is inherently a bimolecular one, in our studies the reactants are expected to be strongly ion-paired, and the efficiencies need not be limited by diffusional processes.[26] Consistent with an associative mechanism, there is a slightly positive correlation between the yields and the nucleophilicities of the halogens in Table I; however, this may reflect relative ion-pairing efficiencies that have not been measured.

More to the point, the quantum yields appear to be incompatible with an associative mechanism as they are much larger than those that have been found in previous studies where associative substitution reactions have been implicated.[11,23] In general, substitution yields are expected to be relatively small for associative processes. In the first place the addition of another ligand is likely to be disfavored by ligand–ligand repulsion effects, especially for systems with a coordination number of 6 or higher. In contrast, the same repulsions would favor ligand expulsion by a dissociative process. Secondly, in the transition state of an associative process there is inevitably a partitioning between two modes of deactivation: return to the initial state and conversion to product.

In view of the quantum yields we have observed, we tentatively ascribe the reaction to a dissociative mechanism, presumably originating from a reactive d–d excited state. No d–d excited states have been identified in the absorption spectrum of $[Re(CNxyl)_6]^+$, but they could be masked by the charge-transfer absorptions, which have much greater oscillator strengths. If the d–d state is not the lowest energy excited state, it is sufficiently low-lying that it can be thermally populated.

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Registry No. $Re(CNxyl)_6{}^+$, 87829-86-5; $Re(CNxyl)_5Cl$, 103904-91-2; $Re(CNxyl)_5Br$, 103904-92-3; $Re(CNxyl)_5I$, 103904-93-4.

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Magnetic Studies of a Linear Chromium(III) Trimer of a Triketone

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The trinuclear chromium(III) triketonate complex, $Cr_3(lig)_2$, where lig = 1,5-diphenyl-1,3,5-pentanetrionato, has been synthesized and characterized by magnetic susceptibility, ESR, and electronic spectra. The complex has $g = 1.977$ and exhibits antiferromagnetic interactions. The magnetic interaction fits an isosceles arrangement of the coupling constants, with $J = -6.00$ cm^{-1} between two pairs of adjacent metal atoms and $J' = -1.35$ cm^{-1} between the third metal pair. This arrangement is compatible with the essentially linear configuration of the metal atoms also expected with the planar ligands.

Introduction

In the past two decades the number of polynuclear complexes of transition metals reported has increased dramatically. Several dimeric chromium(III) complexes have been thoroughly investigated structurally and magnetically,[1] but few trinuclear chromium complexes have been reported. Trinuclear basic carboxylate complexes were studied by various methods. Crystal structures indicate that the three atoms are essentially an equilateral triangle surrounding a central oxygen atom.[2] They have been investigated magnetically[3-6] and were the first compounds in which exchange interactions between the metals were suggested.[3] Although incorrect expressions were occasionally used,[5] a Heisenberg spin-coupling Hamiltonian was shown to give general agreement between magnetic and strutural data. However, a slightly isosceles configuration of the magnetic coupling parameters gives the best agreement, despite the equilateral structural arrangement; moreover, slightly different parameters were required for ESR and specific heat data. Introduction of coupling between adjacent trinuclear molecules gives better agreement.[7-9] Newer basic carboxylates continue to be reported.[10] Recently, Blake and co-workers[11] have also reported magnetic properties of heterotrinuclear basic acetates of Cr(III) with divalent metal ions.

There are few other reports of trinuclear complex formation. Stunzi and Marty[12] report the hydrolytic polymers formed upon addition of OH^- to $[Cr(H_2O)_6]^{3+}$. Connick et al.[13] also report hydrolytic polymerization of Cr(III) and suggest a trinuclear complex on the basis of the magnetic data. However, the essentially constant magnetic moment, between 329 and 274 °C, gives no information on magnetic coupling or on structure. A similar problem voids any structural information from the magnetism of binuclear analogues.[14] Karayannis et al.[15] report the preparation of chromium complexes with purine bases, $Cr_3L_5Cl_4{\cdot}2H_2O$ (purine or adenine) as possible models for DNA–RNA interaction with Cr(III). Despite the trinuclear empirical formula, the complexes are presumed to be infinite polymers,[15] though no structural or magnetic information is available.

We report here the preparation and properties of the first linear trinuclear chromium complex using the ligand 1,5-diphenyl-1,3,5-pentanetrione.

Experimental Section

Synthesis of $Cr_3(C_{17}H_{12}O_3)_2(C_2H_5OH)_2(H_2O)(OH)_5$ and $Cr_3(C_{17}H_{12}O_3)_2(H_2O)_3(OH)_5$. One gram (3.75 mmol) of 1,5-diphenyl-1,3,5-pentanetrione was refluxed in 25 mL of ethanol in a 250-mL RB flask for 20 min. Urea (8.86 g, 0.148 mol), dissolved in 50 mL of a 1:1 mixture

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Table I. Magnetic Properties of $Cr_3(C_{17}H_{12}O_3)_2(H_2O)_3(OH)_5$

temp, K	$10^2\chi_M$, cgsu	μ, μ_B	temp, K	$10^2\chi_M$, cgsu	μ, μ_B
10.9	5.08	2.10	79	1.42	3.00
12	4.73	2.13	86.5	1.34	3.05
14.7	4.10	2.20	94	1.27	3.09
17	3.72	2.25	100	1.22	3.12
21.2	3.22	2.34	125.2	1.05	3.24
24.5	2.93	2.40	150.2	0.92	3.32
27.6	2.73	2.46	175.1	0.82	3.39
33	2.45	2.54	200.4	0.74	3.44
39.5	2.20	2.64	220.77	0.68	3.47
43.2	2.08	2.68	240.2	0.64	3.49
51.9	1.89	2.77	260.4	0.60	3.53
59.9	1.71	2.86	280.25	0.57	3.55
64.12	1.64	2.90	299.25	0.53	3.56
72.5	1.51	2.96	320.2	0.51	3.60

of water and ethanol, was added, and reflux was continued until all urea was dissolved. A solution of 1.5 g (5.65 mmol) of $CrCl_3 \cdot 6H_2O$ in 40 mL of ethanol was slowly added to the refluxing mixture, which was then refluxed for a further 24 h. A burgundy-brown precipitate formed upon cooling, and it was collected by vacuum filtration. The product was washed thoroughly with water and vacuum dried. Mp: >300 °C. Anal. Calcd for $Cr_3(C_{17}H_{12}O_3)_2(C_2H_5OH)_2(H_2O)(OH)_5$: C, 51.88; H, 4.89; Cr, 17.75. Found: C, 51.33; H, 4.86; Cr, 17.66.

Some of the compound was refluxed in H_2O for 30 min to replace the ethanol molecules. The resultant golden yellow precipitate was filtered and dried under a vacuum. Mp: >300 °C. Anal. Calcd for $Cr_3(C_{17}H_{12}O_3)_2(H_2O)_3(OH)_5$: C, 49.57; H, 4.25; Cr, 18.96. Found: C, 49.33; H, 4.29; Cr, 18.71.

Spectroscopy. Infrared spectra were recorded on a Beckman 598 as KBr pellets. The UV–visible spectra were recorded on a Perkin-Elmer Lambda diode-array UV–visible spectrometer as 5×10^{-5} M solutions of methanol.

Electron spin resonance spectra were obtained on a Varian E-109; the spectrum was calibrated with DPPH.

Magnetic Data. Magnetic susceptibilities (4–320 K) were measured on a SQUID magnetometer. The calibration and method of operation are as described elsewhere.[16,17]

Results and Discussion

Lintvedt and Glick[18] have reviewed the metal complexes of 1,3,5-triketones. Planar binuclear complexes of first-row divalent transition metals predominate and have allowed the study of magnetic interactions between two metals in close proximity. Recently, Lintvedt et al.[19] have reported the preparation and magnetic properties of $Ni_2(TFDAA)_2(OH)_2(H_2O)_6$ (TFDAA = 1,1,1-trifluoro-2,4,6-heptanetrionato), the first trinuclear complex of this ligand group. Ferromagnetic interactions between adjacent nickel(II) atoms ($J_{12} = 10$ cm^{-1}) and a somewhat large antiferromagnetic coupling ($J_{13} = -6$ cm^{-1}) between terminal metal atoms are reported. This may be because the function minimized was apparently $\delta = (\mu_{obsd} - \mu_{calcd})^2/n$, instead of an expression involving χ, such as $\delta' = (\chi_{obsd} - \chi_{calcd})^2/n$. Use of δ overweights the high-temperature data, in a situation where the lower temperatures give the highest values of the directly measured quantity and hence the most accurate data. This is probably the reason why improbable values $J = 8.0$ cm^{-1}, $J' = 218$ cm^{-1}, and $g = 1.90$ also fit these data. It was immediately recognized that the latter model was just a mathematical curiosity and had no reality for the complexes, as both the g value and the J values were unreasonable. Lintvedt has also reported a Cr(III) complex of a Schiff base derivative of 1,3,5-triketone.[20] This complex is binuclear with the Cr(III) atoms separated by 10.3 Å, and no magnetic exchange is expected or observed.

We have sought to complete the first-row dimeric transition-metal complexes of triketones by preparing a Cr(III) complex similar to the trivalent Fe(III) dimer.[21] A dimeric chromium complex that was free from ligand impurities was impossible to obtain by a variety of methods; therefore excess chromium was added to ensure the use of all the ligand. In doing so, we obtained a product that analyzed for three chromium atoms per two ligands.

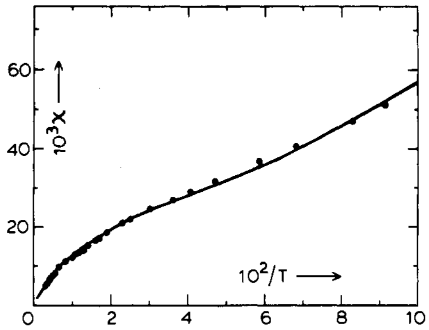


Figure 1. Dependence of the observed and calculated bulk magnetic susceptibility on inverse temperature for $Cr_3(lig)_2(H_2O)_3(OH)_5$.

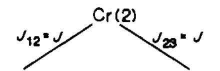
The ESR spectrum of the powdered sample is a broad line, centered at $g = 1.977 \pm 0.005$, which allows no information to be obtained on the directional dependence of the resonance, but it fixes the value of g for the magnetic calculations.

The magnetic susceptibility and magnetic moment per chromium(III) ion, measured on a powdered sample, between 320.2 and 10.9 K are presented in Table I. The dependence of the observed and calculated values of the susceptibility on inverse temperature is shown in Figure 1. This type of plot is chosen because it gives the greatest prominence to the low-temperature data, which are the most accurate. The more conventional $1/\chi$ vs. T plot would lump the most accurate data close together near the origin. Least-squares fits to the data segments above and below 40 K give different slopes. The higher temperature data are less strongly affected by the magnetic coupling, allowing an estimate of some magnetic parameters. The slope gives a Curie constant, C, of 1.86. From the relationship $C = N\beta^2g^2S(S + 1)/3K$ with $S = {}^3/_2$, a calculated value of g of 1.976 ± 0.004 is obtained. The low-temperature data extrapolate to a Weiss constant Θ of −10 K; because of the antiferromagnetism, the plot is nonlinear and the high-temperature data extrapolate to a Θ of −49 K. The calculated values for magnetic coupling are based on the theoretical equations given below, and the fitting procedure is based on δ'.

The exchange coupling between the spins, $S_1 = S_2 = S_3 = {}^3/_2$, for the trinuclear complex may be described by the Hamiltonian

$$H = -2(J_{12}S_1 \cdot S_2 + J_{23}S_2 \cdot S_3 + J_{13}S_1 \cdot S_3)$$

The symmetry of the triketonate ligands requires the environment of the central metal, Cr(2), to be different from that of the other two, producing at most an isosceles symmetry of the coupling constants:



Such will be the case for a linear arrangement of three metal atoms. This leads to the 12 energy levels $E(S)$ for such a system, given by eq 1,[22] where S = total spin and the spin quantum number

$$E(S) = -JS(S + 1) + S_{23}(S_{23} + 1)(J - J') + 15J' + 15J/2 \tag{1}$$

S_{23} applies to either of the short arms of the isosceles triangle. The expession for the variation of susceptibility with temperature is given by eq 2, where $A_1 = 5x^{21}y^{12}$, $A_2 = 4x^{12}y^6(x^6 + y^6)$, A_3

$$\chi = \frac{N\beta^2g^2}{12kT} \frac{33A_1 + 21A_2 + 35A_3 + 5A_4 + A_5}{A_1 + A_2 + 3A_3 + A_4 + A_5} \tag{2}$$

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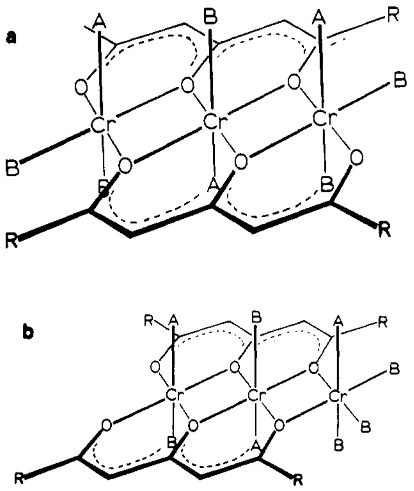

Figure 2. Probable structures for the linear trinuclear complex: (a) symmetrical structure, considered more likely; (b) unsymmetrical structure (A = H_2O, B = OH^-, R = phenyl).

$= x^5(y^{12} + x^6y^6 + x^{10}y^2)$, $A_4 = 2(y^{12} + x^6y^6 + x^{10}y^2 + x^{12})$, $A_5 = x^3y^2(y^4 + x^4)$, $x = e^{2J/kT}$, $y = e^{2J'/kT}$, and the other terms have their usual meaning.

To eliminate g as a fitting parameter, the ESR g value of 1.977 was used, and temperature-independent paramagnetism was taken as zero. Pure antiferromagnetism is observed with $|J| > |J'|$. The best fit is with $J = -6.00$ cm^{-1} and $J' = -1.35$ cm^{-1} with $\delta' = 8.46 \times 10^{-7}$. The g value from the Curie–Weiss and ESR calculations is supported by the observation that the agreement between eq 2 and the observed values becomes worse if the g value is varied significantly from 1.977. Increasing the number of fitting parameters over the two used here necessarily improves the agreement. Thus, with a 3% paramagnetic impurity, a slightly better fit is calculated with $J = -7.35$ cm^{-1} and $J' = -4.06$ cm^{-1}. However, the effect of paramagnetic impurity is likely to be overestimated if other small effects on the magnetism are omitted. These include biquadratic exchange and interactions between adjacent molecules, as well as experimental error. Though none of these would be large, their effects on the magnetism are not independent and not easily evaluated; in the absence of crystallographic data, the intermolecular distance is unknown, but the relatively bulky nature of the ligands should keep intermolecular interaction from being very important.

Table II. UV-Visible Band Positions (cm^{-1}) for $Cr(C_{17}H_{12}O_3)_2(H_2O)_3(OH)_5$ and $Cr(DBM)_3$

trimer (MeOH)	monomer ($CHCl_3$)	assignment[16]
19230	17480	$^4A_{2g} \rightarrow {}^4T_{2g}$
23877	21080	L → M
30057	25810	L → M
39682	32470	$\pi \rightarrow \pi^*$

A decidedly poorer fit is obtained for an equilateral triangle model. The only way to get a fit at all is to assume a paramagnetic impurity. However, an improbably large impurity must be assumed: the best fit in this case is obtained when the impurity is 9% and $J = J' = -14.65$ cm^{-1}; the deviation factor is still doubled ($\delta' = 1.92 \times 10^{-6}$). Therefore, ruling out the equilateral triangular arrangement, we propose a linear trinuclear structure as shown in Figure 2. The linear arrangement can be realized with the two extreme metal atoms identical in the symmetrical structure (Figure 2a). The magnetic model is based on this type of geometry. The unsymmetrical linear structure (Figure 2b) would have three unique metal sites. These three sites may not be sufficiently different to be distinguishable, so that the unsymmetrical structure cannot be ruled out. We have not been able to obtain crystals suitable for X-ray crystallographic study. However, since the ligand remains rigidly planar in all dimeric systems, it is reasonable to assume planarity here also with edge–edge-bound octahedra.

The UV–visible spectral data for the trinuclear complex and for the corresponding mononuclear β-diketonate, $Cr(DBM)_3$,[23] are given in Table II. This also supports the proposed structure. As the spectrum is typical of octahedral Cr(III), the triketonate ligands appear to be coordinated and bridging in the customary manner. This requires a planar molecule with the three Cr(III) species in a linear or very shallow isosceles triangular arrangement. All peaks are shifted to higher energy in the trinuclear complex, as might be expected, attesting to the coupling of the metal atoms in this complex.

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Oxidative Fragmentation of the Cuboid Mo_4S_4 Cluster Core: Synthesis and Structures of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3([9]aneN_3)_3]^{4+}$ and $\{[MoO([9]aneN_3)]_2(\mu\text{-}S)_2\}^{2+}$

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The reaction of the cuboid $[Mo_4S_4]^{6+}$ aquo ion with the terdentate cyclic amine 1,4,7-triazacyclononane ($[9]aneN_3$) initially yields a brown solution from which, depending on the reaction conditions, two fragmentation products were isolated. In acidic solution (pH <2) a trinuclear cluster, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3([9]aneN_3)_3](ZnCl_4)(ZnCl_3OH_2)_2\cdot 3H_2O$, was isolated. It crystallizes in the orthorhombic space group $Pn2_1a$ with $a = 14.116$ (3) Å, $b = 16.417$ (6) Å, $c = 20.773$ (9) Å, $V = 4814$ (5) Å^3, and $Z = 4$. The cluster cation belongs to the M_3X_{13} type (incomplete cube). In neutral medium (pH ≈7) a dinuclear bis(thio)-bridged compound of oxomolybdenum(V) is isolated, $\{[MoO([9]aneN_3)]_2(\mu\text{-}S)_2\}(PF_6)_2$. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.124$ (2) Å, $b = 12.158$ (2) Å, $c = 16.241$ (5) Å, $\beta = 90.88$ (2)°, $V = 1406$ (1) Å^3, and $Z = 4$. The dimeric unit consists of two octahedrally coordinated Mo atoms sharing an edge. The oxo ligands are in an anti configuration with respect to the $Mo(\mu\text{-}S)_2Mo$ plane.

Introduction

It has become apparent recently that an important aspect of the aqueous chemistry of the early transition metals is the presence of polynuclear species, in many of which there are metal–metal bonds.[1,2] The cores of these clusters often are robust entities that can be isolated, in aquated form, by ion-exchange chromatography.

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