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# Quantum-Chemical Study of *trans* Influence in Gold(I) Linear Complexes

**A. Yu. Sokolov and O. V. Sizova**

*St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
*e-mail: ovsizova@mail.ru*

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**Abstract**—Theoretical study of *trans* influence of ligands in Au(I) and Ag(I) complexes is based on quantum-chemical calculations fulfilled within the limits of density functional theory. Metal-ligand bond orders and their σ- and π-components were analyzed for several series of $[L–M(I)–X]^q$ complexes; the participation of *s, p*, and *d* metal orbitals in binding was characterized. The π dative interactions metal→ligand in Ag(I) and Au(I) complexes are weakened, and *trans* influence is caused by a competition of σ-donor ligands for the electronic density transfer from lone pairs of ligands onto $0.9s + 0.4d_{z^2}$ hybrid orbitals of gold.

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Gold(I) complex compounds find wide practical application in medicine, molecular biology, biochemistry, and nanotechnologies. These complexes participate in key stages of fine organic synthesis and are used as building blocks of supramolecular photophysical and photochemical devices. Theoretical calculations aimed at the elucidation of the nature of metal-ligand coordination bonds [1] have played a basic role in understanding the nature of unique properties of Au(I) compounds. The completion of electronic shell filling (formal configuration $d^{10}$) and significant relativistic effects [2–6] determine special features of the chemistry of this element in comparison with the chemistry of other transition metals in low oxidation states, including the fact that complexes with π-acceptor ligands are not characteristic for Ag(I) and Au(I) [1]. At present only a few Au(I) stable carbonyls are known, though the complex [AuCl(CO)] is known even from 1925. The linear cation $[Au(CO)_2]^+$ was obtained only recently in the composition of uranium and antimony salts [1, 7].

Frequencies of the (C–O) stretching vibration in Ag(I) and Au(I) carbonyls [8–11] are higher than that of the free molecule, which proves the absence of strong dative metal→CO interactions [7, 12]. Cyanide complexes of Au(I) are widely used as linear bridging fragments in the synthesis of new polymeric materials, because the cyanide ion forms bonds with metals both through C and N atoms. The theoretical substantiation of the effectiveness of such bridges and the analysis of electronic interactions involving Au(I) touched on the problem of the metal-ligand coordination bond nature and special features of mutual influence of ligands in $d^{10}$ complexes.

The linear structure of $[L–M–X]^q$ complexes reduces an interaction of coordinated ligands to a trans influence. We were able to find only one publication [13], in which the influence of ligands L on the strength of the bond between the gold atom and the ligand $Cl^-$ was studied on the basis of nuclear quadrupole resonance spectroscopy for the series of [L–Au–Cl] complexes [L = RNC, $Cl^-$, $C_5H_5N$, $P(R')_3$; R = Ph, *n*–$CH_3OC_6H_4$, $C_6H_{11}$; R' = $C_2H_5$, Ph, $C_6H_{11}$, Cl, OMe, OPh]. A conclusion was drawn that in these compounds the α-*trans* influence plays the main role in the interaction of ligands. The theoretical study of this problem was undertaken in the only work [14], where metal-ligand bonds in the complexes $[L_1–Au(I)–L_2]$ (L = BF, CO, C≡CH–, pyridine and its derivatives) and $\{HCN–[Au(I)–CN]_n\}$ were considered within the limits of the DFT method with the use of the EDA scheme (Energy Decomposition Analysis). Special attention was given to π interactions transferred through the gold atom valence shell.

In the present work the analysis of chemical bonds and of *trans* influence in linear $[L–Au(I)–X]^q$ complexes is based on the density functional theory (DFT) calculation of bond orders and their σ- and π-com-

**Table 1.** Experimental and calculated [21] Au–P bond lengths (Å) in Au(I) complexes

| Complex | Experiment | Nonrelativistic calculation | Relativistic calculation | Our data |
|---|---|---|---|---|
| $[Au(PMe_3)_2]^+$ | 2.304 [18] | 2.533 | 2.332 | 2.349 |
| $[Au(PMe_3)(Cl)]$ | 2.234 [18] | 2.245 | 2.235 | 2.264 |
| $[Au(PPh_3)(Cl)]$ | 2.235 [19],<br>2.336 [20] | | | 2.272 |

**Table 2.** Optimized metal-ligand bond lengths (Å) found in [14] and in the present work (in brackets)

| [FB–Au–C≡CH] | | [HC≡C–Au–py] | | [FB–Au–$PyO^4$] | |
|---|---|---|---|---|---|
| Au–B | Au–C | Au–C | Au–N | Au–B | Au–N |
| 1.935 | 1.999 | 1.938 | 2.085 | 1.910 | 2.040 |
| (1.936) | (2.004) | (1.944) | (2.101) | (1.911) | (2.041) |

ponents. We set the following tastes: to trace the dependence of Au-L bond orders on the nature of *trans*-ligand X; to characterize σ-donor and π-acceptor power of ligands in compounds under consideration; to characterize electronic configurations of Ag(I) and Au(I) valence shells in the composition of linear $[L–M(I)–X]^q$ complexes; to estimate σ and π contributions into metal-ligand bond orders; to estimate the role of separate gold AOs in the formation of bonds with ligands and in the transmission of the *trans* influence.

Existing and model $[(CN)–Au–X]^q$ complexes with relatively small ligands X (*q* is a total charge of a complex) were selected as subjects of the calculations. The ligand $CN^−$ is characterized by a clearly pronounced σ-donor power and a weak π-acceptor power, the ligand X was varied so that the influence of the following factors on the characteristics of M–CN bonds can be considered:

– electronegativity of a donor atom in the series of ligands X = $NR_3$ (R = H, F), $PR_3$ [R = H, F, $CH_3$ (Me), $C_6H_5$ (Ph)], $AsR_3$ (R = H, F), $H_2O$, $H_2S$, $F^-$, $Cl^−$, $Br^−$, $I^−$;

– nature of substituent R in ligands X;

– charge *q* of a free ligand X (*q* = +1, 0, –1);

– presence or absence of low-lying vacant MOs of ligand X.

To analyze the role of the π–dative interactions in the formation of bonds in complexes of metals with $d^{10}$ electronic configuration, model complexes $[(CO)–Au–X]^q$ were considered. Calculations of the complexes $[X–Ag–Y]^q$ (X = CO, $Cl^−$, $CN^−$; Y = $CN^−$, CO) have allowed us the comparison of characteristics of the electronic structure of Au(I) and Ag(I) complexes. Three com-pounds, [BF–Au–$PyO^4$] ($PyO^4$ = 4-pyridone anion), [CCH–Au–Py] (Py = pyridine), and [BF–Au–CCH], were taken from among those studied in [14] to supplement the description of interfragment interactions in complexes on the basis of a density matrix from EDA positions [14].

*Calculation procedure*. Quantum-chemical calculations were carried out within the limits of density functional theory using the PBE0 hybrid functional [15] and SDD+DZVP combined basis set: the SDD basis with relativistic core pseudopotential [16] for heavy metal atoms and the full-electron DZVP basis [17] for ligand atoms. Test calculations have shown that the selected procedure makes it possible to consider rather complicated compounds and satisfactory reflect their geometrical parameters in the absence of aurophilic interactions in the system. Table 1 contains calculated data for three compounds free from close Au(I)–Au(I) contacts distorting the linear structure of complexes.

Structural parameters of Au(I) complexes optimized within the limits of the selected method are very close to the parameters obtained by the ADF program using the relativistic density functional theory (ZORA), BP86 functional, and TZ2P Slater basis [14] (Table 2). The calculations were carried out using the GAUSSIAN03 software package [22]. Calculations with the complete optimization of geometry without limitations on symmetry have been fulfilled for all complexes.

*Procedure of data handling*. The discussion of the calculated data is based on the analysis of orbital populations (*n*) and orders of bond between A and B atoms according Wiberg, *W*(A–B), [23-24] calculated in the basis of natural atomic orbitals (NAO) [25]. Charges on atoms and fragments and population of AOs were calculated within the limits of NPA (Natural Popula-tion Analysis, analysis of population in the basis of natural atomic orbitals) [25]. To elucidate the nature of nonzero Wiberg indexes between non-adjacent C and X atoms, we applied "bond orders β weighed on overlap integrals" calculated within the

NPA limits by the GAUSSIAN03 program. The calculation of σ and π components of $W$(A–B) indexes was carried out according to the procedure described in [26–28]. To analyze the role of *s, p,* and *d* orbitals of metals in the formation of bonds with ligands, we calculated contributions of *s, p,* and *d* metal AOs (A)) into metal-ligand bond orders: $W(\text{A–B}) = W^{\text{A}}_{s(\sigma)}(\text{A–B}) + W^{\text{A}}_{p(\sigma)}(\text{A–B}) + W^{\text{A}}_{p(\pi)}(\text{A–B}) + W^{\text{A}}_{d(\sigma)}(\text{A–B}) + W^{\text{A}}_{d(\pi)}(\text{A–B})$.

Donor–acceptor power of ligands was estimated according to the procedure offered in [29]. Valence orbitals (VAO in the case of monoatomic blocks and VMO in the case of polyatomic blocks) were constructed by diagonalizaton of density matrix blocks in the NAO orthogonal basis. Their valence activities $\nu_i$ were calculated through their populations $n_i$ by the formula: $\nu_i = 2n_i - n_i^2$. The VMO with the population $n_i = 1$ are involved in bonding to the maximal extent, whereas VMO with the population 0 (vacant) or 2 (localized inside a fragment) form no bonds with surrounding atoms.

*Electronic configuration of metals in [LMX]$^q$ complexes*. The formal electronic configuration $d^{10}$ is assigned to silver and gold ions in the oxidation state +1. According to the calculations, the total population of valence *d*-AOs in silver complexes is close to 10, in most cases $n(d) \approx 9.8$. When ligands have π-acceptor properties, the d-AO population is slightly reduced. The population of *s* AOs is approximately 0.7. The population of gold 6s orbitals in all Au(I) complexes is close to 1, and the metal population *d*-AOs is slightly less than in Ag(I) complexes (Table 3).

**Table 3.** Populations of *s, p,* and *d* orbitals in [(CN)MX]$^q$ complexes (M = Ag, Au)

| X | Ag | | | Au | | |
|---|---|---|---|---|---|---|
| | 5*s* | 5*p* | 4*d* | 6*s* | 6*p* | 5*d* |
| $CN^-$ | 0.74 | 0.01 | 9.80 | 1.02 | 0.01 | 9.65 |
| $HC{\equiv}C^-$ | 0.73 | 0.01 | 9.79 | 1.00 | 0.01 | 9.65 |
| $Cl^-$ | 0.63 | 0.02 | 9.83 | 0.95 | 0.01 | 9.69 |
| CO | 0.67 | 0.01 | 9.76 | 0.98 | 0.01 | 9.58 |
| $PPh_3$ | 0.66 | 0.01 | 9.84 | 0.96 | 0.01 | 9.73 |

Differences in electronic configurations of these two metals with the formal configuration $d^{10}$ are caused by relativistic effects, which are insignificant in Ag(I) complexes, and are very strong in Au(I) complexes [2]. Energy stabilization of *s* AOs results in a raise of their role in the formation of coordination bonds of the gold atom with ligands, and destabilization of gold *d* AOs creates favorable conditions for π-dative interactions.

*Donor-acceptor properties of ligands*. Figure 1 shows σ- and π-valence activities of ligands X in [(CN)AuX]$^q$ complexes. The VMOs of ligands responsible for the appearance of nonzero π-valence activities interact exclusively with $d_\pi$ AO (and VAO) of the metal having the population 2 for free ions. Thus, π-valence activity of all the ligands describes the acceptor power of a ligand, which can be measured by the deviation $\Delta Q_\pi$ of populations of active π VMOs from zero. It is easy to estimate an X→M charge transfer if the total charge $Q$ on a ligand in the complex and the value of $\Delta Q$ are known.

It is readily seen from Fig. 1 that only CO, BF, $PF_3$, $AsF_3$ have pronounced acceptor properties; $H_2O$ and halide ions do not exhibit pronounced π-acceptor power. The ligand BF is remarkable by the fact that even in Au(I) complexes it exhibits pronounced π-acceptor properties, which comprise well with carbonyl π-acceptor power. At the same time its σ-donor power is noticeably higher than that of CO. The resulting quantitative characteristics agree with the generally accepted notions on the donor–acceptor properties of ligands and will be used in the subsequent discussion.

*Metal-ligand bonds in [LAuX]$^q$ complexes*. The calculated data point to the fact that the optimized

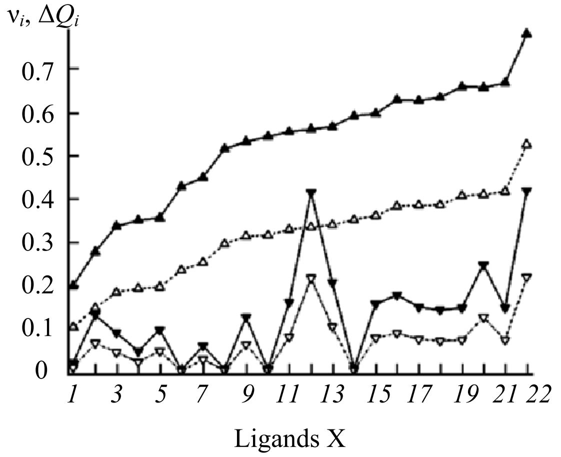

**Fig. 1.** Valence activities $\nu_\sigma$(▲) and $\nu_\pi$(▼) and charge transfer ΔQ by X→M(Δ) σ bonds and by X←M(Δ) π bonds in [(CN)AuX]$^q$ complexes for ligands X: (*1*) $H_2O$, (*2*) $NF_3$, (*3*) $H_2S$, (*4*) $NH_3$, (*5*) Py, (*6*) $F^-$, (*7*) $PyO^-$, (*8*) $Cl^-$, (*9*) $AsH_3$, (*10*) $Br^-$, (*11*) $PH_3$, (*12*) CO, (*13*) $AsF_3$, (*14*) $I^-$, (*15*) $PPh_3$, (*16*) $CNS^-$, (*17*) $PMe_3$, (*18*) $CNO^-$, (*19*) $^-C{\equiv}CH$, (*20*) $PF_3$, (*21*) $CN^-$, and (*22*) BF (ligands are arranged in order of increasing $\nu_\sigma$).

**Table 4.** Bond lengths *r*(A–B), Å, bond orders after Wiberg, *W*, and their σ and π components, $W_\sigma$ and $W_\pi$, in $[(CN)AuX]^q$ complexes

| X | *r*(Au–X) | *r*(Au–C) | *r*(C–N) | Au–X | | | Au–C | | | C–N | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *W* | $W_\sigma$ | $W_\pi$ | *W* | $W_\sigma$ | $W_\pi$ | *W* | $W_\sigma$ | $W_\pi$ |
| $F^-$ | 2.016 | 1.933 | 1.172 | 0.31 | 0.28 | 0.03 | 0.74 | 0.63 | 0.12 | 2.84 | 1.00 | 1.84 |
| $Cl^-$ | 2.345 | 1.958 | 1.171 | 0.37 | 0.35 | 0.02 | 0.68 | 0.59 | 0.10 | 2.86 | 1.00 | 1.86 |
| $Br^-$ | 2.458 | 1.966 | 1.171 | 0.39 | 0.38 | 0.01 | 0.66 | 0.57 | 0.09 | 2.86 | 1.00 | 1.86 |
| $I^-$ | 2.634 | 1.977 | 1.170 | 0.43 | 0.41 | 0.02 | 0.64 | 0.55 | 0.09 | 2.87 | 1.00 | 1.87 |
| $H_2O$ | 2.170 | 1.927 | 1.166 | 0.15 | 0.14 | 0.01 | 0.82 | 0.74 | 0.08 | 2.90 | 1.00 | 1.90 |
| $H_2S$ | 2.376 | 1.954 | 1.166 | 0.28 | 0.24 | 0.04 | 0.75 | 0.68 | 0.07 | 2.91 | 1.00 | 1.91 |
| $NH_3$ | 2.121 | 1.948 | 1.166 | 0.26 | 0.25 | 0.01 | 0.74 | 0.67 | 0.07 | 2.90 | 1.00 | 1.90 |
| $NF_3$ | 2.149 | 1.941 | 1.167 | 0.25 | 0.18 | 0.07 | 0.79 | 0.72 | 0.07 | 2.91 | 2.00 | 1.91 |
| Py | 2.093 | 1.950 | 1.167 | 0.26 | 0.24 | 0.02 | 0.74 | 0.67 | 0.07 | 2.90 | 1.00 | 1.90 |
| $PyO^4$ | 2.067 | 1.960 | 1.170 | 0.31 | 0.30 | 0.01 | 0.70 | 0.61 | 0.09 | 2.87 | 1.00 | 1.87 |
| $PH_3$ | 2.305 | 1.988 | 1.166 | 0.48 | 0.40 | 0.08 | 0.63 | 0.57 | 0.06 | 2.91 | 1.00 | 1.91 |
| $PF_3$ | 2.250 | 1.987 | 1.166 | 0.61 | 0.44 | 0.17 | 0.59 | 0.53 | 0.06 | 2.92 | 1.00 | 1.92 |
| $PMe_3$ | 2.314 | 1.996 | 1.167 | 0.50 | 0.42 | 0.07 | 0.59 | 0.53 | 0.06 | 2.91 | 1.00 | 1.92 |
| $PPh_3$ | 2.305 | 1.998 | 1.167 | 0.47 | 0.40 | 0.07 | 0.60 | 0.54 | 0.06 | 2.91 | 0.99 | 1.91 |
| $AsH_3$ | 2.420 | 1.980 | 1.167 | 0.44 | 0.38 | 0.06 | 0.64 | 0.58 | 0.06 | 2.91 | 1.00 | 1.91 |
| $AsF_3$ | 2.385 | 1.976 | 1.166 | 0.50 | 0.36 | 0.14 | 0.64 | 0.58 | 0.06 | 2.92 | 1.00 | 1.92 |
| $CNO^-$ | 1.997 | 1.988 | 1.171 | 0.53 | 0.46 | 0.07 | 0.59 | 0.51 | 0.08 | 2.87 | 1.00 | 1.87 |
| $CNS^-$ | 1.987 | 1.990 | 1.170 | 0.55 | 0.46 | 0.10 | 0.58 | 0.51 | 0.07 | 2.88 | 1.00 | 1.88 |
| $CN^-$ | 1.997 | 1.997 | 1.170 | 0.56 | 0.49 | 0.07 | 0.56 | 0.49 | 0.07 | 2.87 | 1.00 | 1.87 |
| $HC{\equiv}C^-$ | 1.993 | 2.001 | 1.172 | 0.55 | 0.48 | 0.07 | 0.57 | 0.49 | 0.08 | 2.86 | 1.00 | 1.86 |
| CO | 1.938 | 1.983 | 1.166 | 0.68 | 0.42 | 0.26 | 0.61 | 0.55 | 0.06 | 2.92 | 1.00 | 1.92 |
| BF | 1.942 | 2.022 | 1.167 | 0.91 | 0.58 | 0.33 | 0.49 | 0.44 | 0.05 | 2.92 | 1.00 | 1.92 |

bond length *r*(Au–C) in the {AuCN} fragment varies from 1.93 up to 2.02 Å at the variation of ligand X nature. The bond length *r*(C–N) depends on the X nature to a lesser degree and is preferentially defined by the charge of the complex (Table 4). The bond order indexes *W*(Au–C) and *W*(C–N) depend on X and change in the opposite order than the corresponding *r*(Au–C) and *r*(C–N) values. The data given in Fig. 1 and in Table 4 point to the fact that π-acceptor properties of ligands X are suppressed by special features of Au(I) and Ag(I) electronic structures.

When X is varied, an increase in the Au–X bond order is accompanied by a decrease in the Au–C bond order, appreciable deviations from a linear dependence being obtained only for ligands X with pronounced acceptor properties (CO, BF, and $PF_3$). This dependence is linear for bond σ components (Fig. 2). The highest values of *W*(Au–C) were obtained for the complexes with O-, $N^-$, and S-donor ligands, the least, for the complexes with C-, P-, and As-donor ligands and with the BF ligand. The regions of *W*(Au–C) variation for complexes with various charges q overlap with each other, which points to the fact that the charge of a complex is not the unique characteristic affecting this bond strength. Charge dependence of the C–N bond order is exhibited more clearly.

The data given in Table 4 point to the fact that the range of $W_\sigma$(Au–C) variation exceeds the range of $W_\pi$(Au–C) variation. It confirms the conclusions of [13] that the σ-*trans*-influence of the ligand X in gold complexes is noticeably stronger than the π-trans-influence. The calculated values of the CN→Au charge transfer along σ bonds ($\Delta Q_\sigma$) and of the charge transfer on $CN^-$ π* orbitals ($\Delta Q_\pi$) correlate with σ and π components of the *W*(Au–C) bond order (Fig. 2) that points to the donor-acceptor character of this bond.

The conclusions drawn for $[(CN)AuX]^q$ complexes are also valid for $[(CO)AuX]^{q+1}$ (Table 5), however Au(I) carbonyl complexes have a number of special features:

– $W_\pi$(Au–C) bond indexes in carbonyl complexes are noticeably higher than in corresponding cyanide complexes owing to a higher π-acceptor power of CO;

– $W_\sigma$(Au–CO) bond indexes are noticeably reduced as compared to $W_\sigma$(Au–CN) indexes in compounds with the same ligand X that is caused by a lower σ-donor activity of CO;

– σ-donor power of ligands X in carbonyl complexes is pronounced to a greater extent, and π-acceptor to a smaller extent.

In all considered complexes $[(CO)AuX]^q$ π-acceptor power of a carbonyl group is considerably suppressed as compared to complexes of other heavy metals in low oxidation states [30].

Characteristics of Au–C and Au–P bonds in $[(HC\equiv C)AuX]^q$ complexes (Table 6) are very similar to those obtained for $[(CN)AuX]^q$. In Ag(I) complexes (Table 7) metal–ligand bonds are longer and bond orders are lower than in analogous Au(I) complexes (Table 4); π–components of Au–C and Au–X bonds are also insignificant in this case. The decrease in the bond orders occurs due to both σ and π components.

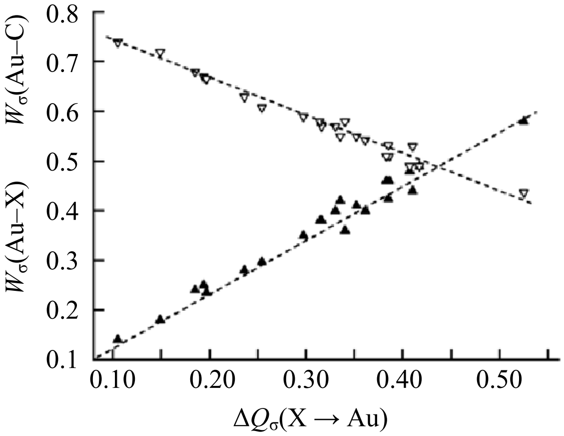

**Fig. 2.** Relations between the value of charge transfer from ligand X by σ bonds, $\Delta Q_\sigma$(X→Au), and σ component of Wiberg indexes, $W_{\sigma(Au–X)}$ and $W_{\sigma(Au–C)}$, in $[(CN)AuX]^q$ complexes.

*Localization and delocalization along L–Au–X bonds.* According to the data [14], π components related to non-adjacent (remote) fragments make a noticeable contribution to the bond energy in complexes with the BF ligand. For all considered compounds we have obtained nonzero (0.05–0.20) *W*(L–X) values for donor atoms of ligands L and X separated from each other by a metal atom (Table 8). Nonzero Wiberg indexes for non-adjacent atoms found earlier for organic compounds with multiple bonds and

**Table 5.** Bond lengths *r*(A–B), Å, bond orders after Wiberg, *W*, and their σ and π components, $W_\sigma$ and $W_\pi$, in $[(CO)AuX]^q$ complexes

| X | *r*(Au–X) | *r*(Au–C) | Au–X | | | Au–C | | |
|---|---|---|---|---|---|---|---|---|
| | | | *W* | $W_\sigma$ | $W_\pi$ | *W* | $W_\sigma$ | $W_\pi$ |
| $Cl^-$ | 2.258 | 1.894 | 0.51 | 0.47 | 0.04 | 0.79 | 0.49 | 0.30 |
| $H_2O$ | 2.100 | 1.905 | 0.22 | 0.21 | 0.01 | 0.83 | 0.60 | 0.22 |
| $NH_3$ | 2.089 | 1.930 | 0.36 | 0.34 | 0.01 | 0.75 | 0.54 | 0.21 |
| $PH_3$ | 2.333 | 1.993 | 0.56 | 0.53 | 0.03 | 0.59 | 0.43 | 0.15 |
| $AsH_3$ | 2.437 | 1.985 | 0.54 | 0.51 | 0.02 | 0.60 | 0.43 | 0.16 |
| $CN^-$ | 1.983 | 1.937 | 0.61 | 0.55 | 0.06 | 0.68 | 0.42 | 0.26 |
| CO | 1.991 | 1.991 | 0.59 | 0.46 | 0.13 | 0.59 | 0.46 | 0.13 |

**Table 6.** Bond lengths $r$(A–B), Å, bond orders after Wiberg, $W$, and their σ and π components, $W_\sigma$ and $W_\pi$, in the complexes (**1**) $[\mathrm{Au(C{\equiv}CH)_2}]^-$, (**2**) $\mathrm{(HC{\equiv}C)Au(PMe_3)}]$, and (**3**) $[\mathrm{Au(PMe_3)_2}]^+$

| Complex | $r$(Au–C) | $r$(Au–P) | $r$(C≡C) | Au–C | | | Au–P | | | C≡C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $W$ | $W_\sigma$ | $W_\pi$ | $W$ | $W_\sigma$ | $W_\pi$ | $W$ | $W_\sigma$ | $W_\pi$ |
| **1** | 1.997 | | 1.228 | 0.56 | 0.48 | 0.08 | | | | 2.92 | 1.01 | 1.91 |
| **2** | 1.985 | 2.314 | 1.222 | 0.59 | 0.54 | 0.06 | 0.50 | 0.42 | 0.08 | 2.95 | 1.01 | 1.94 |
| **3** | | 2.349 | | | | | 0.51 | 0.46 | 0.04 | | | |

**Table 7.** Bond lengths $r$(A–B), Å, bond orders after Wiberg, $W$, and their σ and π components, $W_\sigma$ and $W_\pi$, in $[\mathrm{(CN)AgX}]^q$ complexes

| X | $r$(Ag–X) | $r$(Ag–C) | Ag–X | | | Ag–C | | |
|---|---|---|---|---|---|---|---|---|
| | | | $W$ | $W_\sigma$ | $W_\pi$ | $W$ | $W_\sigma$ | $W_\pi$ |
| $\mathrm{Cl^-}$ | 2.359 | 2.033 | 0.33 | 0.31 | 0.02 | 0.51 | 0.46 | 0.05 |
| $\mathrm{CN^-}$ | 2.048 | 2.048 | 0.47 | 0.43 | 0.04 | 0.47 | 0.43 | 0.04 |
| $\mathrm{HC{\equiv}C^-}$ | 2.041 | 2.052 | 0.46 | 0.42 | 0.04 | 0.47 | 0.43 | 0.05 |
| $\mathrm{PPh_3}$ | 2.391 | 2.041 | 0.35 | 0.31 | 0.04 | 0.52 | 0.49 | 0.03 |
| CO | 2.026 | 2.027 | 0.47 | 0.32 | 0.15 | 0.54 | 0.50 | 0.03 |

caused exclusively by a π component were interpreted as indexes of the electronic density delocalization along a bond line, but not as bond orders [27]. In the case of transition metal complexes the main contribution in $W$(L–X) is introduced by the σ component, therewith the negative (L–X) values point to the antibonding nature of this interaction. For example, $W$(C-B) index for the complex [(FB)–Au–(C≡H)] reaches 0.21, its σ-component $W_\sigma$(C–B) is 0.20 and β(C–B) is –0.05. The molecular orbital introducing the greatest contribution into the total population of overlapping between C and B atoms is shown in Fig. 3.

**Table 8.** Components of Wiberg indexes in complexes with π-acceptor ligands [BF–Au–C≡CH], [HC≡C–Au–Py], and $[\mathrm{BF{-}Au{-}Py{=}O}]^q$

| Pairs of atoms | F–B–Au–C≡C'–H | | H–C≡C'–Au–$\mathrm{NC_5H_5}$ | | F–B–Au–$\mathrm{NC_5H_4}$=O | |
|---|---|---|---|---|---|---|
| | $W_\sigma$ | $W_\pi$ | $W_\sigma$ | $W_\pi$ | $W_\sigma$ | $W_\pi$ |
| Au–B | 0.585 | 0.352 | | | 0.693 | 0.362 |
| Au–N | | | 0.228 | 0.027 | 0.290 | 0.030 |
| Au–C | 0.433 | 0.059 | 0.674 | 0.070 | | |
| C≡C' | 1.009 | 1.924 | 1.005 | 1.930 | | |
| B–F | 0.497 | 0.384 | | | 0.506 | 0.390 |
| Au···F | 0.010 | 0.024 | | | 0.011 | 0.026 |
| Au···C' | 0.007 | 0.024 | 0.009 | 0.057 | | |
| B···C | 0.199 | 0.026 | | | | |
| B···C' | 0.002 | 0.048 | | | | |
| B···N | | | | | 0.141 | 0.045 |
| C···N | | | 0.088 | 0.003 | | |

*Participation of metal s, p, and d AOs in bonds with ligands*. Examination of contributions of gold *s, p,* and *d* AOs in $W$(Au–X) and $W$(Au–C) indexes for $[\mathrm{(CN)AuX}]^q$ and $[\mathrm{(CO)AuX}]^{q+1}$ complexes (Table 9 and Fig. 4) shows:

– Au–X and Au–C bonds are formed mainly due to the electron density transfer from ligands on gold *s*-AOs, whereas contributions of $d_\sigma$-AOs in the metal-ligand bond order are noticeably less and vary only slightly on X variation;

– as the contribution of gold *s* AOs in the Au–X bond order increases, the contribution of these AOs in the Au–C bond order decreases (Fig. 4), which points to a predominant role of gold *s* orbitals in the transmission of σ-*trans* influence in the studied compounds;

– preferential contribution of $W^{\mathrm{Au}}_{d(\sigma)}$(Au–C) in the order of Au–C π bond points to the fact that $d_\pi$ AOs are a source of electronic density for π-acceptor ligands and are responsible for the transmission of the π-*trans* influence;

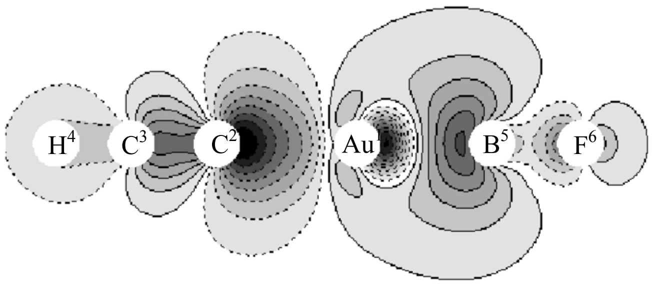

**Fig. 3.** Contour map of MO no. 18 (HOMO-5) of the complex [Au(BF)(C≡CH)]: darker areas correspond to a high function modulo value, continuous isolines show areas with positive function values, and dashed isolines show areas with negative function values (the contour map was constructed using the Chemissian program [31]).

– gold *p* orbitals practically do not participate in bonds with ligands, $W_{p(\sigma)}$ values do not exceed 0.02 and are not shown in Table 9.

**Table 9.** Contributions of gold *s*, $d_\sigma$, and $d_\pi$ AOs [$W_{s(\sigma)}$ and $W_{d(\pi)}$, respectively] in Au–X and Au–C bond orders of $[(CN)AuX]^q$ complexes

| X | Au–X | | | Au–C | | |
|---|---|---|---|---|---|---|
| | $W_{s(\sigma)}$ | $W_{d(\sigma)}$ | $W_{d(\pi)}$ | $W_{s(\sigma)}$ | $W_{d(\sigma)}$ | $W_{d(\pi)}$ |
| $F^-$ | 0.21 | 0.06 | 0.01 | 0.48 | 0.14 | 0.11 |
| $Cl^-$ | 0.29 | 0.06 | 0.01 | 0.47 | 0.10 | 0.09 |
| $Br^-$ | 0.31 | 0.06 | 0.01 | 0.47 | 0.10 | 0.09 |
| $I^-$ | 0.35 | 0.06 | 0.01 | 0.46 | 0.09 | 0.08 |
| $H_2O$ | 0.11 | 0.03 | 0.00 | 0.60 | 0.14 | 0.08 |
| $H_2S$ | 0.19 | 0.04 | 0.04 | 0.58 | 0.10 | 0.06 |
| $NH_3$ | 0.19 | 0.06 | 0.01 | 0.53 | 0.13 | 0.07 |
| $NF_3$ | 0.14 | 0.04 | 0.07 | 0.59 | 0.13 | 0.06 |
| Py | 0.18 | 0.05 | 0.02 | 0.53 | 0.13 | 0.07 |
| $PyO^4$ | 0.23 | 0.06 | 0.01 | 0.48 | 0.12 | 0.08 |
| $PH_3$ | 0.34 | 0.06 | 0.07 | 0.48 | 0.08 | 0.06 |
| $PF_3$ | 0.36 | 0.07 | 0.17 | 0.45 | 0.08 | 0.05 |
| $PMe_3$ | 0.36 | 0.06 | 0.07 | 0.44 | 0.08 | 0.05 |
| $PPh_3$ | 0.34 | 0.06 | 0.07 | 0.46 | 0.08 | 0.06 |
| $AsH_3$ | 0.32 | 0.05 | 0.06 | 0.49 | 0.08 | 0.06 |
| $AsF_3$ | 0.30 | 0.05 | 0.14 | 0.50 | 0.08 | 0.05 |
| $CNO^-$ | 0.37 | 0.09 | 0.07 | 0.41 | 0.09 | 0.08 |
| $CNS^-$ | 0.36 | 0.09 | 0.09 | 0.41 | 0.09 | 0.07 |
| $CN^-$ | 0.39 | 0.09 | 0.07 | 0.39 | 0.09 | 0.07 |
| $HC{\equiv}C^-$ | 0.38 | 0.09 | 0.07 | 0.39 | 0.09 | 0.08 |
| CO | 0.34 | 0.08 | 0.25 | 0.46 | 0.09 | 0.05 |
| BF | 0.48 | 0.09 | 0.32 | 0.37 | 0.06 | 0.05 |

*Interfragment orbital interactions in complexes.* An ion $M^{+1}$ with $d^{10}$ electronic configuration and ligands with closed electronic shells were selected as unbound fragments; VAOs and VMOs were constructed for these structural blocks. An examination of populations and valence activities of these orbitals shows that in all Au(I) and Ag(I) complexes σ bond with both ligands is provided by one hybrid VAO, the basic contribution in which is introduced by metal *s* AOs (Table 10 and Fig. 5).

The contribution of $d_{z^2}$-AO in this orbital and its population increase on passing from Ag(I) compounds to Au(I) compounds. The population of the metal σ VAO is almost exactly equal to the sum $[2 - n(\sigma\text{-VMO})_L] + [2 - n(\sigma\text{-MO})_X]$ (Fig. 5), as it is formed from the electron density transferred from X and L. The *trans*-influence of ligands is reduced to a competition for charge transfer on this VAO. From the metal side only $d_\pi = d_{xz}$, $d_{yz}$ atomic orbitals with the

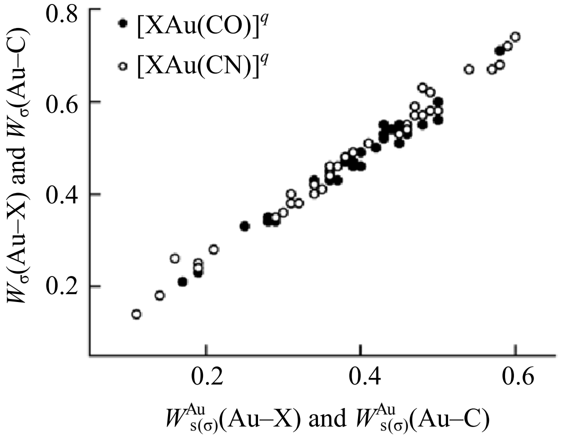

**Fig. 4.** Dependence of σ components of Au–X and Au–C bond orders, $W_\sigma$(Au–X) and $W_\sigma$(Au–C), on the contribution of gold *s* AOs into orders of these bonds, $W^{Au}_{s(\sigma)}$(Au–X) and $W^{Au}_{s(\sigma)}$(Au–C), in the complexes $[XAu(CO)]^q$ and $[XAu(CN)]^q$.

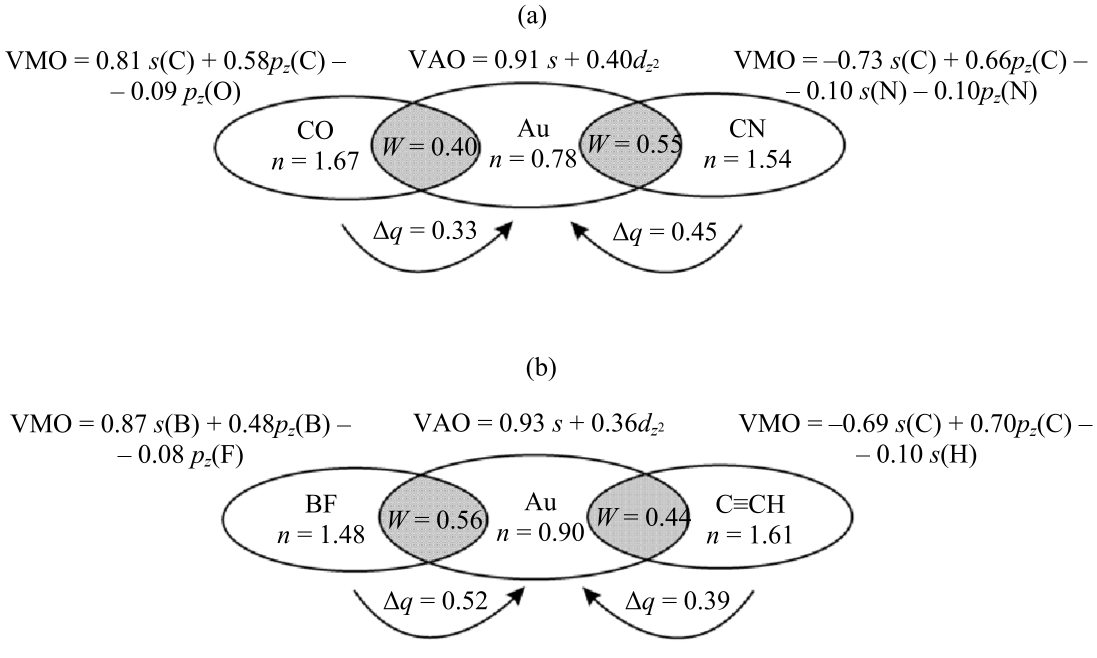

**Fig. 5.** Interaction between σ orbitals of fragments in (a) [CO–Au–CN] and (b) [BF–Au–C≡CH] complexes.

population of ~1.97 in silver compounds and ~1.94 in gold compounds participate in π dative bonds.

The results obtained allow us the following conclusions:

– filling the *d*-electronic shell of Ag(I) and Au(I) [the formal configuration $(n-1)d^{10}ns^0$] results in the fact that the bond of a metal with ligands in these compounds is formed preferentially by metal *s* AOs;

– a metal forms the strongest bonds with strong σ-donor ligands, therewith the electronic configuration becomes $5s^{0.7}4d^{9.8}$ in silver complexes and $6s^{1.05}d^{9.7}$ in gold complexes;

– dative metal→ligand π interactions are weakened;

**Table 10.** Valence atomic orbitals of metals responsible for the formation of σ bonds with ligands: $\text{VAO}_\sigma = as + bd_{z^2}$, *n* is VAO populations (the *Z*-axis passes along the line of the L–M–X bond)

| X | Ag | | | Au | | |
|---|---|---|---|---|---|---|
| | *n* | *a* | *b* | *n* | *a* | *b* |
| $\text{CN}^-$ | 0.61 | 0.95 | 0.31 | 0.80 | 0.90 | 0.43 |
| $\text{HC≡C}^-$ | 0.60 | 0.95 | 0.31 | 0.78 | 0.90 | 0.43 |
| $\text{Cl}^-$ | 0.51 | 0.96 | 0.28 | 0.73 | 0.91 | 0.42 |
| CO | 0.57 | 0.96 | 0.28 | 0.78 | 0.91 | 0.40 |
| $\text{PPh}_3$ | 0.57 | 0.97 | 0.25 | 0.80 | 0.93 | 0.37 |

– the *trans* influence of ligands in Ag(I) and Au(I) complexes is caused by the competition of σ-donor ligands for the electron density transfer from lone pairs of ligands onto hybrid $0.9s + 0.4d_{z^2}$ orbitals of gold.

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