A One-Dimensional Metallopolymer of 2,5-Dimethyl-*N*,*N*′-Dicyanoquinone Diimine (2,5-DM-DCNQI)

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The design of molecule-based materials with interesting conducting, optical, or magnetic properties is a major theme in synthetic organic and inorganic chemistry.[1−7] An intriguing approach to the design of molecular solids that exhibit cooperative behavior is to assemble open-shell metal centers and organic radicals into inorganic/organic "hybrid" structures.[4,5,7a,c,d] An excellent illustration of this strategy is the design of highly conducting covalent solids with σ- as well as dπ−pπ interactions between the metal and organic constituents, for example the class of compounds Cu(R,R′-DCNQI)$_2$ (DCNQI = *N*,*N*′-dicyanoquinone diimine) in which the nitrile functionalities are directly bonded to the Cu centers.[5] These fascinating materials adopt polymeric motifs consisting of tetrahedral mixed-valence Cu$^{+/2+}$ cations connected by partially reduced DCNQI molecules. In addition to the usual 1-D pathway through stacks of DCNQI radicals, the existence of an isotropic 3-D conduction pathway from Robin−Day class III mixed-valence behavior of the Cu$^{I/II}$ ions bridged by DCNQI is thought to contribute to the unusual charge-transport properties.[5a]

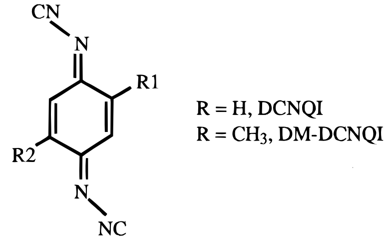

Figure 1. The DCNQI class of organic acceptors that form highly conducting materials.

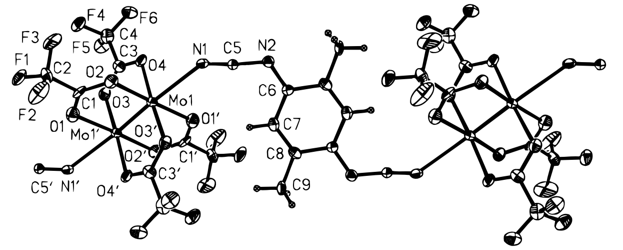

Figure 2. ORTEP view of a segment of the chain in **1**. Thermal ellipsoids are drawn at the 40% probability level. Selected distances (Å) and angles (deg) for **1**: Mo1−Mo1′ 2.127(2); Mo1−O4 2.118(6); Mo1−O3′ 2.105(6); Mo1−O2 2.114(6); Mo1−O1′ 2.131(7); Mo1−N1 2.531(8); N1−C5 1.146(12); C5−N2 1.368(12); Mo1′−Mo1−N1 166.7(2); Mo1′−Mo1−O1 90.4(2); Mo1−N1−C5 140.1(6); N1−C5−N2 173.1(9).

Dinuclear metal building blocks with open-shell electron configurations (*e.g.*, $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$, $S = {}^3/_2$) also present intriguing possibilities for the elaboration of extended arrays.[7−9] Several oligomers that exhibit communication of M−M-bonded units through organic bridges have been structurally characterized,[7a,b,f] but there is a general lack of X-ray data for the polymeric analogues. With respect to the polynitrile acceptors TCNQ, TCNE, and DM-DCNQI,[10] only four metal−metal-bond-containing polymers with TCNE[9a,b] and one with TCNQ are known; there are no crystallographically determined examples for the DCNQI family.[9c] Herein we describe the synthesis and structural characterization of the first 1-D material composed of a quadruply-bonded dimetal complex bridged by an organonitrile acceptor. These results support the formulation of previously reported diruthenium carboxylate/polynitrile materials as infinite-chain structures, as previously suggested by us and by others.[7c−e]

Yellow-brown needles of [Mo$_2$(O$_2$CCF$_3$)$_4$(DM-DCNQI)·C$_6$H$_6$]$_n$ (**1**) are formed instantaneously upon mixing benzene solutions of Mo$_2$(O$_2$CCF$_3$)$_4$ and DM-DCNQI.[11] An infrared spectrum of the sample revealed a ν(C≡N) stretch at 2230 cm^{-1} compared to 2188 cm^{-1} for free DM-DCNQI. A shift to higher energies is typical for coordinated nitriles involved in lone pair σ-donations with little metal-to-ligand back-bonding.[12] The pale color of **1** supports the assignment of DM-DCNQI as a neutral ligand, since DM-DCNQI$^{\bullet-}$ radical compounds are typically dark blue, owing to the characteristic π−π* transition of the reduced form.[5]

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[10] TCNQ = 7,7′,8,8′-tetracyanoquinodimethane, TCNE = tetracyanoethylene, DCNQI = *N*,*N*′-dicyanoquinone diimine, DM-DCNQI = 2,5-dimethyl-*N*,*N*′-dicyanoquinone diimine.

[11] DM-DCNQI (0.018 mg, 0.1 mmol) in C$_6$H$_6$ (15 mL) was added to Mo$_2$(O$_2$CCF$_3$)$_4$ (0.045 g, 0.1 mmol) in C$_6$H$_6$ (10 mL), and the mixture was allowed to stand undisturbed at room temperature for 24 h. After this time, a crop of red-brown needles was harvested, washed with C$_6$H$_6$, and dried (yield 35 mg, 56%).

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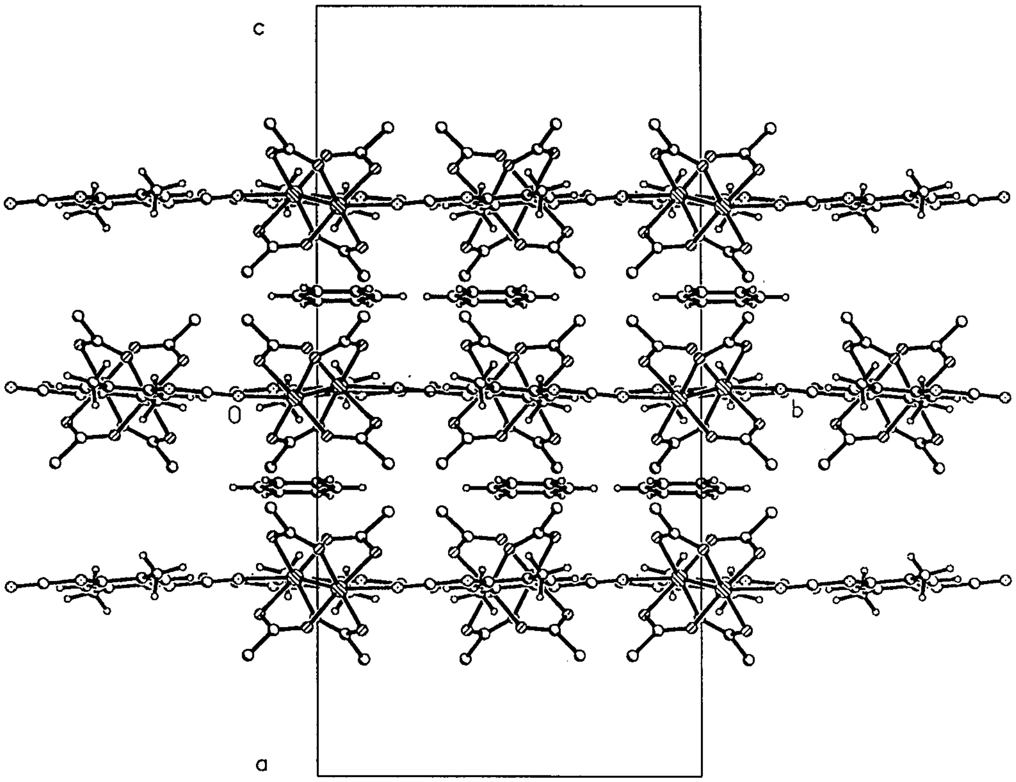

Figure 3. Packing diagram view of **1** along the 101 plane, emphasizing the location of the benzene molecules between the chains. The F atoms have been omitted for clarity.

Single crystals of **1** were grown by slow diffusion of benzene solutions of the constituent molecules. $[Mo_2(O_2CCF_3)_4(DM\text{-}DCNQI)\cdot C_6H_6]_n$ crystallizes in the monoclinic space group *C*2/*c*, with the midpoint of the Mo−Mo bond residing on an inversion center.[13] The structure consists of alternating $Mo_2(O_2CCF_3)_4$ and DM-DCNQI molecules that form a zigzag polymeric chain. An ORTEP plot of a segment of the chain with atom labels is depicted in Figure 2. The axial Mo−N distance of 2.531(8) Å and the Mo−Mo distance of 2.127 (2)Å are in the typical range for molecular $Mo_2(O_2CCF_3)_4$ compounds with axial nitrogen donor ligands, *e.g.*, pyridine (Mo−N 2.548(5) Å, Mo−Mo 2.129(2) Å)[8a] and 4,4′-bipyridine (Mo−N 2.530(9) Å, Mo−Mo 2.124(1) Å).[8b] Of further note in the context of polymeric structures is the Mo−N distance in **1**, which is shorter than the corresponding distances in $[Mo_2(O_2CCF_3)_4(4,4'\text{-bpy})_2]_n$ (2.557(8) Å)[8b] and $[Mo_2(O_2CCF_3)_4(TCNQ)_{0.5}]_n$ (2.622(5) Å).[9c]

One of the more striking aspects of the structure is the Mo−N≡C angle of ~140°, which is unusual for an sp-hybridized nitrile interacting through the N atom lone pair. The several previously reported structures in which a metal is σ-coordinated to DM-DCNQI also exhibit M−N≡C angles that deviate from 180°, although, with one exception, they are all greater than 140°.[5b,14] The M−N≡C bond angle of 140° in the present structure supports an sp^2-hybridized N atom, but curiously, the C≡N bond distance of 1.146(12) Å is essentially the same as the corresponding value for neutral, free DM-DCNQI (1.148(5) Å).[5c]

The structural determination of a 1-D metallopolymer of DM-DCNQI has not been previously reported to our knowledge. The stability of the present compound and the ease with which it crystallizes from benzene are rationalized on the basis of π-stacking of the DM-DCNQI ligands and the benzene molecules (shortest contact = 3.4 Å). A packing diagram that clearly shows the presence of the interstitial benzene is provided in Figure 3. These additional interactions serve to "stitch" the polymeric chains together, hence stabilizing the structure in two dimensions. Of further note is the ...ABAB... pattern of the zigzag chains along the *c* direction, which is evident from the perpendicular arrangement of the Mo_2 units in adjacent chains. The fact that the polymer does not crystallize from solvents other than benzene, coupled with the observation that benzene is involved in stacking interactions with DM-DCNQI, point to the conclusion that **1** is not merely an ordinary solvate, but is a clathrate of benzene which acts as a template for the formation of crystals. Interestingly, toluene does not produce crystals of **1**, which argues that subtle steric factors govern the incorporation of enclathrated solvent in crystals of $[Mo_2(O_2CCF_3)_4(DM\text{-}DCNQI)]_n$. Efforts are underway to extrapolate these experimental conditions for the crystallization[15] of intriguing magnetic materials whose properties are consistent with chains of alternating $[Ru_2(O_2CR_3)_4]^+$ and $DM\text{-}DCNQI^{\bullet -}$ or $TCNQ^{\bullet -}$ groups.[7c−e]

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and torsion angles for **1** and metric parameters for metal−DCNQI compounds and a packing diagram of **1** viewed down the *c* axis (9 pages). Ordering information is given on any current masthead page.

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(13) Crystallographic data for **1**: $a = 20.755(4)$ Å, $b = 13.794(3)$ Å, $c = 13.924(3)$ Å, $\beta = 130.92(3)°$, $V = 3012.1(11)$ Å^3, $Z = 4$, monoclinic, *C*2/*c*, $\rho_{calc} = 1.998$ g cm^{-3}, $\mu = 0.962$ mm^{-1}, $2\theta_{max} = 46.52°$, Mo Kα ($\lambda_{\bar{\alpha}} = 0.710\ 73$ Å), $\theta - 2\theta$ scans, $T = 140(2)$ K, number of unique reflections = 2151, number of data used for refinement = 2151, number of parameters = 256. The structure was collected on a Siemens SMART diffractometer and refined by full-matrix least-squares calculations on F^2 using the Siemens SHELXTL v. 5.03 package. H atoms were calculated and isotropically refined. R (R_w) = 0.071 (0.179) for all data refined on F^2. GOF = 1.10. Disorder in the CF_3 groups was modeled, but its presence contributes to higher R values and accounts for the residual peaks in the difference map.

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(15) Scanning electron microscopy carried out on samples of $[Ru_2(O_2CR)_4TCNX]_n$ (R = CF_3, C_3H_7, C_2H_5; X = E, Q) revealed that the samples are crystalline.