Self-assembly of a Novel 14-Membered Metallamacrobicycle containing Two Chromium(III) Ions as Part of the Ring Skeleton

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A metallamacrocycle, [LCr^{III}μ-{(Hdmg)$_2$(dmg)}Cr^{III}L](ClO$_4$)$_2$·MeOH (L = 1,4,7-trimethyl-1,4,7-triazacyclononane; dmg = dianion of dimethylglyoxime), is synthesized by a one-step high yield template reaction and characterized by X-ray crystallography and magnetic susceptibility measurements.

Since the early work of Pedersen,[1] Cram[2] and Lehn,[3] macrocyclic chemistry has attracted much attention from scientists of different areas, ranging from chemistry to solid-state physics and biology, because of the potential impact on materials science, catalysis and metallo-biochemistry.[4] One of the recent trends has been the use of transition metal centres to control the assembly of macrocyclic structures. Synthesis of macrocycles, containing metals bonded exocyclically to the macrocyclic ring, possessing unusual properties is one of the recent noteworthy advances in this field.[5–8] Synthesis of metallamacrocycles, *i.e.* macrocycles containing transition metals as part of the ring skeleton, is an area as yet relatively unexplored.[9]
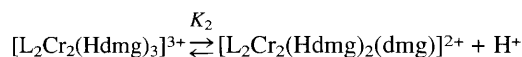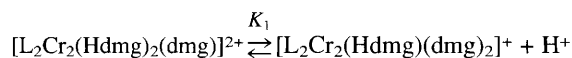
Recently, we have utilized tris(dimethylglyoximato)metal(II) anions, [M(dmg)$_3$]$^{4-}$,† as bridging ligands which are 'capped' by metal complexes, to synthesize linear homo- and heterotrinuclear species in which the central metal ion is encapsulated in a ligand cage.[10,11] Thus, a series of cationic clathrochelates of general formula [LM$_a$μ-{(dmg)$_3$M$_b$}M$_a$L]$^{2+/4+}$ where M$_a$ = Fe^{III}, Mn^{III} or Mn^{IV} and M$_b$ = Zn^{II}, Cu^{II}, Ni^{II}, Fe^{II} or Mn^{II} have been synthesized.

In the course of the synthesis of the aforementioned series with M$_a$ = chromium(III) we encountered an unexpected preparative result which led to the isolation of a novel doubly protonated 14-membered matallamacrobicyclic compound incorporating two chromium(III) ions within the ring skeleton, which is the subject matter of this communication.

[LCr^{III}(Hdmg)$_2$(dmg)Cr^{III}L](ClO$_4$)$_2$·MeOH 1

Complex **1** was synthesized by refluxing a suspension of LCrBr$_3$[12] (2 equiv.), dimethylglyoxime (3 equiv.), triethylamine (6 equiv.) in methanol (60 cm^3) for 10 h until a deep-red solution was obtained. The hot solution was filtered to remove any green solid particles. Red crystalline prisms of **1** were obtained as the perchlorate salt by adding a solution of triethylammonium perchlorate (10 equiv.) in methanol (5 cm^3).‡ The optical spectrum for **1** in acetonitrile shows a CT band at 268 nm (ε = 51300 dm^3 mol^{-1} cm^{-1}) and a d–d band at 525 nm (ε = 244 dm^3 mol^{-1} cm^{-1}). The IR spectrum of **1** exhibits a weak broad band at 3250–3260 cm^{-1} which can be ascribed to the ν(N–H) stretching vibration of the protonated oxime nitrogen atoms.

Values of pK_1 and pK_2 for the following equilibria have been determined by a potentiometric titration§ (Fit program: MINIQUAD) of the bromide salt with sodium hydroxide to be 10.72 ± 0.03 and 4.39 ± 0.08 (T = 25 °C, I = 0.1 mol dm^{-3} KNO$_3$), respectively. The bromide salt was used because of its higher solubility than that of the perchlorate salt in water.

$$[L_2Cr_2(Hdmg)_2(dmg)]^{2+} \overset{K_1}{\rightleftharpoons} [L_2Cr_2(Hdmg)(dmg)_2]^+ + H^+$$

$$[L_2Cr_2(Hdmg)_3]^{3+} \overset{K_2}{\rightleftharpoons} [L_2Cr_2(Hdmg)_2(dmg)]^{2+} + H^+$$

The structure of **1** has been established by a low temperature (193 K) X-ray analysis¶ and is shown in Fig. 1. The asymmetric unit consists of half of the cation, well-separated perchlorate anions and a methanol molecule. The crystal structure analysis of **1** clearly illustrates (Fig. 2) the metallamacrobicyclic nature

of the 14-membered heterocyclic ring. The coordination geometry of the chromium ions, Cr(1) and Cr(1a), is distorted octahedral with three nitrogen atoms [N(4), N(5) and N(6)] from the facially coordinated tridentate macrocyclic amine (L) and three oxygen atoms [O(1), O(2) and O(3)] from three bridging dimethylglyoximato ligands, resulting in *fac*-CrN$_3$O$_3$ cores. The Cr–N [average 2.125(4) Å] and Cr–O [average 1.935(3) Å] distances correspond to the literature values for Cr^{III} complexes with this macrocyclic amine.[12] The chromium centres are nearly coplanar with the nitrogen atoms of a dimethylglyoxime ligand, with a Cr···Cr separation of 7.265 Å. Two significant residual electron densities at a distance of *ca*. 1 Å from N(1) and N(3) have been assigned to two statistically disordered protons (occupancy factor 0.5). The presence of these protons is also in conformity with the pH-metric titration of the complex **1** with NaOH and the charge balance consideration, together with the chemical analysis. Protonation
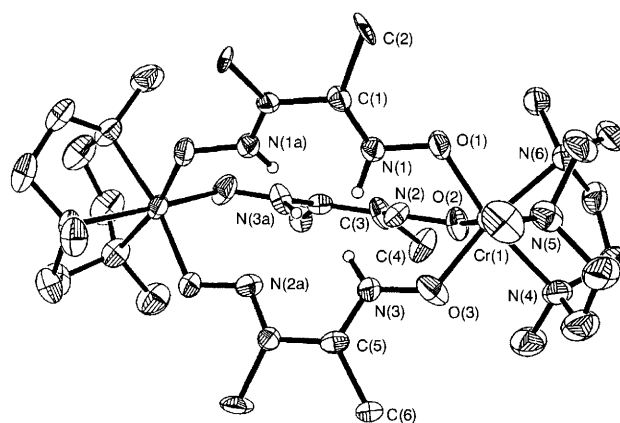

Fig. 1 Structure of the cation [L$_2$Cr$_2$(Hdmg)$_2$(dmg)]$^{2+}$ in **1**. Selected bond lengths (Å) and angles (°): Cr···Cr 7.265, Cr(1)–N(4) 2.115(4), Cr(1)–N(5) 2.130(4), Cr(1)–N(6) 2.129(3), Cr(1)–O(1) 1.940(3), Cr(1)–O(2) 1.925(3), Cr(1)–O(3) 1.939(3), N(1)–O(1) 1.352(4), N(1)–C(1) 1.280(4), N(2)–O(2) 1.362(5), N(2)–C(3) 1.261(5), N(3)–O(3) 1.351(5), N(3)–C(5) 1.279(4), N(4)–Cr(1)–N(5) 82.5(1), N(4)–Cr(1)–N(6) 82.8(1), N(5)–Cr(1)–N(6) 82.2(1), N(4)–Cr(1)–O(1) 168.6(1), N(5)–Cr(1)–O(1) 88.4(1), N(6)–Cr(1)–O(1) 89.3(1), N(4)–Cr(1)–O(2) 90.4(1), N(5)–Cr(1)–O(2) 169.3(1), N(6)–Cr(1)–O(2) 89.1(1), O(1)–Cr(1)–O(2) 97.6(1), N(4)–Cr(1)–O(3) 88.9(1), N(5)–Cr(1)–O(3) 90.9(1), N(6)–Cr(1)–O(3) 169.8(1), O(1)–Cr(1)–O(3) 98.0(1), O(2)–Cr(1)–O(3) 96.9(1), O(1)–N(1)–C(1) 117.6(3), O(2)–N(2)–C(3) 117.4(3), O(3)–N(3)–C(5) 119.7(3).
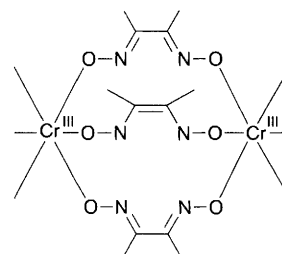

Fig. 2 A schematic view of the 14-membered metallamacrobicycle

of oxime nitrogens has also been described earlier in the literature.[13]

Magnetic susceptibility data for a polycrystalline sample of **1** were collected in the temperature range 2–295 K. The molar paramagnetic susceptibility increases with decreasing temperature and reaches a maximum at *ca.* 20 K with $\chi_M T = 1.347$ cm³ mol⁻¹ K, below which the susceptibility starts to decrease (Fig. 3). At 295 K the μ_{eff} value is 5.425 μ_B, which is slightly lower than the theoretical value of $\mu_{eff} = 5.544$ μ_B, expected for two noncoupled spins of $S_{Cr} = 3/2$. On lowering the temperature, μ_{eff} decreases monotonically with decreasing temperature. Below 70 K, μ_{eff} decreases rapidly with decreasing temperature and approaches the value of 0.226 μ_B ($\chi_M T = 0.6383 \times 10^{-2}$ cm³ mol⁻¹ K). This magnetic behaviour is typical of antiferromagnetically coupled binuclear paramagnetic centres with a diamagnetic ground state, $S_T = 0$. A full-matrix diagonalization approach including magnetic exchange $(-2J \cdot S_1 \cdot S_2)$ and Zeeman interactions was employed to fit the data. The least-squares fits are of good quality (solid lines in Fig. 3) and result in the following values: exchange coupling constant $J = -4.7$ cm⁻¹ and $g = 2.04$. It is noteworthy that the exchange coupling is observed in **1**, in which the chromium(III) centres are separated by a large distance of 7.27 Å.
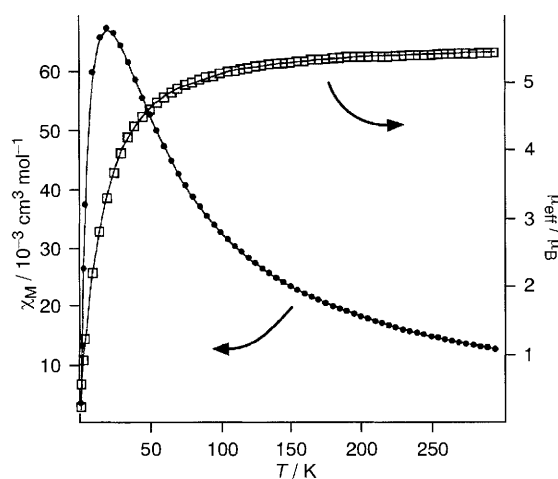

Fig. 3 Plots of χ_M and μ_{eff} *vs.* *T* for **1**. The solid lines represent the best least-squares fits of the experimental data to the theoretical equation.
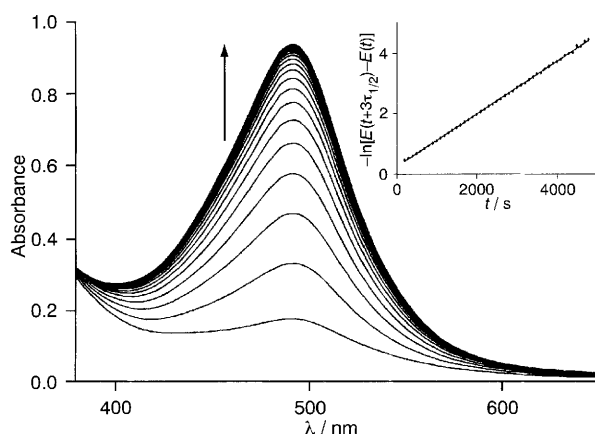

Fig. 4 Time-dependent increase in absorption per cm at ambient temperature during the incorporation of Fe^II into **1**. Experimental conditions: [**1**] = 10⁻⁴ mol dm⁻³, [Fe²⁺] = 5 × 10⁻³ mol dm⁻³, pH = 6.90, *I* = 0.2 mol dm⁻³ (Li₂SO₄), *T* = 40 °C. *Insert*: Guggenheim plot, *k* = 8.8 × 10⁻⁴ s⁻¹.

Formation of complex **1** by simple refluxing of the LCr³⁺ unit with dimethylglyoxime is an example of spontaneous self-assembly, presumably based on the preference of Cr^III ions for oxygen donor atoms to azomethine nitrogens. This stable cyclic derivative **1** has been proved to be an important precursor for generating various heterometallic trinuclear complexes containing Cr^III as the terminal ions by replacing the incorporated protons with different metal ions, *viz.* [L₂Cr₂(dmg)₃M]²⁺/³⁺ (M = Zn^II, Cu^II, Ni^II, Co^III, Fe^II or Mn^II). Interestingly, the incorporation of a labile divalent metal ion, *e.g.* Fe^II, into **1** is kinetically a very slow process. Fig. 4 illustrates the slow substitution kinetics of Fe^II.

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