

# Gas-Phase Metal Cyanide Chemistry: Formation, Reactions, and Proposed Linear Structures of Copper(I) and Silver(I) Cyanide Clusters

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When solid MCN (M = Cu or Ag) is ablated with single pulses of a focused Nd-YAG laser (1064 nm, 470–1600 MW cm<sup>-2</sup>), the ions detected by Fourier transform ion cyclotron resonance mass spectrometry (FTICRMS) are [M<sub>n</sub>(CN)<sub>n+1</sub>]<sup>-</sup> (M = Cu, n = 1–5; M = Ag, n = 1–4), [M<sub>n</sub>(CN)<sub>n-1</sub>]<sup>+</sup> (M = Cu, n = 1–6; M = Ag, n = 1–4), and, for M = Ag, Ag<sub>2</sub><sup>+</sup>, Ag<sub>3</sub><sup>+</sup> and [Ag<sub>4</sub>(CN)]<sup>+</sup>. Several mixed-metal species [Cu<sub>m</sub>Ag<sub>n-m</sub>(CN)<sub>n+1</sub>]<sup>-</sup> and [Cu<sub>m</sub>Ag<sub>n-m</sub>(CN)<sub>n-1</sub>]<sup>+</sup> are produced on ablation of a CuCN:AgCN mixture. Both [M<sub>n</sub>(CN)<sub>n+1</sub>]<sup>-</sup> and [M<sub>n</sub>(CN)<sub>n-1</sub>]<sup>+</sup> lose units of MCN on collision-induced dissociation in Ar(g). Reactions of both [M<sub>n</sub>(CN)<sub>n+1</sub>]<sup>-</sup> and [M<sub>n</sub>(CN)<sub>n-1</sub>]<sup>+</sup> with gaseous NH<sub>3</sub>, H<sub>2</sub>S and CO have been followed using FTICRMS. With the anions no addition was detected but dissociation occurred, again by loss of MCN. Dissociation occurred with the cations also, but was frequently accompanied by addition, with bis-adducts predominant. The ranges of addition products detected are: [M<sub>n</sub>(CN)<sub>n-1</sub>(NH<sub>3</sub>)<sub>x</sub>]<sup>+</sup> (M = Cu, n = 2, x = 1–3, n = 3, x = 1–3, n = 4, x = 1–2; M = Ag, n = 2, x = 1–2, n = 3, x = 1–3, and n = 4, x = 1–3); [M<sub>n</sub>(CN)<sub>n-1</sub>(SH<sub>2</sub>)<sub>x</sub>]<sup>+</sup> (M = Cu or Ag, n = 1–4, x = 1–2); [M<sub>n</sub>(CN)<sub>n-1</sub>(CO)<sub>x</sub>]<sup>+</sup> (M = Cu, n = 3–5, x = 1–2; M = Ag, n = 4, x = 1–2). At long reaction times complexes containing HCN are formed in small amount when [Cu<sub>n</sub>(CN)<sub>n-1</sub>]<sup>+</sup> reacts with H<sub>2</sub>S. Geometry optimizations using density functional theory (DMol) show that the most stable structures for both [M<sub>n</sub>(CN)<sub>n+1</sub>]<sup>-</sup> and [M<sub>n</sub>(CN)<sub>n-1</sub>]<sup>+</sup> are linear alternations of M and CN, in spear topology.

## Introduction

In the last two years a new class of metal-carbon clusters, also known as metallocarbohedrenes, has been formed and detected in mass spectrometric experiments.<sup>2–12</sup> Although there are still no experimental data on the structures of these, considerable theoretical work indicates that many of these are likely to contain C<sub>2</sub> groups, formally C<sub>2</sub><sup>2-</sup>.<sup>13–27</sup> For example,

and of particular relevance to the present work, Yamada and Castleman<sup>9</sup> have reported a series of clusters [Cu<sub>2n+1</sub>C<sub>2n</sub>]<sup>+</sup> (n = 1–10) that can be regarded as containing Cu(I) and C<sub>2</sub><sup>2-</sup>. The ligands involved in the metallocarbohedrene clusters are isoelectronic with CO, N<sub>2</sub> and CN<sup>-</sup>. Metal carbonyl clusters are legion, and a metal cluster with bound N<sub>2</sub> is the focus of the enzyme nitrogenase.<sup>28–32</sup> However, although CN<sup>-</sup> is a key ligand in coordination chemistry, and is known to bridge metal atoms in non-molecular structures,<sup>33</sup> there appear to be no reports of molecular clusters with CN<sup>-</sup> as the predominant ligand.<sup>33,34</sup>

This dearth of information about molecular metal cyanide clusters appears to be anomalous, in view of the fundamental significance of the ligand, and the formal connection to the metallocarbohedrenes. The most obvious reason for this lack of information is a preference for the formation of non-molecular cyanides in condensed phases where multiple electrostatic and van der Waals interactions can occur. The gas phase enforces molecular behavior and favors clustering reactions. Accordingly, we have commenced investigations of metal cyanide

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complexes in the gas phase, where simpler chemistry is anticipated, and report here our results for complexes of Cu(I) and Ag(I). Prior to our study there had been no detailed study of cyano complexes of either Cu(I) or Ag(I) in the gas phase, although the anions  $[\text{Cu}_n\text{CN}]^-$  and  $[\text{Cu}_n(\text{CN})_{n+1}]^-$  ( $n = 1-3$ ) have been identified as products of SIMS measurements on the deposits that occur in copper stills used for grain spirit distillation.<sup>35</sup>

## Experimental Section

The literature method<sup>36</sup> was used for the preparation of CuCN, with the minor modification that  $\text{Na}_2\text{S}_2\text{O}_5$  was substituted for  $\text{Na}_2\text{SO}_3$ . After the CuCN had been dried under vacuum, it was a flocculent light beige powder, which was stored under  $\text{N}_2(\text{g})$ . Samples of CuCN that were allowed to stand in air showed evidence for oxidation (addition of oxygen atoms) in their LA-FTICR (laser ablation Fourier transform ion cyclotron resonance) mass spectra.

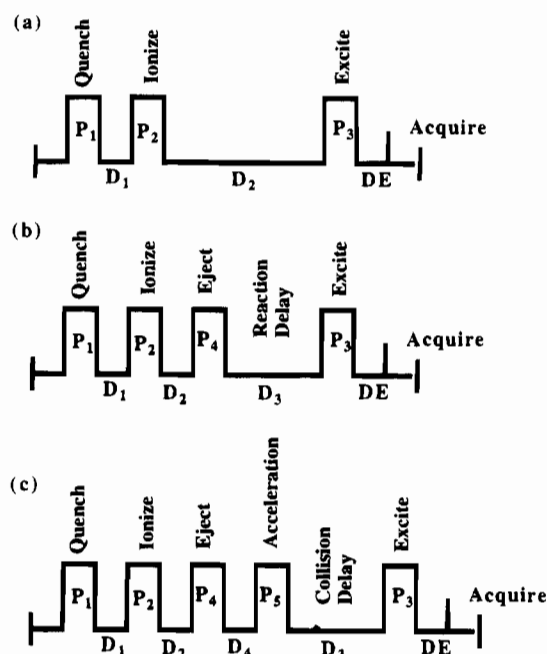
Silver cyanide was precipitated on combination of aqueous solutions of NaCN and an equimolar or slightly larger amount of  $\text{AgNO}_3$ . The flocculent white precipitate of AgCN was washed with  $\text{Me}_2\text{CO}$ , dried under vacuum, and stored in the dark. For some experiments, AgCN was purified by crystallization from concentrated  $\text{NH}_3(\text{aq})$ .<sup>37</sup> Such samples gave spectra not significantly different from spectra obtained using AgCN that had not been crystallized. Pressed disks of AgCN that have been exposed to fluorescent light become silver-rich at the surface (as measured by their LA-FTICR mass spectra) as expected. Use of excess NaCN in the preparation of AgCN led to a product in which  $\text{Na}^+$  and aggregates containing Na could be detected in the LA-FTICR positive-ion mass spectra. The mixed-metal species detected were  $[\text{NaAg}(\text{CN})]^+$ ,  $[\text{Na}_2\text{Ag}(\text{CN})_2]^+$ ,  $[\text{NaAg}_2(\text{CN})_2]^+$ ,  $[\text{Na}_2\text{Ag}_2(\text{CN})_3]^+$  and  $[\text{NaAg}_3(\text{CN})_3]^+$ .

Samples for the LA-FTICR measurements were pressed into stainless steel probe tips. The apparatus and techniques used for the laser desorption and mass spectrometry have been described previously in papers from these laboratories.<sup>38,39</sup> Broad band spectra over a large mass range were normally used to identify the ions. The pulse program is shown in sequence (a) (see Scheme 1). In the case of low abundance ions ( $[\text{Cu}_6(\text{CN})_5]^+$ ,  $[\text{Cu}_m\text{Ag}_{n-m}(\text{CN})_{n-1}]^+$  ( $n = 4, m = 1; n = 5, m = 3, 4$ ),  $[\text{Cu}_5(\text{CN})_6]^-$ ,  $[\text{Ag}_4(\text{CN})_5]^-$  and  $[\text{Cu}_m\text{Ag}_{4-m}(\text{CN})_5]^-$  ( $m = 2, 3$ )) narrow band conditions were used with enhanced receiver gain. For the study of ion-molecule reactions, sequence (b) was used. Collision-induced dissociation experiments were carried out by first selecting an ion and ejecting all unwanted ions from the cell. The selected ion was then accelerated, using a RF pulse, in the presence of argon at a pressure of  $1 \times 10^{-7}$  mbar (sequence (c)).

Electron impact experiments or electron capture experiments (for negative ions) were carried out using a pulse program involving laser desorption followed by flooding the cell with electrons of the required energy.

Positive-ion mass spectra obtained by laser ablation of AgCN were found to be profoundly affected by the power density of the laser. The abundance of  $\text{Ag}^+$  increased with increasing laser power density. For example, in the spectrum of one sample the  $\text{Ag}^+$  ion was not detectable using a power density of  $630 \text{ MW cm}^{-2}$  but became the dominant ion (intensity > 50%) when the power density exceeded ca  $1000 \text{ MW cm}^{-2}$ . For the anions derived from AgCN, the effect of laser power was small, but increase in power increased the percentage abundance of  $[\text{Ag}(\text{CN})_2]^-$  slightly. For both positive and negative ions produced from CuCN, the effect of laser power was again small, but larger aggregates became slightly more abundant as the power was increased.

## Scheme 1



## Results

**1. Products of Laser Ablation of CuCN, AgCN, and a CuCN:AgCN Mixture.** Ablation of solid CuCN and AgCN with single pulses of the focused Nd YAG laser ( $1064 \text{ nm}$ ) at power densities of  $470-1600 \text{ MW cm}^{-2}$  allowed detection of the mass spectra of both anions and cations containing intact CN moieties (Table 1). The anionic series are of the formula  $[\text{M}_n(\text{CN})_{n+1}]^-$ , in which  $n = 1-5$  for  $\text{M} = \text{Cu}$  and  $n = 1-4$  for  $\text{M} = \text{Ag}$ . The cationic series are of the formula  $[\text{M}_n(\text{CN})_{n-1}]^+$ , in which  $n = 1-6$  for  $\text{M} = \text{Cu}$  and  $n = 1-4$  for  $\text{M} = \text{Ag}$ . Individual ions were identified not only by their masses but also by the isotopic patterns arising from the presence of  $^{63/65}\text{Cu}$  or  $^{107/109}\text{Ag}$ .<sup>40</sup> Typical mass spectra, those of  $[\text{Cu}_n(\text{CN})_{n+1}]^-$ ,  $[\text{Cu}_n(\text{CN})_{n-1}]^+$  and  $[\text{Ag}_n(\text{CN})_{n-1}]^+$ , are given in Figure 1a, b, and c, respectively. In electron impact/capture experiments there was a slight improvement in the signal to noise, but the distribution of ions was not significantly affected. Thus, with the absence of  $[\text{M}_n(\text{CN})_n]^\pm$ , we have no evidence for the generation of the neutral electron-precise species  $[\text{M}_n(\text{CN})_n]^0$ .

Apart from the differing extents of the series of ions  $[\text{M}_n(\text{CN})_{n-1}]^+$  that are formed, there is another difference between the cations formed from CuCN and those formed from AgCN. Ablation of AgCN leads to small amounts of bare  $\text{Ag}_2^+$ , bare  $\text{Ag}_3^+$ , and  $[\text{Ag}_4(\text{CN})]^+$ , whereas no copper analogues are formed from CuCN. The relative amounts of the three silver cations are somewhat variable from sample to sample.

When an approximately equimolar mixture of CuCN and AgCN was ablated, several mixed-metal cations and anions,  $[\text{Cu}_m\text{Ag}_{n-m}(\text{CN})_{n-1}]^+$  and  $[\text{Cu}_m\text{Ag}_{n-m}(\text{CN})_{n+1}]^-$ , were detected in addition to the homometallic parent species described above. The heterometallic species are given in Table 1.

**2. Dissociation of  $[\text{M}_n(\text{CN})_{n+1}]^-$  and  $[\text{M}_n(\text{CN})_{n-1}]^+$  in Ar ( $1 \times 10^{-7}$  Torr).** (i) **Collision-Induced Dissociation (CID).** Dissociation of both  $[\text{M}_n(\text{CN})_{n+1}]^-$  and  $[\text{M}_n(\text{CN})_{n-1}]^+$ , induced by collision with Ar, occurs by loss of units of formula MCN, and proceeds as far as  $\text{CN}^-$  and  $\text{M}^+$ , for the anions and cations, respectively (eq 1 and 2). An illustrative spectrum is shown in

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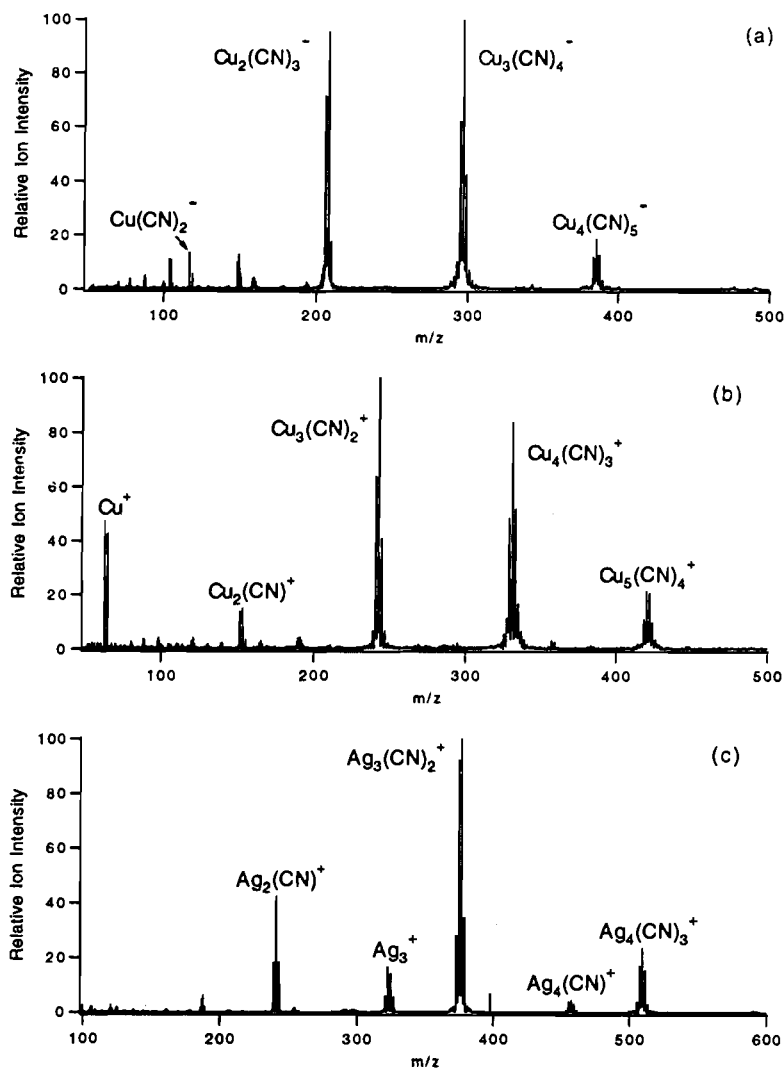
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(40) Percent natural abundances:  $^{63}\text{Cu}$  69.09,  $^{65}\text{Cu}$  30.91;  $^{107}\text{Ag}$  51.35,  $^{109}\text{Ag}$  48.65%.

**Table 1.** Ions Observed in FTICR Mass Spectra after Laser Ablation of MCN (M = Cu or Ag)

M	ions obsd	
	anions	cations
Cu	[Cu(CN) <sub>2</sub> ] <sup>-</sup> , [Cu <sub>2</sub> (CN) <sub>3</sub> ] <sup>-</sup> , [Cu <sub>3</sub> (CN) <sub>4</sub> ] <sup>-</sup> , [Cu <sub>4</sub> (CN) <sub>5</sub> ] <sup>-</sup> , [Cu <sub>5</sub> (CN) <sub>6</sub> ] <sup>- a</sup>	Cu <sup>+</sup> , [Cu <sub>2</sub> (CN)] <sup>+</sup> , [Cu <sub>3</sub> (CN) <sub>2</sub> ] <sup>+</sup> , [Cu <sub>4</sub> (CN) <sub>3</sub> ] <sup>+</sup> , [Cu <sub>5</sub> (CN) <sub>4</sub> ] <sup>+</sup> , [Cu <sub>6</sub> (CN) <sub>5</sub> ] <sup>+</sup> a
Ag	AgCN <sup>- b</sup> , [Ag(CN) <sub>2</sub> ] <sup>-</sup> , [Ag <sub>2</sub> (CN) <sub>3</sub> ] <sup>-</sup> , [Ag <sub>3</sub> (CN) <sub>4</sub> ] <sup>-</sup> , [Ag <sub>4</sub> (CN) <sub>5</sub> ] <sup>- a</sup>	Ag <sup>+</sup> , Ag <sub>2</sub> <sup>+</sup> , Ag <sub>3</sub> <sup>+</sup> , [Ag <sub>2</sub> (CN)] <sup>+</sup> , [Ag <sub>3</sub> (CN) <sub>2</sub> ] <sup>+</sup> , [Ag <sub>4</sub> (CN)] <sup>+</sup> , [Ag <sub>4</sub> (CN) <sub>3</sub> ] <sup>+</sup>
Cu:Ag = 1:1 <sup>c</sup>	[CuAg(CN) <sub>3</sub> ] <sup>-</sup> , [Cu <sub>2</sub> Ag(CN) <sub>4</sub> ] <sup>-</sup> , [CuAg <sub>2</sub> (CN) <sub>4</sub> ] <sup>-</sup> , [Cu <sub>3</sub> Ag(CN) <sub>5</sub> ] <sup>- a</sup> , [Cu <sub>2</sub> Ag <sub>2</sub> (CN) <sub>5</sub> ] <sup>- a</sup>	[CuAg(CN)] <sup>+</sup> , [Cu <sub>2</sub> Ag(CN) <sub>2</sub> ] <sup>+</sup> , [CuAg <sub>2</sub> (CN) <sub>2</sub> ] <sup>+</sup> , [Cu <sub>3</sub> Ag(CN) <sub>3</sub> ] <sup>+</sup> , [Cu <sub>2</sub> Ag <sub>2</sub> (CN) <sub>3</sub> ] <sup>+</sup> , [CuAg <sub>3</sub> (CN) <sub>3</sub> ] <sup>+</sup> , [Cu <sub>4</sub> Ag(CN) <sub>4</sub> ] <sup>+</sup> , [Cu <sub>3</sub> Ag <sub>2</sub> (CN) <sub>4</sub> ] <sup>+</sup> a

<sup>a</sup> Under narrow-band conditions. <sup>b</sup> Only during CID in Ar(g). <sup>c</sup> Only heterometallic species are listed. Parent homometallic complexes were also present.



**Figure 1.** Typical broad band laser ablation FTICR mass spectra: (a) negative ion spectrum of CuCN; (b) positive ion spectrum of CuCN; (c) positive ion spectrum of AgCN.

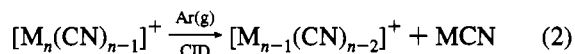
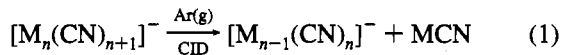
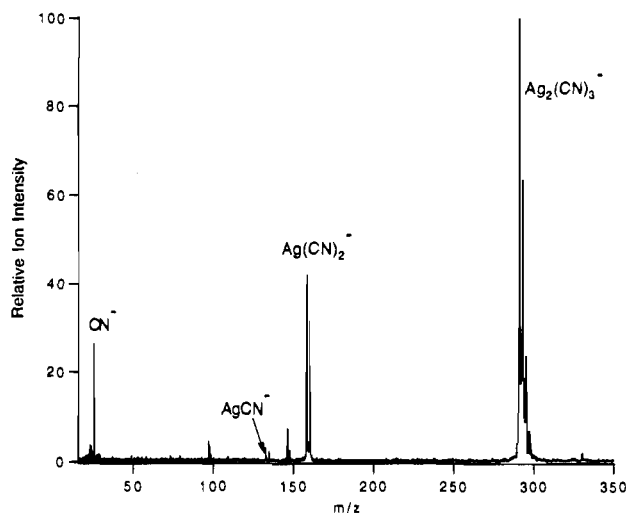


Figure 2. With our instrumentation, the acceleration pulse P5 is neither sharp enough to allow selection of only one line of an isotopic multiplet nor broad enough to allow excitation of the whole multiplet. This makes quantitation of CID rates problematic. However, relative rates can be measured for species giving similar multiplets. For species containing two metal centers, the relative rates of CID at constant center-of-mass energy are  $[\text{Ag}_2(\text{CN})]^+ \approx [\text{Ag}_2(\text{CN})_3]^- > [\text{Cu}_2(\text{CN})_3]^- \geq [\text{Cu}_2(\text{CN})]^+$ .

(ii) **Thermally-Induced Dissociation.** Comparison of dissociation rates in Ar when *no* acceleration is imparted show that larger aggregates dissociate more rapidly, and are thus more fragile. In general, the differences are probably not large, however. In many of the spectra showing collision- or thermally-induced dissociation of an  $M_n$  species, either cationic or anionic, and with M = Cu or Ag, we find the spectra of all possible species of lesser  $n$ , e.g. Figure 2.

**3. Reaction with NH<sub>3</sub>, H<sub>2</sub>S, and CO ( $1 \times 10^{-7}$  mbar).** (a)  $[M_n(\text{CN})_{n+1}]^-$  (M = Cu or Ag). All attempts to react  $[M_n(\text{CN})_{n+1}]^-$  with NH<sub>3</sub>, H<sub>2</sub>S or CO ( $1 \times 10^{-7}$  mbar) produced only evidence for dissociation, in which the products were the same as those observed by collision with Ar. There was no



**Figure 2.** FTICR mass spectrum showing collisionally induced dissociation of  $[\text{Ag}_2(\text{CN})_3]^-$  in  $\text{Ar}(\text{g})$  ( $1 \times 10^{-7}$  mbar) at center of mass energy  $2.5 \times 10^2$  eV.

**Table 2.** Maximum Number of Ligands in  $[\text{M}_n(\text{CN})_{n-1}(\text{L})_x]^+$  Observed by Reaction of Various Ligands L with  $[\text{M}_n(\text{CN})_{n-1}]^+$  or by Dissociation of Higher Species<sup>a</sup> ( $\text{M} = \text{Cu}$  or  $\text{Ag}$ ,  $\text{L} = \text{NH}_3$ ,  $\text{H}_2\text{S}$  or  $\text{CO}$ )

M	L	n	x(max)
Cu	NH <sub>3</sub>	1	4
		2	3
		3	3
		4	2
Ag	NH <sub>3</sub>	1	3
		2	2
		3	3
		4	3
Cu	H <sub>2</sub> S	1	2 <sup>a</sup>
		2	2 <sup>b,c</sup>
		3	2 <sup>d</sup>
		4	2 <sup>e</sup>
Ag	H <sub>2</sub> S	1	2
		3	2
Cu	CO	3	2
		4	2
		5	2
Ag	CO	4	2

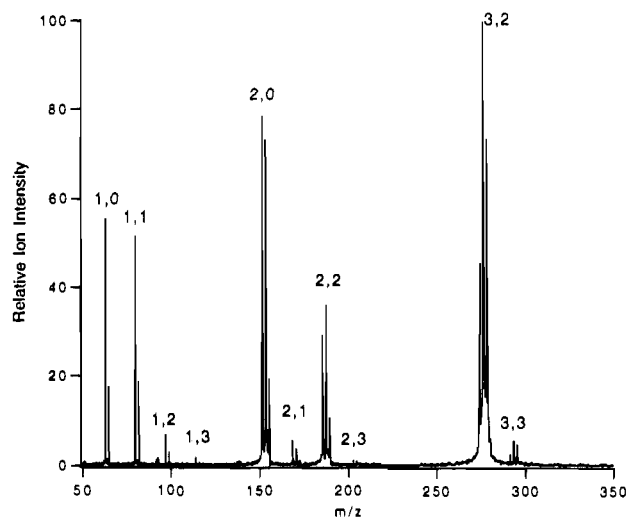
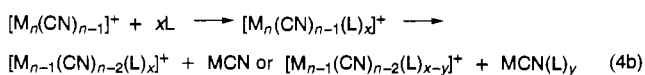
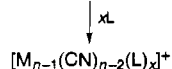
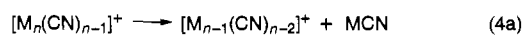
<sup>a</sup> Together with  $[\text{Cu}(\text{NCH})]^+$ . <sup>b</sup> None by direct reaction of  $[\text{Cu}_2(\text{CN})]^+$  with  $\text{H}_2\text{S}$  (see text). <sup>c</sup> Together with  $[\text{Cu}_2(\text{CN})(\text{SH}_2)(\text{NCH})]^+$ . <sup>d</sup> Together with  $[\text{Cu}_3(\text{CN})_2(\text{NCH})]^+$  and  $[\text{Cu}_3(\text{CN})_2(\text{SH}_2)(\text{NCH})]^+$ . <sup>e</sup> Together with  $[\text{Cu}_4(\text{CN})_3(\text{NCH})]^+$  and  $[\text{Cu}_4(\text{CN})_3(\text{SH}_2)(\text{NCH})]^+$ .

evidence for any addition products, but we cannot rule out the possibility that the dissociation is ligand assisted.

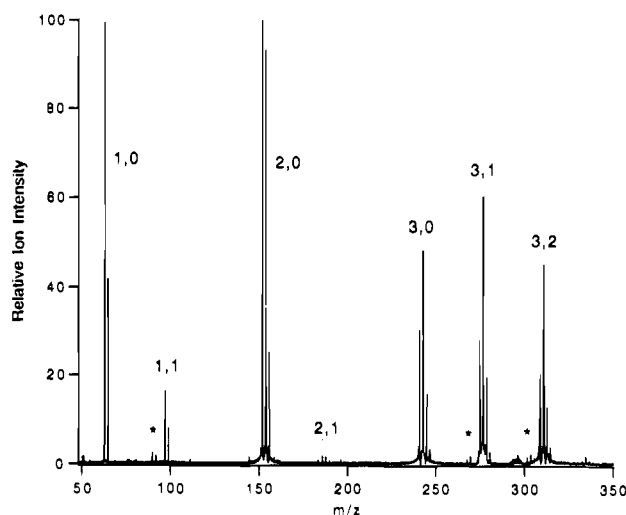
(b)  $[\text{M}_n(\text{CN})_{n-1}]^+$  ( $\text{M} = \text{Cu}$  or  $\text{Ag}$ ). Many of the cations undergo addition with one or more of the three reactant gases (eq 3). A complication of studying the reactions of the cations



with  $n > 1$  is that dissociation to species with lower values of  $n$  accompanies complexation (eq 4a and/or 4b). A summary of the species that have been observed is given in Table 2.



**Figure 3.** FTICR mass spectrum showing complexation and dissociation when  $[\text{Cu}_3(\text{CN})_2]^+$  reacts with  $\text{NH}_3(\text{g})$  ( $1 \times 10^{-7}$  mbar) for 20 s.  $n, x$  for  $[\text{Cu}_n(\text{CN})_{n-1}(\text{NH}_3)_x]^+$  are shown.

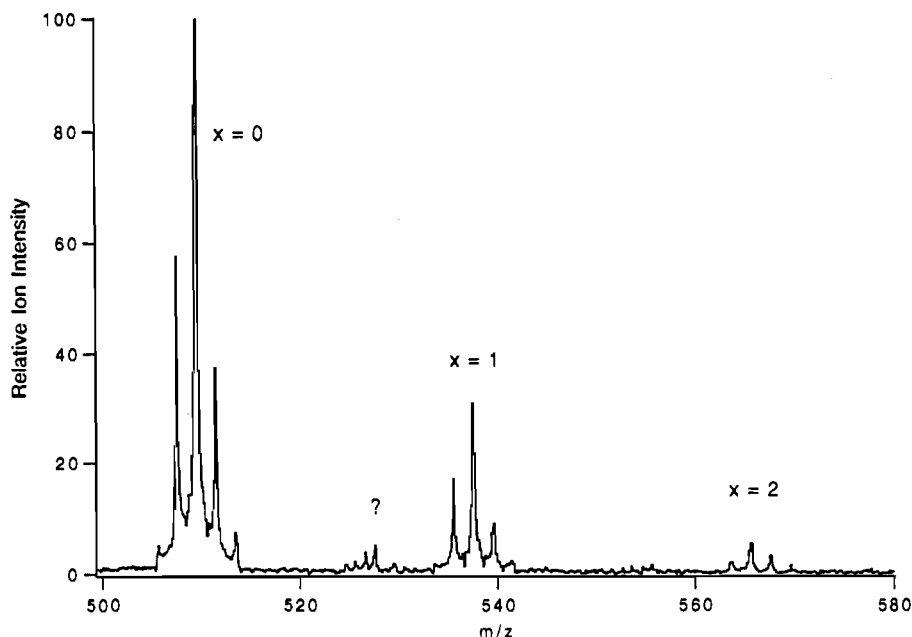


**Figure 4.** FTICR mass spectrum showing complexation and dissociation when  $[\text{Cu}_3(\text{CN})_2]^+$  reacts with  $\text{H}_2\text{S}(\text{g})$  ( $1 \times 10^{-7}$  mbar) for 20 s.  $n, x$  for  $[\text{Cu}_n(\text{CN})_{n-1}(\text{SH}_2)_x]^+$  are shown. \* = complex containing  $\text{HCN}$ .

**I. With NH<sub>3</sub>.** (i)  $\text{M} = \text{Cu}$ . Reaction of  $\text{NH}_3$  with the bare cation  $\text{Cu}^+$  produces the complexes  $[\text{Cu}(\text{NH}_3)_x]^+$  ( $x = 1-4$ ). The complex with  $x = 2$  is apparently particularly stable, while that with  $x = 4$  is only formed in observable amounts at reaction times exceeding ca. 100 s. Exemplifying both of these features, the relative amounts of  $[\text{Cu}(\text{NH}_3)_x]^+$  after  $\text{Cu}^+$  has reacted for 240 s are approximately 0.46:0.33:1:0.16:0.04 for  $x = 0-4$ , respectively.

Under the conditions of our experiment,  $[\text{Cu}_2(\text{CN})]^+$  forms  $[\text{Cu}_2(\text{CN})(\text{NH}_3)_x]^+$  ( $x = 1-3$ ). Again the species with  $x = 2$  is particularly stable. For example, after 20 s the relative amounts of the  $\text{Cu}_2$  species are 1, 0.06 and 0.25 for  $x = 0-2$ , respectively. Dissociation of  $\text{CuCN}$  occurs concurrently with complexation and at 20 s the ratio of  $\text{Cu}_2/\text{Cu}$  is ca 0.29. Addition of up to three  $\text{NH}_3$  ligands to  $[\text{Cu}_3(\text{CN})_2]^+$  is observed, with  $[\text{Cu}_3(\text{CN})_2(\text{NH}_3)_3]^+$  found in only very small amounts. At a reaction time of 20 s, the species with  $x = 1$  is absent and  $[\text{Cu}_3(\text{CN})_2(\text{NH}_3)_2]^+$ :  $[\text{Cu}_3(\text{CN})_2(\text{NH}_3)_3]^+ \approx 18:1$  (Figure 3). Longer reaction times do not yield relatively larger amount of the triammine because of the competing dissociation that is illustrated in Figure 3.

Decomposition is extensive for  $[\text{Cu}_4(\text{CN})_3]^+$  and its ammoniates. This limits the experiments that can be done with this cation. After 4 s reaction time  $[\text{Cu}_4(\text{CN})_3]^+$ ,  $[\text{Cu}_4(\text{CN})_3(\text{NH}_3)]^+$



**Figure 5.** FTICR mass spectrum showing the formation of  $[\text{Ag}_4(\text{CN})_3(\text{CO})_x]^+$  when  $[\text{Ag}_4(\text{CN})_3]^+$  reacts with  $\text{CO}(\text{g})$  ( $1 \times 10^{-7}$  mbar) for 100 s.

and  $[\text{Cu}_4(\text{CN})_3(\text{NH}_3)_2]^+$  are present in a ratio of approximately 1:2:1. However, at this point the percent dissociation of the  $\text{Cu}_4$  species exceeds 90%. After 20 s, the only tetranuclear complex that can be detected is  $[\text{Cu}_4(\text{CN})_3(\text{NH}_3)_2]^+$ , under conditions of poor signal:noise.

(ii) **M = Ag.** Addition of  $\text{NH}_3$  to  $[\text{Ag}_2(\text{CN})]^+$  occurs extremely slowly. After 20 s, the mono- and di-ammoniates are present in small amounts ( $[\text{Ag}_2(\text{CN})]^+ : [\text{Ag}_2(\text{CN})(\text{NH}_3)]^+ : [\text{Ag}_2(\text{CN})(\text{NH}_3)_2]^+ \approx 1:0.02:0.01$ ). However the dissociation products of  $[\text{Ag}_2(\text{CN})]^+$  (and/or its ammoniates) include  $[\text{Ag}(\text{NH}_3)_x]^+$  ( $x = 0-2$ ). After 20 s reaction time (total  $\text{Ag}_2(\text{CN})^+$  complexes):(total  $\text{Ag}^+$  complexes)  $\approx 1:0.25$  and  $\text{Ag}^+ : [\text{Ag}(\text{NH}_3)]^+ : [\text{Ag}(\text{NH}_3)_2]^+ \approx 1:0.26:0.03$ . The cation  $[\text{Ag}_3(\text{CN})_2]^+$  is comparatively more reactive than  $[\text{Ag}_2(\text{CN})]^+$ : after 10 s reaction time, the cations  $[\text{Ag}_3(\text{CN})_2]^+$ ,  $[\text{Ag}_3(\text{CN})_2(\text{NH}_3)]^+$  and  $[\text{Ag}_3(\text{CN})_2(\text{NH}_3)_2]^+$  have relative intensities approximately 1, 0.35 and 0.24. By reaction time 100 s, the only trinuclear species present are  $[\text{Ag}_3(\text{CN})_2(\text{NH}_3)_2]^+$  and  $[\text{Ag}_3(\text{CN})_2(\text{NH}_3)_3]^+$  in the approximate ratio 1:0.06. Tetranuclear  $[\text{Ag}_4(\text{CN})_3]^+$  adds up to three  $\text{NH}_3$  ligands under our experimental conditions. After 20 s, the only tetranuclear species present are  $[\text{Ag}_4(\text{CN})_3(\text{NH}_3)_2]^+$  and a relatively small amount of the corresponding triammine species (diammine:triammine  $\approx 1:0.04$ ). The diammine persists as the major species present in the full spectrum at least up to reaction times of 120 s.

**II. With  $\text{H}_2\text{S}$ .** (i) **M = Cu.** The direct reaction of  $\text{H}_2\text{S}$  with  $\text{Cu}^+$  occurs very slowly. After a reaction time of 100 s,  $[\text{Cu}(\text{SH}_2)]^+$  and  $[\text{Cu}(\text{SH}_2)_2]^+$  are detectable in only very small amounts ( $\text{Cu}^+ : [\text{Cu}(\text{SH}_2)]^+ : [\text{Cu}(\text{SH}_2)_2]^+ \approx 1:0.06:0.02$ ). The cation  $[\text{Cu}_2(\text{CN})]^+$  does not react with  $\text{H}_2\text{S}$  directly at times up to 200 s. The rate of loss of  $\text{CuCN}$  from  $[\text{Cu}_2(\text{CN})]^+$  in  $\text{H}_2\text{S}$  is roughly comparable to the rate in  $\text{NH}_3$ : after 20 s (total  $\text{Cu}_2(\text{CN})^+$  complexes):(total  $\text{Cu}^+$  complexes)  $\approx 0.46:1$ .

Complexation does occur with  $[\text{Cu}_3(\text{CN})_2]^+$ , as shown in Figure 4; complexes up to  $[\text{Cu}_3(\text{CN})_2(\text{SH}_2)_2]^+$  are formed. Two additional features of the  $[\text{Cu}_3(\text{CN})_2]^+ : \text{H}_2\text{S}$  reaction are noteworthy. First, at relatively long reaction times, formation of  $\text{HCN}$  complexes, in minor amounts (Figure 4), accompanies formation of the  $\text{H}_2\text{S}$  complexes of  $[\text{Cu}_3(\text{CN})_2]^+$ . Both  $[\text{Cu}_3(\text{CN})_2(\text{NCH})]^+$  and  $[\text{Cu}_3(\text{CN})_2(\text{SH}_2)(\text{NCH})]^+$  can be detected. Second, dissociation of the  $\text{Cu}_3$  species produces  $\text{H}_2\text{S}$  complexes of  $[\text{Cu}_2(\text{CN})]^+$ . As discussed,  $[\text{Cu}_2(\text{CN})(\text{SH}_2)_x]^+$  are not formed

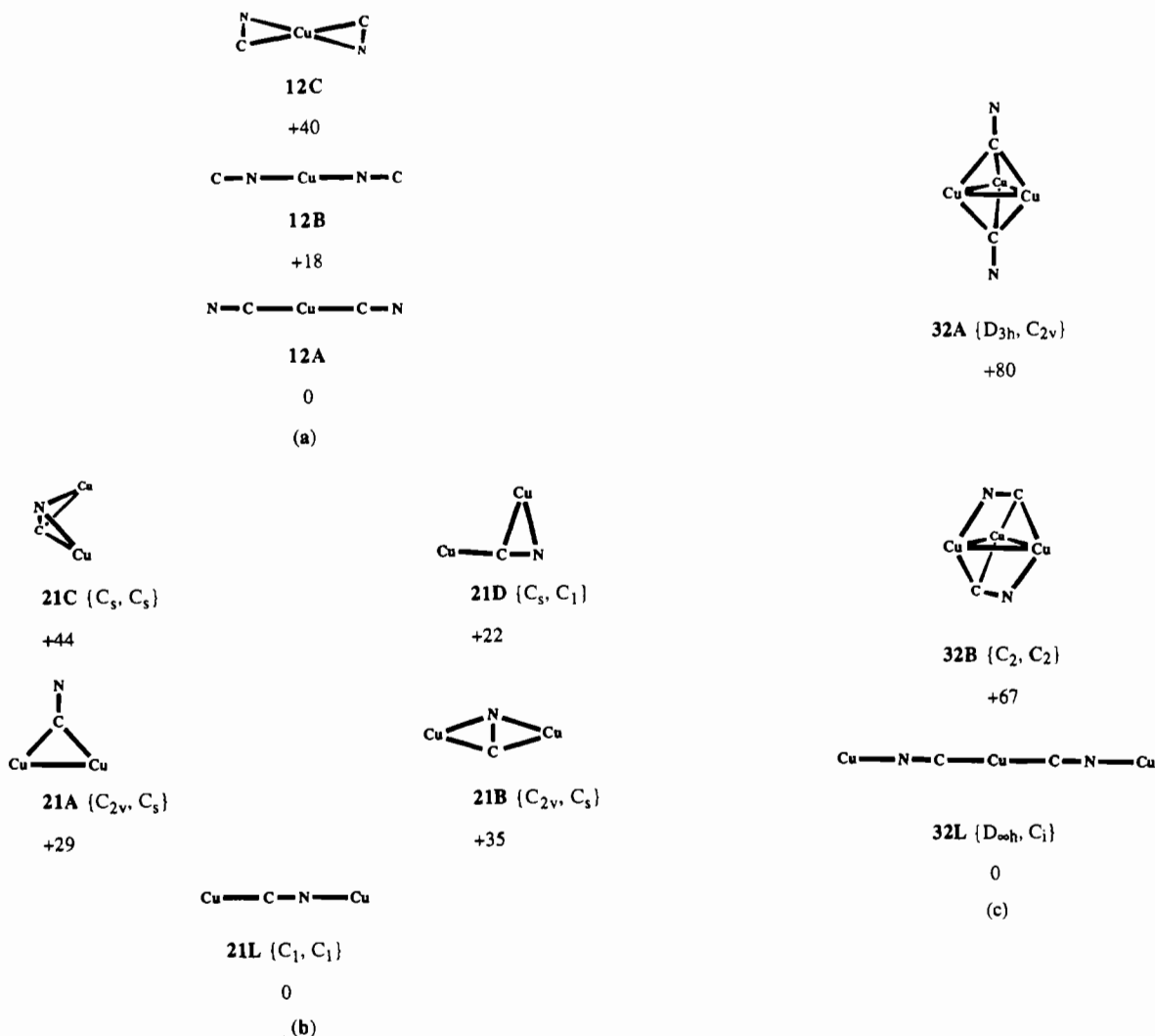
by the direct reaction between  $[\text{Cu}_2(\text{CN})]^+$  and  $\text{H}_2\text{S}$ . Similarly, proportionately larger amounts of  $\text{Cu}(\text{SH}_2)^+$  are formed during decomposition of the trinuclear complexes than by the direct reaction of  $\text{Cu}^+$  with  $\text{H}_2\text{S}$  (Figure 4). In both cases, the decomposition gives  $\text{HCN}$  complexes as well:  $[\text{Cu}_2(\text{CN})(\text{SH}_2)(\text{NCH})]^+$  and  $[\text{Cu}(\text{NCH})]^+$  are found (only the second is shown in Figure 3).

Up to two  $\text{H}_2\text{S}$  ligands can be added to  $[\text{Cu}_4(\text{CN})_3]^+$ . At the reaction times of over 10 s needed for  $[\text{Cu}_4(\text{CN})_3(\text{SH}_2)_2]^+$  to predominate among the  $\text{Cu}_4$  species, dissociation is extensive and in addition another  $\text{HCN}$  complex,  $[\text{Cu}_4(\text{CN})_3(\text{SH}_2)(\text{NCH})]^+$ , is formed.

(ii) **M = Ag.** Complexes of  $\text{Ag}^+$  with  $\text{H}_2\text{S}$  are formed only at long reaction times and then only in very small amounts; after a reaction time of 200 s,  $\text{Ag}^+ : [\text{Ag}(\text{SH}_2)]^+ : [\text{Ag}(\text{SH}_2)_2]^+ \approx 1:0.02:0.01$ . Under no conditions could we find evidence for any  $\text{H}_2\text{S}$  complex of  $[\text{Ag}_2(\text{CN})]^+$ . However, it is interesting to note that dissociation of  $[\text{Ag}_2(\text{CN})]^+$  in the presence of  $\text{H}_2\text{S}$  produces a relatively high proportion of  $[\text{Ag}(\text{SH}_2)]^+$ , e.g. after a reaction time of 5 s,  $\text{Ag}^+ : [\text{Ag}(\text{SH}_2)]^+ \approx 1:0.04$ . As well, decomposition of  $[\text{Ag}_2(\text{CN})]^+$  occurs more rapidly in  $\text{H}_2\text{S}$  than in  $\text{NH}_3$  and is comparable to the rate of decomposition of  $[\text{Cu}_2(\text{CN})]^+$  in  $\text{H}_2\text{S}$ : after 20 s (total  $\text{Ag}_2(\text{CN})^+$  complexes):(total  $\text{Ag}^+$  complexes)  $\approx 0.48:1$ .

The cation  $[\text{Ag}_3(\text{CN})_2]^+$  binds  $\text{H}_2\text{S}$  in a slow reaction that gives detectable amounts of products only at reaction times exceeding ca. 10 s. Up to two  $\text{H}_2\text{S}$  ligands may be bound. No evidence could be obtained for corresponding complexes of  $[\text{Ag}_4(\text{CN})_3]^+$ ; this cation is completely converted to cations with fewer silver atoms in ca. 5 s.

**III. With  $\text{CO}$ .** (i) **M = Cu.** No complex is formed between  $\text{Cu}^+$  and  $\text{CO}$  in reaction times up to 500 s. The same is true of  $[\text{Cu}_2(\text{CN})]^+$ , though this cation does undergo dissociation: after 100 s  $[\text{Cu}_2(\text{CN})]^+ : \text{Cu}^+ \approx 0.72:1$ —decomposition in the presence of  $\text{CO}$  is noticeably slower than in the presence of  $\text{NH}_3$  or  $\text{H}_2\text{S}$ . However, the cation  $[\text{Cu}_3(\text{CN})_2]^+$  does form complexes with  $\text{CO}$ . After a reaction time of 50 s,  $[\text{Cu}_3(\text{CN})_2]^+ : [\text{Cu}_3(\text{CN})_2(\text{CO})]^+ : [\text{Cu}_3(\text{CN})_2(\text{CO})_2]^+ \approx 1:0.44:0.29$  and the degree of decomposition of the  $\text{Cu}_3$  complexes (to  $[\text{Cu}_2(\text{CN})]^+$  and  $\text{Cu}^+$ ) is ca 47%. The dicarbonyl is the major  $\text{CO}$ -containing species after 100 s. The behavior of the  $[\text{Cu}_4(\text{CN})_3]^+$  cation is very similar. However, the dicarbonyl is formed more rapidly—it is



**Figure 6.** Optimized structures and relative energies ( $\text{kcal mol}^{-1}$ ) for structural isomers of the ions (a)  $[\text{Cu}(\text{CN})_2]^-$ , (b)  $[\text{Cu}_2\text{CN}]^+$ , and (c)  $[\text{Cu}_3(\text{CN})_2]^+$ . The symbols in braces describe the idealized symmetry and the symmetry imposed during optimization, respectively.

the only  $\text{Cu}_4$  species after 50 s. Also, the  $\text{Cu}_4$  species are more prone to dissociation: after 50 s, the decomposition (to  $[\text{Cu}_3(\text{CN})_2(\text{CO})_x]^+$ ,  $[\text{Cu}_2(\text{CN})]^+$  and  $\text{Cu}^+$ ) is 82%. Even greater fragility is exhibited by the pentanuclear cations. Nevertheless, after a reaction time of 10 s  $[\text{Cu}_5(\text{CN})_4]^+$  and  $[\text{Cu}_5(\text{CN})_4(\text{CO})]^+$  are detectable in a ratio of ca 1:2, while a reaction time of 20 s yields a trace of  $[\text{Cu}_5(\text{CN})_4(\text{CO})_2]^+$  as the only  $\text{Cu}_5$  species.

(ii)  $\text{M} = \text{Ag}$ . Neither  $\text{Ag}^+$  nor  $[\text{Ag}_2(\text{CN})]^+$  nor  $[\text{Ag}_3(\text{CN})_2]^+$  reacted with CO in reaction times up to 100 s or more. For the  $\text{Ag}_2$  and  $\text{Ag}_3$  species dissociation was observed during this time period, but as for the Cu complexes this occurs more slowly than in the presence of  $\text{NH}_3$  or  $\text{H}_2\text{S}$ . However,  $[\text{Ag}_4(\text{CN})_3]^+$  does undergo slow addition of CO (with concurrent dissociation). After 100 s, both  $[\text{Ag}_4(\text{CN})_3(\text{CO})]^+$  and  $[\text{Ag}_4(\text{CN})_3(\text{CO})_2]^+$  are present, with  $[\text{Ag}_4(\text{CN})_3]^+ : [\text{Ag}_4(\text{CN})_3(\text{CO})]^+ : [\text{Ag}_4(\text{CN})_3(\text{CO})_2]^+ \approx 1:0.31:0.05$  (Figure 5). At this point ca 50% of the  $\text{Ag}_4$  species has undergone dissociation: in CO the silver complex again decomposes more slowly than the corresponding copper complex.

## Discussion

Our principal results, significant for discussion of the laser ablation experiments in the context of other knowledge, can be summarized as follows: 1. The series of ions  $[\text{M}_n(\text{CN})_{n-1}]^+$  and  $[\text{M}_n(\text{CN})_{n+1}]^-$  presumably retain the unfragmented CN group. 2. The largest ions observed are  $[\text{Cu}_6(\text{CN})_5]^+$  and

$[\text{Cu}_5(\text{CN})_6]^-$ . The cation series is not as extensive as the series of copper carbohedrenes described by Yamada and Castleman.<sup>9</sup> A previous study using SIMS<sup>35</sup> provided evidence for the anions  $[\text{Cu}_n(\text{CN})_{n+1}]^-$  ( $n = 1-3$ ), but there has been no other study of the gas-phase chemistry of these species. 3. The ion  $[\text{Ag}_4(\text{CN})]^+$  is unprecedented, but there have been previous reports of  $\text{Ag}_n^+$  ( $n = 2,3$ ),<sup>41,42</sup> also observed in our experiments. 4. When a 1:1 mixture of CuCN and AgCN is ablated the mixed metal:CN stoichiometries (positive and negative) that are formed have the same metal:CN stoichiometries as the single metal ions: no new compositions appear. 5. The cations and anions undergo dissociation of MCN on collision with argon. 6. No anion  $[\text{M}_n(\text{CN})_{n+1}]^-$  ( $\text{M} = \text{Cu}$  or  $\text{Ag}$ ) adds any of the ligands  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  or CO. 7. While the gaseous ammoniates of the bare metals,  $[\text{Cu}(\text{NH}_3)_x]^+$  ( $x = 1-4$ ) and  $[\text{Ag}(\text{NH}_3)_x]^+$  ( $x = 1-3$ ), have been observed previously,<sup>43-47</sup> the gas-phase ammine complexes of  $[\text{M}_2(\text{CN})]^+$  to  $[\text{M}_4(\text{CN})_3]^+$  that we observe for

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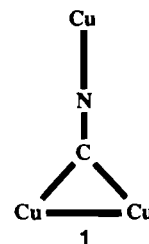
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Cu and Ag have not been observed hitherto in any phase.<sup>48</sup> The series of H<sub>2</sub>S adducts is less extensive than the series of NH<sub>3</sub> adducts, with Ag forming fewer adducts with H<sub>2</sub>S than Cu. When M = Cu, complexes containing HCN are formed in small amount in the reactions of H<sub>2</sub>S with [Cu<sub>n</sub>(CN)<sub>n-1</sub>]<sup>+</sup>. The complexes [M(SH<sub>2</sub>)<sub>x</sub>]<sup>+</sup> (M = Cu or Ag, x = 1–2) and other H<sub>2</sub>S complexes containing one Cu or Ag center have been observed in earlier work from these laboratories,<sup>38a,49</sup> but prior to the present work the only the Cu(I)–HCN complex that has been described is [Cu(NCH)]<sup>+</sup>, which can be produced in anhydrous HF.<sup>50,51</sup> Only the larger cations [M<sub>n</sub>(CN)<sub>n-1</sub>]<sup>+</sup> form mono- and dicarbonyl adducts, none of which has been reported earlier. It is significant that we could obtain no evidence for smaller complexes of either Cu(I) or Ag(I), whereas in condensed phases only mono- and binuclear carbonyl complexes of Cu(I) have been characterized previously,<sup>53</sup> and only mononuclear complexes of Ag(I).<sup>54</sup> 10. In the presence of Ar, CO, NH<sub>3</sub> or H<sub>2</sub>S, dissociation is observed and the rate depends on the nature of the reactant gas in the order Ar < CO < NH<sub>3</sub>, H<sub>2</sub>S. Since this is not simply the order of molecular masses of the gases, apparently dissociation is not a simple collision process in all cases. Probably it is aided by complexation, at least with NH<sub>3</sub> or H<sub>2</sub>S. The involvement of the ligand seems clear for the cases of H<sub>2</sub>S with [Cu<sub>n</sub>(CN)<sub>n-1</sub>]<sup>+</sup> and NH<sub>3</sub> and H<sub>2</sub>S with [Ag<sub>n</sub>(CN)<sub>n-1</sub>]<sup>+</sup>, where the products of dissociation are in some instances different in nature or distribution from those produced by the direct reaction of the same ligand with the appropriate lower cation.

**Structures of the Ions.** What are the structures of the new polymetallic cyanide species? We have no direct data. The CID results can provide guidance, and the numbers of hetero-ligands which add to each species can be interpreted as indication of the numbers of undercoordinated metal atoms. However we recognize that for polymetallic clusters in the gas phase, rearrangement may accompany dissociation or addition reactions, blurring their interpretation in terms of cluster structure.

The complexes [M(CN)<sub>2</sub>]<sup>-</sup> are likely to have the linear structure [NMCN]<sup>-</sup>, which is well-known both in the solid state and in solution for M = Ag,<sup>48</sup> and appears to occur in solution for M = Cu.<sup>55</sup> In liquid NH<sub>3</sub>, linkage isomers of [Ag(CN)<sub>2</sub>]<sup>-</sup> occur; all are thought to be linear,<sup>56</sup> as are both [Ag<sub>2</sub>(CN)]<sup>+</sup> and [Ag<sub>2</sub>(CN)<sub>3</sub>]<sup>-</sup>, which are formed in the same medium.<sup>56</sup> To date the discrete linear [NCCuCN]<sup>-</sup> anion has not been reported in the solid state. The crystal structures of AgCN,<sup>37,57,58</sup> KCu(CN)<sub>2</sub>,<sup>60</sup> NaCu(CN)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>,<sup>61</sup> KCu<sub>2</sub>(CN)<sub>3</sub>(H<sub>2</sub>O),<sup>62</sup> Me<sub>2</sub>PhS<sup>+</sup>[Cu<sub>2</sub>(CN)<sub>3</sub>]<sup>-</sup>,<sup>63</sup> (BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>-

(CN)<sub>3</sub>,<sup>64–66</sup> (BEDT-TTF)Ag<sub>4</sub>(CN)<sub>5</sub>,<sup>67</sup> and [Cu<sub>3</sub>(CN)<sub>3</sub>(H<sub>2</sub>O)]<sup>68</sup> all are nonmolecular, with linear M–CN–M connections. There are only two exceptions to the generality of linear M–CN–M connections (for copper and silver), namely bent bridging of type 1 in CuCN·NH<sub>3</sub>,<sup>69</sup> and a C–Cu connection perpendicular



to approximately linear CuCN, in Me<sub>2</sub>PhS<sup>+</sup>[Cu<sub>2</sub>(CN)<sub>3</sub>]<sup>-</sup>.<sup>63</sup> In postulating structures for the molecular polymetallic cyanides of the gas phase, incorporation of the linear M–CN–M connection common in the solid state would generate open and extended structures. These structures would not have M–M bonds, and would be in strong contrast to the structures of other clusters with similar ligands, such as the metallocarbohedrenes, which are believed on the basis of all calculations so far to be globular and compact, with many M–M bonding connections. Metal carbonyl clusters are globular, with bridging CO ligands and M–M bonds.

The extended structures of crystalline polymetallic cyanides are subject to the stabilizing influences of multiple electrostatic and van der Waals interactions with other lattice species, cations, solvent, and guest molecules. There exist classes of inclusion compounds with very open host lattices based on linear M–CN–M connections stabilized by nonbonded interactions with guest molecules, e.g. refs 70–75. In the gas phase species we observe, none of these factors stabilizing extended M–CN–M connections is present, and therefore our expectation had been that globular rather than extended structures would be the more

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stable. Nevertheless we recognized a fundamental dichotomy: would the topologies of these  $M_x(CN)_y$  species be extended or globular?

We have not been able to find any electron diffraction data on metal cyanide species in the gas phase, and in the absence of other informative data, we have used density functional theory (DFT)<sup>76–80</sup> to develop an understanding of the probable structures and structural principles for the new polymetallic cyanide ions. DFT requires less computation than Hartree–Fock methods, and adequately includes the exchange and correlation effects which are important in large molecules and molecules with large atoms. DFT is able to provide valuable description of metal cluster compounds, and has been applied successfully to comparable metalcarbohedrenes.<sup>14, 24–26</sup> We use DFT as embodied in the program DMol<sup>81,82</sup> to optimize postulated structures, and to estimate relative stabilities by comparison of binding energies. All of the results reported here have non-local corrections to the energy: the VWN functional is used, with the Becke nonlocal corrections to the exchange energies. Double numerical plus polarization basis functions are used, with core orbitals frozen. All calculations are for the even-electron species  $[Cu_n(CN)_{n+1}]^-$ ,  $[Cu_n(CN)_n]^0$  or  $[Cu_n(CN)_{n-1}]^+$  and are spin restricted.

The dichotomy about structure type can be investigated by evaluating the preferred geometries for terminal and bridging CN. Cyanide ligands can be terminal in three idealized ways: linear C bound; linear N bound; or  $\eta^2$ -CN. There are four monohapto bridging possibilities,  $\mu_2$  at C or N, and  $\mu_3$  at C or N, and at least six possibilities for dihapto bridging of  $M_3$  and  $M_4$ . Terminal CN coordination was evaluated in  $[Cu(CN)_2]^-$ , for which the most stable termination is linear  $[NCCuCN]^-$  **12A** (see Figure 6a). The relative total energy of  $[CNCuNC]^-$  (**12B**) is +18 kcal mol<sup>-1</sup>, and for  $[Cu(\eta^2-CN)_2]^-$  (**12C**) is +40 kcal mol<sup>-1</sup>.

The ion  $[Cu_2(CN)]^+$  was the vehicle for investigation of fundamental CN bridging geometries, and the results are presented in Figure 6b. The linear Cu–CN–Cu structure **21L** is the most stable, followed by linear CuCN with one sidebound Cu, **21D**, at +22 kcal mol<sup>-1</sup>.  $Cu(\mu-CN)Cu$ , **21A**, is at +29 kcal mol<sup>-1</sup>, while the two isomers with bridging  $\eta^2$ -CN, planar **21B** and bent **21C**, are less stable. The other linear isomer, CuCuCN, is calculated to have an even less favorable energy of +87 kcal mol<sup>-1</sup> relative to **21L**. Zigzag Cu–CN–Cu isomers straightened on optimization, to **21L**. There is a clear conclusion that the linear Cu–CN–Cu entity prevalent in crystalline compounds is also the most stable in isolation.

Globular structures for the larger positive and negative ions would involve CN bridging  $Cu_3$  or  $Cu_4$ . We have investigated the ion  $[Cu_3(CN)_2]^+$  to evaluate the fundamental bridging geometries,  $\eta^1$  (**32A**,  $\{D_{3h}, C_{2v}\}$ ) and  $\eta^2$  (**32B**,  $\{C_2, C_2\}$ ) shown in Figure 6c. The  $\eta^2$  (**32B**) bridging mode is the more stable by 13 kcal mol<sup>-1</sup>, but both of these structures are much less stable than the linear model **32L**. Again the conclusion is that the bonding stabilization associated with linear Cu–CN–Cu outweighs the formation of other bonding connections.

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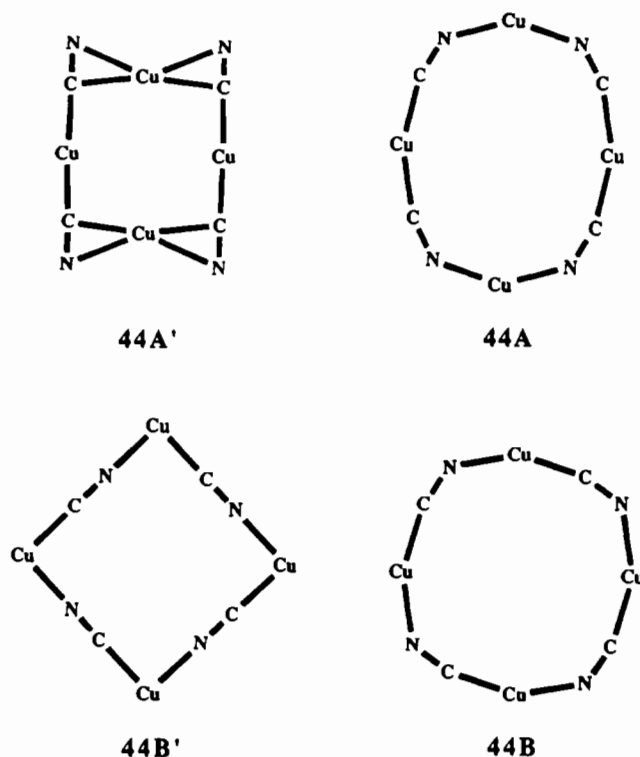
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**Figure 7.** Postulated structures **44A'** and **44B'** and optimized structures **44A** and **44B** for  $[Cu_4(CN)_4]$ .

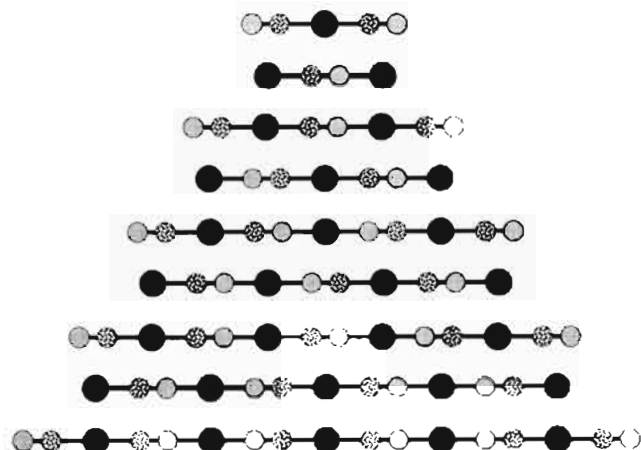
Combinations of these bridging modes with  $Cu_x$  polygons and polyhedra have led to many postulates for structures of the  $[Cu_n(CN)_{n-1}]^+$  and  $[Cu_n(CN)_{n+1}]^-$  ions. However, for all compositions, none of these postulates is more stable than a corresponding linear sequence of Cu and CN groups. For  $[Cu_4(CN)_3]^+$  and  $[Cu_5(CN)_4]^+$  the most stable structures are linear  $[CuNCCuCNCuNCCu]^+$  and  $[CuCNCuNCCuCNCuNCCu]^+$ , while linear  $[NCCuCNCuCN]^-$ ,  $[NCCuCNCuNCCuCN]^-$ ,  $[NCCuCNCuNCCuNCCuCN]^-$  and  $[NCCuCNCuNCCuCN-CuNCCuCN]^-$  are the most stable structures for the  $[Cu_n(CN)_{n+1}]^-$  ions,  $n = 2-5$ . Note that the idealized symmetries and the optimization symmetries are  $\{D_{\infty h}, C_i\}$  for  $n$  odd, and  $\{C_1, C_1\}$  for  $n$  even: we have not yet tested all isomers arising by C/N interchange in the linear geometries.

We have also undertaken calculations for  $Cu_4(CN)_4$ , an unobservable neutral which is very probably present given the observation of the positive ion due to CN decrement and the negative ion from CN increment. The composition  $M_4X_4$  is a paradigm in metal cluster chemistry, and numerous postulates with  $X = CN$  can be tested. In all cases calculated so far, structures which do not have extended Cu–CN–Cu entities are energetically uncompetitive, and some postulates undergo substantial change during the geometry optimization to approach linearity of Cu–CN–Cu as well as linearity at Cu. An illustration of this is presented in the postulates **44A'** and **44B'** (Figure 7), which incorporate linear segments: the optimized structures were **44A** and **44B**, which demonstrate that the requirement for linearity is more pronounced at Cu–C–N than at Cu–N–C.

Details of the calculations and the coordinates for these optimized structures are included in the supplementary material.

The conclusion that the observed cuprous ions have linear structures is supported by their reactivities. All of the positive ions,  $[Cu_n(CN)_{n-1}]^+$  ( $n > 1$ ), which have one-coordinate Cu atoms at each end, add one or two molecules of  $H_2S$  or CO, consistent with completion of digonal coordination. As described above, all the positive ions add at least two  $NH_3$ , with





**Figure 8.** Proposed linear structures for the ions (from the top)  $[\text{Cu}(\text{CN})_2]^-$ ,  $[\text{Cu}_2(\text{CN})]^+$ ,  $[\text{Cu}_2(\text{CN})_3]^-$ ,  $[\text{Cu}_3(\text{CN})_2]^+$ ,  $[\text{Cu}_3(\text{CN})_4]^-$ ,  $[\text{Cu}_4(\text{CN})_3]^+$ ,  $[\text{Cu}_4(\text{CN})_5]^-$ ,  $[\text{Cu}_5(\text{CN})_4]^+$ ,  $[\text{Cu}_5(\text{CN})_6]^-$ : filled circles are Cu, speckled circles are C.

the bis(ammoniate) predominating. The addition of three  $\text{NH}_3$  to the positive ions is restricted, and occurs only in very small proportions, ca. 5%, which could be a consequence of slow rearrangement of the core structure. Other postulated structures possess fewer or more undercoordinated Cu atoms and could be expected to demonstrate differing degrees of addition.

So far we have no structural information for the Ag complexes. It is possible that they have the same structures as their Cu(I) counterparts, since the mixed metal complexes  $[\text{Cu}_m\text{Ag}_{n-m}(\text{CN})_{n+1}]^-$  and  $[\text{Cu}_m\text{Ag}_{n-m}(\text{CN})_{n-1}]^+$  have the same metal:CN<sup>-</sup> stoichiometries as the parent monometallic species (see above). If so then the appearance of  $[\text{Na}_m\text{Ag}_{n-m}(\text{CN})_{n-1}]^+$  ( $m = 1-2$  only) when samples of AgCN containing  $\text{Na}^+$  are ablated (see Experimental Section) can be rationalized in terms of  $\text{Na}^+$  binding to the terminal nitrogen site(s) of  $[\text{Ag}_{n-1}(\text{CN})_{n-1}]$  ( $m = 1$ ) and  $[\text{Ag}_{n-2}(\text{CN})_{n-1}]^-$  ( $m = 2$ ).

Thus we conclude that the gaseous  $\text{Cu}_n(\text{CN})_{n\pm 1}$  ions, and perhaps their Ag analogs, adopt linear structures with "spear" topology, as shown in Figure 8 for all of the observed positive

and negative ions. The  $[\text{Cu}_5(\text{CN})_6]^-$  ion would be almost 30 Å long, and only one atom thick, a singular molecule in all of chemistry. These structures are contrary to experience and conventional thinking for other gaseous polymetallic molecules and ions, and cluster chemistry in general. However the CN<sup>-</sup> ligand is distinctive in favoring linear bridges, and is evidently different from its isoelectronic homologs CO, N<sub>2</sub>, C<sub>2</sub><sup>2-</sup>, and NO<sup>+</sup>. Further, the metals we have investigated here are both d<sup>10</sup>, and digonal coordination stereochemistry is normal for them. There is a clear stoichiometric difference between the copper carbohedrenes,  $[\text{Cu}_{2n+1}(\text{C}_2)_n]^+$ , with less than half as many C<sub>2</sub> ligands as metal atoms, and the copper cyanide complexes with almost equal numbers of CN ligands and metal atoms. Copper carbohedrene structures analogous to those postulated for the cyanides are not possible, and all of the calculations so far have supported symmetrical globular structures for the copper carbohedrenes, with pronounced Cu-Cu bonding, and C<sub>2</sub> entities multiply connected to Cu<sub>4</sub> arrays on the surface.

These results provoke two further experimental programs. One seeks mass spectrometric data on collisional cross sections which relate to the shapes of the ions and thus could support the proposed spear topology. The other approach is to investigate the gas phase cyanide chemistry of other metals, with different coordination preferences and propensities for M-M bonding.

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**Supplementary Material Available:** Details of the density functional calculations, including a listing of the basis sets, text describing the functionals, SCF, and geometry convergence, and listings of the total energies and atomic coordinates for the optimized structures listed in the text (3 pages). Ordering information is given on any current masthead page.