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Dirhodium(II) carboxylate complexes as building blocks. Synthesis and structures of square boxes with tilted walls†

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The crystal structures of four new molecular boxes with substituted benzene-1,4-dicarboxylate side walls are described, showing how substituents larger than hydroxyl cause the walls to tilt in the solid state.

Mononuclear metal complexes are becoming increasingly popular as connection devices for self-assembly in solution and the solid state.[1] In contrast, dinuclear species have scarcely been exploited, although they have potential advantages if both metal atoms can be used to anchor bidentate ligands by two point binding.[2,3] We recently reported the use of the Rh_2^{4+} core to build cyclic arrays of dicarboxylate ligands, exemplified by square macrocycle **1** formed by condensation of a *cis* protected dirhodium corner unit with benzene-1,4-dicarboxylic acid.[2] The walls of **1** are upright in the crystal, with the benzene rings coplanar with the carboxylate groups. A simple way of changing the depth of the box would be to extend the aromatic walls by adding substituents, a strategy previously used to modulate the binding properties of cyclophanes.[4] However it was not clear how substituents would affect the orientation of

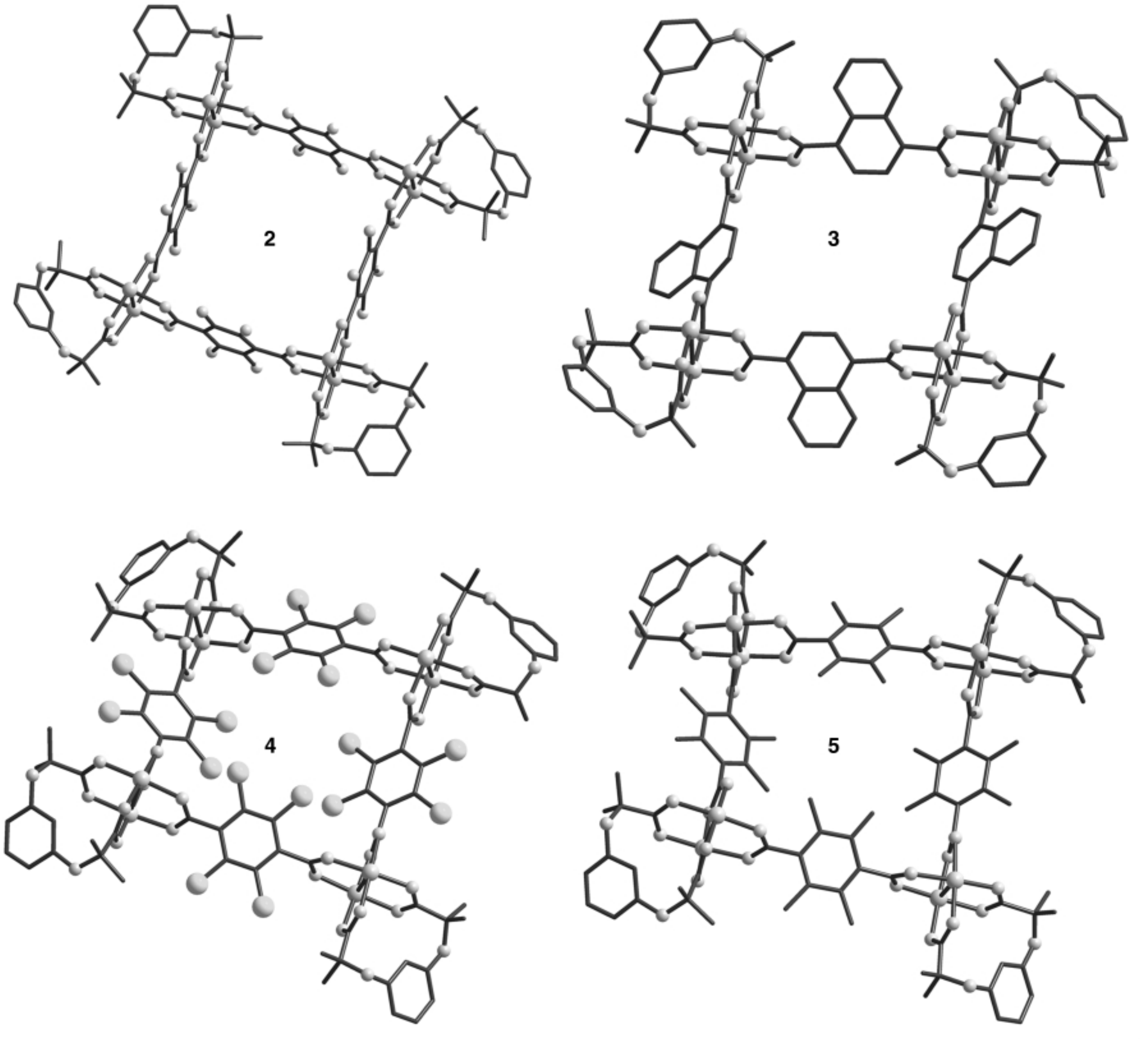

Fig. 1 Crystal structures of **2**–**5** (axial ligands, solvent molecules and hydrogens omitted). The dirhodium corners are spaced 10.9–11 Å apart. The Rh–Rh bonds (2.37–2.39 Å), Rh–O bonds to the axial oxygen ligands (2.24–2.34 Å) and the Rh–O bonds in the Rh–O cages (2.01–2.06 Å) are in the normal range for dirhodium tetracarboxylates.[10]

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† Electronic supplementary information (ESI) available: experimental and analytical data for macrocycles **2**–**5**. See http://www.rsc.org/suppdata/dt/b0/b008060h/

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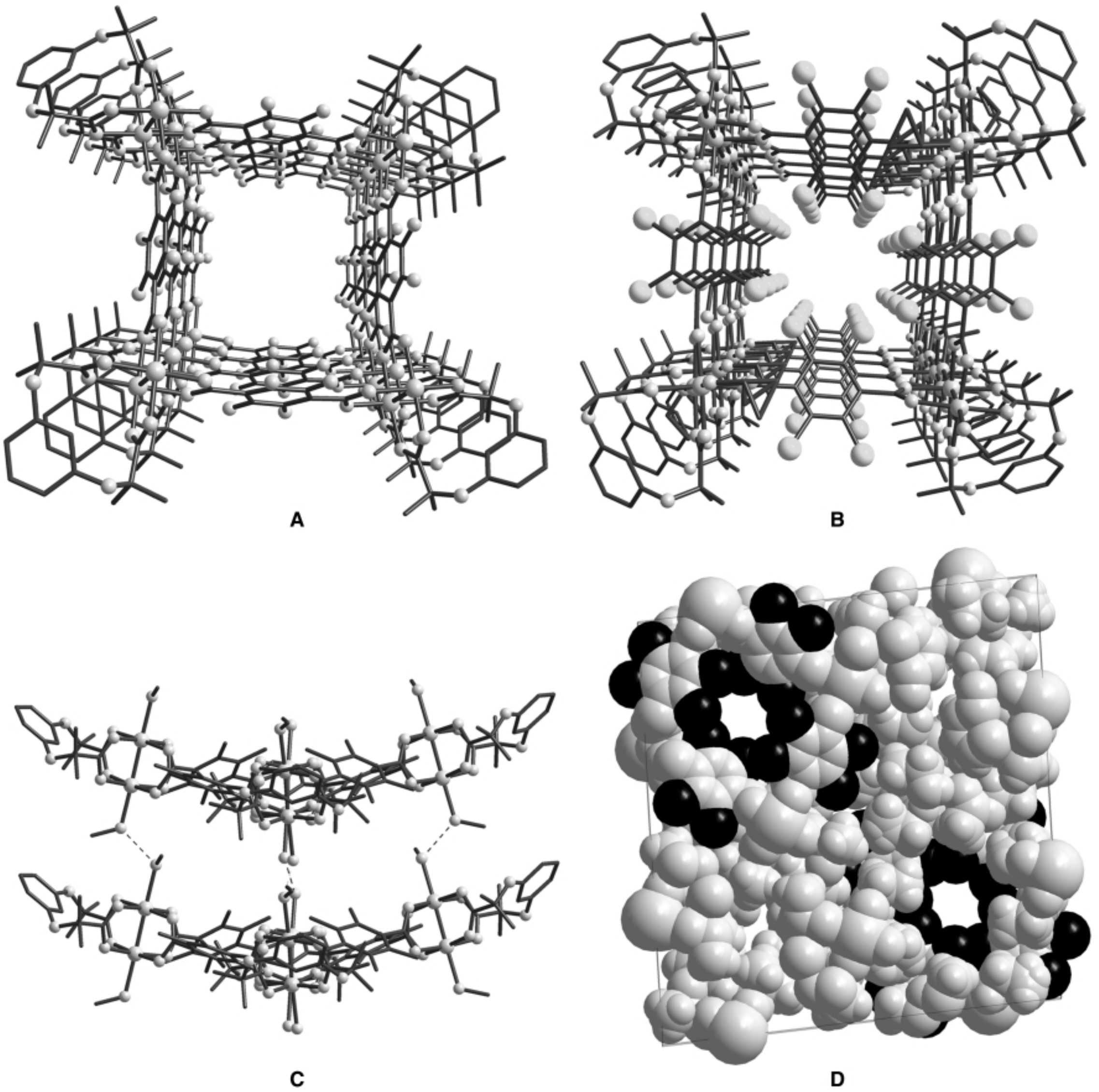
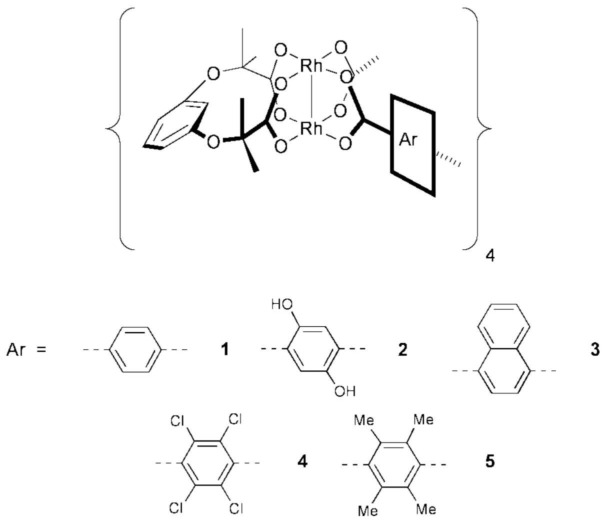


Fig. 2 (A) Offset stacking of **2**, looking down the channel. (B) Vertical stacking of **4**. Box **5** packs in a similar fashion. (C) Two molecules in a stack of **5**, viewed across the box diagonal, showing the saddle distortion of the framework and hydrogen bonds connecting axially coordinated methanol and water ligands. (D) Space filling view of the unit cell of **4**, with chlorines in black, all other atoms light grey.



the walls—how large does the substituent have to be before the walls are forced out of conjugation[5] with the carboxylate groups due to steric repulsion? There was also the question of whether the walls in these macrocycles can rotate—a single peak was observed for the ring protons of **1** in solution, but this could be due to rapid spinning around the carboxylate axis. In order to address these points we prepared boxes **2**–**5** with substituted benzene walls, following the method previously described for **1**,[2] but replacing benzene-1,4-dicarboxylic acid with the appropriate diacids.

The wall protons of all the macrocycles resonate as single sets of sharp peaks in the ^{1}H NMR spectra, implying that the aromatic rings are either fixed in symmetrical environments, or are moving rapidly. The crystal structures are presented in Fig. 1;‡ small crystals of **3**–**5** required the use of synchrotron radiation.[6]§ Box **2**, like **1**, is essentially planar with upright aryl rings, although the walls are bowed in and out slightly by *ca.* 0.3 Å. This macrocycle could exist as several rotameric isomers, but an average is seen in the crystal, with the hydroxyl groups disordered over two positions. The walls may be held upright by intramolecular hydrogen bonds to carboxylate oxygens (O · · · O distances of 2.55–2.65 Å) as found in dirhodium tetrasalicylate,[7] although the phenolic hydrogens were not located in the crystal structure.

Annelation of an aromatic ring causes the naphthalene walls of **3** to tilt by 40–50° from the vertical, resulting in a slight saddle-shaped distortion of the framework, with the sides bowed up and down by *ca.* 0.5 Å from the mean plane of the macrocycle. The structure of boxes **4** and **5** are comparable, with the four substituents making the walls rotate even further out of conjugation, to 60–80°. This is as far as they can twist simultaneously, since the chlorine and methyl groups are in van der Waals contact on the inside of the macrocycles. The frameworks are more obviously saddle-shaped, with out-of-plane deviations of 1.7–1.8 Å, and helically twisted Rh–O cages (twists of 3–9°). The chelating dicarboxylates on the corners of the macrocycles adopt a variety of orientations, two up and two down for **2** and **3**, and all down (as drawn) for **4** and **5**. Single sets of proton resonances are seen for the chelate rings, so these must also be conformationally mobile on the ^{1}H NMR timescale.

The saddle distortions and the relative orientations of corner chelates and side walls combine to make individual molecules of **3**–**5** chiral in the crystal (**3** is C_i, **4** and **5** are C_2), although the unit cells contain both enantiomers. Box **3** packs in zigzag chains, but **2**, **4** and **5** form stacks of macrocycles, neighbouring stacks of **4** and **5** being enantiomeric. Box **2** forms a slipped stack, with successive molecules offset horizontally along the box diagonal by 3.5 Å and held 8.4 Å apart by layers of axially coordinated solvent (Fig. 2A). Boxes **4** and **5** stack vertically 8.6 Å apart (Fig. 2B), connected by hydrogen bonding between axial alcohol and water ligands (Fig. 2C). Numerous more-or-less disordered solvent molecules occupy the space between the boxes, and also extend down the channels of **2** and **5**. A space filling representation of the lattice of **4** (Fig. 2D) illustrates the pore-like nature of the channels, which are large enough for small molecules to pass through.

In summary, a crystallographic survey of the effect of aromatic substituents on the basic square box skeleton shows that groups larger than hydroxyl cause the walls to tilt out of conjugation, providing a simple means of altering the internal dimensions in the solid state. The macrocycles are conformationally mobile in solution at room temperature, although it has yet to be determined if the wall substituents rotate through the ring—this would require a geared motion for boxes **3**–**5**.[8] It is interesting that in three out of four instances the molecules packed to produce channels running through the crystal—such mesoporous arrays of neutral metallomacrocycles have recently been shown to bind volatile organic compounds.[9]

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Notes and references

‡ Crystal data for **2**. $C_{88}H_{70}O_{48}Rh_8{\cdot}(C_2H_6O)_{11}{\cdot}(C_4H_8O_2)_2{\cdot}(H_2O)_2$, $M = 3438.02$, triclinic, space group $P\bar{1}$, $a = 9.5595(12)$, $b = 20.254(3)$, $c = 20.399(3)$ Å, $\alpha = 95.337(17)$, $\beta = 101.800(15)$, $\gamma = 94.735(17)$°, $U = 3828.3(9)$ Å^3, $Z = 1$, $D_c = 1.491$ g cm^{-3}, μ(Mo-K$_\alpha$) 0.827 mm^{-1}, $T = 213(2)$ K. A total of 10115 unique reflections were measured and used in the refinement, which converged to $R = 0.0628$ for the reflections with $F^2 > 2\sigma(F^2)$.

Crystal data for **3**. $C_{104}H_{88}O_{40}Rh_8{\cdot}(CH_4O)_{16}{\cdot}(H_2O)$, $M = 3332.02$, monoclinic, space group $C2/c$, $a = 35.1613(10)$, $b = 18.1227(5)$, $c = 21.5984(6)$ Å, $\beta = 98.2160(10)$°, $U = 13621.6(7)$ Å^3, $Z = 4$, $D_c = 1.625$ g cm^{-3}, μ(Mo-K$_\alpha$) 0.924 mm^{-1}, $T = 213(2)$ K. A total of 11047 unique reflections were measured and used in the refinement, which converged to $R = 0.0959$ for the reflections with $F^2 > 2\sigma(F^2)$.

Crystal data for **4**. $C_{88}H_{62}Cl_{16}O_{40}Rh_8{\cdot}(C_2H_6O)_{10}{\cdot}(C_4H_8O_2)_2$, $M = 3787.02$, monoclinic, space group $P2/n$, $a = 28.7103(12)$, $b = 8.6546(4)$, $c = 30.3073(13)$ Å, $\beta = 93.4120(10)$°, $U = 7517.3(6)$ Å^3, $Z = 2$, $D_c = 1.673$ g cm^{-3}, μ(Mo-K$_\alpha$) 1.105 mm^{-1}, $T = 150(2)$ K. A total of 20907 unique reflections were measured and used in the refinement, which converged to $R = 0.0573$ for the reflections with $F^2 > 2\sigma(F^2)$.

Crystal data for **5**. $C_{104}H_{92}O_{40}Rh_8{\cdot}(CH_4O)_{10}{\cdot}(H_2O)_{12}$, $M = 3341.98$, monoclinic, space group $P2/c$, $a = 28.7494(2)$, $b = 8.5745(7)$, $c = 40.222(3)$ Å, $\beta = 131.477(2)$°, $U = 7428.7(10)$ Å^3, $Z = 2$, $D_c = 1.494$ g cm^{-3}, μ(Mo-K$_\alpha$) 0.850 mm^{-1}, $T = 150(2)$ K. A total of 14311 unique reflections were measured and used in the refinement, which converged to $R = 0.1514$ for the reflections with $F^2 > 2\sigma(F^2)$.

The structures were solved by direct methods and refined by full-matrix least squares against F^2 (G. M. Sheldrick, SHELX-97, Programs for Crystal Structure Solution and Refinement, University of Göttingen, Germany, 1997). Non-hydrogen atoms were refined anisotropically with the exception of disordered ones, which were refined isotropically. Hydrogen positions were set geometrically. The following disordered groups within the asymmetric unit were split in two positions in the refinement, using distance and anisotropic displacement parameter restraints: a methyl and an ethyl group of two ethanol molecules in **4**, the ethyl groups of three ethanol molecules, the ethyl group in the ethyl actetate and the phenolic hydroxyl groups of **2**. CCDC reference number 186/2235. See http://www.rsc.org/suppdata/dt/b0/b008060h/ for crystallographic files in .cif format.

§ The crystals of **5** were very small and also of poor quality leading to a rather high R factor. While the overall connectivity is not in doubt, the quality of the refinement does not allow a detailed discussion of structural parameters.

1 (*a*) C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289; (*b*) *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vögtle, Pergamon, Oxford, 1996, vol. 9, in particular chapters 2, 3, 5, 6 and 7; (*c*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417; (*d*) B. Olenyuk, A. Fechtenkötter and P. J. Stang, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 1707.
2 R. P. Bonar-Law, T. D. McGrath, N. Singh, J. F. Bickley and A. Steiner, *Chem. Commun.*, 1999, 2457.
3 (*a*) F. A. Cotton, L. M. Daniels, C. Lin and C. A. Murillo, *J. Am. Chem. Soc.*, 1999, **121**, 4538; (*b*) H. M. Colquhoun, R. A. Fairman, P. Tootell and D. J. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2651.
4 F. Diederich, *Cyclophanes*, The Royal Society of Chemistry, Cambridge, 1991.
5 S. Böhm and O. Exner, *Chem. Eur. J.*, 2000, **6**, 3391 and references therein.
6 Synchrotron data obtained at SRS Daresbury station 9.8, R. J. Cernik, W. Clegg, C. R. A. Catlow, G. Bushnell-Wye, J. V. Flaherty, G. N. Greaves, I. Burrows, D. J. Taylor, S. J. Teat and M. Hamichi, *J. Synchrotron Rad.*, 1997, **4**, 279.
7 D. P. Bancroft, F. A. Cotton and S. Han, *Inorg. Chem.*, 1984, **23**, 2408.
8 J. Clayden and J. H. Pink, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1937 and references therein.
9 K. D. Benkstein, J. T. Hupp and C. L. Stern, *Angew. Chem.*, *Int. Ed.*, 2000, **39**, 2891 and references therein.
10 (*a*) F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, Clarendon Press, Oxford, 1993, p. 431; (*b*) F. H. Jardine and P. S. Sheridan, *Coord. Chem. Rev.*, 1987, **50**, 109.