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Aurophilicity–Coordination Interplay in the Design of Cyano-Bridged Nickel(II)–Gold(I) Bimetallic Assemblies: Structural and Computational Studies of the Gold(I)–Gold(I) Interactions

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Two polymorphic cyano-bridged Au(I)–Ni(II) bimetallic complexes of formulas $[Ni(en)_2Au(CN)_2][Au(CN)_2]$ (**1**) and $[Ni(en)_2\{Au(CN)_2\}_2]$ (**2**) have been prepared from the 1:2 reaction between $[Au(CN)_2]^-$ and either $[Ni(en)_2Cl_2]Cl$ or $[Ni(en)_3]Cl_2{\cdot}2H_2O$, respectively. The structure of **1** consists of polymeric cationic chains of alternating $[Au(CN)_2]^-$ and $[Ni(en)_2]^{2+}$ units running along the *a* axis and $[Au(CN)_2]^-$ anions lying between the chains. The noncoordinated dicyanoaurate anions are aligned perpendicular to the *ac* plane and involved in aurophilic interactions with the bridging dicyanoaurate groups, ultimately leading to a 2D bimetallic grid. The structure of **2** consists of trinuclear molecules made of two $[Au(CN)_2]^-$ anions linked to $[Ni(en)_2]^{2+}$ unit in trans configuration. Trinuclear units are joined by aurophilic interactions to form 1D zigzag chains. The magnetic properties of these compounds are strongly dominated by the local anisotropy of the octahedral Ni(II) ions, thus indicating that the magnetic exchange interaction mediated by dicyanoaurate bridging groups, if it exits, is very weak. To get insight into the electronic properties of the inter- and intramolecular interactions of the $[Au(CN)_2]^-$ building blocks, the structures of different aggregates of dicyanogold units were optimized and then analyzed by making use of atoms-in-molecules (AIM) theory. Moreover, bond indices were calculated by methods based upon nonlinear population analysis.

Introduction

Crystal engineering of polymetallic coordination polymers has become an area of increasing interest over recent years not only because of their potential applications in catalysis, host–guest chemistry, molecule-based magnets, ion-exchange, gas absorption, etc., but also because of their intriguing structural diversity.[1,2] Among these materials, cyano-bridged systems, prepared from assembling cyanometalates and transition metal complexes, exhibit unique structures. Currently, they are also playing a major role in the areas of molecule-based magnets and photomagnetic

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phenomena.[3,4] The linear diamagnetic $[Au(CN)_2]^-$ anion, however, has been only infrequently used as a building block, despite the fact that gold(I) atoms of dicyanoaurate groups can be involved in weakly bonding aurophilic interactions, which are useful tools in crystal engineering of polymeric structures.[5] Using dicyanoaurate and transition metal complexes as building blocks, new molecular assemblies with novel structural topologies are expected to form by the interplay between coordination bonds and aurophilic interactions. It should be noted that only a few examples of cyano-bridged Au(I)−M(II) (M = Ni(II), Co(II), Cu(II), Zn(II)) bimetallic assemblies have been reported so far which exhibit Au···Au interactions strongly influencing the overall structure.[6] As a continuation of our work along this line, we report herein the structure and magnetic properties of two new Ni(II)−Au(I) heterometallic complexes, $[Ni(en)_2Au(CN)_2][Au(CN)_2]$ (**1**) and $[Ni(en)_2\{Au(CN)_2\}_2]$ (**2**). In addition, the electronic properties of the inter- and intramolecular interactions of the $[Au(CN)_2]^-$ building blocks were analyzed by making use of atoms-in-molecules (AIM) theory.[7] Moreover, bond indices were calculated by methods based upon nonlinear population analysis.[8]

Experimental Section

All reagents were obtained from Aldrich and used without further purification. *Cyanide salts are toxic and should be handled with caution!*

Syntheses of the Complexes. For the preparation of **1**, a 50 mL water/acetone (1:4) solution of $K[Au(CN)_2]$ (0.10 g, 0.35 mmol) was added to an aqueous solution of $[Ni(en)_2Cl_2]Cl$[9] (0.05 g, 0.18 mmol). The resulting solution kept at ambient temperature for several days afforded prismatic light-purple crystals, which were filtered off, washed with water, and air-dried. Yield: 40% based on Ni. Anal. Calcd for $C_8H_{16}N_8Au_2Ni$: C, 14.18; H, 2.36; N, 16.55; Ni, 8.67. Found: C, 14.60; H, 2.57; N, 16.72; Ni, 8.90. IR (KBr, cm^{-1}): 2162 (ν_{CN}), 2143 (ν_{CN}).

Table 1. Crystallographic Data and Structural Refinement Details for the Compounds

	1	2
empirical formula	$C_8H_{16}Au_2N_8Ni$	$C_8H_{16}Au_2N_8Ni$
fw	676.93	676.93
crystal system	monoclinic	monoclinic
space group	$C2/m$ (No. 10)	$C2/c$ (No. 15)
a (Å)	10.265(2)	17.793(2)
b (Å)	13.075(3)	8.119(4)
c (Å)	6.524(2)	12.107(5)
β (deg)	119.21(2)	118.717(14)
V (Å^3)	764.3	1533.9(10)
Z	2	4
T (°C)	−80	−80
λ (Å)	0.710 69	0.710 69
ρ (g cm^{-3})	2.942	2.931
μ (mm^{-1})	20.37	20.30
goodness-of-fit	1.088	1.084
R1^a [$I > 2\sigma(I)$]	0.0558	0.0388
wR2^b [$I > 2\sigma(I)$]	0.1417	0.0984

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Complex **2** was prepared by the same method but using $[Ni(en)_3]Cl_2 \cdot 2H_2O$[9] instead of $[Ni(en)_2Cl_2]Cl$ as light purple crystals. Yield: 50% based on Ni. Anal. Calcd for $C_8H_{16}N_8Au_2Ni$: C, 14.18; H, 2.36; N, 16.55; Ni, 8.67. Found: C, 14.30; H, 2.47; N, 16.67; Ni, 9.02. IR (KBr, cm^{-1}): 2162 (ν_{CN}), 2143 (ν_{CN}).

Physical Measurements. Elemental analyses were carried out on a Fisons-Carlo Erba model EA 1108 analyzer. IR spectra were recorded on a MIDAC progress-IR spectrometer using KBr pellets. Thermogravimetric studies were performed by using a Shimadzu TGA-50H instrument in a flow of air (100 mL/min) and at a heating rate of 20 °C/min. The decomposition gases were analyzed by IR spectroscopy by using a Nicolet 550 spectrophotometer. Magnetization and variable-temperature (1.7−300 K) magnetic susceptibility measurements were carried out with a Quantum Design SQUID operating at different magnetic fields. Experimental susceptibilities were corrected for diamagnetism, temperature-independent paramagnetism, and the magnetization of the sample holder.

Crystallography. Single-crystal data collections for **1** and **2** were performed at −80 °C on a Rigaku AFC7S diffractometer using graphite-monochromatized Mo Kα radiation and the $\omega/2\theta$ scan mode ($2\theta_{max} = 50.5°$). The structures were solved by direct methods and refined on F^2 by the SHELX-97 program package.[10] For both compounds, the metal atoms were refined with anisotropic displacement parameters, but the rest of the non-hydrogen atoms with isotropic displacement parameters, and the hydrogen atoms were treated as riding atoms using the SHELX-97 default parameters.

Crystal data and details of the data collection and refinement for the compounds are summarized in Table 1. Bond lengths and angles for the compounds are gathered in Tables 2 and 3, respectively.

Computational Details

The optimizations were carried out at the MP2/LANL2DZ level of theory by making use of the Gaussian 98 code.[11] Where

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**^{a}

Au1−C2	1.992(13)	N1−C1	1.439(15)
Au2−C3	2.010(16)	N2−C2	1.136(17)
Au2−Au1	3.262(10)	Ni−N1	2.101(8)
Ni−N2	2.124(12)	N3−C3	1.10(2)
C1−C1$^{\#1}$	1.59(2)		
C3−Au2−Au1	90.0	C2−N2−Ni	160.7(12)
C2−Au1−Au2	73.4(4)	N2−C2−Au1	172.1(12)
N1$^{\#1}$−Ni−N1	82.3(5)	N3−C3−Au2	180.0
N1−Ni−N2	87.6(3)		

^{a} Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, y, -z + 1$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 2^a

Au−C3	1.991(10)	N1−C1	1.458(15)
Au−C4	1.993(11)	N2−C2	1.474(14)
Au−Au$^{\#1}$	3.2844(13)	N3−C3	1.134(14)
Ni−N1	2.099(9)	N4−C4	1.150(15)
Ni−N2	2.099(9)	C1−C2	1.524(15)
Ni−N3	2.099(9)		
C3−Au−C4	179.0(4)	N2−Ni−N3	88.9(4)
C3−Au−Au$^{\#1}$	76.5(3)	C3−N3−Ni	166.3(9)
C4−Au−Au$^{\#1}$	102.8(3)	N3−C3−Au	177.8(9)
N1−Ni−N2	82.9(3)	N4−C4−Au	177.6(11)
N1−Ni−N3	91.5(4)		

^{a} Symmetry transformations used to generate equivalent atoms: #1, $-x + 2, y, -z + 1/2$.

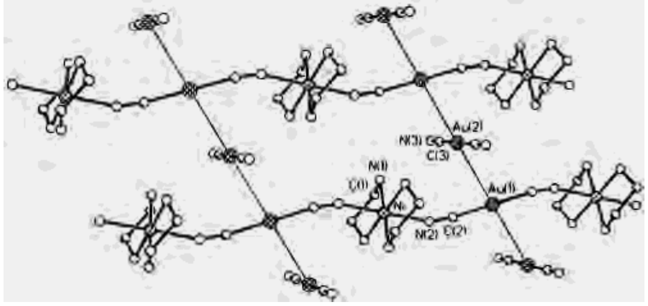

Figure 1. Perspective view of the 2D bimetallic grid of **1**. (Au···Au bonds are drawn as thin lines.) Hydrogen atoms are omitted for clarity.

appropriate, the initial C−Au···Au′−C′ torsion angles were 45° and the Au···Au′ distances 3.3 Å. No symmetry restrictions were applied during the optimizations. According to the calculated IR spectra, all of the optimized structures represent true energy minima. The topological analyses were carried out by making use of the wave functions obtained after the optimizations and applying AIMPAC program package.[12] Pair population analyses were carried out by WinFermi.[13]

Results and Discussion

Compounds **1** and **2** have been prepared as suitable crystals for X-ray analysis from the reaction between 1:1 solutions of K[Au(CN)$_2$] and either [Ni(en)$_2$Cl$_2$]Cl or [Ni(en)$_3$]Cl$_2$, respectively. Although these compounds have the same empirical formula, they exhibit rather different structures and then can be considered as polymorphic forms. This fact is likely due to the different transition metal complexes used in their syntheses and may be tentatively justified as following. When [Ni(en)$_3$]Cl$_2$·2H$_2$O is employed as a precursor, it slowly dissociates in aqueous solution to give [Ni(en)$_2$]$^{2+}$ and free ethylenediamine.[14] In these conditions there would be a great excess of [Au(CN)$_2$]$^-$ with regard to [Ni(en)$_2$]$^{2+}$, which would favor the formation of trinuclear species. When the complex [Ni(en)$_2$Cl$_2$] is used as a building block, however, the chloride ligands are easily replaced by nitrogen atoms of the dicyanoaurate ligand, thus favoring the formation of a 1D chain structure.

The IR spectra of **1** and **2** in the 4000−400 cm^{-1} range are virtually identical, and thus, polymorphs cannot be distinguished by infrared spectroscopy. Both compounds exhibit ν(CN) bands at 2143 and 2162 cm^{-1}, which are due to free (K[Au(CN)$_2$] exhibits a single band at 2141 cm^{-1}) and coordinated [Au(CN$_2$)]$^-$ groups, respectively. Thermogravimetric studies, however, can differentiate between the two polymorphs as the thermal behaviors of these compounds are very similar but not identical. Both polymorphs are stable up to 300 °C, and from this temperature, two weight loss effects corresponding respectively to the elimination of two ethylenediamine ligands and four cyanide occur. For **1**, the TG curve shows the weight loss effects in the 300−350 and 425−500 °C temperature ranges, whereas for **2** the second effect takes place at significantly lower temperatures, between 375 and 450 °C.

Structures. The structure of **1** (Figure 1) consists of polymeric cationic chains of alternating [Au(CN)$_2$]$^-$ and [Ni(en)$_2$]$^{2+}$ units running along the *a* axis and [Au(CN)$_2$]$^-$ anions lying between the chains. Within the chain, the CN$^-$ groups of each [Au(CN)$_2$]$^-$ unit bridges two Ni(II) atoms with Ni(II)···Au(I) and Ni(II)···Ni(II) distances of 5.1325(10) and 10.265(2) Å, respectively, the nickel and gold atoms being located on symmetry elements 2/*m*. The Ni−N2−C2 and Au1−C2−N2 bond angles of 160.7(12) and 172.1(12)°, respectively, for bridging cyanide groups indicate that the chain adopts a zigzag disposition. The Ni(II) center exhibits a distorted octahedral NiN$_6$ environment with equatorial and axial Ni−N distances of 2.101(8) and 2.124(12) Å, respectively, and cis N−Ni−N angles vary from 82.3(5) to 97.7(5)°. The noncoordinated dicyanoaurate anions are aligned perpendicular to the *ac* plane and involved in aurophilic interactions with the bridging dicyanoaurate groups. The Au(1)−Au(2) distance of 3.2620(10) Å is much shorter than

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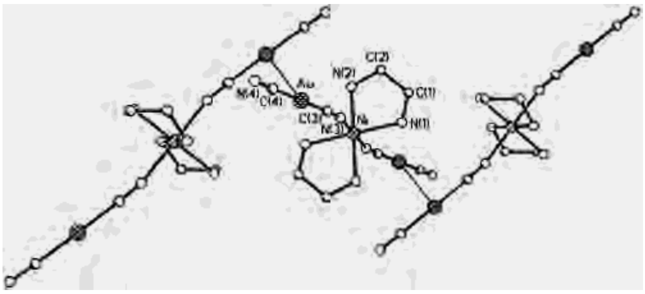

Figure 2. Perspective view of the 1D zigzag chain of **2**. Hydrogen atoms are omitted for clarity.

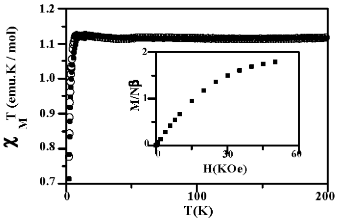

Figure 3. Temperature dependence of the $\chi_M T$ product for **1** (filled circles) and **2** (open circles) and field dependence of M for **2** (inset).

the sum of the van der Waals radii of the gold(I) atoms, thus clearly indicating the existence of Au⋯Au interactions connecting the 1D zigzag chains to form a 2D bimetallic grid in the *ac* plane. As expected from experimental results[5,15] and theoretical calculations,[6g,16] the dicyanoaurate anions involved in aurophilic interactions exhibit a staggered conformation with the C2−Au1⋯Au2−C3 torsion angle of 90°. Because of these aurophilic interactions dicyanoaurate anions form a metal chain that can be viewed as a pseudo-metal wire. Similar structures have been observed for other dicyanoargentate- and dicyanoaurate-containing compounds, such as $[\{Cu(en)_2Au(CN)_2\}\{Au(CN)_2\}]$,[6i] $[\{Cu(en)_2Ag(CN)_2\}\{Ag(CN)_2\}]$,[17] and $[\{Cd(en)_2Ag\ (CN)_2\}\{Ag(CN)_2\}]_n$.[18] A comparison between the crystal structures of $[\{Cu(en)_2Au(CN)_2\}\{Au(CN)_2\}]$ and **1**, both crystallizing in the same space group, shows that Au⋯Au distances for the former are by 0.1 Å shorter than for the latter. This fact might be a consequence of the most important structural difference between these two compounds: the Jahn−Teller tetragonal distortion of the octahedral CuN_6 coordination polyhedron in $[\{Cu(en)_2Au(CN)_2\}\{Au(CN)_2\}]$, with an axial $Cu-N_{cyanide}$ (2.576(6) Å) that is significantly longer than the $Ni-N_{cyanide}$ distance in **1**. Since the interchain Au1⋯Au1 distances for $[\{Cu(en)_2Au(CN)_2\}\{Au(CN)_2\}]$ and **1** are very close, 8.41 and 8.31 Å, respectively, the Jahn−Teller elongation of the $Cu-N_{cyanide}$ distance additionally causes a reduction of the Cu−NC bond angles in the bridging region. These structural changes should yield a more efficient space filling, thus allowing closer Au⋯Au contacts.

The X-ray structure of **2** (Figure 2) consists of trinuclear molecules made of two $[Au(CN)_2]^-$ anions linked to a $[Ni(en)_2]^{2+}$ unit in trans configuration, leading to a Ni(II)⋯Au(I) distance of 5.1816(15) Å. The Ni(II) ion, which is located on a center of inversion, exhibits distorted octahedral NiN_6 coordination polyhedron with equal Ni−N distances of 2.099(9) Å, and cis N−Ni−N angles vary from 82.9(3) to 97.1(3)°. The Ni−N3−C3 bond angle in the bridging region of 166.3(9)° indicates that the trinuclear molecules are far from being linear. Trinuclear units are joined by aurophilic interactions to form 1D zigzag chains with a Au⋯Au′ distance of 3.2844(13) Å and a C3−Au⋯Au^d−$C3^d$ torsion angle of 119.5(7)° ("d" refers to equivalent position $-x + 2$, y, $-z + 1/2$). Gold(I) atoms are additionally involved in a very weak almost negligible aurophilic interaction with a Au⋯Au^e distance of 3.5587(15) Å ("e" refers equivalent position $-x + 2$, $-y + 1$, $-z + 1$). A similar structure has been observed for the compound $[Ni(tren)_2\{Ag(CN)_2\}_2]$ (tren = 1,3-diaminopropane), in which the Ag⋯⋯Ag distance between trinuclear units is 3.267(3) Å, slightly shorter than that of **2**. A comparison among the structures of **1**, **2**, and the above-mentioned structurally similar compounds containing dicyanoargentate groups indicates that, despite Au(I) being smaller than Ag(I),[6i] Ag⋯Ag distances are, in general, shorter than the Au⋯Au analogues. This fact might suggests that argentophilic interactions are, at least, as strong as the aurophilic interactions. Nevertheless, to clarify this point, more examples of dicyanoargentate- and dicyanoaurate-containing isostructural systems are needed to make comparisons of metallophilic bond lengths.

In both compounds, there exist very weak hydrogen bond interactions (donor−acceptor distances bigger than 3.0 Å) involving amino groups of the coordinated ethylenediamine and terminal (or nonbridging) cyanide groups.

It should be noted that, as far as we know, only one cyano-bridged Au(I)−Ni(II) bimetallic complex, $[Ni(tren)Au(CN)_2][Au(CN)_2]$[6g] (tren = tris(2-aminoethyl)amine), has been reported so far. It exhibits a 1D-zigzag chain structure made of $[Au(CN)_2]^-$ bridging anions linked to $[Ni(tren)]^{2+}$ cations in cis positions and uncoordinated $[Au(CN)_2]^-$ anions. In this case, however, the aurophilic interactions are negligible with two different Au⋯Au′ distances of 3.593 and 3.596 Å and C−Au⋯Au′-C′ torsion angles of 106.6 and 163.1°, respectively. The different aurophilic behaviors of the dicyanoaurate anions in $[Ni(tren)Au(CN)_2][Au(CN)_2]$ and **1** might be a consequence of other factors, such as the shape and volume of the cationic building blocks, $[Ni(tren)]^{2+}$ and $[Ni(en)_2]^{2+}$, respectively, as well as the hydrogen-bonding network, which may play an important role in determining the final Au⋯Au distances.

Magnetic Properties. As expected, the temperature dependences of $\chi_M T$ for **1** and **2** are very similar (Figure 3). The $\chi_M T$ values remain almost constant and equal to 1.12 $cm^3\ mol^{-1}$ K in the 300−10 K temperature range. This value agrees well with that expected for one isolated Ni(II) ion with $g = 2.12$. As the temperature is lowered from 10 K, the $\chi_M T$ products gradually decrease to a value near to 0.7

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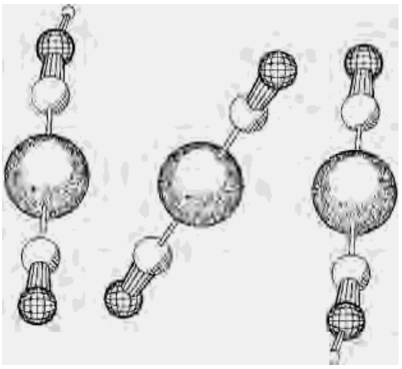

Figure 4. PLUTON picture of the optimized mixed trimer moiety.

$cm^3\ mol^{-1}$ K at 2 K. This behavior is mainly due to the local anisotropy of the octahedral Ni(II) ions promoted by the zero-field splitting, thus suggesting that the magnetic exchange interaction mediated by dicyanoaurate bridging groups, if it exists, is very weak. The same conclusion was drawn from the magnetic study of 1D and 2D bimetallic compounds containing $[Au(CN)_2]^-$ bridging groups.[6g-i] The susceptibility data were fitted by a formula derived directly from Van Vleck equation with only single ion anisotropy (D) involved. The best agreement between calculated and experimental values of the susceptibility was found with $D = 4.10(1)\ cm^{-1}$ and $g = 2.14$ (2) for **1** and $D = 3.89$ (2) cm^{-1} and $g = 2.13(2)$ for **2**. When the magnetic exchange interactions are incorporated into the susceptibility within a molecular-field approximation,[19] the fitting procedure for **1** yielded $D = 4.45(2)\ cm^{-1}$, $g = 2.11(2)$, and $J/k = 0.15(3)$ K. The slight change of D after including J also indicates the dominant role of the paramagnetic anisotropy in this compound. Even though the J value is very small in this case, its positive sign is in agreement with the very weak ferromagnetic exchange interactions observed for $[Ni(en)_2]_3[Fe(CN)_6](PF_6)_2$,[20] $[Cu(en)(H_2O)]_2[Fe(CN)_6]\cdot 4H_2O$,[21] and $(tmen)Cu[Au(CN)_2]_2$,[6d] three cyano-bridged bimetallic compounds containing diamagnetic cyanometalate bridging groups. Field-dependent magnetization measurements for **1** and **2**, performed at 2−5 T, are virtually equal, and thus, only those for **2** are given in the inset of Figure 3. The values at the maximum applied magnetic field of 50 kOe (1.8 $N\beta$) are lower than the expected saturation value of $2N\beta$ for $S = 1$. This is likely due to the effect of the zero-field splitting which is operative at 2 K.

AIM Analysis. In a preliminary communication[6h] we presented a short account on the structure optimizations, at the MP2/LANL2DZ level of theory, for different aggregates of dicyanogold units: neutral dimer; dimer and trimer anions; mixed trimer (anionic form in the middle). To achieve a single neutral complex, one of the two cyanide groups of a dicyanoaurate anion was protonated (see the optimized structure for the mixed trimer in Figure 4). Herein, we report the more detailed results containing also topological analysis of the charge density. Selected geometrical parameters for the optimized moieties are shown in Table 4.

From this study it was concluded that the charge of the moieties has important consequences on the Au···Au distance and C−Au···Au′−C torsion angle. For dimer and trimer anions, as well as for mixed trimer (Figure 4), with Au···Au distances in the range 3.180−3.472 Å, the torsion angles always changed from the initial value of 45° into 90° during the optimization. However, for the neutral dimer, with a Au···Au distance of 3.893 Å, the torsion angle is zero. The long Au···Au distance is indicative of the absence of aurophilic interactions. The theoretical results agree well the available experimental evidence indicating staggered conformation for $[Au(CN)_2]^-$ involved in aurophilic interactions.[6,15] Accordingly, the Au−Au interactions are affected by the torsional angle C−Au···Au′−C′.

To get an insight into the electronic properties of the optimized species, AIM analyses were carried out for them. No AIM analysis was carried out for the neutral dimeric moiety, since the optimized Au−Au distance was clearly too long to indicate any aurophilic interaction. Usually the Au−Au distance of 3.3 Å has been taken as a limit for aurophilic interactions.[22] The results of the AIM analyses are shown in Table 5.

In a bond critical point (BCP) the ellipticity values near zero are interpreted to suggest either a single or a triple bond, whereas the double bonds should have nonzero values. As expected, the ellipticity values are very near zero for the Au−C and C−N bonds. The differences of single and triple bonds are also clearly seen in the electronic charge density values, which are consistently higher for the C−N bonds. The Laplacian values for the C−N bonds are clearly negative, which is in accordance with the expected covalent nature of these bonds. The positive Laplacian values for the Au−C bonds suggest that there is charge depletion at the BCPs indicating closed-shell interaction. This is in accordance with the d^{10} electron configuration of the Au(I) cation.

The Au−Au interactions have very low electronic energy densities at the calculated BCPs. However, the electron charge density at the BCP at the Au−Au interaction increases clearly from dimer to trimer, as does also the Laplacian value. The Laplacian values imply that although the interaction has more closed-shell nature in the trimer, the interaction becomes stronger, which is also seen in the electronic energy density value. For the trimer moiety the negative value indicates even attraction. Moreover, change of the sign of the numerical value for the electron energy value is also in accordance with the suggested limiting value of 3.3 Å for aurophilic interaction. Obviously the aurophilic effect is additive, so that the Au−Au bond length will decrease upon increase of the number of the dicyanogold units.[15] It should be noted, however, that there are nonadditive induction terms involved for large oligomers with several Au(I) centers.[23] The positive values of the Laplacians can also be interpreted

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Table 4. Selected Geometrical Parameters for the Optimized Moieties[a]

moiety	Au···Au	Au−C	AuC(H)[b]	C−N	C−N(H)[b]	C−Au−C	C−Au−Au′−C′
monomer		2.039		1.223		180.0	
dimer anions	3.472	2.045		1.224		173.6	90
dimer neutral	3.893	2.025	2.026	1.221	1.196	170.1	0
trimer mixed	3.180	2.021	2.025	1.221	1.197	178.6	90
trimer anion	3.180	2.036		1.223		180.0	90

[a] The bond lengths are in Å, and the angles, in deg. [b] Refers to the protonated cyanide anion.

Table 5. Ellipticity ϵ, Electron Charge Density $\rho(r)$, Its Laplacian $\nabla^2\rho(r)$), and Electronic Energy Density $E_d(r)$ at the Bond Critical Points for the Optimized Structures at the MP2/LANL2DZ Level of Theory

	ϵ	$\rho(r)$ (e/a_o^3)	$\nabla\rho(r)$ (e/a_o^5)	$E_d(r)$ (hartree/a_o^3)
		Monomer, Anion		
Au−C	0.0000	0.1151	0.3526	−0.0347
C−N	0.0000	0.3869	−0.5981	−0.6014
		Dimer, Dianion		
Au···Au	0.0002	0.0119	0.0375	0.0010
Au−C	0.0002	0.1136	0.3490	−0.0339
C−N	0.0006	0.3855	−0.5920	−0.5981
		Trimer		
Au···Au	0.1009	0.0220	0.0652	−0.0012
anion				
Au−C	0.0025	0.1162	0.3451	−0.1358
C−N	0.0040	0.3873	−0.6058	−0.6008
neutral				
AuCN				
Au−C	0.0042	0.1207	0.3403	−0.0386
C−N	0.0009	0.3884	−0.5974	−0.6049
AuCNH				
Au−C	0.037	0.1160	0.4369	−0.0329
C−N	0.074	0.3725	0.1155	−0.5745

in terms of ionic interaction. Indeed, the ionic component was found to be an important contribution in short distances between gold atoms.[24] Further calculations are in progress to study a possible correlation between the high ellipticity value found here and the ionic contribution in aurophilicity.

To study further the Au···Au interaction, we carried out nonlinear population analyses from geminal expansion of pair densities. The results revealed that in the anionic dimer the Au−Au bond index is very small, only 0.013. In the trimeric species the bond index is again very small, 0.018.[25] Accordingly, the relatively high ellipticity value found for the trimer moiety simple describes the curvature of the bond path rather than the bond order.

As stated before, the AIM description for the Au−C interactions equals that of an ionic bond including closed-shell interactions. It could be possible to describe the interaction in terms of 3c−4e bonding, too. However, WinFermi gives bond indices for the C−Au−C fragments ranging from −0.065 to −0.083. These values are considerably lower than the theoretical value of −0.1875 calculated by Mayer.[26]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds $[Ni(en)_2Au(CN)_2][Au(CN)_2]$ (**1**) and $[Ni(en)_2\{Au(CN)_2\}_2]$ (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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