DALTON
FULL PAPER

Metal–organic co-ordination frameworks based on mixed N- and O-donor ligands: crystal structures of [Co(phth)$_2$(bipy)] and [Co$_2$(mal)$_2$(bipy)(H$_2$O)$_2$] (phth = phthalate, mal = malonate, bipy = 4,4′-bipyridine)†

Philip Lightfoot* **and Alan Snedden**

School of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST.
E-mail: pl@st-and.ac.uk

Received 15th July 1999, Accepted 25th August 1999

Two new metal–organic co-ordination frameworks have been prepared hydrothermally in mixed ligand systems and their crystal structures determined: [Co(phth)$_2$(bipy)] is composed of a complex three-dimensional framework consisting of interlinked Co–phth–Co and Co–bipy–Co chains; [Co$_2$(mal)$_2$(bipy)(H$_2$O)$_2$] is also three-dimensional, being composed of Co–mal sheets which are pillared by bidentate bipy molecules (phth = phthalate, mal = malonate, bipy = 4,4′-bipyridine). Both frameworks enclose small void channels.

Introduction

The crystal engineering of metal–organic co-ordination polymers is now a maturing field. To a modest extent it has been possible to design rationally and build structures with specific architectures in one, two and three dimensions.[1,2] The general strategy for designing such materials relies on the use of multidentate N- or O-donor ligands which have the capacity to bridge between metal centres to form polymeric structures. Hence, many examples exist of 4,4-bipyridine (bipy) acting as a linear bridge between metal centres to form one dimensional chain polymers[3] or "square-box" sheets.[4,5] Polycarboxylic acids have similarly been used to form moderately robust ("zeolitic") frameworks.[6–8]

Extending the scope of this work to systems containing two different organic ligands is so far much less well explored, and it is generally not yet possible to predict either the composition or structure of the product of a reaction consisting of a metal centre and two different, complex organic ligands. In order for some rationalisation and predictive power to be achieved, a much larger database of this type of structure needs to be obtained. However, several very interesting examples have so far been reported including, as ligand combinations, oxalate and pyrazine,[9] oxalate and bipy,[10] pyridine-4-carboxylate and bipy[11] and malonate and bipy.[12]

In the present work we report the outcome of two reactions in mixed ligand systems, one component being the rigid rod-like spacer molecule bipy and the other being a more flexible dicarboxylic acid, specifically phthalate (phth) or malonate (mal).

Experimental

The complexes [Co(phth)$_2$(bipy)] **1** and [Co$_2$(mal)$_2$(bipy)(H$_2$O)$_2$] **2** were synthesized hydrothermally. A 1 : 2 : 1 molar ratio of Co(NO$_3$)$_2$·6H$_2$O (0.2910 g or 1 mmol), dicarboxylic acid (**1** = phthalic, **2** = malonic) and bipy were mixed together in 15 ml water and sealed in a Teflon-lined stainless steel autoclave at 100 °C for 72 h. Autoclaves were removed from the oven and cooled naturally to room temperature. Both compounds crystallised as almost phase-pure materials (Found: C, 57.57; H, 2.98; N, 5.07. Calc. for C$_{26}$H$_{18}$Co$_1$N$_2$O$_8$ **1**: C, 57.26; H, 3.33; N, 5.14%. Found: C, 37.48; H, 3.05; N, 5.18. Calc. for C$_8$H$_8$CoNO$_5$ **2**: C, 37.37; H, 3.14; N, 5.45%).

Table 1 Crystal data and details of structure solution and refinement for complexes **1** and **2**

	1	**2**
Formula	C$_{26}$H$_{18}$CoN$_2$O$_8$	C$_{16}$H$_{16}$Co$_2$N$_2$O$_2$
Crystal system	Tetragonal	Monoclinic
Space group	$I4_122$	$P2_1/n$
a/Å	8.156(5)	7.095(5)
b/Å	8.156(5)	18.735(4)
c/Å	32.927(8)	7.394(5)
β/°		91.53(5)
V/Å^3	2190(2)	982.6(9)
Z	4	2
D_c/g cm^{-3}	1.65	1.74
μ(Mo-Kα)/cm^{-1}	8.44	17.5
Total measured reflections	1593	1948
Total unique reflections	628 (R_{int} = 0.03)	1802 (R_{int} = 0.06)
Observed reflections ($I > 3\sigma(I)$)	566	1113
R,R'	0.025, 0.025	0.070, 0.064

Diffraction data were collected at 25 °C on a Rigaku AFC7S four-circle diffractometer, employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections in the range $15 < 2\theta < 25°$. Further crystallographic details are given in Table 1. Structure solution and refinement was carried out by standard methods using the SIR 92[13] and TEXSAN[14] suites.

CCDC reference number 186/1630.

See http://www.rsc.org/suppdata/dt/1999/3549/ for crystallographic files in .cif format.

Results and discussion

Selected bond lengths and angles for complexes **1** and **2** are given in Tables 2 and 3, respectively. The structure of **1** exhibits a three-dimensional framework structure built up from linear chains of Co–bipy–Co along the ⟨110⟩ directions (Fig. 1) which are bridged to neighbouring chains along the c axis by bidentate phthalate anions. In turn, the Co–phth sublattice forms chains which zigzag between alternate Co–bipy chains (Fig. 2) and effectively interlink the chains into a complex yet highly

---

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3549/

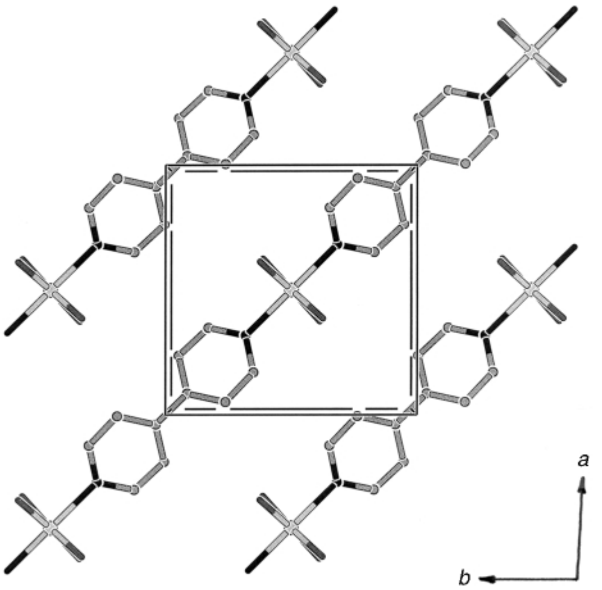

Fig. 1 Polymeric Co–bipy–Co chains in complex **1**.

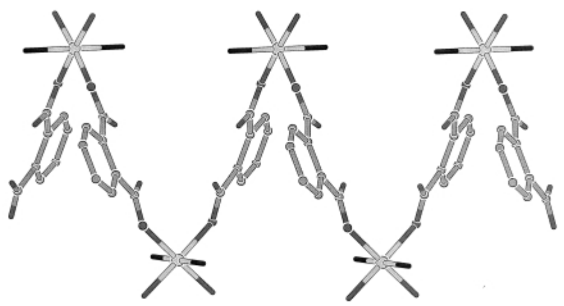

Fig. 2 The Co–phth–Co chain in complex **1**. The cobalt co-ordination is completed by two further phth ligands in *trans* positions to those shown, and two bipy groups. The bipy groups co-ordinated to each of the Co atoms shown belong to *different* Co–bipy–Co chains.

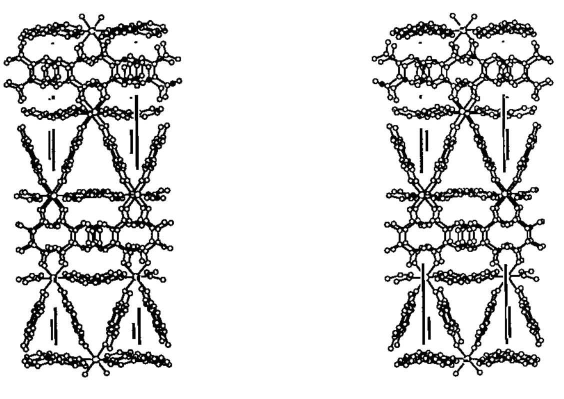

Fig. 3 Stereoplot of the unit cell of complex **1** showing consecutive "end-on" and "face-on" phth bridges, described by the 4_1 screw axis.

symmetrical three-dimensional array (Fig. 3). Within the Co–phth chains there is no π–π interaction between neighbouring rings, the ring centroid–centroid distance being 4.37 Å. The environment around Co is octahedral, being composed of two *trans*-bipy nitrogen atoms and four symmetry-equivalent phthalate oxygens from four different anions (Fig. 4). In order to preserve electroneutrality, the phthalate is required to be monoanionic and a disordered proton position is revealed forming a symmetrical hydrogen-bond between the O(2) positions of one phth group. Atom O(2) therefore does not take part in co-ordination to Co. The framework encloses triangular-shaped void channels along ⟨100⟩, the minimum cross-channel atom–atom contacts being 8.23 and 8.16 Å.

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Co(1)–O(1)	2.100(2) × 4
Co(1)–N(1)	2.206(4) × 2
O(1)–Co(1)–O(1)	175.7(2) × 2
O(1)–Co(1)–O(1)	85.5(1) × 2
O(1)–Co(1)–O(1)	94.7(1) × 2
O(1)–Co(1)–N(1)	87.84(8) × 4
O(1)–Co(1)–N(1)	92.16(8) × 4
N(1)–Co(1)–N(1)	180.0

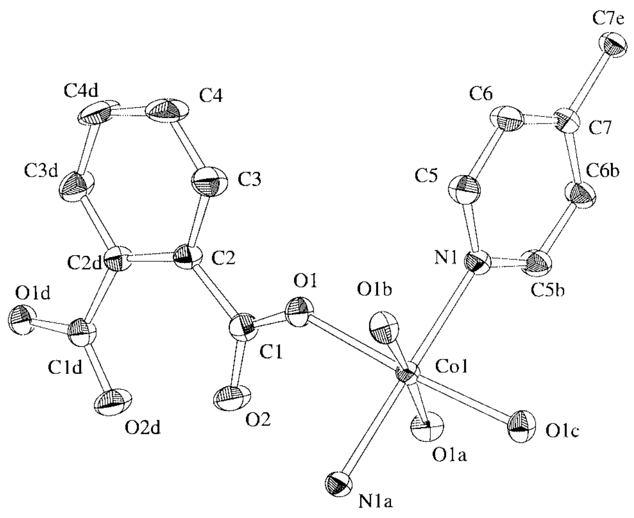

Fig. 4 Building unit of complex **1** with atomic numbering. Symmetry labels: a, $1 - x, -y, z$; b, $\frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2} - z$; c, $\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$; d, $\frac{3}{2} - x, y, \frac{3}{4} - z$; e, $-x, 1 - y, z$.

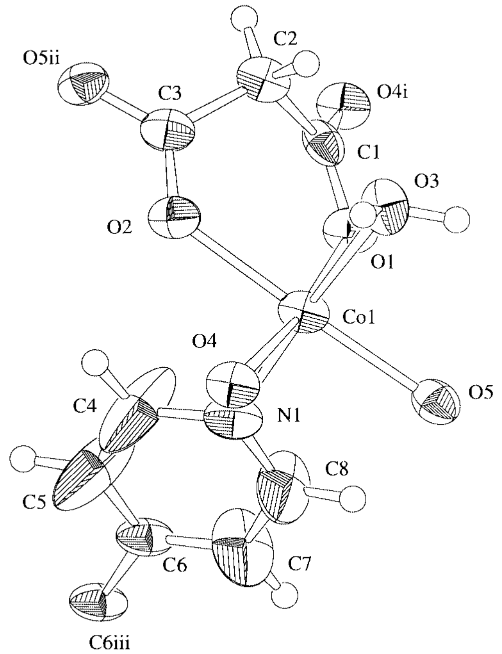

Fig. 5 Building unit of complex **2** with atomic numbering. Symmetry labels: i, $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; ii, $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; iii, $2 - x, -y, 2 - z$.

The asymmetric unit of complex **2**, together with the atom numbering scheme, is shown in Fig. 5. The structure of **2** consists of layers of octahedrally co-ordinated Co atoms bridged by malonate anions within the layers and bipy molecules between layers. A view of the Co–mal layer is shown in Fig. 6. Each malonate chelates a Co, with the remaining two oxygen atoms bridging to two further adjacent Co atoms, thus forming continuous covalently bonded sheets perpendicular to *b*. Correspondingly, each Co atom is co-ordinated by four oxygens from three different malonate anions, with the remaining two *trans*

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Co(1)–O(1)	2.080(7)	Co(1)–O(4)	2.100(6)
Co(1)–O(2)	2.098(7)	Co(1)–O(5)	2.096(7)
Co(1)–O(3)	2.138(7)	Co(1)–N(1)	2.169(9)
O(1)–Co(1)–O(2)	85.7(3)	O(2)–Co(1)–N(1)	92.1(3)
O(1)–Co(1)–O(3)	89.5(3)	O(3)–Co(1)–O(4)	93.7(3)
O(1)–Co(1)–O(4)	170.8(3)	O(3)–Co(1)–O(5)	89.7(3)
O(1)–Co(1)–O(5)	90.0(3)	O(3)–Co(1)–N(1)	175.0(3)
O(1)–Co(1)–N(1)	86.8(3)	O(4)–Co(1)–O(5)	98.7(3)
O(2)–Co(1)–O(3)	91.0(3)	O(4)–Co(1)–N(1)	90.5(3)
O(2)–Co(1)–O(4)	85.6(3)	O(5)–Co(1)–N(1)	86.8(3)
O(2)–Co(1)–O(5)	175.6(3)		

Hydrogen bonds

A H B	A–H/Å	A···B/Å	A–H–B/°
O(3)–H(7)···O(2^{i})	0.95	2.686(9)	148
O(3)–H(8)···O(1^{ii})	0.95	2.663(9)	145

Symmetry relations: (i) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

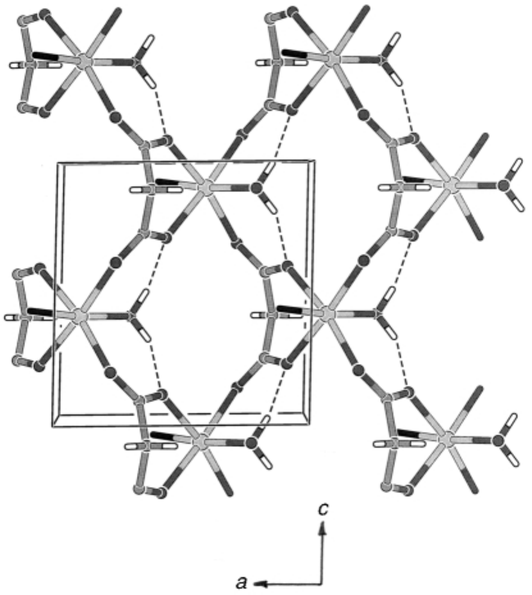

Fig. 6 Projection of a Co–mal layer of complex **2** down the *b* axis.

positions being occupied by a terminal H_2O molecule and the nitrogen of a bridging bipy molecule. The water molecule forms hydrogen bonds to neighbouring malonate groups within the layer. In this case, and in contrast to **1**, the 1:1 Co:anion stoichiometry means that the malonate is not protonated, and is dianionic. The divalent nature of Co in both compounds has been confirmed by bond-valence-sum analysis.[15] A view of the structure perpendicular to the layers is shown in Fig. 7. The bridging bipy molecules can clearly be seen, enclosing void channels of minimum atom–atom cross-section 5.1 × 6.0 Å parallel to the *a* direction.

Conclusion

Two new co-ordination polymers based on mixed O- and N-donor ligands have been synthesized and structurally characterised. Both adopt novel three-dimensional framework topologies. Further systematic work in similar systems, together with studies of the thermal stability and magnetic properties of these and related materials, is ongoing in order to aid the rational design of materials with predictable structure and properties.

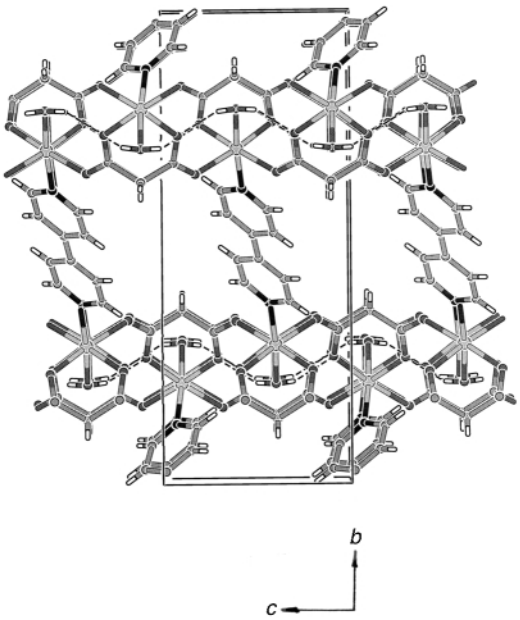

Fig. 7 Unit cell of complex **2** showing channels formed between interlayer bipy bridges.

References

1 C. Janiak, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1431.
2 S. Kitagawa and M. Kondo, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 1739.
3 A. S. Batsanov, M. J. Begley, P. Hubberstey and J. Stroud, *J. Chem. Soc., Dalton Trans.*, 1996, 1947.
4 P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779.
5 O. M. Yaghi, H. Li and T. L. Groy, *Inorg. Chem.*, 1997, **36**, 4292.
6 O. M. Yaghi, H. Li and T. L. Groy, *J. Am. Chem. Soc.*, 1996, **118**, 9096.
7 C. Livage, C. Egger, M. Nogues and G. Ferey, *J. Mater. Chem.*, 1998, **8**, 2743.
8 S. O. H. Gutschke, M. Molinier, A. K. Powell and P. T. Wood, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 991.
9 S. Kitagawa, T. Okubo, S. Kawata, M. Kondo, M. Katada and H. Kobayashi, *Inorg. Chem.*, 1995, **34**, 4790.
10 J. Y. Lu, M. A. Lawandy, J. Li, T. Yuen and C. L. Lin, *Inorg. Chem.*, 1999, **38**, 2695.
11 L. R. MacGillivray, R. H. Groeneman and J. L. Attwod, *J. Am. Chem. Soc.*, 1998, **120**, 2676.
12 J. Li, H. Zeng, J. Chen, Q. Wang and X. Wu, *Chem. Commun.*, 1997, 1213.
13 A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Gugliardi and G. Polidori, *J. Appl. Crystallogr.*, 1993, **26**, 343.
14 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1992.
15 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.

Paper 9/05726I