Non-polymeric molybdenum(ii) complexes of dicarboxylic acids: synthesis, structure and catalytic properties

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$[Mo_2(MeCN)_8][BF_4]_4$ reacts with α,ω-dicarboxylic acids $[HO_2C(CH_2)_nCO_2H$, n = 0–8] to form salts with empirical formula $[Mo_2\{O_2C(CH_2)_nCO_2\}(MeCN)_x][BF_4]_2$; the X-ray crystal structure of the butanedioic salt $[Mo_4\{\eta^2\text{-}\mu\text{-}O_2C\text{-}(CH_2)_2CO_2\text{-}\mu\text{-}\eta^2\}_2(MeCN)_{12}][BF_4]_4\cdot 3MeCN$ is reported together with the use of the complexes as catalysts for the polymerization of norbornene.

The $Mo^{II}Mo^{II}$ quadruply bonded neutral complex $[Mo_2(\mu\text{-}O_2CMe)_4]$ is known to react with dicarboxylic acids to give insoluble polymeric powders[1] which cannot be fully structurally characterized and which have limited subsequent chemical reactivity. Herein we detail the reactions of the tetracationic $Mo^{II}Mo^{II}$ salt $[Mo_2(MeCN)_8][BF_4]_4$[2] with α,ω-dicarboxylic acids $[HO_2C(CH_2)_nCO_2H$, n = 0–8] to form red, soluble complex salts with empirical formula $[Mo_2\{O_2C(CH_2)_nCO_2\}\text{-}(MeCN)_x][BF_4]_2$.‡ The tetranuclear butanedioic salt $[Mo_4\{\pi^2\text{-}\mu\text{-}O_2C(CH_2)_2CO_2\text{-}\mu\text{-}\eta^2\}_2(MeCN)_{12}][BF_4]_4\cdot 3MeCN$ **1** represents the first structurally characterized M–M quadruply bonded dicarboxylate complex (Fig. 1).§ The unit cell contains one centrosymmetric complex ion of formula $[Mo_4\{\eta^2\text{-}\mu\text{-}O_2\text{-}C(CH_2)_2CO_2\text{-}\mu\text{-}\eta^2\}_2(MeCN)_{12}]^{4+}$ along with four BF_4^- counter ions and three MeCN solvent molecules. The Mo^{II} atoms are six-coordinate and their environments are very similar. They are linked by a short [2.1415(6) Å] quadruple bond and, *trans* to this, each has a long interaction with an axial MeCN molecule [Mo(1)–N(50) 2.712(5), Mo(2)–N(60) 2.674(5) Å]. The remaining donors, nitrogen atoms from two MeCN molecules (mean Mo–N 2.162 Å) and an oxygen atom from each of two carboxylate groups (mean Mo–O 2.084 Å) occupy a square plane with *cis* geometry. The two butanedioic dianions each have two bridging functions. First, each of the carboxylate groups bridges the Mo–Mo bond; secondly, each butanedioic ligand links the two halves of the tetranuclear complex together. The coordination environment about each of the quadruply bonded Mo–Mo cores is essentially identical to that of the structurally characterized, red dimolybdenum(ii,ii) monocarboxylate salt *cis*-$[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$.[3] The coordination of the dicarboxylate ligands in **1** is the same as in the tetranuclear ruthenium(i) pentanedioate complex $[Ru_4\text{-}(CO)_8\{O_2C(CH_2)_3CO_2\}_2(PBu_3)_4]$[4] and the polymeric copper(ii) butanedioate complex $\{[Cu_2\{O_2C(CH_2)_2CH_2)_2\}\text{-}(H_2O)_2]\cdot 2H_2O\}_n$,[5] where again the individual bimetallic centres are spanned by two $^-O_2C(CH_2)_nCO_2^-$ ligands in a *cisoid* fashion.

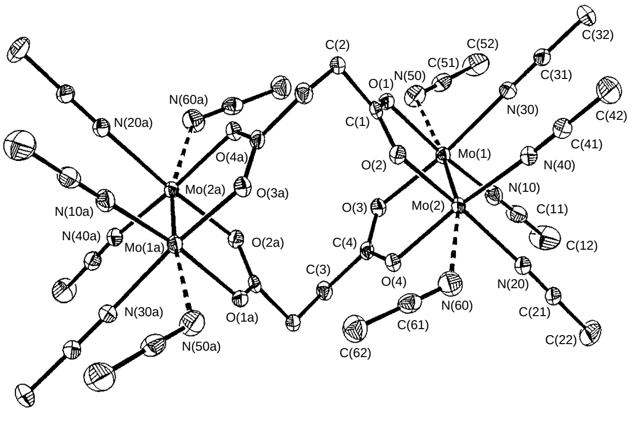

Fig. 1 Crystal structure of **1**. Selected bond lengths (Å) and bond angles (°): Mo(1)–O(1) 2.091(3), Mo(1)–O(3) 2.088(3), Mo(2)–O(2) 2.080(3), Mo(2)–O(4) 2.077(3), Mo(1)–N(10) 2.162(4), Mo(1)–N(30) 2.172(4), Mo(1)–N(50) 2.712(5), Mo(2)–N(20) 2.163(4), Mo(2)–N(40) 2.152(4), Mo(2)–N(60) 2.674(5), Mo(1)—Mo(2) 2.145(6); O(3)–Mo(1)–O(1) 91.53(12), O(3)–Mo(1)–Mo(2) 91.21(9), O(1)–Mo(1)–Mo(2) 91.10(9), O(3)–Mo(1)–N(10) 88.66(14), O(1)–Mo(1)–N(10) 166.2(2), Mo(2)–Mo(1)–N(10) 102.72(13), O(3)–Mo(1)–N(30) 166.3(2), O(1)–Mo(1)–N(30) 89.18(14), Mo(2)–Mo(1)–N(30) 102.43(11), N(10)–Mo(1)–N(30) 87.4(2), O(3)–Mo(1)–N(50) 86.0(2), O(1)–Mo(1)–N(50) 84.01(13), Mo(2)–Mo(1)–N(50) 174.28(11), N(10)–Mo(1)–N(50) 82.2(2), N(30)–Mo(1)–N(50) 80.5(2), O(4)–Mo(2)–O(2) 90.64(12), O(4)–Mo(2)–Mo(1) 90.70(9), O(2)–Mo(2)–Mo(1) 90.80(9), O(4)–Mo(2)–N(40) 166.2, O(2)–Mo(2)–N(40) 86.00(14), Mo(1)–Mo(2)–N(40) 102.75(11), O(4)–Mo(2)–N(20) 90.11(14), O(2)–Mo(2)–N(20) 168.6(2), Mo(1)–Mo(2)–N(20) 100.52(12), N(40)–Mo(2)–N(20) 90.6(2), O(4)–Mo(2)–N(60) 76.1(2), O(2)–Mo(2)–N(60) 83.3(2), Mo(1)–Mo(2)–N(60) 165.43(11), N(40)–Mo(2)–N(60) 90.2(2), N(20)–Mo(2)–N(60) 85.9(2).

The IR spectrum of the solid (KBr matrix) contained prominent carboxylate $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ vibrations at 1536 and 1443 cm^{-1}, respectively, with the value of $\Delta\nu(OCO)$ $\{\nu_{asym} - \nu_{sym} = 93\ cm^{-1}\}$ in keeping with that recorded for complexes in which the carboxylate ligand bridges short M–M bonds {*e.g.* $\Delta\nu(OCO) = 85\ cm^{-1}$ for $[Mo_2(\mu\text{-}O_2CMe)_4]$}. The $[Mo_2\{O_2C(CH_2)_nCO_2\}(MeCN)_x][BF_4]_2$ complexes with n = 3–8 had $\Delta\nu(OCO)$ values in the region 74–99 cm^{-1}, suggesting that the dicarboxylate ligands in these species were also bridging bidentate. $\Delta\nu(OCO)$ values for the ethanedioate (n = 0) and propanedioate (n = 1) complexes were significantly larger (251 and 155 cm^{-1}, respectively), implying a different coordination mode of the dicarboxylate OCO moieties. The shorter hydrocarbon chain linking the two carboxylate functions of the ethanedioate and propanedioate ligands probably imposes steric constraints which inhibit the formation of a discrete tetranuclear entity.

As with *cis*-$[Mo_2(\mu\text{-}O_2CMe)_2(MeCN)_6][BF_4]_2$ complex **1** is quite air-sensitive both in solution (acetonitrile) and in the solid state and therefore must be stored under N_2. However, the cyclic voltammogram of **1** in acetonitrile solution and under N_2 showed the complex to be electroinactive between the switching potentials of +2.0 to −2.0 V (*vs.* Ag/AgCl).¶

In the presence of $EtAlCl_2$ as a cocatalyst the molybdenum complexes (n = 2–8) catalysed the room temperature ring-opening metathesis polymerization of norbornene (as a solution in chlorobenzene). The reactions were instantaneous, and GPC analysis of the products showed that they comprised mainly a mixture of high molecular mass polymer ($\bar{M}_w$ ranged from 125 000 to 691 000) and low molecular mass oligomers ($\bar{M}_w$ *ca.* 500). $^{13}C\{^1H\}$ NMR spectral analysis of the polymers[6] showed them to have a blocky distribution of *cis* and *trans* double bonds. The *cis* content (σ_c) of the polymers was in the narrow range 0.34–0.44, indicating that the microstructure of the polynorbornene was essentially independent of the catalyst composition (*i.e.* the chain length of the dicarboxylate ligand).

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Footnotes

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‡ Procedures conducted under N_2 using dry solvents. $[Mo_2(MeCN)_8][BF_4]_4$ (0.23 mmol), $HO_2C(CH_2)_nCO_2H$ (0.23 mmol) and MeCN (25 cm^3) gently heated for 1 h. The red solution was reduced *in vacuo* to low volume and small amounts of CH_2Cl_2 (or hexane) added periodically to slowly induce product precipitation.

§ *Crystal data* for **1**: $C_{38}H_{53}B_4F_{16}Mo_4N_{15}O_8$, red plate, crystal dimensions 0.68 × 0.30 × 0.18 mm, triclinic, space group $P\bar{1}$, a = 9.842(1), b = 10.744(1), c = 16.792(2) Å, α = 92.35(1), β = 92.77(1), γ = 113.65(1)°, U = 1621.1(3) $Å^3$, μ = 1.617 mm^{-1}, Z = 1, $F(000)$ = 782. Data were collected at 153(2) K on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Unit-cell parameters were determined by non-linear least-squares refinement of 37 accurately centred reflections ($10 < 2\theta < 25°$). Using 1.2° ω-scans at 6° min^{-1}, 6083 reflections were collected in the range $4 < 2\theta < 50°$, 5716 unique reflections (R_{int} = 0.021) were used in the refinement. Crystal stability was monitored by recording three check reflections every 97 reflections and no significant variation was observed, although the crystal cracked towards the end of the data collection. The data were corrected for Lorentz and polarisation effects and a semi-empirical absorption correction was applied (T_{max} = 1.000, T_{min} = 0.838). The structure was solved by direct methods,[7] which revealed most of the structure and the remaining non-hydrogen atoms were located from difference Fourier maps. Hydrogen atoms were inserted at calculated positions (except for those on the partial occupancy acetonitrile) and assigned isotropic temperature factors tied to the equivalent isotropic U of their carrier atoms. The non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All the data were used for refinement on F^2 which converged with $wR2$ = 0.1319, GOF = 1.028 and the conventional R = 0.0463 [$I > 2\sigma(I)$] for 404 parameters. 15 restraints were applied to the geometry and anisotropic displacement parameters of the partial occupancy solvent molecule. The final difference map showed no significant residual electron density, the largest peak (1.0 e $Å^{-3}$) being close to Mo(1). All programs used in the structure refinement are contained in the SHELXL-93 package.[8]

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference nunmber 182/354.

¶ Cyclic voltammetry: glassy carbon disc and platinum wire as working and counter electrodes, respectively; Ag/AgCl as reference electrode; MeCN–$[NBu_4][ClO_4]$ as solvent–supporting electrolyte; $E_{\frac{1}{2}}$ = +0.49 V (*vs.* Ag/AgCl) for the ferrocene–ferrocenium couple.

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