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Substantial Dissociation Energies for the Recently Synthesized NC–Ag–NH₃ and Br–Ag–NH₃ Molecules and Their Isovalent Family Members M(CN)XY₃ and M(Br)XY₃ (M = Cu, Ag, Au; X = N, P; Y = H, F)

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Abstract: Chippindale et al. have recently synthesized the unique molecules (NC)Ag(NH₃) and BrAg(NH₃) and shown the heavy atom skeletal structures to be linear. Here, a theoretical study is reported of 12 members each of the two isovalent series of molecules. For (NC)Ag(NH₃) and BrAg(NH₃), the theoretical structures agree well with those determined by X-ray crystallography. Structures for the 22 yet unknown compounds should be similarly reliable. The dissociation energies for a loss of NH₃ from the two known compounds are significant (34 and 31 kcal/mol), confirming their viability. For the other systems, the ligand dissociation energies are highly variable, ranging from 9 kcal/mol (BrAg–NF₃) to 44 kcal/mol (BrAu–PH₃). The bond dissociation energies for the different metals follow the irregular order Au > Cu > Ag. For the XY₃ ligands, the dissociation energies follow the order NH₃ > PH₃ > PF₃ > NF₃, except for the BrAu–XY₃ complexes. Electronic structure insights are gained via Natural Bond Orbital (NBO) analyses.

Introduction

The metals most frequently forming linear two-coordinate metal complexes are the d¹⁰ metals, particularly the coinage metals Cu, Ag, and Au in their +1 oxidation states.¹ For gold, this linear coordination chemistry dominates the +1 oxidation state, and both symmetrical and unsymmetrical linear Au(I) complexes are known. For example, phosphine complexes of gold(I) halides, namely, R₃PAuX (X = Cl, Br, I), are commonly used reagents in gold chemistry.^{2,3} Such

linear gold(I) complexes are relatively inert kinetically. They are rather unreactive toward increasing their coordination number above two by ligand addition reactions. This characteristic feature of linear Au(I) chemistry may be attributed to relativistic effects.²

The situation is different with the lighter coinage metals copper and silver. Although the organic bis(silver carbene) complexes, such as Ag-based N-heterocyclic carbene complexes, have been reported,^{4–12} before 2008, simple linear asymmetrical complexes of Cu(I) and Ag(I) were unknown because of limitations in synthetic methods, the kinetic lability of such complexes, and the formation of infinite chain complexes or species with higher metal coordination numbers.^{13–19} However, symmetrical linear two-coordinate complexes of copper and silver have been known for more than a century. Using silver as an example, the symmetrical

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linear complexes $\text{Ag}(\text{NH}_3)_2^+$ and AgX_2^- ($\text{X} = \text{CN}, \text{Cl}, \text{Br}, \text{I}$) have been known for many decades and are routinely discussed in inorganic chemistry textbooks.¹

A recent (2008) study of the behavior of silver(I) derivatives in aqueous ammonia reported a breakthrough in the synthesis of asymmetrical linear silver(I) derivatives.¹³ Therein, cautious evaporation of solvent from concentrated solutions of silver(I) halides or pseudohalides in aqueous ammonia led to the derivatives NC-Ag-NH_3 and Br-Ag-NH_3 , which were shown by X-ray crystallography to be discrete molecules rather than infinite chains. The cyanide complex NC-Ag-NH_3 was found to be stable to 100 °C before losing ammonia to form AgCN . The bromide complex Br-Ag-NH_3 was less stable, losing ammonia around room temperature to give AgBr . It thus becomes of interest to investigate factors affecting the stability of NC-Ag-NH_3 and other complexes analogous to it. Recently, the gas-phase monoammoniate of silver chloride ($\text{NH}_3 \cdots \text{Ag-Cl}$) was also observed by Mikhailov et al.,²⁰ and the corresponding *ab initio* calculations performed by the authors.

This paper describes our attempts using density functional theory to explore the possible range of coinage metal derivatives of the type NC-M-XY_3 and Br-M-XY_3 ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$; $\text{X} = \text{N}, \text{P}$; $\text{Y} = \text{H}, \text{F}$).

Theoretical Methods

Two density functional theory (DFT) or hybrid Hatree-Fock/DFT methods were used in this study. The first functional is B3LYP, which incorporates Becke's three-parameter functional (B3)²¹ with the Lee, Yang, and Parr (LYP) correlation functional.²² The second approach is BP86, using the exchange functional of Becke²³ in conjunction with the correlation functional of Perdew.²⁴

For the coinage metals, Cu, Ag, and Au, we adopted the Stuttgart/Dresden double- ζ (SDD) effective core potential (ECP) basis sets.²⁵ In these basis sets, the innermost-electrons (10 for Cu, 28 for Ag, and 60 for Au) for the transition metal atoms are replaced by the effective core potentials (ECP), which include relativistic effects, known to be important for the heavy transition metal atoms.² For the three coinage metals, the SDD basis sets for the 19 valence electrons are $\text{Cu}(8s7p6d/6s5p3d)$, $\text{Ag}(8s7p6d/6s5p3d)$, and $\text{Au}(8s6p5d/7s3p4d)$.

All-electron double- ζ plus polarization basis sets augmented with diffuse functions (DZP++) are used for main group elements. The DZP++ basis sets for carbon, nitrogen, fluorine, and phosphorus are composed of the standard Huzinaga–Dunning double- ζ basis sets^{25–28} plus one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(\text{C}) = 0.75$, $\alpha_d(\text{N}) = 0.80$, $\alpha_d(\text{F}) = 1.00$, and $\alpha_d(\text{P}) = 0.60$ augmented with one set of diffuse functions $\alpha_s(\text{C}) = 0.04302$ and $\alpha_p(\text{C}) = 0.03629$, $\alpha_s(\text{N}) = 0.06029$, and $\alpha_p(\text{N}) = 0.05148$, $\alpha_s(\text{F}) = 0.10490$ and $\alpha_p(\text{F}) = 0.08260$, and $\alpha_s(\text{P}) = 0.03448$ and $\alpha_p(\text{P}) = 0.03346$. For H, the added polarization functions are one set of p-type functions with orbital exponent $\alpha_p(\text{H}) = 0.75$, augmented with one diffuse s function $\alpha_s(\text{H}) = 0.04415$. For bromine, the basis set was composed of Ahlrichs' standard double-spd set plus a set of

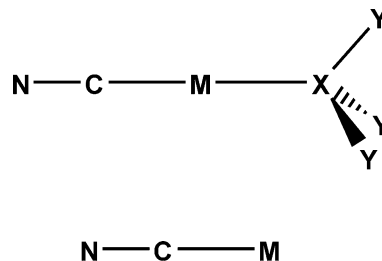


Figure 1. Qualitative structures of $\text{M}(\text{CN})(\text{XY}_3)$ and MCN ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$; $\text{X} = \text{N}, \text{P}$; $\text{Y} = \text{H}, \text{F}$).

Table 1. Geometrical Parameters for $\text{M}(\text{CN})\text{NH}_3$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$)^a

species		B3LYP			BP86		
		Cu	Ag	Au	Cu	Ag	Au
$\text{M}(\text{CN})(\text{NH}_3)$	M–C	1.844	2.021	1.962	1.825	1.997	1.948
	C–N	1.174	1.173	1.172	1.187	1.186	1.186
	M–N	1.954	2.186	2.142	1.943	2.162	2.132
	N–H	1.023	1.022	1.022	1.031	1.029	1.030
	$\angle \text{H–N–H}$	107.1	107.2	107.5	107.0	107.1	107.5

^a Bond distances in Å, bond angles in degrees.

d-type polarization functions $\alpha_d(\text{Br}) = 0.389$ plus diffuse functions $\alpha_s(\text{Br}) = 0.0469$ and $\alpha_p(\text{Br}) = 0.0465$.²⁹ The final contracted basis sets are thus designated as $\text{H}(5s1p/3s1p)$, $[\text{C}, \text{N}, \text{F}](10s6p1d/5s3p1d)$, $\text{P}(12s8p1d/7s5p1d)$, and $\text{Br}(15s12p6d/9s7p3d)$.

Natural bond orbital (NBO) analyses³⁰ have been carried out, with the bond orders and natural charges used to gain some understanding of the bonding in these molecules. All computation employed the Gaussian 03 program suite,³¹ and all results refer to the gas phase at 0 K.

The difference between the B3LYP and BP86 results is generally small, and the two sets of predictions show the same trends. Although all results from the two methods are shown in the tables, the B3LYP results are mainly discussed in the text.

Results and Discussion

$\text{Ag}(\text{CN})\text{NH}_3$. Our theoretical structure for the isolated $\text{Ag}(\text{CN})\text{NH}_3$ molecule is shown in Figure 1, and the corresponding optimized parameters are reported in Table 1. The equilibrium NC-Ag-NH_3 complex is predicted by both the B3LYP and the BP86 methods to be a linear structure with C_{3v} symmetry, in agreement with the experimental crystal structure reported by Chippindale et al. in 2008.¹³ Our theoretical results reproduce the experimental structure reasonably well, with the difference of bond distances less than 0.1 Å. Table 1 shows that the theoretical Ag–C distance (2.021 Å) is 0.03 Å shorter than the experimental value (2.051 Å), while the theoretical Ag–N distance (2.186 Å) is 0.07 Å longer than the corresponding experimental conclusion (2.114 Å).

A key point for this newly observed asymmetric mono-nuclear Ag(I) complex $\text{Ag}(\text{CN})\text{NH}_3$ would be the nature of the bonding between its AgCN and NH_3 fragments. The geometry of the NH_3 fragment in the $\text{Ag}(\text{CN})\text{NH}_3$ complex is comparable with that of the free NH_3 molecule. Table 1 shows that the N–H distance is 1.022 Å in $\text{Ag}(\text{CN})\text{NH}_3$,

Table 2. Geometrical Parameters for Separated MCN (M = Cu, Ag, Au) and XY₃ (X = N, P; Y = H, F) for Comparison^a

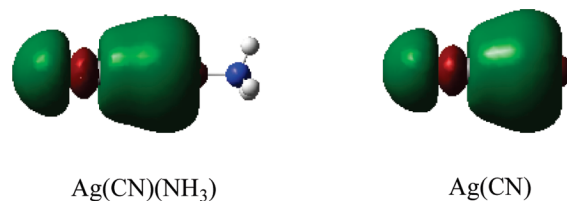
species		B3LYP	BP86	expt ^b	theor ^c
NH ₃	N–H	1.020	1.028		
	∠H–N–H	107.4	106.7		
NF ₃	N–F	1.386	1.411		
	∠F–N–F	101.9	101.8		
PH ₃	P–H	1.423	1.435		
	∠H–P–H	93.6	92.7		
PF ₃	P–F	1.596	1.613		
	∠F–P–F	97.5	97.7		
CuCN	Cu–C	1.832	1.807	1.82962(4)	1.824 (1.8259)
	C–N	1.173	1.187	1.16213(3)	1.164 (1.1665)
AgCN	Ag–C	2.037	2.007	2.031197(23)	2.024
	C–N	1.172	1.186	1.160260(26)	1.164
AuCN	Au–C	1.942	1.922	1.9122519(84)	1.911
	C–N	1.171	1.186	1.1586545(97)	1.162

^a Bond distances in Å, bond angles in degrees. ^b The experimental values for CuCN refer to ref 32, and those for AgCN and AuCN refer to ref 33. ^c The theoretical values for MCN (M = Cu, Ag, and Au) were predicted at the CCSD(T)/cc-pVQZ level of theory in ref 34. The values in parentheses were predicted at the DK-CCSD(T)/cc-pVQZ level of theory (ref 35).

compared with 1.020 Å in the free NH₃ (Table 2). The H–N–H bond angle 107.2° in Ag(CN)NH₃ has only a negligible difference from that in free ammonia (107.4°). This result suggests that there is no significant orbital overlap, but rather a dipole attraction between the NH₃ ligand and AgCN, and this argument is supported by the NBO analysis.

The natural bond orbital (NBO) analysis provides detailed insight into these linear asymmetrical complexes of Ag(CN)–NH₃ (Table 3). The charge distribution of the AgCN fragment in Ag(CN)NH₃ bears a strong resemblance to that of the isolated AgCN molecule. The bonding of NH₃ to AgCN has little influence on the Wiberg Ag–C bond index, changing from 0.60 to 0.58. The highest occupied molecular orbitals (HOMO) of Ag(CN)NH₃ and AgCN are very similar (Figure 2). These similarities between Ag(CN)NH₃ and AgCN show that the Ag 5s orbital mainly takes part in the Ag–C bond, with or without the presence of NH₃. The Wiberg bond index of Ag–N in Ag(CN)NH₃ is as small as 0.20, which also suggests a small overlap between orbitals (or small covalent bonding) of the Ag and N atoms. The natural charge for the ammonia N atom is –1.12, and that for the Ag atom is +0.54 (Table 3), supporting the existence of an ionic attraction between the two fragments AgCN and NH₃. However, σ donation from the ammonia lone pair to the partially vacant Ag 5s hole is not excluded.

The dissociation energy of Ag(CN)NH₃ to free the NH₃ ligand is substantial. Table 4 shows that the dissociation energy for (NH₃)AgCN → AgCN + NH₃ is 33.4 (B3LYP) or 35.3 (BP86) kcal/mol. This value indicates that the simple linear asymmetric Ag(CN)NH₃ complex is quite favorable in energy with respect to such a dissociation. However,

**Figure 2.** The HOMOs for Ag(CN)(NH₃) and AgCN.**Table 4.** Reaction Energies in Kilocalories per Mole^a

	B3LYP	BP86
(NH ₃)AgCN → AgCN + NH ₃	33.4	35.3
(NH ₃)AgCN → 1/2[Ag(NH ₃) ₂] ⁺ + 1/2[Ag(CN) ₂] [–]	–32.1	–32.8
2(NH ₃)AgCN → (NH ₃)AgCN–AgCN + NH ₃	–7.7	–6.9
(NH ₃)AgCN + AgCN → (NH ₃)AgCN–AgCN	–41.1	–42.2
2AgCN → AgCN–AgCN	–36.6	–37.0

^a All of the molecules are in the gas phase.

compared with the long-known symmetrical complexes [Ag(NH₃)₂]⁺ and [Ag(CN)₂][–], the asymmetric NC–Ag–NH₃ complex has relatively high energy. Table 4 shows that the reaction (NH₃)AgCN → 1/2 [Ag(NH₃)₂]⁺ + 1/2 [Ag(CN)₂][–] is exothermic with a significant energy difference, i.e., 32.1 (B3LYP) and 32.8 (BP86) kcal/mol. Thus, the newly prepared Ag(CN)NH₃ complex does not display absolute thermodynamical stability. This may explain why Ag(CN)NH₃ was prepared many years after [Ag–(NH₃)₂]⁺ and [Ag(CN)₂][–] became common chemical reagents.

It is also known that the one-dimensional linear, polymeric chain structures are common for AgCN and the other group 11 metal cyanides.^{36,37} The geometry of the chain structure –Ag–CN–Ag–CN– was determined by the neutron diffraction experiment in 2002.³⁸ Indeed, our theoretical results have confirmed that the linear AgCN–AgCN dimer has a decomposition energy (to two AgCN's) of ~37 kcal/mol (Table 4). Similarly, our theoretical results show that the chain structure (NH₃)AgCN–AgCN has a lower energy than separated (NH₃)AgCN and AgCN by about 42 kcal/mol (Table 4), and thus the monomer Ag(CN)NH₃ is only a metastable structure.

NC–Ag–NF₃. When the NH₃ ligand in Ag(CN)NH₃ is replaced by the more electronegative NF₃ ligand, the linear C_{3v} Ag(CN)NF₃ complex is also predicted as a genuine minimum (Figure 1 and Table 5). However, there are some important differences between Ag(CN)NH₃ and Ag(CN)NF₃. To begin, the NF₃ fragment in Ag(CN)NF₃ is geometrically somewhat different from the isolated NF₃. The N–F distances increase by 0.014 Å, and the F–N–F bond angles increase by more than 1° (Tables 2 and 5). The Ag–NF₃ bond distance (2.294 Å) in Ag(CN)NF₃ is longer than the Ag–NH₃ bond distance (2.186 Å) in Ag(CN)NH₃ (Table 1) by more than 0.1 Å, suggesting a weaker interaction between

Table 3. B3LYP Natural Atomic Charges (Q) and Wiberg Bond Indices (WBI) of Selected Bonds of Ag(CN)XY₃ (X = N and P, Y = H and F)

	Q _{Ag}	Q _C	Q _N	Q _X	Q _Y	Q _{AgCN}	Q _{XY3}	WBI _{Ag–XY3}	WBI _{Ag–CN}
Ag(CN)NH ₃	0.54	–0.16	–0.50	–1.12	0.41	–0.12	0.12	0.20	0.58
Ag(CN)NF ₃	0.57	–0.17	–0.47	0.59	–0.17	–0.06	0.06	0.16	0.60
Ag(CN)PH ₃	0.50	–0.18	–0.49	0.08	0.03	–0.17	0.17	0.36	0.53
Ag(CN)PF ₃	0.45	–0.20	–0.46	1.85	–0.55	–0.21	0.21	0.45	0.52
Ag(CN)	0.67	–0.20	–0.47						0.60

Table 5. Geometrical Parameters for M(CN)NF₃ (M = Cu, Ag, Au)^a

species		B3LYP			BP86		
		Cu	Ag	Au	Cu	Ag	Au
M(CN)(NF ₃)	M–C	1.842	2.021	1.953	1.832	1.998	1.944
	C–N	1.173	1.172	1.171	1.186	1.185	1.184
	M–N	1.978	2.294	2.171	1.907	2.210	2.112
	N–F	1.376	1.372	1.372	1.407	1.397	1.400
	∠F–N–F	103.0	103.2	103.2	102.4	102.9	102.7

^a Bond distances in Å, bond angles in degrees.**Table 6.** Dissociation Energies (in kcal/mol) for M(CN)XY₃ and M(Br)XY₃ (M = Cu, Ag, and Au; X = N and P; Y = H and F)

	B3LYP			BP86		
	Cu	Ag	Au	Cu	Ag	Au
M(CN)(NH ₃) → M(CN) + NH ₃	41.7	33.4	43.4	43.2	35.3	44.5
M(CN)(NF ₃) → M(CN) + NF ₃	15.5	8.6	15.1	18.4	10.0	16.8
M(CN)(PH ₃) → M(CN) + PH ₃	33.5	29.0	41.4	36.1	31.7	43.2
M(CN)(PF ₃) → M(CN) + PF ₃	24.0	18.2	31.6	27.9	21.9	34.6

the NF₃ fragment and the AgCN fragment. On the basis of the NBO analysis, the Wiberg Ag–N bond index (0.16) for Ag(CN)NF₃ is somewhat smaller than that (0.20) for Ag(CN)NH₃. More importantly, the natural charge for the N atom in NF₃ (*Q_N*) is no longer negative, and the charges for the AgCN and NF₃ fragments are only −0.06 and +0.06, respectively, which are only half of those for Ag(CN)NH₃ (Table 3), suggesting that the ionic attraction between the two parts is much weaker. Accordingly, the dissociation energy for Ag(CN)NF₃ to lose NF₃ is only 8.6 (B3LYP) or 10.0 (BP86) kcal/mol (Table 6), compared with the substantial value (~34 kcal/mol) for Ag(CN)NH₃ to lose NH₃. This small dissociation energy may make it difficult to synthesize Ag(CN)NF₃ in a manner analogous to that used for Ag(CN)–NH₃.

NC–M–NH₃ and NC–M–NF₃ (M = Cu, Au). Although CuCN·NH₃ has long been a known compound, the crystal structure for the CuCN·NH₃ complex was reported to have a copper coordination number of four,³⁹ which is quite different from the presently considered linear (NH₃)AgCN complex. For gold, no similar complexes have been reported. In 2007, Mishra used the *ab initio* methods to predict the linear structures for XAuY[−] (X, Y = Cl, Br, and I).⁴⁰

In the present study, like Ag(CN)NH₃, the linear asymmetric Cu(CN)NH₃ and Au(CN)NH₃ structures (with C_{3v} symmetry, Figure 1) are predicted to be genuine minima, and their geometry parameters are reported in Table 1. The NH₃ fragment in Cu(CN)NH₃ or in Au(CN)NH₃ has almost the same geometry as that in Ag(CN)NH₃, with the change less than 0.001 Å for the N–H distance and 0.3° for the H–N–H angle (B3LYP method). This suggests that the interactions between the NH₃ ligand and CuCN and AuCN are also mainly the classical electrostatic attraction.

Energetically, the Cu(CN)NH₃ and Au(CN)NH₃ complexes have dissociation energies for the reaction M(CN)(NH₃) → M(CN) + NH₃ (M = Cu and Au) that are even larger than that predicted for Ag(CN)NH₃. The dissociation energy for Cu(CN)NH₃ is 41.7 (B3LYP) or 43.2 (BP86) kcal/mol, and

Table 7. Geometrical Parameters for M(CN)PH₃ and M(CN)PF₃ (M = Cu, Ag, Au)^a

species		B3LYP			BP86		
		Cu	Ag	Au	Cu	Ag	Au
M(CN)(PH ₃)	M–C	1.867	2.046	2.000	1.852	2.026	1.987
	C–N	1.174	1.173	1.172	1.187	1.186	1.185
	M–P	2.226	2.409	2.333	2.197	2.371	2.315
	P–H	1.410	1.409	1.408	1.423	1.421	1.421
	∠H–P–H	99.1	99.0	100.0	98.7	98.5	99.5
M(CN)(PF ₃)	M–C	1.864	2.040	1.998	1.852	2.022	1.987
	C–N	1.173	1.173	1.171	1.186	1.185	1.184
	M–P	2.186	2.382	2.282	2.157	2.339	2.266
	P–F	1.567	1.568	1.564	1.584	1.585	1.580
	∠F–P–F	100.0	100.0	100.2	100.0	100.1	100.2

^a Bond distances in Å, bond angles in degrees.

that for Au(CN)NH₃ is 43.4 (B3LYP) or 44.5 (BP86) kcal/mol (Table 6). These values are also comparable with the DFT dissociation energy predicted by Frenking et al. for the related metal–carbene bond of XM–L (X = F–I; M = Cu, Ag, Au; L = imidazol-2-ylidene).⁴¹ The energy decomposition analysis (EDA) performed by Frenking et al. shows that the metal–carbene bonds are mainly held together by classical electrostatic attraction (>65%), consistent with our above-noted descriptions of the M–NH₃ bonds in the NC–M–NH₃ (M = Cu, Ag, Au) complexes. Since the copper and gold analogues of the simple linear asymmetric complexes of Ag(CN)NH₃ have properties similar to those of Ag(CN)NH₃, these analogues are likely to be synthesizable.

The NF₃ analogous complexes Cu(CN)NF₃ and Au(CN)–NF₃ have also been studied here, and the results are listed in Table 5. The linear structures are predicted to be genuine minima on their potential hypersurfaces. Like the situation in Cu(CN)NH₃ and Au(CN)NH₃, however, the analogous complexes Cu(CN)NF₃ and Au(CN)NF₃ suggest classical electrostatic attractions between NF₃ and MCN. Table 6 compares the dissociation energies for M(CN)NF₃ (M = Cu, Ag, Au) with those predicted for M(CN)NH₃. The dissociation energies of Cu(CN)NF₃ and Au(CN)NF₃ for losing NF₃ are about 15 kcal/mol (B3LYP, Table 6), substantially smaller compared with the corresponding M(CN)NH₃ complexes (>40 kcal/mol, Table 6), but not as small as the dissociation energy (~9 kcal/mol, Table 6) for Ag(CN)NF₃ to lose NF₃.

M(CN)PH₃ and M(CN)PF₃ (M = Cu, Ag, Au). We extended our studies to the phosphorus analogues (i.e., to replace NH₃ and NF₃ with PH₃ and PF₃). The two DFT methods predict the similar linear C_{3v} minima for Ag(CN)PH₃ and Ag(CN)PF₃, and their structures are reported in Table 7. The geometry parameters for the PH₃ and PF₃ ligands in Ag(CN)PH₃ and Ag(CN)PF₃ (Table 7) are slightly different from the isolated PH₃ and PF₃ species (Table 2). The dissociation energy for Ag(CN)PH₃ is substantial, i.e., 29.0 (B3LYP) or 31.7 (BP86) kcal/mol (Table 6), which is comparable to that for Ag(CN)NH₃. The dissociation energy for Ag(CN)PF₃ is smaller, i.e., 18.2 (B3LYP) or 21.9 (BP86) kcal/mol, but not as small as that for Ag(CN)NF₃ (9 kcal/mol, Table 6). Nevertheless, these complexes are favorable with respect to the loss of the PH₃ and PF₃ ligands. The Ag–P distances in Ag(CN)PH₃ are slightly (~0.03 Å) longer than that in Ag(CN)PF₃, consistent with the corresponding Wiberg bond indices (Table 3).

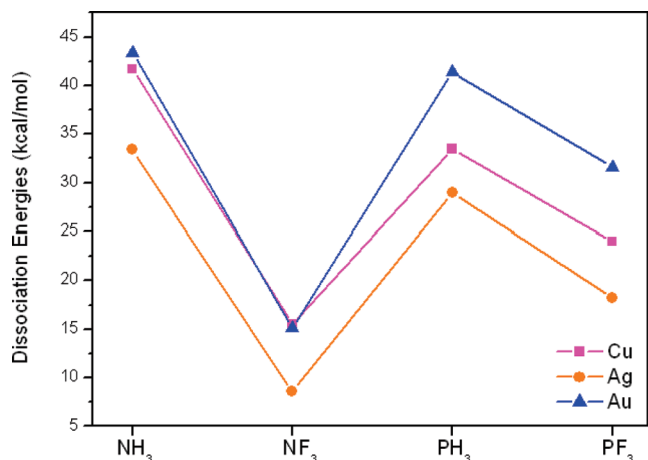


Figure 3. The dissociation energies of $M(\text{CN})(\text{XY}_3)$ ($M = \text{Cu}, \text{Ag}, \text{Au}$; $X = \text{N}, \text{P}$; $Y = \text{H}, \text{F}$).

It may be seen from Table 3 that the positive charges on Ag in $\text{Ag}(\text{CN})\text{PY}_3$ are slightly less than those for $\text{Ag}(\text{CN})\text{NY}_3$, and the Wiberg bond indices of $\text{Ag}-\text{P}$ in $\text{Ag}(\text{CN})\text{PY}_3$ are larger than those of $\text{Ag}-\text{N}$ in $\text{Ag}(\text{CN})\text{NY}_3$. For $\text{Ag}(\text{CN})\text{PF}_3$, the $\text{WBI}(\text{Ag}-\text{P})$ of 0.45 is the largest among the four $\text{Ag}(\text{CN})\text{XY}_3$ ($X = \text{N}$ or P ; $Y = \text{H}$ or F) species, and the P atom has the largest positive charge of +1.85 (Table 3). These results show that the bonds between the Ag and P atoms in $\text{Ag}(\text{CN})\text{PY}_3$ are less ionic but more covalent than the bonds between the Ag and N atoms in $\text{Ag}(\text{CN})\text{NY}_3$.

The Cu and Au analogues $M(\text{CN})\text{PH}_3$ and $M(\text{CN})\text{PF}_3$ ($M = \text{Cu}, \text{Au}$) also have the linear asymmetric structure, and their geometries are reported in Table 7. The PH_3 and PF_3 ligands in the Cu and Au analogues have almost the same geometries as those in $\text{Ag}(\text{CN})\text{PH}_3$ or $\text{Ag}(\text{CN})\text{PF}_3$. The dissociation energies for losing the PH_3 and PF_3 ligands are reported in Table 6, and these values are comparable with (or even larger than) those of $\text{Ag}(\text{CN})\text{PH}_3$ or $\text{Ag}(\text{CN})\text{PF}_3$. Therefore, all of these complexes are energetically viable.

Figure 3 compares the B3LYP bond dissociation energies (BDE) for the 12 $M(\text{CN})\text{XY}_3$ species. The complexes containing the NH_3 ligand, i.e., $M(\text{CN})\text{NH}_3$ for all three metals, have the largest $M-\text{N}$ bond dissociation energies (>33 kcal/mol), while the NF_3 -containing complexes have the smallest BDEs (as small as 8.6 kcal/mol for $\text{Ag}(\text{CN})\text{NF}_3$). This is consistent with the NBO analysis mentioned above. The ionic interaction between M and N is believed to play an important role in stabilizing these complexes. The dissociation energies for $M(\text{CN})\text{PH}_3$ are larger than those for $M(\text{CN})\text{PF}_3$, but the difference is not as large as those between the $M(\text{CN})\text{NH}_3$ and $M(\text{CN})\text{NF}_3$ species. Thus, the BDE values for the complexes containing the different ligands are in the order $\text{NH}_3 > \text{PH}_3 > \text{PF}_3 > \text{NF}_3$. Comparing complexes among the three different coinage metals, the theoretical BDE values show the order $\text{Au} > \text{Cu} > \text{Ag}$. This is in agreement with the general trend for the bond dissociation energies of the first, second, and third transition metal rows.⁴² On the basis of energy considerations, the linear asymmetric complexes for Cu and Au should be even more favorable species than their Ag analogues.

Ag(Br)NH₃ and Analogues. In Chippindale et al.'s 2008 paper,¹³ the other critical new structure synthesized was the

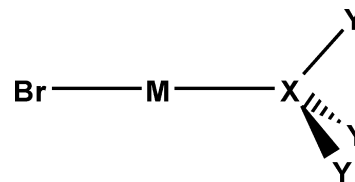


Figure 4. Qualitative structures of $\text{BrM}(\text{XY}_3)$ ($M = \text{Cu}, \text{Ag}, \text{Au}$; $X = \text{N}, \text{P}$; $Y = \text{H}, \text{F}$).

analogous asymmetric complex of $\text{Ag}(\text{I})$, namely, $\text{Ag}(\text{Br})\text{NH}_3$. The molecular units in the crystal slightly distort from linearity with an experimental $\text{Br}-\text{Ag}-\text{N}$ bond angle of $165.01(12)^\circ$. However, in the present research, the theoretically optimized geometry for the isolated $\text{Ag}(\text{Br})\text{NH}_3$ remains a linear structure with C_{3v} symmetry (Figure 4 and Table 8). Chippindale et al. have suggested that the slight distortion from the linear geometry for the crystal $\text{Ag}(\text{Br})\text{NH}_3$ is caused by a weak intermolecular interaction, i.e., between a silver atom and a bromine atom in a neighboring molecule (with 2.971 Å being the intermolecular $\text{Ag} \cdots \text{Br}$ distance).¹³ Our predicted $\text{Ag}-\text{N}$ distance (2.204 Å by B3LYP or 2.171 Å by BP86) is close to the crystal $\text{Ag}-\text{N}$ distance 2.192 Å. Our predicted $\text{Ag}-\text{Br}$ distance (2.435 Å by B3LYP and 2.413 Å by BP86) is somewhat shorter than the crystal $\text{Ag}-\text{Br}$ distance (2.536 Å),¹³ and the $\text{Ag}-\text{Br}$ distance (2.49 Å) in the $[\text{AgBr}_2]^-$ anion.⁴³ The dissociation energy for $\text{Ag}(\text{Br})\text{NH}_3$ to lose NH_3 is predicted to be 29.6 (B3LYP) or 32.0 (BP86) kcal/mol (Table 10), which is ~ 2 kcal/mol smaller than that for $\text{Ag}(\text{CN})\text{NH}_3$. This may explain why the $\text{Ag}(\text{Br})\text{NH}_3$ complex, while also successfully prepared experimentally, decomposes at lower temperature than $\text{Ag}(\text{CN})\text{NH}_3$.

Like for the $M(\text{CN})\text{XY}_3$ analogues, we have investigated a total of 12 $M(\text{Br})\text{XY}_3$ analogues ($M = \text{Cu}, \text{Ag}, \text{Au}$; $\text{XY}_3 = \text{NH}_3, \text{NF}_3, \text{PH}_3, \text{PF}_3$) with the same methods. All of these complexes are predicted to be linear in the heavy atoms, with C_{3v} symmetry, and their geometry parameters are reported in Table 8. The $M-X$ distances and the geometry parameters for XY_3 in the 12 $M(\text{Br})\text{XY}_3$ complexes are very close to the corresponding geometry parameters in $M(\text{CN})\text{XY}_3$ (Tables 1, 5, and 7). Comparing the geometries of the $M(\text{Br})\text{XY}_3$ complexes with the free MBr and XY_3 , the trend of the changes of the corresponding geometrical parameters is similar to that for the $M(\text{CN})\text{XY}_3$ species.

The natural bond orbital (NBO) analyses were also carried out for the $\text{Ag}(\text{Br})\text{XY}_3$ complexes (Table 9). It is interesting to compare the natural atomic charges and Wiberg bond indices (WBI) for the $\text{Ag}(\text{Br})\text{XY}_3$ complexes with those for their CN analogues (Table 3). These two tables are remarkably similar with a deviation of less than 0.04 for natural atomic charges and 0.07 for WBIs, if CN is considered the analogue of Br. Similar to the above discussion for the $\text{Ag}(\text{CN})\text{XY}_3$ complexes (Table 3), there is primarily ionic bonding between AgBr and XY_3 . The $\text{Ag}-\text{NH}_3$ interaction is stronger than that for $\text{Ag}-\text{NF}_3$, since the latter has significantly smaller atomic charges for Q_X , Q_Y , Q_{AgBr} , and Q_{XY_3} (Table 9). For the complexes with PH_3 and PF_3 ligands, the absolute values of the fragment natural charges Q_{AgBr} and Q_{XY_3} are substantial (>0.14), suggesting strong bonding. However, the larger

Table 8. Geometrical Parameters for M(Br)XY₃ (M = Cu, Ag, Au; X = N, P; Y = H, F)^a

species		B3LYP			BP86		
		Cu	Ag	Au	Cu	Ag	Au
M(Br)(NH ₃)	M–Br	2.229	2.435	2.411	2.216	2.413	2.398
	M–N	1.951	2.204	2.136	1.932	2.171	2.118
	N–H	1.023	1.021	1.022	1.031	1.029	1.030
	∠H–N–H	107.2	107.4	107.8	107.0	107.2	107.8
M(Br)(NF ₃)	M–Br	2.210	2.424	2.390	2.199	2.399	2.376
	M–N	1.956	2.326	2.150	1.872	2.201	2.063
	N–F	1.379	1.374	1.377	1.417	1.402	1.410
	∠F–N–F	102.7	103.0	102.7	101.9	102.6	102.0
M(Br)(PH ₃)	M–Br	2.237	2.441	2.431	2.224	2.422	2.419
	M–P	2.197	2.397	2.292	2.161	2.350	2.268
	P–H	1.411	1.410	1.409	1.424	1.422	1.422
	∠H–P–H	98.8	98.7	99.8	98.3	98.2	99.3
M(Br)(PF ₃)	M–Br	2.221	2.421	2.411	2.211	2.402	2.399
	M–P	2.156	2.364	2.242	2.122	2.312	2.222
	P–F	1.570	1.570	1.567	1.588	1.588	1.584
	∠F–P–F	99.6	99.7	99.8	99.5	99.7	99.8
MBr	M–Br	2.216	2.449	2.412	2.198	2.428	2.394

^a Bond distances in Å, bond angles in degrees.**Table 9.** B3LYP Natural Atomic Charges (*Q*) and Wiberg Bond Indices (WBI) of Selected Bonds of Ag(Br)XY₃ (X = N and P, Y = H and F)

	<i>Q</i> _{Ag}	<i>Q</i> _{Br}	<i>Q</i> _X	<i>Q</i> _Y	<i>Q</i> _{AgBr}	<i>Q</i> _{XY3}	WBI _{Ag–XY3}	WBI _{Ag–Br}
Ag(Br)NH ₃	0.58	−0.68	−1.13	0.41	−0.10	0.10	0.20	0.51
Ag(Br)NF ₃	0.60	−0.65	0.59	−0.18	−0.04	0.04	0.15	0.57
Ag(Br)PH ₃	0.53	−0.68	0.06	0.03	−0.14	0.14	0.37	0.49
Ag(Br)PF ₃	0.48	−0.65	1.83	−0.55	−0.17	0.17	0.46	0.50
AgBr	0.66							0.60

WBI_{Ag–XY3} values (>0.37) suggest that the bonding between AgBr and PY₃ possesses more covalent character.

The bond dissociation energies (BDE) for all 12 M(Br)XY₃ complexes are reported in Table 10 and displayed in Figure 5. Compared with those in Table 6 and Figure 3 for M(CN)XY₃, the BDEs of M(Br)XY₃ (Figure 5) have a very similar pattern. As for the three different coinage metals, Figure 5 shows that the theoretical BDE values for M(Br)XY₃ follow the irregular order Au > Cu > Ag, as was the case for the M(CN)XY₃ complexes. On the basis of energy considerations, the linear asymmetric M(Br)XY₃ complexes for Cu and Au have good prospects for preparation.

Summary

The present research shows that Ag(CN)NH₃ has a C_{3v} linear asymmetric structure, with theoretical bond distances in good agreement with the experimental crystal structure. Our structure for Ag(Br)NH₃ is linear in the three heavy atoms, while the experimental structure is slightly bent (165.0°). The difference between the theory and experiment has been rationalized in terms of the intermolecular interactions.¹³

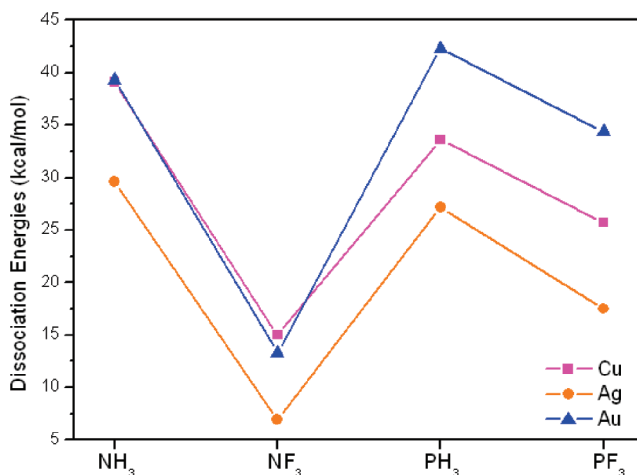
The bond dissociation energies (BDE) are shown in Tables 6 and 10, as well as in Figures 3 and 5. For Cu and Ag, the dissociation energies fall in the order NH₃ > PH₃ > PF₃ > NF₃. However, for Au, the dissociation energies for Au(CN)XY₃ are in the order NH₃ ~ PH₃ > PF₃ > NF₃, and those for Au(Br)XY₃ become different, i.e., PH₃ > NH₃ ~ PF₃ > NF₃ (Tables 6 and 10). Thus, it is understandable that the dissociation energies were reported in the order PH₃ > PF₃ > NH₃ > NF₃ for ClAu–L reported by Pyykkö et al. at the BP86/cc-pVDZ level of theory.⁴⁴

Table 10. Dissociation Energies (in kcal/mol) for M(Br)L (M = Cu, Ag, and Au; L = NH₃, NF₃, PH₃, PF₃)

	B3LYP			BP86		
	Cu	Ag	Au	Cu	Ag	Au
M(Br)(NH ₃) → M(Br) + NH ₃	39.1	29.6	39.3	41.7	32.0	42.2
M(Br)(NF ₃) → M(Br) + NF ₃	15.0	6.9	13.3	20.3	9.1	17.7
M(Br)(PH ₃) → M(Br) + PH ₃	33.6	27.2	42.3	38.0	31.2	46.8
M(Br)(PF ₃) → M(Br) + PF ₃	25.7	17.5	34.4	31.8	22.9	40.3

The NBO analysis shows that the interaction between AgCN and NH₃ (or AgBr and NH₃) is essentially ionic, and this is in agreement with the EDA analysis for related carbenes by Frenking et al.⁴¹ The dissociation energy of Ag(CN)NH₃ for losing NH₃ is predicted to be substantial (>30 kcal/mol), suggesting an energetically viable species.

We have also studied a series of analogues of Ag(CN)NH₃ and Ag(Br)NH₃, i.e., XML (X = CN, Br; M = Cu, Ag, Au; L = NH₃, NF₃, PH₃, PF₃), most of which are experimentally unknown. All of these analogous compounds are predicted to have similar C_{3v} linear asymmetric minima. Except for the NF₃-containing complexes, the dissociation energies for these analogous complexes are substantial, and they should have synthetic potential, as recently discovered experimentally for Ag(CN)NH₃ and Ag(Br)NH₃.

**Figure 5.** Dissociation energies of M(Br)XY₃ (M = Cu, Ag, Au; X = N, P; Y = H, F).

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