CHEMISTRY
A EUROPEAN JOURNAL

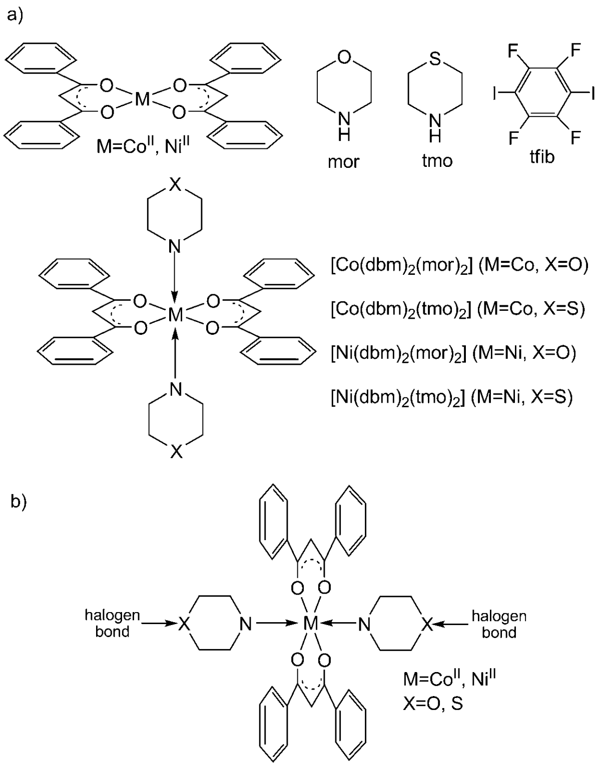
DOI: 10.1002/chem.201000049

A Three-Component Modular Strategy to Extend and Link Coordination Complexes by Using Halogen Bonds to O, S and π Acceptors

Giuseppe Lapadula,[a] Nenad Judaš,[b] Tomislav Friščić,*[a] and William Jones*[a]

We report a metal–organic design that allows decoration and cross-linking of metal centres through halogen-bond-directed co-crystallisation. Halogen bonds have emerged as reliable and directional interactions, alternative to hydrogen bonds, in supramolecular engineering of organic solids.[1] Halogen bonds that form between a polarisable and electron-deficient halogen atom (the halogen-bond donor) and an electron-rich Lewis base (the halogen-bond acceptor)[2] have been utilised to construct co-crystals,[3] salts,[4] ionic inclusion frameworks[5] and liquid crystals.[6] An attractive target in halogen-bond-based materials engineering is the inclusion of transition metals, which are expected to introduce interesting magnetic, electrical and optical properties. So far, formation of halogen-bonded co-crystals with metal–organic species has proven difficult.[7,8] Although the self-assembly of metal–organic molecules with self-complementary halogen-bonding functionalities was demonstrated,[9] attempts to construct multicomponent molecular materials have not been successful.[10] This difficulty was explained by competition with other non-covalent interactions, such as hydrogen bonds[11] and halogen–halogen interactions.

In our search for a suitable strategy to decorate metal–organic complexes using halogen bonds we sought to achieve the highest possible generality. Thus, we were interested in a modular[12] approach that would allow adding different halogen-bonding functionalities onto a given metal–organic fragment. We recognised planar complexes of divalent metals with dibenzoylmethanate anions (dbm$^-$) as suitable candidates. In particular, nickel(II) and cobalt(II) dibenzoylmethanates ([Ni(dbm)$_2$] and [Co(dbm)$_2$], Scheme 1 a) provide a coordinatively unsaturated and equatorially protected platform onto which a molecule with a halogen-bonding functionality could be attached. We targeted the ditopic molecules morpholine (mor) and thiomorpholine (tmo) as suitable ligands[13] that would attach through Co–N (or Ni–N) bonds to form coordinatively saturated complexes:[14] [Co(dbm)$_2$(mor)$_2$], [Co(dbm)$_2$(tmo)$_2$], [Ni(dbm)$_2$(mor)$_2$] and [Ni(dbm)$_2$(tmo)$_2$] (Scheme 1 a). These complexes would then



Scheme 1. Molecular diagrams of: a) a metal(II) dibenzoylmethanate, morpholine (mor), thiomorpholine (tmo), halogen-bond donor tfib and tmo- or mor-substituted metal(II) dibenzoylmethanate; b) expected assembly by coordination and halogen bonds.

---

[a] G. Lapadula, Dr. T. Friščić, Prof. W. Jones
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB2 1EW (UK)
Fax: (+44) 1223-336-017
E-mail: tf253@cam.ac.uk
wj10@cam.ac.uk

[b] Dr. N. Judaš
Department of Chemistry, University of Zagreb
Horvatovac 102a, HR-10000 Zagreb (Croatia)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000049.

contain oxygen or sulfur atoms as potential halogen-bond acceptors that could link to donors such as 1,4-diiodotetrafluorobenzene (tfib) (Scheme 1 b). A simpler design was previously utilised for coordination- and hydrogen-bond-driven assembly of metal complexes,[15,16] but was never used for the assembly of more than two types of molecules.

The tmo- or mor-substituted [Co(dbm)$_2$] and [Ni(dbm)$_2$] complexes were obtained by re-crystallisation of the metal dibenzoylmethanate dihydrate from liquid mor or tmo. The materials could also be prepared from stoichiometric amounts of reactants by liquid-assisted grinding (LAG).[17] Initial attempts to form halogen-bonded co-crystals of tfib and [Co(dbm)$_2$(tmo)$_2$] from solutions in chloroform resulted only in the re-crystallisation of [Co(dbm)$_2$(tmo)$_2$]. However, LAG of [Co(dbm)$_2$(tmo)$_2$] and tfib provided a new material (**1**), evidenced by X-ray powder diffraction (XRPD) pattern (Figure 1 a).[18,19]

Varying the stoichiometric ratio of the reactants in LAG indicated that **1** is formed from [Co(dbm)$_2$(tmo)$_2$] and tfib in the stoichiometric ratio 1:6. Subsequently, single crystals of **1** were obtained from solutions in chloroform involving [Co(dbm)$_2$(tmo)$_2$] and tfib in ratios between 1:6 and 1:10.

Single-crystal X-ray crystal structure determination revealed the success of our modular strategy. Each [Co(dbm)$_2$(tmo)$_2$] molecule in **1** is attached to two tfib molecules through a short S···I separation of 3.15 Å. The resulting five-component [Co(dbm)$_2$(tmo)$_2$(tfib)$_2$] assemblies have a wheel-and-axle shape and are about 3 nm in length. In addition to tfib attached to the [Co(dbm)$_2$(tmo)$_2$] fragments, **1** also contains additional tfib molecules as guests,[20,21] resulting in the overall composition [Co(dbm)$_2$(tmo)$_2$(tfib)$_2$]·4 tfib (Figure 1 b,c). In that way, **1** represents a halogen-bonded analogy of a metal-based wheel-and-axle inclusion compounds.[22,23]

The [Co(dbm)$_2$(tmo)$_2$(tfib)$_2$] assemblies in **1** stack in the [110] direction through short C···I contacts (3.49 Å) between the phenyl rings of dbm and iodine atoms of tfib (Figure 1 d,e). These contacts are significantly shorter than the sum of the van der Waals radii (≈3.7 Å)[24] and can be classified as weak halogen bonds of the C···I type.[8a,25] To test this interpretation, we performed a search of the Cambridge Structural Database (CSD)[26,27] for C−I···C contacts, with the acceptor carbon atom defined as a part of a π system (i.e., aromatic ring, sp^2 or sp hybridised). The results revealed two peaks in the distribution of I···C distances with respect to the C−I···C angle. The first peak occurs at C···I distance close to 3.6 Å and an angle of 90°, corresponding to van der Waals I···C contacts (**I**, Figure 2 a). The second peak (**II**, Figure 2 a) occurs at significantly shorter separations of about 3.3 Å and is associated with linear arrangements expected for halogen bonds.[1,2,8a,25] Consequently, the assembly of [Co(dbm)$_2$(tmo)$_2$(tfib)$_2$] units is best described as a one-dimensional chain held by coordination and halogen bonds.

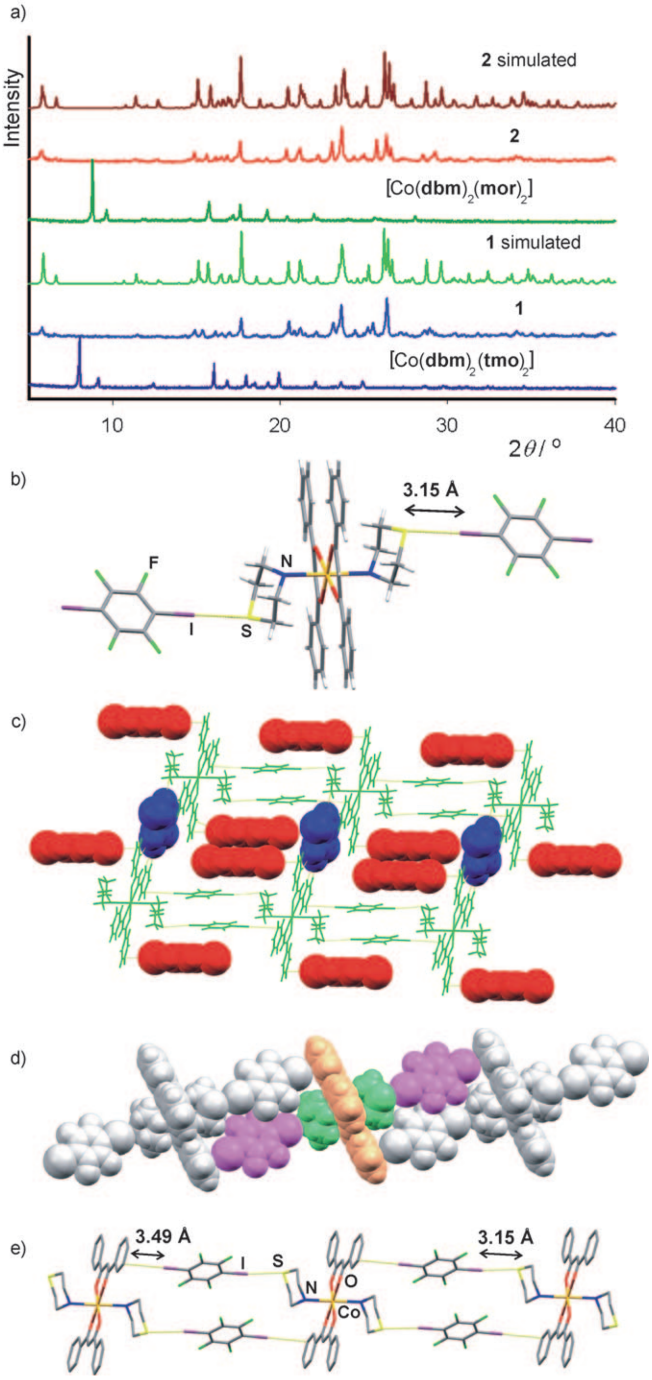


Figure 1. a) XRPD patterns[18] (bottom to top): [Co(dbm)$_2$(tmo)$_2$]; **1** prepared by LAG; simulated for the crystal structure of **1**; [Co(dbm)$_2$(mor)$_2$]; **2** prepared by LAG and simulated for the crystal structure of **2**; b) a single [Co(dbm)$_2$(tmo)$_2$(tfib)$_2$] assembly; c) guest tfib molecules (space-filling) between the chains of [Co(dbm)$_2$(tmo)$_2$(tfib)$_2$] (wireframe). Symmetrically different tfib guests are shown in blue and red; d) stacking of [Co(dbm)$_2$(tmo)$_2$(tfib)$_2$] assemblies (in the central assembly: orange = [Co(dbm)$_2$], green = tmo, purple = tfib) and e) S···I and C···I interactions in **1**.

Liquid-assisted grinding of [Co(dbm)$_2$(mor)$_2$] with tfib provided a material of composition [Co(dbm)$_2$(mor)$_2$(tfib)$_2$]·4 tfib (**2**), isostructural to **1**. The isostructural nature of **2**, confirmed by single-crystal X-ray diffraction, is consistent with the structural similarity of O and S acceptors in halogen bonding.[13] In the crystal of **2**, the [Co(dbm)$_2$(mor)$_2$]

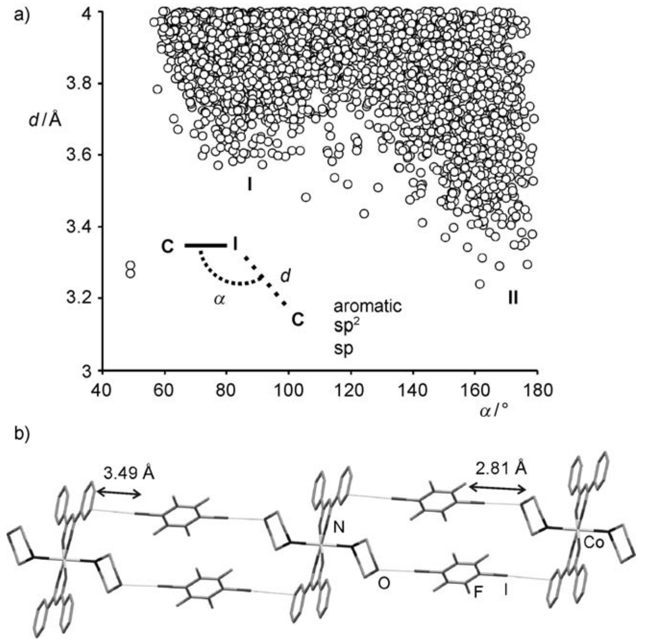


Figure 2. a) Scatterplot of C···I separations (d) versus the C–I···C angle (α) in C–I···C fragments involving aromatic, sp^2- or sp-hybridised carbon acceptors. The maximum **I** corresponds to van der Waals contacts, while **II** is assigned to halogen-bonding interactions and b) a halogen- and coordination-bonded chain in $[Co(dbm)_2(tmo)_2(tfib)_2]$.

units are crosslinked by short O···I (O···I separation: 2.81 Å) and C···I (3.49 Å) interactions to tfib (Figure 2b).

Similarly, LAG of $[Ni(dbm)_2(mor)_2]$ with tfib provided a material (**3**) that was identified as $[Ni(dbm)_2(mor)_2(tfib)_2]\cdot 4\,tfib$, as it is isostructural its cobalt analogue. In contrast, $[Ni(dbm)_2(tmo)_2]$ did not react with tfib, either in solution or by grinding. Presumably, the lack of reactivity could be related to the relative weakness of S···I interactions[13] compared to O···I ones.[28] Consequently, our strategy resulted in altogether three halogen-bonded co-crystals of substituted metal dibenzoylmethanates. Co-crystals **1** and **2** could also be synthesised in a one-pot LAG reaction[16] involving $[Co(dbm)_2]\cdot 2H_2O$, tfib and tmo or mor, in respective stoichiometric ratio 1:2:6.

In summary, we have demonstrated a modular approach to decorate neutral metal complexes of Ni^{II} and Co^{II} with I···O or I···S halogen bonds. Our approach resulted in a coordination and halogen-bonded analogy of inclusion materials based on wheel-and-axle units. The unexpected association of the five-component building blocks into a supramolecular polymer highlights the importance of weak interactions in the design of halogen-bonded materials. We are currently investigating the generality of our design.

Experimental Section

In a typical LAG[17] experiment, $CHCl_3$ (75 µL) was added to of the mixture of solid reactants (0.200 g), along with two stainless steel balls of 7 mm diameter. The mixture was ground for 30 min in a stainless steel jar using a Retsch MM200 mill at 30 Hz. The samples were subsequently analysed using XRPD, FTIR-ATR spectroscopy and thermogravimetric analysis.[18] CCDC-760938 (**1**), -760938 (**2**) and -760940 (low-temperature re-determined $[Co(dbm)_2(tmo)_2]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The Herchel Smith Fund is acknowledged for a research fellowship (T.F.) and the Erasmus programme is acknowledged for funding (G.L.). Professor Pierangelo Metrangolo from the Politecnico di Milano is acknowledged for a fruitful discussion. Dr Mary Vickers, University of Cambridge, is acknowledged for help in addressing the problems of X-ray fluorescence of prepared materials.

Keywords: cocrystals · coordination compounds · halogen bonding · solid-state structures · supramolecular chemistry

---

[1] a) P. Metrangolo, G. Resnati, *Science* **2008**, *321*, 918; b) P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, *Angew. Chem.* **2008**, *120*, 6206; *Angew. Chem. Int. Ed.* **2008**, *47*, 6114.
[2] a) R. Cabot, C. A. Hunter, *Chem. Commun.* **2009**, 2005; b) P. Metrangolo, H. Neukirch, T. Pilati, G. Resnati, *Acc. Chem. Res.* **2005**, *38*, 386.
[3] a) T. Caronna, R. Liantonio, T. A. Logothetis, P. Metrangolo, T. Pilati, G. Resnati, *J. Am. Chem. Soc.* **2004**, *126*, 4500; b) R. B. Walsh, C. W. Padgett, P. Metrangolo, G. Resnati, T. W. Hanks, W. T. Pennington, *Cryst. Growth Des.* **2001**, *1*, 165; c) D. Cinčić, T. Friščić, W. Jones, *Chem. Mater.* **2008**, *20*, 6623.
[4] a) G. Mínguez Espallargas, L. Brammer, D. R. Allan, C. R. Pulham, N. Robertson, J. E. Warren, *J. Am. Chem. Soc.* **2008**, *130*, 9058; b) G. Mínguez Espallargas, L. Brammer, P. Sherwood, *Angew. Chem.* **2006**, *118*, 449; *Angew. Chem. Int. Ed.* **2006**, *45*, 435.
[5] P. Metrangolo, Y. Carcenac, M. Lahtinen, T. Pilati, K. Rissanen, A. Vij, G. Resnati, *Science* **2009**, *323*, 1461.
[6] C. Präsang, H. L. Nguyen, P. N. Horton, A. C. Whitwood, D. W. Bruce, *Chem. Commun.* **2008**, 6164.
[7] L. Brammer, G. Mínguez Espallargas, S. Libri, *CrystEngComm* **2008**, *10*, 1712.
[8] Halogen bond-driven co-crystallisation of organometallic molecules has been reported, see: a) M. Amati, F. Lelj, R. Liantonio, P. Metrangolo, S. Luzzati, T. Pilati, G. Resnati, *J. Fluorine Chem.* **2004**, *125*, 629; b) S. Libri, N. A. Jasim, R. N. Perutz, L. Brammer, *J. Am. Chem. Soc.* **2008**, *130*, 7842.
[9] a) S. Muniappan, S. Lipstman, I. Goldberg, *Chem. Commun.* **2008**, 1777; b) P. Smart, G. Mínguez Espallargas, L. Brammer, *CrystEngComm* **2008**, *10*, 1335.
[10] C. B. Aakeröy, N. Schultheiss, J. Desper, C. Moore, *CrystEngComm* **2007**, *9*, 421.
[11] a) C. B. Aakeröy, M. Fasulo, N. Schultheiss, J. Desper, C. Moore, *J. Am. Chem. Soc.* **2007**, *129*, 13772; b) C. B. Aakeröy, N. C. Schultheiss, A. Rajbanshi, J. Desper, C. Moore, *Cryst. Growth Des.* **2009**, *9*, 423; c) C. B. Aakeröy, J. Desper, B. A. Helfrich, P. Metrangolo, T. Pilati, G. Resnati, A. Stevenazzi, *Chem. Commun.* **2007**, 4236.
[12] T. Friščić, L. R. MacGillivray, *Croat. Chem. Acta* **2006**, *78*, 327.
[13] D. Cinčić, T. Friščić, W. Jones, *Chem. Eur. J.* **2008**, *14*, 747.
[14] a) N. Judaš, I. Halasz, D.-K. Bučar, *Acta Crystallogr. Sect. E* **2006**, *62*, m283; b) B. Kaitner, E. Meštrović, *Acta Crystallogr. Sect. E* **2007**, *63*, m1549.
[15] a) C. B. Aakeröy, N. Schultheiss, J. Desper, *Inorg. Chem.* **2005**, *44*, 4983; b) C. B. Aakeröy, J. Desper, J. Valdés-Martínez, *CrystEngComm* **2004**, *6*, 413.

[16] a) T. Friščić, E. Meštrović, D. Škalec-Šamec, B. Kaitner, L. Fábián, *Chem. Eur. J.* **2009**, *15*, 12644; b) T. Friščić, L. Fábián, *CrystEngComm* **2009**, *11*, 743.

[17] a) D. Cinčić, T. Friščić, W. Jones, *J. Am. Chem. Soc.* **2008**, *130*, 7524; b) T. Friščić, A. V. Trask, W. Jones, W. D. S. Motherwell, *Angew. Chem.* **2006**, *118*, 7708; *Angew. Chem. Int. Ed.* **2006**, *45*, 7546.

[18] XRPD measurements were made difficult by the fluorescence of **1**, **2** and **3**. Consequently, XRPD patterns of acceptable quality were obtained by using a secondary monochromator.[19] Such problems were not encountered with [Co(dbm)$_2$(tmo)$_2$], [Co(dbm)$_2$(mor)$_2$], [Ni(dbm)$_2$(tmo)$_2$], [Ni(dbm)$_2$(mor)$_2$] or tfib.

[19] P. Norby, *J. Appl. Crystallogr.* **1994**, *27*, 129.

[20] One of the included tfib molecules participates in another set of short C···I contacts (C···I separation: 3.53 Å) with the phenyl groups of the supramolecular chain, while the other participates in C−H···F interactions (C···F separation range: 3.08–3.30 Å).[21]

[21] J. D. Dunitz, W. B. Schweizer, *Chem. Eur. J.* **2006**, *12*, 6804.

[22] a) D. V. Soldatov, *J. Chem. Crystallogr.* **2006**, *36*, 747; b) A. Bacchi, M. Carcelli, T. Chiodo, F. Mezzadri, *CrystEngComm* **2008**, *10*, 1916.

[23] a) D. V. Soldatov, P. Tinnemans, G. D. Enright, C. I. Ratcliffe, P. R. Diamente, J. A. Ripmeester, *Chem. Mater.* **2003**, *15*, 3826; b) A. Bacchi, E. Bosetti, M. Carcelli, P. Pelagatti, D. Rogolino, G. Pelizzi, *Inorg. Chem.* **2005**, *44*, 431.

[24] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[25] Linear C−Cl···π and C−Br···π contacts have recently been recognised as important contributors to molecular recognition in biological systems, see: H. Matter, M. Nazaré, S. Güssregen, D. W. Will, H. Schreuder, A. Bauer, M. Urmann, K. Ritter, M. Wagner, V. Wehner, *Angew. Chem.* **2009**, *121*, 2955; *Angew. Chem. Int. Ed.* **2009**, *48*, 2911.

[26] Cambridge Structural Database, version 5.30 (November 2008), update 1.

[27] a) F. H. Allen, R. Taylor, *Chem. Soc. Rev.* **2004**, *33*, 463; b) F. H. Allen, *Acta Crystallogr. Sect. B* **2002**, *58*, 380.

[28] This is not the only difference in mechanochemistry of tmo- and mor-based adducts of [Co(dbm)$_2$] and [Ni(dbm)$_2$]. For example, while mechanosynthesis yields [Co(dbm)$_2$(tmo)$_2$] and [Ni(dbm)$_2$(tmo)$_2$] as isostructural solids, [Ni(dbm)$_2$(mor)$_2$] differs from [Co(dbm)$_2$(mor)$_2$] by forming two polymorphs, one isostructural to [Co(dbm)$_2$(mor)$_2$] and the other isostructural to [Co(dbm)$_2$(tmo)$_2$].

Received: January 8, 2010