COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Intermolecular recognition and crystal packing in molybdenum and tungsten coordination polymers as deduced from powder X-ray diffraction data†‡

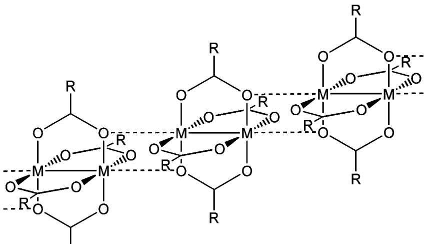
Malcolm H. Chisholm,* Paul J. Wilson and Patrick M. Woodward*

Department of Chemistry, The Ohio State University, Newman and Wolfrom Laboratory, 100 W. 18th Avenue, Columbus OH 43210-1185, USA. E-mail: chisholm@chemistry.ohio-state.edu

Received (in Purdue, IN, USA) 9th January 2002, Accepted 24th January 2002
First published as an Advance Article on the web 25th February 2002

The molecular conformations and packing of [(^{t}BuCO$_2$)$_3$M$_2$(μ-X)M$_2$(O$_2$C^{t}Bu)$_3$], where M = Mo and W, and X = oxalate and perfluoroterephthalate, determined in the solid-state from powder X-ray diffraction analysis, reveal one-dimensional coordination polymers involving pivalate-oxygen to metal interactions (X = perfluoroterephthalate), and oxalate- as well as pivalate-oxygen to metal bonds (X = oxalate), and allows explanation of the unusual state-dependent chromic properties of these compounds.

In the solid-state, $M_2(O_2CR)_4$ compounds tend to associate to form laddered structures involving weak intermolecular $M_2\cdots O$ interactions (see **I**).[1] Thus bridged compounds of the type



I

[(^{t}BuCO$_2$)$_3$M$_2$(μ-X)M$_2$(O$_2$C^{t}Bu)$_3$] would be expected to form coordination polymers in the solid-state. However, predicting the specific details of these structures with any certainty is not possible. If one aspires to understand the crystal packing forces at work in coordination polymers of this type it is essential to know the solid-state structures. However, in many instances such knowledge is not available due to the lack of crystals suitable in size and/or quality for single crystal diffraction analysis. This describes the impasse that we encountered in our understanding of the compounds that are described in this paper.[2]

In this work we describe our attempts to use X-ray powder diffraction data (XRPD) in order to determine the solid-state structures of the compounds [(^{t}BuCO$_2$)$_3$M$_2$(μ-X)M$_2$(O$_2$C^{t}Bu)$_3$], where M = Mo and W and X = oxalate and perfluoroterephthalate (M_4OXA and M_4PFT, respectively). This work was motivated by recent advances in direct-space techniques for solving the crystal structures of molecular solids from XRPD,[3] and the development of the program DASH.[4,5]

Samples of all four compounds (Mo_4OXA, W_4OXA, Mo_4PFT, W_4PFT) were ground in a mortar and pestle and sealed in 0.7 mm diameter capillaries inside a dry box. Monochromatic XRPD data were collected on a Bruker D8 diffractometer. In addition, synchrotron XRPD data were collected on the oxalate bridged compounds.† Based on the observed peak positions and intensities the related tungsten and molybdenum compounds may be considered isostructural, although the diffraction patterns of the molybdenum species were superior to those obtained for the tungsten analogues, whose broad peaks and relatively poor signal-to-noise were not conducive to structure solution attempts. Thus the analysis was carried through in full only for Mo_4OXA and Mo_4PFT.

The data analysis proceeded by the following steps: (a) peak positions were determined using the profile fitting functionality of DASH, (b) potential unit cell dimensions were obtained using the autoindexing package DICVOL,[6] (c) space group symmetries were inferred from the systematic absences, (d) peak intensities were extracted using DASH according to the Pawley method,[7] (e) input models were derived by taking the optimised gas-phase geometries of the model compounds [(HCO$_2$)$_3$Mo$_2$-(μ-X)Mo$_2$(O$_2$CH)$_3$], determined by density functional theory (DFT), and replacing the formate protons with *tert*-butyl groups,[8] (f) the location, orientation and torsional degrees of freedom were then optimised using default simulated annealing parameters provided in DASH, (g) finally constrained Rietveld refinements were carried out using GSAS.[9] The final fits to the observed diffraction patterns are shown in Fig. 1, and the final structural parameters are summarized in Table 1. Full crystallographic details and procedures are provided as ESI.†§

The crystal packing and intermolecular interactions within the two compounds are compared and contrasted in Fig. 2 and 3. While both compounds are coordination polymers in the solid-state, their intermolecular interactions differ significantly (see Fig. 3). In the oxalate structure, each molecule is linked to its neighbours through the agency of four oxalate and two pivalate oxygen-to-metal bonds on either side forming an

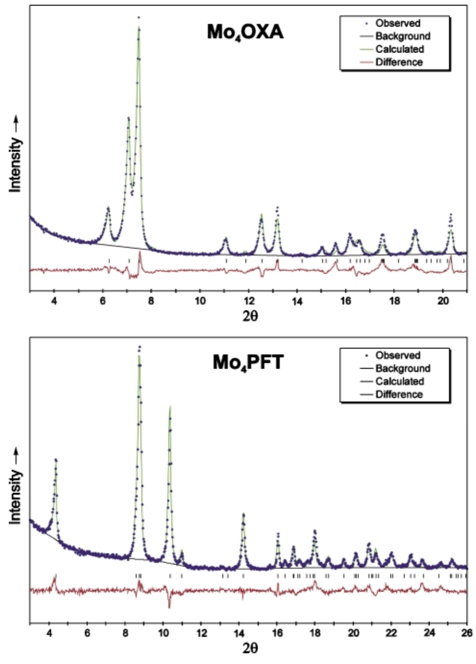


Fig. 1 Fits to the X-ray powder diffraction patterns for [(^{t}BuCO$_2$)$_3$Mo$_2$(μ-X)Mo$_2$(O$_2$C^{t}Bu)$_3$]. The black ticks mark the expected peak positions.

---

† Electronic supplementary information (ESI) available: full details of the X-ray structure determinations. See http://www.rsc.org/suppdata/cc/b2/b200362g/

‡ Dedicated to Drs. Kirsten Folting and William E. Streib on the occasion of their retirement.

DOI: 10.1039/b200362g

infinite chain. The five-membered rings involving the oxalate oxygen-to-metal intermolecular interactions are often seen in mononuclear metal–oxalate complexes,[10] although the six Mo···O distances, which fall in the range 2.9–3.1(1) Å, are relatively long. The oxalate group is slightly twisted, having a C–C torsional angle of ~18°. In the perfluoroterephthalate structure, only pivalate oxygen-to-metal interactions of 3.0(1) Å are present as observed for $\text{M}_2(\text{O}_2\text{CR})_4$ compounds. However, the molecule undergoes a significant twist at the bridging perfluoroterephthalate group such that the two Mo_2 axes are offset by a dihedral angle of ~54°, leading to a twisted double staircase structure. Although the orientation of the aromatic rings is not fully ordered, the refinement suggests that they prefer to align in such a way as to remain nearly planar with one of the two Mo_2 groups in each molecule.

Table 1 Crystallographic data for $[(^t\text{BuCO}_2)_3\text{Mo}_2(\mu\text{-X})\text{Mo}_2(\text{O}_2\text{C}^t\text{Bu})_3]$

X	O_2CCO_2	$\text{O}_2\text{CC}_6\text{F}_4\text{CO}_2$
Formula	$\text{Mo}_4\text{C}_{32}\text{H}_{54}\text{O}_{16}$	$\text{Mo}_4\text{C}_{38}\text{H}_{54}\text{F}_4\text{O}_{16}$
Space group	*Pc*	*C*2
a/Å	16.045(2)	21.011(3)
b/Å	5.8170(6)	5.7245(8)
c/Å	26.817(2)	20.586(3)
β/°	118.826(7)	101.307(7)
V/Å^3	2192.7(5)	2427.8(7)
Z	2	2
Calculated density/g cm^{-3}	1.51	1.68
χ^2 (DASH)	9.73	5.82
χ^2 (GSAS)	8.70	3.31

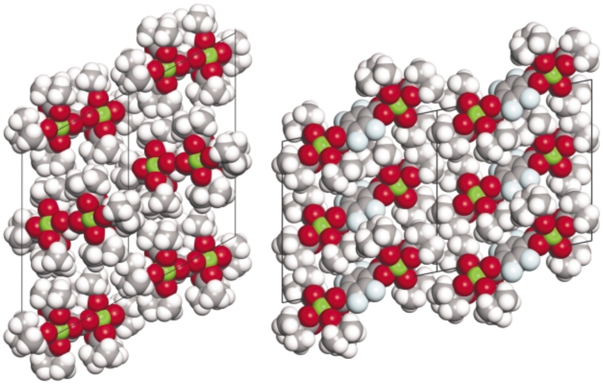


Fig. 2 Space filling representations of the crystal packing in Mo_4OXA (left) and Mo_4PFT (right) showing one layer of molecules viewed down the *b*-axis. Atomic colour scheme: Mo = green, O = red, C = grey, F = pale blue, H = white. For Mo_4PFT only one of the two possible orientations of the aromatic rings is shown for clarity.

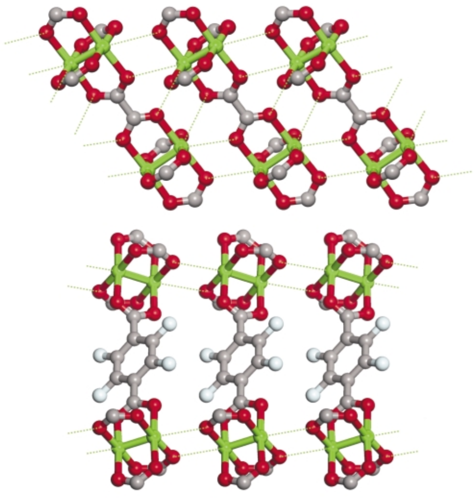


Fig. 3 Intermolecular Mo–O interactions in Mo_4OXA (top) and Mo_4PFT (bottom), which run parallel to the *b*-axis. For clarity, the *tert*-butyl groups have been omitted and only one of the two possible orientations of the aromatic rings is shown for Mo_4PFT. The colour scheme is as in Fig. 2.

The solid-state structures reported here shed light on the origin of the unusual chromic properties of these compounds which are dominated by intense metal-to-ligand bridge charge transfer bands, M_2 δ to bridge π^*, in the visible region of the spectrum.[2] The mull spectra of the oxalate compounds show bathochromic shifts relative to their solution spectra, whereas the perfluoroterephthalate species show strong hypsochromic shifts in the solid-state relative to solution.[11] For example, Mo_4PFT is yellow in the solid-state (λ_{max} ~ 390 nm) but red in tetrahydrofuran solution (λ_{max} ~ 480 nm), whereas Mo_4OXA is maroon in the solid-state (λ_{max} ~ 575 nm) but red in tetrahydrofuran solution (λ_{max} ~ 475 nm). These phase chromic properties can be correlated with the fact that, in solution, there are low barriers to rotation of the two M_2 units. DFT calculations on the models for the oxalate species predict planar D_{2h} structures to be favoured by 3–8 kcal mol^{-1} over fully twisted D_{2d} structures.[8] In the planar structures, there is π-conjugation within the bridge and the LUMOs are low-lying bridge π^* MOs. In the D_{2d} structure of the oxalate species the conjugation is removed. A similar effect is seen for the perfluoroterephthalate compound *via* rotation of the aryl ring. Consequently, the near-planar oxalate structure in the solid-state gives rise to a lower energy MLCT spectrum than in solution. In contrast, the twisted structure seen in the solid-state perfluoroterephthalate structure removes some of the π-conjugation leading to a hypsochromic shift in the mull spectrum, again compared to that in solution.

In conclusion, the present study illustrates the potential importance of the emerging developments in powder diffraction techniques that allow the elucidation of intermolecular interactions within coordination polymers. Based upon both the relatively large unit cells adopted by these compounds and the relatively modest degree of crystallinity of these samples, there can be no doubt that this work represents a very challenging application of this technique. The results, while not of sufficient resolution to obtain highly accurate bond distances and angles, as one could obtain from a single crystal structure determination, do unambiguously reveal the details of the intermolecular interactions which determine the extended structures of these materials. This information is absolutely essential if one hopes to rationally design coordination polymers at the molecular level as so many investigators currently do.

We thank the National Science Foundation for financial support and the Cambridge Crystallographic Data Centre for providing an evaluation copy of DASH.

Notes and references

§ The compounds Mo_4OXA and Mo_4PFT have CCDC reference numbers 178245–178246. See http://www.ccdc.cam.ac.uk/ for more details.

1 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Oxford University Press, London, 1993.

2 R. H. Cayton, M. H. Chisholm, J. C. Huffman and E. B. Lobkovsky, *J. Am. Chem. Soc.*, 1991, **113**, 8709.

3 K. D. M. Harris, M. Tremayne and B. M. Kariuki, *Angew. Chem., Int. Ed.*, 2001, **40**, 1626.

4 DASH was written by W. I. F. David and K. Shankland, and can be purchased from the Cambridge Crystallographic Data Centre, see http://www.ccdc.cam.ac.uk/ for more details.

5 W. I. F. David, K. Shankland and N. Shankland, *Chem. Commun.*, 1998, 931.

6 A. Boultif and D. Louer, *J. Appl. Crystallogr.*, 1991, **24**, 987.

7 G. S. Pawley, *J. Appl. Crystallogr.*, 1981, **14**, 357.

8 B. E. Bursten, M. H. Chisholm, C. M. Hadad, J. Li and P. J. Wilson, *Chem. Commun.*, 2001, 2382.

9 A. C. Larson and R. B. Von Dreele, GSAS Software Suite, Los Alamos, NM, 1987.

10 M. J. S. Dewar and Y. J. Zheng, *THEOCHEM*, 1990, **68**, 157.

11 B. E. Bursten, M. H. Chisholm, R. J. H. Clark, C. M. Hadad, S. Firth, A. M. Macintosh, P. M. Woodward, P. J. Wilson and J. M. Zaleski, *J. Am. Chem. Soc.*, in press.