

MS29 Crystal engineering: structural flexibility, phase transitions and non-standard manipulation of synthons

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Metal centres as electron donors in σ -hole interactions

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Abstract

In this communication, the role of metal centres as electron donors is analyzed from two perspectives. Firstly, it highlights recent studies discovering unconventional halogen and chalcogen bonding (HaB and ChB, respectively) that involves positively charged metal centres. These centres provide their filled d-orbitals for HaB/ChB, and thus behave as nucleophilic components toward the σ -holes at the halogen or chalcogen atoms (see Figure 1a). This role of some electron-rich transition metal centres can be regarded as an oxymoron in the sense that the metal is, in most cases, formally cationic; consequently, its nucleophilic function is surprising. The importance of Ha \cdots d-[M] (Ha=halogen; M is Group 9 (Rh, Ir), 10 (Ni, Pd, Pt), or 11 (Cu, Au)) interactions in crystal engineering is emphasized by showing remarkable examples reported and uncovered by processing of the Cambridge Structural Database (CSD),[1] where this Ha \cdots d-[M] directional interaction guides the formation of solid supramolecular assemblies of different dimensionalities.

Secondly, by exploring the CSD and using DFT calculations it is shown that the metal centre can also enhance the σ -hole interaction (in particular ChBs) by metal coordination (see Figure 1b). Moreover, the new σ -hole that is formed opposite to the M–Ch bond provides an extra possibility of binding. In fact, an example where Pd–Te \cdots Cl chalcogen bond is provided that has a strong directing role and is responsible for the formation of an interesting supramolecular polymer.

The results derived from this study might be useful to those scientists working in the fields of supramolecular chemistry and crystal engineering as well as to inspire chemists working in supramolecular catalysis.

References

[1] D. M. Ivanov, N. A. Bokach, V. Yu. Kukushkin, A. Frontera, Metal Centers as Nucleophiles: Oxymoron of Halogen Bond-Involving Crystal Engineering. *Chem Eur. J.*, 2022, 28, e202103173.

