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Unprecedented $[d^9]Cu \cdots [d^{10}]Au$ coinage bonding interactions in $\{Cu(NH_3)_4[Au(CN)_2]\}^+[Au(CN)_2]^-$ salt[†]

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The X-ray structure of the {Cu(NH₃)₄[Au(CN)₂]⁺[Au(CN)₂]⁻ salt is reported showing an unprecedented [d⁹]Cu···[d¹⁰]Au coinage bond. The physical nature of the interaction has been studied using DFT calculations, including the quantum theory of atoms-inmolecules, the noncovalent interaction plot and the natural bond orbital analysis, revealing the nucleophilic role of the [d¹⁰]Au metal and the electrophilic role of [d⁹]Cu metal.

Noncovalent metal…metal interactions (metallophilicity) are well known forces that can be utilized to generate unique structures with advanced functionalities.¹⁻⁴ Homo-metallophilicity, such as aurophilicity,² argentophilicity,³ and cuprophilicity,⁴ has been traditionally utilized for the construction of metal clusters. On the other hand, heterometallophilicity allows the generation of diverse structures and functionalities, particularly in the d¹⁰–d¹⁰ heterometallic complexes.⁵ Among them, supramolecular architectures through Au…Cu interactions have been developed to construct phosphorescent materials.^{5,6} The dispersive nature of metallophilic interactions, which take place between closed electron shell atoms, has been proposed by Pyykkö.⁷ An alternative orbital explanation was also proposed by Hoffmann⁸ and reinforced by the investigation of Fonseca-Guerra's group.⁹

Several theoretical and experimental investigations^{10–15} have shown that nanoparticles¹⁶ and halide salts of Cu, Ag, and Au form attractive noncovalent interactions (NCIs) with a variety of Lewis bases and anions, where the coinage atoms act as Lewis acids. These NCIs involving Group 11 elements acting as electron acceptors are named either regium bonds¹⁰ or coinage bonds¹³ in the literature.

Herein we report experimental and theoretical results that reveal the existence of coinage-bond (CiB) between two cationic species where $Cu(\pi)$ functions as an acceptor of electron density and Au(I) as a donor of electron density. The $[d^9]Cu \cdots [d^{10}]Au$ contacts involving Au and Cu atoms of different units drive the formation of supramolecular cationic polymers. Theoretical calculations prove the electrophilic role of copper and nucleophilic role of gold as well as the attractive nature of the [d⁹]Cu...[d¹⁰]Au interaction. These findings show that CiBs involving two coinage atoms (one as the donor and another as the acceptor) are robust enough to drive the formation of attractive cation ... cation NCIs, which determine the crystal packing of the salt. To the best of our knowledge, there is no previous report in the literature describing Cu(II) ··· Au(I) attractive NCIs. In contrast, linear 1D polymeric assemblies formed by alternating [CuBr₂]...[AuL₂] units (see Scheme 1) guided by [d¹⁰]Cu···[d¹⁰]Au NCIs have been described.¹⁷

As part of our continuous investigations on NCIs involving coinage elements, we obtained the single-crystal X-ray structure of dicyanoaurate salt of $\{Cu(NH_3)_4[Au(CN)_2]\}^+$ (1), see Fig. 1a. It was synthesized in a good yield (99%) by mixing $[Cu(NH_3)_4]^{2+}$ with K[Au(CN)₂] in water (see the ESI[†] for further experimental details). In the solid state, the $Cu(\pi)$ metal centre of the cationic unit is coordinated to four ammonia ligands in the basal plane and to a dicyanoaurate metalloligand in the apical position. The cationic and anionic units of 1 are connected through quite long N-H···C contacts. The N-H···C angles are 146.3° and 150.3° and the H···C distances are 2.811 Å and 2.927 Å, which could be classified as long H-bonds or C-H··· π (C \equiv N) interactions. Fig. 1b depicts the location of the five $[Au(CN)_2]^-$ anions that surround the cation. Two of them are located opposite to the coordinated $[Au(CN)_2]^-$ metalloligand, establishing the aforesaid long N-H···C contacts. The other three anions are

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Fig. 1 (a) X-ray structure of compound **1** with the atom numbering scheme. (b) Partial view of the X-ray structure showing the cationic $\{Cu(NH_3)_4[Au(CN)_2]^+$ unit surrounded by five $[Au(CN)_2]^-$ anions. Aurophilic interactions indicated using red dashed lines and $N-H\cdots C$, N contacts using black dashed lines. (c) Representation of the zig-zag supramolecular polymer of **1** containing CiBs (shown in black dashed lines) and aurophilic interactions in red. Distances in Å.

located close and parallel to the coordinated $[Au(CN)_2]^-$ metalloligand, forming a combination of N-H···N bonds (H···N distances ranging 2.27 to 2.34 Å) and classical $[d^{10}]Au \cdot \cdot [d^{10}]Au$ aurophilic interactions (Au···Au separation 3.37 and 3.67 Å).

In the crystal packing, the Cu(II) atom of $\{Cu(NH_3)_4 [Au(CN)_2]\}^+$ forms a short contact with the Au(I) atom of the adjacent cationic unit (see Fig. 1c). The Au···Cu separation is 3.329 Å, shorter than Batsanov's¹⁸ sum of van der Waals radii

 $[\Sigma R_{vdw} = 1.73 (Cu) + 1.86 (Au) = 3.59 Å]$ and quite longer than the sum of covalent radii ($\Sigma R_{cov} = 2.68$ Å), thus suggesting the formation of a Cu···Au NCI. The Cu1 ion in the cationic unit adopts the classical square-pyramidal arrangement and the Au2 atom of another cationic unit gets close to the copper centre, along the direction of the apical CN–Cu bond (N5–Cu1···Au2 is 186.7°) and almost orthogonal to the CuN₄ mean plane (*i.e.*, the N5–Cu1···Au2 angle is 84.9° and the N6–Cu1···Au2 angle is 86.7°). Therefore, the interaction might be rationalized as σ -hole CiB. These CiBs dictate the formation of an infinite zig-zag supramolecular chain (see Fig. 1c) bearing the anions as appended residues.

First, the theoretical study (see the ESI[†] for details) was focused on the analysis of the molecular electrostatic potential (MEP) surfaces of the $\{Cu(NH_3)_4[Au(CN)_2]\}^+$ cationic unit and the ion-pair. The MEP results are summarized in Fig. 2. As expected, the MEP values of the isolated cation are positive almost over the entire surface because of its net positive charge. Only the non-coordinated N-atom of the cyano ligand remains negative $(-29 \text{ kcal mol}^{-1})$. The MEP maxima are located at the Cu-atom opposite to the coordinated cyano group (σ -hole) and the H-atoms of coordinated ammonia ligands $(+144 \text{ kcal mol}^{-1})$, thus explaining the location of the counterions in the solid state. The MEP surface analysis of the salt (the closest anion has been used in this model) shows that the value of the potential at the σ -hole of the Cu center is reduced to +88 kcal mol⁻¹. The MEP maxima are located at the H-atoms of the coordinated ammonia ligands (+105 kcal mol $^{-1}$). The MEP minimum is located between



Fig. 2 MEP surfaces of the $\{Cu(NH_3)_4[Au(CN)_2]\}^+$ cationic unit (a) and the ion-pair (b) using 0.00 a.u. isovalues at the PBE0-D3/def2-TZVP level of theory. The values are given in kcal mol⁻¹ at some points of the surface.

the terminal N-atoms of the coordinated and non-coordinated $[{\rm Au}({\rm CN})_2]^-$ moieties $(-100~{\rm kcal~mol^{-1}}).$ It is interesting to highlight that the MEP at the Au-atoms becomes negative, and thus adequate for acting as an electron donor.

Second, for both cation...cation and cation...anion dimers, the Cu---Au and Au---Au contacts were further characterized by using the quantum theory of "atoms-in-molecules" (QTAIM)¹⁹ and the noncovalent interaction index (NCIplot).²⁰ By using the X-ray geometries, Fig. 3 shows the results of using QTAIM and NCIplot index computational tools combined in the same representation. The interaction energies are also indicated in Fig. 3. The QTAIM analysis confirms the existence of both the Au. Au and Cu. Au contacts, each one characterized by a bond critical point (CP) and a bond path connecting the Au2 atom to the Cu1 or Au1 atom (cation ··· cation or cation ··· anion, respectively). The analysis also reveals the existence of four N-H···C contacts in the cation ··· cation complex (distances range from 2.72 to 2.82 Å). The shortest ones are characterized by the corresponding bond critical points (CPs) and bond paths connecting the N-H bonds to the C atoms (see Fig. 3). The longest ones are characterized by green (attractive) NCIplot index isosurfaces located between the H and C-atoms. The presence of Cu-...Au and Au-...Au is also confirmed by the



Fig. 3 QTAIM distribution of the bond and ring CPs (red and yellow spheres, respectively) and bond paths for the cation—cation (a) and cation—anion (b) dimers of compound **1**. The superimposed NClplot isosurfaces (RDG isovalue = 0.4) are shown. The cut-off ρ = 0.04 a.u. has been used. Colour range: -0.035 a.u. $\leq (\text{sign}\lambda_2)\rho \leq 0.035$ a.u. Level of theory: PBE0-D3/def2-TZVP. The second-order perturbation energies $E^{(2)}$ along with the donor and acceptor orbitals obtained from the NBO analysis are indicated.

NCIplot analysis, which reveals the existence of light blue isosurfaces located between the interacting atoms. The comparison of the different colours of the isosurfaces reveals that Cu---Au shows the strongest interaction. The interaction energy of the cation $\cdot \cdot \cdot$ cation dimer is repulsive (+23 kcal mol⁻¹, see Fig. 3a), as expected. However, it is significantly smaller than the electrostatic repulsion originating from two point charges of the same sign located at the centre of masses of both molecules (+58.9 kcal mol^{-1}), thus confirming the attractive nature of the NCIs (Cu···Au and N-H···C contacts). The interaction energy of the ion-pair dimer is attractive $(-67.4 \text{ kcal mol}^{-1})$ and slightly larger (in absolute value) than the electrostatic attraction of two point charges of opposite sign located at the centre of masses of both molecules $(-64.9 \text{ kcal mol}^{-1})$, thus suggesting that the Au \cdots Au aurophilic interaction is weaker than that in the Cu--Au one, in line with the NCIplot analysis.

We have also studied if orbital contributions are important in the aforementioned Cu...Au interaction. For this purpose, a natural bond orbital (NBO) second-order perturbation analysis has been performed, since it is adequate for analysing donoracceptor interactions.²¹ Remarkably, the NBO analysis reveals two orbital contributions in the cation...cation dimer, which are also indicated and represented in Fig. 3. These contributions come from electron donations from one lone pair (LP) of electrons located on the $5d_{x^2-y^2}$ Au atomic orbital to the empty 4s and 4p atomic orbitals of Cu. The second-order stabilization energies $E^{(2)}$ associated with the orbital donor-acceptor interactions are also shown in Fig. 3. The LP(Au) \rightarrow 4p(Cu) donation (2.79 kcal mol⁻¹) is larger than the LP(Au) \rightarrow 4s(Cu) donation $(1.80 \text{ kcal mol}^{-1})$. Therefore, the total stabilization energy due to the orbital contribution to the Cu---Au contact is 4.59 kcal mol⁻¹. This NBO analysis evidences the CiB nature of the Cu-Au interaction, where the Cu atom acts as an acceptor and the Au atom acts as a donor of electron density.

These results are in line with recent theoretical investigations that have demonstrated that gold in the oxidation state +1 can behave as a Lewis base and, particularly, as an excellent HaB acceptor.²² It has been estimated that the strength of the halogen bonds involving I_2 as a σ -hole donor and Au(I) as an electron donor in the cationic $[(H_3N-Au-NH_3)\cdots I_2]^+$ adduct is -5.9 kcal mol⁻¹,²³ which is similar to the CiB energy derived from the NBO analysis in **1**. In addition, experimental findings and DFT calculations have recently shown that cationic species (iodonium cations, L–I⁺–L) are able to act as nucleophiles in co-crystals with Ag(I) complexes, establishing I⁺…Ag⁺ interactions.²⁴ This NCI has been termed as "nucleophilic iodonium interaction" (NII).

In conclusion, experimental evidence is provided for the first time demonstrating that $\{Cu(NH_3)_4[Au(CN)_2]\}^+$ cations form short $Cu\cdots Au$ interactions in the solid state. DFT calculations show that these interactions are attractive, and their directionality is consistent with σ -hole CiBs. The combined experimental and theoretical results reported here prove that cation \cdots cation CiB interactions involving $\{Cu(NH_3)_4[Au(CN)_2]\}^+$ are relevant in guiding the crystalline structure and are

responsible for the formation of zig-zag supramolecular polymers. The unprecedented Cu[d⁹]···Au[d¹⁰] CiBs reported here in addition to CiBs recently described in anion···anion AuCl₄⁻ salts²⁵ are important extensions of the potential of gold interactions, which are currently dominated by aurophilic bonds.^{2c}

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Conflicts of interest

There are no conflicts to declare.

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