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Letter

Novel series of hexanuclear M^{III} complexes (M = V, Cr, Mn, Fe) with the $[M_6O_2]$ core as exemplified by the Cr^{III} complex†

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The hexanuclear M^{III} complexes containing the structural core $[M^{III}{}_6(\mu_3\text{-O})_2]$ are obtained for V^{III}, Cr^{III}, Mn^{III} and Fe^{III} through a general synthetic route.

Polynuclear complexes are of current interest both to biologists and bioinorganic chemists investigating the structure and function of polynuclear metal centres in proteins,[1] and to physicists or physical inorganic chemists searching for new materials[2] displaying interesting electronic properties.

Our continuing interest in the polynuclear and oxime-based complexes[3] has enabled us to discover that the hexanuclear M^{III} complexes containing the structural core $[M^{III}{}_6(\mu_3\text{-O})_2]$ are not rather unusual species and can be obtained for V^{III}, Cr^{III}, Mn^{III} and Fe^{III} through a general synthetic route. The hexanuclear compounds with the general composition $[M^{III}{}_6(\mu_3\text{-O})_2(\text{Salox})_6(\mu_2\text{-OOC}\cdot\text{R})_2(\text{OH}_2)_2(\text{RCN})_2]$ (M = V^{III}, Cr^{III}, Mn^{III}, Fe^{III}), where Salox^{2-} represents the dianion of salicylaldoxime, RCOO^- carboxylate anions such as triphenylacetate, pivalate, benzilate, benzoate or propionate, and RCN a nitrile solvent such as acetonitrile, propionitrile or butyronitrile, have been structurally characterized and found to be isotypic.

We describe in this preliminary communication only the preparation and characterization of the chromium(III) complex, **1**, as a representative one. All operations for the synthesis of **1** were performed under an argon atmosphere unless otherwise mentioned. **1** was prepared by refluxing a suspension of CrF_2 (2 mmol) and $CaCl_2$ (2 mmol) in dry methanol for 2 h. The suspension was filtered to remove the precipitated CaF_2 and the filtrate was stirred at room temperature with propionic acid (2 mmol) for 0.5 h, until a clear green solution was obtained. The green solution, charged with salicylaldoxime (3 mmol) and triethylamine (3 mmol), was stirred at room temperature for 3 days, whereupon a clear brown solution was obtained. The brown solution was kept open to air to yield a brown solid,[4] which was recrystallized twice from propionitrile to obtain brown crystals of **1** (yield $\approx 15\%$)‡. Besides the $\nu(\text{C=N})$ vibrations at 1597 cm^{-1}, strong sharp bands at 675 and 650 cm^{-1}, probably due to the $\nu_{as}(\text{Cr}_3\text{O})$ vibrations,[5] are observed in the IR spectrum.

The molecular structure§ of **1** is shown in Fig. 1, while Fig. 2 highlights only the coordination spheres of the chromium centres. The six chromium atoms in the hexanuclear structure are distributed in two μ_3-oxo-centred trinuclear arrays $[\text{Cr}_3(\mu_3\text{-O})]$, related through an inversion centre situated in the middle of the plane comprising the Cr(2)O(3)O(3a)Cr(2a) atoms; thus the $[\text{Cr}_3(\mu_3\text{-O})]$ units are bridged through the oxygen atoms O(3) and O(3a) of the oxime moiety. The doubly-bridging mode of the oxime oxygens O(3) and O(3a) present in **1** represents a rare coordination type for the oximato ligand.[6] The most common mode is the two-atom bridge, through the *N*- and *O*-donors, for metal oximato complexes.[7] In addition, the oximato group functioning as a μ_4-bridging ligand with N and O bonded to two metal atoms is also known.[8] The chromium atoms Cr(2) and Cr(2a), belonging to the two separate $\text{Cr}_3(\mu_3\text{-O})$ units and bridged by two oximato oxygens O(3) and O(3a), are separated by a distance of 3.275(1) Å. The angle Cr(2)—O(3)—Cr(2a) is 99.3(2)°. The chromium atoms Cr(1), Cr(2) and Cr(3) form an isosceles triangle with the following separations: Cr(1)···Cr(2) 3.148(1), Cr(1)···Cr(3) 3.263(1) and Cr(2)···Cr(3) 3.252(1) Å.

The dispositions of the μ_3-oxide, O(1), are nearly symmetrical, the difference being insignificant within the 3σ range, and the average Cr—O(1) bond, 1.873 Å, is distinctly shorter than that in the $\text{Cr}_3(\mu_3\text{-O})$ core present in Cr^{III} carboxylate complexes.[9] Moderate hydrogen bonding may be envisaged between the water molecule, O(10), coordinated to Cr(3), and O(4a) of the phenoxy group, and also O(3) of the oximato group, with distances of 2.978 and 3.063 Å, respectively.

The chromium atoms Cr(2) and Cr(3) are in distorted octahedral environments having Cr(2)NO_5 and $\text{Cr(3)N}_2\text{O}_4$ coordination spheres, whereas Cr(1) is in an unusual square-pyramidal Cr(1)NO_4 environment. The five-coordinated Cr(1)

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† Non-SI units employed: $\mu_B \approx 9.27 \times 10^{-24}\ \text{J T}^{-1}$.

‡ Anal. calcd for $C_{60}H_{64}N_{10}O_{20}Cr_6$: C, 46.10; H, 4.13; N, 8.96; Cr, 20.34. Found: C, 47.0; H, 4.1; N, 8.9; Cr, 20.0. UV/VIS in CH_3CN: ≈ 600 nm sh (2019 $M^{-1}\ cm^{-1}$), ≈ 370 nm sh (20600 $M^{-1}\ cm^{-1}$).

§ Crystal data for **1**: $C_{60}H_{64}N_{10}O_{20}Cr_6$, $M = 1557.2$, triclinic, space group $P\bar{1}$, $a = 12.064(2)$, $b = 12.458(3)$, $c = 12.482(3)$ Å, $\alpha = 65.57(3)$, $\beta = 77.20(3)$, $\gamma = 75.24(3)°$, $U = 1637.2(6)$ Å^3, $Z = 1$, $D_c = 1.579$ g cm^{-3}, $\mu = 1.042$ mm^{-1}, $T = 103(2)$ K. Of 6571 reflections collected [Siemens SMART, MoKα radiation ($\lambda = 0.71073$ Å)], 4618 were used [$F > 4.0\ \sigma(F)$]. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (SHELXTL-PLUS package; G. M. Sheldrick, Universität Göttingen). All non-hydrogen atoms were refined anisotropically; $R = 0.065$ and R' (all data) = 0.102 with 430 parameters. CCDC reference number 440/026.

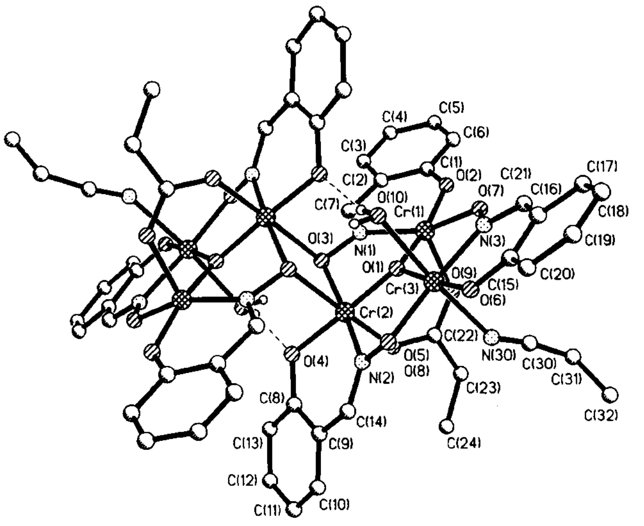


Fig. 1 Structure of **1**. Selected bond lengths/Å and angles/°: Cr(1)—O(2) 1.859(5), Cr(1)—O(1) 1.860(4), Cr(1)—O(7) 1.897(5), Cr(1)—N(1) 2.003(6), Cr(1)—O(9) 2.103(5), Cr(2)—O(4) 1.874(4), Cr(2)—O(1) 1.874(4), Cr(2)—O(3) 1.958(5), Cr(2)—N(2) 1.998(6), Cr(2)—O(8) 2.107(5), Cr(2)—O(3a) 2.327(5), Cr(3)—O(6) 1.862(5), Cr(3)—O(1) 1.884(5), Cr(3)—O(5) 1.931(5), Cr(3)—N(3) 2.003(6), Cr(3)—N(30) 2.303(6), Cr(3)—O(10) 2.338(5), O(2)—Cr(1)—O(1) 169.3(2), O(2)—Cr(1)—O(7) 87.1(2), O(1)—Cr(1)—O(7) 90.9(2), O(2)—Cr(1)—N(1) 89.5(2), O(1)—Cr(1)—N(1) 89.0(2), O(7)—Cr(1)—N(1) 160.4(2), O(2)—Cr(1)—O(9) 95.8(2), O(1)—Cr(1)—O(9) 94.9(2), O(7)—Cr(1)—O(9) 105.5(2), N(1)—Cr(1)—O(9) 94.0(2), O(4)—Cr(2)—O(1) 177.1(2), O(4)—Cr(2)—O(3) 89.9(2), O(1)—Cr(2)—O(3) 89.7(2), O(4)—Cr(2)—N(2) 91.2(2), O(1)—Cr(2)—N(2) 88.6(2), O(3)—Cr(2)—N(2) 168.4(2), O(4)—Cr(2)—O(8) 91.0(2), O(1)—Cr(2)—O(8) 91.9(2), O(3)—Cr(2)—O(8) 96.7(2), N(2)—Cr(2)—O(8) 94.8(2), O(4)—Cr(2)—O(3a) 89.5(2), O(1)—Cr(2)—O(3a) 87.7(2), O(3)—Cr(2)—O(3a) 80.7(2), N(2)—Cr(2)—O(3a) 87.8(2), O(8)—Cr(2)—O(3a) 177.3(2), O(6)—Cr(3)—O(1) 174.0(2), O(6)—Cr(3)—O(5) 89.4(2), O(1)—Cr(3)— O(5) 92.2(2), O(6)—Cr(3)—N(3) 90.8(2), O(1)—Cr(3)—N(3) 87.9(2), O(5)—Cr(3)—N(3) 176.2(2), O(6)—Cr(3)—N(30) 92.8(2), O(1)—Cr(3)—N(30) 93.0(2), O(5)—Cr(3)—N(30) 90.4(2), N(3)—Cr(3)—N(30) 85.9(2), O(6)—Cr(3)—O(10) 90.6(2), O(1)—Cr(3)—O(10) 83.5(2), O(5)—Cr(3)—O(10) 95.6(2), N(3)—Cr(3)—O(10) 88.2(2), N(30)—Cr(3)—O(10) 173.2(2), Cr(1)—O(1)—Cr(2) 114.9(2), Cr(2)—O(1)—Cr(3) 119.9(2), Cr(1)—O(1)—Cr(3) 121.3(2)

is bonded to the azomethine nitrogen N(1), phenolate oxygen O(2), hydroxo oxygen O(7) and μ_3-oxo group O(1) in the basal plane, and an oxygen O(9) of the bridging carboxylate group in the apical position. The Cr(1) atom is displaced by 0.25 Å from the mean basal plane comprising the N(1)O(2)O(7)O(1) atoms toward the apical atom O(9) of the carboxylate. The Cr(1) centre provides another of the very few examples of an authenticated nonoctahedral Cr^{III} complex.[10]

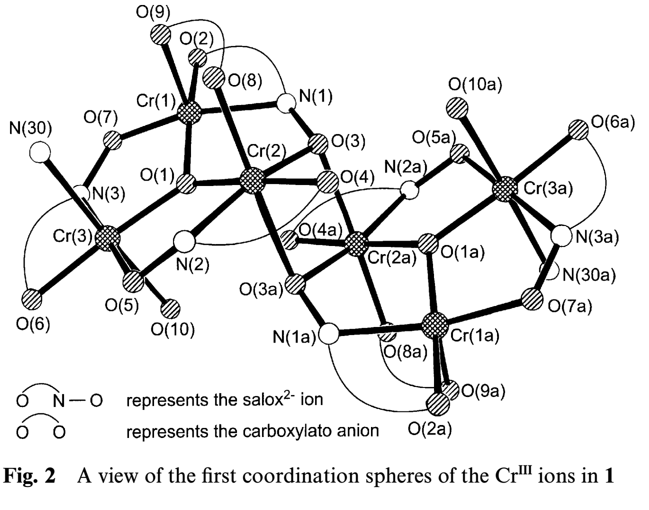
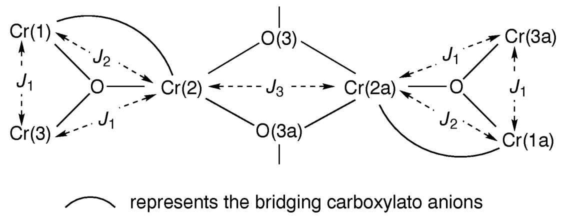


Fig. 2 A view of the first coordination spheres of the Cr^{III} ions in **1**

Magnetic susceptibility data for a polycrystalline sample of **1** were collected in the temperature range 2–290 K with an applied field of 1 T; the data are displayed in Fig. 3 as μ_{eff} *vs.* *T*. On lowering the temperature the μ_{eff} value of 9.19 μ_B at 290.3 K decreases monotonically, approaching a minimum around ≈ 30 K ($\mu_{eff} = 6.75\mu_B$), and increases upon further cooling to 6.93 μ_B at 10 K. Below 10 K there is a decrease in μ_{eff} for **1**, reaching a value of 4.89μ_B at 2 K; this behaviour is attributable to the effect of the zero-field splitting of the ground state $S_t = 3$. The experimental magnetic data were simulated using a least-squares fitting computer program, which uses the irreducible tensor operator (ITO)[11] with the $H = -2JS_i \cdot S_j$ convention. The exchange coupling model is shown in the scheme:



The best fit, shown as the solid line in Fig. 3, yields the following parameters: $g = 2.13$, $J_1 = -14.2$ cm^{-1}, $J_2 = +12.8$ cm^{-1} and $J_3 = +5.3$ cm^{-1}. At this point, we like to mention that the reduction of the number of '*J*' parameters from three to two does not yield an acceptable simulation of the experimental data. We also performed a systematic search in parameter space to determine the global nature of the fit minimum. Using the evaluated exchange coupling constants, the first and the second excited states are found to be $S_t = 2$ and $S_t = 1$, respectively, which lie 18.4 and 31 cm^{-1} above the ground state with $S_t = 3$. The ground state, $S_t = 3$, is also confirmed by the field-dependent magnetization study at 5 K in the 0.5–6.5 T magnetic field range, which yields a value for the zero-field splitting parameter *D* of 3.03 cm^{-1}.

The antiferromagnetic coupling between the Cr^{III} centres reported in the literature[5] for $[Cr_3O]^{7+}$ cores, typically $J = -9.5$ cm^{-1}, is weaker than $J_1 = -14.2$ cm^{-1} for **1**, although it is generally accepted that in compounds of this type the μ_3-oxo ion provides the principal superexchange pathway. It is interesting to note that J_2 and J_3 are of ferromagnetic nature. As the interpretation of magnetic data for the hexanuclear Cr^{III} is difficult at the present stage of knowledge, we are refraining from discussing the individual coupling constants.

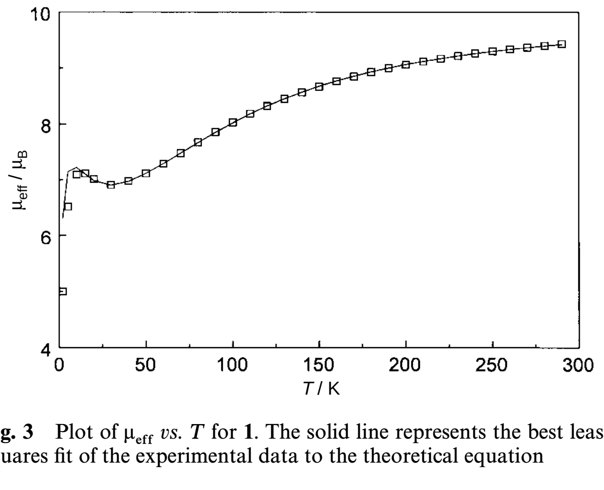


Fig. 3 Plot of μ_{eff} *vs.* *T* for **1**. The solid line represents the best least-squares fit of the experimental data to the theoretical equation

To conclude, this work describing the hexanuclear[12] series $[M^{III}_6(\mu_3\text{-}O)_2(Salox)_6(\mu\text{-}COOR)_2(OH_2)_2(RCN)_2]$ with the structural and physical properties of the Cr^{III} analog clearly expands our knowledge of polynuclear metal complexes, showing the importance of bridging ligands like carboxylato anions for cooperation with the ancillary ligand, *viz*., salicylaldoxime, to build up high-nuclearity metal clusters. To our knowledge, this is the first report of paramagnetic trivalent metal complexes with salicylaldoxime as a ligand.

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4 The brown solid upon recrystallization from *methanol* yields also brown crystals, but with a slightly different structure. The structures of both the manganese and iron complexes have been solved. The triclinic packing, space group $P\bar{1}$, exhibits six molecules in the unit cell, two of type A, $M_6(\mu_3\text{-}O)_2(Salox)_6(benzoate)_2(OH_2)_5$, and four of type B, $M_6(\mu_3O)_2(Salox)_6(benzoate)_2(OH_2)_4$, which differ from A in the coordination sphere of one M^{III} atom. The A and two B molecules (B_1) lie on general sites, the remaining two B molecules (B_2) are situated on a crystallographic inversion centre, thus implying exact molecular inversion symmetry C_i. The molecules B_1 also exhibit C_i symmetry, although not imposed by space group symmetry, whereas those of A are unsymmetrical with respect to the ligands coordinated to the metal atoms. So the asymmetric unit contains one complete molecule A as well as one molecule B_1 plus two halves of type B_2.

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