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Controlling the Dimensionality of Metal−Metal Bonded Rh_2^{4+} Polymers by the Length of the Linker. A Disciplined Example of Crystal Engineering

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Reaction of the molecular loop $[Rh_2(\textit{cis}\text{-DAniF})_2(CH_3CN)]_2(\text{malonato})_2$, DAniF = *N*,*N*′-di-*p*-anisylformamidinate, with 2 equiv of 2,2′,3,3′,5,5′,6,6′-octafluoro-4,4′-biphenyldinitrile gives a linear tubular structure with Rh−Rh distances of 2.435(1) Å. A comparison of the structures obtained with this molecular loop but employing other linkers support the idea that longer linkers favor one-dimensional structures while shorter linkers favor two-dimensional structures because of the increased clashing between the large *p*-anisyl groups. Crystallographic data at 213(2) K for $\{[Rh_2(\textit{cis}\text{-DAniF})_2]_2(O_2CCH_2CO_2)_2(NCC_6F_4C_6F_4CN)_2\}\cdot 6.8nCH_2Cl_2$ are: monoclinic, $P2_1/m$, $a = 11.802(1)$, $b = 28.303(2)$, $c = 18.820(2)$ Å, $\beta = 95.673(2)°$, and $Z = 2$.

Introduction

There is now great interest in creating new materials and supramolecular assemblies in which metal units are found at the corners or apices of polygonal, polyhedral, or more complex 1-, 2-, or 3-dimensional structures. By far the majority have been made with mononuclear coordination centers such as Pd^{2+}, Pt^{2+}, Cd^{2+}, Zn^{2+}, and Ag^{+} as the geometry-setting elements in the arrays. Often the isolated compounds have very large charges per formula unit, with values of 8+ and upward being common.[1−8]

We recognized some time ago that by using partially complexed metal−metal bonded M_2 entities, many architectures similar to those obtained from mononuclear units, e.g. pairs, loops, triangles, and squares, could be made (as well as some that are different). However, many of the properties of this new class of compounds cannot be easily attained with mononuclear building blocks; an example is the extensive electronic communication commonly found in many neutral species prepared from dimetal units.[9]

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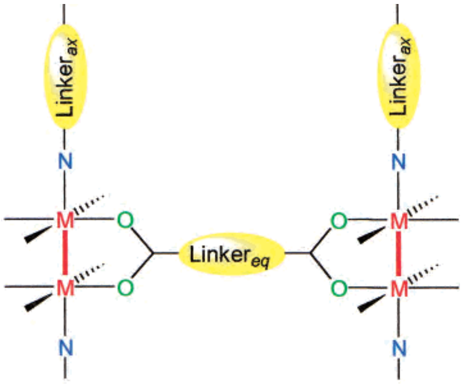
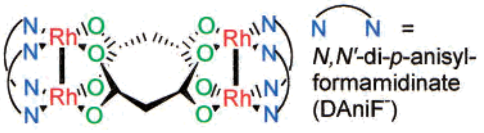
Also, some metal−metal bonded species (e.g., Rh$_2^{4+}$) can be manipulated in unique ways. An example is the possibility of utilizing both equatorial and axial connections, as shown in **I** for a system with dicarboxylate anions as equatorial linkers and N-donor ligands as axial linkers.



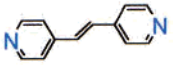
I

Recently we reported on a series of compounds in which simultaneous utilization of equatorial and axial connections led to the formation of extended one- and two-dimensional polymers.[10] These were prepared by reaction of the tetranuclear molecular loop, **II**, where two (*cis*-DAniF)$_2$Rh$_2^{2+}$ units are joined equatorially by two dicarboxylate (malonate) anions.

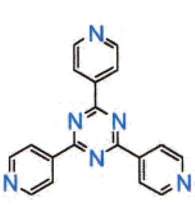


II

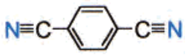
When this loop reacts with ligands **III** and **IV** 1-D polymers are formed,[10] whereas reaction with **V** gives a 2-D polymer.[10a]



III



IV



V

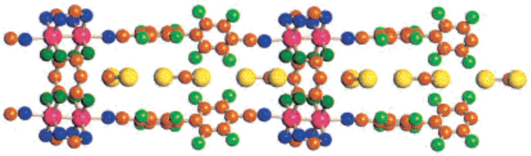


Figure 1. A view of the extended one-dimensional structure in **1** showing interstitial solvent molecules. The *p*-anisyl groups have been omitted.

Table 1. Crystal and Structure Refinement Data for **1**

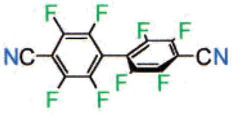
compound	**1**·6.8CH$_2$Cl$_2$
chemical formula	C$_{100.8}$H$_{77.6}$Cl$_{13.6}$F$_{16}$N$_{12}$O$_{16}$Rh$_4$
formula weight	2910.71
cryst syst	monoclinic
space group	$P2_1/m$
a, Å	11.802(1)
b, Å	28.303(2)
c, Å	18.820(2)
β, deg	95.673(2)
V, Å^3	6256(1)
Z	2
T, K	213(2)
λ, Å	0.71073
ρ_{calcd}, g cm^{-3}	1.545
μ, mm^{-1}	0.894
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.095, 0.217

[a] $R1 = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

Table 2. Selected Bond Distances (Å) for **1**

Rh(1)−Rh(2)	2.435(1)	Rh(2)−N(2)	2.011(9)
Rh(1)−N(1)	2.016(9)	Rh(2)−N(4)	2.031(9)
Rh(1)−N(3)	2.022(9)	Rh(2)−N(6)	2.24(1)
Rh(1)−N(5)	2.204(9)	Rh(2)−O(104)	2.074(8)
Rh(1)−O(103)	2.086(8)	Rh(2)−O(202)	2.066(7)
Rh(1)−O(201)	2.088(7)		

We suggested that the length of the linker determined the dramatic difference in the type of polymer formed and postulated that the shorter linker, **V**, would require unacceptable contact between the aromatic rings of the formamidinate ligands of the molecular loops should the structure remain one dimensional. Here we report on the result of a control experiment done by using a ligand chemically similar to **V**, but with a longer unit between the two cyanide groups, namely 2,2′,3,3′,5,5′,6,6′-octafluoro-4,4′-biphenyldicarbonitrile, **VI**.



VI

By using the longer linker having two phenyl rings, **VI**, instead of one phenyl ring, **V**, the structure changes from two- to one-dimensional. It is also interesting that even with the extensive fluorination in **VI** it is still basic enough to serve as an effective linker.

Experimental Section

General Considerations. All the syntheses were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried, then distilled under nitrogen following conventional methods. Chemicals were purchased from Aldrich and used as received. The dirhodium molecular loop [Rh$_2$(DAniF)$_2$(CH$_3$CN)]$_2$(O$_2$CCH$_2$CO$_2$)$_2$ (DAniF = *N,N′*-di-*p*-anisylformamidinate) was prepared by following

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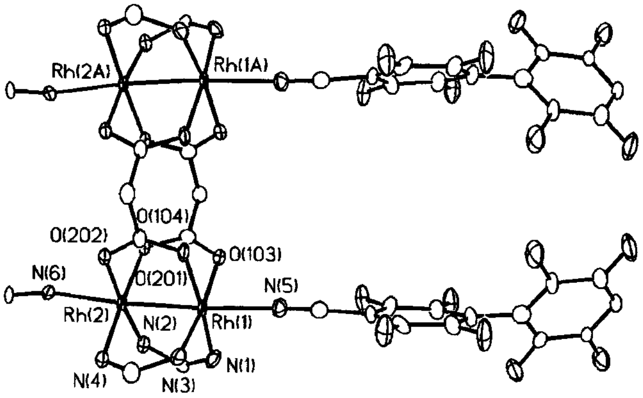

Figure 2. A thermal ellipsoid plot of a portion of the tube **1** with solvent and *p*-anisyl groups omitted. Note there is a mirror plane perpendicular to the paper bisecting the tube. Displacement ellipsoids for non-carbon atoms are given at the 50% probability level.

published procedures.[10a] Elemental analysis was performed by Canadian Microanalytical Service, Delta, British Columbia, on samples that had been heated under vacuum; the results were satisfactory.

Preparation of Complexes. $\{[\mathrm{Rh_2}(cis\text{-DAniF})_2]_2(\mathrm{O_2CCH_2CO_2})_2(\mathrm{NCC_6F_4C_6F_4CN})_2\}\cdot 6.8n\mathrm{CH_2Cl_2}$ (**1**). A green $\mathrm{CH_2Cl_2}$ solution (10 mL) of $[\mathrm{Rh_2(DAniF)_2(CH_3CN)}]_2(\mathrm{O_2CCH_2CO_2})_2$ (82 mg, 0.050 mmol) was carefully layered with a $\mathrm{CH_2Cl_2/Et_2O}$ solution (1:1, 20 mL) of 2,2′,3,3′,5,5′,6,6′-octafluoro-4,4′-biphenyldicarbonitrile (35 mg, 0.10 mmol). Red crystals were formed after several days diffusion. The yield was essentially quantitative.

Crystallographic Procedures. Single-crystal X-ray work on compound **1** was performed on a Bruker SMART 2000 CCD detector system. Cell parameters were measured using the SMART[11] software. Data were corrected for Lorentz and polarization effects using the program SAINT.[12] Absorption corrections were applied using SADABS.[13]

The positions of some or all of the non-hydrogen atoms were found via direct methods by way of the program package SHELXTL.[14] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Hydrogen atoms were used in idealized positions on the metal cluster for structure factor calculations. Other details of data collection and refinement are given in Table 1. Selected atomic distances and angles are provided in Table 2. Other crystallographic data are available as Supporting Information.

Results and Discussion

The red complex was prepared in essentially quantitative yield by treating the singly bonded $[\mathrm{Rh_2}(cis\text{-DAniF})_2(\mathrm{CH_3CN})]_2$(malonato)$_2$ molecular loop[15] with the 2,2′,3,3′,5,5′,6,6′-octafluoro-4,4′-biphenyldicarbonitrile linker in a mixture of $\mathrm{CH_2Cl_2/Et_2O}$ according to the following reaction:

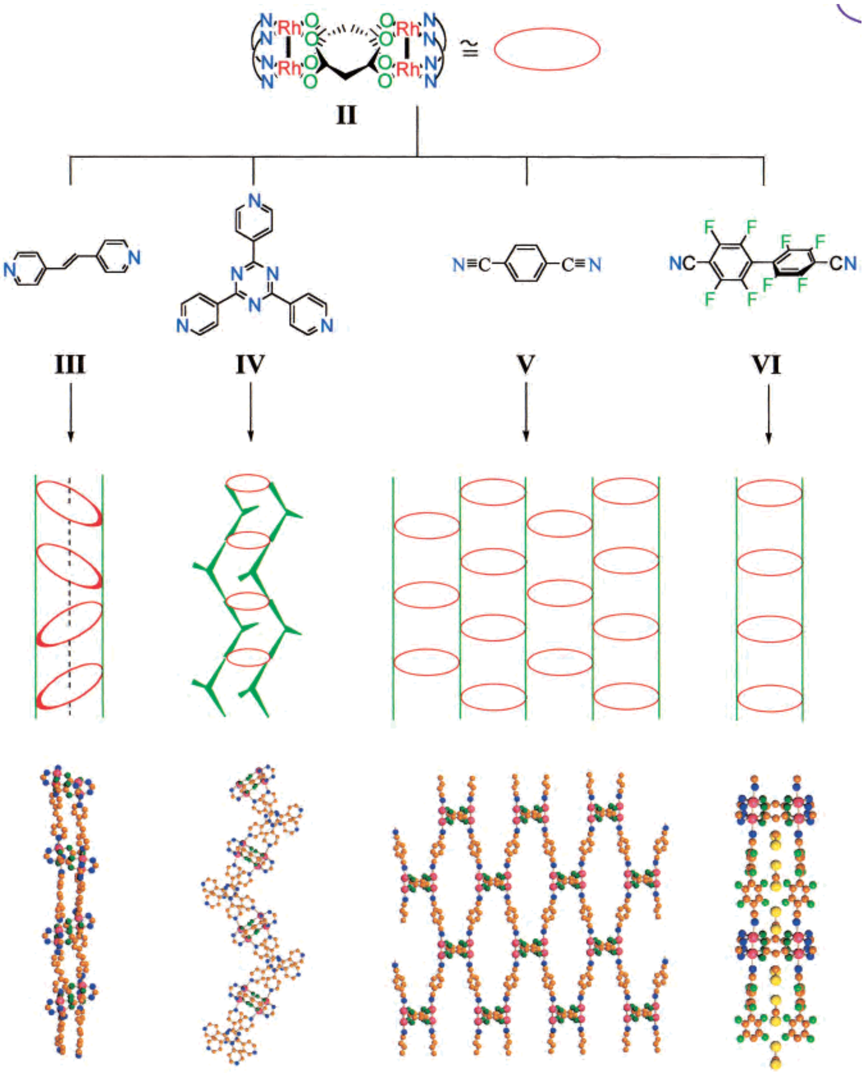

Figure 3. A comparison of the structures of the various polymers prepared so far by reacting molecular loops with 2 equiv of N-donor linkers. For linkers **III** and **V** see ref 10a and for **IV** see ref 10b.

$$n\,[\mathrm{Rh_2}(cis\text{-}\mathrm{DAniF})_2(\mathrm{CH_3CN})]_2(\mathrm{O_2CCH_2CO_2})_2 + 2n\,\mathrm{NCC_6F_4C_6F_4CN} \xrightarrow{-\mathrm{CH_3CN}} \{[\mathrm{Rh_2}(cis\text{-}\mathrm{DAniF})_2]_2(\mathrm{O_2CCH_2CO_2})_2(\mathrm{NCC_6F_4C_6F_4CN})_2\}_n$$

The crystalline material is very insoluble in most common organic solvents. Thus, preparation of crystals is best accomplished by diffusion of solutions of the two reactants.

The X-ray structure, without the aromatic rings of the formamidinate groups, is shown in Figure 1. In the one-dimensional polymer, the metal−metal bonded molecular loops are joined by axially coordinated octafluoro-4,4′-biphenyldicarbonitrile ligands forming a 1-D tube. As shown in Figure 2, a mirror plane perpendicular to the plane of the paper bisects the tube. All metrical parameters are as expected; the crystallographically unique Rh−Rh distance of 2.435(1) Å is typical of those in singly bonded dirhodium complexes. An interesting feature is the presence of interstitial $\mathrm{CH_2Cl_2}$ molecules within the tubes. This contrasts with the compounds formed by **II** and **III**, which did not have solvent molecules within the tube.

It is also informative to compare the extended structures of all the products prepared so far by reacting 1 equiv of the molecular loop **II** with 2 equiv of the neutral N-donor linkers **III**−**VI**. This is done schematically in Figure 3.

For linker **III**, the tubular structure has loops related alternately by centers of inversion and two-fold axes in an overall linear structure. When the reaction is done with linker **IV** and the stoichiometry is carefully controlled, a zigzag tunnel forms, having one loop and two triazine ligands alternating to form the walls of the tube.

For the shorter linker, **V**, the structure is very different than those previously described. Now a sheetlike structure is formed. In our earlier communication, we speculated that this structure was adopted to avoid clashes between the bulky *p*-anisyl groups from the formamidinate ligands. We also indicated that such clashes could only be avoided if the linkers were long enough. Indeed, we now show that simply by increasing the length of the linker, using **VI**, the resulting structure is tubular. This is a very significant result, as it proves that we can now control the nature of the polymeric structure by choosing axial ligands of the appropriate length and shape.

In conclusion, this work demonstrates that linking molecular loops with polydentate ligands is a process amenable to a high degree of control. It is thus a good example of the currently very active enterprise called crystal engineering.

Acknowledgment. We are grateful to the National Science Foundation for support of work and to Johnson Matthey for a generous loan of $\mathrm{RhCl_3}$.

Supporting Information Available: An X-ray crystallographic file for compound **1**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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