Structural and magnetic characterization of an adamantane-like complex ion of chromium(III) and 1,3,5-triaminocyclohexane, $[Cr_4(tach)_4(OH)_6]^{6+}$

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Abstract

The synthesis and characterization of a tetranuclear chromium(III) complex of the ligand 1,3,5-triaminocyclohexane, (tach), $C_6H_{15}N_3$, are described. The complex $[Cr_4(tach)_4(OH)_6](ClO_4)_n(CF_3SO_3)_{6-n}$, where n refines to approximately 3.57, has been isolated and its structure has been determined from three-dimensional crystallographic data. The complex crystallizes in space group $P2_1/c$ of the monoclinic system with four tetranuclear species in a cell of dimensions $a=22.365(4)$, $b=12.581(3)$, $c=22.508(5)$ Å, $\beta=101.75(3)$°. The structure has been refined to a final R factor of 0.0737 based on 6023 observed independent reflections. Each chromium(III) center is pseudo-octahedrally bonded to the three nitrogen atoms of the ligand and to three hydroxo groups; each hydroxo group acts as a bridge between two chromium atoms. The complex adopts the adamantane structure in which all four chromium atoms are chemically equivalent, as are all six hydroxide groups. The six independent Cr···Cr separations in the tetramer are in the narrow range 3.660–3.685 Å. The temperature dependence of the magnetic susceptibility of the complex is consistent with the observed structure, the tetranuclear complex exhibiting an antiferromagnetic interaction with a J value of 8.91(2) cm^{-1}. A model is presented which makes it possible to compare the antiferromagnetic interaction in complexes containing different numbers of metal atoms.

Introduction

The chemistry of hydroxo-bridged chromium(III) complexes continues to be of great current interest, largely because of the development of models attempting to correlate the magnetic properties of these systems with their structures [1] but also because of the large variety of geometries that have been uncovered [2]. As shown in Fig. 1, the binuclear complexes $[Cr_2(OH)_2]$ can exist as either μ-hydroxo (open form) (I) [3] or di-μ-hydroxo (closed form) (II) [4], and in some systems there is a pH-dependent equilibrium relating these two geometries [5]. The trinuclear system, $[Cr_3(\mu\text{-}OH)_4]$ also adopts two different geometries, one of which (III) can be viewed as being formed from the tetrameric chromium analog of Werner's brown salt by removal of one metal and two OH groups [6] while the other (IV) is similarly generated from the rhodoso tetrameric array [7]. The tetranuclear $[Cr_4(\mu\text{-}OH)_6]$ systems have been shown to adopt four different geometries; these are the chromium analog of the cobalt brown salt (V), in which one central chromium(III) center is bound by two OH bridges to each of three chemically equivalent external chromium(III) centers [8]; the rhodoso structure (VI), in which two central chromium(III) ions are joined to each other by two *cis*-hydroxo bridges and this di-μ-hydroxo unit is capped above and below the plane by two additional chromium atoms [9]; the extended structure (VII), in which each metal in this same central di-μ-hydroxo unit is doubly bridged to an external chromium center [6]; and the adamantane structure (VIII) in which each chromium(III) atom is singly bridged to each of three other chromium atoms, and all four chromium atoms are chemically equivalent [10]. These geometric frameworks have been expertly summarized by Andersen [2], and are depicted in Fig. 1.

While examples of the adamantane geometry (VIII) are known in the chemistry of tantalum [11], titanium [12], indium [13] and manganese [14], the only example of this structure in chromium(III) chemistry involves the organometallic cluster $[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6]^{2+}$

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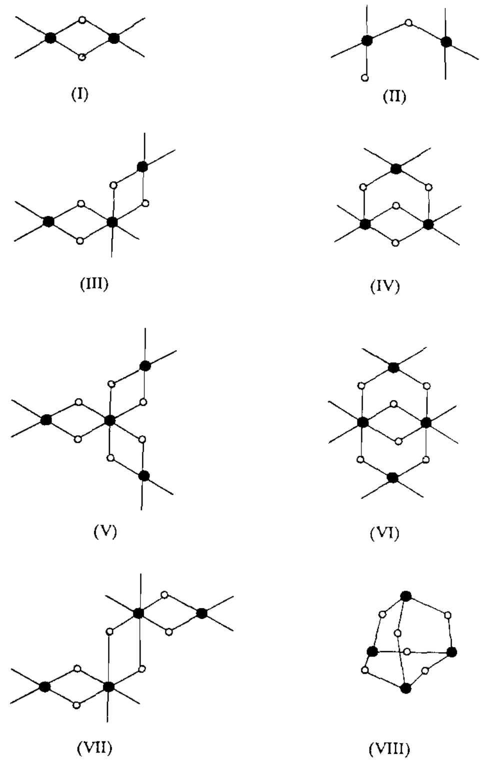

Fig. 1. The geometries observed for binuclear $Cr_2(OH)_2$, trinuclear $Cr_3(\mu\text{-}OH)_4$ and tetranuclear $Cr_4(\mu\text{-}OH)_6$ clusters of chromium(III).

[10]. We have been continuing our long association with the coordination chemistry of chromium(III), and have uncovered another example which represents the first coordination complex of chromium to adopt the adamantane structure. We report here the synthesis and the structural and magnetic properties of this interesting new complex, $\{[Cr(tach)]_4(OH)_6\}^{6+}$, where tach is *cis,cis*-1,3,5-triaminocyclohexane.

Experimental

Synthetic methods

Tetrahydrofuran (THF) was dried by addition of molecular sieves (4 Å). 1,3,5-Triaminocyclohexane [15] (tach) and $[Cr(THF)Cl_3]$ [16] were synthesized according to literature procedures.

$[Cr(tach)Cl_3]$

To a suspension of 2.4 g (0.01 mol) $tach(HCl)_3$ in 50 ml THF was added 1.62 g (0.03 mol) of sodium methylate. The suspension was refluxed for 30 min and then filtered through a sintered glass filter. 3.75 g (0.01 mole) of $[Cr(THF)_3Cl_3]$ were added and the solution was refluxed for 20 min. The green product was filtered off and washed with THF. Yield 2.8 g.

$[Cr(tach)(CF_3SO_3)_3]$

The previous product (2.8 g) was stirred with triflic acid (Htrf) (4 ml) for 24 h in a flask equipped with a bubble trap. To the cold suspension was slowly added 150 ml ether. The pale red product was filtered off and washed with ether. Yield 6.0 g.

$[Cr_4(tach)_4(OH)_6](ClO_4)_n(CF_3SO_3)_{6-n}$

The 6 g were dissolved in acetone containing 10% water, causing the tristriflate complex to be hydrolyzed to the triaqua complex. When the acetone had evaporated the complex was dissolved in a few ml of water and sodium hydroxide (0.57 g, 0.014 mol) was added. The solution was cooled in ice and the crystals were filtered off. Yield 2.0 g. The product was heated in an oven to 120 °C, causing the color to change from violet to brick-red. Suitable crystals for X-ray crystallography were obtained by slow evaporation of an aqueous solution of the compound to which 2 g of sodium perchlorate were added. Yield 1.1 g.

X-ray structure determination

The structure of the complex was determined at room temperature 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. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with four tetranuclear cations in the unit cell. Crystal data and experimental parameters are presented in Table 1. The data were corrected for Lorentz–polarization effects and absorption. The structure was solved by direct methods and refined by least-squares techniques; the programs used were from the SHELXTL system [17]. All hydrogen atoms except the hydroxyl hydrogens were placed in calculated positions (C–H = 0.96 Å). All non-hydrogen atoms were refined anisotropically. At a late stage in the refinement

TABLE 1 Crystallographic data for the complex

Formula	$[C_{24}H_{60}N_{12}Cr_4(OH)_6](ClO_4)_{3\ 57}(SO_3CF_3)_{2\ 43}$
a (Å)	22 365(4)
b (Å)	12 581(3)
c (Å)	22.508(5)
β (°)	101.75(3)
V (Å^3)	6200(7)
Z	4
Formula weight	1600 4
Space group	$P2_1/c$
T (°C)	22
μ (mm^{-1})	1 033
NO[a]	10909
NO ($I > 3\sigma(I)$)	6023
R[b]	0.0737
R_w[c]	0.0939

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

it was determined that one of the anion sites was partially occupied by both perchlorate and triflate; the model adopted involved full occupancy by three oxygen atoms (assumed common to the $O_3S–CF_3$ and $O_3Cl–O$ entities) and linked refinement of the other atoms with the occupancy of the S and CF_3 moieties defined as α and that of the Cl and O as $(1-\alpha)$, the parameter α being allowed to refine. The refined model led to a value of 0.43 for α. The final values of the conventional R factors were $R=0.0737$, $R_w=0.0939$, based on 6023 independent reflections with $I>3\sigma(I)$. Positional parameters are listed in Table 2.

Physical measurements

Magnetic susceptibility measurements were performed by the Faraday method on equipment described elsewhere [18]. The molar susceptibilities were corrected for ligand diamagnetism using Pascal's constants.

Results and discussion

Synthesis

We have recently [19] briefly discussed the feasibility of forming triols (tri-μ-hydroxobischromium(III) complexes) as a function of the structure of the coordinated tridentate amine ligands, and we have made the C_{3h} isomer of the triol with the amine Me_3-tame (1,1,1-tris(*N*-methylaminomethyl)ethane). Moreover, Andersen *et al.* [20] have prepared the triol isomer with D_3 symmetry by a new route. This route can be described by the equations:

$$(Me_3\text{-tame})Cr(OH_2)_2(OH)^{2+}$$

$$+(H_2O)(HO)_2Cr(Me_3\text{-tame})^{+}+3trf^{-}\longrightarrow$$

$$[(Me_3\text{-tame})Cr(HO\cdot\cdot H\cdot\cdot OH)_3Cr(Me_3\text{-tame})](trf)_3$$

$$\xrightarrow{120\ ^\circ C}$$

$$[(Me_3\text{-tame})Cr(OH)_3Cr(Me_3\text{-tame})](trf)_3+3H_2O$$

In the past we have unsuccessfully tried to prepare triols with the tach ligand, and inspired by the above route we tried this scheme, however, the compound obtained turned out not to be the triol (*vide infra*).

The magnetic susceptibility of the prepared compound showed that it contained an even number of chromium atoms. The EPR spectrum was measured on the crystalline powder and on a frozen glass of the compound dissolved in *N*-methylformamide at different temperatures. It was obvious to us that the EPR spectrum was not dominated by quintet spectra as is usually seen in binuclear chromium complexes [19, 21–23]. We therefore concluded that the compound was at least a tetramer and we tentatively proposed an adamantane structure.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2\times 10^3$)

	x	y	z	U_{eq}[a]
Cr(1)	2761(1)	327(1)	4225(1)	25(1)
N(1)	3250(3)	1734(6)	4221(3)	33(3)
N(2)	2127(3)	1196(7)	4592(4)	37(3)
N(3)	3226(4)	53(6)	5106(3)	34(3)
Cr(2)	2038(1)	−117(1)	2634(1)	24(1)
N(4)	2329(3)	1150(6)	2176(3)	33(3)
N(5)	1196(3)	658(6)	2504(3)	32(3)
N(6)	1713(4)	−834(7)	1803(3)	37(3)
Cr(3)	2005(1)	−2210(1)	3761(1)	25(1)
N(7)	1138(4)	−2131(7)	3959(4)	39(3)
N(8)	2251(4)	−3151(6)	4525(3)	37(3)
N(9)	1716(4)	−3579(6)	3262(3)	36(3)
Cr(4)	3449(1)	−1548(1)	3314(1)	25(1)
N(10)	4155(3)	−713(7)	3026(4)	39(3)
N(11)	4124(3)	−2316(7)	3935(3)	35(3)
N(12)	3516(3)	−2721(7)	2687(4)	37(3)
O(1)	2307(3)	665(5)	3401(3)	29(2)
O(2)	2270(3)	−950(5)	4272(3)	31(2)
O(3)	3414(3)	−431(5)	3925(3)	27(2)
O(4)	1722(3)	−1331(5)	3032(3)	30(2)
O(5)	2838(3)	−806(5)	2686(3)	32(2)
O(6)	2827(3)	−2421(5)	3587(3)	31(2)
C(1)	3343(5)	2433(8)	4763(5)	46(4)
C(2)	2729(5)	2815(8)	4872(5)	48(4)
C(3)	2355(5)	1958(8)	5096(5)	40(4)
C(4)	2719(5)	1367(9)	5641(5)	45(4)
C(5)	3321(5)	960(9)	5540(5)	43(4)
C(6)	3698(5)	1803(9)	5321(5)	45(4)
C(7)	856(5)	−3116(8)	4138(5)	44(4)
C(8)	1233(5)	−3545(10)	4723(5)	51(4)
C(9)	1837(5)	−4027(9)	4648(5)	45(4)
C(10)	1754(5)	−4819(8)	4122(5)	47(4)
C(11)	1381(5)	−4412(8)	3538(5)	45(4)
C(12)	774(5)	−3926(9)	3633(5)	46(4)
C(13)	1928(4)	1539(9)	1592(5)	42(4)
C(14)	1350(5)	1974(9)	1734(5)	44(4)
C(15)	929(4)	1117(8)	1909(5)	37(3)
C(16)	807(4)	256(9)	1423(5)	40(4)
C(17)	1390(5)	−195(9)	1285(4)	42(4)
C(18)	1805(4)	669(9)	1127(4)	39(4)
C(19)	4684(5)	−1346(9)	2921(5)	49(4)
C(20)	5017(4)	−1855(10)	3509(5)	51(4)
C(21)	4665(5)	−2758(9)	3723(5)	41(4)
C(22)	4450(5)	−3572(9)	3237(5)	47(4)
C(23)	4138(5)	−3112(9)	2635(5)	44(4)
C(24)	4485(5)	−2201(10)	2429(6)	56(5)
S(1)	4878(1)	6193(3)	717(2)	64(1)
O(7)	4577(6)	5840(11)	1209(6)	135(7)
O(8)	4529(5)	5961(9)	128(5)	110(5)
O(9)	5500(4)	5877(8)	831(4)	79(4)
C(1S)	4865(9)	7529(15)	796(9)	94(8)
F(1)	5120(7)	7991(10)	345(6)	166(7)
F(2)	4311(6)	7927(11)	708(8)	194(9)
F(3)	5171(6)	7919(10)	1274(6)	156(7)
S(2)	2961(2)	4119(3)	3122(2)	71(2)
O(10)	3397(7)	4016(9)	3709(5)	125(6)
O(11)	2487(5)	3359(9)	3056(6)	126(6)
O(12)	2829(4)	5193(7)	2975(4)	75(4)
C(2S)	3416(8)	3671(12)	2620(7)	83(7)

(*continued*)

TABLE 2. (*continued*)

	x	y	z	U_{eq}[a]
F(4)	3053(8)	3638(11)	2076(5)	188(8)
F(5)	3893(5)	4236(9)	2620(6)	154(7)
F(6)	3578(5)	2656(8)	2728(5)	122(5)
Cl(5)	2499(2)	6777(4)	1161(2)	97(2)
O(25)	2343(7)	6502(11)	571(5)	145(7)
O(26)	2985(8)	6138(16)	1424(7)	202(10)
O(27)	2550(9)	7809(12)	1260(12)	247(15)
O(28)	2337(28)	6924(49)	1683(25)	280(23)
C(3S)	1892(19)	6291(31)	1388(18)	77(11)
F(7)	1426(14)	6646(23)	1173(13)	146(12)
F(8)	1764(15)	5083(29)	1353(15)	184(15)
F(9)	1884(19)	6266(34)	1953(19)	210(17)
Cl(2)	3649(2)	359(3)	1351(2)	78(2)
O(13)	3406(7)	1382(9)	1410(6)	133(7)
O(14)	4210(6)	240(15)	1518(13)	282(16)
O(15)	3376(5)	−340(10)	1691(6)	121(6)
O(16)	3421(11)	58(14)	737(6)	226(12)
Cl(3)	9602(2)	7976(4)	492(2)	99(2)
O(17)	10185(5)	7527(13)	504(8)	228(13)
O(18)	9581(10)	9000(10)	209(7)	331(21)
O(19)	9548(7)	8158(13)	1117(4)	201(11)
O(20)	9127(7)	7334(16)	199(9)	398(25)
Cl(4)	233(2)	4272(4)	2064(2)	113(2)
O(21)	232(13)	5394(7)	2037(9)	429(35)
O(22)	190(6)	3835(12)	1469(4)	190(9)
O(23)	764(7)	3882(18)	2450(6)	497(27)
O(24)	−295(7)	3927(18)	2286(9)	392(26)
O(1W)	8525(4)	7454(6)	1556(4)	72(4)
O(2W)	6504(4)	825(7)	554(5)	77(4)
O(3W)	849(6)	7466(9)	2112(6)	140(6)
O(4W)	8816(6)	4643(10)	125(7)	141(7)

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

The X-ray structure determination showed that the complex is in fact an adamantane-like tetranuclear chromium(III) cation with the composition $[Cr_4(tach)_4(OH)_6]^{6+}$.

Description of the structure

The structure of this tetranuclear chromium(III) complex consists of $[Cr_4(tach)_4(OH)_6]^{6+}$ cations, perchlorate and triflate anions, and water molecules. A view of the cation is shown in Fig. 2. Principal bond distances and angles are listed in Table 3.

As is shown most clearly in Fig. 3, the tetrameric $Cr_4(\mu\text{-}OH)_6$ unit adopts the adamantane-like skeleton in which the four chromium atoms are placed at the apices of an approximate tetrahedron and the six hydroxyl oxygen atoms are sitting above the edges of this tetrahedron. The geometry about each chromium atom is distorted octahedral, with ligation provided by the three nitrogen atoms of the tach ligands and by the oxygen atoms of three hydroxyl groups. As can be seen in Fig. 2, the isomer at Cr is the *fac* isomer. The twelve independent Cr–N bond lengths are observed to lie in the range 2.067(8)–2.104(9) Å, with an average value of 2.080(10) Å. The twelve independent Cr–O bond lengths are in the range 1.961(6)–1.987(6), with an average value of 1.973(6) Å. This value is clearly longer than those of 1.942–1.959 Å in the organometallic chromium adamantane complex $[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6]^{2+}$ [10]. The Cr···Cr separations in the cluster are 3.660 to 3.685 Å, with an average value of 3.668(9) Å. Five of the six Cr···Cr distances are in the very narrow range of 3.660 to 3.668 Å, the Cr(2)···Cr(4) separation being the exception at 3.685 Å. These values are comparable to the value of 3.669(2) Å in $[(C_5Me_5)_4Cr_4(\mu\text{-}OH)_6]^{2+}$ [10].

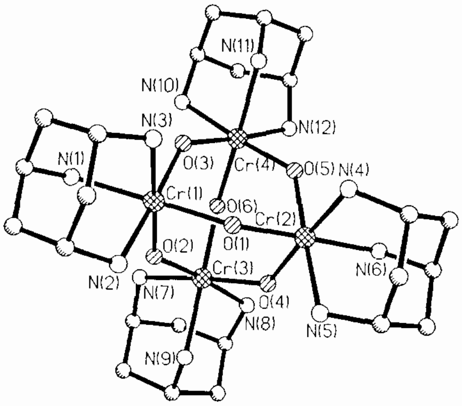

Fig. 2. View of the $[Cr_4(tach)_4(\mu\text{-}OH)_6]^{6+}$ cation in the crystals of the mixed perchlorate triflate salt. Carbon atoms are unlabelled, and hydrogen atoms are omitted for clarity

As would be expected, the steric requirements of the tach ligand cause the angles at chromium to be distorted from those anticipated for a regular octahedron. Thus, the N–Cr–N angles are all less than 90°, falling between 86.4(3) and 89.1(3)° with an average value of 87.8(10)°, but the distortion is not as severe as is seen in tridentate ligands related to 1,4,7-triazacyclononane, where the *cis* bond angles at chromium are frequently found to be about 82° [24]. This complex cation could, in principle, be expected to have S_4 symmetry, but in fact the chromium centers are all crystallographically independent. The metrical parameters at the four chromium centers are not significantly different, however.

Magnetic susceptibility

The temperature dependence of the magnetic susceptibility of powdered samples of the complex was measured in the range 4–296 K. As is shown in Fig. 4, the effective magnetic moment at room temperature is approximately 6.9 μ_B. For four independent, non-interacting $S=3/2$ ions, the effective magnetic moment would be $\sqrt{60}$, or 7.75 μ_B; the slightly lower value of 6.9 μ_B shows that the antiferromagnetic coupling can be observed even at room temperature. The effective

TABLE 3 Principal bond lengths (Å) and angles (°) ın the catıon

Bond lengths			
Cr(1)–N(1)	2.081(8)	Cr(1)–N(2)	2.089(9)
Cr(1)–N(3)	2.072(7)	Cr(1)–O(1)	1.971(6)
Cr(1)–O(2)	1.961(6)	Cr(1)–O(3)	1.974(6)
N(1)–C(1)	1.484(13)	N(2)–C(3)	1.494(13)
N(3)–C(5)	1.489(13)	Cr(2)–N(4)	2.074(8)
Cr(2)–N(5)	2.088(8)	Cr(2)–N(6)	2.070(7)
Cr(2)–O(1)	1.972(6)	Cr(2)–O(4)	1.973(6)
Cr(2)–O(5)	1.971(6)	N(4)–C(13)	1.513(12)
N(5)–C(15)	1.468(12)	N(6)–C(17)	1.478(12)
Cr(3)–N(7)	2.079(9)	Cr(3)–N(8)	2.067(8)
Cr(3)–N(9)	2.087(8)	Cr(3)–O(2)	1.976(6)
Cr(3)–O(4)	1.974(6)	Cr(3)–O(6)	1.973(7)
N(7)–C(7)	1.483(14)	N(8)–C(9)	1.500(14)
N(9)–C(11)	1.495(14)	Cr(4)–N(10)	2.104(9)
Cr(4)–N(11)	2 076(7)	Cr(4)–N(12)	2.069(9)
Cr(4)–O(3)	1.979(6)	Cr(4)–O(5)	1.987(6)
Cr(4)–O(6)	1.967(7)	N(10)–C(19)	1.485(14)
N(11)–C(21)	1.495(14)	N(12)–C(23)	1.503(13)
Bond angles			
N(1)–Cr(1)–N(2)	87.5(3)	N(1)–Cr(1)–N(3)	89.1(3)
N(2)–Cr(1)–N(3)	87.5(3)	N(1)–Cr(1)–O(1)	89.0(3)
N(2)–Cr(1)–O(1)	89.9(3)	N(3)–Cr(1)–O(1)	176.9(3)
N(1)–Cr(1)–O(2)	175.8(3)	N(2)–Cr(1)–O(2)	88.6(3)
N(3)–Cr(1)–O(2)	89.4(3)	O(1)–Cr(1)–O(2)	92.3(2)
N(1)–Cr(1)–O(3)	89.0(3)	N(2)–Cr(1)–O(3)	175.2(3)
N(3)–Cr(1)–O(3)	89.1(3)	O(1)–Cr(1)–O(3)	93.3(3)
O(2)–Cr(1)–O(3)	94.9(3)	Cr(1)–N(1)–C(1)	119.1(7)
Cr(1)–N(2)–C(3)	118 9(6)	Cr(1)–N(3)–C(5)	118.5(6)
N(4)–Cr(2)–N(5)	86.4(3)	N(4)–Cr(2)–N(6)	88.5(3)
N(5)–Cr(2)–N(6)	86.4(3)	N(4)–Cr(2)–O(1)	88.9(3)
N(5)–Cr(2)–O(1)	89.8(3)	N(6)–Cr(2)–O(1)	175.5(3)
N(4)–Cr(2)–O(4)	176.8(3)	N(5)–Cr(2)–O(4)	91.6(3)
N(6)–Cr(2)–O(4)	88.9(3)	O(1)–Cr(2)–O(4)	93.6(3)
N(4)–Cr(2)–O(5)	89.7(3)	N(5)–Cr(2)–O(5)	175.1(3)
N(6)–Cr(2)–O(5)	90.6(3)	O(1)–Cr(2)–O(5)	93.1(2)
O(4)–Cr(2)–O(5)	92.1(3)	Cr(2)–N(4)–C(13)	119.3(6)
Cr(2)–N(5)–C(15)	119.9(6)	Cr(2)–N(6)–C(17)	120.0(6)
N(7)–Cr(3)–N(8)	87.2(3)	N(7)–Cr(3)–N(9)	87.4(3)
N(8)–Cr(3)–N(9)	88.6(3)	N(7)–Cr(3)–O(2)	91.1(3)
N(8)–Cr(3)–O(2)	88.8(3)	N(9)–Cr(3)–O(2)	177.0(3)
N(7)–Cr(3)–O(4)	89.7(3)	N(8)–Cr(3)–O(4)	176.7(3)
N(9)–Cr(3)–O(4)	90.1(3)	O(2)–Cr(3)–O(4)	92.4(2)
N(7)–Cr(3)–O(6)	175.0(3)	N(8)–Cr(3)–O(6)	89.3(3)
N(9)–Cr(3)–O(6)	88.9(3)	O(2)–Cr(3)–O(6)	92.4(3)
O(4)–Cr(3)–O(6)	93.7(3)	Cr(3)–N(7)–C(7)	119.0(6)
Cr(3)–N(8)–C(9)	120.3(6)	Cr(3)–N(9)–C(11)	118.8(6)
N(10)–Cr(4)–N(11)	87.2(3)	N(10)–Cr(4)–N(12)	89.0(3)
N(11)–Cr(4)–N(12)	89.1(3)	N(10)–Cr(4)–O(3)	89.9(3)
N(11)–Cr(4)–O(3)	89.3(3)	N(12)–Cr(4)–O(3)	178.1(3)
N(10)–Cr(4)–O(5)	89.8(3)	N(11)–Cr(4)–O(5)	176.6(3)
N(12)–Cr(4)–O(5)	89.1(3)	O(3)–Cr(4)–O(5)	92.4(2)
N(10)–Cr(4)–O(6)	175.8(3)	N(11)–Cr(4)–O(6)	89.6(3)
N(12)–Cr(4)–O(6)	88.2(3)	O(3)–Cr(4)–O(6)	92.8(3)
O(5)–Cr(4)–O(6)	93.3(3)	Cr(4)–N(10)–C(19)	117.0(7)
Cr(4)–N(11)–C(21)	118.9(6)	Cr(4)–N(12)–C(23)	118.9(6)
Cr(1)–O(1)–Cr(2)	136.4(3)	Cr(1)–O(2)–Cr(3)	136.9(4)
Cr(1)–O(3)–Cr(4)	135.8(3)	Cr(2)–O(4)–Cr(3)	136.7(3)
Cr(2)–O(5)–Cr(4)	137.2(4)	Cr(3)–O(6)–Cr(4)	137.2(3)

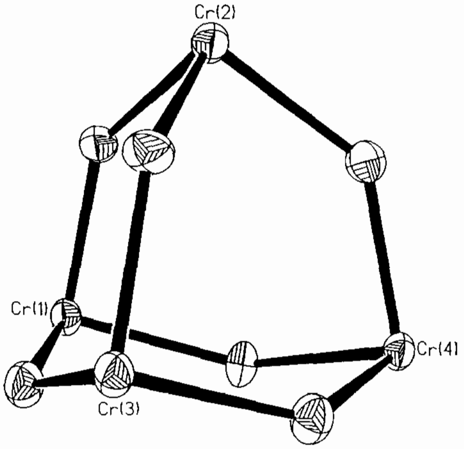

Fig. 3. Vıew of the $[Cr_4(\mu\text{-}OH)_6]$ framework in the cation, showing the adamantane skeleton.

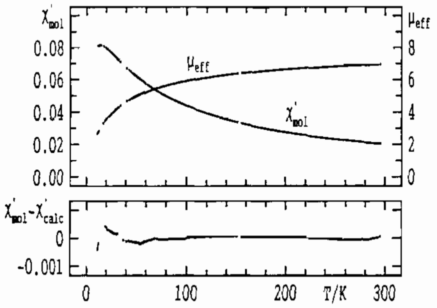

Fig. 4. Magnetic susceptibılıty (left scale) and effectıve magnetic moment (rıght scale) for the complex. The lower curve shows the fit of the susceptıbilıty data to the values calculated using the parameters $g=1.95$, $J=8.91$ cm^{-1} and 0.5% monomerıc ımpurity.

magnetic moment declines monotonically to a value of 1.5 μ_B at 4.5 K and the susceptibility curve shows a maximum at 14 K. These properties are consistent with the existence of a singlet ground state in the complex.

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

$$\chi_{\text{mol exp}} \approx \chi_{\text{mol calc}} = -\frac{N}{H}\,\frac{\sum\limits_{i} \frac{\partial E_i}{\partial H}\exp(-E_i/kT)}{\sum\limits_{i}\exp(-E_i/kT)} + K + C/T \qquad (1)$$

by minimization of the function

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

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 correction for the diamagnetism of the atoms. The energies E_i of the various components of the ground-state manifold were obtained using the Hamiltonian operator

$$H=\mu_B\sum_{i=1}^{4}g_i\hat{S}_i\cdot H+J\sum_{i<j}^{j=4}\hat{S}_i\cdot\hat{S}_j \tag{3}$$

where we have assumed that the g values for the four chromium atoms are identical and isotropic. Since we have four $S=3/2$ centers in the complex, the Heisenberg term $J\hat{S}_i\cdot\hat{S}_j$ in the Hamiltonian gives rise to the following states: four singlets, nine triplets, eleven quintets, ten septets, six nonets, three undecets and one tridecet, with the energies 0, J, $3J$, $6J$, $10J$, $15J$, $21J$, respectively. The energy for each level and its derivative with respect to the magnetic field are calculated from the expression

$$E(S)=J/2\,S(S+1)+M_s g\mu_B H \tag{4}$$

The fitting resulted in a variance per degree of freedom (var/f) of 1.87 and gave the values of $J=8.91(2)$ cm^{-1}, $g=1.95(1)$ and $C=9.64\times10^{-3}$, which is equivalent to 0.5% of monomeric chromium(III) impurity.

The J value for this complex looks relatively small compared to those found for binuclear chromium(III) complexes with one, two or three bridging hydroxo groups. For a μ-hydroxo complex [25] $J=32$ cm^{-1}, for di-μ-hydroxo complexes [1] $J=0$–40 cm^{-1}, and for tri-μ-hydroxo complexes [19, 26] $J=96$–147 cm^{-1}. The small and variable values for the diols have been accounted for by the GHP model [1] (the position of the protons on the bridging hydroxo groups is the important factor).

Magnetic interactions

We can now compare the magnetic interactions of the dimeric triol complex and the tetrameric adamantane complex on the basis of the magnetic orbitals. The geometries of each chromium atom in the two complexes are almost identical, with three facially-bonded hydroxo groups, and in both complexes all three t_{2g} orbitals on one metal can interact with the t_{2g} orbitals on another metal via the p-orbitals on the bridging hydroxo groups. For simplicity, we will assume that the triol has idealized D_{3h} symmetry and the tetramer has T_d symmetry.

The magnetic interactions in the μ-oxo-bis[pentaamminechromium(III)] cation ('the Basic Rhodo' cation) [27] and in the di-μ-hydroxo complexes [1, 28] have been interpreted as a result of configuration interaction between charge-transfer levels (metal to metal) and the ground state levels. The two-centered one-electron matrix elements are calculated on the basis of the angular overlap model. In analogy with the ligand field matrix elements for a single center [28, 29] the two-center interaction can be defined as

$$\langle d_{ia}|V_{ab}|d_{jb}\rangle\cong\sum_q\sum_{\lambda\omega}\sum_n(e_{\lambda\omega nqa})^{1/2}(e_{\lambda\omega nqb})^{1/2}\,F_{\lambda\omega}(d_{ia},L_{nq})F_{\lambda\omega}(d_{jb},L_{nq}) \tag{5}$$

where d_i refers to the d-orbitals, $\lambda\omega$ to σ, π_x, π_y bonding, n counts the common ligands L, and q refers to the orbitals on these ligands that have a common overlap with the d-orbitals on both metal atoms $F_{\lambda\omega}$ is a fractional overlap factor, and $e_{\lambda\omega}$ is a semi-empirical radial dependence parameter.

In the basic rhodo complex, the most important interaction is the π-interaction, which can be expressed as

$$\langle\xi_a|V_{ab}|\xi_b\rangle=\langle\eta_a|V_{ab}|\eta_b\rangle=e_{\pi\mathrm{OH}} \tag{6}$$

where the z-axis is defined as the fourfold axis through the Cr–O–Cr vector and ξ, η, ζ are orbitals that transform as the d-orbitals yz, zx, xy, respectively.

For the triol complex and for the adamantane complex we will only consider the oxygen p-orbitals perpendicular to the Cr–O–Cr planes, because the in-plane p-orbitals are used to bind the hydrogen atoms and therefore any interaction through these orbitals is considered to be unimportant.

On the basis of eqn. (5) we can write the following interaction matrix, where all the elements have to be multiplied by $e_{\pi,\mathrm{OH}}$:

$$\begin{array}{ccccccc}
\xi_a & 1 & -1/2 & -1/2 & 1 & -1/2 & -1/2\\
\eta_a & -1/2 & 1 & -1/2 & -1/2 & 1 & -1/2\\
\zeta_a & -1/2 & -1/2 & 1 & -1/2 & -1/2 & 1\\
\xi_b & 1 & -1/2 & -1/2 & 1 & -1/2 & -1/2\\
\eta_b & -1/2 & 1 & -1/2 & -1/2 & 1 & -1/2\\
\zeta_b & -1/2 & -1/2 & 1 & -1/2 & -1/2 & 1
\end{array} \tag{7}$$

This matrix can then be used to calculate the non-diagonal elements between the ground levels and the charge-transfer levels. The results are:

$$\begin{aligned}
\langle{}^5A_1'|V_{ab}|{}^5A_1'\,\mathrm{C.T.}\rangle&=-\sqrt{6}e_{\pi\mathrm{OH}}\\
\langle{}^3A_2''|V_{ab}|{}^3A_2''\,\mathrm{C.T.}\rangle&=-\sqrt{10}e_{\pi\mathrm{OH}}\\
\langle{}^1A_1'|V_{ab}|{}^1A_1'\,\mathrm{C.T.}\rangle&=-\sqrt{12}e_{\pi\mathrm{OH}}
\end{aligned} \tag{8}$$

The J value in the operator $JS_a\cdot S_b$ can then be related to these non-diagonal elements and the energy of the charge-transfer states E_{CT} by the equation

$$J=\frac{2e_{\pi\mathrm{OH}}^2}{E_{CT}} \tag{9}$$

For the adamantane complex we can make a similar matrix (10) as for the triol.

In this matrix many of the elements are zero because each d-orbital can only interact with two other d-orbitals on two other metals. The ground levels and charge-

$$
\begin{array}{lcccccccccccc}
\xi_1 & 1 & -1/2 & -1/2 & 0 & 1/2 & -1/2 & 0 & 0 & 0 & -1/2 & 1/2 & 0 \\
\eta_1 & -1/2 & 1 & -1/2 & 0 & 0 & 0 & 1/2 & 0 & -1/2 & 1/2 & -1/2 & 0 \\
\zeta_1 & -1/2 & -1/2 & 1 & 0 & -1/2 & 1/2 & -1/2 & 0 & 1/2 & 0 & 0 & 0 \\
\xi_2 & 0 & 0 & 0 & 1 & -1/2 & -1/2 & 0 & 1/2 & -1/2 & 0 & -1/2 & 1/2 \\
\eta_2 & 1/2 & 0 & -1/2 & -1/2 & 1 & -1/2 & 0 & 0 & 0 & 0 & 1/2 & -1/2 \\
\zeta_2 & -1/2 & 0 & 1/2 & -1/2 & -1/2 & 1 & 0 & -1/2 & 1/2 & 0 & 0 & 0 \\
\xi_3 & 0 & 1/2 & -1/2 & 0 & 0 & 0 & 1 & -1/2 & -1/2 & 1/2 & 0 & -1/2 \\
\eta_3 & 0 & 0 & 0 & 1/2 & 0 & -1/2 & -1/2 & 1 & -1/2 & -1/2 & 0 & 1/2 \\
\zeta_3 & 0 & -1/2 & 1/2 & -1/2 & 0 & 1/2 & -1/2 & -1/2 & 1 & 0 & 0 & 0 \\
\xi_4 & -1/2 & 1/2 & 0 & 0 & 0 & 0 & 1/2 & -1/2 & 0 & 1 & -1/2 & -1/2 \\
\eta_4 & 1/2 & -1/2 & 0 & -1/2 & 1/2 & 0 & 0 & 0 & 0 & -1/2 & 1 & -1/2 \\
\zeta_4 & 0 & 0 & 0 & 1/2 & -1/2 & 0 & -1/2 & 1/2 & 0 & -1/2 & -1/2 & 1
\end{array}
\tag{10}
$$

transfer levels can be calculated as for the triol, but this is very time consuming. We have calculated the non-diagonal matrix element for the undecet state to be

$$\left\langle {}^{11}\mathrm{T}_2 \left| \sum_{i<j}^{4} V_{ij} \right| {}^{11}\mathrm{T}_2\mathrm{C.T.} \right\rangle = -\frac{2}{\sqrt{6}}\, e_{\pi\mathrm{OH}} \tag{11}$$

Comparing this value to $6J$, the tridecet–undecet energy separation, gives

$$J = \frac{1}{9}\frac{e^2_{\pi\mathrm{OH}}}{E_{\mathrm{CT}}} \tag{12}$$

If we assume that the two sets of parameters e_{OH} and E_{CT} have the same values in the two complexes, the calculated relationship between the magnitudes of the J values is $J_{\mathrm{triol}} = 18J_{\mathrm{adamantane}}$, in excellent agreement with the experimental value of 147/8.9, or $J_{\mathrm{triol}} = 16.5J_{\mathrm{adamantane}}$.

The above process is a rather tedious comparison, and a more simplified (but, necessarily, less satisfying) model can be obtained by comparison of the energy gain per metal atom as a result of the antiferromagnetic coupling. For a binuclear system we can use the septet state as the reference state because its energy is not affected by the configuration interaction. For the triol, the quintet is lowered in energy by $3J$, the triplet by $5J$, and the singlet by $6J$. The total energy gain per dimeric unit is then $36J$, or $18J$ per atom for an infinitely high temperature where all states are equally populated. When T approaches 0 K the energy gain is $3J$ per chromium atom, since only the singlet state is populated.

For the tetranuclear adamantane complex, where the tridecet state is our reference point, the gain is energy as a result of the antiferromagnetic coupling is $2456J$ per tetrameric unit, or $864J$ per chromium atom for an infinitely high temperature. When T approaches 0 K the energy gain is $21J$ per chromium atom. In the high temperature limit the ratio between the tetramer and the dimer gain in energy is 48:1 and in the low temperature limit this ratio is 7:1. For intermediate temperatures, the energy gains can be calculated by appropriate use of the Boltzmann distribution.

To conclude, therefore, one cannot directly compare the J values between complexes with different numbers of interacting metal atoms, but must either compare the energy gains per atom or more thoroughly make a calculation on the basis of the interacting orbitals.

Supplementary material

Tables S1 (hydrogen atom parameters), S2 (anisotropic thermal parameters) and S3 (listing of observed and calculated structure amplitudes) are available from D.J.H. on request.

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