

A paramagnetic Cu(I)/Cu(II)/Zn(II) coordination polymer with multiple CN-binding modes and its solid-state NMR characterization†

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Received (in Columbia, MO, USA) 1st September 2005, Accepted 28th November 2005

First published as an Advance Article on the web 5th January 2006

DOI: 10.1039/b512430a

A Cu(I)/Cu(II)/Zn(II) mixed-valent $[\text{Cu}(\text{en})_2][\text{Zn}(\text{NC})_4(\text{CuCN})_2]$ polymer, which has a 2-D layer structure with six structurally inequivalent cyanides in four distinct bonding modes, has been prepared; structurally informative ^{13}C and ^{15}N MAS NMR spectra of this paramagnetic system are readily observable.

Cyanometallates have been ubiquitous building blocks in coordination polymers for decades because the wide choice of available geometries, compatible metal centers, and excellent bridging ability facilitates the modular and rational design of supramolecular systems.^{1–3} However, compared to heavily utilized octahedral and square planar units, tetrahedral cyanometallates have received scant attention as potential building blocks. Given their intrinsic non-centrosymmetric geometry, potential use in constructing polar crystals with associated non-linear optical properties, and the proven ability of tetrahedral nodes to form porous 3-D diamondoid lattices in organic supramolecular systems,⁴ it is surprising that there are so few reported coordination polymers using tetrahedral $[\text{M}(\text{CN})_4]^{n-}$ building blocks.^{5–13} Continuing our interest in d^{10} -cyanometallate coordination polymers,^{14,15} we hereby report the synthesis and structure of a cyano-Cu/Zn-containing coordination polymer using the d^{10} tetrahedral $[\text{Zn}(\text{CN})_4]^{2-}$ starting material and the ^{13}C and ^{15}N MAS NMR spectra of this paramagnetic compound.

The addition of an aqueous solution of $\text{K}_2[\text{Zn}(\text{CN})_4]$ (1 equiv.) to an aqueous solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 equiv.) containing three equiv. of ethylenediamine (en) produced dark purple crystals of **1** overnight. If the reaction is performed with two or fewer equiv. of en, the dark blue Cu(II) solution completely decolorizes.¹⁶ The IR spectrum of **1** in the νCN region shows six different peaks, indicating an unexpected structural complexity. Indeed, the X-ray crystal structure of **1** reveals the formation of a mixed-valent Cu(I)/Cu(II)/Zn(II) polymer with the formula $[\text{Cu}(\text{en})_2][\text{Zn}(\text{NC})_4(\text{CuCN})_2]$ (**1**) and six inequivalent cyanide groups.¹⁷ The anionic $[\text{Zn}(\text{NC})_4(\text{CuCN})_2]^{2-}$ moiety forms a 2-D puckered sheet and the $[\text{Cu}(\text{en})_2]^{2+}$ cations lie in the cavities between and within the sheets, perhaps templating their formation (Fig. 1).¹⁸ The axial sites of the paramagnetic $[\text{Cu}(\text{en})_2]^{2+}$ are unligated; the closest contact is the *N*-terminus of cyanide CN(10) at 2.73 and 2.95 Å from the two $[\text{Cu}(\text{en})_2]^{2+}$ in the unit cell. Within the anionic cyanometallate layer, the two Cu(I) centers have four-coordinate, distorted

tetrahedral geometries (Fig. 2). All CN^- groups are *C*-bound to the Cu(I) centers, which build a dinuclear $[\text{Cu}_2(\text{CN})_6]^{4-}$ cyanide-bridged cluster within the 2-D array, with a Cu(3)–Cu(4) distance of 2.6458(10) Å – well within the range for reported “cuprophilic interactions”.^{19,20} Three of the cyanides (CN6,7,8) are μ_2 -bridging to a Zn(II) center, and the fourth cyanide (CN5) μ_3 -bridges from two Cu(I) centers to the Zn(II) node. Thus, the Zn(II) metal center is also tetrahedrally coordinated but is *N*-bound to four cyanides rather than to the *C*-bound cyanides as in the starting material $[\text{Zn}(\text{CN})_4]^{2-}$, which does not survive the reaction conditions. The direction of the cyanide binding (*C*-terminus on Zn(II) or Cu(I)) was unambiguously determined by X-ray crystallography (the NMR and IR spectra are also definitive; see below); in the related 3-D zincblende-type $\text{Me}_4\text{N}[\text{ZnCu}(\text{CN})_4]$ polymer, the switch in CN-directionality from Zn–CN–Cu to Zn–NC–Cu could only be

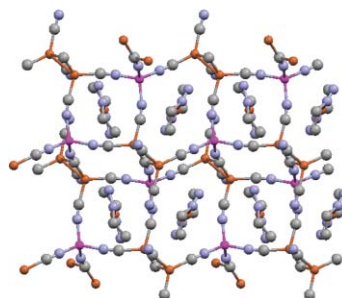


Fig. 1 Polymer **1** viewed along the *b*-axis, showing the anionic 2-D array of $[\text{Zn}(\text{NC})_4(\text{CuCN})_2]^{2-}$ and embedded $[\text{Cu}(\text{en})_2]^{2+}$ cations. Colour scheme: Cu, orange; Zn, pink; C, gray; N, blue. Hydrogen atoms were omitted for clarity.

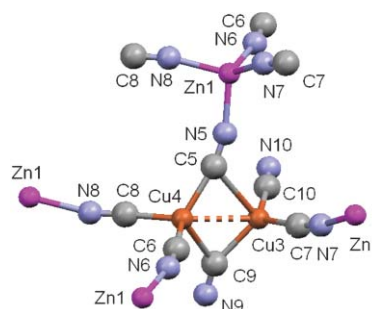


Fig. 2 Detailed structure of anionic layer $[\text{Zn}(\text{NC})_4(\text{CuCN})_2]^{2-}$ with numbering scheme. Selected bond lengths (Å): Zn(1)–N(5) 1.985(4), Zn(1)–N(6) 1.976(4), Zn(1)–N(7) 1.960(4), Zn(1)–N(8) 1.966(4), Cu(3)–C(5) 2.493(5), Cu(3)–C(7) 1.936(4), Cu(3)–C(9) 2.025(5), Cu(3)–C(10) 1.935(5), Cu(4)–C(5) 1.970(5), Cu(4)–C(6) 1.970(5), Cu(4)–C(8) 1.959(5), Cu(4)–C(9) 2.237(5), Cu(3)–Cu(4) 2.6458(10).

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† Electronic supplementary information (ESI) available: full experimental details. See DOI: 10.1039/b512430a

determined by MAS NMR techniques due to disordered metal and cyanide sites.^{12,13} Regarding the two remaining Cu(I)-cyanide ligands in the structure: C9–N9 forms a μ_2 -C-bridge between the two Cu(I) centers, thereby supporting the dicopper(I) cluster, and C10–N10 is terminal to Cu(3). Thus, there are *six* inequivalent CN groups, sporting four different binding modes in one compound! Although various cyanide binding modes¹ have been reported in other systems,²¹ the simultaneous existence of such a diverse range in a single complex is remarkable.

This variation in CN-bonding is reflected in six ν CN peaks at 2136, 2128, 2111, 2089, 2082 and 2067 cm^{-1} ; these are all red-shifted compared to the 2153 cm^{-1} of $\text{K}_2[\text{Zn}(\text{CN})_4]$ but generally blue-shifted relative to $\text{K}_3[\text{Cu}(\text{CN})_4]$ (2075, 2081, 2094 cm^{-1}),³ consistent with the change to C-bound Cu(I) centers, as ν CN peaks usually blue-shift upon binding of the M–CN *N*-terminus to a second metal.^{1,2} For comparison, the ν CN peak for the Cu(I)–CN–Zn(II) moiety in $\text{Me}_4\text{N}[\text{ZnCu}(\text{CN})_4]$ is observed⁶ at 2130 cm^{-1} . Also, the μ_2 -C-bridging cyanides in $(\text{CuCN})_2$ dimer groups in a series of diamine–CuCN polymers²⁰ are found between 2045–2080 cm^{-1} , red-shifted relative to terminal Cu–CN groups in three- or four-coordinate Cu(I) systems. In this light, the lowest vibration for **1** is likely the μ_2 -C-bridging CN9 and the three highest vibrations probably correspond to μ_2 -Cu/Zn bridging units; the terminal and μ_3 -bridging cyanides are difficult to differentiate due to competing red- and blue-shifting factors for the μ_3 -CN5.

At 300 K, the μ_{eff} for **1** is 1.8 μ_{B} and it obeys the Curie Law down to 10 K, consistent with the presence of isolated copper(II) centers. Despite this paramagnetism, ^{13}C and ^{15}N MAS NMR spectra were successfully recorded at natural isotopic abundance (Fig. 3). NMR of paramagnetic solids is rare due to rapid nuclear spin relaxation caused by unpaired electrons, which can broaden the signals of interest to invisibility. This problem can sometimes

be overcome by very fast MAS, which effectively averages dipolar interactions in spite of large paramagnetic shifts and anisotropies.²² Even with an observable spectrum, peak assignments are sometimes complicated by significant shifts from their “normal” positions due to paramagnetic interactions. For example, the CH_2 resonances of the en backbone on the Cu(II) appear at –303 ppm (spinning rate: 20 kHz; $T = 25^\circ\text{C}$), far from their peak position in typical diamagnetic systems. (This peak is significantly attenuated in the echo spectrum shown due to a very short relaxation time; it appears more prominently in the single-pulse Bloch-decay spectrum (see inset, Fig. 3a).) The ^{13}C cyanide centerband region displays three peaks at 122, 165 and 182 ppm, spanning a range much larger than the usual CN region in diamagnetic compounds, but not as shifted as the en carbon, presumably due to the relative isolation of the anionic framework from the paramagnetic Cu(II) center. Based on our work with a series of paramagnetic metal-cyanide compounds,²³ it has become clear that the observed shifts are dominated by their proximity to the paramagnetic ion, with their coordination mode a secondary effect. Hence, the broad resonance at 122 ppm represents both C10 and C9, which have weak interactions with the Cu(II) through the *N*-termini ($r_{\text{CuC}} = 3.9$ and 4.9 Å). Moreover, this signal splits into two distinct peaks at higher temperatures, and exhibits more pronounced temperature dependence than the other peaks. The two other peaks are harder to assign since they are farther from the paramagnetic center, and their bonding modes have not been well characterized by ^{13}C NMR.

The ^{15}N MAS NMR spectrum (Fig. 3b) reveals four CN signals at 231, 243, 246 and 255 ppm in a 1 : 2 : 2 : 1 intensity ratio. The comparatively small spread of ^{15}N chemical shifts with respect to the ^{13}C shifts can be understood in terms of the electron–nucleus dipolar coupling constants. This coupling varies with the inverse cube of the electron–nucleus distance, and directly with their respective magnetogyric ratios. Since the carbon and nitrogen distances to the Cu(II) center are comparable, the larger $\gamma(^{13}\text{C})$ results in dipolar coupling constants roughly twice as large for ^{13}C than for ^{15}N . In fact, the observed ^{15}N CN chemical shifts are not very different from the known range of CN shifts in diamagnetic compounds. The two center peaks with relative intensity of 4 may represent the zinc-bound bridging *N*-bound cyanides (CN5–8), with the two other cyanides (CN9,10) at higher and lower frequencies; however, insufficient ^{15}N NMR data exist to be confident about precise CN assignments. Remarkably, despite being *directly bonded to the paramagnetic Cu(II)*, the ethylenediamine NH_2 peak can be seen at 85 ppm.

The observed peak widths in the ^{13}C and ^{15}N NMR spectra provide information on the cyanide orientation. $^1J(^{13}\text{C}, ^{63/65}\text{Cu})$ ²⁴ are known to range from 300 to 700 Hz.^{25,26} While no resolved quartet is observed, the peak breadth (1200–2000 Hz) is sufficiently large to accommodate such a coupling. By contrast, $^1J(^{15}\text{N}, ^{63/65}\text{Cu})$ ranges from 120 to 250 Hz,^{23,25} and would result in a total quartet breadth of 360–750 Hz. The observed widths (120–160 Hz) are too narrow to permit such one-bond *J*-couplings. On the other hand, ^{67}Zn is only 4% naturally abundant and possesses a spin quantum number of 5/2, hence any hexet produced by coupling would be very low in intensity. From these observations, it can be concluded that all cyanide nitrogens are bound to Zn, and all CN carbons are bound to Cu. The successful acquisition and partial assignment of the NMR spectra in these paramagnetic

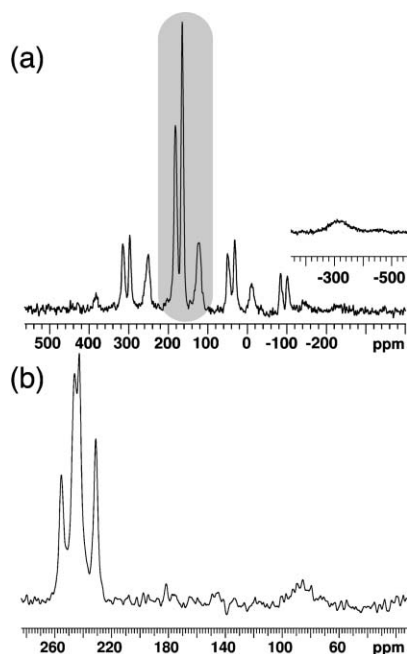


Fig. 3 (a) ^{13}C spin-echo MAS NMR spectrum. Shaded region highlights isotropic peaks; all other peaks are spinning sidebands. The en signal, as obtained from the Bloch-decay spectrum, is displayed in the inset; (b) ^{15}N MAS NMR spectrum of $[\text{Cu}(\text{en})_2][\text{Zn}(\text{NC})_4(\text{CuCN})_2]$ (**1**).

solids suggests that, contrary to conventional wisdom, NMR can be a structurally informative technique for materials containing stoichiometric paramagnetic constituents.

One reason for the paucity of reported d^{10} - $[\text{Zn}(\text{CN})_4]^{2-}$ -based coordination polymers in general may lie with the relatively low stability of aqueous $\text{K}_2[\text{Zn}(\text{CN})_4]$, which has an overall aqueous formation constant $\beta_4 = 3.7 \times 10^{21} \text{ M}^{-4}$. Although not particularly labile ($K_4 = 7.7 \times 10^4 \text{ M}^{-1}$ for $\text{KZn}(\text{CN})_3 + \text{KCN} \rightarrow \text{K}_2[\text{Zn}(\text{CN})_4]^{3,27}$), when $[\text{Zn}(\text{CN})_4]^{2-}$ is reacted with other metals with a higher cyanide-affinity, some or all of its bound cyanide groups are released upon interacting with the other metal present; a related situation exists in the case of the labile $[\text{Ag}(\text{CN})_2]^-$ system.¹⁵ Thus, in the case of Cu(I) with $\text{K}_2[\text{Zn}(\text{CN})_4]$, the $[\text{Cu}(\text{CN})_4]^{3-}$ anion ($\beta_4 = 10^{30.7} \text{ M}^{-4}$)³ readily forms and is incorporated into the final $[\text{ZnCu}(\text{CN})_4]^-$ product with no C-bound Zn(II) remaining,¹² as is the case for **1**. Similarly, the reaction of $\text{K}_2[\text{Zn}(\text{CN})_4]$ with $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and en generates the previously reported²⁸ zinc-free $\text{Ni}(\text{en})_2\text{Ni}(\text{CN})_4$; the β_4 for d^8 - $[\text{Ni}(\text{CN})_4]$ is ca. 10^{10} larger than that for the zinc-analogue and it is also inert once formed.³ Indeed, $[\text{Zn}(\text{pyridine})_2][\text{Zn}(\text{CN})_4]$ is, to our knowledge, the only reported $[\text{Zn}(\text{CN})_4]$ -based polymer; in this case, the companion metal is another Zn(II) center, obviating any competing formation constant or lability issues.⁹

The facile release of cyanide from $[\text{Zn}(\text{CN})_4]^{2-}$ is likely also responsible for the presence of Cu(I) in **1** in the first place. It is well-known that CN^- reacts with aqueous Cu(II) to generate Cu(I) and cyanogen and that this reaction is attenuated by amineligation to Cu(II),^{11,16,29,30} in this light, the mechanism for Cu(I) generation as well as the requirement for three equiv. of en both become clear. This reaction has been used more directly (i.e. addition of CN^- to a Cu(II) solution) to generate cyanide-bridged mixed-valent Cu(I)–Cu(II) coordination polymers in which the sizes of templating neutral molecules or cations play a crucial role in determining the structure and CN-binding modes;^{11,16,30} many cyanocuprate(I) polymers have also been reported from the direct reaction of CuCN/CN^- and nitrogen-based ligands.^{10,20,31} The synthesis of bimetallic **1** is more complicated since, in the reaction of $\text{Cu}(\text{II})/\text{en}$ and $\text{K}_2\text{Zn}(\text{CN})_4$, the latter acts both as an indirect reducing agent (via its CN^-) and as a source of Zn(II) and CN^- units.

In summary, the mixed-valent $[\text{Cu}(\text{en})_2][\text{Zn}(\text{NC})_4(\text{CuCN})_2]$ polymer exhibits exceptionally diverse cyanide binding modes and structurally informative ^{13}C and ^{15}N MAS NMR spectra, despite its paramagnetic nature. It is clear that, in order to rationally utilize $[\text{Zn}(\text{CN})_4]^{2-}$ and related d^{10} -tetracyanometallates as building blocks for coordination polymers, their stability and lability with respect to a proposed companion metal need to be taken into account or controlled. We are currently exploring such methodologies.

Financial support from NSERC of Canada (SK, DBL) is gratefully acknowledged. SK thanks the Canada Foundation for Innovation for infrastructure support. We are grateful to Michael Katz for assistance with the X-ray structural data.

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