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Evidence of Significant Covalent Bonding in $Au(CN)_2^-$

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Recently there has been intense interest in the homogeneous catalytic chemistry of Au(I) complexes.[1] Among the Au(I) molecules, the $Au(CN)_2^-$ ion is the most stable and has been widely used in gold extraction back to ancient times. Although AuCN in the condensed phase has been studied via both solution-phase vibrational spectroscopy[2] and crystal structures,[3] the free AuCN molecule has been studied only very recently by microwave spectroscopy.[4] The important $Au(CN)_2^-$ complex has not been observed and studied in the gas phase. Because of relativistic effects,[5] Au-containing molecules exhibit distinctly different properties among the coinage elements. To elucidate the nature of the Au−ligand binding, high-level ab initio calculations are needed because of the complicated electron correlation and relativistic effects.[6−8] The structure and bonding of the AuCN molecule were first examined computationally by Frenking and co-workers.[7] Recent high-precision calculations by Pyykkö and co-workers[8] suggested multiple-bond character in the Au−C bonds in AuCN because the Au−C bond length is only slightly longer than the sum of the triple-bond covalent radii.

Photoelectron spectroscopy (PES) combined with high-level ab initio calculations is a powerful method for probing the electronic and structural properties of metal complexes without the complication of condensed-phase environments.[9] Our previous PES studies of the Au−halogen complexes AuX_2^- (X = Cl, Br, and I)[10] have stimulated several theoretical calculations,[11] and the well-resolved spectra have served as benchmarks for calibrating theoretical methods for Au-containing systems. A recent PES and high-level ab initio study of AuO^- and AuS^- revealed surprising covalent bonding character in these simple diatomic systems.[12] To probe the nature of the chemical bonding in $Au(CN)_2^-$, here we performed a joint PES and theoretical [including ab initio and density functional theory (DFT) methods] study of the three coinage-metal cyanide complexes $M(CN)_2^-$ (M = Cu, Ag, Au). We obtained PES spectra of $Au(CN)_2^-$ at three detachment photon energies, 6.424 eV (193 nm), 7.866 eV (157 nm), and 10.488 eV (118 nm), and compared them with those of its lighter congeners, $Cu(CN)_2^-$ and $Ag(CN)_2^-$, at 193 and 157 nm. The PES spectra of $Au(CN)_2^-$ display well-resolved vibrational progressions due to the Au−C stretching, in sharp contrast to the atomic-like transitions observed for the mainly ionic $Cu(CN)_2^-$ complex, and thus provide direct experimental evidence of significant covalent bonding character in $Au(CN)_2^-$. Theoretical calculations were carried out to provide insight into the nature of the chemical bonding in $Au(CN)_2^-$ in comparison with that in $Cu(CN)_2^-$ and $Ag(CN)_2^-$.

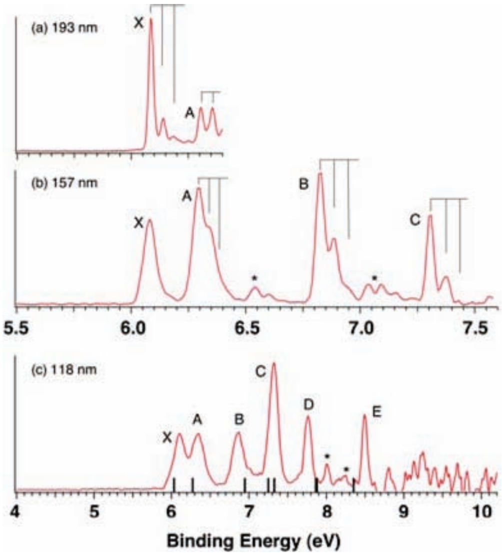

Figure 1. Photoelectron spectra of $Au(CN)_2^-$ at (a) 193 and (b) 157 at 12 K and (c) at 118 nm at room temperature. Resolved vibrational features in the 12 K spectra are labeled. The short bars in (c) represent the positions of theoretical vertical detachment transitions. Features marked with * are likely due to multielectron processes.

The $M(CN)_2^-$ (M = Cu, Ag, Au) complexes were produced via electrospray of 10^{-4} M water/methanol solutions of the respective potassium salts. All of the 193 and 157 nm PES spectra were obtained using our low-temperature PES apparatus operated at 12 K,[13] whereas the 118 nm spectrum for $Au(CN)_2^-$ was taken using our room-temperature instrument.[14] The 118 nm photons were generated via tripling of the 355 nm output from a Nd:YAG laser, as described previously,[15] allowing high-binding-energy features beyond 7.8 eV to be probed. Figure 1 presents the PES spectra of $Au(CN)_2^-$ at three photon energies: 193, 157, and 118 nm. Six major detachment bands (labeled as X and A−E) were observed in the energy range from 6 to 8.5 eV (Table 1). A weak broad feature around 9.2 eV was also discernible, but the signal-to-noise ratio in the high-binding-energy region was poor because of strong background electrons at 118 nm. Vibrational progressions were observed for bands X and A at 193 nm (Figure 1a) and for A, B, and C at 157 nm (Figure 1b), with frequencies of 400 cm^{-1} for X and A, 480 cm^{-1} for B, and 520 cm^{-1} for C. The vibrational features should correspond to Au−C stretching according to solution-phase data[6] and our calculated vibrational frequencies. The adiabatic detachment energy (ADE) of $Au(CN)_2^-$ [or the electron affinity of $Au(CN)_2$] was determined from the 0−0 transition of band X to be 6.09 eV (Table 1). The vertical detachment energies (VDEs) for bands X, A, B, and C are the same as the corresponding ADEs

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Table 1. Observed and Calculated Vertical Detachment Energies (VDEs) for $M(CN)_2^-$ (M = Au, Ag, Cu), Observed Vibrational Frequencies, and Final State Assignments

	feature	state	VDE (eV)[a]		vib freq (cm^{-1})[a]
			exptl	calcd	
$Au(CN)_2^-$	X	$^2\Sigma_{1/2g}$	6.09(1)[b]	6.02	400(40)
	A	$^2\Pi_{3/2g}$	6.30(1)	6.28	400(40)
	B	$^2\Delta_{5/2g}$	6.83(1)	6.94	480(40)
	C	$^2\Pi_{1/2g}$	7.31(1)	7.24	520(40)
		$^2\Sigma_{1/2u}$		7.32	
	D	$^2\Pi_{3/2u}$	7.76(2)	7.87	
		$^2\Pi_{1/2u}$		7.88	
	E	$^2\Delta_{3/2g}$	8.50(2)	8.35	
$Ag(CN)_2^-$	X	$^2\Sigma_{1/2g}$	6.06(1)[b]	6.07	400(40)
	A	$^2\Pi_{3/2g}$	6.87(2)	6.92	
	B	$^2\Sigma_{1/2u}$	6.96(1)	7.04	
	C	$^2\Pi_{1/2g}$	7.21(1)	7.13	
	D	$^2\Pi_{3/2u}$	7.67(1)	7.71	
		$^2\Pi_{1/2u}$		7.71	
		$^2\Delta_{5/2g}$		8.09	
		$^2\Delta_{3/2g}$		8.51	
$Cu(CN)_2^-$	X	$^2\Sigma_{1/2g}$	5.29(1)[b]	5.22	
	A	$^2\Pi_{3/2g}$	5.80(1)	5.76	
	B	$^2\Pi_{1/2g}$	5.92(1)	5.88	
	C	$^2\Delta_{5/2g}$	~6.15	6.10	
	D	$^2\Delta_{3/2g}$	~6.4	6.29	
	E	$^2\Sigma_u$	7.10(1)	7.07	
	F	$^2\Pi_u$	7.51(1)	7.61	

[a] Each number in parentheses represents the experimental uncertainty in the last digit. [b] Also the adiabatic detachment energy of the $M(CN)_2^-$ anions or electron affinity for neutral $M(CN)_2$.

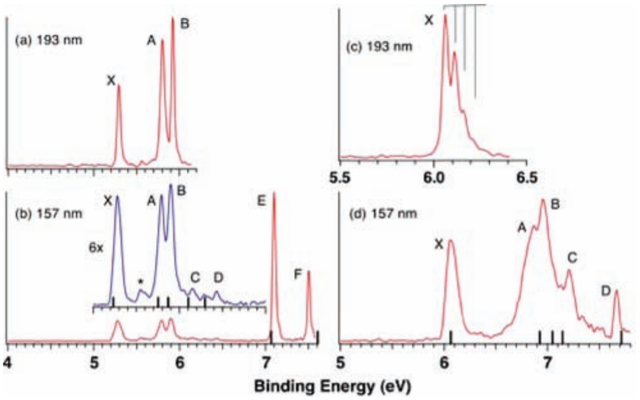

Figure 2. Photoelectron spectra of (a, b) $Cu(CN)_2^-$ and (c, d) $Ag(CN)_2^-$ at 193 and 157 nm at 12 K. The short bars in (b) and (d) represent the calculated vertical detachment energies. The feature marked with * in (b) is likely due to multielectron processes.

because of the short vibrational progressions, whereas the VDEs for bands D and E observed in the 118 nm spectrum (Figure 1c) were measured from the maximum of each band.

The spectrum of $Cu(CN)_2^-$ at 193 nm shows three sharp transitions, designated X, A, and B (Figure 2a). At 157 nm, two strong peaks (E and F) were found at high binding energies (Figure 2b). All of these PES transitions are atomic-like (with the spectral width limited only by the instrumental resolution), in sharp contrast to the vibrationally resolved bands for $Au(CN)_2^-$. Some weak features between the X and A bands (labeled by *) and between B and E (labeled as C and D; see the inset in Figure 2b) were also discernible. The 193 nm spectrum of $Ag(CN)_2^-$ (Figure 2c) exhibits a well-resolved vibrational progression with a spacing of 400 cm^{-1}, most likely due to the Ag−C stretching. The 157 nm spectrum (Figure 2d) shows congested spectral features around 7 eV with three overlapping bands (A, B, and C) and a sharp peak (D) at the high-binding-energy side. The VDEs for all of the observed PES features for $Cu(CN)_2^-$ and $Ag(CN)_2^-$ are also given in Table 1 along with computed values for comparison.

High-level calculations were carried out to optimize structures, compute VDEs, and analyze chemical bonding.[16] The optimized geometries of $M(CN)_2^-$ (M = Cu, Ag, Au) and the corresponding neutrals are all linear (Table S1 in the Supporting Information). The calculated Au−C bond length is 1.99 Å, which lies in the range of experimentally measured Au−C distances in solid $Au(CN)_2^-$ salts (1.98−2.12 Å).[3] The electron binding energies corresponding to one-electron transitions from the closed-shell ground states of the anions to the ground and excited states of the neutrals were obtained using a CASSCF/CCSD(T)/spin−orbit (SO) approach, where the SO splittings were calculated on the basis of CASSCF wave functions with the diagonal matrix elements replaced by the UCCSD(T) energies.[17] The calculated ADEs of $Cu(CN)_2^-$, $Ag(CN)_2^-$, and $Au(CN)_2^-$ were 5.22, 6.03, and 6.02 eV, respectively, in excellent agreement with the experimental data (Table 1). While there is almost no Cu−C bond length change in going from the anion to the neutral (1.89 to 1.88 Å), the Au−C and Ag−C bonds shorten appreciably (1.99 to 1.97 and 2.07 to 2.05 Å, respectively, at the SO PW91 level) (Table S1), consistent with the observed vibrational progressions in the Au−C and Ag−C stretching modes (Figures 1 and 2c). The calculations also predicted electron binding energies for the excited states of the neutrals, which are compared to the spectra as vertical bars in Figures 1 and 2. For $Au(CN)_2^-$ and $Ag(CN)_2^-$, the predicted VDEs agree well with the experimental data, and their assignments are given in Table 1. For $Cu(CN)_2^-$, there is a one-to-one correspondence between the calculated VDEs and the X, A, and B peaks as well as the E and F peaks. However, the calculations also predicted two transitions ($^2\Delta_g$) at 6.10 and 6.29 eV, which lie in between the two major spectral features B and E and are tentatively assigned to the two very weak features C and D (see the Figure 2b inset). However, the relatively small detachment cross sections for C and D were surprising. These two transitions correspond to detachment from the nonbonding δ_g orbitals, and the small detachment cross sections may be correlated with the tightly contracted character of the Cu 3d orbitals. For $Ag(CN)_2^-$, the corresponding detachment channels occur at much higher binding energies (Table 1) and were not observed in the 157 nm spectrum. For $Au(CN)_2^-$, the detachments from the δ_g orbitals have much larger cross sections, occur at a much lower VDE with a large SO splitting, and correspond to the B and E bands, respectively (Table 1). The B band was resolved with a short vibrational progression, suggesting significant covalent bonding character that is very different from the atomic-like nature in $Cu(CN)_2^-$. Features marked with * in Figures 1 and 2 are likely due to multielectron transitions, suggesting strong electron-correlation effects.

The vibrational progressions observed in the spectra of $Au(CN)_2^-$ provide a striking contrast to the atomic-like transitions in the spectra of $Cu(CN)_2^-$. Although the molecular orbital pictures (Figure S1) for the three $M(CN)_2^-$ species look similar, their electronic structures as revealed by the PES data are very different. Table S2 shows that the SO effects in $Au(CN)_2^-$ are much stronger than those in its lighter congeners, which is also reflected in Table S1, where the Au−C bond length in $Au(CN)_2$ shows a sizable reduction upon inclusion of SO effects, resulting in an appreciable Au−C bond length change in going from the anion to the neutral (1.99 to 1.97 Å), in accord with the observed Au−C vibrational progression (Figure 1). The observed vibrational progressions in the photodetachment transitions of $Au(CN)_2^-$ provide direct experimental evidence for covalency in the Au−C bonding. The Au−C bond length (1.99 Å) in $Au(CN)_2^-$ is significantly smaller

Table 2. Theoretical Charge Populations and Bond-Order Analysis for $M(CN)_2^-$ (M = Cu, Ag, Au)[18]

		Charge Population		
M	NPA	Hirshfeld	Voronoi	MDC-q
Cu	0.49	0.14	0.19	0.30
Ag	0.44	0.14	0.20	0.43
Au	0.31	0.04	0.11	0.22
		Bond Order		
M−C	Wiberg		G-J	N-M (3)
Cu−C	0.49		0.51	0.49
Ag−C	0.48		0.50	0.48
Au−C	0.58		0.58	0.57

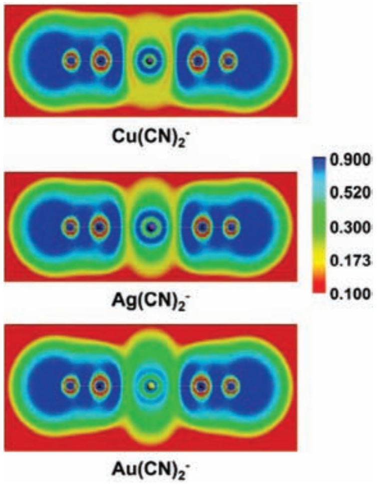

Figure 3. ELFs for $M(CN)_2^-$ (M = Cu, Ag, Au).

than the Ag−C bond length (2.07 Å) in $Ag(CN)_2^-$ and is similar to the Au−C bond length in monoligated AuCN (1.91 Å), which has been suggested to possess triple-bond character.[8] The atomic-like PES transitions in $Cu(CN)_2^-$ are consistent with the ionic bonding nature of this system,[9b] whereas the bonding in $Ag(CN)_2^-$ should be in between.

The nature of the chemical bonding in $M(CN)_2^-$ (M = Cu, Ag, Au) can also be inferred from the population and bond-order analysis results given in Table 2. There is clearly less positive charge on Au and a larger Au−C bond order in $Au(CN)_2^-$ than in the $Cu(CN)_2^-$ and $Ag(CN)_2^-$ complexes. Electron localization functions (ELFs)[19] reflecting the probability to find electron pairs reveal more vividly the increased covalency in the Au−C bonding in $Au(CN)_2^-$, as shown in Figure 3. Fragment orbital analysis and orbital interaction analysis (Table S3) both reveal that the covalent character of Au−C and the remarkable stability of $Au(CN)_2^-$ stem from the strong relativistic effects in gold. The s−d hybridization significantly enhances the ability of Au to form covalent bonds with multiple-bond character. The covalent nature of the Au−C bonding is consistent with the high stability of the $Au(CN)_2^-$ complex.

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Supporting Information Available: Experimental and theoretical methods; Cartesian coordinates, bond lengths, and stretching vibrational frequencies for $M(CN)_2^-$ (M = Cu, Ag, Au) at the PW91 level of theory; frontier occupied molecular orbitals of $M(CN)_2^-$ (M = Cu, Ag, Au); assignments of the photoelectron spectra and contributions of SO-free states to SO eigenstates; and fragment analysis for $M(CN)_2^-$ (M = Cu, Ag, Au) with the M and CN neutrals as fragments. This material is available free of charge via the Internet at http://pubs.acs.org.

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