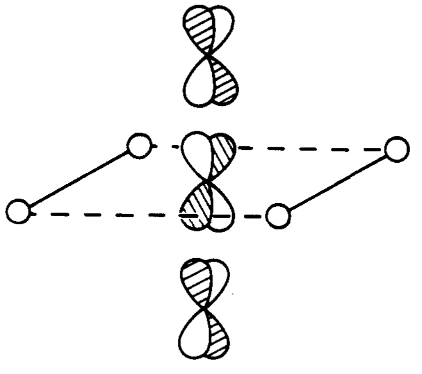
in II, the elongation of the octahedra along the chain (dashed)



II

means that the d_{yz} orbital in particular is most effective in bonding axial Pr to Ru, thereby enhancing the observed Pr–Ru bonding distortion. These distinctions would not enter in with a main-group interstitial.

Recognition of the versatility of interstitially stabilized clusters and condensed clusters continues apace, and the complexity of the synthetic problems is increasing too. For example, just the components Pr, Os, and I are known to produce four ternary cluster and condensed cluster phases. The most important factor determining the stability, or not, of these compounds appears to be the stability of alternate phases. The absence of, for example, a Pr_4I_5Z phase for Z = Re, Ir, Rh, Pt, Fe, or Cu, all of which are known as $Pr_7I_{12}Z$, and of any cluster compound for Z = Ag is accordingly very difficult to explain or correlate. Obviously, theoretical calculations will not provide electronic "explanations" unless the stabilities of all alternatives can also be considered in a reliable way. Even trends with Z when no other cluster phases exist may be complex in origin when binary R–Z components change with the selection of interstitial.

Acknowledgment. Arnold Guloy provided considerable assistance in the calculational part of the research. Jerome Ostensen was instrumental in securing the magnetic susceptibility data. This research was supported by the National Science Foundation, Solid State Chemistry, via Grants DMR-8318616 and -8902954, and was carried out in facilities of Ames Laboratory, DOE.

Supplementary Material Available: Tables of data collection and refinement details and anisotropic thermal parameters for Pr_4I_5Ru (2 pages); a table of structure factor data for Pr_4I_5Ru (6 pages). Ordering information is given on any current masthead page.

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Crystal Structure of a Novel Copper(I) Cyanide Complex with Hexamethylenetetramine, $(CuCN)_3(C_6H_{12}N_4)_2$

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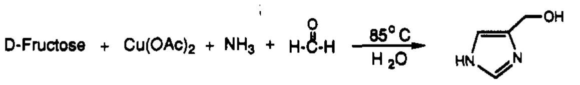
The crystal structure of $(CuCN)_3(C_6H_{12}N_4)_2$ (**1**) consists of infinite chains of alternating copper(I) and CN which are bound into infinite sheets by hexamethylenetetramine. The CN groups appear to be totally end-for-end disordered. The preparation of the complex is unusual by the fact that none of the final constituent species is present in the starting material; i.e. the copper(I) ion, the cyanide ion, and the hexamethylenetetramine are all created in situ. The crystal is monoclinic, space group $C2/c$, with a = 14.812 (10) Å, b = 11.445 (3) Å, c = 14.784 (7) Å, β = 126.78 (5)°, and Z = 4; R was 0.042 for 2065 independent reflections.

Introduction

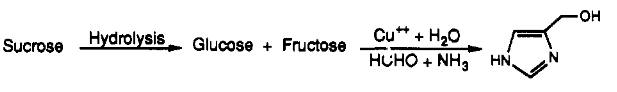
While performing an adaptation of the Parrod synthesis[1-4] of imidazoles (Scheme I), which normally employs hexoses (especially D-fructose) with copper(II) salts, ammonia, and formaldehyde, I inadvertently discovered a novel copper complex. In my adaptation I planned to hydrolyze sucrose to form a mixture of glucose/fructose prior to performing the Parrod synthesis (Scheme II). On one occasion during my preliminary work on this modification, sucrose was inadvertently used in the Parrod synthesis due to an error in the hydrolysis experiment. Instead of the expected olive brown precipitate of the sparingly soluble copper–imidazole complex, colorless needles began separating out of the deep blue aqueous solution shortly after the temperature reached 85–90 °C. The slow production of the crystalline product continued over the 8-h reaction period. That this material contained copper was shown by its dissolution in nitric acid to produce a blue solution that turned to deep blue in the presence of ammonia. Although I knew of no pathway consistent with current theory that would allow a nonreducing sugar such as sucrose to react in a Parrod synthesis, I repeated the reaction with sucrose (omitting the hydrolysis procedure) several times before definitive analytical data became available on the new complex. When elemental analysis confirmed the presence of copper, carbon, hydrogen, and nitrogen and the absence of oxygen, I felt certain that sucrose was not involved in the reaction. I confirmed that theory by isolating the complex from a reaction system that omitted sucrose (Scheme III).

Scheme I



(Isolated as cuprous salt)

Scheme II



(Isolated as cuprous salt)

Scheme III

$$Cu(OAc)_2 + NH_3 + HCHO \xrightarrow[H_2O]{85\ °C} (CuCN)_3(C_6H_{12}N_4)_2$$

The physical properties of the salt were quite interesting. It was found to be very stable under atmospheric conditions and highly insoluble in all the common solvents including water, acetone, lower alcohols, DMSO, DMF, acetonitrile, haloalkanes, aromatics, etc. The infrared spectrum of the salt revealed a strong cyanide vibration (KBr 2075 cm^{-1}, Nujol 2070 cm^{-1}) and a magnetic susceptibility study showed the salt to be diamagnetic, consistent with its absence of color.

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0020-1669/91/1330-1472$02.50/0

It dissolved with decomposition in concentrated nitric acid producing a clear blue solution along with evolution of a gas that was shown subsequently to be formaldehyde.[5] It also dissolved in aqueous sodium cyanide, producing a stable colorless solution. Extraction of the latter solution with chloroform allowed isolation of a white organic solid that proved to be hexamethylenetetramine (HMTA). Comparison of the infrared spectrum (KBr) of the copper salt with the infrared spectrum (KBr) of HMTA showed correlation of more than a dozen peaks.

Elemental analysis of the title compound was in accord with the empirical formula $C_{15}H_{24}Cu_3N_{11}$ or $(CuCN)_3(C_6H_{12}N_4)_2$. The appearance of Cu(I) is easily explained by the well-known reduction of Cu(II) by formaldehyde. The formation of HMTA was to be expected given the presence of ammonia and formaldehyde. The explanation for the production of cyanide ion, however, was not immediately obvious. After some reflection on this matter I now propose the following pathway for cyanide formation:

(a) imine formation

$$NH_3 + HCHO \rightarrow [H_2C{=}NH] + H_2O$$

(b) redox process

$$2Cu^{2+} + [H_2C{=}NH] \rightarrow HCN + 2H^+ + 2Cu^+$$

The copper(I) ion produced here would be in addition to that produced by the reduction of copper(II) ion by formaldehyde.

The stoichiometry of the formation of the complex requires that the following reactions must take place:

(a) HMTA production (2 equiv)

$$12HCHO + 8NH_3 \rightarrow 2C_6H_{12}N_4 + 12H_2O$$

(b) Cu(I) and cyanide production (minimum of 3 equivs)

$$6Cu^{2+} + 3[H_2C{=}NH] \rightarrow 6Cu^+ + 3HCN + 6H^+$$

(c) concomitant imine formation

$$3HCHO + 3NH_3 \rightarrow 3[H_2C{=}NH] + 3H_2O$$

Adding reactions a–c together gives the following overall reaction (disregarding the copper ammonia complex):

$$6Cu^{2+} + 15HCHO + 11NH_3 \rightarrow (CuCN)_3(HMTA)_2 + 15H_2O + 3Cu^+ + 9H^+$$

With Cu(I), cyanide ion, and ammonia together in this reaction mixture, a number of other species could potentially be in competition with the actual product. Among these are the stable soluble complexes $Cu(CN)_2^-$, $Cu(CN)_4^{3-}$, and $Cu(NH_3)_2^+$ and highly insoluble CuCN. Considering the competing equilibria, it is remarkable that **1** separates out during the reaction.

Experimental Section

General Considerations. Commercial chemicals were used without further purification. Infrared spectra were recorded on a Beckman IR 5A spectrometer, and ^1H NMR spectra were recorded on a JEOL C-60HL spectrometer. Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN, unless otherwise indicated.

Preparation of $(CuCN)_3(C_6H_{12}N_4)_2$ (1). a. In the Presence of Sucrose. The reaction flask was cooled in an ice bath during the time the reactants were being mixed together. To concentrated aqueous ammonia (500 mL, 7.68 mol of NH_3) was added $Cu(OAc)_2{\cdot}H_2O$ (199.65 g, 1.00 mol), sucrose (250 g, 0.730 mol), and 200 mL of 37% formalin (2.67 mol of H_2CO). The reaction mixture was placed on a boiling water bath and stirred throughout the reaction process. No effort was made to reduce the losses of volatiles during the reaction. Not long after the reaction mixture reached 85–90 °C, crystal formation began. After 15 h the reaction mixture was filtered with suction through a fritted glass funnel. (Filter paper (cellulose) disintegrates in the presence of the copper–ammonia complex.) While on the filter, the crystals were washed free of the mother liquor with a large quantity of a 1% solution of ammonia. The first crop of white crystals amounted to 10.55 g. After an additional 14.5 h of reaction time another crop of white crystals (7.73 g) was isolated. The total of 18.28 g represents a 19.98% yield based on copper as the limiting reagent. IR (cm^{-1}): KBr 2075 s, 2092 sh; Nujol 2070 s, 2088 sh. Anal. Calcd for $C_{15}H_{24}Cu_3N_{11}$: C, 32.81; H, 4.41; Cu, 34.72; N, 28.06. Found: C, 32.81; H, 4.34; Cu, 33.39, 34.60;[6] N, 28.20.

Table I. Summary of X-ray Diffraction Data

formula	$C_{15}H_{24}Cu_3N_{11}$	D(calcd), g/cm^3	1.817
fw	549.07	temp, K	189
space group	$C2/c$	λ(Mo Kα radiation), Å	0.71069
a, Å	14.812 (10)		
b, Å	11.445 (3)	μ, cm^{-1}	31.88
c, Å	14.784 (7)	R	0.042
β, deg	126.78 (5)	R_w	0.052
V, Å^3	2007 (4)	abs cor factors	0.78–1.16
Z	4	cryst dimens, mm	0.50 × 0.20 × 0.15

b. In the Absence of Sucrose. By use of the above procedure, the following reagents were mixed: $Cu(OAc)_2{\cdot}H_2O$ (19.97 g, 0.100 mol), 50 mL of concentrated aqueous ammonia (0.768 mol of NH_3), 20 mL of 37% formalin (0.267 mol of H_2CO), and 20 mL of distilled water. The reaction was carried out on a boiling water bath without mixing for a 30-h period. The product was collected on a filter and washed as described above, producing nearly white crystals (with a faint blue tint) amounting to 0.64 g (6.99% yield based on copper as the limiting reagent). The IR spectrum of this material was identical with that of the compound made in the presence of sucrose. Found:[7] C, 32.9; H, 4.4; Cu, 31.8; N, 28.4.

Isolation of Hexamethylenetetramine. To a solution of 5.00 g (102 mmol) of NaCN dissolved in 30 mL of distilled water was added 3.972 g (7.23 mmol) of the copper complex. The complex dissolved exothermically giving a colorless solution. After extraction with four 30-mL portions of chloroform, the combined extracts were dried and evaporated to dryness to yield 171 mg (1.22 mmol, 8.44%) of white crystals. The solid did not exhibit a melting point but did sublime at temperatures over 200 °C. The spectra (IR and ^1H NMR) recorded for this substance were identical with the spectra taken of an authentic sample of hexamethylenetetramine.

X-ray Structure Determination. A colorless prismatic crystal of **1** having approximate dimensions of 0.50 × 0.20 × 0.15 mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 22 carefully centered reflections in the range $25.00 < 2\theta < 50.00°$ and were found to correspond to a monoclinic cell. Systematic absences were consistent with space group $C2/c$ (No. 15). The data were collected at 189 K by using the ω scan technique to a maximum 2θ value of 59.9°.

A total of 3845 unique reflections were collected, of which the 2065 with $I > 3.00\sigma(I)$ were used in the calculations. No duplicate reflections were measured. The intensities of three representative reflections measured after every 100 min of X-ray exposure time remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo Kα is 31.9 cm^{-1}. An empirical absorption correction, using the program DIFABS,[8] was applied, which resulted in correction factors ranging from 0.78 to 1.16. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods using the program MITHRIL.[9] The asymmetric unit is half of the formula unit with the other half related by a 2-fold rotation. The non-hydrogen atoms were refined anisotropically. Both CN groups appear to be disordered completely. The atoms at the C and N positions, C1N, C2N, and C3N, were refined by using a 50/50 average of the scattering factors for C and N. Hydrogen atoms were included in the structure factor calculation in idealized positions and were assigned isotropic thermal parameters which were 20% greater than the B_{eq} value of the atom to which they were bonded. Atomic scattering factors and anomalous-dispersion corrections for all

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(5) The gas evolved when **1** dissolved in 7.5% nitric acid was passed into a solution of chromotropic acid dissolved in concentrated sulfuric acid. A positive test for formaldehyde was indicated by the change in color from yellow to violet to deep purple. The results were comparable to those observed with a control experiment using pure formaldehyde gas.

(6) This copper determination was performed by electrodeposition (80 min, 2 A) from a solution prepared by dissolving **1** in 7.5% nitric acid.

(7) We are grateful for this analysis, which was performed by the Analytical Research Department, 3M Central Research Laboratories, St. Paul, MN, while the author was in residence at 3M Central Research Laboratories during a sabbatical leave.

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Table II. Selected Bond Distances (Å) and Bond Angles (deg) for **1**

A. Tetracoordinate Cu (Cu on a 2-fold Axis)			
Cu1–C1N	1.906 (4)	N1–Cu1–C1N	106.3 (1)
Cu1–N1	2.172 (3)	C1N–Cu1–C1NA	132.9 (2)
		C1N–Cu1–N1A	100.9 (1)
		N1–Cu1–N1A	108.1 (2)
B. Tricoordinate Cu			
Cu2–C2N	1.883 (4)	C2N–Cu2–C3N	138.1 (2)
Cu2–C3N	1.867 (4)	N2A–Cu2–C3N	114.6 (1)
Cu2–N2	2.104 (3)	C2N–Cu2–N2A	106.8 (1)
C. C–N Bond			
C1N–C2N	1.161 (5)	Cu1–C1N–C2N	173.4 (3)
C3N–C3NA	1.168 (7)	Cu2–C2N–C1N	175.3 (4)
		Cu2–C3N–C3NA	174.4 (2)

Table III. Positional and Isotropic Thermal Parameters for **1**

atom	*x*	*y*	*z*	*B*(eq), Å^2
Cu1	0	0.39511 (6)	3/4	2.04 (2)
Cu2	0.29483 (4)	0.58173 (5)	1.11288 (4)	2.13 (2)
C1N	0.1232 (3)	0.4617 (3)	0.8886 (3)	2.4 (1)
C2N	0.1913 (3)	0.5031 (4)	0.9758 (3)	2.4 (1)
C3N	0.4509 (3)	0.5961 (3)	1.2184 (3)	2.0 (1)
N1	0.0732 (2)	0.2837 (3)	0.6905 (2)	1.53 (8)
N2	0.2010 (2)	0.3015 (3)	0.6366 (2)	1.64 (9)
N3	0.2025 (3)	0.1243 (3)	0.7300 (3)	2.2 (1)
N4	0.0416 (3)	0.1656 (3)	0.5359 (3)	2.0 (1)
C12	0.1441 (3)	0.3625 (3)	0.6780 (3)	1.5 (1)
C13	0.1474 (3)	0.1895 (3)	0.7697 (3)	1.9 (1)
C14	−0.0109 (3)	0.2290 (3)	0.5790 (3)	1.9 (1)
C23	0.2712 (3)	0.2063 (4)	0.7181 (3)	2.1 (1)
C24	0.1115 (3)	0.2463 (3)	0.5265 (3)	1.9 (1)
C34	0.1155 (4)	0.0750 (3)	0.6188 (4)	2.6 (1)

atoms were taken from ref 10. All calculations were performed by using the TEXSAN[11] crystallographic software package of the Molecular Structure Corp.

The ORTEP plot of the asymmetric unit (plus the next contacts), including the atom labeling scheme, is shown in Figure 1. Figure 2, which views the structure along *b*, shows the infinite chains of –CuCN– bound into infinite sheets by HMTA. Table II shows selected bond distances and angles, and Table III shows positional and isotropic thermal parameters for **1**.

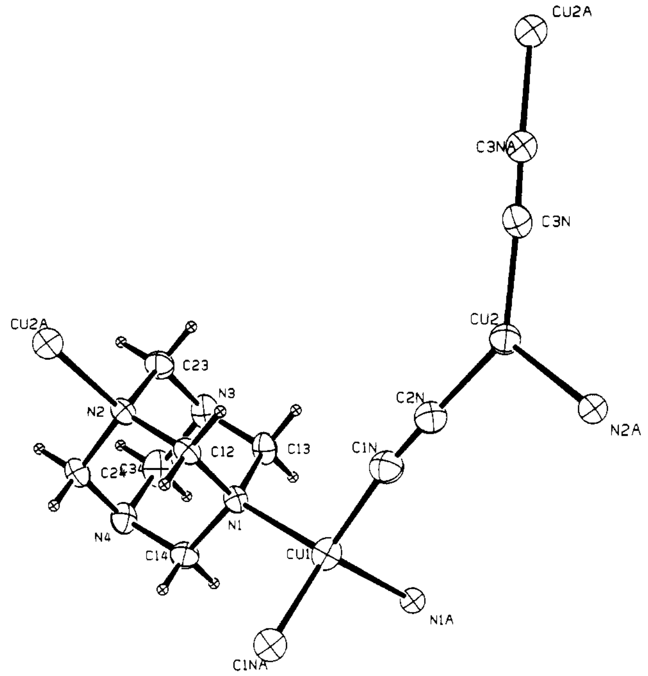

Figure 1. ORTEP plot of the structure of **1**, showing the atom labeling scheme and 50% probability ellipsoids. Hydrogen atoms have been given arbitrary thermal parameters for clarity. The atoms C1N, C2N, and C3N are 50/50 mixtures of disordered C and N atoms.

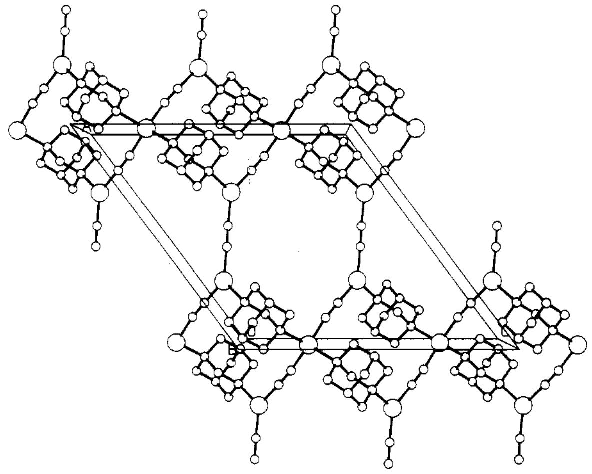

Figure 2. Structure of **1** viewed along *b*. The chains of Cu and CN are approximately parallel to the [101] direction, and these chains are bound into infinite sheets perpendicular to the *b* axis by HMTA bridges. The fragment in Figure 1 is in the same orientation as the equivalent fragment in this figure.

Discussion

The common feature to most of the previously reported copper cyanide complexes is a one-dimensional chain ···Cu–CN–Cu–CN··· where the Cu atoms are either two-coordinate, although this is rare, three-coordinate, or four-coordinate. Examples of the two-coordinate Cu occur in $Cu^{II}Cu^{I}_4(CN)_6(NH_3)_2$,[12] $Cu^{II}Cu^{I}_3(CN)_5(NH_3)_2(H_2O)$,[12] and $(CuCN)_3(H_2O)$.[13] The three-coordinated Cu atoms have a third ligand that is either another cyanide, $KCu(CN)_2$,[14] $NaCu(CN)_2(H_2O)$,[15] $Cu^{II}Cu^{I}_2(CN)_4(NH_3)_3$,[16] or a different base, $CuCN(NHEt_2)$,[17] $CuCN(NEt_3)$,[17] $(CuCN)_2(4\text{-Mepy})_3$[17] (py = pyridine), or $(CuCN)_2(DMSO)_2$.[18] The four-coordinated complexes are similar to the three-coordinated ones except that the Cu is now coordinated to two additional atoms as in CuCN(phen)[17] (phen = 1,10-phenanthroline), $(CuCN)_2(4\text{-Mepy})_3$,[17] and CuCN(dmphen)[19] (dmphen = 2,9-dimethyl-1,10-phenanthroline). In $CuCN{\cdot}N_2H_4$,[20] $KCu_2(CN)_3(H_2O)$,[21] $Cu^{II}Cu^{I}_4(CN)_6(NH_3)_2$,[12] and $Cu^{II}Cu^{I}_3(CN)_5(NH_3)_2(H_2O)$,[12] the same four-coordinated Cu occurs but the other ligands cross-link the one-dimensional copper cyanide polymers to form two-dimensional sheets. In the latter three examples, additional cyanides are the extra ligands. In $Cu^{II}Cu^{I}_2(CN)_4(en)_2(H_2O)$[22] cyanide also increases the coordination number to 4 but the cross-linking leads to a three-dimensional polymer. Two examples, $CuCN{\cdot}NH_3$[23] and $(CuCN)_3{\cdot}H_2O$,[13] are different from

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all of the above in that four-membered Cu_2C_2 rings occur with the C atoms coming from CN groups. The only monomeric example of a CuCN complex is the $Cu(CN)_4^{3-}$ ion in $K_3Cu(CN)_4$.[24] The 1987 reference work edited by Wilkinson[25] contains an excellent review of copper(I) chemistry including a considerable amount of information about copper cyanide complexes.

X-ray Structure Results. In the structure of $(CuCN)_3(HMTA)_2$ reported here, the same sort of ···Cu-CN-Cu-CN··· chains as described in the section above are found, with two-thirds of the Cu atoms three-coordinate and one-third four-coordinate. The three-coordinate coppers have a N from HMTA as the third ligand, and the four-coordinate coppers have two N atoms from two different HMTA molecules as the third and fourth ligands. This results in the one-dimensional HMTA molecules as the third and fourth ligands. This results in the one-dimensional CuCN chains being bound into a two-dimensional sheet by the HMTA molecules. The binding between chains utilizes, in repeating order, a four-coordinate Cu atom followed by two three-coordinate Cu atoms, which give rise to a repeating sequence of ring structures consisting of a Cu_6 ring followed by a Cu_4 ring.

It can be seen from the data in Table II for the three-coordinate copper that the bond distances and bond angles are quite similar to comparable copper(I) complexes. For example, three-coordinate copper atoms in double stalts[14,15,21] typically have Cu-C(cyanide) distances of 1.90-1.92 Å and Cu-N distances of 1.99-2.05 Å, whereas three-coordinate copper atoms in CuCN·L complexes (where L is a nitrogen base)[17] exhibit Cu-C distances of 1.86-1.90 Å, Cu-N distances of 1.89-2.00 Å, and Cu-L distances of 2.07-2.21 Å. Compound **1**, at the three-coordinate copper Cu2, shows Cu-C(N) distances of 1.867 (4) and 1.883 (4) Å and a Cu-L distance of 2.104 (3) Å. Turning to four-coordinate copper, the majority of previously reported complexes[17,19,20] have Cu-C(cyanide) distances of 1.88-1.99 Å, Cu-N distances of 1.99-2.00 Å, and Cu-L distances of 2.11-2.17 Å. In compound **1**, at the four-coordinate copper Cu1, the Cu-C(N) distances ae 1.905 (4) and 1.906 (4) Å and the Cu-L distance is 2.172 (3) Å. The ring structures within **1** show similarities to ring structures contained in other copper cyanide complexes . The $(CuCN)_6$ ring in $K[Cu_2(CN)_3]\cdot H_2O$[21] resembles the Cu_6 ring exhibited by **1**, and the Cu_4 ring in $CuCN\cdot N_2H_4$[20] resembles the Cu_4 ring in **1**.

Acknowledgment. I was fortunate to receive guidance during this project from specialists in coordination chemistry and/or X-ray crystallography since I am working outside of my specialty of organic synthesis. I am indebted to Professor Doyle Britton of the Department of Chemistry at the University of Minnesota for determining the X-ray crystal structure and also for reading and providing helpful comments on this paper. I also owe thanks to Professor Louis H. Pignolet, also of the University of Minnesota, for encouragement and for performing the magnetic susceptibility experiment. I am grateful to the following Macalester students who assisted with the experimental work on this project: Larry M. Rue, Michael W. Fordice, Jerry K. Larson, Bruce Williams, and Larry W. Dahl. I also wish to thank Professor Wayne C. Wolsey of Macalester College for encouragement and helpful discussions.

Supplementary Material Available: Figure 3 of Cu_4 and Cu_6 rings in **1**, a stereoview of the crystal packing, and tables of hydrogen atom coordinates, anisotropic thermal parameters, bond distances and angles, least-squares planes, and intermolecular distances for **1** (11 pages); a listing of observed and calculated structure factors of **1** (15 pages). Ordering information is given on any current masthead page.

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A New Hydrogen-Bonded Dinuclear Complex Involving Copper(II) Ions in a Pseudotetrahedral N_3O Environment: Molecular and Crystal Structure and Magnetic and Spectroscopic Properties

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The preparation, spectroscopic and magnetic properties, and crystal structure of $[CuLpy]_2\cdot 0.5H_2O$ are described (L stands for the dideprotonated form of 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracil and py stands for pyridine). Crystals are monoclinic, of space group $P2_1/c$, with cell constants a = 9.740 (3) Å, b = 19.258 (7) Å, c = 10.361 (3) Å, β = 108.57 (3)°, and Z = 2. The structure was solved and refined to R = 0.059. The structure comprises discrete dinuclear entities resulting from pairwise association of mononuclear fragments via two extended bridging networks Cu-O-C-O···H-N-Cu, which comprise long hydrogen bonds. The geometry of each CuN_3O chromophore is intermediate between square planar and tetrahedral. The magnetic study points to an antiferromagnetic (singlet) ground state. The magnitude of the magnetic interaction is discussed on the basis of structural data.

Introduction

Formation of dinuclear complexes between mononuclear transition-metal fragments via hydrogen bonding was first suggested by Yoneda and Kida[1] for the series of complexes $[Co_2(Eta)_3(EtaH)_3]X_3$, where EtaH represents 2-aminoethanol and Eta the related anion. The occurrence of this bonding scheme was definitively established by structural studies performed on various copper(II), nickel(II), and cobalt(III) complexes involving amino and/or imino alcohols as ligands.[2-7] In these complexes

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