Crystal Structures of AuCN and AgCN and Vibrational Spectroscopic Studies of AuCN, AgCN, and CuCN[†]

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The crystal structures of AuCN and AgCN have been determined by powder neutron diffraction measurements. The structure of AuCN consists of rows of linear AuCN chains parallel to [001] with alternating long Au−C = 2.06(2) and short Au−N = 1.82(2) Å. The Au atoms form sheets and are bonded to 6 other Au atoms at a distance of 3.396(2) Å, so that the local environment of each Au atom can be described as a compressed scalehedron. The Au- - -Au distance is within the range expected for an "aurophilic attraction" between these atoms. The AgCN structure is very similar to that for AuCN, in that it consists of rows of AgCN chains with alternating long Ag−C = 2.15(6) and short Ag−N = 1.86(8) Å. The major difference is that the Ag- - -Ag separation within the Ag sheets is noticeably longer, 3.881(5) Å, so that there are no significant Ag- - -Ag interactions. The IR spectra of MCN show ν(CN) at 2170, 2164, 2236; ν(MC,MN) at 591, 480, 598; δ(MCN) at 326, 272, 358; and δ(NMC) = 168, 112, 224 cm^{-1} for M = Cu, Ag, and Au, respectively. This pattern of band positions strongly suggests that CuCN has the same infinite linear chain structure as AgCN and AuCN. Anomalies in the previously reported IR spectrum of CuCN are shown to be due to the formation of an unusual CuCN/KBr/H_2O product in KBr disks, which is possibly an intercalation compound involving incorporation of KBr and H_2O between the chains in the CuCN structure.

Introduction

The chemistry of the group 11 metal cyanide systems has been of considerable interest as a result of the commercial importance of some of the complexes formed in these systems. The ready formation of $[Au(CN)_2]^-$ from gold, cyanide, and oxidizing agents has been exploited in the extraction of gold from its ores, and solutions of $[Au(CN)_2]^-$ are also commonly used in gold electroplating applications. Studies into the mechanisms of these processes have suggested AuCN as a probable intermediate.[1] Cyanide solutions form the basis for an important method of extracting silver metal from silver ore, by leaching the ore with dilute sodium cyanide solutions followed by treatment of the solutions with zinc to recover the silver, and are also used in silver electroplating.[2] The copper(I) cyanide system has been studied extensively as a result of the ease of preparation of CuCN from copper(II) and KCN,[3] and there has been some recent interest in CuCN as a precursor in the synthesis of ceramic superconductors.[4] The structural diversity exhibited by other univalent group 11 complexes[1−3] is also evident in the cyanides, an example of this being the $K[M(CN)_2]$ (M = Cu, Ag, Au) complexes. The structures for the silver(I)[5,6] and gold(I)[7,8] species both contain linear $[M(CN)_2]^-$ ions, but the copper(I)[9] complex contains a helical anion chain in which each copper is three-coordinate.

It is therefore something of an anomaly that details of the solid-state structures of the group 11 metal cyanides MCN (M = Cu, Ag, Au) remain unknown. Text and reference books on inorganic and coordination chemistry generally state that AgCN and AuCN have polymeric structures with linear −MCNMCN− chains,[1,10−14] but further details of the structures are apparently unavailable. The structural information that has been published to date on these systems is summarized below.

A preliminary report on two forms of copper(I) cyanide, described as a dark red crystal and a dark green crystal, gave only unit cell information.[15] Another more recent report on a colorless form also reported only unit cell information.[16] There is considerable difference between the three reported forms, and none of them provide any structural information. Recently the crystal structure of what has been described as a hydrated form

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[†] This paper is dedicated to Professor Warren Roper on the occasion of his 60th birthday.

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(1) Puddephatt, R. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 5, p 861.
(2) Lancashire, R. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 5, p 775.
(3) Hathaway, B. J. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Vol. 5, p 533.
(4) Khan, N. A.; Baber, N.; Iqbal, M. Z.; Mazhar, M. *Chem. Mater.* **1993**, *5*, 1283.
(5) Staritzky, E. *Anal. Chem.* **1956**, *28*, 419.
(6) Hoard, J. L. *Z Krist*. **1933**, *84*, 231.
(7) Staritzky, E.; Ellinger, F. H. *Anal. Chem.* **1956**, *28*, 420.
(8) Rosenzweig, A.; Cromer, D. T. *Acta Crystallogr.* **1959**, *12*, 709.
(9) Cromer, D. T. *J. Phys. Chem.* **1957**, *61*, 1388.
(10) Puddephatt, R. J. *The Chemistry of Gold*; Elsevier: New York, 1978; p 37.
(11) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1988; p 941.
(12) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984; p 1104.
(13) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Oxford, U.K., 1984; p 1388.
(14) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic Press: London, 1976; Chapter 10.
(15) Norberg, B.; Jacobson, B. *Acta Chem. Scand.* **1949**, *3*, 174.
(16) Cromer, D. T.; Douglass, R. M.; Staritzky, E. *Anal. Chem.* **1957**, *29*, 316.

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of copper(I) cyanide has been reported, with a suggested composition of $[Cu_3(CN)_3(H_2O)]_\infty$.[17] This complex is comprised of a two-dimensional polymer with both linearly coordinated and bridging cyanide groups. Both two- and four-coordinate copper atoms are observed, and portions of the structure are comprised of the linear chain segment −CN−Cu−CN−Cu−CN−. Theoretical calculations of the structures of a series of clusters obtained as the result of a laser ablation mass spectrometry investigation into copper(I) and silver(I) cyanide indicated that the most likely structures for the $[Cu_x(CN)_{x\pm1}]$ ions are those involving one-dimensional linear-chain structures of the type $-(CN-Cu)-_n$.[18] The structure of the largest observed copper cyanide cluster, $[Cu_5(CN)_6]^-$, would therefore be a chain almost 30 Å long and only one atom thick.

For AgCN there is a more comprehensive set of structural information, but a complete picture still remains elusive. Two old reports indicate that silver cyanide crystallizes from aqueous ammonia in the trigonal system with $a = 3.88$ Å, $\alpha = 101°11'$, and $Z = 1$; on hexagonal indexing the unit cell has $a = 5.99$ Å, $c = 5.26$ Å, and $Z = 3$.[19,20] The structure was described as being comprised of infinite linear chains of AgCN with apparently disordered CN groups arranged in parallel lines in the structure. However the positions of the light atoms were not identified in the analysis.

A similar situation exists for the gold(I) cyanide complex, where the results of a powder diffraction study are ambiguous because of the difficulty in differentiating between the C and N atoms.[21] The AuCN structure is thought to be closely related to, but not isomorphous with, the AgCN structure. The structure consists of infinite linear chains −Au−CN−Au−CN− arranged in parallel chains in the crystal.

Given the dearth of detailed structural information about these MCN complexes, it was the aim of this investigation to gain a more detailed insight into the structures of these complexes. X-ray and neutron powder diffraction techniques and vibrational spectroscopy have been used in the investigation.

Experimental Section

Preparation of Compounds. **Copper(I) Cyanide**. This was prepared via the literature method.[22] A 25 g (160 mmol) amount of copper(II) sulfate was dissolved in 80 mL of water at 50 °C, 7 g (37 mmol) of sodium bisulfite was dissolved in 20 mL of water at 50 °C, and 7 g (110 mmol) of potassium cyanide was dissolved in 20 mL of water at 50 °C. The sodium bisulfite solution was slowly added to the copper sulfate solution, with stirring, over a 2-min period, followed immediately by the potassium cyanide solution. The complex began to precipitate immediately as a fine cream powder, which was collected by filtration, washed thoroughly with boiling water and then ethanol, and dried in vacuo over P_2O_5.

Silver(I) Cyanide. A 10.25 g (60 mmol) amount of silver nitrate was dissolved in 50 mL of water. To this was added a solution of 3.89 g (60 mmol) of potassium cyanide in 50 mL of water. A fine white precipitate of the compound formed immediately. This was collected by filtration, washed thoroughly with water and then with ethanol, and dried in vacuo over P_2O_5.

Gold(I) Cyanide. This was prepared by the literature method.[23] A 1.29 g (6.5 mmol) amount of gold metal was dissolved in a mixture of 4.5 mL of concentrated HCl and 2.1 mL of concentrated HNO_3. Concentrated ammonia was added to the resultant solution until the solution was slightly basic. A yellow precipitate formed and was collected by filtration and washed with water. The precipitate was then dissolved in a solution of 1.35 g (20 mmol) of KCN in water, and the solution was filtered. The filtrate was slowly evaporated to crystallize $KAu(CN)_2$. The $KAu(CN)_2$ was then dissolved in water and the solution made slightly acidic with concentrated HCl, causing AuCN to precipitate out, which was collected by filtration, washed with water, and dried in vacuo over P_2O_5. Anal. Found: C, 5.59; N, 6.43. Calcd for CNAu: C, 5.39; N, 6.28. A commercial sample of AuCN (Degussa) was used for the X-ray and neutron diffraction studies; this gave an infrared spectrum that was identical to that of the product synthesized by the method described above.

Reaction of CuCN with Aqueous KBr. To a solution of KBr (1.9 g, 16 mmol) dissolved in water (5 mL) in a small sample vial was added CuCN (0.76 g, 8.4 mmol). The mixture was allowed to stand for 1 h at room temperature, after which time there was a noticeable increase in the volume of the insoluble CuCN, which “cemented” together to some extent. The solid was collected by vacuum filtration and air-dried without washing. The yield of dry product was about 1 g. The IR spectrum (Nujol mull) showed bands at 3590, 3522, 2164, 2119, 1610, and 529 cm^{-1}. Washing of a sample of this product with water resulted in quantitative recovery of CuCN, whose identity was verified by means of its Nujol mull IR spectrum.

Diffraction Studies. The neutron powder diffraction patterns were recorded at room temperature using neutrons of wavelength 1.664 Å in 0.10° steps over the range $10° < 2\theta < 135°$ on the medium-resolution powder diffractometer (MRPD)[24] on the HIFAR reactor operated by Australian Nuclear Science and Technology Organisation. The lightly ground sample was contained in a thin-walled vanadium can that was slowly rotated during the measurement to minimize the effects of preferred orientation. The room-temperature synchrotron XRD patterns were recorded at a wavelength of 0.99981 Å in 0.010045° steps in the range $5° < 2\theta < 85°$ on the Australian National Beamline Facility (ANBF) powder diffractometer, BL-20B, at the KEK Photon Factory, Tsukuba, Japan. The data were collected using two image plates as the detectors covering the angular ranges 5−45° and 45−85°. The finely ground sample was housed in a 0.5-mm-diameter glass capillary and was rotated during the measurements. A full description of the diffractometer and the use of the image plate detectors has been given previously.[25,26]

The Rietveld refinements[27] were undertaken with a version of the computer program LHPM[28] operating on a PC. LHPM has been modified for combined X-ray and neutron refinements and can handle multiple data sets with independent scale factors, background functions, and zero corrections. The background was defined by a fourth-order polynomial in 2θ and was refined simultaneously with the other profile parameters. A Voigt function was chosen to generate the line shape of the neutron diffraction patterns. The Gaussian component varied as $(\text{fwhm})^2 = U \tan^2\theta + V \tan\theta + W$, where U, V, and W are refinable parameters,[29] and the width of the Lorentzian component was varied as $\eta \sec\theta$. The coherent neutron scattering lengths [fm (10^{-15} m)] used were as follows: Au, 0.763; Ag, 0.5922; C 0.6646; N, 0.9360.[30]

Spectroscopy. Infrared spectra were recorded at 4 cm^{-1} resolution as Nujol mulls between KBr plates on a Digilab FTS-60 Fourier transform infrared spectrometer employing an uncooled deuteriotriglycine sulfate detector. Far-infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as polythene disks on a Digilab FTS-

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(17) Kildea, J. D.; Skelton, B. W.; White, A. H. *Aust. J. Chem*. **1985**, *38*, 1329.
(18) Dance, I. G.; Dean, P. A. W.; Fisher, K. J. *Inorg. Chem*. **1994**, *33*, 6261.
(19) West, C. D. *Z. Krist*. **1934**, *88*, 173.
(20) West, C. D. *Z. Krist*. **1935**, *90*, 555.
(21) Zhdanov, G. S.; Shugam, E. A. *Acta Physicochim. URSS* **1945**, *20*, 253.
(22) Barber, H. J. *J. Chem. Soc*. **1943**, 79.
(23) Bradley, R. S.; Munro, D. C.; Spencer, P. N. *Trans. Faraday Soc*. **1969**, *65*, 1920.
(24) Kennedy, S. J. *Adv. X-ray Anal*. **1995**, *38*, 35.
(25) Garret, R. F.; Cookson, D. J.; Foran, G. J.; Sabine, T. M.; Kennedy B. J.; Wilkins, S. W. *Rev. Sci. Instrum*. **1995**, *66*, 1351.
(26) Sabine, T. M.; Kennedy, B. J.; Garrett, R. F.; Foran, G. J.; Cookson, D. J. *J. Appl. Crystallogr*. **1995**, *28*, 513.
(27) Rietveld, H. M. *J. Appl. Crystallogr*. **1969**, *2*, 65.
(28) Hill R. J.; Howard, C. J. Australian Atomic Energy Commission Report No. M112, AAEC (now ANSTO); Lucas Heights Research Laboratories: New South Wales, Australia, 1986.
(29) Caglioti, G.; Paoletti A.; Ricci, F. P. *Nucl. Instrum*. **1958**, *3*, 223.
(30) Sears, V. F. Atomic Energy of Canada Limited Report AECL-8490, 1984.

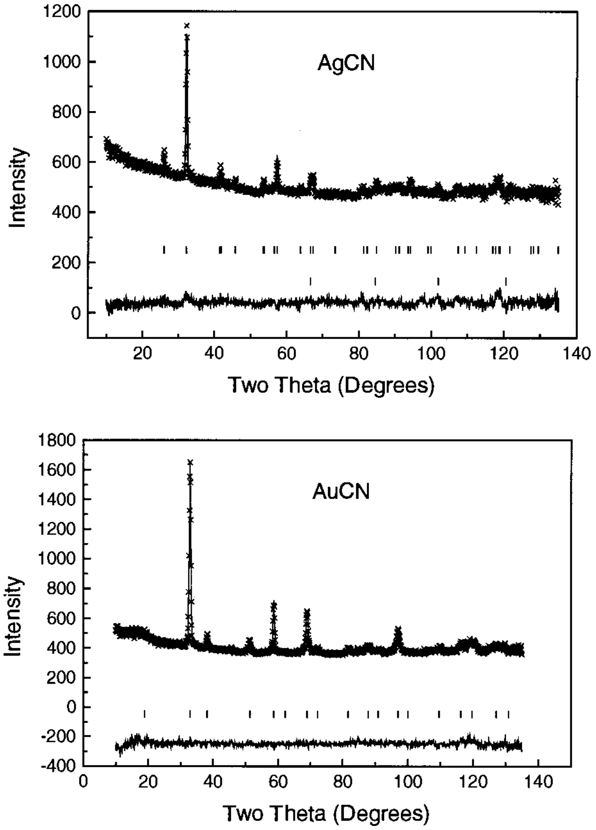

Figure 1. Observed (×), calculated, and difference (lower trace) neutron profiles for (a, top) AgCN and (b, bottom) AuCN. The vertical markers show the positions of the allowed Bragg reflection. The lower set of reflection markers in AgCN indicates the presence of peaks from the V sample holder.

60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 6.25 μm Mylar film beam splitter, a mercury lamp source, and a pyroelectric triglycine sulfate detector. Raman spectra were recorded at 4.5 cm^{-1} resolution using a Jobin-Yvon U1000 spectrometer equipped with a Spectrolab Laserspec III premonochromator and a cooled photomultiplier (RCA C31034A) detector. The samples were presented in a rotating glass capillary, mounted in a macrochamber, and excited with 25 mW of 514.5 nm radiation from a Spectra-Physics model 2016 argon ion laser.

Results and Discussion

Diffraction Studies. Synchrotron powder X-ray and neutron diffraction measurements were carried out on the compounds. The half-widths of the Bragg reflections in the X-ray diffraction patterns for AuCN and AgCN showed considerable variation due to anisotropic particle size effects. This effect may be compounded by translational disorder of the MCN chains; see below. The diffraction patterns of CuCN exhibited only very broad bands indicative of very poor crystallinity. Consequently, it was not possible to determine the crystal structure of this compound.

The X-ray powder diffraction pattern of AuCN corresponds to a hexagonal compound, the systematic absences being compatible with the space group $P6mm$ with $a = 3.396$ and $c = 5.092$ Å. These results are consistent with the earlier report of Zhdanov and Shugam.[21] The X-ray diffraction pattern of AgCN shows that this compound is not isostructural with AuCN. The data were indexed on the basis of a trigonal cell, space group $R3m$ with $a = 5.996$ and $c = 5.259$ Å, in reasonable agreement with the early work of West.[19] In both cases no unindexed peaks were observed in the synchrotron diffraction patterns. Attempts to refine the structures of AuCN and AgCN using the powder X-ray data were unsuccessful, with the C and N positions being very poorly described.

Table 1. Crystallographic Data for AuCN and AgCN[a]

	AuCN	AgCN
	Lattice Constants	
space group	$P6mm$	$R3m$
a, Å	3.396(2)	5.996(9)
c, Å	5.092(2)	5.259(4)
V, Å^3	50.85(4)	163.8(3)
	Refinement Information	
data points	1250	1250
reflcns	28	39
variables	20	20
R_p	2.37	2.18
R_{wp}	2.68	2.55
R_{exp}	1.67	1.50
R_{Bragg}	0.99	1.28
	Positional and Thermal Parameters (Å^2)	
M, B	3.0(3)	7.7(9)
C, z	0.404(5)	0.408(12)
C, B	0.3(2)	0.8(3)
N, z	−0.358(5)	−0.353(15)
N, B	3.9(3)	8.1(9)
	Selected Bond Distances (Å)	
M−C	2.06(2)	2.15(6)
M−N	1.82(2)	1.86(8)
C−N	1.21(3)	1.26(9)
M−M	3.396(2)	3.881(5)

[a] The unique atoms have the following positions: M (0, 0, 0), C (0, 0, z), and N (0, 0, z). Standard errors are in parentheses and refer to the least significant decimal.

The neutron diffraction patterns for AuCN and AgCN are shown in Figure 1. Refinements of the structures were commenced using the previously proposed models.[19,21] The high background in the neutron diffraction pattern of AgCN is due to poor crystallinity, and while a less than optimal signal-to-noise resulted from this, an acceptable fit to the pattern was obtained. In the analysis of these data it was necessary to include vanadium, from the sample holder, as a second phase. The final structural parameters for both compounds are listed in Table 1, and the agreement between the observed and calculated neutron diffraction profiles is shown in Figure 1.

The structures of AuCN and AgCN are shown in Figure 2. Both structures consist of rows of linear MCN chains parallel to [001] with alternating long M−C and short M−N distances. In AuCN the Au atoms form sheets and are bonded to 6 other Au atoms at a distance of 3.396 Å, so that the local environment of each Au atom can be described as a compressed scalehedron. In AgCN the chains are displaced up and down relative to the AuCN structure, and the Ag- - -Ag distances are longer at 3.881 Å.

The fact that d(M−C) > d(M−N) in both compounds is at first sight surprising. An attempt was made to obtain a fit involving d(M−C) < d(M−N) by exchanging the C and N positions, but the structures simply reconverged by moving the z parameters in the appropriate way to give identical fits and M−L distances (note that in the structural refinements it was necessary to fix the metal at $z = 0$). A possible explanation for this observation is that the “lone pair” on C is larger than that of N in CN$^-$.[31] The calculated structures of CuCN and

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(31) Bickelhaupt, F. M.; Nibbering, N. M. M.; van Wezenbeek, E. M.; Baerends, E. J. *J. Phys. Chem.* **1992**, *96*, 4864.

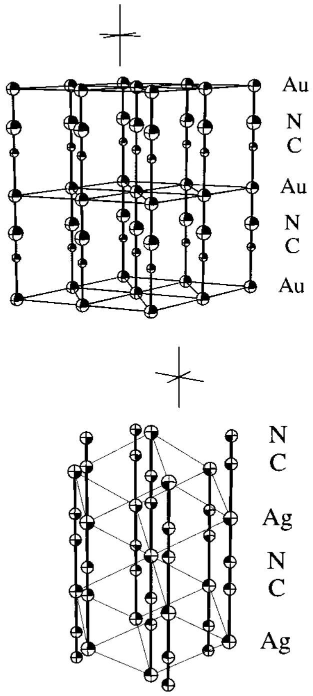

Figure 2. View of the structure of (a, top) AuCN and (b, bottom) AgCN.

CuNC monomers yield $d(\mathrm{M{-}C}) > d(\mathrm{M{-}N})$, despite the fact that the Cu−C bond is stronger than the Cu−N bond in these species.[32]

The M−C and M−N distances in AgCN are longer than the corresponding distances in AuCN. This is consistent with observations on other complexes of Ag(I) and Au(I) and can be attributed, at least in part, to the greater importance of relativistic effects in the case of the gold compounds.[33,34] Furthermore, it has been noted previously, that in linear two-coordinate complexes involving two different ligands, the bond length contraction from the Ag to the corresponding Au compound is greater for the bond involving the more electropositive ligand atom.[34] It is therefore of interest to note the same trend in the present results, i.e., a greater reduction in the M−C than in the M−N bond length, Table 1.

The fact that the Au- - -Au distance within the Au sheets in AuCN is significantly less than the corresponding Ag- - -Ag distance in AgCN suggests the presence of a bonding interaction between the Au atoms. It is now widely recognized that the gold atoms in Au(I) complexes often experience a mutual attraction, the “aurophilic attraction”, which may result in inter- or intramolecular association involving relatively short Au- - -Au contacts.[35−37] The energy of interaction has been estimated at about 35 kJ mol^{-1} for d(Au- - -Au) = 3.0 Å.[35] In AuCN a significantly longer d(Au- - -Au) = 3.4 Å is observed, but this is still within the range expected for the aurophilic attraction, which has been shown to be significant beyond d(Au- - -Au) = 3.5 Å.[38] The existence of the aurophilic attraction has been attributed to relativistic effects,[39] so it appears that such effects are responsible for the contraction of the Au−C, Au−N, and Au- - -Au distances in AuCN relative to the corresponding distances in AgCN. Due to the different preferred coordination numbers of Ag(I) and Au(I), it is very unusual to find compounds of these two metals with the same molecular structure that allow such comparisons to be made.[33,34] The present case is the first that allows a comparison of metal−metal interactions under such circumstances.

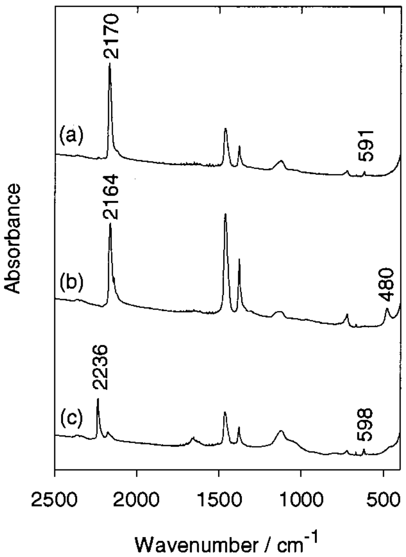

Figure 3. IR spectra recorded as Nujol mulls of (a) CuCN, (b) AgCN, and (c) AuCN.

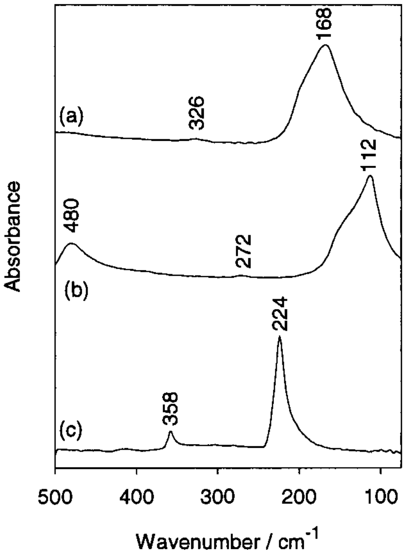

Figure 4. Far-IR spectra of (a) CuCN, (b) AgCN, and (c) AuCN.

Vibrational Spectroscopy. The vibrational spectra of MCN (M = Cu, Ag, Au) are shown in Figures 3−5. Although aspects of the vibrational spectra of these compounds have been reported in previous studies,[4,40−46] the majority of these are concerned

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(32) Bouslama, L.; Daoudi, A.; Mestdagh, H.; Rolando, C.; Suard, M. *J. Mol. Struct.* (*THEOCHEM*) **1995**, *330*, 187.

(33) Bayler, A.; Schier, A.; Bowmaker, G. A.; Schmidbaur, H. *J. Am. Chem. Soc.* **1996**, *118*, 7006.

(34) Bowmaker, G. A.; Schmidbaur, H.; Krüger, S.; Rösch, N. *Inorg. Chem.* **1997**, *36*, 1754.

(35) Schmidbaur, H.; Graf, W.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 417.

(36) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11.

(37) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(38) Schwerdtfeger, P.; Bruce, A. E.; Bruce, M. R. M. *J. Am. Chem. Soc.*, in press.

(39) Pyykkö, P.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 604. Li, J.; Pyykkö, P. *Chem. Phys. Lett.* **1992**, *197*, 586. Pyykkö, P.; Li, J.; Runeberg, N. *Chem. Phys. Lett.* **1994**, *218*, 133.

(40) Murray, C. A.; Bodoff, S. *J. Chem. Phys.* **1986**, *85*, 573.

(41) El-Hinnawi, M. A.; Peter, L.; Meyer, B. *J. Raman Spectrosc.* **1985**, *16*, 272.

(42) Billman, J.; Otto, A. *Surf. Sci.* **1984**, *138*, 1.

(43) Penneman, R. A.; Jones, L, H. *J. Chem. Phys.* **1956**, *24*, 293.

(44) Jones, L. H.; Penneman, R. A. *J. Chem. Phys.* **1954**, *22*, 965.

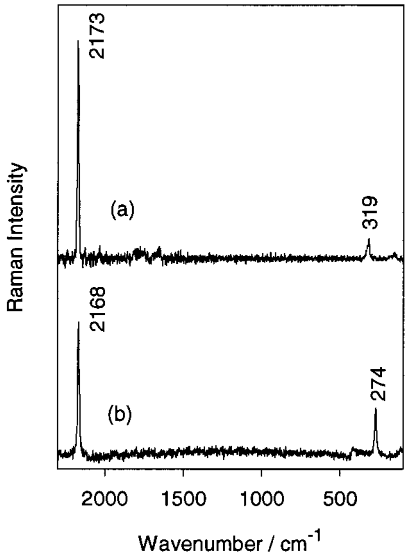

Figure 5. Raman spectra of (a) CuCN and (b) AgCN.

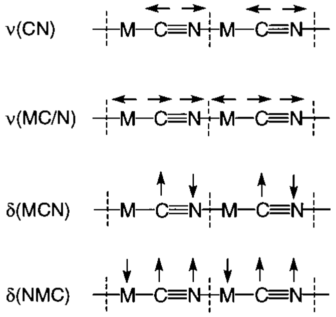

Figure 6. Normal modes of vibration of an infinite linear MCN chain.

solely with the ν(CN) stretching mode. There are relatively few reports containing data on other bands in the spectra. An assignment has been made for the ν(CuC) band at 525 cm^{-1}.[4] For AgCN the δ(AgCN) bending mode has been assigned in two different reports, with values of 269 and 273 cm^{-1}.[40,42] However a third report has assigned a band at 273−274 cm^{-1} to the ν(AgC) stretching mode.[46] For AuCN the ν(AuC) and δ(AuCN) modes have been assigned at 471 and 229 cm^{-1}, respectively.[40]

In the present study we have made a consistent set of assignments for all of the observed bands in the vibrational spectra. These assignments are made in terms of the allowed vibrations of an infinite −MCN− polymer chain. It was shown above that such chains that are present in the structures of AuCN and AgCN and the vibrational spectra show that this is the case for CuCN as well (see below). For these chain structures, the zero wave vector selection rule ($k = 2\pi/\lambda = 0$) applies,[47,48] meaning that only vibrations with wavelength $\lambda = \infty$ are active. The forms of the allowed vibrations are shown in Figure 6.

Table 2. Calculated (MCN) and Observed [(MCN)$_\infty$] Vibrational Frequencies (cm^{-1})

	assgnt	MCN	(MCN)$_\infty$
M = Cu	ν(CN)	2033^a	2170
	ν(MC)	468^a	591
	δ(MCN)	315^b	326
	δ(NMC)		168
M = Ag	ν(CN)	2094^c	2164
	ν(MC)	364^c	480
	δ(MCN)	182^c	272
	δ(NMC)		112
M = Au	ν(CN)	2105^c	2236
	ν(MC)	464^c	598
	δ(MCN)	279^c	358
	δ(NMC)		224

[a] Reference 32. [b] Calculated using the corresponding M = Ag force constant from ref 49 (see text). [c] Reference 49.

The vibrational frequencies of the triatomic monomers MCN (M = Cu, Ag, Au) provide a useful starting point for the assignment of the vibrations of the chains. Although there are no reports of the experimental isolation and characterization of such species, they have been the subject of a number of theoretical studies. Calculated band positions and bond lengths have been reported for the AgCN and AuCN monomers by Veldkamp and Frenking.[49] For the CuCN monomer the ν(MC) band position was calculated from the force constants and bond lengths determined by Bouslama et al.[32] Since this latter work did not include a calculation of the bending force constant, the corresponding force constant for the AgCN monomer[49] was used in this study to calculate the position of the δ(MCN) band for the CuCN monomer. The calculated frequencies for all three species are listed, together with our assignments of the bands in the corresponding MCN solids, in Table 2. There is a good correlation between the wavenumbers of the corresponding modes that are present in both the monomers and the infinite chains in the solids, ν(CN), ν(MC), and δ(MCN), but the wavenumbers in the solid are greater than those in the trimers. In the case of the ν(CN) mode, this is readily explained as a consequence of the change in the nature of the vibration when the trimeric units are linked into an infinite chain. As is clearly evident in Figure 6, the ν(MC) vibration within a unit cell is accompanied by a ν(MN) vibration between the N and M atoms of adjacent cells, so that only one mode is associated with the stretching of these two bonds. Moreover, it can be shown that the force constant for this mode is the sum of the M−C and M−N force constants $k_{MC} + k_{MN}$, whereas that for the ν(MC) vibration of the isolated monomer is just k_{MC}. This accounts for the observed substantial increase in the wavenumber of this mode in the solid relative to that in the isolated trimer. The situation is similar for the other modes, although additional effects may also be present. Thus, in the case of the ν(CN) mode, the frequency of this mode is partly affected by that of the ν(MC) mode through coupling of the coordinates involved in these vibrations. However, the frequency of the ν(CN) mode also increases as a result of "stiffening" of the CN bond when the cyano group acts as a σ-donor. In the case of the infinite chains, a greater frequency increase occurs relative to the monomer because the CN group is involved in a σ-donor interaction with both of the metal atoms that it bridges.

The δ(MCN) bending mode can also be described as a restricted rotation of the CN groups within the chains. The resulting bands are very weak in the IR spectra (326, 272, 358 cm^{-1}; Figure 4) but are relatively strong in the Raman spectra (Figure 5).

There is no vibrational mode in the MCN monomer that corresponds to the intense low-frequency band observed in the far-IR spectrum of each of these compounds (168, 112, 224 cm^{-1}; Figure 4). These bands are the result of a vibration in the polymer that is analogous to the δ(CMC) bending mode

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(45) Hormann-Arendt, A. L.; Shaw, C. F. *Inorg. Chem.* **1990**, *29*, 4683.
(46) Otto, A. *Surf. Sci.* **1978**, *75*, L392.
(47) Sherwood, P. M. A. *Vibrational Spectroscopy of Solids*; Cambridge University Press: Cambridge, U.K., 1972.
(48) Painter, P. C. *The Theory of Vibrational Spectroscopy and Its Application to Polymeric Materials*; Wiley: New York, 1982.
(49) Veldkamp, F. C.; Frenking, G. *Organometallics* **1993**, *12*, 4613.

observed in $[M(CN)_2]^-$ (107 and 123 cm^{-1} for M = Ag and Au, respectively[50,51]), although for the infinite linear chain structure this vibration is more properly described as a δ(NMC) mode (Figure 6). An alternative description of this vibration is as a countervibration of the M and CN sublattices, and this is consistent with the high IR intensities of the bands concerned (Figure 4). The δ(NMC) IR bands for CuCN and AgCN are considerably broader than that for AuCN, and there is evidence for some unresolved splitting of these bands in the former two compounds. The δ(NMC) mode is a perpendicular vibration (the atoms vibrate perpendicular to the chain axis) and is therefore doubly degenerate in an isolated chain. The crystal structures show that the chains in AuCN and AgCN lie on 6- and 3-fold symmetry axes respectively, so the degeneracy of the perpendicular vibrations should be maintained in the solid. Another possible explanation for the apparent splitting of these bands is an LO/TO splitting effect, which is often observed in such lattice vibrations.[47] However, this does not normally lead to splitting of the IR bands, and there is no obvious reason it should not occur in the case of AuCN. A final possibility is a symmetry-lowering effect induced by disorder. In an early X-ray crystallographic study of AgCN it was stated that the chains are "translationally disordered".[20] As indicated previously, particle size effects have resulted in severe anisotropic broadening of the Bragg reflections. Disorder of the chains, as suggested by West, would contribute to this broadening and would result in a loss of the 3-fold symmetry about the chain axes and, thus, to a possible splitting of the perpendicular vibrations. Whatever the reason for this splitting, the close similarity of the spectra of AgCN and CuCN strongly suggests that these both have the same structure.

This latter point is supported by the overall pattern of band positions in the spectra of the three compounds. For any particular mode the frequencies of the M = Cu and Au compounds are higher than those for M = Ag. This reversal of the trend in properties from M = Cu, Ag to M = Au is typical of isostructural group 11 compounds and is generally attributed to relativistic effects in the gold compound.[52,53] The observation of this trend in the present study suggests that the chain structures found in AgCN and AuCN also occur in CuCN.

A further indication that a linear chain structure exists in CuCN comes from nuclear quadrupole resonance (NQR) data. The ^{63}Cu NQR resonances in CuCN at room temperature are 37.85, 40.80, and 44.40 MHz, respectively.[54] These are in the region expected for linear coordination of copper.[55] The large linewidths and the multiplicity of the resonances indicate the presence of disorder in the structure.[54] This suggests a possible reason the X-ray diffraction patterns for this compound contain very broad peaks.

The mid-IR spectra of the MCN solids were initially recorded as samples in alkali-metal halide disks. However, these spectra showed evidence of an unusual interaction of MCN with the alkali-metal halide. The case of CuCN in a KBr disk is described here, as this sheds some light on the assignment of bands in a recently reported IR study of the thermal decomposition of CuCN.[4]

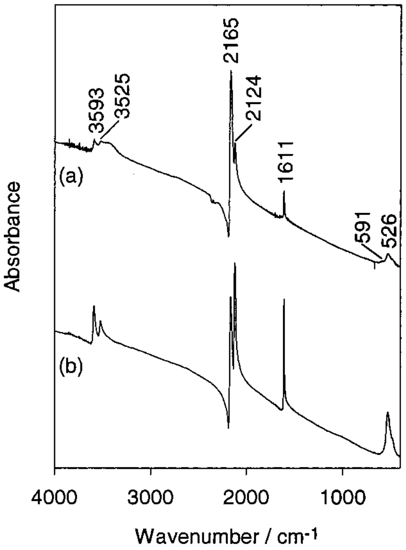

Figure 7. IR spectra of CuCN as a KBr disk (a) immediately after preparation and (b) 24 h after preparation of the disk.

The IR spectra of CuCN recorded as a KBr disk both immediately upon preparation and ca. 24 h after disk preparation are shown in Figure 7. The main features of both spectra are two bands (2165, 2124 cm^{-1}) in the region normally associated with ν(CN) bands, a band at 526 cm^{-1}, a sharp band at 1611 cm^{-1}, and two bands in the 3500 cm^{-1} region of the spectra. Immediately after preparation the band at 2165 cm^{-1} is the dominant feature in this region, with the band at 2124 cm^{-1} being considerably weaker. After 24 h the situation is essentially reversed, with the band at 2124 cm^{-1} now being the more intense. The bands at 1611 and 525 cm^{-1} also appear to show a marked increase in intensity, relative to the band at 2165 cm^{-1}, as time progresses. The bands at ca. 3500 cm^{-1} form a broad, poorly resolved feature immediately after disk preparation; however, after 24 h they also show an increase in intensity relative to the band at 2165 cm^{-1}, and this is accompanied by an decrease in the widths of these two bands. The ν(CuC) mode for CuCN was assigned above to a band at 591 cm^{-1}, and in the KBr disk spectrum this band is visible as a weak shoulder on the band at 525 cm^{-1}. After 24 h the band at 525 cm^{-1} has become stronger and the shoulder is no longer visible.

The bands at 1611, 3525, and 3593 cm^{-1} in Figure 7 are attributed to the presence of water that is initially present in the KBr and which gradually reacts with the CuCN over a period of time after the disk has been prepared. A hydrated form of CuCN has been reported previously,[17] and an attempt was made to prepare this hydrated form and record its previously unreported IR spectrum to see if it matched the CuCN/KBr disk spectrum. However, the product obtained from heating a mixture of CuCN and H_2O to 150 °C in a sealed reaction vessel for 48 h yielded IR (Nujol mull) and far-IR spectra identical to those of CuCN. This indicates that the reaction occurring in pressed disks requires the presence of KBr to proceed. To test this, CuCN was added to an aqueous solution of KBr (see Experimental Section). The product, which was collected after 1 h, showed a substantial increase in mass compared to that of the CuCN initially placed in the solution. The Nujol mull IR spectrum of this product showed bands that were the same as those observed in the CuCN/KBr disk spectrum after standing, Figure 7b. Washing the CuCN/KBr/H_2O product with water resulted in quantitative recovery of the CuCN (the IR spectrum, as a Nujol mull, was identical to that of CuCN) indicating that the CuCN had not undergone an irreversible change (e.g. hydrolysis of cyanide to amide) in this reaction.

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(50) Jones, L. H. *J. Chem. Phys.* **1957**, *26*, 1578.
(51) Chadwick, B. M.; Frankiss, S. G. *J. Mol. Struct.* **1976**, *31*, 1.
(52) Pyykko, P. *Chem. Rev.* **1988**, *88*, 563.
(53) Baker, L. J.; Bott, R. C.; Bowmaker, G. A.; Healy, P. C.; Skelton, B. W.; Schwerdtfeger, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1995**, 1341.
(54) Kroeker, S.; Wasylishen, R. E.; Hanna, J. V. Manuscript in preparation.
(55) Bowmaker, G. A. *Adv. Spectrosc.* **1987**, *14*, 1.

Although the spectra are insufficient to determine the structure of the CuCN/KBr/H_2O product, the similarity in the positions of the 2124 and 525 cm^{-1} bands to those of the ν(CN) and ν(CuC) bands of CuCN suggests that the CuCN chains remain intact in this compound. Thus the compound is possibly an intercalation compound involving incorporation of KBr and H_2O between the chains in the CuCN structure. The structure of AgCN·2$AgNO_3$ contains infinite −Ag−CN−Ag−CN− chains such as those thought to occur in AgCN, but Ag^+ and NO_3^- ions are dispersed between the chains,[56] showing the ability of these linear chains to remain intact while incorporating other species. The fact that washing the CuCN/KBr/H_2O product with water converts it back to CuCN is consistent with an intercalation compound in which the KBr is weakly bound and the water is only bound in the presence of the KBr.

The IR spectrum of CuCN as a KBr disk has been reported previously in an investigation of the thermal decomposition of CuCN.[4] Although not all regions of the spectrum were discussed in this report, those that were showed features identical to those of the CuCN/KBr disk spectrum recorded in the present study. The band at 2160 cm^{-1} was assigned to the ν(CN) stretch, while a second band at 2120 cm^{-1} was attributed to an "unknown impurity" in the CuCN. A band at 525 cm^{-1} was assigned to the ν(CuC) stretch. However, it is very likely that the 2120 and 525 cm^{-1} IR bands are due to the same interaction of CuCN with KBr that was observed in the present study.

Conclusion

The structures of MCN (M = Ag, Au) in the solid state have been determined by powder neutron diffraction studies. The presence of one-dimensional chains, as proposed in earlier studies, has been confirmed, and additional details concerning bond lengths and interchain M- - -M separations have been obtained. The structure of CuCN appears to be disordered, but vibrational spectroscopic studies show that this compound also has a one-dimensional chain structure. These compounds undergo unusual reactions with alkali-metal halides in the presence of water, and this behavior accounts for some previously unexplained features in the IR spectra of CuCN suspended in KBr disks. The complete assignment of the vibrational spectra for the MCN chains provides a basis for understanding the spectra of MCN complexes in which a chain structure is also present.

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[56] Britton, D.; Dunitz, J. D. *Acta Crystallogr.* **1965**, *19*, 815.