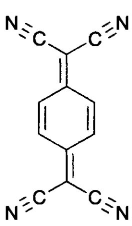
A novel one-dimensional structure involving μ_4-TCNQ ligands and quadruply bonded dimolybdenum units (TCNQ = 7,7,8,8-tetracyanoquinodimethane)

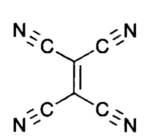
Charles Campana, Kim R. Dunbar* and Xiang Ouyang

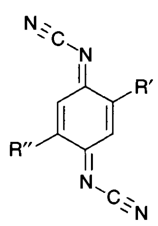
Department of Chemistry and Centre for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824, USA

Reaction of $Mo_2(O_2CCF_3)_4$ with TCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) in xylenes yields $[Mo_2(O_2CCF_3)_4(TCNQ)_{0.5}\cdot m\text{-xylene}]_2\cdot[Mo_2(O_2CCF_3)_4\cdot(m\text{-xylene})]$ 1, an unprecedented one-dimensional μ_4-TCNQ polymer, which is characterized by X-ray crystallography.

Polynitriles such as TCNQ, TCNE and DCNQI are interesting ligands for the assembly of transition-metal centres into inorganic–organic 'hybrid' structures.[1–4]


TCNQ


TCNE


DCNQI

Among the TCNQ materials that form extended solids with direct metal–nitrile interactions, the only crystallographically determined compound with μ_4-TCNQ bridges is the three-dimensional material $[Ag(\mu_4\text{-TCNQ})]_n$ prepared by electrocrystallization methods.[5] The one-dimensional Mn(salen) complex also contains μ_4-TCNQ ligands, but two of the four CN groups are capped off and not involved in extended bonding.[6] The μ_4-TCNQ mode has also been detected in solution for manganese and ruthenium complexes.[7]

Work in our laboratories has focused on the direct binding of redox-active polynitriles to dimetal complexes with σ, π and δ components to their metal–metal bonding.[8–12] The objective is to match the orbital symmetries of the dimetal units with the nitrile acceptors to build arrays with electronically coupled M_2 units. To date, a 'dimer-of-dimers' of TCNQ,[8] one-dimensional chains of TCNE[9] and DMDCNQI,[10] and two-dimensional layer structures of TCNE[11] have been structurally characterized. Herein we report a unique one-dimensional μ^4-TCNQ polymer with quadruply bonded dimolybdenum units.

Treatment of $[Mo_2(O_2CCF_3)_4]$ with TCNQ in refluxing xylenes produces a red solution which yields dark red crystals upon slow cooling. An X-ray crystallographic study revealed that the compound is composed, in part, of a chain of μ_4-TCNQ ligands bound to the axial positions of four independent $Mo_2(O_2CCF_3)_4$ molecules to give a one-dimensional polymeric motif. A second type of $Mo_2(O_2CCF_3)_4$ molecule is situated in a cavity with two *m*- xylene ligands perpendicularly oriented near the axial positions. The midpoint of the Mo–Mo bond in the unique Mo_2 unit and the centre of the μ_4-TCNQ rings reside on inversion centres. The ORTEP of **1** is depicted in Fig. 1 along with a listing of important bond distances and bond angles.

The Mo–Mo bond length of 2.1126(8) Å in the polymeric chain and 2.1131(11) Å in the molecule of $Mo_2(O_2CCF_3)_4$ $(m\text{-xylene})_2$ are not statistically different from each other, but they are longer by *ca.* 0.023 Å than the M–M bond in $[Mo_2(O_2CCF_3)_4]$ [2.090(4) Å].[13] The Mo–N(TCNQ) bond length of 2.627(5) Å is longer than the corresponding distances reported for polymeric $Mo_2(O_2CCF_3)_4L_2$ complexes containing other axial nitrogen donor ligands [Mo–Mo 2.127(2), Mo–N 2.531(8) Å, L = DMDCNQI;[10] Mo–Mo 2.128(1), Mo–N 2.557(8) Å, L = 4,4'-bpy[14]). These observations taken together with the ν(C≡N) stretching frequencies of 2243 and 2220 cm^{-1} for **1** [for neutral TCNQ, ν(C≡N) 2230 cm^{-1}] imply that the interactions between the nitrile and the Mo–Mo unit in **1** are weak σ interactions. The TCNQ ligand is also involved in π-stacking interactions with interstitial *m*-xylene solvent molecules, with the shortest distance from the *m*-xylene to TCNQ being 3.43(2) Å. The presence of these π interactions helps to stabilize the structure, and, indeed, crystals do not form in the absence of xylenes. The xylenes used in the reaction is a mixture of isomers (bp 138.2–141.7 °C), but only *m*-xylene is incorporated. Furthermore, neither benzene nor toluene is suitable as a medium for crystal growth. These collective

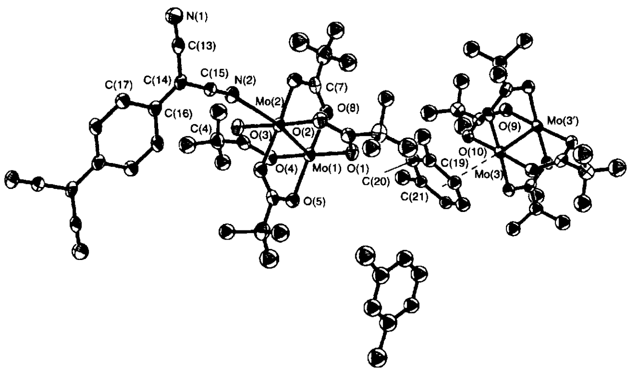


Fig. 1 Bond lengths (Å) and angles (°) in **1**: Mo(1)–Mo(2) 2.1126(8), Mo(1)–O(1), 2.127(4), Mo(2)–O(2), 2.109(4), Mo(2)–N(2) 2.623(5), Mo(3)–Mo(3)' 2.1131(11), Mo(3)–O(10) 2.107(4), N(2)–C(15) 1.126(8), N(1)–C(13) 1.148(8), C(14)–C(15) 1.453(8), C(14)–C(16) 1.361(9), C(17)–C(16) 1.451(8), O(4)–Mo(1)–O(5) 90.6(2), Mo(1)–Mo(2)–N(2) 171.15(12), C(15)–N(2)–Mo(2) 163.5(5), O(10)–Mo(3)–(O)9 91.3(2). Mo(3) distance to the least square plane of C(19)–C(24), 2.994(10).

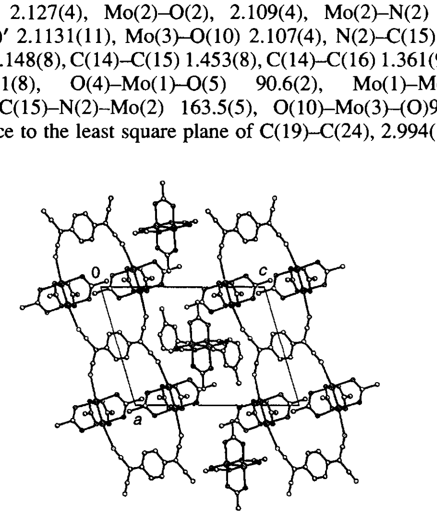


Fig. 2 Packing diagram of **1** in the *ac* plane emphasizing the 24-membered metallocyclic ring. The CF_3 groups and interstitial *m*-xylene solvent involved in π stacking with TCNQ are omitted for clarity.

observations point to the selective enclathration of *m*-xylenes in the formation of this rather unusual inclusion compound.

Metal–metal bonded complexes involved in axial coordination to arenes are rare. In fact only two examples, $[Cr_2(O_2CCF_3)_4]\cdot C_6H_6$[15] and $[Mo_2\{O_2CP(Bu^t)_2\}_4]\cdot 2C_6H_6$,[16] have been reported for Group 6 metals. As was observed for the interactions involving benzene, the *m*-xylenes in **1** are oriented with the planes of the rings perpendicular to the Mo–Mo axis. The average distance from the least-squares plane of the xylene ring to the Mo atom is 2.99(1) Å and the shortest Mo···C distance is essentially the same, *viz*., 3.00 Å. These values are much less than the corresponding M···C distances in the earlier examples.[15,16] Furthermore, a lengthening of the Mo–Mo bond from 2.090(4) Å in $[Mo_2(O_2CCF_3)_4]$ to 2.1131(11) Å in **1** is in accord with the presence of axial interactions.[15]

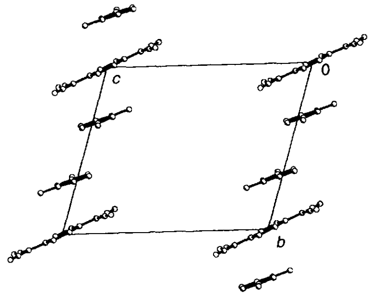
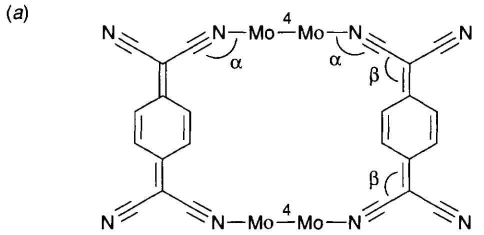
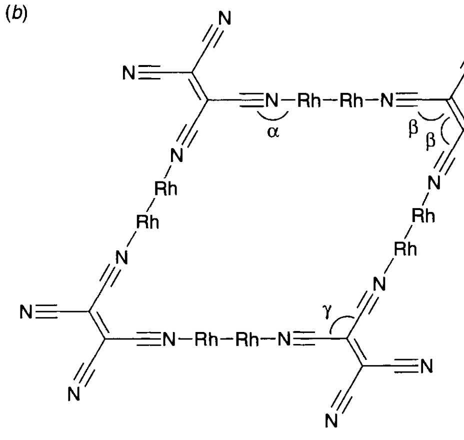


Fig. 3 Packing diagram in the *bc* plane emphasizing the planar stacking of *m*-xylene and coordinated TCNQ ligands. All the other interactions are omitted for clarity.



24-membered octagonal ring
$\alpha = 150$, $\beta = 120$



30-membered square ring
$\alpha = 180$, $\beta = \gamma = 120$

Fig. 4 Metallocyclic rings of polynitriles with dimetal units in idealized angles; (*a*) $Mo_2(O_2CCF_3)_4(TCNQ)$, (*b*) $Rh_2(O_2CCF_3)_4(TCNE)$

This study supports the feasibility of using TCNQ to connect dimetal units in extended arrays. The 24-membered metallocyclic ring that forms in **1** is a consequence of the Mo–N≡C angles. These angles are expected to vary from one nitrile to another, thereby giving rise to different metallocyclic ring sizes, *e.g*. the structure of $Rh_2(O_2CCF_3)_4(TCNE)$[9] involves a 30-membered ring in a two-dimensional motif [Fig. 4(*b*)], due to the Rh–N–C angle of 180°. In compound **1**, the two independent Mo–N≡C angles of 147.5 and 163.5° are closer to 150°, which permits ring closure with only two ligands [Fig. 4(*a*)], hence the formation of a one-dimensional polymer.

The financial support of the Alfred P. Sloan Foundation, the Camille and Henry Dreyfus Foundation and ACS-PRF is gratefully acknowledged. This research is also supported by the Center for Fundamental Materials Research, Michigan State University. We also thank Dr Donald Ward for helpful discussions regarding the refinement of the structure.

Footnote

† *Crystal data* for **1**: $C_{34}H_{22}F_{18}Mo_3N_2O_{12}$, $M_r = 1280.36$, triclinic, space group $P\bar{1}$, $a = 11.712(2)$, $b = 12.831(3)$, $c = 15.882(3)$ Å, $\alpha = 73.88(3)$, $\beta = 73.87(3)$, $\gamma = 87.87(3)°$, $U = 2200.8(8)$ Å^3, $Z = 2$, $D_c = 1.932$ g cm^{-3}, $F(000) = 1248$, $\mu = 0.978$ mm^{-1}, Mo-Kα ($\lambda_\alpha = 0.710\ 73$ Å). $T = -108$ °C, ω–2θ, $4 \leqslant 2\theta \leqslant 50°$ on a Siemens P3V diffractometer. Reflections measured = 6908; independent reflections = 6536; data used for refinement = 6532; parameters = 625. The structure was solved by direct methods and refined on F^2 using the Siemens SHEXTL v5.03 package. The disorder in the CF_3 groups and *m*-xylene molecules was modelled and the atoms involved were refined isotropically. $R = 0.0478$ ($R_w = 0.119$) for $I > 2\sigma(I)$ and GOF = 1.232. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/220.

References

1 W. Kaim and M. Moscherosch, *Coord. Chem. Rev.*, 1994, **129**, 157.
2 J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385.
3 J. M. Manriquez, G. T. Yee, R. S. McClean, A. J. Epstein and J. S. Miller, *Science*, 1991, **252**, 1415.
4 A. Aumüller and S. Hünig, *Liebigs Ann. Chem.*, 1986, **142**; K. Sinzger, S. Hünig, M. Jopp, D. Bauer, W. Bietsch, J. U. von Schütz, H. C. Wolf, R. K. Kremer, T. Metzenthin, R. Bau, S. I. Khan, A. Lindbaum, C. L. Lengauer and E. Tillmanns, *J. Am. Chem. Soc.*, 1993, **115**, 7696.
5 L. Shields, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1.
6 H. Oshio, E. Ino, T. Ito and Y. Maeda, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 889.
7 M. Moscherosch, E. Waldhör, H. Binder, W. Kaim and J. Fiedler, *Inorg. Chem.*, 1995, **34**, 4326, and references therin.
8 S. L. Bartley and K. R. Dunbar, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 448.
9 F. A. Cotton, Y. Kim and J. Lu, *Inorg. Chim. Acta*, 1994, **221**, 1.
10 K. R. Dunbar and X. Ouyang, *Inorg. Chem.*, submitted.
11 F. A. Cotton and Y. Kim, *J. Am. Chem. Soc.*, 1993, **115**, 8511.
12 K. R. Dunbar and X. Ouyang, *Proc. Conf. on Ferromagnetic and High Spin Molecular Based Materials*, ed. J. S. Miller and A. J. Epstein, *Mol. Cryst. Liq. Cryst.*, 1995, **273**, 21.
13 F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, 1971, **1**, 161.
14 M. Handa, K. Yamada, T. Nakao, K. Kasuga, M. Mikuriya and T. Kotera, *Chem. Lett.*, 1993, 1969.
15 F. A. Cotton, X. Feng, P. Kibala and M. Matusz, *J. Am. Chem. Soc.*, 1988, **110**, 2807.
16 W. E. Buhro, M. H. Chisholm, J. D. Martin, J. C. Huffman, K. Folting and W. E. Streib, *J. Am. Chem. Soc.*, 1989, **111**, 8149.

Received, 10th June 1996; Com. 6/04084E