DALTON COMMUNICATION

Supramolecular squares with Rh_2^{4+} corners

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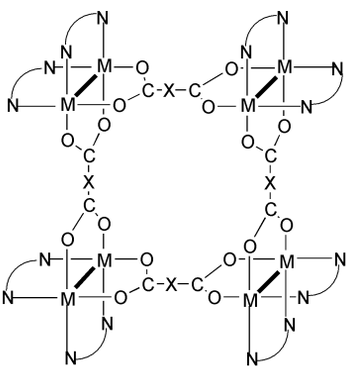
Received 27th November 2000, Accepted 24th January 2001
First published as an Advance Article on the web 12th February 2001

Six molecular squares were obtained by reacting the singly metal–metal-bonded complex $[Rh_2(cis\text{-}DAniF)_2(CH_3CN_{eq})_4(CH_3CN_{ax})_2](BF_4)_2$ (DAniF = *N*,*N*′-di-*p*-anisylformamidinate), and $(Et_4N^+)_2(Carb^{2-})$ where $Carb^{2-}$ represents the dicarboxylate anion bicyclo[1.1.1]pentane-1,3-dicarboxylate, 1; tetrafluoroterephthalate, 2; 1,4-cubanedicarboxylate, 3; terephthalate, 4; fumarate, 5; *trans*-1,4-cyclohexanedicarboxylate, 6; these squares stack in the crystal forming square channels capable of accommodating solvent molecules and the NMR spectra are consistent with the presence of highly symmetrical structures even in solution.

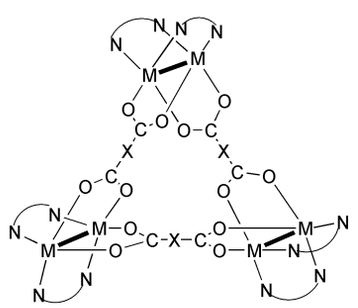
The use of metal atoms (or ions) as key elements in the assembly of supramolecular arrays has emerged as an area of great interest, and much effort has been devoted to the assemblage of molecules having a great variety of polygons and polyhedra.[1] So far, practically all of the effort has been directed to the use of mononuclear coordination centers (*i.e.*, mainly metal ions such as Pd^{2+}, Pt^{2+}, Ag^+, Cd^{2+}) as the geometry-setting elements in the arrays,[1,2] but a few isolated examples containing non- and metal–metal-bonded units exist.[2] In this laboratory we have pioneered the use of metal–metal bonded dimetal units (*e.g.* $M_2(DArF)_n^{(4-n)+}$, M = Mo and Rh and DArF = *N*,*N*′-diarylformamidinate) to dictate geometric patterns,[4] for five major reasons. (1) With dinegative linkers, these can be used to create neutral rather than highly positive oligomers and networks, which can then be oxidized in a controlled way without loss of structural integrity. (2) An enormous range of transition metals[5] is potentially available to form homologous structures. (3) Many organic ligands may be used to vary solubility and other properties. (4) The spectroscopic and magnetic properties of dimetal units are extremely varied and the arrays containing them can be designed with an even more varied range of such electronic properties. (5) By suitable choice of both equatorial and axial connecting elements, the nature and degree of interaction between adjacent dimetal units can be finely controlled.

Since we first reported[6] that Rh_2^{4+} units, appropriately ligated to assure stability, can be used to form molecular squares, **I**, (as well as triangles, **II**) others have reported such squares by employing exactly the same[7] or a similar[3d,8] approach. We therefore considered it appropriate to communicate some other results that have been obtained in this laboratory. It should be noted that there is now a considerable body of results concerning similar compounds containing Mo_2^{4+} units.[9] However, Rh_2^{4+} species offer one very important advantage, architecturally speaking, over Mo_2^{4+} species, namely, that because the Rh_2^{4+} compounds engage in much stronger axial interactions they readily lend themselves to building multidimensional structures. One such example, employing squares, that we have already reported is shown schematically as **III**,[10] and there are others employing Rh_2^{4+} loops.[10,11]

In this report we discuss the reactions† of the singly bonded Rh_2^{4+} compound $[Rh_2(cis\text{-}DAniF)_2(CH_3CN_{eq})_4(CH_3CN_{ax})_2](BF_4)_2$ (DAniF = *N*,*N*′-di-*p*-anisylformamidinate) with tetraethyl ammonium salts of dicarboxylic acids in acetonitrile in a 1:1 ratio to produce a series of diamagnetic molecular squares‡ of composition $[Rh_2(DAniF)_2(CH_3CN_{ax})_2(O_2CXCO_2)]_4$, according to eqn. (1).



I



II

III

$$4[Rh_2(cis\text{-}DAniF)_2(CH_3CN_{eq})_4(CH_3CN_{ax})_2](BF_4)_2 + 4(NEt_4)_2(O_2CXCO_2) \xrightarrow{CH_3CN} \{[(cis\text{-}Rh_2(DAniF)_2)(CH_3CN_{ax})_2](O_2CXCO_2)\}_4 + 8NEt_4BF_4 \quad (1)$$

As noted by the carboxylate linker (see Chart 1), the compounds are: bicyclo[1.1.1]pentane-1,3-dicarboxylate, **1**; tetrafluoroterephthalate, **2**; 1,4-cubanedicarboxylate, **3**; terephthalate, **4**; fumarate, **5**; *trans*-1,4-cyclohexanedicarboxylate, **6**.

Yields for these reactions are very high, essentially quantitative, and the purity of the red crystalline materials is satisfactory as determined by ^1H NMR spectroscopy. The latter show the characteristic singlets of the methine and methoxy

 DOI: 10.1039/b009613j

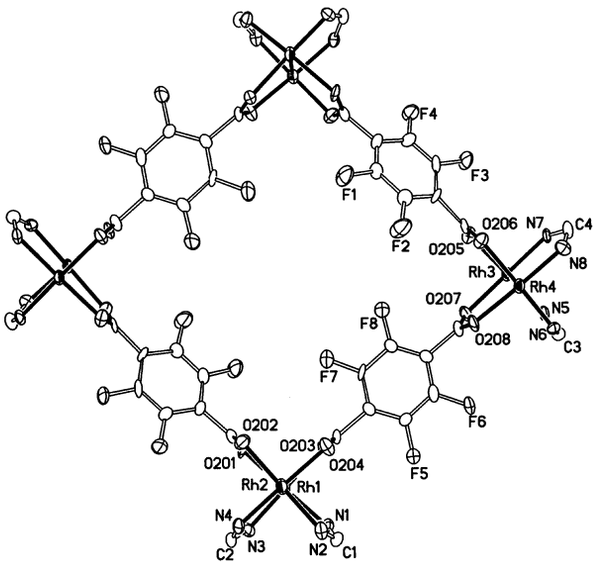


Fig. 1 A thermal ellipsoid plot of the core of the molecular square **2** in **2**·3CH_2Cl_2. The *p*-anisyl groups of the two formamidinate ligands bridging the singly-bonded Rh_2^{4+} units, the axially coordinated CH_3CN molecules on each Rh atom and the interstitial solvent molecules have been removed for clarity. Average distances for compounds **1**–**4** are: Rh–Rh, 2.449[3]; Rh–O, 2.073[3]; Rh–$N_{(eq)}$, 2.02[1]; and Rh–$N_{(ax)}$, 2.24[3] Å.

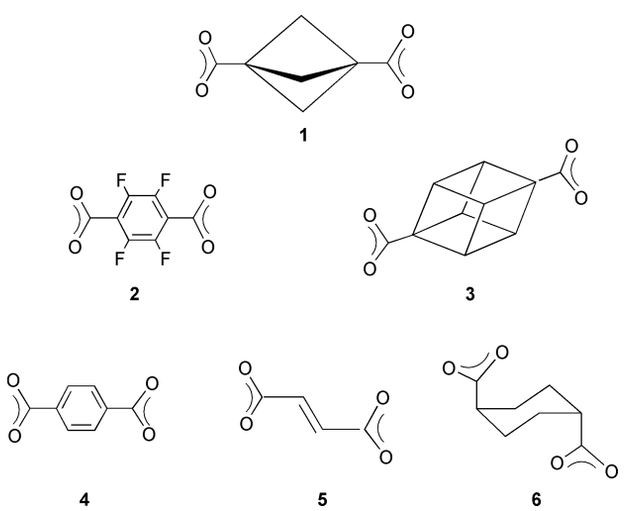


Chart 1 Dicarboxylate linkers used in $[Rh_2(DAniF)_2(CH_3CN)_8(O_2CXCO_2)]_4$ squares **1**–**6**.

groups as well as the pairs of doublets corresponding to the aryl protons of the *p*-anisyl groups in the expected ratios of 1 : 6 : 8. Other signals corresponding to the individual dicarboxylate linkers are also observed in the appropriate ratio. In all cases, the ^{1}H NMR pattern is consistent with the presence, in solution, of only these highly symmetrical molecules.

Complexes reported here are quite soluble in organic solvents such as CH_2Cl_2, $CHCl_3$, benzene and toluene but insoluble in CH_3CN. They are stable to oxygen both as solids and in solution. However, upon exposure to moisture, some of the axial CH_3CN molecules are substituted by H_2O as shown by ^{1}H NMR. The color also changes from red to green. This can be reversed by pumping under vacuum and then adding CH_3CN. All compounds are electrochemically active and show 2 quasi-reversible waves, each corresponding to 4e oxidations. The first wave is in the range of 240–390 mV, the second is in the range of 1040–1170 mV. Further details of the electrochemistry and the electronic communication in these molecular squares will be provided elsewhere.

The structures of all of these compounds have been established for **1**–**4** by X-ray crystallography.§ For **5** and **6**, refinement is still incomplete because of extensive disorder of solvent molecules but the presence of squares has been unequivocally

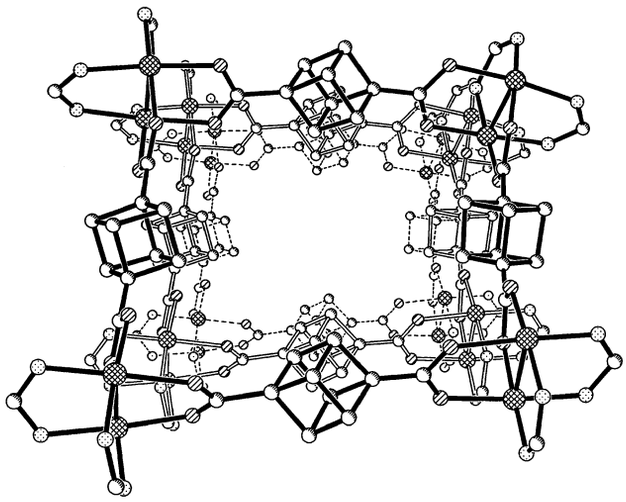


Fig. 2 A packing diagram of **3**·2.8CH_3CN showing how the cores of the molecular squares stack forming an infinite tunnel. A similar drawing for **1**·8CH_3CN is shown in the table of contents.

established. In all cases the local structure of the $(DAniF)_2Rh_2$ is as shown in Fig. 1 for the molecule of **2**, and the bridging dicarboxylic acids have the expected dimensions. Also, in all cases, the packing in the crystals is such as to create infinite tunnels, as shown in Fig. 2 for **3**. This is an important property as we have demonstrated that the walls of such tunnels can be closed to give molecular columns of type **III**[10] which are capable of enclosing solvent molecules.

We are grateful to Prof. Josef Michl of the University of Colorado for the sample of $HO_2CC(CH_2)_3CCO_2H$. We also acknowledge the assistance of Dr X. Wang with the crystallography and the assistance of Mr P. Lei with NMR spectroscopy. We also thank the National Science Foundation for financial support and Johnson Matthey for a generous loan of $RhCl_3$.

Notes and references

† All complexes were prepared by following a method similar to that for **1** with a ratio of dimetal unit to dicarboxylate of 1 : 1. To a stirred solution of $[Rh_2(cis\text{-}DAniF)_2(CH_3CN_{eq})_4(CH_3CN_{ax})_2](BF_4)_2$[12] (57 mg, 0.050 mmol) in CH_3CN (4 cm^3) was added dropwise 0.050 M $(Et_4N)_2(O_2CC(CH_2)_3CCO_2)$ in CH_3CN (1.0 mL, 0.050 mmol). The reaction mixture was stirred at ambient temperature for *ca.* 24 h. Self-assembly took place gradually with the formation of a reddish precipitate, which was collected by filtration, and then washed several times with CH_3CN. The crude product was dissolved in CH_2Cl_2 (2 × 5 cm^3) and layered with CH_3CN (5 cm^3). Then a very slow stream of N_2 was allowed to pass over the mixture. One week later, dark-red needle-like crystals of **1**·8CH_3CN suitable for X-ray structural analysis were collected by filtration. After the solvent of crystallization was removed by pumping, the yield was essentially quantitative. ^{1}H NMR (CD_2Cl_2): δ 7.34 (s, 8H, –NC*H*N–), 6.93 (m, 32H, aromatic), 6.68 (d, 32H, aromatic), 3.72 (s, 48H, –OCH_3), 2.10 (s, 24H, –C(CH_2)$_3$C–). For **2**, ^{1}H NMR (CD_2Cl_2): δ 7.32 (s, 8H, –NC*H*N–), 6.96 (d, 32H, J = 8.70 Hz, aromatic), 6.67 (d, 32H, J = 8.70 Hz, aromatic), 3.70 (s, 48H, –OCH_3). For **3**, ^{1}H NMR (CD_2Cl_2): δ 7.38 (s, 8H, –NC*H*N–), 6.96 (d, 32H, J = 8.77 Hz, aromatic), 6.67 (d, 32H, J = 8.77 Hz, aromatic), 3.97 (s, 24H, CH of cubane), 3.72 (s, 48H, –OCH_3). For **4**, ^{1}H NMR (CD_2Cl_2): δ 7.91 (s, 16H, Ph–*H* of terephthalate), 7.30 (br, 8H, –NC*H*N–), 6.92 (d br, 32H, aromatic), 6.67 (d br, 32H, aromatic), 3.66 (s, 48H, –OCH_3). For **5**, ^{1}H NMR (CD_2Cl_2): δ 7.33 (s, 8H, –NC*H*N–), 6.69 (d, 32H, J = 8.85 Hz, aromatic), 6.59 (s, 8H, –*H*C=C*H*–), 3.74 (s, 48H, –OCH_3). For **6**, ^{1}H NMR ($CDCl_3$): δ 7.34 (s br, 8H, –NC*H*N–), 6.90 (d, 32H, J = 8.78 Hz, aromatic), 6.68 (d, 32H, J = 8.78 Hz, aromatic), 3.76 (s, 48H, –OCH_3), 2.23 (br, 8H, cyclohexyl C*H*), 1.80 (d br, 16H, cyclohexyl C*H*), 1.40 (t br, 16H, cyclohexyl C*H*).

‡ In a previous study[6] we found that by varying the ratio of reactants shown in eqn. (1) for the oxalate linker, it was possible to obtain either a molecular square or a molecular triangle. So far all attempts to change the reaction conditions for all six linkers reported in this paper have failed to provide any evidence supporting the presence of molecular triangles.

§ Crystal data for **1**, **2** and **4** were collected at 213(2) K and that for **3** at

293(2) K using Mo-Kα radiation. For **1**·8CH_3CN, $C_{180}H_{192}N_{32}O_{32}Rh_8$, space group = $P\bar{1}$, a = 14.2593(4), b = 18.608(5), c = 20.147(3) Å, α = 80.59(2), β = 75.51(1), γ = 71.45(1)°, V = 4886.3(15) Å^3, Z = 1, refinement converged at a final R = 0.062 [$wR2(I > 2\sigma(I))$ = 0.142]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were used in calculated positions. For two of the "corners" of the square (one unique corner) the entire corner was slightly disordered, such that the two opposite corners are slightly buckled above and below the plane of the molecule. The two sets of metal positions are displaced by approx. 0.6 Å. The disorder ratio refined to 56 : 44. At the other corner, two of the four *p*-anisyl groups are disordered (a common occurrence in nearly every structure containing the DAniF ligand). CCDC reference number 154477. For **2**·3CH_2Cl_2, $C_{171}H_{150}Cl_6F_{16}N_{24}O_{32}Rh_8$, space group = $P2_1/n$, a = 19.732(1), b = 13.518(1), c = 34.938(2) Å, β = 90.052(1)°, V = 9319(1) Å^3, Z = 2, refinement converged at a final R = 0.080 [$wR2(I > 2\sigma(I))$ = 0.182]. Except for one half-occupied CH_2Cl_2 molecule, all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were used in calculated positions. CCDC reference number 154478. **3**·2.8CH_3CN, $C_{181.60}H_{200.40}N_{26.80}O_{32}Rh_8$, space group = $P\bar{1}$, a = 20.426(2), b = 22.682(4), c = 25.315(3) Å, α = 96.909(5), β = 100.978(6), γ = 96.077(9)°, V = 11330(3) Å^3, Z = 2, refinement converged at a final R = 0.141 [$wR2(I > 2\sigma(I))$ = 0.348]. CCDC reference number 154479. **4**·3CH_3CN·2CH_2Cl_2, $C_{176}H_{173}Cl_4N_{27}O_{32}Rh_8$, space group = $P\bar{1}$, a = 14.681(3), b = 18.661(3), c = 20.742(4) Å, α = 77.818(3), β = 75.205(4), γ = 74.440(3)°, V = 5230(2) Å^3, Z = 1, refinement converged at a final R = 0.164 [$wR2(I > 2\sigma(I))$ = 0.485]. CCDC reference number 154480. For both **3** and **4**, only the metal atoms were refined anisotropically. In both, four of the *p*-anisyl groups were disordered. Hydrogen atoms were not included in the models. While no peaks recognizable as solvent molecules remain in the difference Fourier maps, it is likely that the large void volumes include more disordered or partially-occupied solvent sites. See http://www.rsc.org/suppdata/dt/b0/b009613j/ for crystallographic data in CIF or other electronic format.

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