

Dinuclear complexes as connectors for carboxylates. Self-assembly of a molecular box

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A dinuclear complex derived from dirhodium(II) tetraacetate has been used as a corner unit for the synthesis of metallomacrocycles, including a square box with aromatic side walls.

Metal complexes are versatile building blocks in supramolecular chemistry.¹ Apart from the range of geometries available, coordination chemistry is well suited to self-assembly² since metal–ligand bonds are often formed cleanly and reversibly. Recent examples include one-pot syntheses of macrocycles from square-planar Pt and Pd complexes and polydentate nitrogen ligands.³ These and related macrocycles are of particular interest in having internal cavities large enough to accommodate other molecules.^{1–3} Although metallomacrocycles are being prepared from an increasing variety of metals and ligands,⁴ metal–amine coordination remains the dominant structural motif.⁵ It occurred to us that a common functional group which has not been exploited for metalloassembly in solution is carboxylic acid/carboxylate.⁶ One reason for this may be that two carboxylates rarely coordinate to a single metal atom in a predictable, symmetrical fashion.⁷ In this respect dinuclear complexes such as Rh₂(OAc)₄ **1** seemed promising, since acids can be joined in well defined orientations, either in

species based on Mo₂, W₂, Ru₂ or Cu₂ cores have also been prepared recently.⁹ We chose to concentrate on dirhodium compounds¹⁰ because they are neutral, diamagnetic, kinetically stable with respect to carboxylate exchange at room temperature,¹¹ and most importantly for practical applications, not appreciably air or water sensitive. A very recent report¹² by Cotton and Murillo *et al.* on diacid-linked Rh₂ and Mo₂ macrocycles with formamidinate ligands [M₂(O₂C–R–CO₂)(ArNCHNAr)₂]_n prompts the communication of our efforts.

The first step was to reduce the possibility of uncontrolled polymerisation by blocking substitution of a pair of *cis*-acetates in **1**. We elected to retain the basic tetracarboxylate structure, and designed dicarboxylic acid **2** to act as a substitution-inert corner ligand.¹³ Heating **1** with 1 equivalent of **2** in hot *N,N*-dimethylaniline provided diacetate **3** in 60% yield with liberation of acetic acid, along with roughly equal amounts of unreacted **1** and a complex in which all the acetates had been replaced by two molecules of **2**. The choice of solvent was important—a polar coordinating solvent was found to be necessary to keep reactants and intermediates in solution. Heating **3** with an excess of benzoic acid displaced only the acetate groups, demonstrating the kinetic stability of the chelating dicarboxylate. In the solid state structure of **3**·2(4-*tert*-butylpyridine) (Fig. 1),[†] the phenyl ring of the dicarboxylate is strongly tilted, although in solution the geminal methyl groups of **3** (with or without axial ligands) appear as a sharp singlet in ¹H NMR spectra at room temperature, suggesting that the chelate ring is flexible.

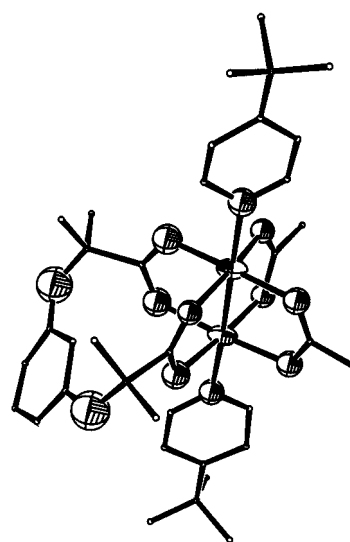
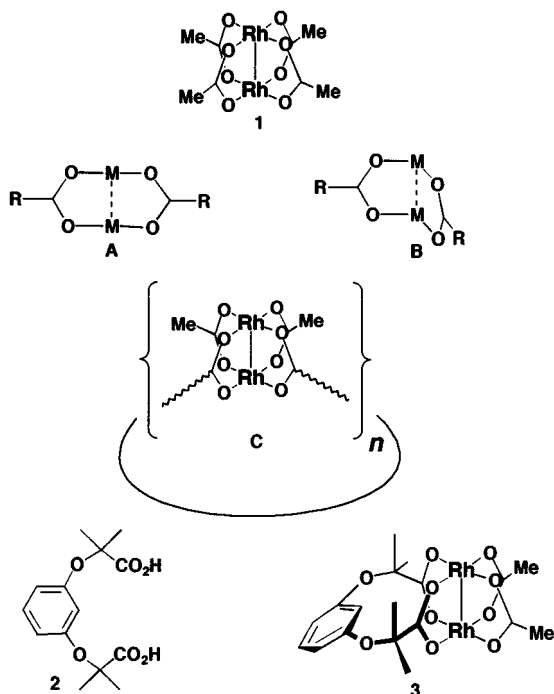


Fig. 1 Crystal structure of **3**·2(4-*tert*-butylpyridine).

a linear fashion, **A** (an analogue of the classical hydrogen bonded dimer) or at right-angles, **B**. Anticipating that cyclic species would have interesting properties, our initial goal was to exploit geometry **B** to connect dicarboxylic acids at right angles to give macrocycles, **C**. At the outset of our work, two small cyclic ‘dimers-of-dimers’ had been structurally characterised, [Mo₂{O₂C(CH₂)₂CO₂}(MeCN)₆]₂[BF₄]₄^{8a} and [Ru₂{O₂C(CH₂)₃CO₂}(CO)₄(PBu₃)₂]₂.^{8a} Several linear or polymeric

Heating **3** with 1.1 equivalents of benzene-1,4-dicarboxylic acid in *N,N*-dimethylaniline produced a cyclic tetramer **4** in 80% yield after chromatography. The structure of **4**·8(4-*tert*-butylpyridine)·2(hexane) (Fig. 2)[†] shows a box 1.1 nm wide (measured between adjacent Rh₂ centres) with one pair of chelates pointing up and the other down. Like **3**, this asymmetry

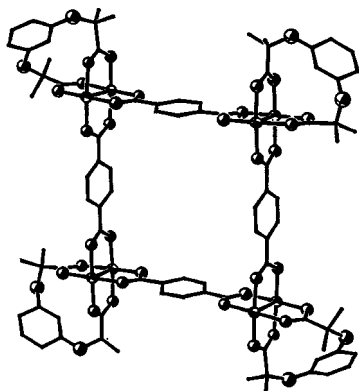


Fig. 2 Crystal structure of 4-8(4-*tert*-butylpyridine):2(hexane). The 4-*tert*-butylpyridine ligands and solvent molecules have been removed for clarity.

in the solid state is not evident in solution by ^1H NMR. In the crystal the boxes pack in two-dimensional layers, with hexane molecules between adjacent boxes, and nothing inside the macrocycles. The layers are held apart by axial pyridine ligands. The assembly of **4** was shown to be reversible: addition of excess acetic acid to the reaction mixture regenerated starting complex **3**, and subsequent heating to evaporate excess acid reformed **4**. The yield of **4** was insensitive to reactant concentration and **4** was still the main product with excess diacid, consistent with assembly under thermodynamic control.

Cyclocondensation of **3** with rigid diacids appears to be fairly general. Crystalline macrocycles have been obtained from benzene-1,3-dicarboxylic acid, naphthalene-1,4-dicarboxylic acid, naphthalene-2,6-dicarboxylic acid, biphenyl-4,4'-dicarboxylic acid and adamantane-1,3-dicarboxylic acid, among others. A characteristic feature of these species is aggregation in non-polar solvents. ^1H NMR spectra in chloroform are broad, but sharp in the presence of polar additives (methanol, acetone, pyridine) which can coordinate to the Lewis acidic metal centres. Monomeric dinuclear carboxylates are known to associate in the solid state *via* intermolecular metal–oxygen coordination;¹⁴ this effect may be amplified in cyclic arrays to the extent that it becomes observable in solution.

In summary, a simple strategy for connecting carboxylic acids at right angles has been developed, illustrated by the synthesis of air- and water-stable metallomacrocycles. We are currently extending the synthetic studies, and plan to investigate the physical properties of these macrocycles, in particular inclusion chemistry and further supramolecular assembly.

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Notes and references

† Data were collected on a Stoe-IPDS diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$), $T = 293$ K, full-matrix least squares refinements on F^2 using all data (G. M. Sheldrick, SHELX97, Crystal structure determination program, Göttingen, 1997). Non-hydrogen atoms were refined anisotropically except the methyl groups of 4-*tert*-butylpyridine ligands in **3** and all atom positions of 4-*tert*-butylpyridine ligands and the crystallographically independent hexane molecule in **4**. Hydrogen positions were set geometrically. The structure of **3** is twinned both racemically and across a pseudo mirror along c (Flack parameter = 0.42(12)). Crystals of **4** were weakly diffracting leading to poorly defined bond lengths and angles.

Crystal data: for **3**-2(4-*tert*-butylpyridine): $\text{C}_{36}\text{H}_{48}\text{N}_2\text{O}_{10}\text{Rh}_2$, $M = 874.58$, rhombohedral, space group $R\bar{3}$, $a = 31.600(4)$, $c = 12.700(3)$, $U = 10983(3) \text{ \AA}^3$, $Z = 9$, $\mu(\text{Mo-K}\alpha) = 0.720 \text{ mm}^{-1}$, 19768 reflections collected 6376 unique ($R_{\text{int}} = 0.0331$), $R1 = 0.047$ ($F > 4\sigma F$), $wR2 = 0.1422$ (all data). For **4**-8(4-*tert*-butylpyridine)-hexane, red plates from dichloromethane–hexane: $\text{C}_{160}\text{H}_{184}\text{N}_8\text{O}_{40}\text{Rh}_8 \cdot 2(\text{C}_6\text{H}_{14})$, $M = 3855.20$, triclinic,

space group $P\bar{1}$, $a = 13.485(2)$, $b = 19.834(3)$, $c = 23.522(5)$, $\alpha = 69.66(2)$, $\beta = 75.12(2)$, $\gamma = 83.331(19)^\circ$, $U = 5698.5(18) \text{ \AA}^3$, $Z = 1$, $\mu(\text{Mo-K}\alpha) = 0.553 \text{ mm}^{-1}$, 31008 reflections collected, 14177 unique ($R_{\text{int}} = 0.178$), $R1 = 0.056$ ($F > 4\sigma F$), $wR2 = 0.168$ (all data).

CCDC 182/1442. See <http://www.rsc.org/suppdata/cc/1999/2457/> for crystallographic files in .cif format.

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