Crystal Structures and Vibrational Spectroscopy of $[NBu_4][Cu(CN)X]$ (X = Br, I) and $[NBu_4][Cu_3(CN)_4]\cdot CH_3CN$

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The new compounds $[NBu_4][Cu(CN)X]$ (X = Br (**1**), I (**2**)) and $[NBu_4][Cu_3(CN)_4]\cdot CH_3CN$ (**3**) have been prepared by reaction of $[NBu_4]X$ with CuCN in acetone (**1**, **2**) or acetonitrile (**3**), and have been characterized by X-ray crystallography and vibrational spectroscopy. Compounds **1** ($C_{34}H_{72}Br_2Cu_2N_4$, $a = 17.4956(11)$ Å, $b = 12.1741(8)$ Å, $c = 19.2434(12)$ Å, orthorhombic, $Pna2_1$, $Z = 4$) and **2** ($C_{34}H_{72}Cu_2I_2N_4$, $a = 21.683(2)$ Å, $b = 12.233(2)$ Å, $c = 17.632(3)$ Å, $\beta = 111.710(10)°$, monoclinic, $P2_1/c$, $Z = 4$) contain infinite one-dimensional (zigzag) $-Cu^I-CN-Cu^I-CN-$ chains which run parallel to the crystallographic *a* (X = Br) or *c* (X = I) axis. Each Cu^I center within these chains is additionally bound to an X = Br or I atom, and the whole network is planar, with successive planar units stacked in the *b* direction. Bands in the IR and Raman spectra are assigned to ν(CN), ν(CuC/N), δ(CuCN), and δ(NCuC) modes of the CuCN chains. The IR spectra of the products of the reversible reaction of CuCN with aqueous KX (X = Br, I) show ν(CN) and δ(NCuC) as well as bands due to coordinated water, suggesting that these $CuCN/KX/H_2O$ compounds are mixed halogeno(cyano)cuprates with hydrated K^+ counterions whose structures are similar to those observed in $[NBu_4][Cu(CN)X]$. The structure of **3** ($C_{22}H_{39}Cu_3N_6$, $a = 16.8572(4)$ Å, $b = 14.1180(3)$ Å, $c = 13.39100(10)$ Å, $\beta = 113.30(3)°$, monoclinic, $C2$, $Z = 4$) consists of two-dimensional polymeric sheets of composition $[Cu_3(CN)_4^-]_\infty$ in the *ac* plane, which are made up of infinite one-dimensional (zigzag) $-Cu^I-CN-Cu^I-CN-$ chains parallel to the *a* axis, with each Cu^I center within these chains being additionally bound to a linear $[CN-Cu-CN^-]$ group which links adjacent chains, so that the structure contains both two-coordinate and three-coordinate copper atoms. Successive planar sheets are stacked in the *b* direction, with the $[NBu_4]^+$ cations and noncoordinating acetonitrile molecules lying within rings of composition $(CuCN)_8$.

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.[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]

A number of complexes of copper(I) cyanide have been reported over the years,[3] but recent studies have shown that there is still much to be learned about such systems.[4−6] Copper(I) cyanide has shown promise in the construction of self-assembling zeolitic frameworks,[7] and as a precursor in the synthesis of $YBa_2Cu_3O_{7-x}$ superconductors.[8] It is also important in synthetic organic chemistry, where it is a component of cyanocuprate reagents such as Li[Cu(CN)R] (R = alkyl), one of the class of organocopper reagents which are among the most important organometallic compounds used to form carbon−carbon bonds.[9]

In comparison to the case of group 11 halogenometalates(I), where a large number of compounds with a remarkable diversity of structures have been reported,[10] relatively little work has been done on the corresponding cyanometalates(I). Early studies showed unexpected differences in the structures of the solid

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compounds $K[M(CN)_2]$ (M = Cu, Ag, Au). Thus, the silver(I)[11,12] and gold(I)[13,14] compounds both contain linear $[M(CN)_2]^-$ ions, but the copper(I)[15] complex contains a helical anion chain in which each copper is three-coordinate. Three-coordinate copper(I) is also observed in $[NBu_4][Cu(CN)_2]$,[16] $Na_2[Cu(CN)_3]\cdot 3H_2O$,[17] and $K[Cu_2(CN)_3]\cdot H_2O$,[18] while four-coordinate copper(I) occurs in $K[Cu(CN)_4]$.[19] There have been some references in the past to the existence of mixed halogeno(cyano)cuprates of the types $[Cu(CN)X]^-$, $[Cu(CN)_2X]^{2-}$, and $[Cu(CN)_3X]^{3-}$,[20−22] but no direct structural evidence for these has yet been presented. In a recent study of the vibrational spectra of the group 11 metal cyanides, evidence for the interaction of copper(I) cyanide with potassium bromide was obtained, but the exact nature of the product of this interaction was not determined.[23] In the present study we report the synthesis and structure of the compounds $[NBu_4][Cu(CN)X]$ (X = Br, I). Comparison of the vibrational spectra of these with those of the products of interaction of CuCN with KX (X = Br, I) yields information about the structure of the latter compounds. We also report the structure and vibrational spectra of the new cyanocuprate(I) complex $[NBu_4][Cu_3(CN)_4]$, which was discovered in the course of the present work, and which has a structure that is related to the $[NBu_4][Cu(CN)X]$ compounds.

Experimental Section

Preparation of Compounds. Tetra(*n*-butyl)ammonium Bromo(cyano)cuprate(I), $[NBu_4]^1_\infty[Cu(CN)Br]$ (1). A mixture of copper(I) cyanide (0.125 g, 1.4 mmol) and tetra(*n*-butyl)ammonium bromide (0.52 g, 1.6 mmol) was heated under reflux with stirring in acetone (30 mL) for 20 h. The resulting solution was filtered while hot to remove some undissolved residue, and the filtrate was gradually cooled to room temperature. After several days the product separated from the clear solution in the form of colorless plate- and rod-shaped crystals. Anal. Calcd for $C_{17}H_{36}BrCuN_2$: C, 49.57; H, 8.81; N, 6.80. Found: C, 49.64; H, 8.62; N, 7.15. Suitable crystals for the X-ray structure analysis were selected under the microscope. The cell constants of the different crystal forms were identical.

Tetra(*n*-butyl)ammonium Iodo(cyano)cuprate(I), $[NBu_4]^1_\infty[Cu(CN)I]$ (2). A mixture of copper(I) cyanide (1.0 g, 11.0 mmol) and tetra(*n*-butyl)ammonium iodide (4.1 g, 11.0 mmol) was heated under reflux with stirring in acetone (50 mL) for 30 h. The resulting yellow solution was filtered while hot to remove some undissolved residue, and the filtrate was gradually cooled to room temperature. After several days the product separated in the form of colorless needle-shaped crystals. Anal. Calcd for $C_{17}H_{36}CuIN_2$: C, 44.49; H, 7.91; N, 6.10. Found: C, 44.99; H, 7.94; N, 6.06.

Tetra(*n*-butyl)ammonium Tetracyanotricuprate(I) Acetonitrile Solvate, $[NBu_4]^2_\infty[Cu_3(CN)_4]\cdot CH_3CN$ (3). A mixture of copper(I) cyanide (1.0 g, 11.0 mmol) and tetra(*n*-butyl)ammonium iodide (4.1 g, 11.0 mmol) was heated under reflux with stirring in acetonitrile (50 mL) for 30 h. The resulting clear solution was filtered while hot to remove some undissolved residue, and the filtrate was gradually cooled to room temperature. After 4 days the product separated in the form of large colorless crystals. Anal. Calcd for $C_{22}H_{39}Cu_3N_2$: C, 45.70; H, 6.79; N, 14.53. Found: C, 45.03; H, 6.95; N, 14.20.

Potassium Tricyanodicuprate Monohydrate, $K[Cu_2(CN)_3]\cdot H_2O$, and Potassium Tricyanodicuprate, $K[Cu_2(CN)_3]$. A mixture of KCN (0.65 g, 10.0 mmol), CuCN (1.79 g, 20.0 mmol), and water (5 mL) was heated briefly, and allowed to cool. The white microcrystalline compound $K[Cu_2(CN)_3]\cdot H_2O$ was collected by vacuum filtration and washed with a little water. Yield: 2.29 g. A sample of this was dehydrated at 110 °C to yield anhydrous $K[Cu_2(CN)_3]$.

Reaction of CuCN with Aqueous KBr or KI. To a solution of KBr (1.9 g, 16 mmol) or KI (2.7 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 (KBr product) and about 1.5 g (KI product). The IR spectra (Nujol mull) showed bands at 3590, 3522, 2119, 1610, and 529 cm^{-1} (KBr product) and 3590, 3523, 2127, 2109, 1593, and 442 cm^{-1} (KI product). Washing of samples of these products with water results in quantitative recovery of CuCN, whose identity was verified by means of its Nujol mull IR spectrum.

X-ray Structure Determinations. X-ray single-crystal data were obtained by mounting a suitable crystal (**1** and **3**) at low temperature by applying a stream of cold nirogen on a Bruker SMART CCD 1000 TM diffractometer. Measurement conditions were as follows: Mo Kα (λ = 71.073 pm), scan width 0.3° in ω, exposure time 20 s/frame, and detector-crystal distance 4.0 cm. A full sphere of data up to $2\theta = 55°$ (**1**) and $2\theta = 53°$ (**3**) was measured by 1800 frames. Data were reduced to intensities and corrected for background, and an empirical absorption correction based on multiple observation of symmetry-equivalent reflections ("Sadabs") was applied.

A suitable single crystal of **2** obtained by crystallization from acetone was mounted at low temperature on an Enraf-Nonius CAD 4 four-cycle diffractometer by applying a stream of cold nitrogen. Mo Kα (λ = 71.073 pm) radiation with a graphite monochromator was used. Lattice constants were obtained by fine adjustment of 25 reflections. X-ray intensities were measured with the $\omega/2\theta$ scan method, with maximal 55 s/reflection. Lorentz, polarization, and ψ scan absorption corrections (transmission, max/min 0.97/0.93) were applied. Structures **1**−**3** were solved[24] and refined[25] by the SHELX programs; positional parameter and temperature factors were refined against F^2. All non-hydrogen atoms in **2** and **3** were refined anisotropically. In structure **1** all non-hydrogen atoms were also refined anisotropically except carbon and nitrogen atoms of the bridging cyanide groups. The positions of all hydrogen atoms were calculated.

Crystallographic data for compounds **1**−**3** are given in Table 1. Selected bond lengths and angles for **1** and **2** are given in Table 2, and those for **3** are given in Table 3.

Spectroscopy. Infrared spectra were recorded at 4 cm^{-1} resolution at room temperature as Nujol mulls between KBr plates or as KBr disks on a Perkin-Elmer Spectrum 1000 Fourier transform infrared spectrometer or on a Digilab FTS-60 Fourier transform infrared spectrometer employing an uncooled deuteriotriglycine sulfate detector. Far-infrared spectra were recorded with 2 cm^{-1} resolution at room temperature as pressed Polythene disks on a Digilab FTS-60 Fourier transform infrared spectrometer employing an FTS-60V vacuum optical bench with a 5 lines/mm wire mesh 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 cooled photomultiplier (RCA C31034A) detector, with 514.5 nm argon ion laser excitation (Spectra-Physics

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Table 1. Crystallographic Data for Compounds **1**−**3**

	1	**2**	**3**
empirical formula	$C_{34}H_{72}Br_2Cu_2N_4$	$C_{34}H_{72}Cu_2I_2N_4$	$C_{22}H_{39}Cu_3N_2$
fw	411.93	458.93	578.21
cryst size (mm)	0.4 × 0.5 × 0.3	0.2 × 0.3 × 0.25	0.32 × 0.21 × 0.11
space group (no.)	$Pna2_1$ (33)	$P2_1/c$ (14)	$C2$ (5)
a (Å)	17.4956(11)	21.683(2)	16.8572(4)
b (Å)	12.1741(8)	12.233(2)	14.1180(3)
c (Å)	19.2434(12)	17.632(3)	13.39100(10)
α (deg)	90	90	90
β (deg)	90	111.710(10)	113.30(3)
γ (deg)	90	90	90
V (Å^3), Z	4098.7(5), 4	4345.1(11), 4	2927.11(10), 4
T (K)	143	143	203
λ (Å)	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.335	1.403	1.312
μ (mm^{-1})	3.013	2.424	2.178
R_1,[a] wR_2[b] (%)	4.06, 8.13	3.44, 7.88	3.61, 8.62

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Model 2016), or with a Bruker RFS 100 S FT Raman spectrometer, with 1064 nm Nd:YAG laser excitation (300 mW).

Results and Discussion

Syntheses. The compounds $[NBu_4][Cu(CN)X]$ (X = Br (**1**), I (**2**)) crystallize from solutions of the products of the reaction of $[NBu_4]X$ with CuCN in a 1:1 mole ratio in acetone. The exact nature of the species present in such solutions is not clear at present, but it is likely that an equilibrium exists among a range of halogenocuprate(I), cyanocuprate(I), and mixed halogeno(cyano)cuprate(I) species. The species that crystallizes from such solutions is clearly solvent dependent, as the reaction yields the compound $[NBu_4][Cu_3(CN)_4]\cdot CH_3CN$ (**3**) when the solvent is changed from acetone to acetonitrile (see the Experimental Section). Attempts to obtain $[NBu_4][Cu(CN)X]$ with X = Cl under conditions similar to those that yield the X = Br and I compounds were not successful.

Crystal Structure Determinations. The structures of the anions in $[NBu_4]^1_\infty[Cu(CN)X]$ (X = Br, (**1**), I (**2**)) are shown in Figure 1. Selected bond lengths and angles for **1** and **2** are given in Table 2. The structures of these complexes consist of infinite one-dimensional (zigzag) $-Cu^I-CN-Cu^I-CN-$ chains which run parallel to the a (X = Br) or c (X = I) axis (Figure 1). Each Cu^I center within these chains is additionally bound to an X = Br or I atom, and the whole network is planar, with successive planar units stacked in the b direction. The $[NBu_4]^+$ cations fill the voids between these stacks. There are two Cu(CN)Br entities in the asymmetric unit. The distorted trigonal-planar coordination environments of the two inequivalent copper atoms are quite similar, with C−Cu−N angles significantly greater than 120°, and C−Cu−X and N−Cu−X angles significantly less than this value (Table 2). The structure can be considered to be derived from that of solid CuCN, which is believed to contain infinite linear $-Cu^I-CN-Cu^I-CN-$ chains,[23,26] by addition of X^- in a side-on fashion to each of the copper atoms in the chain. The binding of the halide ion causes a "bending" of the N−Cu−C angle in the chain from 180° to a value of about 130°. The structure is similar to those observed in a number CuCN:L adducts $[L_nCuCN]$ (n = 1, 1.5, 2; L = amine base).[27,28] The three-coordinate copper sites in these latter complexes show coordination geometries similar to those observed in **1** and **2**, with N−Cu−C angles in the range 128−149°.[27,28]

As is often the case for structures of this type,[27,28] the C and N atoms in the bridging CN groups cannot be distinguished crystallographically. Assignments based on d(Cu−C) < d(Cu−N) have been made (Figure 1, Table 2), but it is possible that these groups are fully disordered, as in solid CuCN.[26]

The structure of the anion in $[NBu_4]^2_\infty[Cu_3(CN)_4]\cdot CH_3CN$ (**3**) is shown in Figure 2, and selected bond lengths and angles are given in Table 3. The structure of this complex consists of polymer sheets of composition $^2_\infty[Cu_3(CN)_4^-]$ in the ac plane. These can be viewed as consisting of infinite one-dimensional (zigzag) $-Cu^I-CN-Cu^I-CN-$ chains which run parallel to the a axis (similar to the CuCN chains in **1** and **2**). Each Cu^I center within these chains is additionally bound to a linear $[CN-Cu(2)-CN^-]$ group which links adjacent chains via Cu(1) and Cu(3) (Figure 2). The resulting sheet structure is planar, with successive planar units stacked in the b direction, and the cation and the noncoordinating acetonitrile molecule lie within rings of composition $(CuCN)_8$. Two of the butyl chains of each interconnected $^2_\infty[Cu_3(CN)_4]$ layer penetrate the $(CuCN)_8$ rings (Figure 2b). The structure is related to that of $K[Cu_2(CN)_3]\cdot H_2O$, which can similarly be regarded as consisting of zigzag $-Cu^I-CN-Cu^I-CN-$ chains, but linked by CN^- groups, instead of by $[CN-Cu-CN^-]$ groups, and with K^+ ions lying within rings of composition $(CuCN)_6$.[15] In this case all of the Cu atoms are three-coordinate, whereas in **3** there are both two-coordinate copper (Cu(2)) and three-coordinate copper (Cu(1), Cu(3)) atoms present. The presence of the linear $[CN-Cu(2)-CN^-]$ group in the structure is of some interest, given that cyanocuprate(I) compounds containing isolated linear $[Cu(CN)_2]^-$ have not yet been observed. The ability of the cyanocuprate(I) system to form the $^1_\infty[Cu_2(CN)_3^-]$ and $^2_\infty[Cu_3(CN)_4^-]$ structures described above is clearly dependent on the well-known ability of copper(I) to adopt a variety of coordination numbers.[29] The driving force that determines the formation of the structures is possibly the "template" effect of the cation. The $(CuCN)_8$ rings in **3** are of a size suitable for accommodation of $[NBu_4]^+$, whereas the $(CuCN)_6$ rings in $K[Cu_2(CN)_3]\cdot H_2O$ match the smaller size of the K^+ ion.

The Cu−C/N bond lengths about the three-coordinate copper atoms in **3** (average 1.91 Å) are significantly longer than those about the two-coordinate copper atoms (average 1.82 Å). The bond angles about the three-coordinate copper atoms are closer to the ideal trigonal angle, 120°, than those in **1** and **2** (Table 2) or in $K[Cu_2(CN)_3]\cdot H_2O$,[18] although there is still quite a significant variation, from 116° to 126° (Table 3).

Vibrational Spectroscopy. The IR and Raman band assignments for the vibrations of the infinite $-CuCN-CuCN-$ chains in $[NBu_4][Cu(CN)X]$ are given in Table 4. The spectra show strong ν(CN) bands, whose frequencies are listed in Table 4. We have recently shown that a correlation exists between the ν(CN) frequencies and the Ag−C/N bond lengths in a number of AgCN complexes, such that ν(CN) increases with decreasing Ag−C/N bond length.[30] A similar trend is evident in the data for a number of CuCN complexes with amine and phosphine ligands.[28,31] From these results, ν(CN) for a linear bridging CN group with d(Cu−C/N) = 1.9 Å (the average value observed for **1** and **2**) is expected at about 2115 cm^{-1}, which agrees well with the observed values (Table 4). These structures show two

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[NBu_4][Cu(CN)X]$ (**1**, **2**)[a]

	1 (X = Br)	**2** (X = I)		**1** (X = Br)	**2** (X = I)
X(1)−Cu(1)	2.4448(6)	2.6219(9)	Cu(2)−C(1)	1.898(4)	1.910(7)
Cu(1)−C(2)	1.908(5)	1.897(7)	Cu(2)−N(2)	1.902(4)	1.894(6)
Cu(1)−N(1)	1.914(5)	1.907(7)	C(1)−N(1)	1.169(5)	1.147(7)
X(2)−Cu(2)	2.4427(7)	2.6226(9)	C(2)−N(2)#1	1.167(5)	1.175(7)
C(2)−Cu(1)−N(1)	128.4(2)	130.4(2)	N(2)−Cu(2)−X(2)	116.29(14)	117.84(15)
C(2)−Cu(1)−X(1)	118.73(14)	119.16(15)	N(1)−C(1)−Cu(2)	171.6(4)	173.3(6)
N(1)−Cu(1)−X(1)	112.81(13)	110.35(16)	C(1)−N(1)−Cu(1)	173.3(4)	172.5(6)
C(1)−Cu(2)−N(2)	129.0(2)	130.8(2)	N(2)#1−C(2)−Cu(1)	176.2(4)	175.3(5)
C(1)−Cu(2)−X(2)	114.54(14)	111.07(16)	C(2)#2−N(2)−Cu(2)	176.5(4)	174.0(5)

[a] Symmetry transformations: (**1**) #1, $x + {}^1/_2$, $-y + {}^1/_2$, z; #2, $x - {}^1/_2$, $-y + {}^1/_2$, z. (**2**) #1, x, $-y + {}^3/_2$, $z - {}^1/_2$; #2, x, $-y + {}^3/_2$, $z + {}^1/_2$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[NBu_4][Cu_3(CN)_4]$ (**3**)[a]

Cu(1)−C(3)	1.888(11)	Cu(3)−C(5)	1.912(9)	N(2)−C(2)	1.181(11)
Cu(1)−N(1)	1.889(11)	Cu(3)−N(3)	1.918(10)	N(3)−C(3)#3	1.162(5)
Cu(1)−C(4)	1.942(9)	N(1)−C(1)	1.140(11)	C(5)−N(5)#4	1.176(19)
Cu(2)−N(2)	1.789(10)	C(4)−N(4)#1	1.119(17)	C(5)−C(5)#4	1.176(19)
Cu(2)−C(1)	1.846(10)	C(4)−C(4)#1	1.119(17)		
Cu(3)−C(2)	1.911(10)	C(3)−N(3)#2	1.162(5)		
C(3)−Cu(1)−N(1)	126.2(4)	C(1)−N(1)−Cu(1)	174.2(12)	C(3)#3−N(3)−Cu(3)	176.5(5)
C(3)−Cu(1)−C(4)	115.9(4)	N(4)#1−C(4)−C(4)#1	0.0(19)	N(5)#4−C(5)−C(5)#4	0.0(13)
N(1)−Cu(1)−C(4)	117.9(4)	N(4)#1−C(4)−Cu(1)	172.7(3)	N(5)#4−C(5)−Cu(3)	173.2(4)
N(2)−Cu(2)−C(1)	176.4(9)	C(4)#1−C(4)−Cu(1)	172.7(3)	C(5)#4−C(5)−Cu(3)	173.2(4)
C(2)−Cu(3)−C(5)	118.3(4)	N(1)−C(1)−Cu(2)	174.5(12)	N(2)−C(2)−Cu(3)	173.5(11)
C(2)−Cu(3)−N(3)	124.1(4)	N(3)#2−C(3)−Cu(1)	176.4(6)		
C(5)−Cu(3)−N(3)	117.6(4)	C(2)−N(2)−Cu(2)	174.7(11)		

[a] Symmetry transformations: #1 $-x + 1$, y, $-z + 1$; #2 x, y, $z + 1$; #3, x, y, $z - 1$; #4, $-x$, y, $-z - 1$.

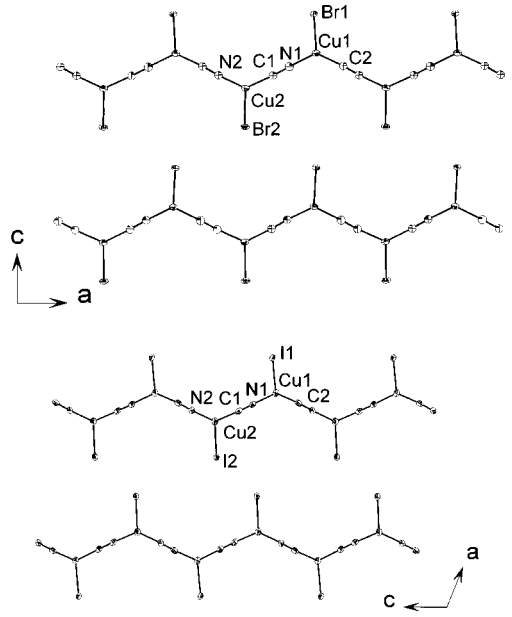

Figure 1. View of the structure (ORTEP, 50% probability level) of (a, top) $[NBu_4][Cu(CN)Br]$ (**1**) and (b, bottom) $[NBu_4][Cu(CN)I]$ (**2**).

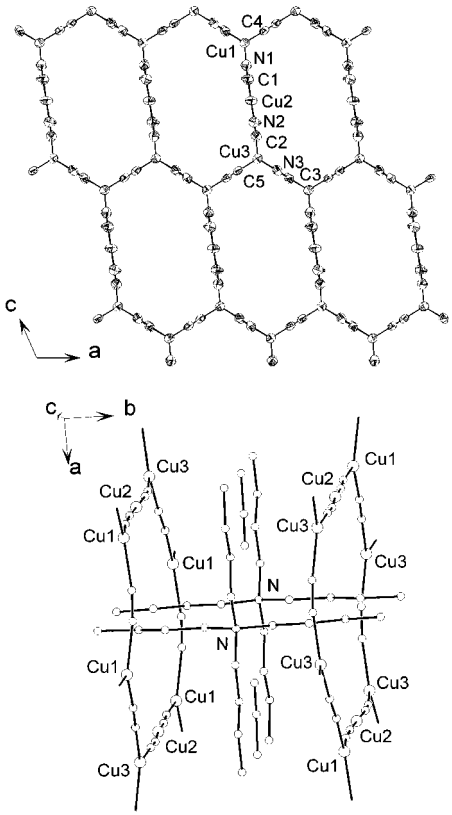

Figure 2. Structure of $[NBu_4][Cu_3(CN)_4]\cdot CH_3CN$ (**3**) (ORTEP, 50% probability level): (a, top) anionic network, viewed along *b*; (b, bottom) a view along *c*, showing the locations of the cation and solvent molecules.

crystallographically inequivalent CN groups, so that two ν(CN) bands should be observed. Two closely spaced bands are observed in the IR and Raman spectra in both cases (Table 4).

It has recently been shown by vibrational spectroscopy that solid CuCN contains infinite linear −CuCN−CuCN− chains, with ν(CN) = 2170 cm^{-1}.[23] The ν(CN) frequencies for the chain polymers in Table 4 are lower than this, as a result of the fact that the binding of the halide donor ligands to the copper weakens the Cu−C/N bonds, and thus lowers the ν(CN) frequency.

The far-IR spectra of complexes **1** and **2** are shown in Figure 3. The following low-frequency vibrational modes have previously been assigned in the infinite linear −CuCN−CuCN− chains present in solid CuCN: ν(CuC/N) = 591 cm^{-1}, involving vibration of the CN group between its two neighboring Cu atoms; δ(CuCN) = 326 cm^{-1}, which can be described as a restricted rotation of the CN group; δ(NCuC) = 168 cm^{-1},

Table 4. Wavenumbers (cm^{-1}) of Bands Assigned to the CuCN Chains in the Vibrational Spectra of $[NBu_4][Cu(CN)X]$, $KX/CuCN/H_2O$ (X = Br, I), $[NBu_4][Cu_3(CN)_4]\cdot CH_3CN$, and $K[Cu_2(CN)_3]\cdot xH_2O$ ($x = 0$, 1)'

compound			ν(CN)	ν(CuC/N)	δ(CuCN)	δ(NCuC)
CuCN[a]		IR	2170	591	326	168
$[NBu_4][Cu(CN)Br]$	**1**	IR	2118, 2111	476, 465	326, 289	181, 164
		R	2122, 2114		331	
$KBr/CuCN/H_2O$		IR	2122, 2116	*b*	*b*	173
$[NBu_4][Cu(CN)I]$	**2**	IR	2122, 2115	484, 468	329, 298	175
		R	2127, 2118	484	323	
$KI/CuCN/H_2O$		IR	2127, 2110	*b*	*b*	160
$[NBu_4][Cu_3(CN)_4]\cdot CH_3CN$	**3**	IR	2159, 2125, 2086	565, 463	355, 331, 288	200, 175
		R	2157, 2138, 2128, 2085			
$K[Cu_2(CN)_3]$		IR	2121, 2081	463, 419	355, 330, 279	201, 164, 147
		R	2124, 2086	470, 434	300, 287	196, 157
$K[Cu_2(CN)_3]\cdot H_2O$		IR	2113, 2093	*b*	*b*	202, 159
		R	2127, 2117, 2095	478, 452	289	207, 167

[a] Reference 23. [b] Obscured by strong H_2O bands (see the text).

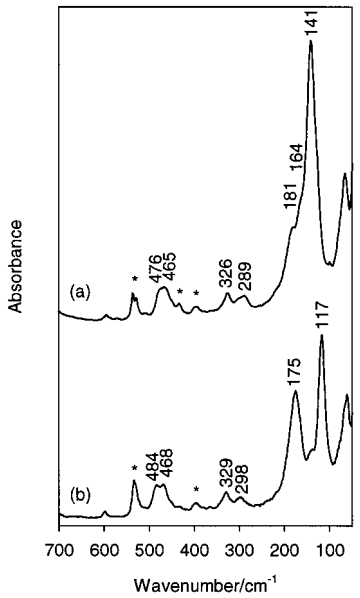

Figure 3. Far-IR spectra of $[NBu_4][Cu(CN)X]$: (a) X = Br, (b) X = I. The bands marked with an asterisk are due to the NBu_4^+ ion.

which can be described as a countervibration of the Cu sublattice against the CN sublattice, in a direction perpendicular to the CuCN chains.[23] In the infinite chain compounds in which the copper atoms are coordinated to the halide ligands, shifts in the above frequencies and splitting of the bending modes (which are doubly degenerate in the isolated linear chains) are expected. For the ν(CuC/N) mode, a downward frequency shift is expected because the binding of the halide ligand weakens the Cu−C/N bonds, as has been observed in analogous complexes with amine bases.[28] According to a correlation that has been established for these latter complexes, ν(CuC/N) for a linear bridging CN group with d(Cu−C/N) = 1.90−1.91 Å (the range of values observed for **1** and **2**) is expected in the range 480−490 cm^{-1}. Bands in the range 465−485 cm^{-1} are therefore assigned to this mode. The splitting of these bands into doublets relative to the single ν(CuC/N) band observed in CuCN is due to the nonlinearity of the zigzag chain in the complexes.

The far-IR spectra also contain bands below 400 cm^{-1}, some of which can be assigned to vibrations of the CuCN chains: Weak bands at about 325 cm^{-1} are assigned to δ(CuCN), close to the value of 326 cm^{-1} for solid CuCN. Stronger bands at about 175 cm^{-1} are assigned to δ(NCuC). These doubly degenerate (perpendicular) modes give rise to a single band at 168 cm^{-1} in the linear chains of CuCN itself due to the fact that the chains lie on 3-fold symmetry axes,[23] but this symmetry is lost in the present complexes. The observed multiplicity of the δ(CuCN) bands, and of the δ(NCuC) band for X = Br (Figure 3), can be attributed to this loss of axial symmetry.

According to a previously established correlation between ν(CuX) and the Cu−X bond length,[32] ν(CuX) bands for **1** and **2** are expected at 173 and 146 cm^{-1} for X = Br and I, respectively. The predicted value for X = Br overlaps with the bands assigned to the δ(NCuC) mode of the CuCN chain (Table 4). However, a strong band is observed at 141 cm^{-1}, and this is assigned as ν(CuBr). A strong band at 117 cm^{-1} in the iodide complex is likewise assigned to ν(CuI). The unexpectedly low frequencies for these modes are probably due to their coupling with the δ(NCuC) modes.

The results for compounds **1** and **2** described above shed some light on the nature of the product of interaction of copper(I) cyanide with potassium bromide that was reported in a previous study.[23] This product was first detected in the IR spectrum of CuCN recorded as a KBr disk in the presence of moisture. The main features of the spectrum 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. It was subsequently found that the same product was obtained by adding CuCN to an aqueous solution of KBr, and that an iodide analogue is obtained if KI is used in place of KBr (see the Experimental Section). The product shows a substantial increase in mass compared to that of the CuCN initially placed in the solution. Washing the products with water resulted in quantitative recovery of the CuCN (the IR spectrum, as a Nujol mull, was identical to that of CuCN). The same compounds are produced when KBr or KI disks containing deliberately moistened CuCN are prepared for IR spectroscopy. Partially deuterated samples can be prepared by premoistening the CuCN with D_2O instead of H_2O. Assignments of the CuCN modes in the IR spectra of these compounds are given in Table 4. The presence of water in the KBr compound is indicated by the bands ν(OH) = 3590 and 3522 cm^{-1}, $\delta(OH_2)$ = 1610 cm^{-1}, and ρ_w = 526 cm^{-1} (the wagging mode of H_2O bound to K^+). Corresponding bands in the KI compound occur at 3590, 3523, 1593, and 438 cm^{-1}. Corresponding bands due to HDO and D_2O are observed in the spectra of samples prepared using D_2O. The water molecules are quite labile; D_2O/HDO can be replaced by H_2O by simply allowing the partially deuterated solid to stand in the air for a few hours. However, the water molecules are reasonably strongly bound, and are not removed by heating the compounds to 110 °C. This contrasts with the situation for

(32) Bowmaker, G. A.; Healy, P. C.; Kildea, J. D.; White, A. H. *Spectrochim. Acta, Part A* **1988**, *44*, 1219.

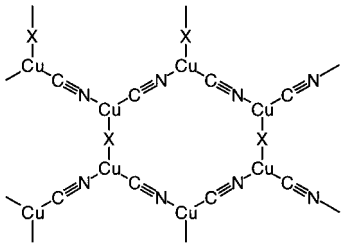

Figure 4. Proposed structure of the anion network in the CuCN/KX/H_2O complexes.

$K[Cu_2(CN)_3]\cdot H_2O$, where the water molecule bound to the K^+ ion is readily removed under these conditions.

The above results suggest that the CuCN/KX/H_2O compounds are mixed halogeno(cyano)cuprates with a structure similar to those observed in $[NBu_4][Cu(CN)X]$, the cations in the former compounds being hydrated K^+ ions. The presence of $-CN-Cu(X)-$ groups in these compounds is supported by the close similarity of the wavenumbers of the bands assigned to these groups to those of $[NBu_4][Cu(CN)X]$ (Table 4). Although a number of the lower frequency modes expected in the far-IR spectra of the CuCN/KX/H_2O compounds are masked by stronger bands due to H_2O, strong δ(NCuC) bands in the 160−175 cm^{-1} region that are characteristic of $-CN-Cu-CN-Cu-$ chain structure[23] are clearly observed (Table 4).

The stoichiometry of the CuCN/KBr/H_2O compound is not easy to determine, as some CuCN remains unreacted even after a long reaction time. However, for the corresponding KI compound, the IR spectrum shows that the reaction goes essentially to completion. The product cannot be obtained in a pure form because it cannot be washed with water to remove the excess KI, since water extracts the KI and converts the product back to CuCN. However, an estimate of the stoichiometry can be obtained from the yield of product, and this indicates a CuCN:KI ratio of 2:1 (see the Experimental Section). A possible structure for a compound of this stoichiometry is a sheet containing $-Cu-CN-Cu-CN-$ chains such as those in $[NBu_4][Cu(CN)I]$, but with the chains cross-linked by bridging iodide in a way that retains three-coordinate copper. The vibrational spectroscopy indicates the same structure for the KBr compound. These structures would contain $(CuCN)_2(CuX)$-$(CuCN)_2(CuX)$ rings (analogous to the $(CuCN)_6$ rings in $K[Cu_2(CN)_3]\cdot H_2O$) which would accommodate the potassium ions and water molecules. A likely stoichiometry would therefore be $K[Cu_2(CN)_2X]\cdot H_2O$. The proposed structure of the anion network is shown in Figure 4. The anion structure in $[NBu_4][Cu_3(CN)_4]$ (**3**) (see above) is related to that in these complexes by replacing the bridging X^- by $Cu(CN)_2^-$.

The IR and Raman band assignments for the vibrations of the CuCN networks in $[NBu_4][Cu_3(CN)_4]$ (**3**) and in $K[Cu_2(CN)_3]\cdot xH_2O$ ($x = 0, 1$) are given in Table 4. The far-IR spectra, containing bands due to the lower frequency vibrations, are shown in Figure 5. The water molecules in $K[Cu_2(CN)_3]\cdot H_2O$ give rise to bands in the IR spectra at 3584, 3524, 1628, 580, and 477 cm^{-1}. The last two of these are assigned to the ρ_w mode of H_2O bound to K^+, and these obscure the bands in the ν(CuC/N) region. However, the overall similarity of the vibrational spectra for the hydrated and dehydrated forms (Figure 5, Table 4), and the fact that the hydrate can be reversibly dehydrated and rehydrated, indicates that the hydrate maintains its structural integrity upon dehydration.

The ν(CN) bands in **3** include a component at 2159 cm^{-1} that can be assigned to the bridging $[CN-Cu(2)-CN^-]$ units. These occur at higher frequency than the corresponding bands in isolated $[Cu(CN)_2]^-$ (ca. 2125 cm^{-1})[33] because the terminal CN groups in the free ion become linear bridging CN groups in **3**. The absence of bands above 2130 cm^{-1} in $K[Cu_2(CN)_3]\cdot xH_2O$ ($x = 0, 1$) is consistent with the absence of linear bridging $[Cu(CN)_2]^-$ in these compounds. The far-IR spectrum of **3** shows a band at 463 cm^{-1}, which is assigned to the ν(CuC/N) vibrations. This is consistent with the results for $K[Cu_2(CN)_3]$, which has a similarly assigned band at 463 cm^{-1} (Table 4). A second ν(CuC/N) band is assigned in this compound at 419 cm^{-1}. The band at 565 cm^{-1} in **3** is assigned to ν(CuC/N) of the bridging $[CN-Cu(2)-CN^-]$ units. As noted above, the Cu−C/N bond lengths about the three-coordinate copper atoms in the chains are significantly longer than those about the two-coordinate copper atoms in the bridges, so a higher ν(CuC/N) frequency would be expected for the latter. In fact, the structure of the linear bridges is similar to that in solid CuCN,[23,26] and this is reflected in the values of the ν(CN) and ν(CuC/N) frequencies for this unit, which are only slightly less than those in CuCN itself (Table 4).

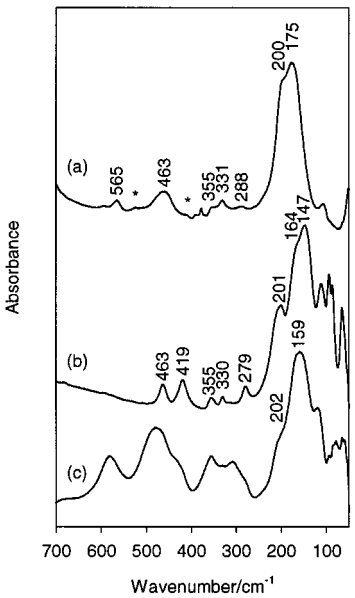

Figure 5. Far-IR spectra of (a) $[NBu_4][Cu_3(CN)_4]\cdot CH_3CN$, (b) $K[Cu_2(CN)_3]$, and (c) $K[Cu_2(CN)_3]\cdot H_2O$. The bands marked with an asterisk are due to the NBu_4^+ ion.

Conclusion

Mixed-ligand halogeno(cyano)cuprates $[Cu(CN)X]^-$, whose existence has been postulated several times in the past, have been prepared and structurally characterized for the first time. The solid-state structures contain $^1_\infty[Cu(CN)X]^-$ with infinite zigzag $-Cu^I-CN-Cu^I-CN-$ chains in which each copper is bound to a halide ligand. The structures indicate that the halide ion is only relatively weakly coordinated to the copper atom, and slight variations in the synthesis conditions (e.g., change of solvent) yield compounds with different anion structures, such as $^2_\infty[Cu_3(CN)_4]^-$, in which the halide is completely excluded. The present results shed some light on the nature of the products formed when CuCN absorbs alkali-metal halide salts from aqueous solution. Infrared spectroscopic results suggest that, in the case of potassium halides, these are compounds of the type $K[Cu_2(CN)_2X]\cdot H_2O$ containing $(CuCN)_2(CuX)(CuCN)_2$-

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

(CuX) rings (analogous to the $(CuCN)_6$ rings in $K[Cu_2(CN)_3]\cdot H_2O$), which accommodate the potassium ions and water molecules.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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