One-Dimensional Assemblies of Dirhodium Units Bridged by *N,N′*-Dicyanoquinonediimine Ligands

Hitoshi Miyasaka,[†] Cristian S. Campos-Fernández, José Ramón Galán-Mascarós, and Kim R. Dunbar*

Department of Chemistry, Texas A&M University,
P.O. Box 30012, College Station, Texas 77842-3012

Received June 27, 2000

Introduction

Polymeric assemblies consisting of metal ions coordinated to polycyanide ligands are of interest for their conducting and magnetic properties.[1−5] Unusual behavior results from dπ−pπ interactions between open-shell metal ions and organic radicals as illustrated by the family of 3-D metals Cu(R,R′-DCNQI)$_2$ (DCNQI = *N, N′*-dicyanoquinone diimine).[5] The presence of π-stacked columns of DCNQI radicals is an important component of the conducting pathway, but interactions through the metal−organic skeleton are essential for leading to the extraordinarily high metallic conductivities exhibited by these coordination polymers.

Metal−metal bonded complexes of the second- and third-row transition series are excellent prospects for reactions with nitrile acceptor ligands because of the fact that (1) they possess diffuse d orbitals that can engage in back-donation with ligand pπ orbitals, (2) they possess HOMO/LUMO levels whose energies can be easily varied, and (3) they undergo redox as well as simple ligand substitution reactions. There are a number of papers in the current literature on the subject of linked metal−metal bonded structures,[6−9] but only a few instances of polycyano-bridged systems have been reported.[10−18] To our knowledge, there are five structurally characterized polymers: the 1-D chains *cis*-[Rh$_2$(O$_2$CCH$_3$)$_4$(TCNE)]$_\infty$, *trans*-[Rh$_2$(O$_2$CCH$_3$)$_4$(TCNE)]$_8$,[14] and [Mo$_2$(O$_2$CCF$_3$)$_4$(DM-DCNQI)]$_\infty$,[16] the

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* To whom correspondence should be addressed. Phone: (979) 845-5235. Fax: (979) 845-7177. E-mail: dunbar@mail.chem.tamu.edu.

[†] Current address: Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-Ohsawa 1-1, Hachioji, Tokyo 192-0397, Japan.

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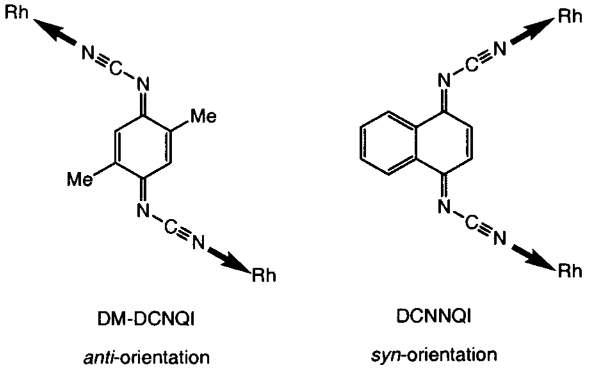
Chart 1. Schematic Drawings that Emphasize the Binding Preferences of DM-DCNQI and DCNNQI



1-D ladder [{$Mo_2(O_2CCF_3)_4(TCNQ)_{0.5}$·*m*-xylene}$_2$·$Mo_2(CF_3CO_2)_4$·(*m*-xylene)]$_\infty$,[15] and the 2-D network compound [{$Rh_2(O_2CCF_3)_4$}$_2$(TCNE)]$_\infty$.[13]

Herein we describe two new 1:1 polymers, [$Rh_2(O_2CCF_3)_4$(DM-DCNQI)]$_8$·(C_6H_6) (**1**) and [$Rh_2(O_2CCF_3)_4$(DCNNQI)]$_\infty$·(C_7H_8) (**2**), derived from reactions of $Rh_2(O_2CCF_3)_4$ with 2,5-dimethyl-*N*,*N*′-dicyanoquinone diimine (DM-DCNQ) and *N*,*N*′-dicyanonaphthaquinone diimine (DCNNQI). The different polymeric frameworks of the two products reflect the steric preferences for anti-oriented nitrile groups in DM-DCNQI versus syn-oriented nitrile substituents in DCNNQI (Chart 1).

Experimental Section

Chemicals and Reagents. Reactions were carried out under a dinitrogen atmosphere unless otherwise indicated. Solvents were dried and freshly distilled under N_2 before use. $Rh_2(O_2CCF_3)_4$ was purchased from Pressure Chemical Co. The dicyanodiimine ligands DM-DCNQI and DCNNQI were synthesized according to a literature method.[19]

Preparation of [$Rh_2(O_2CCF_3)_4$(DM-DCNQI)]$_\infty$·(C_6H_6) (1). $Rh_2(O_2CCF_3)_4$ (66 mg, 0.1 mmol) was dissolved in 20 mL of dichloromethane/benzene (1:1 v/v). This solution was placed in a narrow Schlenk tube and layered with a benzene solution of DM-DCNQI (18 mg, 0.1 mmol). After standing undisturbed for 1 week, the solution yielded a crop of reddish-brown crystals. Yield, 92%. IR (cm^{-1}) (Nujol mull): ν(C≡N), 2216; ν(C−O), 1537; δ(C−H) (phenyl), 844.

Preparation of [$Rh_2(O_2CCF_3)_4$(DCNNQI)]$_\infty$·(C_7H_8) (2). This compound was prepared in the same manner as described for **1** except that DCNNQI (21 mg, 0.1 mmol) was used instead of DM-DCNQI and toluene was used in place of benzene. Reddish-brown rectangular-shaped crystals were obtained. Yield, 86%. IR (cm^{-1}) (Nujol mull): ν(C≡N), 2192; ν(C−O), 1545, 1515; δ(C−H) (phenyl), 842.

X-ray Structural Studies. Both crystals for the single-crystal analyses were cut from larger rectangular crystals and secured on glass fibers with Dow-Corning grease. Data were collected on a Bruker SMART CCD area detector diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.710 69 Å) operated at 100 ± 1 K for **1** and 90 ± 1 K for **2**. The structures were solved by direct methods (SIR97 and SHELXS-97)[20] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[21] Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. Full-matrix least-squares refinements based on 2117 data with $I > 2\sigma(I)$ for **1** and 3322 data with $I > 4\sigma(I)$ for **2** were employed. Crystallographic parameters and refinement details for **1** and **2** are summarized in Table 1.

Table 1. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{24}H_{14}N_4O_8F_{12}Rh_2$	$C_{27}H_{14}N_4O_8F_{12}Rh_2$
fw	920.21	956.24
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2/c$
temp/K	100	90
λ/Å	0.710 69	0.710 69
a/Å	8.570(5)	8.534(2)
b/Å	9.135(5)	8.427(2)
c/Å	11.871(5)	22.693(5)
α/deg	67.555(5)	90
β/deg	88.810(5)	96.92(3)
γ/deg	63.899(5)	90
V/Å^3	759.1(7)	1620.1(6)
Z	1	2
D_{cal}/g cm^{-3}	2.013	1.960
μ(Mo Kα)/cm^{-1}	12.15	11.43
R^a	0.0558	0.0287
$R_w{}^b$	0.1312	0.0710

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Results and Discussion

Synthesis and Infrared Spectroscopy. Both compounds were isolated as reddish-brown crystals by slow diffusion of the reactants in either benzene or toluene. The choice of these solvents reflects the fact that coordinating solvents such as alcohols, MeCN, and THF compete with the dicyanodiimine ligands for axial ligation.[22] Furthermore, compounds **1** and **2** are insoluble in aromatic solvents, which renders their isolation convenient.

An IR spectrum of **1** revealed a ν(C≡N) stretch at 2216 cm^{-1}, which is at a higher energy than the mode for free DM-DCNQI (2188 cm^{-1}). The related 1-D compound [$Mo_2(O_2CCF_3)_4$(DM-DCNQI)]$_\infty$ exhibits a ν(C≡N) stretch at an even higher energy, namely, 2230 cm^{-1}.[16] The ν(C≡N) stretch for **2** at 2192 cm^{-1} is also at a higher energy than the mode for free DCNNQI (2169 cm^{-1}). A shift to higher energies is typical for nitrile ligands involved in lone pair σ donations with little or no metal-to-ligand back-bonding. As a further indication of the oxidation state, we note that ν(C≡N) stretches in reduced DM-DCNQI compounds are shifted to lower energies compared to that of the neutral molecule. For example, [$Ru_2(O_2CR)_4$(DM-DCNQI)]$_\infty$ (R = H, Me, Et, Pr, Ph), which contains [DM-DCNQI]$^{\bullet-}$, exhibits ν(C≡N) stretches in the range 2098−2136 cm^{-1}.[10a] The dark-blue color of these Ru compounds is also indicative of the redox state of the organocyanide as being the reduced form, [DM-DCNQI]$^{\bullet-}$, which exhibits a characteristic $\pi-\pi^*$ transition. Conversely, the reddish-brown color of both **1** and **2** is in accord with the assignment of the DCNQI ligands as being neutral in these polymers.

X-ray Crystallographic Studies. Compound **1** crystallizes in the triclinic space group $P\bar{1}$, with the midpoint of the Rh−Rh bond and the DM-DCNQI bridge residing on an inversion center ($Z = 1$). A perspective view of the asymmetric unit in one of the chains in **1** is shown in Figure 1 with selected bond distances and angles being provided in Table 2. The main structural unit is a chain of alternating $Rh_2(O_2CCF_3)_4$ and DM-DCNQI molecules arranged along the c axis. The anti orientation of nitrile groups in DM-DCNQI leads to a fairly regular linear

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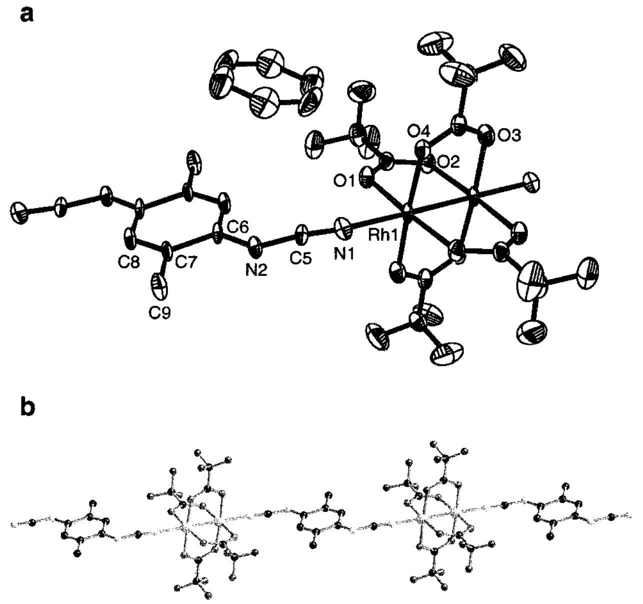

Figure 1. Views of (a) the asymmetric unit (50% probability thermal ellipsoids) and (b) the 1-D linear chain motif in **1** with the atom-labeling scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **2** with the Estimated Standard Deviations in Parentheses

	1		
Rh1−O1	2.039(5)	N1−C5	1.157(9)
Rh1−O2	2.041(5)	N2−C5	1.337(9)
Rh1−O3	2.036(6)	N2−C6	1.310(9)
Rh1−O4	2.031(5)	C6−C7	1.462(9)
Rh1−N1	2.189(7)	C6−C8	1.453(10)
Rh1−Rh1*	2.4125(14)	C7−C8	1.334(10)
Rh1*−Rh1−N1	179.0(5)	N1−C5−N2	172.6(9)
Rh1−N1−C5	161.9(6)	C5−N2−C6	118.3(6)
	2		
Rh1−O1	2.0362(15)	N2−C5	1.329(5)
Rh1−O2	2.0438(16)	N3−C8	1.299(5)
Rh1−O3	2.0349(16)	N3−C12	1.344(6)
Rh1−O4	2.0330(16)	C5−C6	1.433(3)
Rh1−N1	2.212(2)	C5−C10	1.428(3)
Rh1−Rh1*	2.4221(8)	C6−C7	1.405(5)
N1−C11	1.283(5)	C7−C8	1.433(3)
N1−C12	1.211(5)	C8−C9	1.429(3)
N2−C11	1.336(6)	C9−C10	1.358(4)
Rh1*−Rh1−N1	178.08(5)	N1−C11−N2	169.6(4)
Rh1−N1−C11	137.4(2)	N1−C12−N3	167.5(5)
Rh1−N1−C12	137.6(3)	C11−N2−C5	118.8(4)
		C12−N3−C8	119.1(4)

chain. The Rh−Rh bond distance of 2.4125(14) Å is very close to the typical value of ~2.40 Å found in the adducts $Rh_2(O_2CCF_3)_4(L)_2$.[22] The Rh−N(nitrile) distance is 2.189(7) Å, and the bond angles are Rh−Rh−N = 179.05(19) Å and Rh−N−C = 161.9(6) Å. The axial Rh−N(nitrile) distance is comparable to the values of 2.16(1) and 2.19(1) Å found in crystals of $[\{Rh_2(O_2CCF_3)_4\}_2(TCNE)]_\infty$.[13] The related compound $[Mo_2(O_2CCF_3)_4(DM\text{-}DCNQI)]_\infty\cdot(C_6H_6)$ is very similar to **1** in terms of the symmetry of the binding and the chain packing, but it crystallizes in the monoclinic space group *C*2/*c*.[16] There is a considerable difference, however, in the M−N(nitrile) distances and the M−N−C angles in these two compounds. The M−N(nitrile) distance of **1** is much shorter than the corresponding Mo−N(nitrile) distance of 2.531(8) Å, which is not surprising given that Mo_2^{4+} compounds do not have an electronic preference for axial interactions and, when present, the $M{-}L_{axial}$ distances are quite long (Mo−N = 2.5−2.6 Å). The Rh−N−C = 161.9(6) Å bond angle in **1** is wider than the Mo−N−C angle of 140°, but it is still much less than 180°.[13−18] A packing diagram of **1** is shown in Figure 2 where it can be observed that the interstitial benzene molecules engage in *π*-stacking with DM-DCNQI ligands along the *b* axis (stacking distances of ~3.8−4.0 Å). As in the earlier case with the Mo_2 compound, the benzene helps to stabilize the solid-state structure.

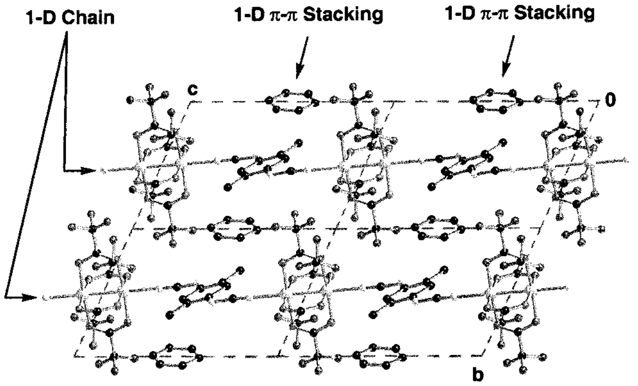

Figure 2. Packing diagram view of **1** along the *a* axis, showing alternating *π*−*π* stacking columns along the *b* axis.

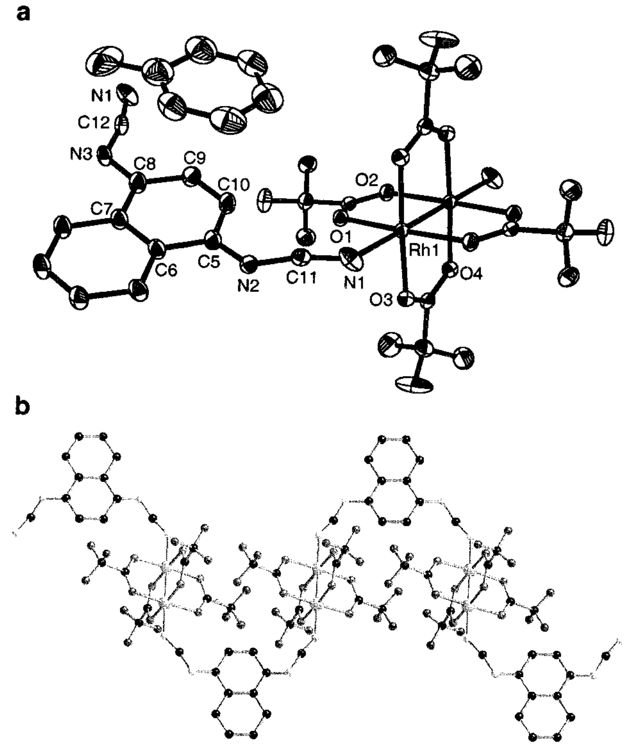

Figure 3. Views of (a) the asymmetric unit (50% probability thermal ellipsoids) and (b) the 1-D chain in **2** with the atom-labeling scheme.

Compound **2** crystallizes in the monoclinic space group *P*2/*c*, with an inversion center located at the midpoint of the Rh−Rh bond and a 2-fold axis bisecting the DCNNQI molecule (*Z* = 2). The presence of a crystallographic C_2 across the DCNNQI bridge leads to a static disorder. A view of the asymmetric unit and one of the chains in **2** is shown in Figure 3, and a packing diagram is provided in Figure 4. Selected bond distances and angles are given in Table 2. The structure consists of alternating $Rh_2(O_2CCF_3)_4$ and DCNNQI molecules in a snakelike chain along the *b* axis. The Rh−Rh bond distance is 2.4221(8) Å and Rh−N(nitrile) = 2.212(2) Å. The bond angles

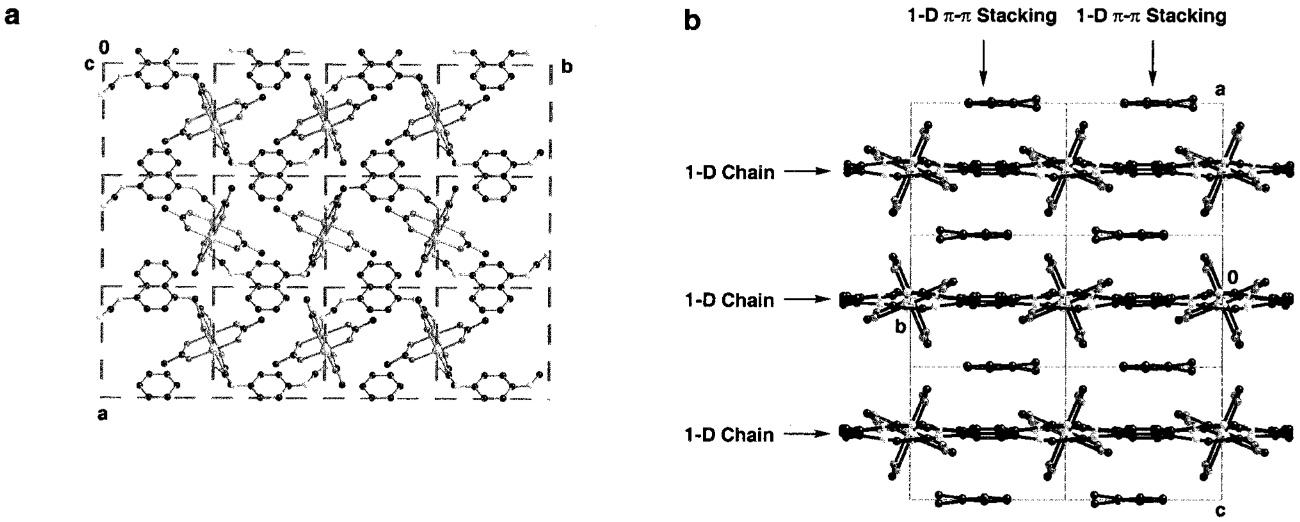

Figure 4. Packing diagram of **2** (a) along the *c* axis and (b) along the 101 plane, emphasizing the alternating $\pi-\pi$ stacked columns along the *a* axis. The CF_3 groups of $[Rh_2(CF_3CO_2)_4]$ moieties are omitted for the sake of clarity.

are Rh−Rh−N = 178.08(5) Å and Rh−N−C = 137.6(3), 137.4(2) Å. A striking aspect of the structure is the low Rh−N−C angle, which is the lowest value among this class of polymeric dinitrile compounds. The toluene molecules of crystallization are situated between chains as part of a 1-D π-stacked column with DCNNQI ligands along the *a* axis (stacking distance of ca. 3.4 Å).

It had earlier been shown that electron-rich dirhodium carboxylate compounds can form π-delocalized polymers with electron-rich polycyanide acceptors as in the case of $[\{Rh_2(CF_3CO_2)_4\}_2(TCNE)]_\infty$.[13] In the present compounds, however, it appears that only σ donation from the DCNQI ligands to the dirhodium complex is occurring. Further exploration of these compounds is required for a full understanding of the different electronic properties among members of this family and related materials with Mo and Ru.

Acknowledgment. K.R.D. thanks the National Science Foundation for financial support (CHE-9906583) and for the CCD X-ray equipment (CHE-9807975). H.M. was supported by a JSPS Research Fellowship for Young Scientists. J.R.G.-M. thanks the Ministerio de Educacion y Cultura for a Postdoctoral Fellowship.

Supporting Information Available: X-ray crystallographic files for **1** and **2**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0007097