometry about the zinc is slightly distorted from regular square-pyramidal. The base "plane" defined by the bridging oxygen atoms O(1), O(2), O(3), and O(4) exhibits a small distortion toward tetrahedral geometry, with two atoms [O(1) and O(3)] lying 0.07 Å above the least-squares plane while the other two [O(2) and O(4)] lie 0.07 Å below it. As is normal for square pyramidal complexes,[16,17] the zinc atom lies above this plane, on the side of the axial ligand O(11); in the present case, the central metal atom is 0.248 Å above the plane. This value is consistent with those observed in a variety of five-coordinate transition metal complexes.[16-20] The axial O(11)–Zn–O angles range from 94.3 (3) to 103.7 (3)°, while the O–Zn–O angles between oxygens that bridge to the same chromium are each 77.6 (3)°. This latter value can be compared with similar angles at copper of 80.8 (1)° in the related copper chromium complex.[6]

The bonds between the zinc atom and the oxygen atoms in the bridging hydroxo groups range from 1.993 (7) to 2.028 (11) Å. These values are slightly longer than the corresponding values in the copper chromium trimer[6] and account for the slightly more acute angle between hydroxo bridges to the same chromium noted above. The zinc–chromium separation is 3.032 (4) Å, slightly longer than the value in the bispictn copper(II) chromium(III) trimer.[6] Trans angles at zinc are 169.9 (4) and 161.9 (3)°.

The geometry about each chromium atom is approximately octahedral with cis angles ranging from 80.9 (4) to 95.8 (3)°. The O–Cr–O bond angles of 80.9 (4) and 82.5 (4)° are similar to those discussed elsewhere for analogous species,[6,7] as are the Cr–O bond lengths from 1.911 (8) to 1.953 (9) Å. The bridging Zn–O–Cr angles are unsymmetric, lying in the range 98.2 (3)–101.5 (3)°, with an average value of 100.0°; all of these values are within the range normally associated with bis(μ-hydroxo)-

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(15) Solà, M.; Lledós, A.; Duran, M.; Bertrán, J. *Inorg. Chem.* **1991**, *30*, 2523–2527.

(16) See, for example: Marsh, W. E.; Eggleston, D. S.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chim. Acta* **1983**, *70*, 137–142.

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(18) Oki, A. R.; Hodgson, D. J. *Inorg. Chim. Acta* **1990**, *170*, 65–73.

(19) Marsh, W. E.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1982**, *21*, 2679–2684 and references therein.

(20) Pecoraro, V. L.; Butler, W. M. *Acta Crystallogr.* **1986**, *C42*, 1151–1154.

Table X. Bond Lengths (Å) for $[Zn\{(OH)_2Cr(cyclam)\}_2](S_2O_6)_2$

Cr(1)–Zn	3.032 (4)	Cr(1)–O(1)	1.911 (8)
Cr(1)–O(2)	1.953 (9)	Cr(1)–N(1)	2.081 (9)
Cr(1)–N(4)	2.078 (12)	Cr(1)–N(8)	2.108 (10)
Cr(1)–N(11)	2.076 (10)	Cr(2)–Zn	3.035 (4)
Cr(2)–O(3)	1.939 (9)	Cr(2)–O(4)	1.948 (8)
Cr(2)–N(1A)	2.099 (10)	Cr(2)–N(4A)	2.081 (10)
Cr(2)–N(8A)	2.089 (8)	Cr(2)–N(11A)	2.088 (10)
Zn–O(1)	2.004 (10)	Zn–O(2)	2.059 (8)
Zn–O(3)	2.028 (11)	Zn–O(4)	1.993 (7)
Zn–O(11)	2.217 (9)	N(1)–C(2)	1.484 (17)
N(1)–C(14)	1.508 (18)	C(2)–C(3)	1.483 (22)
C(3)–N(4)	1.467 (18)	C(5)–N(4)	1.478 (18)
C(5)–C(6)	1.482 (22)	C(6)–C(7)	1.537 (22)
C(7)–N(8)	1.487 (15)	N(8)–C(9)	1.463 (17)
C(9)–C(10)	1.488 (21)	C(10)–N(11)	1.495 (17)
N(11)–C(12)	1.454 (16)	C(12)–C(13)	1.537 (22)
C(13)–C(14)	1.480 (22)	N(1A)–C(2A)	1.504 (16)
N(1A)–C(14A)	1.473 (15)	C(2A)–C(3A)	1.453 (20)
C(3A)–N(4A)	1.503 (17)	N(4A)–C(5A)	1.485 (15)
C(5A)–C(6A)	1.456 (22)	C(6A)–C(7A)	1.514 (19)
C(7A)–N(8A)	1.454 (15)	N(8A)–C(9A)	1.508 (15)
C(9A)–C(10A)	1.506 (17)	C(10A)–N(11A)	1.483 (16)
N(11A)–C(12A)	1.476 (15)	C(12A)–C(13A)	1.504 (21)
C(13A)–C(14A)	1.479 (22)	S(1)–O(11)	1.429 (9)
S(1)–O(12)	1.418 (11)	S(1)–O(13)	1.408 (17)
S(1)–S(2)	2.125 (5)	S(2)–O(21)	1.434 (12)
S(2)–O(22)	1.445 (8)	S(2)–O(23)	1.465 (9)
S(3)–O(31)	1.457 (10)	S(3)–O(32)	1.449 (10)
S(3)–O(33)	1.443 (8)	S(3)–S(4)	2.124 (4)
S(4)–O(41)	1.418 (12)	S(4)–O(42)	1.449 (8)
S(4)–O(43)	1.427 (12)		

dichromium(III) species.[21] Complete listings of bond lengths and bond angles are given in Tables X and XI, respectively.

The dithionate anions are ordered. The S–S separations are 2.124 (4) and 2.125 (5) Å, while the S–O bond lengths range from 1.408 (17) to 1.465 (9) Å. These values are all consistent with a number of recent characterizations.[22-25] As is shown in Figure 2, one of the dithionate anions is coordinated to the central zinc atom, the Zn–O(11) bond length being 2.217 (9) Å. As is universally found in dithionate structures,[22-25] both anions exhibit approximate D_{3d} geometry. Thus, in the coordinated anion, the ideally ±60° torsion angles are in the range 52.6–66.9°, and the ideally 180° torsion angles range from 172.6 to 178.9°; in the uncoordinated ion the corresponding values are 51.9–68.5 and 171.9–176.3°.

While transition metal coordination to oxyanions in the solid state is well established, the coordination of dithionate ion to transition metals is uncommon. Axial coordination to copper(II) has been observed in $Cu(NH_3)_4(S_2O_6)$, in which the dithionate anions link adjacent copper centers through Cu–O–S–S–O–Cu bonding to form a chain structure.[26] Both O-bound[27] and S-bound[28] complexes of the reduced ion, dithionite $[S_2O_4^{2-}]$, have been observed, and dithionate coordination to alkali metals is well-known.[29] The present example, with a Zn–O(11) bond length of 2.217 (9) Å, clearly demonstrates that strong metal–dithionate bonding is possible in the solid state.

Table XI. Bond Angles (deg) for $[Zn\{(OH)_2Cr(cyclam)\}_2](S_2O_6)$

Zn–Cr(1)–O(1)	40.4 (3)	Zn–Cr(1)–O(2)	42.2 (2)
O(1)–Cr(1)–O(2)	82.5 (4)	Zn–Cr(1)–N(1)	132.1 (3)
O(1)–Cr(1)–N(1)	171.8 (4)	O(2)–Cr(1)–N(1)	90.3 (4)
Zn–Cr(1)–N(4)	94.4 (3)	O(1)–Cr(1)–N(4)	94.4 (4)
O(2)–Cr(1)–N(4)	95.8 (4)	N(1)–Cr(1)–N(4)	82.5 (4)
Zn–Cr(1)–N(8)	132.3 (3)	O(1)–Cr(1)–N(8)	91.9 (4)
O(2)–Cr(1)–N(8)	172.5 (4)	N(1)–Cr(1)–N(8)	95.6 (4)
N(4)–Cr(1)–N(8)	89.7 (4)	Zn–Cr(1)–N(11)	96.7 (3)
O(1)–Cr(1)–N(11)	93.7 (4)	O(2)–Cr(1)–N(11)	92.8 (4)
N(1)–Cr(1)–N(11)	90.4 (4)	N(4)–Cr(1)–N(11)	168.9 (5)
N(8)–Cr(1)–N(11)	82.5 (4)	Zn–Cr(2)–O(3)	41.2 (3)
Zn–Cr(2)–O(4)	40.2 (2)	O(3)–Cr(2)–O(4)	80.9 (4)
Zn–Cr(2)–N(1A)	131.8 (3)	O(3)–Cr(2)–N(1A)	91.7 (4)
O(4)–Cr(2)–N(1A)	171.5 (4)	Zn–Cr(2)–N(4A)	89.3 (3)
O(3)–Cr(2)–N(4A)	93.5 (4)	O(4)–Cr(2)–N(4A)	93.2 (4)
N(1A)–Cr(2)–N(4A)	83.1 (4)	Zn–Cr(2)–N(8A)	132.0 (3)
O(3)–Cr(2)–N(8A)	172.3 (4)	O(4)–Cr(2)–N(8A)	92.0 (3)
N(1A)–Cr(2)–N(8A)	95.6 (4)	N(4A)–Cr(2)–N(8A)	89.8 (3)
Zn–Cr(2)–N(11A)	101.9 (3)	O(3)–Cr(2)–N(11A)	94.6 (4)
O(4)–Cr(2)–N(11A)	95.8 (3)	N(1A)–Cr(2)–N(11A)	88.9 (4)
N(4A)–Cr(2)–N(11A)	168.7 (4)	N(8A)–Cr(2)–N(11A)	83.1 (3)
Cr(1)–Zn–Cr(2)	168.8 (1)	Cr(1)–Zn–O(1)	38.1 (2)
Cr(2)–Zn–O(1)	140.0 (2)	Cr(1)–Zn–O(2)	39.6 (2)
Cr(2)–Zn–O(2)	138.6 (3)	O(1)–Zn–O(2)	77.6 (3)
Cr(1)–Zn–O(3)	139.8 (2)	Cr(2)–Zn–O(3)	39.0 (2)
O(1)–Zn–O(3)	169.9 (4)	O(2)–Zn–O(3)	100.6 (3)
Cr(1)–Zn–O(4)	137.3 (2)	Cr(2)–Zn–O(4)	39.1 (2)
O(1)–Zn–O(4)	101.0 (3)	O(2)–Zn–O(4)	161.9 (3)
O(3)–Zn–O(4)	77.6 (3)	Cr(1)–Zn–O(11)	94.0 (3)
Cr(2)–Zn–O(11)	97.2 (3)	O(1)–Zn–O(11)	95.2 (4)
O(2)–Zn–O(11)	94.3 (3)	O(3)–Zn–O(11)	94.8 (4)
O(4)–Zn–O(11)	103.7 (3)	Cr(1)–O(1)–Zn	101.5 (3)
Cr(1)–O(2)–Zn	98.2 (3)	Cr(2)–O(3)–Zn	99.8 (4)
Cr(2)–O(4)–Zn	100.7 (3)	Cr(1)–N(1)–C(2)	106.4 (6)
Cr(1)–N(1)–C(14)	114.7 (9)	C(2)–N(1)–C(14)	111.4 (10)
N(1)–C(2)–C(3)	108.1 (10)	C(2)–C(3)–N(4)	109.1 (15)
Cr(1)–N(4)–C(3)	109.4 (8)	Cr(1)–N(4)–C(5)	118.7 (8)
C(3)–N(4)–C(5)	112.1 (14)	N(4)–C(5)–C(6)	114.5 (11)
C(5)–C(6)–C(7)	114.5 (15)	C(6)–C(7)–N(8)	112.4 (10)
Cr(1)–N(8)–C(7)	115.6 (7)	Cr(1)–N(8)–C(9)	106.8 (9)
C(7)–N(8)–C(9)	109.7 (9)	N(8)–C(9)–C(10)	108.3 (9)
C(9)–C(10)–N(11)	109.3 (9)	Cr(1)–N(11)–C(10)	108.9 (9)
Cr(1)–N(11)–C(12)	118.7 (8)	C(10)–N(11)–C(12)	113.4 (9)
N(11)–C(12)–C(13)	113.5 (14)	C(12)–C(13)–C(14)	114.5 (11)
N(1)–C(14)–C(13)	114.1 (11)	Cr(2)–N(1A)–C(2A)	106.3 (9)
Cr(2)–N(1A)–C(14A)	115.5 (7)	C(2A)–N(1A)–C(14A)	111.8 (8)
N(1A)–C(2A)–C(3A)	109.8 (9)	C(2A)–C(3A)–N(4A)	109.7 (9)
Cr(2)–N(4A)–C(3A)	108.8 (9)	Cr(2)–N(4A)–C(5A)	115.9 (8)
C(3A)–N(4A)–C(5A)	113.8 (9)	N(4A)–C(5A)–C(6A)	115.2 (14)
C(5A)–C(6A)–C(7A)	115.4 (10)	C(6A)–C(7A)–N(8A)	112.8 (10)
Cr(2)–N(8A)–C(7A)	116.6 (8)	Cr(2)–N(8A)–C(9A)	106.6 (5)
C(7A)–N(8A)–C(9A)	111.6 (8)	N(8A)–C(9A)–C(10A)	107.4 (9)
C(9A)–C(10A)–N(11A)	107.9 (12)	Cr(2)–N(11A)–C(10A)	108.6 (6)
Cr(2)–N(11A)–C(12A)	117.5 (7)	C(10A)–N(11A)–C(12A)	111.4 (11)
N(11A)–C(12A)–C(13A)	115.3 (9)	C(12A)–C(13A)–C(14A)	114.3 (15)
N(1A)–C(14A)–C(13A)	115.1 (10)	O(11)–S(1)–O(12)	108.6 (6)
O(11)–S(1)–O(13)	113.1 (7)	O(12)–S(1)–O(13)	119.1 (8)
O(11)–S(1)–S(2)	105.0 (4)	O(12)–S(1)–S(2)	105.0 (5)
O(13)–S(1)–S(2)	104.8 (5)	Zn–O(11)–S(1)	151.2 (5)
S(1)–S(2)–O(21)	105.5 (3)	S(1)–S(2)–O(22)	104.5 (4)
O(21)–S(2)–O(22)	113.6 (6)	S(1)–S(2)–O(23)	106.5 (4)
O(21)–S(2)–O(23)	112.3 (6)	O(22)–S(2)–O(23)	113.5 (5)
O(31)–S(3)–O(32)	114.3 (5)	O(31)–S(3)–O(33)	114.0 (6)
O(32)–S(3)–O(33)	113.4 (5)	O(31)–S(3)–S(4)	105.5 (3)
O(32)–S(3)–S(4)	103.9 (4)	O(33)–S(3)–S(4)	104.2 (4)
S(3)–S(4)–O(41)	106.9 (5)	S(3)–S(4)–O(42)	104.4 (4)
O(41)–S(4)–O(42)	112.7 (5)	S(3)–S(4)–O(43)	104.2 (4)
O(41)–S(4)–O(43)	116.9 (6)	O(42)–S(4)–O(43)	110.5 (6)

$[Mn\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2\cdot{}^1/_2H_2O$ (2g) and $[Co\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2\cdot{}^1/_2H_2O$ (3g). As was noted above, these two complexes are isomorphous and can be discussed together. The central metal (Mn or Co) atom is located on a crystallographic inversion center. It is coordinated in a roughly octahedral arrangement to four water molecules and two trans hydroxo groups. The hydroxo groups link the central metal atom to two chromium atoms, each of which is coordinated to four nitrogen atoms from the ligands and one terminal hydroxo group. A view of the entire cation is given in Figure 3.

The bond lengths and angles in the two complexes are given in Tables XII and XIII, respectively. Cis angles at cobalt range from 84.3 (4) to 89.0 (4)°, while those at manganese are 84.9 (1)–88.6 (1)°. The cobalt–chromium separation is 3.669 (2) Å, and the bridging angle Co–O(1)–Cr is 135.2 (5)°; the oxygen

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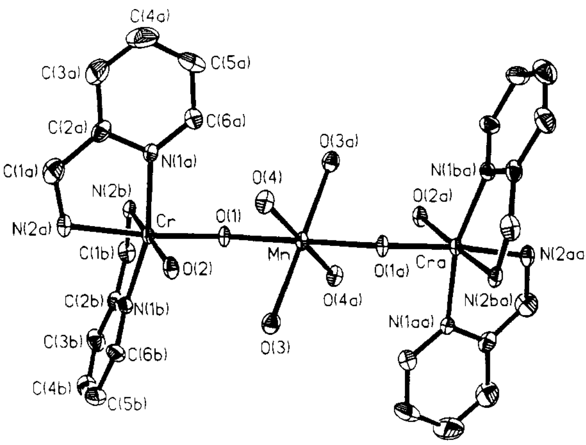

Figure 3. View of the cation in the structure of $[Mn\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2\cdot{}^1/_2H_2O$. Hydrogen atoms are omitted for clarity. The structure of the cation in the analogous Co complex is substantially similar to that shown here.

Table XII. Selected Bond Lengths (Å) for $[M\{(OH)Cr(pico)_2\}_2](S_2O_6)_2\cdot 0.5H_2O$ (M = Mn, Co)

	Mn	Co		Mn	Co
Cr–N(1A)	2.076 (4)	2.069 (14)	Cr–N(2A)	2.092 (5)	2.089 (13)
Cr–N(1B)	2.072 (4)	2.070 (15)	Cr–N(2B)	2.087 (4)	2.092 (12)
Cr–O(1)	1.935 (4)	1.934 (10)	Cr–O(2)	1.930 (3)	1.927 (9)
M–O(1)	2.110 (4)	2.034 (10)	M–O(3)	2.274 (4)	2.172 (10)
M–O(4)	2.212 (3)	2.134 (10)	S(1)–S(2)	2.130 (2)	2.163 (7)
S(1)–O(11)	1.440 (4)	1.431 (10)	S(1)–O(12)	1.428 (6)	1.423 (12)
S(1)–O(13)	1.418 (5)	1.394 (12)	S(2)–O(21)	1.442 (4)	1.443 (11)
S(2)–O(22)	1.435 (4)	1.418 (12)	S(2)–O(23)	1.445 (5)	1.417 (10)

atom in the bridging hydroxo group lies somewhat closer to the chromium atom than the cobalt atom, the bond lengths being 2.034 (10) Å for Co–O(1) and 1.934 (10) for Cr–O(1) Å. In the manganese complex, for which the structure is more precisely determined, the corresponding metrical parameters are 3.728 (1) Å, 134.3 (2)°, 2.110 (4) Å, and 1.935 (4) Å. These Cr–O values can be compared to those of 1.941 (16)–1.989 (4) Å in a variety of (μ-hydroxo)dichromium(III) complexes.[21,30] The differences in the M–O bond lengths presumably reflect the decreasing metal ion radius in the order Mn(II) > Co(II) > Cr(III).

The dithionate anions are not coordinated to the metal centers, and they show very regular geometries with approximate D_{3d} symmetry. The ideally ±60° torsion angles range from ±57.5 to ±62.9°, and the ideally 180° torsion angles range from 178.3 to 179.1°. The S–O bond lengths range from 1.417 (10) to 1.443 (11) Å, and the S–S bond length is 2.163 (7) Å. These values are comparable to those discussed above.

The most surprising feature of these two complexes, of course, is that the chromium atoms are bridged to the central metal atom by only one hydroxo group. This is unique in the series of metal clusters involving *cis*-$[Cr(OH)_2(A)_4]^+$ complexes, where A is a nitrogen donor. The series of trimers, discussed above and elsewhere,[6,7] and larger clusters prepared and characterized by us[2,3,5] and by Müller and Thewalt[31] had invariably shown ions of this type to be bidentate chelating agents. However, in these particular compounds with the ligand 2-picolylamine [2-(aminomethyl)pyridine], this ion is monodentate with the terminal hydroxo group involved in hydrogen bonding with the water molecules attached to the central metal ion. Complexes most nearly showing this type of bonding include the classical dimers of chromium chemistry, Jorgensen's rhodo and erythro ions isolated in 1882, $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ and $[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]^{5+}$,[21,30] and the dimer $[(H_2O)(en)_2Cr(OH)Cr(en)_2(OH)]^{4+}$ of Springborg and Toftlund (en = ethylenediamine).[32] The last complex is rather more pertinent, as it also contains a terminal hydroxo group. The pH-dependent equilibrium between singly- and doubly-bridged hydroxo species has been discussed in detail by Springborg and Toftlund,[32] and the present result can be readily interpreted in terms of their model.

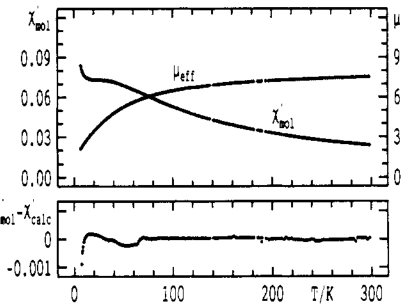

Figure 4. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) for the complex $[Mn\{(OH)Cr(pico)_2(OH)\}_2(OH_2)_4](S_2O_6)_2\cdot{}^1/_2H_2O$. The lower curve shows the fit to the values calculated using the parameters J = 9.93 and J' = 1.52 cm^{-1}.

Magnetic Properties. The magnetic properties of the trinuclear complexes may lend some valuable clues to their structures. For the μ-hydroxo "open-form" complexes **2g** and **3g**, the temperature dependence of the magnetic susceptibility demonstrates significant antiferromagnetic coupling between the central metal and the exterior chromium(III) centers. The data for the Mn(II) complex **2g** are presented in Figure 4; those for the Co complex **3g** are qualitatively similar. The effective magnetic moment of **2g** at room temperature is approximately 7.6 μ_B, close to the expected value of 8.06 μ_B for three independent spins with $S = {}^5/_2, {}^3/_2, {}^3/_2$. The effective magnetic moment decreases to a value of approximately 1.8 μ_B at 5 K, consistent with the existence of a doublet ground state. It is noteworthy that the analogous Ni(II) complex, which is known from X-ray powder patterns to be isomorphous with **2g** and **3g**, also exhibits a significant antiferromagnetic interaction, leading to the conclusion that these "open-form" complexes may all be assumed to give rise to antiferromagnetic coupling.

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

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

by minimization of the function

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

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

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Table XIII. Selected Bond Angles (deg) for $[M\{(OH)Cr(pico)_2\}_2](S_2O_6)_2 \cdot 0.5H_2O$ (M = Mn, Co)

	Mn	Co		Mn	Co
N(2A)–Cr–N(1A)	80.1 (2)	79.8 (5)	N(1B)–Cr–N(1A)	163.6 (2)	162.8 (5)
N(1B)–Cr–N(2A)	88.2 (2)	87.6 (5)	N(2B)–Cr–N(1A)	89.0 (2)	88.6 (5)
N(2B)–Cr–N(2A)	91.6 (2)	91.6 (5)	N(2B)–Cr–N(1B)	79.7 (2)	80.0 (6)
O(1)–Cr–N(1A)	93.6 (2)	94.7 (5)	O(1)–Cr–N(2A)	173.6 (2)	174.2 (6)
O(1)–Cr–N(1B)	98.2 (2)	98.2 (5)	O(1)–Cr–N(2B)	89.5 (2)	90.2 (4)
O(2)–Cr–N(1A)	95.4 (2)	95.6 (5)	O(2)–Cr–N(2A)	91.8 (2)	91.8 (5)
O(2)–Cr–N(1B)	96.5 (2)	96.5 (5)	O(2)–Cr–N(2B)	174.9 (2)	175.0 (6)
O(2)–Cr–O(1)	87.5 (2)	86.8 (4)	O(3)–M–O(1)	84.9 (1)	84.6 (4)
O(4)–M–O(1)	88.6 (1)	89.0 (4)	O(3)–M–O(4)	85.4 (1)	84.2 (4)

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 atom.

For the manganese complex the energies $E(S,S')$ of the 15 states of the ground-state manifold were obtained using the formula

$$E(S,S') = (1/2)J[S(S+1) - S_b(S_b+1) - S'(S'+1)] + (1/2)J'[S'(S'+1) - S_a(S_a+1) - S_c(S_c+1)]$$

which has been derived from the Hamiltonian operator above. In this formula 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 values from $^{11}/_2$ to $^1/_2$.

The fitting of the data to this model gives values for J of 9.93 (3), 16 (1), and 8.43 (3) cm^{-1} for Mn, Co, and Ni, respectively, and for J' of 0.29 (3), 1.5 (2), 0, and 2.94 (4) cm^{-1} for Zn, Mn, Co, and Ni, respectively.[4] This result means that the ground states for the Mn, Co, and Ni complexes are $E(^1/_2,3)$, $E(^3/_2,3)$, and $E(2,3)$, respectively, but for the nickel case the states $E(1,2)$ and $E(0,1)$ are only slightly higher in energy than the ground state.

If we look at the magnetic interaction on the basis of the structure as seen in Figure 3, we can describe the cation as consisting of two halves, each of which is a μ-hydroxo complex. The magnetic interactions in (μ-hydroxo)chromium(III) complexes[30] and in mixed-metal bis(μ-hydroxo) complexes[33] have been discussed before, and the GHP[34] model developed for bis(μ-hydroxo)chromium(III) complexes can (with minor modifications) be used for complexes of this kind.

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 chromium(III) 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. In the present chromium(III)/maganese(II) case, the π–π interaction is also between the half-filled π orbitals on chromium(III) and the half-filled π orbitals on manganese(II), which again results in an antiferromagnetic interaction. In this case, however, the σ–π interaction between the half-filled e_g orbitals on manganese(II) and the half-filled t_{2g} orbitals on chromium(III) also gives rise to an antiferromagnetic coupling. The possible magnetic interaction between the empty e_g orbitals on chromium and the half-filled t_{2g} orbitals on manganese gives rise to a ferromagnetic coupling, but this interaction is expected to be very small. Finally, we should note the interaction between the two chromium atoms, even though they are far apart, can be significant, as we have shown elsewhere.[35,36] In the GHP model a very important parameter is the position of the hydrogen atoms relative to the plane formed by the two metal atoms and the bridging oxygen atom. In this case the angle between the OH bond and the plane formed by Mn–O–Cr is 6.7°, which means that the antiferromagnetic contribution is at its maximum. To conclude, therefore, we anticipate that the chromium–manganese interactions in this μ-hydroxo complex will be antiferromagnetic, which is also what we observe.

The room-temperature effective magnetic moment of the cobalt/chromium complex has approximately the expected value for three noninteracting ions (with $S = {}^3/_2, {}^3/_2, {}^3/_2$), which is $\sqrt{45}$. This shows that the ground state for the cobalt atom must be $^4T_{1g}$ in O_h symmetry. We have therefore treated the cobalt(II) atom as an $S = {}^3/_2$ system, even though this is obviously a crude approximation; this approximation, however, will improve as the symmetry around cobalt departs from octahedral. For the cobalt complex two of the three π orbitals are filled and one is half-filled. In this case the interaction with the half-filled π orbital would be expected to be more important than that with the filled π orbitals. The σ–π interaction must give an antiferromagnetic contribution, as discussed for the manganese case. The overall result is an antiferromagnetic coupling in agreement with the experiment. In this case the location of the hydrogen atom on the bridge is less reliably established, but it is certainly not in a position to block the interaction.

For the nickel complex with filled π orbitals and with the half-filled σ orbitals, the π–π interaction will be ferromagnetic while the σ–π interaction between the half-filled σ orbital on nickel and the half-filled π orbital on chromium will be *antiferromagnetic*; the experimental observation of an antiferromagnetic interaction shows that the latter interaction is the more important.

The zinc cyclam complex, **5h**, which differs from the above complexes both in its bridging structure and in the presence of a diamagnetic metal in the central site, exhibits weak antiferromagnetic coupling between the two Cr(III) centers. The effective magnetic moment of **5h** at room temperature is approximately 5.5 μ_B, as expected for two $S = {}^3/_2$ ions, and this value declines slowly to 5.0 μ_B at 20 K; below 20 K the effective magnetic moment decreases rapidly. The susceptibility data do not show a maximum above 4 K, but they can be fitted to the normal expressions for a binuclear chromium(III) complex[21] to give a value of 1.61 (9) cm^{-1} for the singlet–triplet splitting.

As was noted above, there are evidently two distinct forms of the other cyclam complexes, and the magnetic data allow us to distinguish between these two forms. One form of complexes with Mn, Co, and Ni (**2h**, **3h'**, **4h**) exhibits magnetic properties that approximate Curie–Weiss behavior, the effective magnetic moment remaining approximately constant in the temperature range 20–300 K. The observed value of 8.0 μ_B for the Mn complex, for example, is consistent with the value of $\sqrt{65}$ μ_B expected for the spin-only moment of three noninteracting centers with $S = {}^5/_2, {}^3/_2, {}^3/_2$. Hence, in this form of the complex, there is apparently

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no discernible magnetic interaction between the central metal and the chromium centers. Another form (e.g., **3h**) exhibits weak ferromagnetic interactions, the effective magnetic moment increasing as the temperature decreases in the range 300–20K. All of these complexes may be expected to be bis(μ-hydroxo) "closed forms" consistent with the structure of **5h**. As discussed above, the GHP model places great emphasis on the angle between the O–H bonds and the M–O–Cr planes. In the absence of additional structural data, we do not know the relevant angles, but we would note that if the angles are of the order of 40–50°, the antiferromagnetic π–π interaction is effectively blocked.

Unlike the cyclam complexes, the complexes with en and NH_3 all exhibit antiferromagnetic interactions. In the absence of any structural data in either of these series, we are unable to offer any convincing structural conclusion on the basis of these magnetic results alone.

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Supplementary Material Available: Tables S1–S6, listing hydrogen atom parameters and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.