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Supramolecular structures based on dimetal units: simultaneous utilization of equatorial and axial connections†

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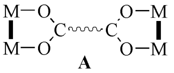
As determined by X-ray crystallography, tetranuclear metal–metal bound molecular loops $[Rh_2(DAniF)_2]_2(O_2CCH_2CO_2)_2$ (DAniF = *N,N′*-di-*p*-anisylformamidinate) react with 2-*N* donor linkers to give a tubular structure $\{[Rh_2(DAniF)_2]_2(O_2CCH_2CO_2)_2(NC_5H_4CHCHC_5H_4N)_2\}_n$ 1, and a sheet-like structure with interstitial dichloromethane molecules for $[Rh_2(DAniF)_2]_2(O_2CCH_2CO_2)_2(NCC_6H_4CN)_2\}_n$ 2; when the assembly unit was changed from $[Rh_2(DAniF)_2(O_2CCH_2CO_2)]_2$ to the square $[Rh_2(DAniF)_2(O_2CCO_2)]_4$ and the linker $NCC_6F_4C_6F_4CN$ was used, the compound $\{[Rh_2(DAniF)_2]_4(O_2CCO_2)_4(NCC_6F_4C_6F_4CN)_4\}_n$ 3, was formed, in which there are infinite tubes of square cross section having entrained CH_2Cl_2 molecules.

Oligomers and polymers in which a key organizing element is a coordinated metal atom, for example, a square-coordinated Pd^{II} or Pt^{II} atom or a tetrahedral zinc atom, are currently the subjects of vigorous study in many laboratories.[1] This work is driven by the search for novel materials, distinguished by special magnetic properties,[2] micro- and meso-porous structures,[3] or catalytic properties.[4]

Several years ago we began to explore the possibilities of employing strongly bonded dimetal units, such as Mo_2^{4+} and Rh_2^{4+}, that can be suitably complexed to control their reactivity and then linked to form linear,[5a,b] square,[5c,d] triangular[5c] and polyhedral[5e] structures. The linking process entails the use of di- and tri-carboxylic acids which attach themselves to adjacent pairs of equatorial sites in the M_2^{4+} entities, as shown schematically in **A**. The arrays that can be built up in this way have as great a range of sizes as those previously made[2] but differ from most of those in forming initially as neutral species rather than as highly charges ones. However, charge may readily be introduced—in a controlled, stepwise fashion[5b,d]—by oxidation of the Mo_2^{4+} units.



A

B

Here we report that by using axial linking, as shown schematically in **B**, it is possible to take simple oligomers and connect them to form one- and two-dimensional polymers. These, again, are initially neutral but can be oxidized. This is the first time such architectures have been created by using dimetal building blocks. We also show how the nature of the polymeric structure can be controlled by choosing axial linkers of the right length, a principle that will be of importance in all future work.

In the examples reported here we have utilized dirhodium, Rh_2^{4+}, building blocks shown as **II** and **III** in Fig. 1. The square, **III**, has been reported before[5c] but the loop, **II**, is a new unit, not reported before, though it is somewhat similar to loops that have been made with Mo_2^{4+} units.[6] Dirhodium units were used here because they have a strong affinity for axial ligands, unlike Mo_2^{4+} units. As axial linkers we have employed **IV**, **V**, and **VI**, (Fig. 1).

With **IV**, $\{[Rh_2(DAniF)_2]_2(O_2CCH_2CO_2)_2(NC_5H_4CHCHC_5H_4N)_2\}_n$ **1** is obtained.‡ It has a tubular structure shown in Fig. 1(a). In Fig. 1(b) there is a schematic representation of this structure§ showing how the rings (**II**) are related alternately by centers of inversion and two-fold axes.

While the formation of such tubes might be considered the 'obvious' outcome of linking units of type **II** by axial bridges, it can only result when the linkers are long enough to keep the bulky *p*-anisyl groups from clashing with each other. With a shorter linker, **V**, major clashes would occur and therefore a different structure arises in $\{[Rh_2(DAniF)_2]_2(O_2CCH_2CO_2)_2(NCC_6H_4CN)_2\}_n$ **2**. This sheet-like structure is shown as 2(a), where dichloromethane molecules are omitted, as 2(b) where the sheets are viewed edge-on and the CH_2Cl_2 molecules are included, and in schematic form as 2(c). The CH_2Cl_2 molecules were well ordered and refined without difficulty. The sheet belongs to the two-dimensional space group C*mm*, the highest symmetry possible in a rectangular sheet structure.

When the assembly unit was changed from **II** to **III** and the linker **VI** was used, the compound $\{[Rh_2(DAniF)_2]_4(O_2CCO_2)_4(NCC_6F_4C_6F_4CN)_4\}_n$, **3** was formed, in which there are infinite tubes of square cross section. A portion of the entire structure is shown as 3(a) while 3(b) shows a portion of one of the units, including one of the entrained CH_2Cl_2 molecules; 3(c) shows a schematic representation of this structure.

Other studies of these compounds and the syntheses of other assemblies of different topologies containing different dimetal units and axial ligands are in progress.

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Notes and references

‡ The general experimental conditions were described in ref. 1. Elemental analyses were satisfactory for all compounds. The following procedure describes the preparation of $1\cdot 3CH_2Cl_2\cdot 0.5Et_2O$. A CH_2Cl_2 solution (10 mL) of **II** (82 mg, 0.05 mmol) was carefully layered with a CH_2Cl_2–Et_2O solution (1:1, 20 mL) of *trans*-1,2-bis(4-pyridyl)ethylene (18 mg, 0.10 mmol). Red crystals formed after several days. A similar method was used for $2\cdot 4CH_2Cl_2$ and $3\cdot 12.36CH_2Cl_2$. The yields are essentially quantitative.

§ *Crystal data*: for $1\cdot 3CH_2Cl_2\cdot 0.5Et_2O$: $C_{95}H_{95}Cl_6N_{12}O_{16.5}Rh_4$, M = 2293.17, monoclinic, space group $C2/c$, a = 56.521(4), b = 19.016(2), c = 19.564(2) Å, β = 103.053(2)°, V = 20484(3) Å^3, Z = 8, μ(Mo-Kα) = 0.857 mm^{-1}, T = 213(2) K. The structure, refined on F^2, converged for 13458 unique reflections and 613 parameters to give $R1$ = 0.082 and $wR2$ = 0.182 and a goodness-of-fit = 1.031.

For $2\cdot 4CH_2Cl_2$: $C_{86}H_{80}Cl_8N_{12}O_{16}Rh_4$, M = 2232.86, triclinic, space group $P\bar{1}$, a = 12.708(2), b = 14.378(2), c = 14.997(3) Å, α = 65.810(3), β = 72.693(3), γ = 74.766(3)°, V= 2355.0(7) Å^3, Z = 1, μ(Mo-Kα) = 0.984 mm^{-1}, T = 213(2) K. The structure, refined on F^2, converged for

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† Most of the results reported here were presented in a poster at *Contemporary Inorganic Chemistry, II*, March 12–15, 2000, College Station, TX, USA.

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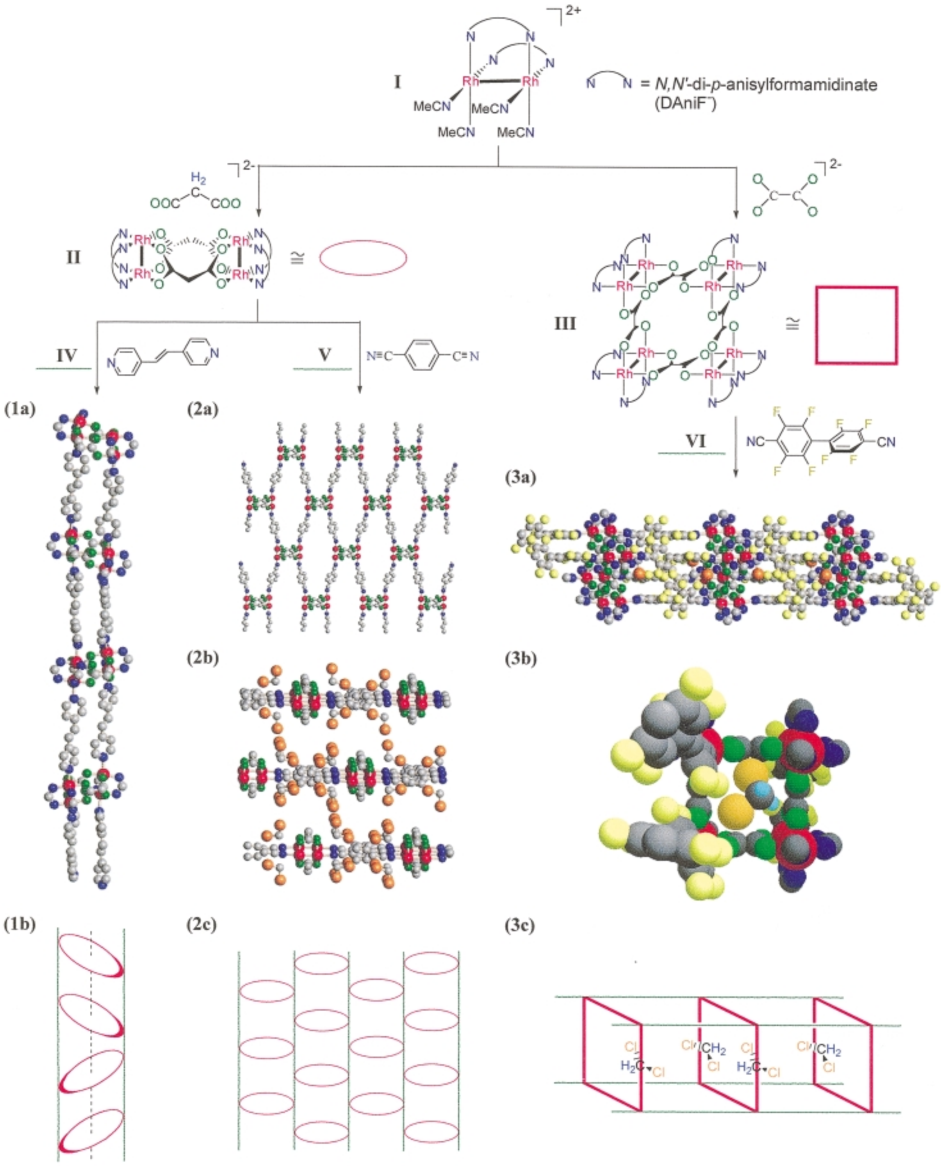

Fig. 1 Synthesis of compounds **1**·$3CH_2Cl_2$·$0.5Et_2O$, **2**·$4CH_2Cl_2$ and **3**·$12.36CH_2Cl_2$. Views of the extended structures are given in the middle section as follows: (1a) structure of **1**; (2a) structure of **2**; (2b) intercalating architecture in **2**; (3a) structure of **3** and (3b) a space filling drawing of **3** showing CH_2Cl_2 molecules inside the square tube. A schematic view of the corresponding structure is shown in the lower section. In the top section, there are axial CH_3CN molecules (not shown for clarity) at each Rh atom in **I** and **III**. For **II**, there are two CH_3CN molecules distributed on the four Rh atoms. The *p*-anisyl or DAniF groups have also been omitted for clarity. Color labels: Rh, red; N, blue; O, green; C, gray; F, yellow; Cl, orange; H, turquoise.

6163 unique reflections and 578 parameters to give $R1 = 0.051$ and $wR2 = 0.119$ and a goodness-of-fit = 1.010.

For **3**·$12.36CH_2Cl_2$: $C_{196.36}H_{144.72}Cl_{24.72}F_{32}N_{24}O_{32}Rh_8$, $M = 5660.01$, triclinic, space group $P\bar{1}$, $a = 18.235(6)$, $b = 18.430(6)$, $c = 18.665(6)$ Å, $\alpha = 81.839(7)°$, $\beta = 81.775(6)$, $\gamma = 80.742(7)°$, $V = 6082(3)$ Å^3, $Z = 1$, μ(Mo-Kα) = 0.891 mm^{-1}, $T = 223(2)$ K. The structure, refined on F^2, converged for 15333 unique reflections and 814 parameters to give $R1 = 0.094$ and $wR2 = 0.211$ and a goodness-of-fit = 1.014. CCDC 182/1852. See http://www.rsc.org/suppdata/cc/b0/b007347o/ for crystallographic files in .cif format.

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