

Magnetic Exchange through Hydrogen Bonds: Structural and Magnetic Characterization of *cis*-Hydroxo-aquachromium(III) Complexes of Tetradentate and Monodentate Ligands

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The syntheses and characterization of a series of chromium(III) complexes of the general type *cis*-[CrA₄(OH)(OH₂)]²⁺ are described. The ligands A₄ used include 1,4,8,11-tetraazacyclotetradecane (cyclam), *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine (bispictn), *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen), *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine (bispicMe₂en), and ammonia. The binuclear complex [Cr(bispicMe₂en)(OH)(OH₂)](ClO₄)₂, [CrC₁₆H₂₅N₄O₂](ClO₄)₂ (**3**), crystallizes in space group *P*2₁/*n* of the monoclinic system with eight mononuclear formula units in a cell of dimensions *a* = 14.381(4) Å, *b* = 15.054(4) Å, *c* = 21.547(6) Å, and β = 105.94(2)°. The structure has been refined to a final *R* factor of 0.0606 based on 3346 observed independent reflections. The central chromium(III) atom is pseudooctahedrally bonded to the four nitrogen atoms of the ligand and to two *cis* oxygen atoms from the nominal water and hydroxo ligands. The complex adopts the *cis*-α geometry in which the pyridine nitrogen atoms of the ligand are mutually *trans*. The complex [Cr(cyclam)(OH)(OH₂)](ClO₄)₂·0.5H₂O (**4a**) and the corresponding dithionate (**4b**), and iodide chloride salt (**4c**) have also been isolated, and the structure of the iodide chloride salt (**4c**) has been determined. The complex, [Cr(cyclam)(OH)(OH₂)](Cl)(I), [CrC₁₀H₂₇N₄O₂](Cl)(I) (**4c**), crystallizes in space group *P*2₁/*c* of the monoclinic system with four formula units in a cell of dimensions *a* = 10.361(2) Å, *b* = 11.125(2) Å, *c* = 15.211(2) Å, and β = 104.880(10)°. The structure has been refined to a final *R* factor of 0.0379 based on 2519 observed independent reflections. Both of these complexes **3** and **4c** are binuclear in the solid state, the two adjacent chromium(III) centers being doubly bridged by hydrogen bonds between hydroxo and aqua ligands. The Cr...Cr separations are 4.999 and 4.925 Å in **3** and **4c**, respectively. The complexes exhibit surprisingly strong antiferromagnetic interactions, with triplet energies in the range 2–7 cm⁻¹, with the exception of the tetraammine complexes **5** and complex **4c**, which show only very weak antiferromagnetic coupling with triplet energies of 0–7 cm⁻¹. The bispicen complex (**2**) is known from other work to adopt a chain structure in the solid state, while the other complexes are binuclear, but magnetic susceptibility measurements alone are hard pressed to distinguish between these two structures. The EPR spectra of the complexes, however, can be used to readily distinguish between the chain and dimer forms of aggregation.

Introduction

In a recent series of papers^{2–5} it was shown that, in the solid state, compounds of the general formula *cis*-[CrA₄(OH₂)(OH)]²⁺ (where A₄ represents the four nitrogen ligands from an appropriate number of monodentate or polydentate ligands) have a dimeric structure where two formula units are bound together by hydrogen bonds. This solid-state structure has at least two implications: First, heating this kind of compound to 100–140 °C is a general procedure^{6,7} to prepare bis(μ-hydroxo) complexes ("diols"), and second, the hydrogen bonds are so powerful that they can transmit an antiferromagnetic interaction between the two chromium(III) ions even though the separation between them approximates 5 Å. In addition to interactions in these aqua hydroxo complexes, Wieghardt and co-workers⁸ have described weak antiferromag-

netic interactions in complexes with one, two, or three hydrogen-bonded bridges. We had originally proposed⁵ that the observation of antiferromagnetic coupling is indicative of this hydrogen bonded dimeric structure, but our more recent work suggested that the situation is more complex than it originally appeared. One exception to our proposed guideline has already been established, since there is now at least one known example of a complex of this type that exhibits antiferromagnetic coupling but forms an infinite chain rather than a dimeric structure.⁹ Moreover, in the present paper we demonstrate that while the ammonia complexes [A₄ = (NH₃)₄] form diols upon heating, they exhibit *J* values that are so small that they cannot be used to distinguish between dimeric and chain structures.

In this work we will demonstrate that EPR spectroscopy provides an excellent method to prove the existence of a dimeric structure both in the solid state and in frozen solutions. To obtain narrow lines in EPR spectroscopy, it is in general necessary to dilute the compound in a diamagnetic host. However, crystals of these antiferromagnetically coupled systems become magnetically diluted when cooled to 4 K. At this temperature the spectra observed are definitely not from monomeric chromium(III) complexes but from the quintet states which emerge from the magnetic interaction in the hydrogen-bonded dimeric units. Recently we¹⁰ and others¹¹ discussed the EPR spectra of binuclear chromium(III) complexes held together by bridging ligands (rather than by hydrogen bonds) and showed that the spectrum

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from the quintet state is the dominant feature. In addition, we will demonstrate that the complexes adopt the dimeric structure in frozen glasses of some organic solvents independent of their original structure in the solid. The equilibrium between monomeric and dimeric species in different solvents is also discussed.

The specific systems used for our investigation were salts of *cis*-[Cr(NH₃)₄(OH)(H₂O)]²⁺, *cis*-[Cr(cyclam)(OH)(H₂O)]²⁺, *cis*-β-[Cr(bispictn)(OH)(H₂O)]²⁺, *cis*-α-[Cr(bispicen)(OH)(H₂O)]²⁺, and *cis*-α-[Cr(bispicMe₂en)(OH)(H₂O)]²⁺, where cyclam, bispictn, bispicen, and bispicMe₂en represent 1,4,8,11-tetraazacyclotetradecane, *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine, *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine, and *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine, respectively.

Experimental Section

Physical Measurements. Electronic absorption spectra in the visible region were recorded on a Perkin-Elmer Lambda 17 spectrophotometer. The spectra are characterized by their maxima (ϵ, λ)_{max}, where the molar absorption coefficient ϵ is in units of L mol⁻¹ cm⁻¹ and λ is in nm. The compounds were dissolved in water ($c \sim 3 \times 10^{-3}$ M), and spectra were recorded immediately thereafter. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 2–300 K at a field strength of 1.3 T. The susceptibility data were corrected for diamagnetism by Pascal's constants. The magnetic field was calibrated with Hg[Co(NCS)₄].¹² A more detailed description of the equipment is published elsewhere.¹³ EPR spectra were recorded on a Bruker ESP-300 spectrometer equipped with an Oxford ESR-9 gas-flow cryostat. The metal analyses were performed on a Perkin-Elmer 403 atomic absorption spectrometer. The microanalytical laboratory of the H. C. Ørsted Institute carried out analyses for carbon, nitrogen, hydrogen, halogen, and sulfur by standard methods.

Syntheses. Caution! Some of the compounds described were isolated as perchlorate salts and should be handled as potentially explosive compounds. Mother liquors containing even small amounts of perchloric acid should never be mixed with washing liquors containing ethanol.

Ligands. 1,4,8,11-Tetraazacyclotetradecane (cyclam) was purchased from Fluka. *N,N'*-Bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen) and *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine (bispictn) were prepared according to methods described previously.^{14,15}

The ligand *N,N'*-bis(2-pyridylmethyl)-*N,N'*-dimethyl-1,2-ethanediamine (bispicMe₂en)¹⁶ was prepared by direct methylation of bispicen with formic acid and formaldehyde using a standard method.¹⁷ From 24.2 g of bispicen (100 mmol) was obtained 31 g of a crude product, which was purified in the following way: The crude amine was dissolved in ethanol (200 mL, 99%). Concentrated hydrochloric acid was added to the cooled solution to precipitate 34.5 g of the amine hydrochloride. This compound was washed with ethanol (99%). Anal. Calcd for C₁₆H₂₂N₄·4HCl: C, 46.17; N, 13.46; H, 6.30; Cl, 34.07. Found: C, 45.08; N, 13.23; H, 6.18; Cl, 34.88. The compound was evidently slightly contaminated with hydrochloric acid. The free amine was obtained by redissolving the hydrochloride in a solution of potassium hydroxide (95 mL, 30%). Solid potassium hydroxide (60 g) was added, and the layer of free amine that separated was isolated with a separatory funnel. Toluene (400 mL) was then added, and the solution was dried over anhydrous Na₂SO₄. After 60 min of stirring, the solution was filtered, and the solvent was evaporated on a rotary evaporator. Yield of free amine: 18 g (66%). This product was sufficiently pure for the syntheses described below.

Complexes. The following compounds (starting materials and others) have been prepared previously: *cis*-β-[Cr(bispictn)(OH)(H₂O)](ClO₄)₂·2H₂O,¹⁸ *cis*-α-[Cr(bispicen)Cl₂]Cl·3H₂O,¹⁹ *trans*-[Cr(py)₄F₂]NO₃,²⁰ *cis*-[Cr(cyclam)Cl₂]Cl,²¹ *cis*-[Cr(NH₃)₄(OH)(H₂O)](S₂O₆)·H₂O,²² *cis*-[Cr(NH₃)₄(OH)(H₂O)](ClO₄)₂,¹⁸ *cis*-β-[Co(bispictn)(OH)(H₂O)](ClO₄)₂·2H₂O,¹⁸ *cis*-α-[Co(bispicen)Cl₂]Cl·1 1/3 H₂O.¹⁹

cis-β-[Cr(bispictn)(OH)(H₂O)]₂·2H₂O (1) could be obtained by the same procedure as the corresponding perchlorate,¹⁸ when sodium perchlorate and perchloric acid were replaced by sodium iodide and hydrochloric acid. Yield: 71%. The compound was recrystallized from boiling water with a loss of 40%. Anal. Calcd for [Cr(C₁₃H₂₀N₄)(OH)(H₂O)]₂·2H₂O: Cr, 8.21; C, 28.45; N, 8.85; H, 3.66; I, 40.08. Found: Cr, 8.17; C, 27.73; N, 8.83; H, 4.21; I, 39.60. (ϵ, λ)_{max} = (75.8, 513), (65.7, 395).

cis-α-[Cr(bispicen)(OH)(H₂O)](ClO₄)₂·0.5H₂O (2) was prepared by the same method as *cis*-β-[Cr(bispictn)(OH)(H₂O)](ClO₄)₂·2H₂O¹⁸ from *cis*-α-[Cr(bispicen)Cl₂]Cl·3H₂O (0.30 g, 0.66 mmol). Yield: 0.29 g (83%). The compound was recrystallized from water with a loss of 50%. Anal. Calcd for [Cr(C₁₄H₁₈N₄)(OH)(H₂O)](ClO₄)₂·0.5H₂O: Cr, 9.68; C, 31.30; N, 10.43; H, 3.56; Cl, 13.20. Found: Cr, 9.75; C, 31.13; N, 10.46; H, 3.79; Cl, 13.28. (ϵ, λ)_{max} = (84.3, 522), (58.6, 398).

cis-α-[Cr(bispicMe₂en)(OH)(H₂O)](ClO₄)₂. (3) *trans*-[Cr(py)₄F₂]NO₃ (0.94 g, 2.00 mmol) was dissolved in 2-methoxyethanol (10 mL) by heating. bispicMe₂en (0.54 g, 2.00 mmol) was added, and the solution was heated for 4 h at 90 °C with supplementary addition of 2-methoxyethanol. Afterward, the solvent was evaporated to leave a sticky mass presumed to contain impure *cis*-[Cr(bispicMe₂en)F₂]NO₃. This residue was heated for 3 h at 90 °C with concentrated hydrochloric acid (10 mL). Finally, the heating was continued to leave a blue, sticky mass presumed to consist of impure *cis*-[Cr(bispicMe₂en)Cl₂]Cl. The new residue was heated gently (75–80 °C) with 50 mL of a solution of mercury(II) perchlorate (0.1 M) in perchloric acid (0.5 M). When a bright red solution had formed, the pH of the solution was adjusted to 4–5 with a solution of sodium hydroxide (2 M) and of sodium acetate (2 M). Solid sodium perchlorate (7 g) was added, and the solution was cooled on ice. Red crystals formed. They were filtered off and washed with a solution of sodium perchlorate (1 M) and with ethanol (96%). Yield: 0.77 g (69%). The practically pure compound was recrystallized from boiling water with a loss of 20%. Anal. Calcd for [Cr(C₁₆H₂₂N₄)(OH)(H₂O)](ClO₄)₂: Cr, 9.35; C, 34.55; N, 10.07; H, 4.53; Cl, 12.75. Found: Cr, 9.32; C, 34.51; N, 10.01; H, 4.51; Cl, 12.72. (ϵ, λ)_{max} = (59.7, 532), (53.9, 408).

cis-[Cr(cyclam)(OH)(H₂O)](ClO₄)₂·0.5H₂O (4) was prepared as described for *cis*-β-[Cr(bispictn)(OH)(H₂O)](ClO₄)₂·2H₂O¹⁸ but from *cis*-[Cr(cyclam)Cl₂]Cl (0.36 g, 1.0 mmol). Yield: 0.38 g (78%). The crude product was extracted on a filter with hot water and reprecipitated with a concentrated solution of sodium perchlorate. Anal. Calcd for [Cr(C₁₀H₂₄N₄)(OH)(H₂O)](ClO₄)₂·0.5H₂O: Cr, 10.50; C, 24.25; N, 11.31; H, 5.69; Cl, 14.32. Found: Cr, 10.51; C, 24.20; N, 11.28; H, 5.64; Cl, 14.17. (ϵ, λ)_{max} = (114, 519), (47.7, 388), (45.9, 365) sh.

cis-[Cr(cyclam)(OH)(H₂O)]S₂O₆·3H₂O (4a) was prepared as the corresponding perchlorate except that a saturated solution of sodium dithionate and concentrated hydrochloric acid was used instead of a solution of sodium perchlorate and perchloric acid. The crystals were washed with ethanol (50% and 96%). From *cis*-[Cr(cyclam)Cl₂]Cl (0.36 g, 1.0 mmol) was obtained a yield of 0.24 g (48%). Anal. Calcd for [Cr(C₁₀H₂₄N₄)(OH)(H₂O)]S₂O₆·3H₂O: Cr, 10.37; C, 23.95; N, 11.17; H, 6.63; S, 12.79. Found: Cr, 10.43; C, 24.03; N, 11.15; H, 6.06; S, 12.99.

cis-[Cr(cyclam)(OH)(H₂O)]₂·2H₂O (4b) was prepared as the corresponding perchlorate except that a solution of sodium iodide (1 g) and hydrochloric acid was used instead of a solution of sodium perchlorate and perchloric acid. The crystals were washed with ethanol (50% and 96%). From *cis*-[Cr(cyclam)Cl₂]Cl (0.36 g, 1.0 mmol) was obtained a yield of 0.46 g (80%). Anal. Calcd for [Cr(C₁₀H₂₄N₄)(OH)(H₂O)]₂·2H₂O: Cr, 9.01; C, 20.81; N, 9.71; H, 5.41; I, 43.97. Found: Cr, 8.89; C, 20.69; N, 9.72; H, 5.12; I, 42.68. When a smaller amount of sodium iodide (0.23 g) was used to precipitate the complex, a mixed chloride iodide (4c) resulted. This same complex also separated

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Table 1. Crystallographic Data for Complexes 3, 4a, and 4c

	3	4c	4a
formula	C ₁₆ H ₂₅ Cl ₂ CrN ₄ O ₁₀	C ₁₀ H ₂₇ ClCrIN ₄ O ₂	C ₁₀ H ₃₃ CrN ₄ O ₁₁ S ₂
color, habit	burgundy prism	red prism	red plate
a, Å	14.381(4)	10.361(2)	8.785(2)
b, Å	15.054(4)	11.125(2)	9.511(2)
c, Å	21.547(6)	15.211(2)	13.665(3)
α, deg	90	90	86.27(3)
β, deg	105.94(2)	104.88(1)	86.47(3)
γ, deg	90	90	73.41(3)
V, Å ³	4485(2)	1694.4(5)	1090.8(4)
Z	8	4	2
fw	556.3	449.7	501.5
space group	P2 ₁ /n	P2 ₁ /c	P1̄
T, °C	-100	22	22
ρ _{calc}	1.648	1.763	1.527
μ, mm ⁻¹	0.796	2.626	0.765
NO ^a	7937	3348	3079
NO [I > 3σ(I)]	3346	2519	2339
R ^b	0.0606	0.0379	
R _w ^c	0.0649	0.0507	

^a NO = number of observed reflections. ^b $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^c $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$.

slowly from the mixture to give well-shaped crystals when a concentrated solution of the iodide salt in hydrochloric acid was neutralized. Anal. Calcd for [Cr(C₁₀H₂₄N₄)(OH)(H₂O)]Cl: Cr, 11.47; C, 26.70; N, 12.46; H, 6.05; Cl, 7.88; I, 28.02. Found: Cr, 11.70; C, 24.12; N, 11.53; H, 6.02; Cl, 8.0; I, 29.4. (ϵ, λ)_{max} = (112, 519), (47.9, 388), (46.1, 365 sh). The analysis for carbon, nitrogen, and hydrogen was carried out in a thermostated room of high humidity. As the compound readily takes up crystal water, this may account for the low observed values for carbon and nitrogen. In the sample examined crystallographically (*vide infra*), there is no water of crystallization.

cis-[Cr(NH₃)₄(OH)(H₂O)]₂ (5) was prepared as the corresponding perchlorate (5a) as described previously¹⁸ (see also preparation 1). Yield: 62% based on *cis*-[Cr(NH₃)₄(OH)(H₂O)]S₂O₈·H₂O, prepared via *cis*-[Cr(NH₃)₄(H₂O)]Br₃. Anal. Calcd for [Cr(NH₃)₄(OH)(H₂O)]₂: Cr, 12.72; N, 13.70; H, 3.70; I, 62.07. Found: Cr, 12.80; N, 13.64; H, 3.70; I, 64.05. (ϵ, λ)_{max} = (42.6, 521), (38.1, 396).

cis-α-[Co(bispicen)(OH)(H₂O)](ClO₄)₂ (6) was prepared as the corresponding chromium complex, but from *cis*-α-[Co(bispicen)Cl₂]-Cl·1.33H₂O (0.45 g, 1.04 mmol). Yield: 0.42 g (78%). Recrystallization from water gave a loss of 55%. Anal. Calcd for [Co(C₁₄H₁₈N₄)(OH)(H₂O)](ClO₄)₂: Co, 11.01; C, 31.42; N, 10.47; H, 3.96; Cl, 13.25. Found: Co, 11.00; C, 31.63; N, 10.56; H, 3.97; Cl, 13.38. (ϵ, λ)_{max} = (131, 498), (94.7, 379).

cis-[Co(bispicMe₂en)(OH)(H₂O)](ClO₄)₂·H₂O (7) was prepared by the same procedure as *cis*-β-[Co(bispicn)(OH)(H₂O)](ClO₄)₂·2H₂O,¹⁸ but from a crude product of *cis*-[Co(bispicMe₂en)Cl₂Cl] (0.30 g, ~0.7 mmol) obtained in the same way as *cis*-α-[Co(bispicen)Cl₂Cl]·1/3H₂O.¹⁹ Yield: 0.15 g (~37%). Anal. Calcd for [Co(C₁₆H₂₂N₄)(OH)(H₂O)](ClO₄)₂·H₂O: Co, 10.14; C, 33.06; N, 9.64; H, 4.68; Cl, 12.20. Found: Co, 9.58; C, 32.79; N, 9.73; H, 4.32; Cl, 11.82. The content of crystal water varied with the humidity of the air. (ϵ, λ)_{max} = (68.3, 520), (75.4, 398).

X-ray Structure Determinations. The structure of complex 3 was determined at 173 K while those of complexes 4a and 4c were determined at room temperature (295 K) on a Nicolet R3m/V diffractometer equipped with a molybdenum tube [$\lambda(K\alpha_1) = 0.70926$ Å; $\lambda(K\alpha_2) = 0.71354$ Å] and a graphite monochromator. Crystal data and experimental parameters are presented in Table 1. The data were corrected for Lorentz-polarization effects and absorption. The structures were solved by direct methods and refined by least-squares techniques; the programs used were from the SHELXTL system.²³

cis-α-[Cr(bispicMe₂en)(OH)(H₂O)](ClO₄)₂ (3). The complex crystallizes in the centrosymmetric monoclinic space group P2₁/n with eight mononuclear formula units in the unit cell. Data were collected in the range 4 < 2θ < 50°, the data gathered having -17 ≤ h ≤ 0, 0 ≤ k ≤ 17, -24 ≤ l ≤ 24. All hydrogen atoms except those associated with the coordinated water and hydroxo groups were placed in calculated positions (C-H = 0.96 Å). All non-hydrogen atoms were refined anisotropically. The final values of the conventional R factors were R = 0.0606, R_w =

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for [Cr(bispicMe₂en)(OH)₂(OH)]₂(ClO₄)₄ (3)

	x	y	z	U(eq) ^a
Cr(1)	2115(1)	7593(1)	186(1)	20(1)
O(1)	1066(5)	8415(4)	140(3)	28(3)
O(2)	1327(5)	6627(4)	346(3)	28(3)
N(1)	3402(6)	6836(5)	405(4)	23(3)
N(2)	2979(6)	8556(6)	-104(4)	26(3)
N(11)	2677(6)	7845(5)	1154(4)	21(3)
N(21)	1707(6)	7420(6)	-808(4)	28(3)
Cr(2)	-736(1)	7471(1)	1087(1)	20(1)
O(3)	-278(5)	6682(4)	529(3)	25(3)
O(4)	-109(5)	8450(5)	778(3)	26(3)
N(3)	-1569(6)	6463(6)	1358(4)	28(3)
N(4)	-1092(6)	8199(5)	1831(4)	27(3)
N(31)	-2044(6)	7605(6)	374(3)	27(3)
N(41)	456(6)	7231(5)	1852(4)	22(3)
C(1)	4207(6)	7460(8)	383(4)	26(3)
C(2)	3877(7)	8093(7)	-170(5)	30(4)
C(11)	3392(8)	6062(7)	-35(5)	33(4)
C(12)	3344(7)	7252(7)	1476(5)	24(4)
C(13)	3808(7)	7333(8)	2129(5)	30(4)
C(14)	3555(8)	8052(8)	2462(5)	32(4)
C(15)	2877(8)	8659(8)	2134(5)	36(5)
C(16)	2434(8)	8524(7)	1487(5)	30(4)
C(17)	3548(7)	6511(7)	1074(5)	26(4)
C(21)	3262(8)	9343(7)	317(5)	39(5)
C(22)	1919(8)	8079(7)	-1151(5)	28(4)
C(23)	1669(8)	8075(8)	-1818(5)	38(5)
C(24)	1190(8)	7359(8)	-2142(5)	40(5)
C(25)	971(9)	6670(8)	-1785(6)	46(5)
C(26)	1211(8)	6727(7)	-1130(5)	30(4)
C(27)	2411(7)	8872(7)	-760(5)	26(4)
C(3)	-2167(8)	6907(8)	1760(5)	36(4)
C(4)	-1515(7)	7550(7)	2209(4)	29(4)
C(31)	-1057(8)	5672(7)	1691(5)	40(5)
C(32)	-2635(7)	6905(7)	298(5)	28(4)
C(33)	-3523(8)	6886(8)	-156(5)	35(5)
C(34)	-3795(8)	7608(9)	-558(5)	43(5)
C(35)	-3173(9)	8335(8)	-491(5)	40(5)
C(36)	-2292(8)	8308(8)	-23(5)	34(4)
C(37)	-2254(8)	6143(7)	741(5)	32(4)
C(41)	-1795(8)	8962(7)	1606(5)	36(5)
C(42)	573(7)	7811(7)	2340(5)	24(4)
C(43)	1326(8)	7723(7)	2909(5)	32(4)
C(44)	1959(8)	7038(8)	2958(5)	37(4)
C(45)	1837(8)	6421(7)	2455(5)	30(4)
C(46)	1086(7)	6550(7)	1905(5)	29(4)
C(47)	-155(7)	8532(7)	2247(5)	31(4)
Cl(1)	1569(2)	4339(2)	988(1)	31(1)
O(5)	2368(7)	4602(6)	1512(4)	70(4)
O(6)	705(6)	4514(5)	1150(5)	60(4)
O(7)	1603(6)	3399(5)	861(4)	50(4)
O(8)	1599(7)	4824(5)	421(4)	54(4)
Cl(2)	673(2)	714(2)	1288(1)	34(1)
O(9)	1383(6)	534(6)	963(5)	61(4)
O(10)	1007(7)	417(6)	1934(4)	70(4)
O(11)	490(6)	1656(5)	1269(4)	57(4)
O(12)	-223(5)	272(5)	976(4)	46(3)
Cl(3)	5787(2)	4918(2)	1514(1)	33(1)
O(13)	5073(8)	4264(7)	1255(4)	94(5)
O(14)	5677(6)	5484(6)	871(4)	56(4)
O(15)	6736(6)	4521(6)	1572(4)	62(4)
O(16)	5682(7)	5397(6)	1962(4)	69(4)
Cl(4)	5620(2)	-20(2)	1509(2)	43(1)
O(17)	6518(6)	282(8)	1901(4)	85(5)
O(18)	5602(9)	-111(10)	879(5)	142(8)
O(19)	5333(13)	-741(10)	1760(6)	185(9)
O(20)	4946(10)	540(13)	1547(8)	211(11)

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

0.0649, based on 3346 independent reflections with I > 3σ(I). Positional parameters are listed in Table 2.

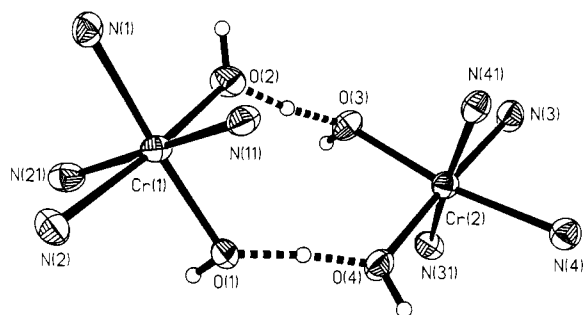
cis-[Cr(cyclam)(OH)(H₂O)](I)(Cl) (4c). The complex crystallizes in the centrosymmetric monoclinic space group P2₁/c with four mononuclear formula units in the cell. Data were collected in the range 4 < 2θ < 52°, the data gathered having -12 ≤ h ≤ 0, 0 ≤ k ≤ 13, -18 ≤ l

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

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for $[\text{Cr}(\text{cyclam})(\text{OH}_2)(\text{OH})_2(\text{ClO}_4)_2(\text{Cl})_2]_2(\text{4c})$

	x	y	z	$U(\text{eq})^a$
Cr(1)	3283(1)	-3824(1)	8923(1)	24(1)
O(1)	3697(4)	-3830(4)	10266(3)	38(1)
O(2)	4080(4)	-5402(3)	8941(3)	35(1)
N(1)	2607(5)	-2046(4)	8958(3)	31(2)
N(4)	5099(5)	-2969(4)	8975(3)	33(2)
N(8)	2878(5)	-3913(4)	7511(3)	35(2)
N(11)	1318(5)	-4459(5)	8691(3)	35(2)
C(2)	3799(6)	-1308(5)	9359(4)	38(2)
C(3)	4870(6)	-1648(5)	8911(4)	39(2)
C(5)	5901(6)	-3380(6)	8359(4)	47(2)
C(6)	5137(7)	-3393(6)	7360(4)	51(2)
C(7)	3987(7)	-4241(6)	7120(4)	49(2)
C(9)	1771(6)	-4779(6)	7219(4)	48(2)
C(10)	715(6)	-4500(6)	7704(4)	47(2)
C(12)	424(5)	-3859(6)	9192(4)	40(2)
C(13)	287(6)	-2523(6)	9023(5)	46(2)
C(14)	1511(6)	-1809(6)	9414(4)	41(2)
I(1)	1993(1)	2201(1)	9129(1)	46(1)
Cl(1)	2116(1)	-1207(1)	6773(1)	32(1)

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

**Figure 1.** View of the inner coordination sphere of the binuclear $[\text{Cr}(\text{bispicMe}_2\text{en})(\text{OH}_2)(\text{OH})_2]_2^{4+}$ cation in the crystals of the perchlorate salt **3**. Atoms N(11) and N(21) are ligand pyridine nitrogen atoms while N(1) and N(2) are ligand amine nitrogen atoms.**Table 4.** Bond Lengths (\AA) for $[\text{Cr}(\text{bispicMe}_2\text{en})(\text{OH}_2)(\text{OH})_2(\text{ClO}_4)_2(\text{Cl})_2]_2(\text{3})$

Cr(1)-O(1)	1.933(7)	Cr(1)-O(2)	1.931(7)
Cr(1)-N(1)	2.113(8)	Cr(1)-N(2)	2.113(9)
Cr(1)-N(11)	2.055(8)	Cr(1)-N(21)	2.074(8)
N(1)-C(1)	1.501(13)	N(1)-C(11)	1.500(14)
N(1)-C(17)	1.483(13)	N(2)-C(2)	1.507(14)
N(2)-C(21)	1.480(14)	N(2)-C(27)	1.503(12)
N(11)-C(12)	1.355(12)	N(11)-C(16)	1.349(14)
N(21)-C(22)	1.323(15)	N(21)-C(26)	1.344(13)
Cr(2)-O(3)	1.930(7)	Cr(2)-O(4)	1.939(7)
Cr(2)-N(3)	2.112(9)	Cr(2)-N(4)	2.118(9)
Cr(2)-N(31)	2.087(7)	Cr(2)-N(41)	2.058(7)
N(3)-C(3)	1.532(16)	N(3)-C(31)	1.478(13)
N(3)-C(37)	1.500(12)	N(4)-C(4)	1.503(14)
N(4)-C(41)	1.519(13)	N(4)-C(47)	1.486(12)
N(31)-C(32)	1.336(14)	N(31)-C(36)	1.346(14)
N(41)-C(42)	1.341(13)	N(41)-C(46)	1.352(13)
C(1)-C(2)	1.498(14)	C(12)-C(13)	1.386(13)
C(12)-C(17)	1.490(15)	C(13)-C(14)	1.400(16)
C(14)-C(15)	1.381(15)	C(15)-C(16)	1.380(14)
C(22)-C(23)	1.382(15)	C(22)-C(27)	1.519(14)
C(23)-C(24)	1.363(16)	C(24)-C(25)	1.378(18)
C(25)-C(26)	1.360(16)	C(3)-C(4)	1.501(14)
C(32)-C(33)	1.379(13)	C(32)-C(37)	1.496(14)
C(33)-C(34)	1.378(17)	C(34)-C(35)	1.395(18)
C(35)-C(36)	1.387(14)	C(42)-C(43)	1.402(13)
C(42)-C(47)	1.482(14)	C(43)-C(44)	1.361(16)
C(44)-C(45)	1.401(16)	C(45)-C(46)	1.380(13)

≤ 18 . Hydrogen atoms associated with the nitrogen and oxygen atoms were located from a difference Fourier map and were refined isotropically, while hydrogen atoms bound to carbon atoms were placed in fixed calculated positions ($\text{C}-\text{H} = 0.96 \text{\AA}$) and all non-hydrogen atoms were

Table 5. Bond Angles (deg) for $[\text{Cr}(\text{bispicMe}_2\text{en})(\text{OH}_2)(\text{OH})_2(\text{ClO}_4)_2(\text{Cl})_2]_2(\text{3})$

O(1)-Cr(1)-O(2)	90.2(3)	O(1)-Cr(1)-N(1)	168.5(3)
O(2)-Cr(1)-N(1)	94.3(3)	O(1)-Cr(1)-N(2)	93.4(3)
O(2)-Cr(1)-N(2)	172.3(3)	N(1)-Cr(1)-N(2)	83.4(3)
O(1)-Cr(1)-N(11)	91.0(3)	O(2)-Cr(1)-N(11)	92.5(3)
N(1)-Cr(1)-N(11)	78.3(3)	N(2)-Cr(1)-N(11)	94.2(3)
O(1)-Cr(1)-N(21)	91.8(3)	O(2)-Cr(1)-N(21)	94.4(3)
N(1)-Cr(1)-N(21)	98.3(3)	N(2)-Cr(1)-N(21)	78.7(3)
N(11)-Cr(1)-N(21)	172.5(3)	Cr(1)-N(1)-C(1)	106.9(6)
Cr(1)-N(1)-C(11)	115.0(5)	C(1)-N(1)-C(11)	109.9(8)
Cr(1)-N(1)-C(17)	106.0(6)	C(1)-N(1)-C(17)	109.4(7)
C(11)-N(1)-C(17)	109.4(8)	Cr(1)-N(2)-C(2)	107.4(6)
Cr(1)-N(2)-C(21)	117.0(7)	C(2)-N(2)-C(21)	109.3(8)
Cr(1)-N(2)-C(27)	106.5(6)	C(2)-N(2)-C(27)	108.4(8)
C(21)-N(2)-C(27)	108.0(8)	Cr(1)-N(11)-C(12)	115.1(7)
Cr(1)-N(11)-C(16)	126.4(6)	C(12)-N(11)-C(16)	118.5(8)
Cr(1)-N(21)-C(22)	116.1(7)	Cr(1)-N(21)-C(26)	126.2(7)
C(22)-N(21)-C(26)	117.6(9)	O(3)-Cr(2)-O(4)	89.0(3)
O(3)-Cr(2)-N(3)	92.6(3)	O(4)-Cr(2)-N(3)	173.5(3)
O(3)-Cr(2)-N(4)	170.1(3)	O(4)-Cr(2)-N(4)	95.7(3)
N(3)-Cr(2)-N(4)	83.7(3)	O(3)-Cr(2)-N(31)	89.6(3)
O(4)-Cr(2)-N(31)	94.8(3)	N(3)-Cr(2)-N(31)	78.9(3)
N(4)-Cr(2)-N(31)	98.7(3)	O(3)-Cr(2)-N(41)	92.3(3)
O(4)-Cr(2)-N(41)	92.6(3)	N(3)-Cr(2)-N(41)	93.6(3)
N(4)-Cr(2)-N(41)	78.8(3)	N(31)-Cr(2)-N(41)	172.4(4)
Cr(2)-N(3)-C(3)	106.9(6)	Cr(2)-N(3)-C(31)	117.9(7)
C(3)-N(3)-C(31)	111.1(9)	Cr(2)-N(3)-C(37)	105.7(6)
C(3)-N(3)-C(37)	107.9(8)	C(31)-N(3)-C(37)	106.9(8)
Cr(2)-N(4)-C(4)	106.9(6)	Cr(2)-N(4)-C(41)	115.3(6)
C(4)-N(4)-C(41)	109.4(8)	Cr(2)-N(4)-C(47)	105.2(7)
C(4)-N(4)-C(47)	109.2(7)	C(41)-N(4)-C(47)	110.6(8)
Cr(2)-N(31)-C(32)	115.4(6)	Cr(2)-N(31)-C(36)	124.9(7)
C(32)-N(31)-C(36)	119.6(8)	Cr(2)-N(41)-C(42)	114.2(6)
Cr(2)-N(41)-C(46)	126.4(6)	C(42)-N(41)-C(46)	119.4(8)
N(1)-C(1)-C(2)	110.2(7)	N(2)-C(2)-C(1)	108.1(9)
N(11)-C(12)-C(13)	122.5(10)	N(11)-C(12)-C(17)	114.8(8)
C(13)-C(12)-C(17)	122.6(9)	C(12)-C(13)-C(14)	117.9(9)
C(13)-C(14)-C(15)	119.8(9)	C(14)-C(15)-C(16)	118.9(11)
N(1)-C(16)-C(15)	122.4(9)	N(1)-C(17)-C(12)	108.7(8)
N(21)-C(22)-C(23)	123.0(10)	N(21)-C(22)-C(27)	115.1(9)
C(23)-C(22)-C(27)	121.9(10)	C(22)-C(23)-C(24)	119.1(11)
C(23)-C(24)-C(25)	118.1(11)	C(24)-C(25)-C(26)	120.0(11)
N(21)-C(26)-C(25)	122.2(11)	N(2)-C(27)-C(22)	108.8(8)
N(3)-C(3)-C(4)	107.3(8)	N(4)-C(4)-C(3)	110.1(8)
N(31)-C(32)-C(33)	122.5(10)	N(31)-C(32)-C(37)	114.7(8)
C(33)-C(32)-C(37)	122.8(10)	C(32)-C(33)-C(34)	118.4(11)
C(33)-C(34)-C(35)	119.4(9)	C(34)-C(35)-C(36)	118.9(11)
N(31)-C(36)-C(35)	121.0(10)	N(3)-C(37)-C(32)	110.9(8)
N(41)-C(42)-C(43)	121.6(9)	N(41)-C(42)-C(47)	116.1(8)
C(43)-C(42)-C(47)	122.3(9)	C(42)-C(43)-C(44)	118.6(10)
C(43)-C(44)-C(45)	120.3(9)	C(44)-C(45)-C(46)	118.2(10)
N(41)-C(46)-C(45)	121.9(10)	N(4)-C(47)-C(42)	108.9(8)

refined anisotropically. The final values of the conventional R factors were $R = 0.0379$, $R_w = 0.0507$ based on 2519 independent reflections with $I > 2\sigma(I)$. Positional parameters are listed in Table 3.

cis- $[\text{Cr}(\text{cyclam})(\text{OH})(\text{H}_2\text{O})\text{S}_2\text{O}_6\text{3H}_2\text{O}(\text{4a})]$. The complex crystallizes in the triclinic space group $P\bar{1}$ with two mononuclear formula units in the cell. Data were collected in the range $3.5 < 2\theta < 45^\circ$, the data gathered having $0 \leq h \leq 9$, $-10 \leq k \leq 10$, $-14 \leq l \leq 14$. The locations of the chromium and bridging oxygen atoms were revealed with reasonable clarity, but it soon became apparent that the cyclam ligands were severely disordered. Since the result of importance to us, that the salt is dimeric like that in (4c) above (*vide infra*), was apparent from this preliminary analysis, and since it seemed improbable that great metrical precision would be obtained from a more detailed analysis, further refinement was not undertaken.

Results and Discussion

Description of the Structures. *cis*- α - $[\text{Cr}(\text{bispicMe}_2\text{en})(\text{OH})(\text{H}_2\text{O})](\text{ClO}_4)_2(\text{3})$. The structure consists of *binuclear* units of the complex and perchlorate ions. A view of the inner coordination sphere in the cation is shown in Figure 1. Principal bond distances and angles are listed in Tables 4 and 5, respectively.

The geometry about the chromium(III) centers is roughly octahedral, with ligation provided by the pyridine and the amine

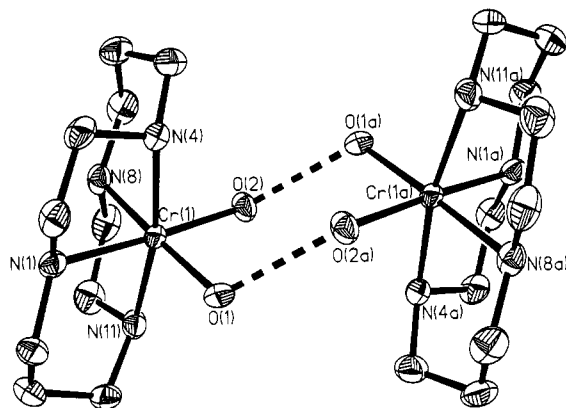


Figure 2. View of the binuclear $[\text{Cr}(\text{cyclam})(\text{OH}_2)(\text{OH})]_2^{4+}$ cation in the crystals of the chloride iodide salt **4c**.

Table 6. Bond Lengths (Å) for $[\text{Cr}(\text{cyclam})(\text{OH}_2)(\text{OH})]_2(\text{I})_2(\text{Cl})_2$ (**4c**)

Cr(1)–O(1)	1.976(4)	Cr(1)–O(2)	1.937(4)
Cr(1)–N(1)	2.104(5)	Cr(1)–N(4)	2.092(5)
Cr(1)–N(8)	2.082(5)	Cr(1)–N(11)	2.097(5)
N(1)–C(2)	1.478(7)	N(1)–C(14)	1.498(9)
N(4)–C(3)	1.488(7)	N(4)–C(5)	1.475(9)
N(8)–C(7)	1.469(9)	N(8)–C(9)	1.476(8)
N(11)–C(10)	1.472(7)	N(11)–C(12)	1.499(8)
C(2)–C(3)	1.492(9)	C(5)–C(6)	1.522(8)
C(6)–C(7)	1.490(10)	C(9)–C(10)	1.500(10)
C(12)–C(13)	1.508(9)	C(13)–C(14)	1.485(8)

nitrogen atoms of the ligand and the oxygen atoms of the “water” and “hydroxo” ligands. As can be seen in Figure 1, the isomer is the *cis-α* species in which the pyridine nitrogen atoms N(11) and N(21) are *trans*. The two chromium(III) centers are bridged by hydrogen bonds to form the dimeric unit $\text{Cr}(\text{HO}\cdots\text{H}\cdots\text{OH})_2\text{Cr}$. The O(1)⋯O(4) and O(2)⋯O(3) separations are 2.455 and 2.448 Å, respectively, for an average value of 2.452(5) Å, and the Cr(1)⋯Cr(2) distance is 4.999 Å. Although the oxygen atoms nominally come from two water and two hydroxo ligands, it is apparent from the structure that all oxygen atoms in the bridges are chemically equivalent. Thus, the Cr(1)–O(1) and Cr(1)–O(2) bonds of 1.933(7) and 1.931(7) Å, respectively, are equal, as are the Cr(2)–O(3) and Cr(2)–O(4) separations of 1.930(7) and 1.939(7) Å, respectively, the average value of these Cr–O lengths is 1.933(4) Å. The O(1)–Cr(1)–O(2) and O(3)–Cr(2)–O(4) bond angles are 90.2(3) and 89.0(3)°, respectively.

The four crystallographically-independent perchlorate ions in the structure are reasonably ordered at this temperature (–100 °C), although there is very high apparent librational motion associated with the oxygen atoms on Cl(4), suggestive of some disorder. The sixteen independent Cl–O bond lengths are in the range 1.303–1.445 Å, with an average value of 1.41(4) Å; if the distances associated with Cl(4) are omitted, the average of the other twelve lengths is 1.426(16) Å. If we again omit the observations associated with Cl(4), the eighteen O–Cl–O bond angles are in the range 107.9–111.5°, with an average of 109.5–(11)°; all of these metrical parameters are consistent with earlier observations of this anion.²⁴

***cis*-[Cr(cyclam)(OH)(H₂O)](I)(Cl) (**4c**).** The structure consists of *binuclear* units of the complex cations and chloride and iodide anions. A view of the inner coordination sphere in the cation is shown in Figure 2. Principal bond distances and angles are listed in Tables 6 and 7, respectively.

The structure of the binuclear cation in the present complex is substantially similar to that in complex **3** above, the principal difference being the presence, in the case of **4c**, of a crystallographic inversion center in the middle of the dimeric array relating

Table 7. Bond Angles (deg) for $[\text{Cr}(\text{cyclam})(\text{OH}_2)(\text{OH})]_2(\text{I})_2(\text{Cl})_2$ (**4c**)

O(1)–Cr(1)–O(2)	90.2(2)	O(1)–Cr(1)–N(1)	87.8(2)
O(2)–Cr(1)–N(1)	174.4(2)	O(1)–Cr(1)–N(4)	90.5(2)
O(2)–Cr(1)–N(4)	92.1(2)	N(1)–Cr(1)–N(4)	82.7(2)
O(1)–Cr(1)–N(8)	177.0(2)	O(2)–Cr(1)–N(8)	86.8(2)
N(1)–Cr(1)–N(8)	95.2(2)	N(4)–Cr(1)–N(8)	90.1(2)
O(1)–Cr(1)–N(11)	96.7(2)	O(2)–Cr(1)–N(11)	95.1(2)
N(1)–Cr(1)–N(11)	90.3(2)	N(4)–Cr(1)–N(11)	169.8(2)
N(8)–Cr(1)–N(11)	83.2(2)	Cr(1)–N(1)–C(2)	106.6(3)
Cr(1)–N(1)–C(14)	118.3(4)	C(2)–N(1)–C(14)	111.3(4)
Cr(1)–N(4)–C(3)	108.7(4)	Cr(1)–N(4)–C(5)	118.8(3)
C(3)–N(4)–C(5)	111.8(5)	Cr(1)–N(8)–C(7)	117.2(3)
Cr(1)–N(8)–C(9)	106.0(4)	C(7)–N(8)–C(9)	110.2(5)
Cr(1)–N(11)–C(10)	108.8(4)	Cr(1)–N(11)–C(12)	117.7(3)
C(10)–N(11)–C(12)	112.1(4)	N(1)–C(2)–C(3)	108.2(5)
N(4)–C(3)–C(2)	110.2(5)	N(4)–C(5)–C(6)	113.8(5)
C(5)–C(6)–C(7)	115.3(6)	N(8)–C(7)–C(6)	113.8(5)
N(8)–C(9)–C(10)	109.0(5)	N(11)–C(10)–C(9)	109.6(5)
N(11)–C(12)–C(13)	113.3(5)	C(12)–C(13)–C(14)	115.2(5)
N(1)–C(14)–C(13)	113.1(5)		

one end to the other. Thus, the geometry about the chromium(III) centers is again roughly octahedral, with ligation provided by the four nitrogen atoms of the ligand and the oxygen atoms of the “water” and “hydroxo” ligands. The two chromium(III) centers are again bridged by hydrogen bonds to form the dimeric unit $\text{Cr}(\text{HO}\cdots\text{H}\cdots\text{OH})_2\text{Cr}$. In the present case, the O(1)⋯O(2a) separation is 2.462 Å, slightly larger than the average value of 2.452(5) Å in **3**, and the Cr(1)⋯Cr(2) distance is 4.925 Å, which is significantly shorter than that of 4.999 Å in **3**, above. In this structure, there is apparently some asymmetry in the bridge, the Cr–O(1) bond of 1.976(4) Å being significantly longer than the Cr–O(2) distance of 1.937(4) Å. This might lead to the conclusion that O(1) is associated with the water ligand while O(2) comes from the hydroxo ligand, although the difference of 0.04 Å between these two bond lengths is much less than would be predicted for a localized system. The O(1)–Cr(1)–O(2) bond angle is 90.2–(2)°, very similar to those in **3**.

***cis*-[Cr(cyclam)(OH)(H₂O)]₂O₆·3H₂O (**4a**).** As was noted above, the cations are disordered in the crystals, and the structure was not refined; however, it is apparent from the space group and unit cell information that the system again contains the dimeric *cis*-[Cr(cyclam)(OH)(OH₂)]₂⁴⁺ cation with a Cr⋯Cr separation of 5.033 Å.

These binuclear structures are, therefore, similar to those observed earlier for the iodide salts of the bipyridine,² picolylamine,³ and bispicn⁵ (**1**) complexes, in which the Cr⋯Cr separations are in the range 4.797–5.12 Å. In the bispicn structure,⁵ the asymmetry noted here in the Cr–O bond lengths for **4c** is also observed, the difference between the two Cr–O bond lengths being 0.055 Å. These structures are, however, in contrast with those of the bispicn complex (**2**), which exhibits a linear chain structure in the solid state,⁹ and of the monomeric dithionate salt of picolylamine.⁴ The structures of the binuclear units in **3** and **4c** are compared with those in related binuclear complexes in Table 8.

Magnetic Susceptibility. The susceptibility data are given *per* monomeric formula unit in cgsu (cm³/mol). The temperature dependence of the magnetic susceptibility of powdered samples of complexes **1**, **2**, **3**, **4–4c**, **5**, and **5a** were measured in the range 2–300 K. Complexes **3** and **5a** may be regarded as demonstrating the extrema of the observed magnetic properties, and the magnetic susceptibility data for these two complexes are plotted as a function of temperature in Figures 3 and 4, respectively. As is shown in Figure 3, for the bispicMe₂en complex **3**, the effective magnetic moment at room temperature is approximately 3.9 μ_B, declining monotonically to a value of 0.8 μ_B at 2 K. Alternatively, the magnetic susceptibility increases with decreasing temperature in the range 300–18 K, reaches a maximum at this temperature, and then declines on further temperature reduction. These

(24) See, for example: Glerup, J.; Goodson, P. A.; Hodgson, D. J.; Michelsen, K.; Nielsen, K. M.; Weihe, H. *Inorg. Chem.* **1992**, *31*, 4611–4616.

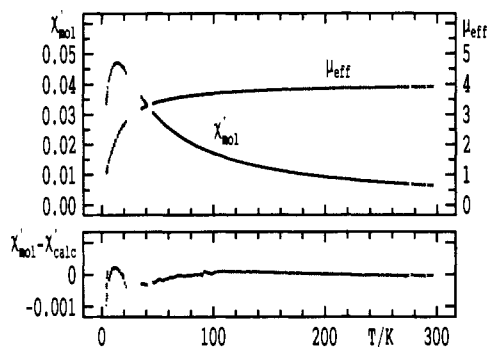


Figure 3. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) for the complex $[\text{Cr}(\text{bispicMe}_2\text{en})(\text{OH})_2(\text{OH})]_2(\text{ClO}_4)_4$ (**3**). The lower curve shows the fit of the susceptibility data to the values calculated using the parameters $g = 2.000$, $J = 6.67 \text{ cm}^{-1}$.

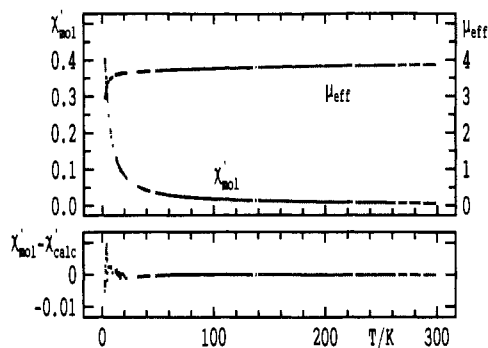


Figure 4. Magnetic susceptibility (left scale) and effective magnetic moment (right scale) for the complex $[\text{Cr}(\text{NH}_3)_4(\text{OH})_2(\text{OH})]_2(\text{ClO}_4)_4$ (**5a**). The lower curve shows the fit of the susceptibility data to the values calculated using the parameters $g = 1.98$, $J = 0.5 \text{ cm}^{-1}$.

Table 8. Structural and Magnetic Properties of Binuclear $[\text{CrA}_4(\text{OH})_2(\text{OH})]_2^{4+}$ Cations

A ₄	Cr–O, Å	O···O, Å	Cr···Cr, Å	J, cm ⁻¹	ref
(bpy) ₂	1.925(3)	2.446(5)	5.03		2
	1.928(3)				
(pico) ₂	1.932(7)	2.50(1)	5.12	2.27	3
	1.934(9)	2.48(1)			
bispictn	1.906(3)	2.472(5)	4.797(1)	4.58	5
	1.961(4)				
bispicMe ₂ en	1.933(7)	2.455	4.999	6.67	this work
	1.931(7)				
	1.930(7)	2.448			
	1.939(7)				
cyclam	1.976(4)	2.462	4.925	~0	this work
	1.937(4)				
(NH ₃) ₄				0.5	this work

properties are consistent with the presence of an antiferromagnetic interaction and the existence of a singlet ground state in the complex. The properties of the binuclear complexes **1** and **4–4b** are qualitatively similar to those shown in Figure 3, although the temperature at which the susceptibility maximum occurs is lower in all of these cases. For complex **4c** the antiferromagnetic interaction is practically zero, as is also the case for the tetraammine complexes. In Figure 4 complex **5a** is used as an example, where the susceptibility increases with decreasing temperature throughout the range 300–2 K and no maximum is observed in the susceptibility.

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

$$\chi_{\text{mol,exp}} \approx \chi_{\text{mol,calc}} = -\frac{\sum_i \frac{\partial E_i}{\partial H} \exp(-E_i/kT)}{2 \sum_i \exp(-E_i/kT)} + K + C/T \quad (1)$$

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 factor 2 appears in the denominator of eq 1 because our calculations are based on monomeric formula units. The term C/T accounts for the presence of small quantities of 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 sixteen components of the ground-state manifold which emerge as a result of the antiferromagnetic coupling between two monomeric entities were obtained from the following Hamiltonian operator with an isotropic Zeeman term

$$H = \mu_B \sum_i g_i \hat{S}_i H + J \hat{S}_1 \cdot \hat{S}_2$$

where we have assumed that the g values for the two chromium atoms are identical. Since we have two $S = 3/2$ centers in the complexes, the Heisenberg Hamiltonian gives rise to states with $S = 0, 1, 2, 3$, with energies of $0, J, 3J$, and $6J$, respectively.

The results of the data fittings are presented in Table 8 together with some structural data. The K values were all small compared to the diamagnetic corrections. The C values could be interpreted as indicating the presence of up to 1% monomeric chromium(III) impurities. For the bispicMe₂en complex **3**, the fitting leads to a value of $J = 6.67(1) \text{ cm}^{-1}$ with $g = 2.000$. The magnitude of J for this complex is the largest we have observed for this kind of hydrogen-bonded binuclear complex and is comparable in magnitude to that observed in some bis(μ -hydroxo)dichromium(III) complexes (“diols”)²⁵ where the two chromium(III) centers are bridged by genuine bonds to the hydroxo groups.

The small coupling observed in the ammonia complexes, as exemplified by **5a** with $J = 0.5 \text{ cm}^{-1}$ and $g = 1.98$, is relatively easy to understand. When the bulky amine ligands in **3** and **4** are replaced by small flexible ligands (e.g. ammonia), oxyanions can more readily approach the bridging groups to form intermolecular hydrogen bonds, thereby weakening the intramolecular magnetic interaction by pulling the proton of the hydroxo group out of the plane of the binuclear unit. This effect has been discussed elsewhere for the simple bis(μ -hydroxo)dichromium(III) complexes and forms a basis for the Glerup–Hodgson–Pedersen (GHP) model.²⁵

Surprisingly, even the bispicen complex **2** appears to fit a binuclear model reasonably well, despite the fact that this complex adopts a chain structure in the solid state.⁹ The unexpected success of these dimer models for **2** presumably comes about because the chains are very asymmetric, with O···O separations of 2.33 and 3.45 Å.⁹ In all cases, except those of the ammonia complexes and **4c**, the magnitude of the exchange coupling is relatively large, and comparable to those observed for bis(μ -hydroxo) complexes of chromium(III).²⁵ This observation clearly demonstrates that these O–H–O bridges are entirely capable of providing significant magnetic exchange pathways. To our knowledge, the complexes of this type reported here and elsewhere^{2,3,5,8} are the only chromium(III) complexes that interact magnetically through hydrogen bonds. From the data in Table 8 it can be seen that the linear relationship between $\log J$ and the Cr···Cr distance proposed by Wiegardt and co-workers⁸ is not observed. As we have discussed elsewhere, the positions of the hydrogen atoms on the bridges are of crucial importance in determining the magnitude of the antiferromagnetic interaction

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

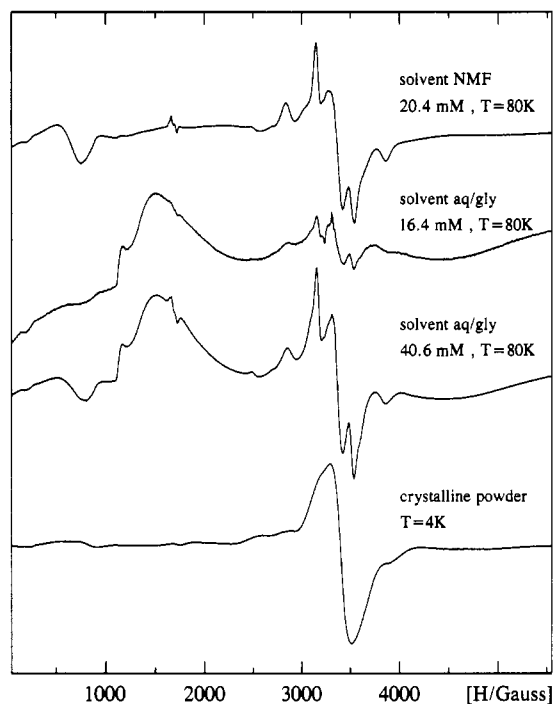


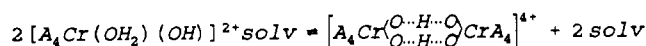
Figure 5. EPR spectra of the complex $[\text{Cr}(\text{cyclam})(\text{OH}_2)(\text{OH})]_2^+(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$ (**4**). The top curve shows the spectrum in NMF at 80 K at a concentration of 20.4 mM, the second curve shows the spectrum in water/glycerol at 80 K at a concentration of 16.4 mM, the third curve shows the spectrum in water/glycerol at 80 K at a concentration of 40.6 mM, and the bottom curve shows the solid state spectrum at 4 K.

between the chromium atoms in the diols.²⁵ Regrettably, in the hydrogen-bonded structures presented here we know the positions of too few of the protons on the bridges (not *in* the bridges) to make a similar correlation at this stage.

EPR Spectra. The EPR spectrum recorded on a frozen glass of *cis*- $[\text{Cr}(\text{cyclam})(\text{OH}_2)(\text{OH})]_2^{2+}$ dissolved either in NMF (*N*-methylformamide) or in a mixture of water/glycerol (1:1 v/v) is shown in Figure 5. The NMF spectrum is a typical spectrum of a dinuclear chromium(III) complex. We have previously shown that the EPR spectra of dinuclear chromium(III) are dominated by transitions within the quintet state which emerge as a result of the antiferromagnetic coupling.¹⁰ The solid-state spectrum at 4 K is solely a quintet spectrum, in accordance with the dimeric units found in the crystal structure.

From an examination of the frozen glass spectrum of the complex dissolved in a water/glycerol mixture, it is apparent that the spectrum consists of two parts: the first part is the same spectrum as observed in NMF; the second part centered around 1000–2000 G is a typical monomeric chromium(III) spectrum with a considerable zfs (zero-field splitting). Furthermore, it can be seen that the intensity of the dimeric spectrum increases relative to that of the monomeric species as the concentration of the complex is increased.

These observations can be rationalized as an equilibrium between a monomeric and a dimeric form. In solvents like DMF, DMSO, and NMF, which are poor hydrogen-bond donors and relatively poor hydrogen-bond acceptors, the equilibrium is toward the dimeric hydrogen-bonded units, while in a solvent like the water/glycerol mixture, which is a much better hydrogen-bond donor and acceptor, the equilibrium is toward the monomeric unit. The equilibrium can be described by the following equation:



To check whether this effect is caused by hydrogen-bond formation or by the dielectric constants of the media (which reflect the ability of the media to separate ions), we have compared the

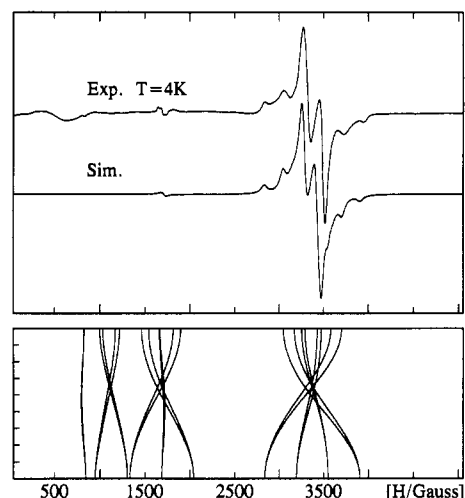


Figure 6. EPR spectrum of the complex $[\text{Cr}(\text{bispicMe}_2\text{en})(\text{OH}_2)(\text{OH})]_2^+(\text{ClO}_4)_4$ (**3**) in NMF at 4 K. The top curve is the observed spectrum, while the center curve is the spectrum simulated with the dimer model (see text). The lower portion of the figure shows the resonance conditions as a function of the angle between the molecular *z*-axis and the applied magnetic field.

spectra measured in DMF and NMF and shown that the relative amounts of binuclear and mononuclear species are the same in these two solvents even though the dielectric constants of these media are very different (37 and 182, respectively²⁶). The equilibrium constant is the same in these two media, which means that the hydrogen-bond formation is the important factor and not the dielectric properties of the solvent.

The EPR spectrum at 4 K of complex **2** (which contains an infinite chain of hydrogen-bonded units) shows a featureless broad line centered around $g = 2$. This spectrum could be interpreted either as that of a mononuclear complex with nearly octahedral symmetry broadened by nearest neighbor interactions or as the result of interactions between several chromium atoms. However, it cannot be interpreted as a spectrum from the quintet state that emerges as a result of the coupling between two chromium ions, even though the magnetic susceptibility data can be interpreted as an interaction between pairs of chromium centers. The frozen-glass spectrum of complex **2** dissolved in NMF is typical of a spectrum from the quintet state of a dinuclear complex, while the solid-state spectrum of **2** dissolved in the similar diamagnetic cobalt(III) complex **6** is typical of the spectrum from a monomeric complex.

The solid-state EPR spectrum of complex **3**, however, which is shown in Figure 6, is from the quintet state that results from the magnetic coupling between two chromium centers bound to each other.

Simulation of EPR Spectra. The EPR spectra of the mononuclear complexes were interpreted by the spin Hamilton operator

$$H = \mu_B (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z) + D[S_z^2 - 1/3 S(S+1)] + E[S_x^2 - S_y^2]$$

and for the dinuclear complexes this operator was used for each of the two metal atoms together with the following exchange term which accounts for the interaction between the two metal atoms:

$$H_{ex} = J S_a \cdot S_b + D_e [2 S_{az} S_{bz} - S_{ax} S_{bx} - S_{ay} S_{by}] + E_e [S_{ax} S_{bx} - S_{ay} S_{by}]$$

In Figure 6 is shown the spectrum of *cis*- $[\text{Cr}(\text{bispicMe}_2\text{en})(\text{OH}_2)(\text{OH})]_2^{4+}$ dissolved in NMF at 4 K. The quintet spectrum

(26) Covington, A. K.; Dickinson, T. In *Physical Chemistry of Organic Solvent Systems*; Covington, A. K., Dickinson, T., Eds.; Plenum: London, 1973, p 5.

was simulated with the parameters $g = 1.985$, $J = 5 \text{ cm}^{-1}$, $D_e = 0.011 \text{ cm}^{-1}$, and $E_e = 0.0025 \text{ cm}^{-1}$ by diagonalization of the energy matrix generated on the basis of the spin Hamiltonian operator. The band form was represented by a Lorentzian curve with a half-width of 80 G. The striking similarity between the observed spectrum and that simulated for a dimer demonstrates conclusively that this observed spectrum is due to the binuclear species. We were unable to determine the single atom zfs parameters, because zfs parameters only influence the transition within the quintet state as a second-order effect.

Conclusion. The present work demonstrates that magnetic susceptibility measurements can be used as a diagnostic tool for the detection of magnetic interaction through hydrogen bonds, but the method cannot be reliably used to distinguish between dimeric and chain structures. Moreover, the magnitude of the antiferromagnetic interaction is so small in some complexes that

it is hardly observable by magnetic susceptibility measurement. Consequently, EPR spectra are a significantly more reliable diagnostic tool to demonstrate the formation of dimeric units both in the solid state and in solution (frozen glasses).

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Supplementary Material Available: Tables S1–S4 (hydrogen atom parameters and anisotropic thermal parameters for complexes **3** and **4c**) (7 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure amplitudes are available from D.J.H.