Poster

Charge transfer causes bulk conductivity through π-hole interactions

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π-hole interactions involving metal-bound electron donor are studied for the first time on four isomorphous co-crystals of [Cu(terpy)Cl*X*] (terpy = 2,2′:6′,2″-terpyridine; *X* = Br, I) and perhalogenquinone *X*′$_4$Q (*X*′ = Cl, Br). Close contact between the halide *X* from [Cu(terpy)Cl*X*] and the quinoid ring (Fig. 1a) has geometry similar to those observed previously for free halides [1,2]. This is an *n*→π* interaction [3] with a partial charge transfer from the halide to the quinone. Therefore, it weakens the Cu–*X* bond: in [Cu(terpy)ClI]·Cl_4Q the length of Cu–I bond is 2.844 Å, which represents an elongation of 0.18 Å.

The extreme elongation indicates charge transfer from the Cu–*X* bond to the quinone, which then has a partial semiquinoid radical character. This is indicated by black colour of the crystals; the neutral quinone and the [Cu(terpy)Cl*X*] complex are yellow. Degree of charge transfer is probably similar to previously studied charge transfer between an uncoordinated iodide and tetrabromoquinone, which is approximately 10 % [3]. Energy of the π-hole interaction in [Cu(terpy)ClI]·Cl_4Q is estimated to −20.8 kcal mol^{-1}, comparable to the strongest hydrogen bonds.

A weaker π-hole interaction between Cl atom of the complex and a symmetry-equivalent quinoid ring helps form π-hole-bonded chains parallel to [100] (Fig. 1b). Since the crystals grow as rods extended along the *a* axis, electrical contacts could be attached to a single crystal, allowing study of electrical properties by impedance spectroscopy. The compounds are weak semiconductors: room-temperature DC conductivity of [Cu(terpy)ClI]·Cl_4Q is 10^{-9} S cm^{-1}.

This is the first documented case of conductivity through a π-hole interaction and shows that it may find use in materials chemistry.

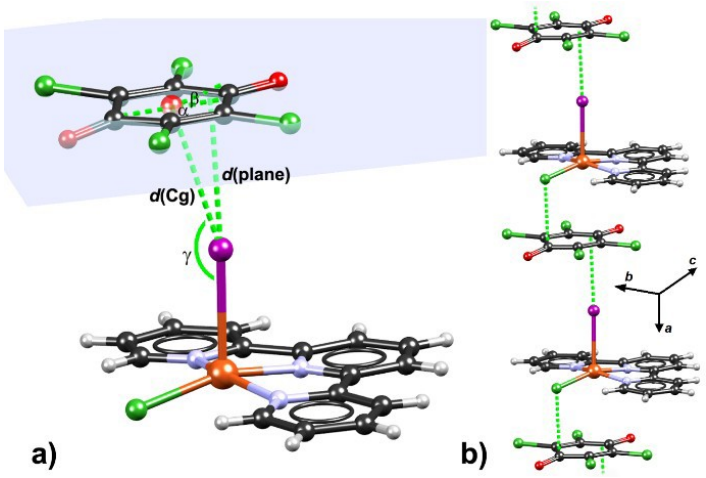

Figure 1. a) Short halogen-quinone π-hole contact in [Cu(terpy)ClI]·Cl_4Q with relevant geometric parameters marked. Offset is calculated as *d*(Cg)·*cos*(α); b) an infinite chain of π-hole interactions parallel to the axis *a*.

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[2] Milašinović, V. & Molčanov, K. (2021). *CrystEngComm* **23**, 8209-8214.

[3] Milašinović, V., Vuković, V., Krawczuk, A., Molčanov, K., Hennig C. & Bodensteiner, M. (2023). *IUCrJ* **10**, 156-163.

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