

Article

Isolated Dicyanoaurate(I) as a Polycentered σ -Hole Interaction Acceptor: A Combined Crystallographic and Theoretical Survey

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Abstract

The nucleophilic properties of the isolated dicyanoaurate(I) anion in σ -hole interactions were investigated using theoretical calculations of models from 19 crystalline literature structures. The study focuses on the ability of $[\text{Au}(\text{CN})_2]^-$ to participate in various noncovalent interactions, including halogen, chalcogen, pnictogen, and tetrel bonds. The research reveals that both nitrogen atoms of the cyanide ligands and the gold(I) center exhibit nucleophilic behavior. The nature of all interactions and philicities of interacting atoms were confirmed using a set of theoretical methods, including QTAIM topological analysis, noncovalent interaction plots (NCIplot), electrostatic potential (ESP) surfaces, electron localization function (ELF), analysis of electron density (ED), and electrostatic potential (ESP) minima in their 1D profiles along the bond paths, BSSE corrected dimerization energies, and NBO charge-transfer analysis. The study demonstrates that the dicyanoaurate(I) anion can act as a versatile building block in supramolecular chemistry, participating in multiple types of noncovalent interactions through different sites, including first confirmed examples of gold(I)-involving intermolecular chalcogen bonds.

Keywords: dicyanoaurate(I); σ -hole interactions; QTAIM; DFT; metal-involving interactions; halogen bonding; chalcogen bonding; pnictogen bonding; tetrel bonding

1. Introduction

σ -Hole interactions represent a major class of noncovalent interactions, analogous to hydrogen bonding (HB) [1], where the role of the hydrogen atom is played by atoms from other groups of the periodic table. Recognizing the importance and diversity of these interactions, the IUPAC has established formal definitions for several subtypes, including halogen bonding (XB) [2], chalcogen bonding (ChB) [3], and pnictogen bonding (PnB) [4]; tetrel interactions (TrB) have also been mentioned [5–7].

Homoleptic cyanometallates are particularly significant as acceptors in σ -hole interactions [8–13]. The negatively charged, sterically accessible *sp*-hybridized orbitals of nitrogen atoms enable these complexes to serve as structural elements in the supramolecular assembly of crystals. Our recent investigations have highlighted the involvement of dicyanoargentate(I) in σ -hole interactions with diaryliodonium cations [14], while they also provided theoretical validation for previously reported $\text{Br} \cdots \text{N}$ [15], $\text{Te} \cdots \text{N}$ [16], and $\text{I} \cdots \text{N}$ [17] interactions involving $[\text{Ag}(\text{CN})_2]^-$ anion.

Linear dicyanoaurate(I), structurally isomorphic with dicyanoargentate(I), demonstrates a wide range of noncovalent contacts, including hydrogen bonding [18–30] and metallophilic interactions [31]. Notably, this anion exhibits pronounced self-aggregation



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behavior driven by Au(I)···Au(I) aurophilic interactions [18–27,32–38], and similar Au(I)···Au(I) interactions have been observed between dicyanoaurate(I) and gold(I)-containing cations [30,32,39–41]. Furthermore, heterometallic interionic interactions involving dicyanoaurate(I), including Rh(I)···Au(I) [29], Ag(I)···Au(I) [32,42], and Pt(II)···Au(I) [28,35,43] were characterized, and interactions between [Ag(CN)₂][−] and π -systems were also reported [36].

To the best of our knowledge, only two cases of XBs with dicyanoaurate(I) have been described, namely C–I···N $\equiv$ C interactions in a co-crystal of potassium dicyanoaurate(I) with 15-crown-5 and 1,4-FIB [44] (structure code: XEDDIW) and C–Cl···Au contacts [45] in the solvate [(Ph₃P)₂N][Au(CN)₂].CH₂Cl₂ (structure code: XULBIP), which were confirmed in subsequent theoretical work [46] as XB with gold(I). Possible ChBs, including the anion, were described in the study of Fujita [47] where the S···N and S···Au interactions were mentioned as short interatomic contacts in the structure of [BBDTA][Au(CN)₂] (BBDTA = benzo [1,2-d:4,5-d']bis [1–3]dithiazolium radical, structure code: KUBDOC), and by Shirahata et al., who described [48] the Se···N contacts in [Q]₂[M(CN)₂] (Q = 2-isopropylidene-1,3-dithiolo [4,5-d]-4,5-ethylenediselenotetrathiafulvalene/-ium radical) as anion–donor interactions (structure codes: HODZIL, HODZIL01). Despite detailed characterization of various noncovalent contacts in dicyanoaurate systems, there are no descriptions of PnB or TrB formation involving this anion in the available scientific literature.

In this study, we systematically analyze the role of isolated [Au(CN)₂][−] in σ -hole interactions, excluding metallophilic interactions and additional coordination. Our approach combines an analysis of crystal structures with DFT calculations.

We hypothesize that [Au(CN)₂][−] can act as a versatile σ -hole interaction partner, serving as

- (1) A σ -hole acceptor through its nitrogen atoms (e.g., in XB and ChB with I···N, S···N contacts);
- (2) A π -system nucleophile via the C $\equiv$ N triple bond (e.g., in S··· π (C $\equiv$ N) interactions);
- (3) A nucleophilic center at Au(I) (e.g., in C–Cl···Au, C–S/Se···Au contacts), expanding the classical σ -hole interaction framework. The C–S/Se···Au^I, as the first examples of intermolecular gold(I)-involving ChBs, represent a significant advancement in our understanding of gold-involving noncovalent interactions.

2. Materials and Methods

Computational Details

Prior to calculations, hydrogen atoms were added to all structures in idealized positions, based on neutron diffraction statistics [49], using the OLEX2 program (version 1.5) [50] package (UK).

DFT calculations for all clusters were performed using experimental X-ray geometries in ORCA 5.0 [51] program (Germany) with the TPSS-D3 [52,53] functional and jorge-TZP-ZORA [54,55] basis set. The resolution-of-identity (RI) [56] approximation was employed, along with AutoAux-generated [57] auxiliary basis sets. Zero-order regular approximation (ZORA) [58–62] was employed to account for relativistic effects. The SCF calculations were tightly converged (TightSCF).

The topological analysis of the electron density distribution with the help of the quantum theory of atoms in molecules (QTAIM) method developed by Bader [63–65], ELF [66–68] projection analysis, and ED/ESP [69–74] profile analysis was performed using the Multiwfn program (version 3.8) (People's Republic of China) [75,76]. Electrostatic surface potentials were calculated in the Multiwfn program (version 3.8) and visualized in VMD 1.9.3 (USA) [77]. Natural bond orbital (NBO) charge-transfer [78,79] analysis was performed in NBO 7.0 (USA) [80] in conjunction with ORCA 5.0. The basis set superposition

error (BSSE) [81] for the calculation of interaction energies has been corrected using the counterpoise method in ORCA 5.0.

The Cartesian atomic coordinates for the clusters are given in the Supplementary Materials.

3. Results and Discussion

3.1. Identification of Noncovalent Interactions

Before the investigation of available literature data, we checked the possible nucleophilicity of atoms in dicyanoaurate(I) by calculation of its electrostatic potential (ESP) [82–84] on the surface where $\rho = 0.001 \text{ e/Bohr}^3$ (Figure 1) [85]. The ESP minima (-112.8 kcal/mol) are localized at the N atoms, while the ESP maxima (-82.1 kcal/mol) remain negative and are positioned in a toroidal region around the Au atom. Thus, all three types of atoms (N, C, and Au) are electrostatically favorable as nucleophilic centers for σ -hole interactions.

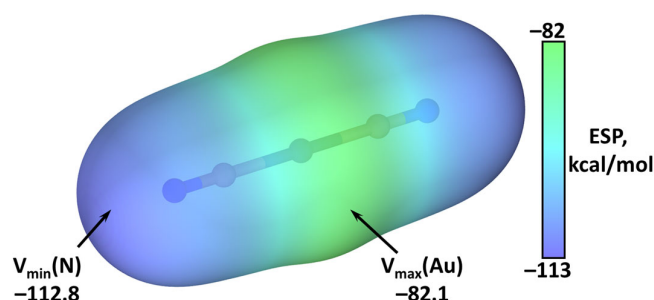
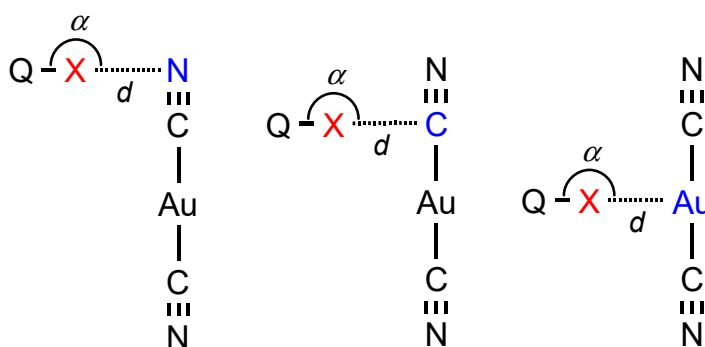


Figure 1. ESP surface ($\rho = 0.001 \text{ e/Bohr}^3$) for optimized (TPSS-D3/jorge-TZP-ZORA [52–55]) dicyanoaurate(I).

To find the structures that contain possible σ -hole interactions with dicyanoaurate(I), we use three schemes (Scheme 1). In all cases, Au and C atoms demonstrate only two coordinative/covalent neighbors, whereas N atoms demonstrate only C cyano atoms as neighbors. X atoms are C, Si, Ge, Sn, Pb, P, As, Sb, Bi, S, Se, Te, Cl, Br, and I; Q atoms are any nonmetals. The d distances are less than the sum of Bondi vdW radii [86], and the α angles are in the range 150 – 180° .



Scheme 1. Schemes of search for N-involved (left), C-involved (center), and Au-involved (right) contacts.

As a result, we found 19 structures, where possible $\text{Cl} \cdots \text{Au}$ and $\text{I} \cdots \text{N}$ XBs, possible $\text{S} \cdots \text{N}$, $\text{S} \cdots \text{C}$, $\text{S} \cdots \text{Au}$, $\text{Se} \cdots \text{N}$, and $\text{Se} \cdots \text{Au}$ ChBs, possible $\text{Sb} \cdots \text{N}$ PnBs, and possible $\text{C} \cdots \text{N}$ TrBs were detected, and their parameters were found using Olex2 1.5 [50] software (Table 1).

Table 1. Parameters of σ -hole interactions with $[\text{Au}(\text{CN})_2]^-$.

N ^a	Code	Contact	Distance, Å	Nc *	$\angle E, ^\circ$	$\angle Nu, ^\circ$
1	XEDDIW [44]	C1–I1...N22=C21	2.846(6)	0.81	177.0(2)	175.4(7)
		C7–I2...N24=C23	2.960(5)	0.84	174.7(2)	167.2(6)
2	XULBIP [45]	C3–C12...Au1–C1/C2	3.381(4)	0.99	175.0(5)	77.84(17)/102.56(17)
3	BAQBIE [87]	C13–S11...N1=C19	3.217(13)	0.96	165.6(5)	133.3(12)
		C16–C15...N1=C19	3.2125(7)	0.99	167.317(7)	116.698(18)
4	CITPEC [88]	C(6)–S(5)...N(1)=C(24)	3.299(9)	0.98	153.3(3)	112.6(6)
		N7–S4...N6=C13	2.975(5)	0.89	159.06(19)	118.8(3)
5	KUBDOC [47]	C10–S4...Au1–C16/C13	3.4459(16)	0.99	167.24(15)	105.69(14)/72.19(14)
6	SUHDAB [89]	C6–S6...N2=C13	3.258(11)	0.97	172.0(3)	125.0(8)
7	SUHDEF [89]	C18–S12...N3=C25	3.22(2)	0.96	170.7(7)	127.7(16)
8	SUHDIJ [89]	C6–S6...N4=C26	3.268(17)	0.98	169.9(4)	125.8(11)
9	TAYXOH [90]	C(1)–S(1)...N(1)=C(13)	3.184(9)	0.95	166.8(3)	155.5(8)
10	ZIGKIJ [91]	C4–S1...N1=C1	3.04(4)	0.91	174.3(13)	133(6)
		C3–C2...N1=C1	3.17(6)	0.95	155(3)	142(4)
11	HODZIL [48]	C3–Se1...N1=C13	2.995(7)	0.87	168.88(16)	137.0(4)
		C2–C1...N1=C13	3.214(8)	0.99	172.8(3)	154.9(4)
12	HODZIL01 [48]	C3–Se1...N1=C13	2.959(4)	0.86	169.33(13)	136.0(3)
		C2–C1...N1=C13	3.177(5)	0.98	171.2(2)	155.6(3)
13	QIGMUO [92]	C(2)–Se(1)...N(33)=C(32)	3.42(3)	0.99	159.4(9)	89(2)
		C12–Se1...Au(3)–C(32)/C(34)	3.450(3)	0.97	178.9(6)	80.9(7)/99.0(7)
14	DUSBIC [93]	C5–S7... π -C11=N1/Au1	3.4378(9)	0.98	161.327(11)	77.70(4)/101.77(4)
15	DUSBIC02 [94]	C4–S5... π -C1=N1/Au1	3.417(11)	0.98	161.7(4)	79.0(8)/101.4(4)
		C61–Sb2...N4=C164	2.88(4)	0.8	175.6(11)	169(4)
16	CUCNIA [95]	C61–Sb3...N6=C166	2.86(4)	0.79	175.3(12)	173(3)
		C131–Sb4...N7=C167	2.98(9)	0.83	174.7(12)	173(3)
		C31–Sb1...N0AA=C162	2.91(4)	0.81	175.9(11)	168(3)
17	CECLAB [33]	C13–C16...N1=C1	3.238(10)	0.99	169.9(4)	109.8(5)
18	PILFAR [96]	O1–C9...N2=C12	3.19(6)	0.98	160(2)	106(3)
19	WEJZOA [97]	O1–C14...N1=C1	3.22(3)	0.99	159.7(12)	117.5(15)

* The normalized contact parameter (Nc) is defined as the ratio of the experimental interatomic distance (d) to the sum of the Bondi [86] van der Waals radii for the interacting atoms: $Nc = d/\Sigma_{vdW}$.

In the following sections, we analyzed different types of σ -hole interactions with dicyanoaurate(I) in detail.

3.2. Halogen Bonding with Nitrogen Atom

The halogen bonds (XB) with the isolated dicyanoaurate anion were identified in one structure of XEDDIW (1) and reviewed by the authors in the corresponding article [44]. However, the nature of interactions and philicity of participants were not confirmed by computational methods, so hereinafter we employ the meta-GGA functional TPSS complemented with the D3 dispersion correction in combination with the jorge-TZP-ZORA basis set [52–55]. TPSS is a well-established non-empirical meta-GGA that has been successfully used for describing molecular structures, thermochemistry, and noncovalent interactions of transition-metal and main-group systems, while the jorge-TZP-ZORA basis provides a balanced triple-dzeta description optimized for scalar-relativistic ZORA calculations on heavy atoms. This level of theory offers a favorable compromise between accuracy and computational cost for the present series of clusters, which contain Au and I atoms. The presence of interactions and the role of interacting atoms were confirmed by a combination of methods, including QTAIM topological analysis, NCIPLOT analysis (Figure 2), and electron localization function (ELF) projections. Hereinafter for visualization of QTAIM topological and NCIPLOT analyses blue dots correspond to (3; −1) bond critical points, orange dots to (3; +1) ring critical points, bond paths are shown by black lines, and RDG semitransparent surfaces with 0.4 values were colored from blue ($\text{sign}(\lambda_2)\rho(\mathbf{r}) = -0.01 \text{ e/Bohr}^3$) to red ($\text{sign}(\lambda_2)\rho(\mathbf{r}) = +0.01 \text{ e/Bohr}^3$).

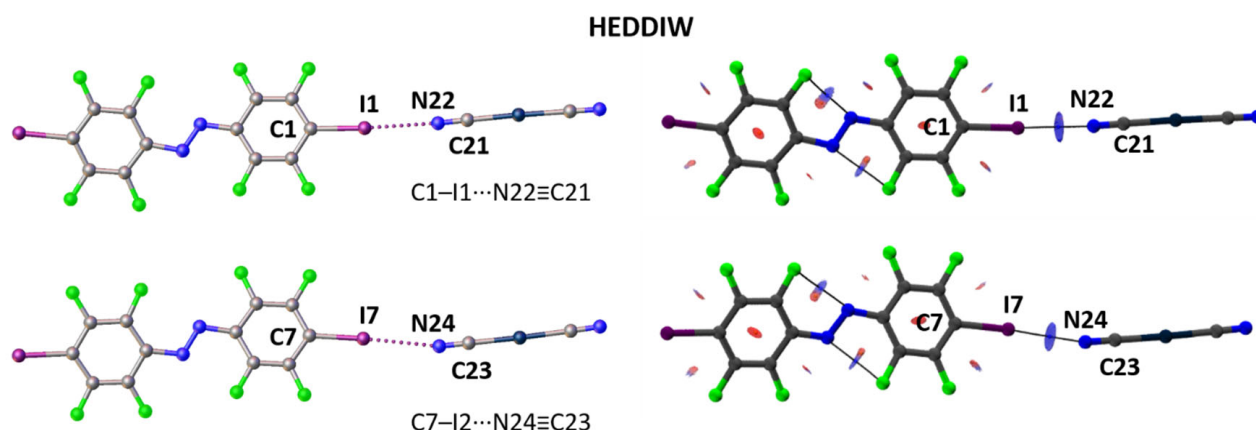


Figure 2. The C-I...N≡C XBs in the structure of **1** (left panel) and visualization of QTAIM topological and NCIPLOT analyses for the **1** (right panel) clusters.

QTAIM analysis reveals the presence of bond critical points (3, −1) (BCPs) for C-I...N noncovalent interactions (Table 2). The BCPs exhibit small negative values of $\text{sign}(\lambda_2)\rho$, which is consistent with attractive, noncovalent interactions [98]. Additionally, their near-zero positive energy density and, in most cases, the balance of the Lagrangian kinetic energy $G(r)$ and the potential energy density $V(r)$ ($-G(r)/V(r) > 1$) on the corresponding BCPs further support their classification as typical noncovalent interactions [65].

Table 2. Parameters in (3, −1) bond critical points (the electron density multiply by sign of λ_2 $\text{sign}(\lambda_2)\rho(r)$ in e/Bohr^3 , Laplacian of electron density $\nabla^2\rho(r)$ in e/Bohr^5 , the local electronic energy density H_b , local electronic potential energy density $V(r)$, local electronic kinetic energy density $G(r)$ in Hartree/Bohr³) corresponding to the C-I...N interactions in cluster models.

Structure	Bond	$\text{Sign}(\lambda_2)\rho(r)$	$\nabla^2\rho(r)$	$G(r)$	$V(r)$	H_b
XEDDIW	C1-I1...N22	−0.0256	0.0663	0.0174	−0.0182	−0.0008
	C7-I2...N24	−0.0206	0.0555	0.0137	−0.0135	0.0002
BAQBIE	C13-S11...N1	−0.0084	0.0277	0.0056	−0.0043	0.0013
KUBDOC	N7-S4...N6	−0.0143	0.0412	0.0090	−0.0077	0.0013
ZIGKIJ	C1-S1...N1	−0.0117	0.0384	0.0081	−0.0065	0.0016
HODZIL	C3-Se1...N1	−0.0143	0.0433	0.0096	−0.0083	0.0013
HODZIL01	C3-Se1...N1	−0.0153	0.0461	0.0102	−0.0090	0.0012
QIGMUO	C12-Se1...N33	−0.0071	0.0228	0.0045	−0.0033	0.0012
PILFAR	O1-C9...N2≡C12	−0.0064	0.0184	0.0036	−0.0027	0.0009
DUSBIC	C4-S5... π -C1≡N1	−0.0069	0.0225	0.0044	−0.0031	0.0013
DUSBIC02	C5-S7... π -C11≡N1	−0.0069	0.0227	0.0044	−0.0032	0.0012
XULBIP	C3-Cl2...Au1	−0.0096	0.0306	0.0063	−0.0049	0.0014
KUBDOC	C10-S4...Au1	−0.0106	0.0265	0.0057	−0.0048	0.0009
QIGMUO	C7-Se1...Au3	−0.0114	0.0271	0.0060	−0.0052	0.0008

The RDG value equal to 0.4 shows that all bond critical points (BCPs) are surrounded by surfaces characterized by negative $\text{sign}(\lambda_2)\rho(r)$ values, thus providing evidence for the relevant noncovalent interactions (Figure 2).

Analysis of structure **1** reveals that the I...N bond paths pass through regions of high electron localization function (ELF) at the nitrogen atoms and depleted ELF regions at the iodine atoms. This observation lends support to the idea that nitrogen acts as a nucleophile in these interactions (Figure 3). Hence, both I...N contacts qualify as XBs.

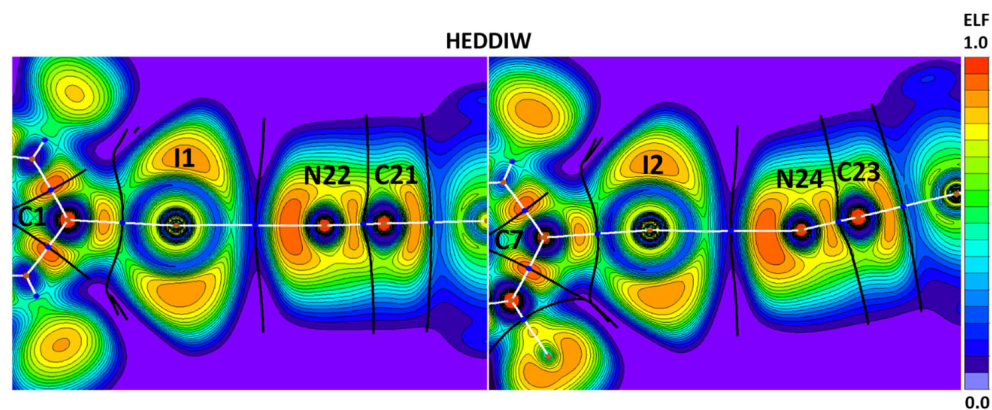


Figure 3. Visualization of ELF, BCPs, and bond paths for C–I $\cdots$ N XBs in cluster **1**. BCPs (3, -1) are shown in blue; nuclear critical points (3, -3) are shown in pale brown; ring critical points (3, $+1$) are shown in orange; bond paths are shown as white lines.

3.3. Chalcogen Bonding with Nitrogen Atom

Chalcogen bonding with $[\text{Au}(\text{CN})_2]^-$ was most often found in structures that were obtained by the electrochemical crystallization of so-called organic metals, since dicyanoaurate anion as a linear anion was popular among researchers of such objects (refcodes: BAQBIE (**3**), KUBDOC (**5**), ZIGKIJ (**10**), HODZIL (**11**), HODZIL01 (**12**), and QIGMUO (**13**)). In some cases, these contacts were mentioned, so we decided to further understand their nature using computational methods.

The QTAIM analysis (Table 2) demonstrates the presence of bond critical points (3, -1) (BCP) between a N in dicyanoaurate anion and an S or Se atom in corresponding heterocycles. The negative and small values of the $\text{sign}(\lambda_2)\rho$ on the other BCPs favor the attractive and noncovalent nature of the interactions [98]. They can also be considered as typical noncovalent interactions due to their close to zero positive energy density (0.001 – 0.002 Hartree/Bohr³) and the balance of the Lagrangian kinetic energy $G(\mathbf{r})$ and the potential energy density $V(\mathbf{r})$ ($-G(\mathbf{r})/V(\mathbf{r}) > 1$) on the corresponding BCPs [65].

The RDG = 0.4 surfaces with a negative $\text{sign}(\lambda_2)\rho(\mathbf{r})$ values on them surround all the BCPs, confirming the existence of the corresponding noncovalent interactions (Figures 4–10).

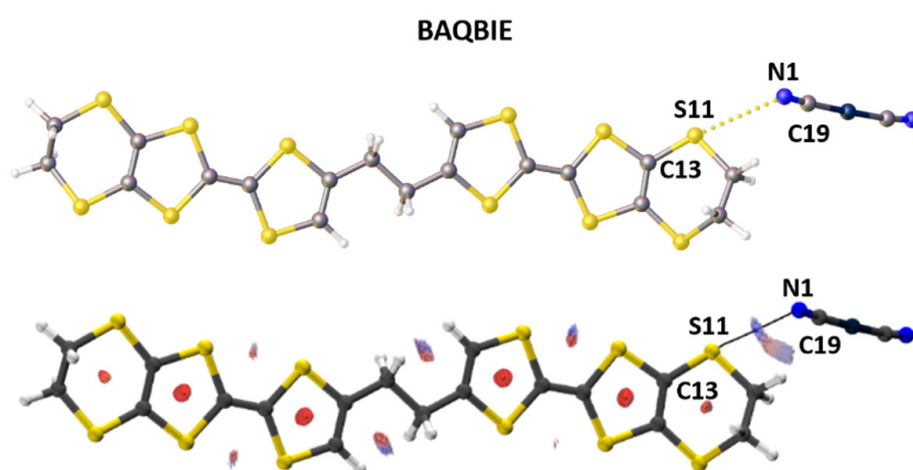


Figure 4. The C–S $\cdots$ N $\equiv$ C ChBs in the structures of **3** (top panel) and visualization of QTAIM topological and NCIPLOT analyses for cluster **3** (bottom panel).

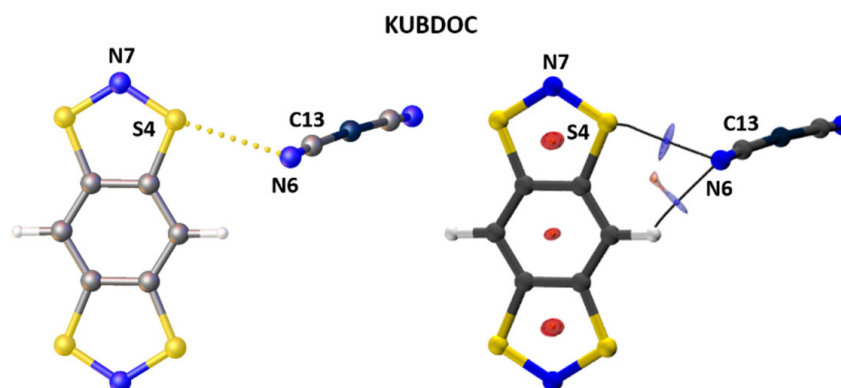


Figure 5. The C–S···N≡C ChBs in the structures of **5** (left panel) and visualization of QTAIM topological and NCIPLOT analyses for cluster **5** (right panel).

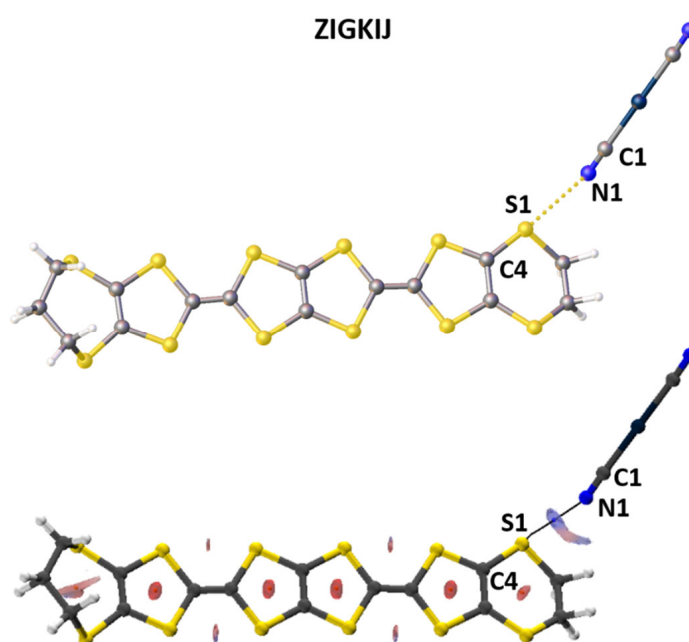


Figure 6. The C–S···N≡C ChBs in the structures of **10** (top panel) and visualization of QTAIM topological and NCIPLOT analyses for the **10** (bottom panel) clusters.

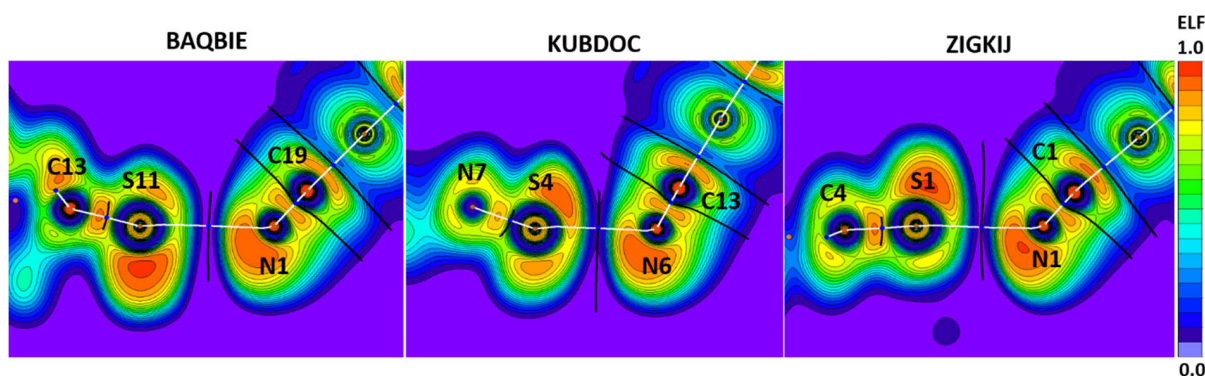


Figure 7. Visualization of ELF, BCPs, and bond paths for X–S···N interactions in clusters **3**, **5**, **10**. BCPs (3, −1) are shown in blue; nuclear critical points (3, −3) are shown in pale brown; ring critical points (3, +1) are shown in orange; bond paths are shown as white lines.

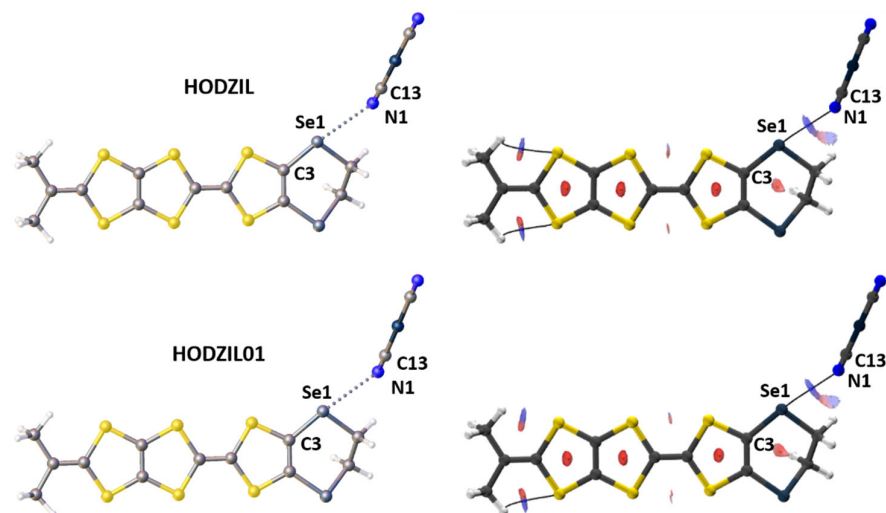


Figure 8. The C–Se···N≡C ChBs in the structures of **11** and **12** (left panel) and visualization of QTAIM topological and NCIplot analyses for clusters **11** and **12** (right panel).

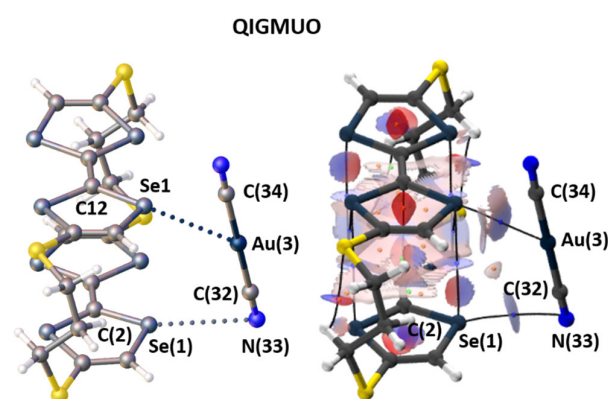


Figure 9. The C–Se···N and C–Se···Au contacts in the structure of **13** (left panel) and visualization of QTAIM topological and NCIplot analyses for cluster **13** (right panel).

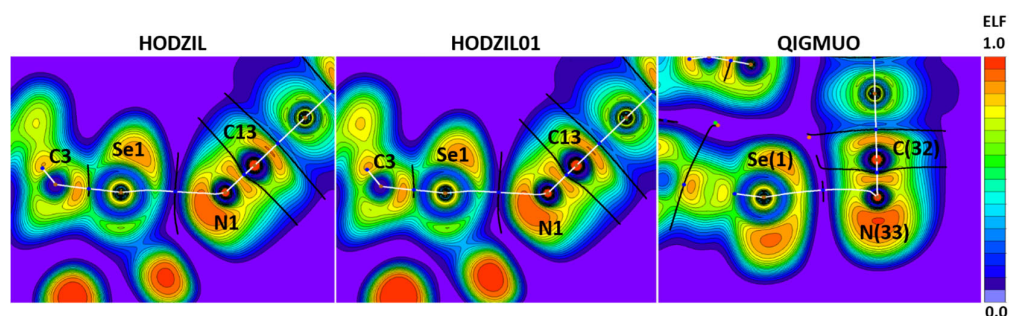


Figure 10. Visualization of ELF, BCPs, and bond paths for C–S···N and C–Se···N ChBs in clusters **11**–**13**. BCPs (3, −1) are shown in blue; nuclear critical points (3, −3) are shown in pale brown; ring critical points (3, +1) are shown in orange; bond paths are shown as white lines.

3.4. Pnictogen Bonding with Nitrogen Atom

The pnictogen bonding (PnB) with the dicyanoaurate anion is represented by a single structure (refcode: CUCNIA [95]) in which the antimony atom acts as an electrophile (Figure 11). Unfortunately, we were unable to carry out theoretical calculations due to the low quality of the structure, $R > 10\%$. For a more detailed study of the PnB with dicyanoaurate anion, additional research is needed.

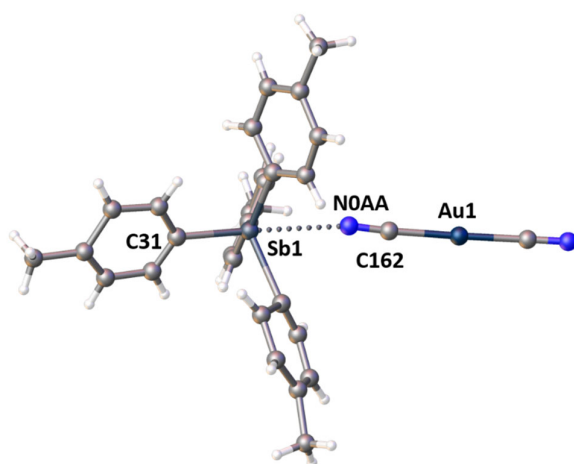


Figure 11. The C–Sb···N≡C PnB in **16**.

3.5. Tetrel Bonding with Nitrogen Atom

Based on geometric features such as the distance between interacting atoms less than the sum of their van der Waals radii and the angle around the nucleophilic center close to 180° , we identified three structures (refcodes: CECLAB (**17**), PILFAR (**18**), WEJZOA (**19**)) with potential tetrel bonds involving a dicyanoaurate anion. However, theoretical calculations confirmed the presence of bond critical points (BCPs) only in one of these cases: in the structure of **18** (Table 2, Figure 12). The combination of QTAIM and NCIPLOT analyses confirms the presence of BCP (3, -1) between the nitrogen atom in $[\text{Au}(\text{CN})_2]^-$ and the carbon atom in EOST (EOST = 4,5-ethylenedithio-4',5'-(2-oxatrimethylenedithio)-diselenadithiafulvalene). The structures of **17** and **19** demonstrate the presence of $\text{H} \cdots \text{N}$ hydrogen bonds, corresponding to the visualization of QTAIM topological and NCIPLOT analyses shown in Supplementary Materials Figures S1 and S2.

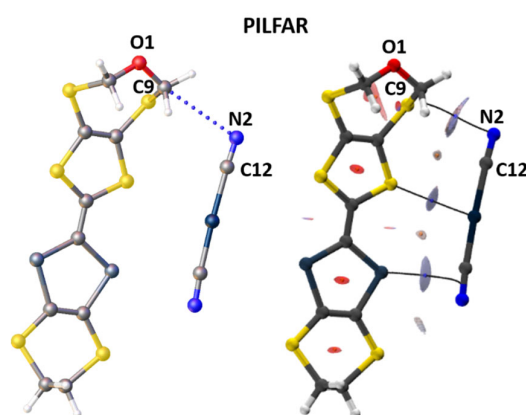


Figure 12. The O–C···N interaction in the structure of **18** (left panel) and visualization of QTAIM topological and NCIPLOT analyses for cluster **18** (right panel).

The philicities of participating atoms in O–C···N interaction can be better understood through a combined use of the electron localization function (ELF) and topological analysis of electron density. Such a synergistic approach reveals the spatial distribution of shared and unshared electron pairs and bond paths.

The ELF visualization combined with the QTAIM analysis for the structure of **18** shows that the bond path extends from the nitrogen nuclear point to the carbon nuclear point. Based on this topological feature, we propose that the interaction should be classified as a tetrel bond rather than a hydrogen bond (Figure 13).

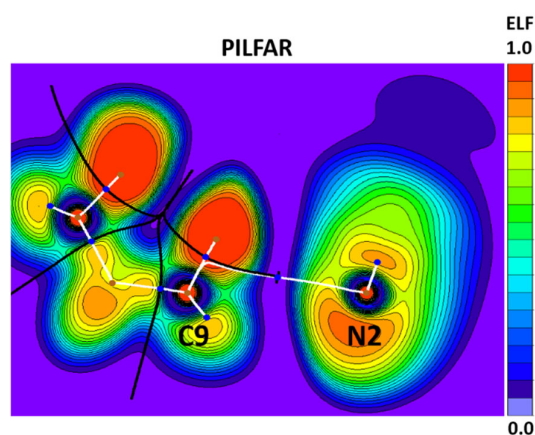


Figure 13. Visualization of ELF, BCPs, and bond paths for O–C···N contact in cluster **18**. BCPs (3, −1) are shown in blue; nuclear critical points (3, −3) are shown in pale brown; ring critical points (3, +1) are shown in orange; bond paths are shown as white lines.

To confirm the nature of partners in the studied noncovalent interaction, we employed the analysis of electron density (ED) and electrostatic potential (ESP) minima in their 1D profiles along the bond paths [69–74]. The change in the boundaries of the ED/ESP basins illustrates the interatomic and intermolecular electrostatic interactions in XBs in supramolecular clusters. Minimum of ED is closer to the electrophile, while the minimum of ESP is closer to the nucleophilic partner, and the region between these two minima corresponds to the lone pair of nucleophile [74]. The ED/ESP profiles (Figure 14) along C···N bond paths indicate that the ESP minima shifted to the ρ -basin of the nitrogen atom in $[\text{Au}(\text{CN})_2]^-$. The shift can be explained by the nucleophilicity of the N atom. The ED minimum is shifted to the carbon atom, which confirms the electrophilicity of this atom. Therefore, C···N contacts can be attributed to tetrel bonds involving the dicyanoaurate anion.

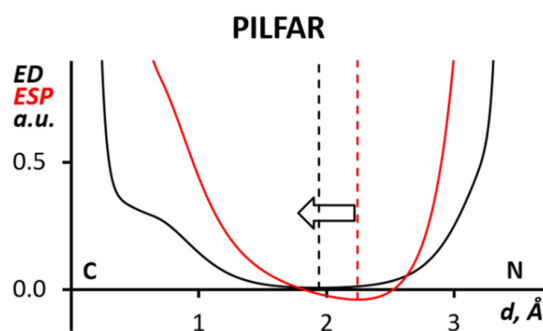


Figure 14. The ED (black) and ESP (red) 1D profiles along the C···N bond paths for the **18** cluster.

3.6. σ -Hole Interactions with π -Electrons of $\text{C}\equiv\text{N}$ Triple Bond

The nucleophilicity of the cyanide ligand arises not only from the nitrogen atom lone pair but also from the π -bonding orbitals of the $\text{C}\equiv\text{N}$ triple bond. Notably, we identified two structures in which the S···C distances are shorter than the sum of the van der Waals radii rather than the S···N distances. Nevertheless, topological analysis shows that the bonding path in both structures extends from the S nuclear point to the N nuclear point (Table 2, Figure 15). The observed twist of the bond path towards a more electronegative atom (or an atom exhibiting a more diffuse charge distribution), despite the increased intermolecular distance, is consistent with prior observations. This phenomenon has previously been reported in the works of Jabłonski [99,100]. The π -orbitals of $\text{C}\equiv\text{N}$ act as additional nucleophilic sites, expanding the σ -hole interaction repertoire of $[\text{Au}(\text{CN})_2]^-$.

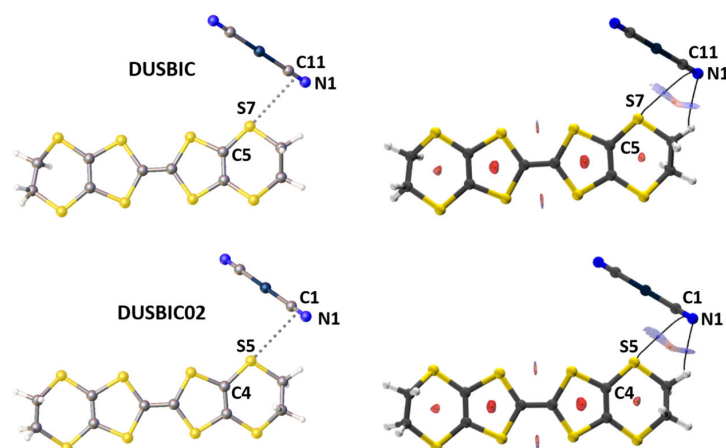


Figure 15. The C–S $\cdots$ N interaction in the structures of **14** and **15** (left panel) and visualization of QTAIM topological and NCIplot analyses for the **14** and **15** (right panel) clusters.

Supporting the argument that π -bonding orbitals contribute to the nucleophilicity of the cyanide ligand of $[\text{Au}(\text{CN})_2]^-$, we examine the ELF projections in combination with QTAIM topological analysis. The visualizations reveal that the bond paths pass the region between the carbon and nitrogen nuclear points precisely through an area identified by ELF as the π -bond domain of the $\text{C}\equiv\text{N}$ moiety (Figure 16).

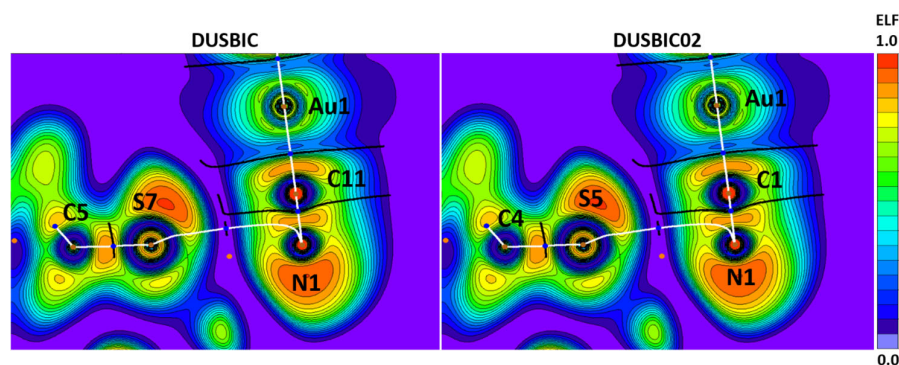


Figure 16. Visualization of ELF, BCPs, and bond paths for C–S $\cdots$ π -C $\equiv$ N interactions in clusters **14** and **5**. BCPs (3, -1) are shown in blue; nuclear critical points (3, -3) are shown in pale brown; ring critical points (3, $+1$) are shown in orange; bond paths are shown as white lines.

Analysis of the electron density (ED) and electrostatic potential (ESP) minima in their 1D profiles along the corresponding bond paths provides additional evidence for the nucleophilicity of the cyanide ligand. The minimum of ESP is closer to the nitrogen atom, and the shift clearly demonstrates the nucleophilic character of the N atom toward the S atom in both cases (Figure 17).

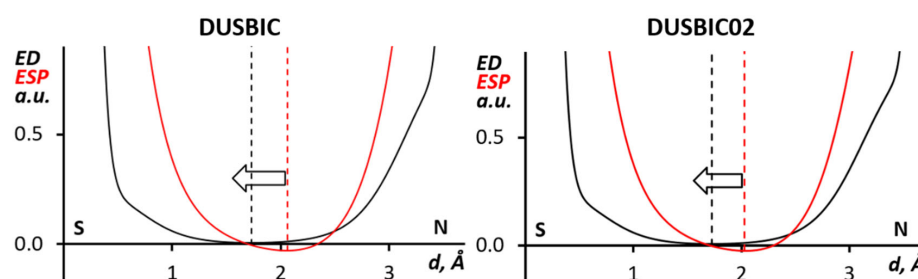


Figure 17. The ED (black) and ESP (red) 1D profiles along the C–S $\cdots$ π -C $\equiv$ N bond paths for clusters **14** and **15**.

3.7. Au Nucleophilicity in σ -Hole Interactions

The C–Cl $\cdots$ Au(I) short contacts were detected in the crystal structure of [PPN][Au^I(CN)₂] CH₂Cl₂ (PPN = bis(triphenylphosphino)iminium) [45]. These contacts are formed between a chlorine atom of CH₂Cl₂ and the gold(I) center of [Au(CN)₂][−], the QTAIM data [46] confirmed the noncovalent nature of these interactions. However, to verify the XB nature of C–Cl $\cdots$ Au(I) contact and the philicities of interacting atoms, we also performed additional theoretical calculations. The occurrence of C–Cl $\cdots$ Au(I) noncovalent interactions was proved by topological analysis of electron density distribution in the QTAIM approach, followed by NCIPLOT analysis of reduced density gradient (RDG). The results are shown in Figure 18 and summarized in Table 2.

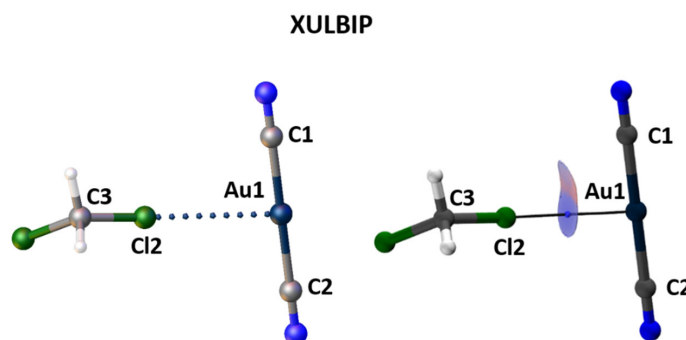


Figure 18. The C–Cl $\cdots$ Au(I) interaction in the structure of **2** (left panel) and visualization of QTAIM topological and NCIPLOT analyses for cluster **2** (right panel).

The QTAIM analysis (Table 2) demonstrates the presence of bond critical points (3, −1) (BCP) between an Au(I) center in dicyanoaurate anion and a chlorine atom in dichloromethane. The negative and small values of the sign(λ_2) ρ on the other BCPs favor the attractive and noncovalent nature of the interactions. They can also be considered as typical noncovalent interactions due to their close to zero positive energy density (0.001–0.002 Hartree/Bohr³) and the balance of the Lagrangian kinetic energy $G(\mathbf{r})$ and the potential energy density $V(\mathbf{r})$ ($-G(\mathbf{r})/V(\mathbf{r}) > 1$) on the corresponding BCPs [65].

The RDG = 0.4 surfaces with a negative sign(λ_2) $\rho(\mathbf{r})$ values on them surround all the BCPs, confirming the existence of the corresponding noncovalent interactions.

To further verify whether the observed Cl $\cdots$ Au contacts belong to the XB, we calculated the electron localization function (ELF) [66–68] projections with assigned critical points and bond paths from QTAIM analysis for the **2** model cluster (Figure 19). The Cl $\cdots$ Au bond path passes through the depletion ELF region (σ -hole) and between the enlargement ELF regions (LPs) on the Cl atom. Inspection of these data supports the hypothesis on the electrophilic nature of the chlorine atom in the gold(I)-involving XB.

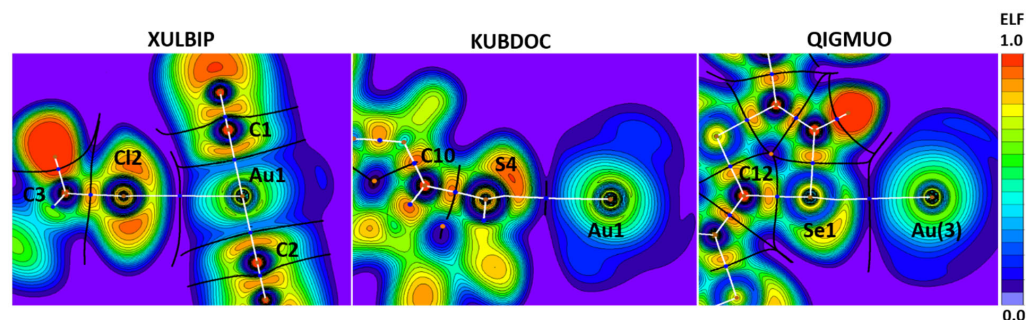


Figure 19. Visualization of ELF, BCPs, and bond paths for C–X $\cdots$ Au (X = Cl, S, Se) interactions in the **2**, **5**, and **13** clusters. BCPs (3, −1) are shown in blue; nuclear critical points (3, −3) are shown in pale brown; ring critical points (3, +1) are shown in orange; bond paths are shown as white lines.

The change in ED/ESP-basins boundaries illustrates the interatomic and intermolecular electrostatic interactions in XB-involving supramolecular clusters (Figure 20). ESP minimum is always placed at the side of the electron-donating atom, while ED minimum is closer to the electrophilic site [72]. A region between the minima is mainly associated with the nucleophile lone pair [74]. The ED/ESP profiles along the Cl $\cdots$ Au bond paths in **2** indicate that the ESP minima shifted to the Au ρ -basin. This shift is probably due to the nucleophilicity of the Au(I) center toward the Cl atom, and Cl $\cdots$ Au interactions can be attributed to Au-involving XB.

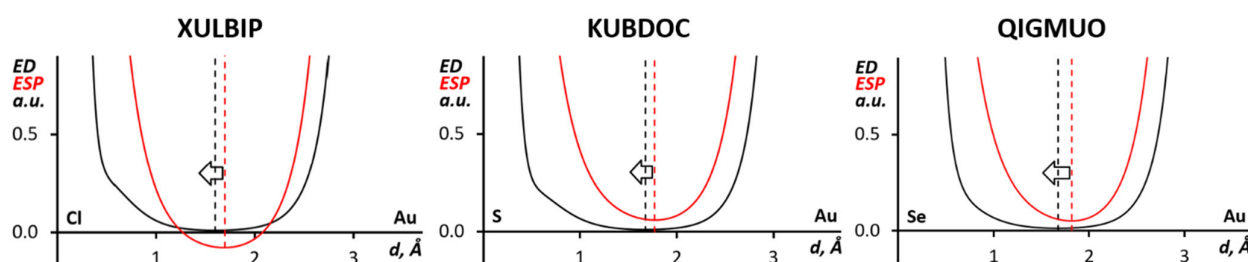


Figure 20. The ED (black) and ESP (red) 1D profiles along the C-X $\cdots$ Au (X = Cl, S, Se) bond paths for the **2** (left panel), **5** (center panel), and **13** (right panel) clusters.

The Se $\cdots$ Au(I) (Figure 9) and S $\cdots$ Au(I) (Figure 21) interactions were detected in the structures of **5** and **13**, respectively. In contrast to the S $\cdots$ N contact, the S $\cdots$ Au interaction in the structure of **5** was not identified or reported by the author of the original work [47]. Analogously, the Se $\cdots$ Au contact in **13**, which can also be interpreted as an example of ChB involving the gold(I) center (Table 2), was not observed and described in the relevant article [92].

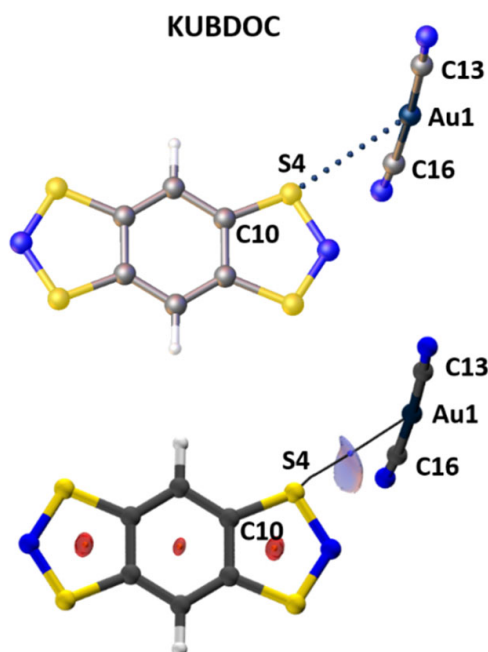


Figure 21. The C-S $\cdots$ Au interaction in the structure of **5** (top panel) and visualization of QAIM topological and NCIPLOT analyses for cluster **5** (bottom panel).

The ELF projections in combination with QAIM topological analysis demonstrate that in both structures, bond paths pass between areas of lone electron pairs of S or Se atoms, which confirms the electrophilicity of these atoms in Au(I)-involving ChBs (Figure 19).

The analyses of electron density (ED) and electrostatic potential (ESP) minima in their 1D profiles along the S...Au(I) and Se...Au(I) bond paths (Figure 20) also confirm the nucleophilicity of gold(I) atoms in these ChBs.

We also applied an alternative approach, namely NBO charge-transfer analysis, to verify the philicities of noncovalent participants. This analysis was performed for the heterodimeric **2**, **5**, and **13** clusters in the natural atomic partitioning scheme (Table 3). In all cases, we found charge-transfer interactions corresponding to the XBs and ChBs between X atoms (X = Cl, S, Se) and the Au center in dicyanoaurate(I), where LPs, located on the gold(I) center, interact with empty σ^* -orbitals of X–C bonds.

Table 3. NBO charge transfer, energy of charge transfer (E_{NBO}), where LP is lone pair and σ^* is antibonding σ^* -orbital in **2**, **5**, and **13** clusters.

Cluster	Charge Transfer	E_{NBO} , kcal/mol
XULBIP	LP(Au1) $\rightarrow$ σ^* (Cl2–C3)	1.21
KUBDOC	LP(Au1) $\rightarrow$ σ^* (S4–C10)	1.00
QIGMUO	LP(Au3) $\rightarrow$ σ^* (Se1–C12)	2.55

The observation of both S...Au and Se...Au ChBs, confirmed by multiple computational methods, underscores the versatility of dicyanoaurate(I) anion as a platform for exploring novel metal-involving noncovalent interactions. These findings significantly expand understanding of gold(I) chemistry, as they demonstrate for the first time that Au(I) centers can act as nucleophilic participants in intermolecular ChBs. Previously, the scientific literature only documented intramolecular ChBs with Au(I), specifically S/Se...Au [101] and Te...Au [102] interactions.

Additionally, intermolecular ChBs had been observed in systems containing other metal centers, i.e., Se...Pt(II) [103,104], Se...Pd(II) [103], Te...Pt(II) [104–106], and Te...Pd(II) [107].

3.8. Calculated Dimerization Energies

The strength of the noncovalent interactions can be calculated as a difference between the energy of a complex and the sum of monomer energies (in the geometry of a complex, i.e., without consideration of the monomer relaxation energies), taking into account the basis set superposition error (BSSE [81]) using a counterpoise procedure. The energies were calculated for all cluster models.

The studied systems are divided into two groups: those comprising an anion and a neutral molecule acting as a σ -hole interaction donor, and those containing an anion and a cation. Calculations of BSSE-corrected dimerization energies revealed a significant energy difference (Table 4) between the two groups. This discrepancy can be rationalized by the enhanced contribution of strong electrostatic attraction between oppositely charged ions in the latter systems [108]. In contrast, for interactions involving neutral molecules (XEDDIW), a strong σ -hole I-centered donors lead to a higher interaction E_{BSSE} , compared with the dicyanoaurate(I)–dichloromethane pair (XULBIP). The latter energy (−1.48) aligns with previously reported value (−1.58) for the dichloroaurate(I)–dichloromethane system [109]. The strongest E_{BSSE} among interionic interactions was found for the dimer from the KUBDOC structure, where electrostatically favorable N–S...N $\equiv$ C ChB is followed by C–H...N $\equiv$ C hydrogen bonding.

Table 4. BSSE-corrected dimerization energies E_{BSSE} (in kcal/mol) for cluster models.

Structure	Bond	σ -Hole Donor	E_{BSSE} , kcal/mol
XEDDIW	C1–I1...N22	neutral	−14.15
	C7–I2...N24	neutral	−15.84
XULBIP	C3–Cl2...Au1	neutral	−1.48
BAQBIE	C13–S11...N1	cationic	−43.23
KUBDOC	N7–S4...N6	cationic	−69.31
ZIGKIJ	C1–S1...N1	cationic	−49.84
HODZIL	C3–Se1...N1	cationic	−53.62
HODZIL01	C3–Se1...N1	cationic	−53.75
QIGMUO	C12–Se1...N33	cationic	−62.99
	C7–Se1...Au3	cationic	−62.99
PILFAR	O1–C9...N2≡C12	cationic	−68.26
DUSBIC	C4–S5... π -C1≡N1	cationic	−54.67
DUSBIC02	C5–S7... π -C11≡N1	cationic	−54.63
KUBDOC	C10–S4...Au1	cationic	−59.45

4. Conclusions

The study identified multiple types of σ -hole interactions, including halogen, chalcogen, pnictogen, and tetrel bonds formed through different sites of the $[\text{Au}(\text{CN})_2]^-$ anion. Theoretical validation using set independent computational methods, including QTAIM and NCI analysis, confirmed the nature of these interactions as noncovalent. Philicities of participants were attributed by both geometrical parameters and further computational methods, including ELF projections, ED/ESP analysis minima, and NBO charge-transfer analysis.

Among all observed and theoretically confirmed interactions, the C–S...Au (structure KUBDOC) and C–Se...Au (structure QIGMUO) are of special interest since this type of intermolecular gold(I)-involving chalcogen bond interactions has never been described before, which expands the known scope of gold(I) supramolecular behavior and fills a major gap in transition metal chemistry.

The observed nucleophilicity of gold(I) centers is consistent with previously established nucleophilic character of this metal center in the formation of interionic metal-philic interactions, including dicyanoaurate(I) as well as Au-centered nucleophilicity of dichloroaurate(I) [109], dibromoaurate(I) [46], and other gold(I) complexes [110,111] in XBs. Since not only gold(I), but also gold(0) and gold(III) are known [112] to participate in the related halogen bonds, we believe the investigation of gold-involving σ -hole interactions can be further expanded in future studies.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/chemistry8070091/s1>: Cartesian atomic coordinates for model supramolecular associates; Figure S1: The C–H...N≡C interactions in the structure of **17** (left panel) and visualization of QTAIM topological and NCIPLOT analyses for cluster **17** (right panel). Hereinafter, blue dots correspond to (3; −1) bond critical points, orange dots to (3; +1) ring critical points, and bond paths are shown by black lines. For noncovalent interactions, RDG half-transparent surfaces with 0.4 values were colored from blue ($\text{sign}(\lambda_2)\rho(\mathbf{r}) = -0.01 \text{ e/Bohr}^3$) to red ($\text{sign}(\lambda_2)\rho(\mathbf{r}) = +0.01 \text{ e/Bohr}^3$). Figure S2: The C–H...N≡C interactions in the structure of **19** (top panel) and visualization of QTAIM topological and NCIPLOT analyses for cluster **19** (bottom panel).

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