

s9.m3.p37 Hexagonal and Pseudo-Hexagonal Grid Motifs in Inorganic Crystal Engineering: Cobalt(II) Cupferronato Complexes Incorporating Neutral N-Donors with Intermolecular NH₂ Connectors.

A. Deák,^a A. Kálmán,^a L. Párkányi,^a M. Venter^b and I. Haiduc,^b
^a*Institute of Chemistry, Chemical Research Center of the Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary,* ^b*Babes-Bolyai University, Department of Inorganic Chemistry, Arany János 11, RO-3400 Cluj-Napoca, Romania.*

Keywords: molecular interactions, supramolecular assemblies.

Aakeröy and co-workers^[1] have outlined the possibilities of creating infinite hydrogen-bonded 1D, 2D and 3D metal-containing frameworks based on metal complexes in which the specific coordination geometry propagates through the crystal structure by intermolecular connectors of the ligands. In these examples the complementary functions of the same ligands govern the self-assembly of complexes *via* hydrogen-bonded interactions.

We have supplemented this strategy by using different multifunctional hydrogen-bond acceptor and donor ligands, as well as octahedral coordination geometries around the metal ions. Employing this strategy neutral donor molecules with NH₂ functions, such as 2-amino-pyridine (2-NH₂Py) and 2,6-diamino-4-phenyl-1,3,5-triazine (dpt) were tested as potentially versatile ligands. In addition, we have recently studied the coordination behavior and hydrogen-bond acceptor ability of cupferronato (PhN₂O₂⁻) ligand.^[2]

The cobalt(II) cupferronato complexes [Co(PhO₂N₂)₂(2-NH₂Py)₂] (**1**) and [Co(PhO₂N₂)₂(dpt)₂]·[Co(PhO₂N₂)₂(EtOH)₂] (**2**) were characterised by X-ray diffraction analysis. Intra- and intermolecular N–H···O and N–H···N interactions between symmetry related molecules of **1** lead to hexameric aggregates which connect through common edges into a 2D supramolecular network of hexagonal-grid type. The crystal lattice of **2** contains the [Co(PhO₂N₂)₂(dpt)₂] (**2a**) and [Co(PhO₂N₂)₂(EtOH)₂] (**2b**) molecular subunits self-assembled by hydrogen-bonds. In complex **2** the complementary dpt units of **2a** molecules are connected by intermolecular N–H···N hydrogen-bonds, generating infinite linear chains. The **2a** and **2b** subunits are self-assembled by N–H···O and O–H···N hydrogen-bondings, completing a 2D supramolecular network consisting of pseudo-hexagonal grid sheets. Intramolecular N–H···O hydrogen-bondings between the NH₂ groups and the oxygen atom of the cupferronato anion can be observed in both **1** and **2**.

[1] C. B. Aakeröy, A. M. Beatty, D. S. Leinen, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1815–1819.

[2] a) A. Deák, I. Haiduc, L. Párkányi, M. Venter, A. Kálmán, *Eur. J. Inorg. Chem.* **1999**, 1593–1596; b) A. Deák, M. Venter, A. Kálmán, L. Párkányi, L. Radics, I. Haiduc, *Eur. J. Inorg. Chem.* **2000**, 127–132; c) A. Deák, L. Párkányi, A. Kálmán, M. Venter, I. Haiduc, *Acta Crystallogr.* **1998**, *C54*, IUC9800036.