

Gold(III) as an effective electrophilic site, namely coinage bond donor: assembly of AuCl_4^- units into supramolecular anionic polymers

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The distribution of the electron density at the outer regions of bonded atoms is anisotropic. This feature was first proposed for explaining the noncovalent interactions formed by bonded atoms early nineteen nineties [1] and now it is successfully used for rationalizing interactions of elements of all groups of the p block of the periodic table [2]. This mindset began to be extended to d block elements four years ago, being first applied to elements of group 11, then to elements of groups 10 and 12 [3]. For instance, some theoretical studies and experimental results have shown that gold can behave as an effective acceptor of electron density in some of its derivatives, e.g., attractive interactions, named coinage bond (CiB) [3], can be formed between donors of electron density and regions of most positive electrostatic potential at the outer surface of gold nanoparticles and halides.

In this communication we describe that *gold can function as acceptor of electron density not only in neutral species, as mentioned above, but also in negatively charged species*. It will be proven that the *Au(III)···nucleophile supramolecular synthon is quite robust and effectively controls the packing of ionic crystals* [4]. This synthon may complement the opportunities offered by the aurophilic interactions which are now dominating the interactional landscape of gold. Specifically, we report single crystal structures wherein AuCl_4^- anions act as self-complementary tectons, chlorine and gold atoms functioning as donors and acceptors of electron density, respectively. Au and Cl atoms of different units form short $\text{Au}\cdots\text{Cl}$ contacts and construct supramolecular anionic polymers (**Figure**) wherein gold forms a second CiB with a lone pair possessing atom (the oxygen of an ester group). The electrophilic role of gold and the attractive nature of $\text{Au}\cdots\text{Cl}/\text{O}$ interactions will be proven by some modelling. A survey of the Cambridge Structural Database (CSD) will be reported suggesting that this behaviour is quite general. Indeed, a non-minor fraction of CSD structures containing the AuCl_4^- anion show the presence of the $\text{Au}\cdots\text{nucleophile}$ supramolecular synthon and the same holds for structures containing the AuBr_4^- and $\text{Au}(\text{CN})_4^-$ anions.

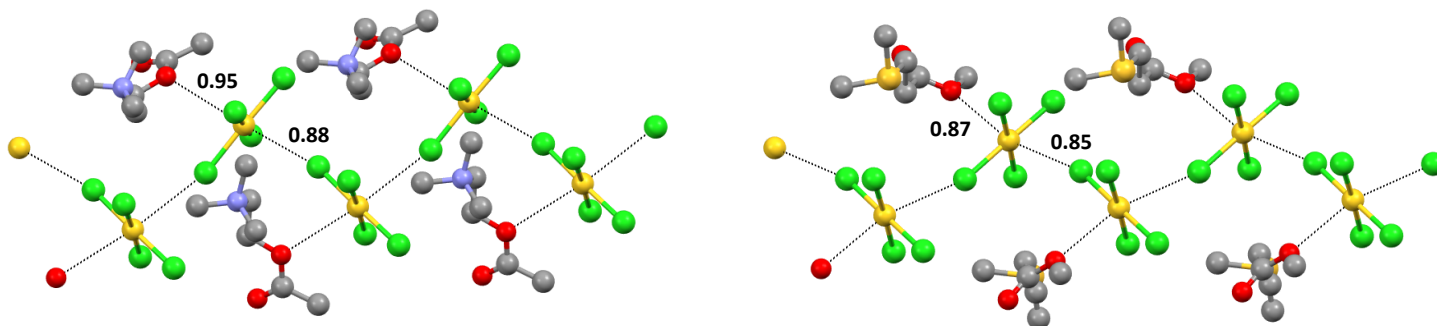


Figure. Coinage bonded anionic supramolecular polymers in the tetrachloridoaurates of acetylcholine (left) and the methyl ester of propiothetin (right). Coinage bonds are black dashed lines; normalized contact (Nc) values are reported close to the interactions (Nc for an interaction involving atoms i and j is the ratio $D_{ij}/(\text{rvd}W_{i,j})$, where D_{ij} is the experimental distance between i and j and $\text{rvd}W_{i,j}$ are the van-der-Waals radii of i and j. If the electron donor j is an anionic atom, $\text{rvd}W_{i,j}$ is substituted by the Pauling ionic radius of the anion atom j). H atoms are omitted for sake of clarity. Color code: grey, carbon; red, oxygen; light blue, nitrogen; green, chloride; yellow, gold; ocher, sulfur.

[1] Brinck, T., Murray, L. S., Politzer, P. (1992) *Int. J. Quantum Chem.* **44**, 57.

[2] Cavallo, G., Metrangolo, P., Pilati, T., Resnati, G., Terraneo, G. (2014) *Cryst. Growth Des.* **14**, 2697.

[3] Daolio, A., Scilabra, P., Terraneo, G., Resnati, G. (2020) *Coord. Chem. Rev.* **413**, 213265.

[4] Daolio, A., Pizzi, A., Terraneo, G., Ursini, M., Frontera, A., Resnati, G. (2021) *Angew. Chem. Int. Ed.* **2021**, 60, 14385–14389.

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