Bis(β-diketonate) ligands for the synthesis of bimetallic complexes of Ti^{III}, V^{III}, Mn^{III} and Fe^{III} with a triple-helix structure

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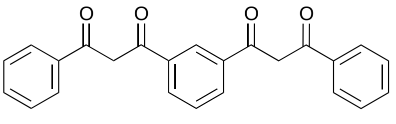
Addition of the bis(β-diketone) ligand L [L = 1,3-bis(3-phenyl-3-oxopropanoyl)benzene] to a suitable source of M^{III} ions (M = Ti, V, Mn, Fe) in a L : M = 3 : 2 ratio gives the dinuclear products [M_2L_3], which have a triple-helical structure.

The use of oligopyridyl, oligo-2,2′-bipyridyl and related ligands in transition-metal chemistry has been receiving a great deal of attention in recent years.[1–7] Their products with mononuclear metal ions have displayed a variety of fascinating structures such as double[1,2,4,8] or triple helices,[1,2,3,6,9] and ‘cylindrical’,[10] ‘capped’[11] or ‘circular’[12] architectures. As such, these ligands have been amongst the central players in the supramolecular chemistry field.

Bis(β-diketonate) ligands offer similar potential for the preparation of supramolecular assemblies, and we herein report the initial use of the ligand L for the synthesis of bimetallic complexes of formula [M_2L_3] (M = Ti^{III}, V^{III}, Mn^{III}, Fe^{III}) with a triple-helix structure. Ligand L† was prepared from a Claisen condensation employing dimethyl isophthalate and acetophenone in the presence of NaH, a method related to that in the early literature of bis(β-diketonates).[13] Addition of L to a convenient source of M^{III} [$MCl_3(thf)_3$][14] (M = Ti, V), $Mn(O_2CMe)_2\cdot 4H_2O$/$NBu^n_4MnO_4$, $Fe(ClO_4)_2\cdot 6H_2O$/air] in dmf or CH_2Cl_2 gave dark coloured solutions from which could be isolated crystalline [M_2L_3] (M = Ti **1**, V **2**, Mn **3**, Fe **4**) in 30–70% yields, followed by recrystallisation from dmf–MeOH (**1**–**3**) or thf–Me_2CO (**4**).‡ Complexes **1**–**4** are isostructural§ (Fig. 1) and consist of two six-coordinate M^{III} ions chelated and bridged by three L^{2-} groups. The M···M separations are very similar [7.222(2) **1**, 7.224(2) **2**, 7.350(2) **3**, 7.262(4) Å **4**] and the molecules are in a triple-helix conformation, as emphasized by the view along the M···M vector (Fig. 2). The average ligand twist angles (defined as the angles between the two M–M–C(methine) planes for each ligand) are 42.8 **1**, 44.0 **2**, 47.4 **3** and 40.8° **4**. The structural parameters show only the small differences expected from varying the M^{III} ion and the presence in **3** of a Jahn–Teller axial elongation along the O(3)–Mn(1)–O(35) and O(8)–Mn(2)–O(40) axes. The metal geometries are essentially octahedral. The series could undoubtedly be extended to other M^{III} ions (*e.g.*, Cr^{III}, Co^{III}) and this is currently being explored. The triple-helix structures of **1**–**4** with the ligand L^{2-} are new additions to the relatively small but growing family of dinuclear metal complexes with a triple-helix structure, hitherto with ligands other than β-diketonates.[2,3,6,9,15–17]



L

Detailed characterisation of **1**–**4** by a variety of spectroscopic and physical methods is in progress. Preliminary electrochemical studies by cyclic voltammetry in dmf confirm that the two M^{III} ions are interacting. The ‘richest’ CV scans belong to **1** and **2** which show very similar electrochemical behaviour (Fig. 3). Both exhibit two pairs of closely spaced reversible reductions: −1.076, −1.212 V (Δ*E* = 0.136 V) and −1.720,

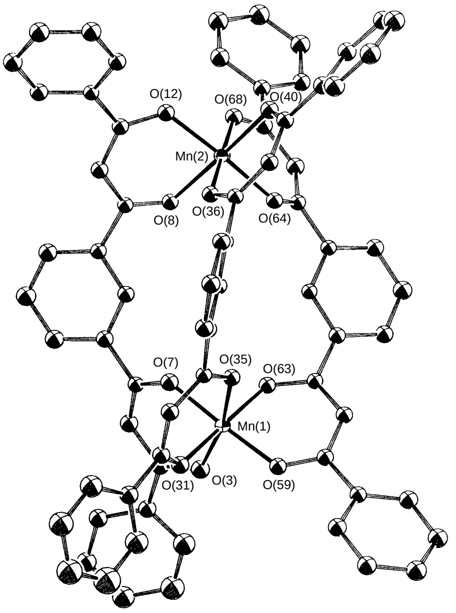


Fig. 1 The structure of [Mn_2L_3] **3**; complexes **1**, **2** and **4** are isostructural

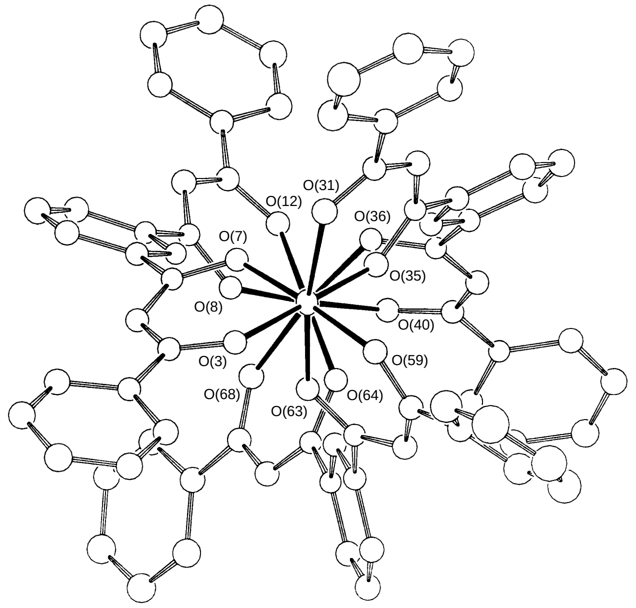


Fig. 2 A view down the Mn···Mn vector of**3** emphasizing the triple-helical conformation of the molecule

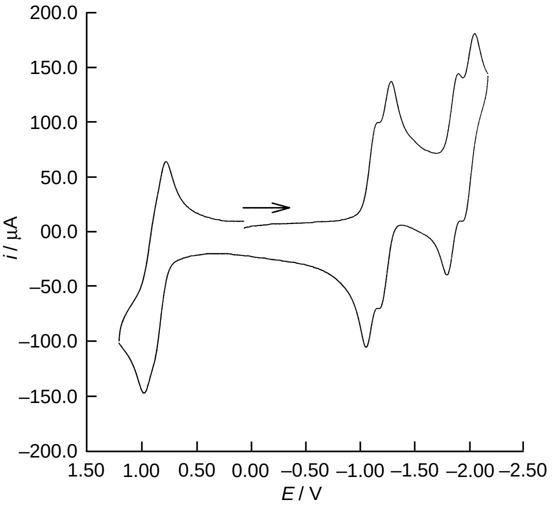


Fig. 3 Cyclic voltammogram at 100 mV s^{-1} for complex **2** in dmf at a glassy carbon electrode and with $NBu^n_4PF_6$ as supporting electrolyte

−1.900 V (ΔE = 0.180 V) for **1** and −1.104, −1.240 V (ΔE = 0.136 V) and −1.840, −2.000 V (ΔE = 0.160 V) for **2** *vs.* SCE. In addition, for both complexes, there is a less well resolved pair of oxidation processes: +0.016, +0.092 V for **1** (ΔE = 0.076 V) and +0.808, +0.884 V for **2** (ΔE = 0.080 V). The large ΔE values are indicative of intramolecular interactions between the two M^{III} ions. Complex **4** shows only a single pair of reversible reductions, at −0.460 and −0.584 V. Complex **3** shows a broad, quasi-reversible reduction process at −0.018 V ($E_{pc} - E_{pa}$ = 0.520 V), with an additional irreversible oxidation at approximately +1.238 V. For all four species, additional reductions are observed at < −2.0 V. The redox behaviour of **1–4** is related to that of the corresponding mononuclear $M(dbm)_3$ (dbm = anion of dibenzoylmethane), which exhibit single redox processes at similar processes to **1–4**. Variable-temperature magnetic susceptibility studies on **1–4** are currently in progress to quantitate the strength of intramolecular interactions within these molecules.

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Footnotes and References

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† *Selected spectroscopic data* for L: ^1H NMR (CD_2Cl_2, 500 MHz): δ 6.98 (s, 2 H), 7.53 (t, *J* 8 Hz, 4 H), 7.61 (t, *J* 8 Hz, 2 H), 7.66 (t, *J* 8 Hz, 1 H), 8.04 (d, *J* 8 Hz, 4 H), 8.19 (d, *J* 8 Hz, 2 H), 8.60 (s, 1 H); EI-MS (M^+) 370.1 ($C_{24}H_{18}O_4$ requires 370.1).

‡ The complexes analysed satisfactorily.

§ *Crystal data* **1**: $C_{72}H_{48}O_{12}Ti_2$, M_r = 1200.90, monoclinic, space group $C2/c$, a = 22.924(3), b = 17.721(2), c = 18.870(2) Å, β = 129.60(1)°, U = 5906.7 Å^3, Z = 4, T = 106 K, μ = 3.293 cm^{-1}, 1689 reflections with $F > 4\sigma(F)$, $R(F)$ = 0.0645, $R_w(F^2)$ = 0.1030. **2**·0.72 MeOH: $C_{72}H_{48}O_{12}V_2$·0.72 MeOH, M_r = 1207.06 (excl. solv), monoclinic, space group $C2/c$, a = 22.982(4), b = 17.906(3), c = 18.057(3) Å, β = 127.09(1)°, U = 5945.7 Å^3, Z = 4, T = 106 K, μ = 3.829 cm^{-1}, 3038 reflections with $F > 3\sigma(F)$, $R(F)$ = 0.0481, $R_w(F)$ = 0.0510. **3**·CH_2Cl_2: $C_{73}H_{50}O_{12}Cl_2Mn_2$, M_r = 1300.0, triclinic, space group $P\bar{1}$, a = 15.682(3), b = 16.850(4), c = 13.843(3) Å, α = 105.63(1), β = 102.92(1), γ = 113.93(1)°, U = 2980.5 Å^3, Z = 2, T = 102 K, μ = 5.806 cm^{-1}, 8025 reflections with $F > 3\sigma(F)$, $R(F)$ = 0.0657, $R_w(F)$ = 0.0589. **4**·thf: $C_{76}H_{56}O_{13}Fe_2$, M_r = 1293.00, triclinic, space group $P\bar{1}$, a = 16.151(5), b = 16.982(6), c = 11.817(4) Å, α = 108.50(2), β = 103.54(2), γ = 87.24(2)°, U = 2987.0 Å^3, Z = 2, T = 103 K, μ = 5.561 cm^{-1}, 4128 reflections with $F > 3\sigma(F)$, $R(F)$ = 0.0911, $R_w(F)$ = 0.0835. CCDC 182/522.

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