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Large family of halogen-bonded cocrystals involving $CoCl_2L_2$ building blocks

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An overwhelming majority of reported studies and strategies for incorporating metals into halogen-bonded architectures have focused on single component metal-organic solids which include the formation of metal-organic complexes using ligands with pendant halogen bond donor groups (e.g. acetylacetonate derivatives or halopyridines) [1,2]. On the other hand, synthesis of multi-component metal–organic materials with organic halogen bond donors has received much less attention. Most reports on such materials have focused on the formation of ionic structures involving metal complexes with simple inorganic ligands (e.g., Cl^-, CN^-, SCN^- etc.) and cations as halogen bond donors (e.g. halopyridines) [1,2]. Much less explored systems are neutral metal–organic cocrystals. Few approaches have been presented as promising and they have generally been focused on cocrystals of neutral halogen bond donors and metal complex subunits with pendant acceptor groups: halogen atoms [3], chelating ligands such as imines and acetylacetonate derivatives [4,5], neutral molecules coordinated to metal centre such as morpholine or thiomorpholine [6]. Following our previous study where we described the halogen bonding proclivity of the chlorine atom coordinated to the Co(II) metal centre, in this work we demonstrate a strategy for synthesis of halogen-bonded metal-organic cocrystals by utilizing metal complexes whose pendant chloride group enables halogen bonding [7]. A series of 12 cocrystals involving octahedral $CoCl_2L_2$ complexes [L = 2,2' bipyridine (**1**) or 1,10 phenantroline (**2**)] as halogen bond acceptors were prepared by both liquid-assisted grinding and conventional solution-based methods. The efficacy of this strategy is evident by the assembly of a large family of cocrystals involving six perfluorinated halogen bond donors: 1,4-diiodotetrafluorobenzene (**14tfib**), 1,3-diiodotetrafluorobenzene (**13tfib**), 1,2-diiodotetrafluorobenzene (**12tfib**), 1,3,5-triiodotrifluorobenzene (**135tfib**), iodopentafluorobenzene (**ipfb**) and octafluoro-1,4-diiodobutane (**ofib**). Single crystal X-ray diffraction experiments have shown that cocrystals display different crystal packing, governed by Cl···I halogen bonds involving halogen bond donor iodine atoms and metal complex chlorine atoms (varying from 3.061 to 3.471 Å). The monotopic donor **ipfb** and ditopic donor **12tfib** form discrete 2:1 or 1:1 halogen bonded complexes with both acceptors. The exception is **12tfib** which, with **1,** acts as both monotopic and ditopic donor thus forming two cocrystals, 2:1 (discrete complex) and 1:1 (chains). The halogen bond motifs in cocrystals based on **14tfib**, **13tfib**, **135tfib** and **ofib** exhibit higher dimensionality, halogen bonded chains. The exceptions are two cocrystals of **1**, one with **13tfib** forming a two-dimensional layered halogen-bonded structure, and with **ofib** forming a three-dimensional halogen-bonded structure.

References:

[1] Bertani, R. et al. (2010) Coord. Chem. Rev., 254, 677-695.
[2] Li, B. et al (2016) Coord. Chem. Rev., 308, 1-21.
[3] Ghosh, B. N. et al. (2016) Cryst. Growth Des., 16, 2527-2534.
[4] Cinčić, D. & Friščić, T. (2014) CrystEngComm, 16, 10169-10172.
[5] Nemec, V. et al. (2017) Cryst. Growth Des., 17, 6169-6173.
[6] Lapadula, G. et al. (2010) Chem. Eur. J., 16, 7400-7403.
[7] Lisac, K. & Cinčić, D. (2017) Crystals, 7, 363.

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