DALTON
COMMUNICATION

The first dirhodium-based supramolecular assemblies with interlocking lattices and double helices

F. Albert Cotton,*[a] Chun Lin[a] and Carlos A. Murillo *[ab]

[a] *Department of Chemistry and Laboratory for Molecular Structure and Bonding,*
PO Box 30012, Texas A&M University, College Station, TX 77842-3012, USA.
E-mail: cotton@tamu.edu
[b] *Department of Chemistry, University of Costa Rica, Ciudad Universitaria, Costa Rica.*
E-mail: murillo@tamu.edu

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

One dimensional zig-zag tunnels or three-dimensional lattices with double helices can be made by controlling the stoichiometry of the reaction of the metal–metal bonded loop, 1, $[Rh_2(DAniF)_2(CH_3CN)]_2(O_2CCH_2CO_2)_2$ (DAniF = *N*,*N*′-di-*p*-anisylformamidinate) and tri(4-pyridyl)triazine, 2.

The synthesis and structural characterization of supramolecular assemblies which are coordination oligomers and polymers is an intensely active research area at present.[1–11] Practically all of the effort has been directed to the use of mononuclear coordination centers (*i.e.*, metal ions such as Pd^{2+}, Pt^{2+}, Ag^+, Cd^{2+}) as the geometry-setting elements in the arrays.[1,2] In this laboratory we have pioneered the use of metal–metal bonded dimetal units (*e.g.* Mo_2^{4+} and Rh_2^{4+}) to dictate geometric patterns,[12] for five major reasons. (1) 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 metals (*i.e.*, V, Nb, Cr, Mo, W, Tc, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Cu) 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.

While most of our previous work has dealt with oligomeric structures (*i.e.*, pairs,[12d,g] loops,[12a] triangles,[12b,f] squares,[12c,f] and closed polyhedra [12e]), we have recently entered the realm of extended structures. In this report we describe the first example based on dimetal units of extended structures that entail the existence of interpenetrating lattices.

In previous work carried out in our laboratory, the dirhodium molecular loop, $[Rh_2(DAniF)_2(CH_3CN)]_2(O_2CCH_2CO_2)_2$ (DAniF = *N*,*N*′-di-*p*-anisylformamidinate), **1**, has been used to assemble 1-D tubular and 2-D sheet-like architectures by using bidentate ligands such as dipyridyl or dinitrile as axial linkers.[13] A question that naturally occurred to us is, what can be constructed if a tridentate axial linker is applied? Earlier results had shown us that the self-assembly process in this system can be stepwise and controllable by varying the stoichiometric ratio of the reactants. In the following, monoptic views of the new structures are shown in Fig. 1 and dioptic (stereoscopic) views in Fig. 2.

When loop **1** was combined with tri(4-pyridyl)triazine (**2**) in a 1 : 2 molar ratio of CH_2Cl_2–$CHCl_3$, followed by layering with ether, red cube-shaped crystals formed after one week.† X-Ray crystallography showed the formation of a 1-D, zig-zag molecular tunnel (**3**) having the composition $[Rh_2(DAniF)_2]_2(O_2CCH_2CO_2)_2[C_3N_3(C_5H_4N)_3]_2\cdot 3CHCl_3\cdot CH_2Cl_2$. A schematic representation of the core is shown as 3a in Fig. 1. There are several outstanding features in this structure. (1) One loop and two triazine ligands alternate to form a zig-zag 1-D tunnel. (2) The planes of two triazine molecules connecting the dirhodium loops are essentially parallel to each other having an interplanar separation of 3.8 Å, but these two triazine molecules are not superimposed. Instead, within each pair there is a *ca.* 60° rotation of one relative to the other along a common three-fold axis. (3) Loops are aligned from end to end as shown in 3c. There are no solvent molecules inside the tunnel. (4) Each triazine linker uses only two of its three pyridyl nitrogen atoms for coordination. The availability of an unused coordination site on each linker (as indicated by arrows on 3a and 3b) allows for the possibility of assembling the 1-D tunnels into a 3-D interpenetrating lattice structure as described below.

When a CH_2Cl_2 solution of loop **1** was combined with **2** in a 3 : 4 molar ratio, followed by layering with ether, dark-red crystals of $\{[Rh_2(DAniF)_2]_2(O_2CCH_2CO_2)_2\}_3[C_3N_3(C_5H_4N)_3]_4\cdot 4.1CH_2Cl_2\cdot Et_2O\cdot H_2O$, **4**, formed after one week.‡ The X-ray structure shows that the additional loop links two zig-zag tunnels by using the open N coordination sites of the triazine ligands. The two essentially parallel triazine planes are staggered, so that the two zig-zag tunnels do not lie in the same plane. Two schematic drawings of this grid assembly are shown as 4a and 4b, and more realistically as 4c, When viewed along the *b* axis, there is a spiral hexagon-like stacking as emphasized by the bold lines. A stereoscopic view is presented in Fig. 2A. The left- and right-handed spiral hexagonal units alternate in space and are related by crystallographic inversion centers. Each spiral hexagonal unit has an edge length of *ca.* 18 Å, and is surrounded by six other units. When these units are observed from another direction, a large ring of dimensions *ca.* 31 × 63 Å and consisting of ten loops and twenty triazine linkers appears, shown as 4d.

However, all the above description tells only half the story. The two networks 4a and 4b are both present and interpenetrate each other in such a way that they are realated by two-fold axes. These two-fold axes are along *b* at *c* equals 1/4, and 3/4, and they are at the center of each spiral hexagonal unit. The interpenetration of 4a and 4b is shown schematically in 4e and a stereoscopic view is shown in Fig. 2B. Therefore, when viewed along the *b* axis, a single spiral hexagonal unit becomes a double helix, as shown in space filling diagram 4f. The pitch of the helix is *ca.* 45 Å and the width is *ca.* 27 Å. Each such helix is surrounded by six other helices.

The structure of **4** is one of the most elaborate self-assembled structures we are aware of, and demonstrates that the use of dimetal building blocks offers abundant opportunities for creating extremely elaborate three-dimensional structures.

We are grateful to the National Science Foundation for support of this work.

DOI: 10.1039/b009612l

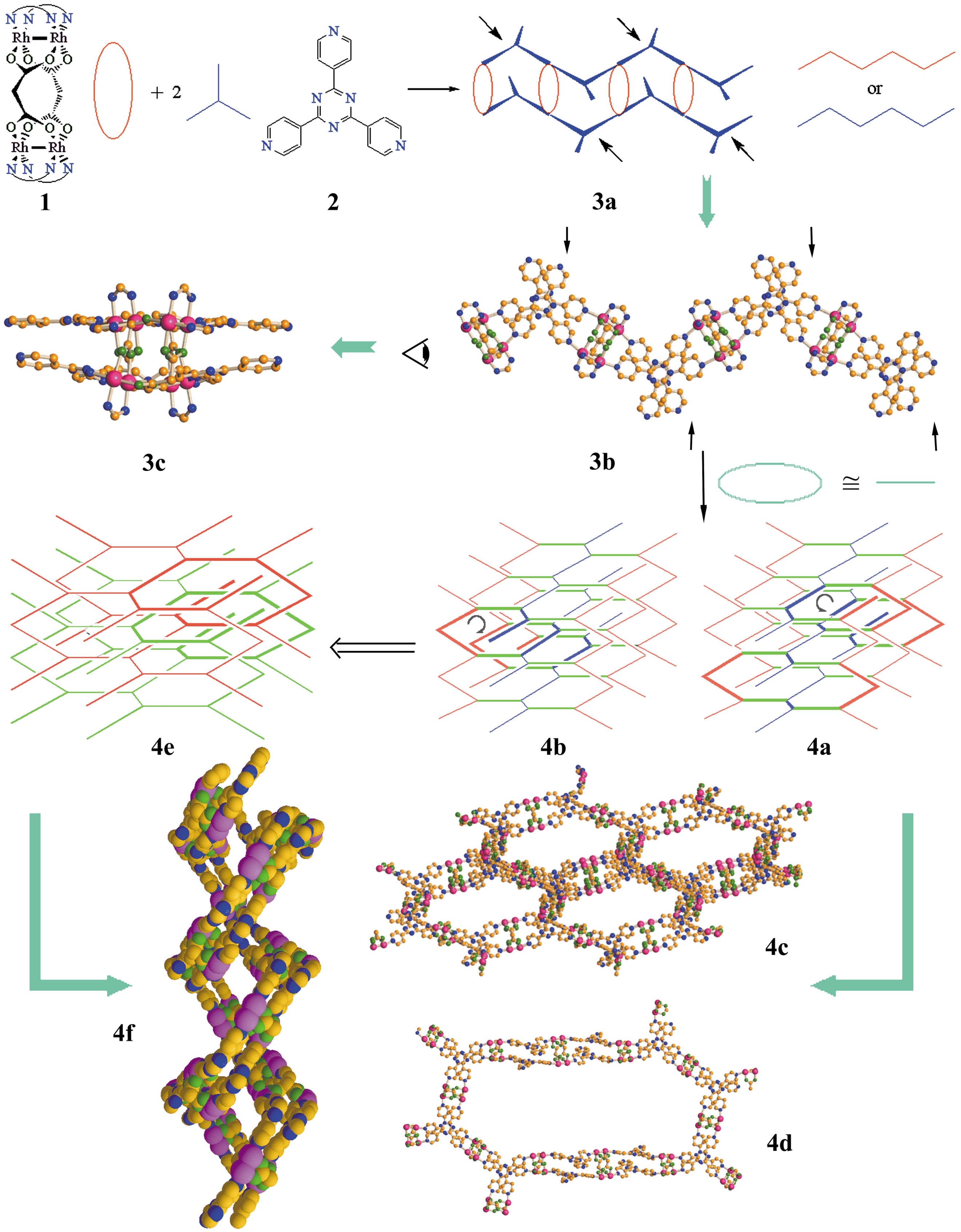

Fig. 1 Schematic representation of the products of the reaction between **1** and **2**. Images 3b and 3c are different views of the X-ray structure of **3** without the anisyl and interstitial solvent molecules. The eye on 3b indicates the direction that generates view 3c. Images 4a and 4b are representations of the two helices that form the interpenetrating lattice, 4e, in compound **4**. Views 4c and 4d are generated from one of the helices while 4f shows the core of the double helix in **4**. Color code: Rh, pink; N, blue; O, green; C, orange. Average metrical parameters (in Å) are: for **3**, Rh–Rh, 2.465[2]; Rh–N$_{\text{formamidinate}}$, 2.008[6]; Rh–N$_{\text{triazine}}$, 2.35[5]; and for **4**, Rh–Rh, 2.460[5]; Rh–N$_{\text{formamidinate}}$, 2.022[4]; Rh–N$_{\text{triazine}}$, 2.31[1].

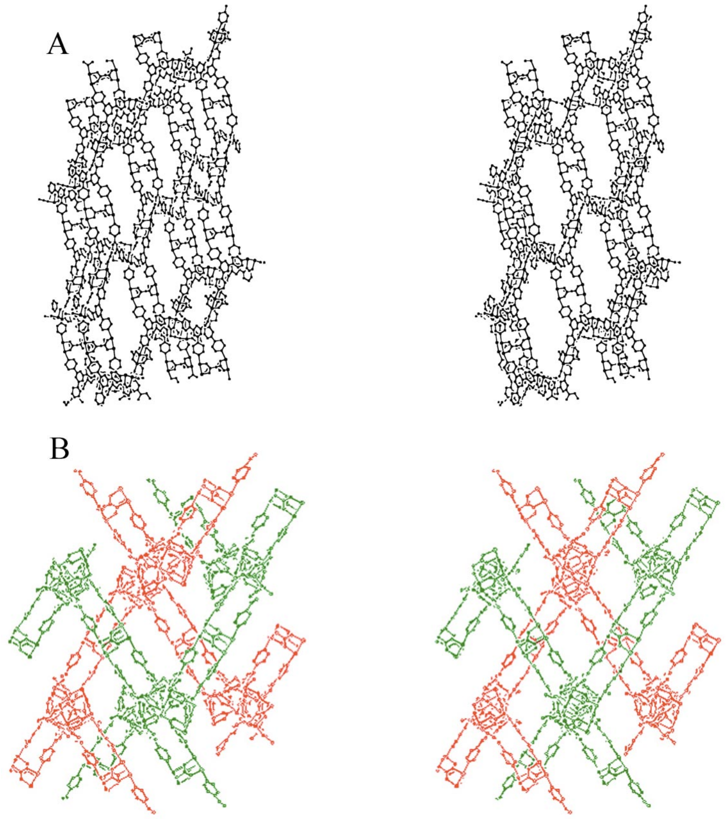

Fig. 2 Stereoscopic views of (A) one of the helices in **4** emphasizing the spiral hexagon-like stacking; (B) the core of the double helix. For clarity the right- and left-handed helices are shown in different color ink.

Notes and references

† Complex **3**: A solution of **1** (82 mg, 0.050 mmol) and **2** (32 mg, 0.10 mmol) in 20 cm^3 CH_2Cl_2–$CHCl_3$ (v : v, 1 : 1) was carefully layered with Et_2O. Red crystals were formed in essentially quantitative yield after one week of diffusion. Elemental analysis calcd. for $C_{102}H_{88}N_{20}O_{16}Rh_4$: C 54.17, H 3.92, N, 12.39; found: C 53.71, H 3.88, N 12.28%. Crystal data for **3**·3CHCl$_3$·CH$_2$Cl$_2$: $C_{212}H_{186}Cl_{22}N_{40}O_{32}Rh_8$, $M_r = 5409.19$, orthorhombic, space group *Pbca*, $a = 28.777(2)$, $b = 28.965(3)$, $c = 29.868(3)$ Å, $V = 24896(4)$ Å^3, $Z = 4$, μ(Mo-Kα) = 0.823 mm^{-1}, $T = 293(2)$ K. The structure, refined on F^2, converged for 15808 unique reflections and 743 parameters to give $R1 = 0.084$ and $wR2 = 0.197$ and a goodness-of-fit = 0.873.

‡ Complex **4**: A CH_2Cl_2 solution (20 cm^3) containing **1** (98 mg, 0.060 mmol) and **2** (25 mg, 0.080 mmol) was carefully layered with Et_2O. Dark-red crystals were formed after one week of diffusion. The yield is essentially quantitative. Elemental analysis calcd. for $C_{270}H_{240}N_{48}O_{48}Rh_{12}$: C 52.64, H 3.93, N 10.92; found: C 52.25, H 3.89, N 10.77%. Crystal data for **4**·4.1CH$_2$Cl$_2$·Et$_2$O·H$_2$O: $C_{278.1}H_{260.2}Cl_{8.2}N_{48}O_{50}Rh_{12}$, $M_r = 6600.35$, monoclinic, space group *P*2/*c*, $a = 19.458(1)$, $b = 22.577(1)$, $c = 45.763(2)$ Å, $V = 19980(2)$ Å^3, $Z = 2$, μ(Mo-Kα) = 0.594 mm^{-1}, $T = 243(2)$ K. The structure, refined on F^2, converged for 24998 unique reflections and 931 parameters to give $R1 = 0.086$ and $wR2 = 0.244$ and a goodness-of-fit = 1.047.

For both **3** and **4**, only the metal atoms were refined anisotropically. Hydrogen atoms were not included in the models. In both, five of the *p*-anisyl groups were disordered. The disordered groups were each refined as a pair, comprising a major and a minor orientation, but the members of each pair were constrained to have the same bond distances and angles. CCDC reference numbers 154475 for **3** and 154476 for **4**. See http://www.rsc.org/suppdata/dt/b0/b009612l/ for crystallographic data in CIF or other electronic format.

1 S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853 and references therein.

2 M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417 and references therein.

3 P. Espinet, K. Soulantica, J. P. H. Charmant and A. G. Orpen, *Chem. Commun.*, 2000, 915.

4 J. A. R. Navarro and B. Lippert, *Coord. Chem. Rev.*, 1999, **185–186**, 653.

5 D. Whang and K. Kim, *J. Am. Chem. Soc.*, 1997, **119**, 451.

6 S. Mann, G. Huttner, L. Zsolnai and K. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2808.

7 M. Scherer, D. L. Caulder, D. W. Johnson and K. N. Raymond, *Angew. Chem., Int. Ed.*, 1999, **38**, 1588.

8 K. D. Benkstein, J. T. Hupp and C. L. Stern, *Inorg. Chem.*, 1998, **37**, 5404.

9 S.-W. Lai, M. C.-W. Chan, S.-M. Peng and C.-M. Che, *Angew. Chem., Int. Ed.*, 1999, **38**, 669.

10 C. J. Jones, *Chem. Soc. Rev.*, 1998, **27**, 289.

11 K. K. Klausmeyer, S. R. Wilson and T. B. Rauchfuss, *J. Am. Chem. Soc.*, 1999, **121**, 2705.

12 (*a*) F. A. Cotton, C. Lin and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 472; (*b*) F. A. Cotton, C. Lin and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 575; (*c*) F. A. Cotton, C. Lin and C. A. Murillo, *Inorg. Chem.*, 2001, **40**, 478; (*d*) F. A. Cotton, J. P. Donahue, C. Lin and C. A. Murillo, *Inorg. Chem.*, 2001, in press; (*e*) F. A. Cotton, L. M. Daniels, C. Lin and C. A. Murillo, *Chem. Commun.*, 1999, 841; (*f*) F. A. Cotton, L. M. Daniels, C. Lin and C. A. Murillo, *J. Am. Chem. Soc.*, 1999, **121**, 4538; (*g*) F. A. Cotton, C. Lin and C. A. Murillo, *J. Chem. Soc., Dalton Trans.*, 1998, 3151.

13 F. A. Cotton, C. Lin and C. A. Murillo, *Chem. Commun.*, 2001, 11.