1685 (1974)] establishes a *decrease* in Fe–C distance of 0.026 (8) Å from $Fe(CN)_6^{3-}$ to $Fe(CN)_6^{4-}$, ascribed by these authors to an increase in π bonding in the Fe(II) state. This should be the final entry in Table VII and is consistent with the interpretation presented here.

Registry No. $[Fe(H_2O)_6](NO_3)_3 \cdot 3H_2O$, 60803-54-5.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Spectral Properties of Sodium Dicyanocuprate(I) Dihydrate. A Planar Polymeric Three-Coordinated Copper(I) Anion

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The structure of sodium dicyanocuprate(I) dihydrate, $NaCu(CN)_2 \cdot 2H_2O$, has been determined crystallographically. The space group is $P2_1/c$ with $a = 3.598$ (3) Å, $b = 19.655$ (4) Å, $c = 8.515$ (5) Å, $\beta = 103.35$ (5)°, $Z = 4$, $V = 585.9$ Å^3, and a density of 1.97 g/cm^3. Based on 714 unique Weissenberg reflections, the structure was refined by full-matrix least-squares techniques to give $R = 0.058$ and $R_w = 0.064$. The structure is characterized by the existence of a polymeric $[Cu(CN)_2^-]_\infty$ chain having the symmetry of the glide plane c, with copper atoms in a trigonal-planar coordination. On each copper are fixed one terminal cyano group, Cu–C = 1.902 (7) Å, and two bridging groups, Cu–C = 1.904 (9) Å and Cu–N = 1.992 (8) Å. The sodium atom has an octahedral cis geometry formed by three oxygens and three nitrogens from terminal cyano groups. Two different types of water molecules are present. The Raman and infrared spectra as well as the reflectance spectrum are given.

Introduction

The cyanocuprate(I) ions $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$ exist as such in aqueous solution,[1] but only the geometrical structure of the last anion is known in the potassium compound $K_3Cu(CN)_4$[2] where it is tetrahedral. The main characteristic of the other known cyanocuprates is the existence of polymeric anions containing bridging cyano groups. The coordination number around copper(I) is 3 (as in $KCu(CN)_2$[3]) or 4 (as in the mixed-valence complex $[Cu^I(CN)_2]_2[Cu^{II}(en)_2H_2O]$[4]). However very few data are available on the sodium salts of cyanocuprates and only ref 5 points out the two salts $NaCu(CN)_2 \cdot 2H_2O$ and $Na_2Cu(CN)_3 \cdot 3H_2O$ but without any structural information; on the other hand in the case of potassium salts a compound with a ratio CN:Cu = 3 is unknown[6] and the complex $KCu(CN)_2$ with a ratio CN:Cu = 2 is polymeric. Therefore it was interesting to investigate these two sodium salts and we report here the preparation, structure, and spectral properties of sodium dicyanocuprate(I) dihydrate. We hoped to find the monomeric anion $Cu(CN)_2^-$ on the basis of the following considerations: (1) It is a hydrated salt and the cation $Na(OH_2)_n^+$ has a size that compares much more favorably with the anion than does the "naked" potassium ion. (2) The measured density (1.97 g/cm^3) is lower than those of polymeric potassium cyanocuprates (2.38 g/cm^3 for $KCu(CN)_2$ and 2.39 g/cm^3 for $KCu_2(CN)_3 \cdot H_2O$) and very close to the value found for the monomeric potassium tetracyanocuprate (2.02 g/cm^3). (3) For the CN:Cu ratio lower than 3, the solubility of the sodium cyanocuprates in water (where the ions are monomeric) is higher than for the potassium salts.[7] (4) The mononuclear planar tricyanocuprate ion $Cu(CN)_3^{2-}$ exists in solution as well as in the solid compound $Na_2Cu(CN)_3 \cdot 3H_2O$.[8]

Unfortunately our purpose was not successful and we found a new polymeric structure which we will describe herein.

Experimental Section

Preparation. Copper cyanide (2.25 g, 25 mmol) was dissolved in an aqueous solution (15 ml) of sodium cyanide (1.95 g, 40 mmol). After one night of cooling, a precipitation of needles occurred. The

Table I. Final Atomic Coordinates and Equivalent Isotropic Temperature Factors

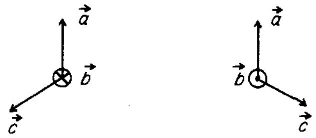
Atom	*x*	*y*	*z*	*B*, Å^2
Cu	0.1457 (4)	0.1830 (1)	0.2155 (2)	2.1
Na	0.3211 (8)	0.0533 (2)	0.6523 (4)	1.9
O(1)	0.4770 (34)	0.0660 (4)	0.9368 (10)	6.3
O(2)	0.8063 (15)	0.3643 (3)	0.1384 (8)	2.2
N(1)	0.1724 (19)	0.0362 (3)	0.3404 (9)	2.0
C(1)	0.1630 (21)	0.0917 (4)	0.2905 (10)	1.4
N(2)	0.1286 (23)	0.2483 (4)	0.3928 (10)	2.7
C(2)	0.1409 (27)	0.2243 (4)	0.0127 (11)	2.3
H(1)	0.77 (4)	0.167 (6)	0.55 (2)	5[a]
H(2)	0.83 (4)	0.173 (7)	0.74 (2)	5[a]
H(3)	0.69 (4)	0.417 (7)	0.55 (2)	5[a]

[a] Hydrogen atoms were assigned a fixed isotropic temperature factor of 5.0.

$NaCu(CN)_2{\cdot}2H_2O$ crystals were filtered and dried on a filter paper. The thermogravimetric analysis showed the loss of the two water molecules at 50 °C.

Spectra. The spectra were recorded with the following spectrometers and methods: infrared spectrum, Perkin-Elmer Model 521 with Nujol mulls and KBr pellets; Raman spectrum, Coderg Model T 800 with an ionized argon laser (λ 4880 Å) and a rotating cell; electronic spectrum, Beckman DK 2 A fitted with a reflectance attachment.

Crystal Data. A first examination under a polarizing microscope revealed that the crystals were twinned, and attempts to obtain single crystals failed. The needles were studied with the De Jong and Bouman method and the systematic absences ($h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$) led to the space group $P2_1/c$; the spindle axis of the needles corresponds to the $\vec{a}$ axis. The accurate determination of the parameters was done with a Weissenberg camera, using Ni-filtered Cu Kα_1 and Kα_2 radiations (λ 1.54051 and 1.54433 Å). The calibration was performed with a superimposed powder pattern of aluminium. The cell constants at 20 °C are $a = 3.598$ (3) Å, $b = 19.655$ (4) Å, $c = 8.515$ (5) Å, $\beta = 103.35$ (5), and $V = 585.9$ Å^3. Standard deviations on the last significant digits, here and in the tables, are given in parentheses. The experimental density determined by the flotation method in a mixture of carbon tetrachloride and 1,2-dibromoethane is 1.97 (1) g/cm^3 compared to the calculated value, 1.979 g/cm^3, assuming $Z = 4$. The twinning can be seen in the reciprocal space by the mixing of the two networks with different intensities. The orientation of one network related to the other in the real space is (the axis system is right handed)



This orientation corresponds to a rotation of π around the $\vec{a}$ axis and the twinning plane contains the $\vec{a}$ and $\vec{b}$ axes. For the intensity measurements we have disregarded the spots of the weaker network. For the very few cases where the reflections for the two twin fragments coincided, we have substracted the contribution (calculated by comparison of the intensities of the two networks) of the reflection corresponding to the weaker network.

Collection of Intensity Data. A crystal (0.4 × 0.3 × 0.2 mm) was mounted on an integrating Nonius Weissenberg camera and the $0kl$ to $3kl$ levels were recorded with the multiple-film method. The intensities of the reflection spots were measured with a Macbeth Model TD 504 densitometer. The levels were first approximately scaled by considering the exposure times, and for the last computations, a scale factor was used for each level which was rescaled after each cycle of refinements. A total of 714 independent measurable reflections were collected in the range $0° \leq \theta \leq 75°$ and were corrected for the Lorentz and polarization effects. No absorption corrections have been made ($\mu = 53.8$ cm^{-1}).

Structure Determination and Refinement. The structure was solved and refined using standard Patterson, Fourier, and least-squares methods.[9] In all least-squares refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure amplitudes and w is the weight. The agreement indices are defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors for neutral Cu, C, N, and O and for Na^+ were used and corrections for anomalous dispersion were made for Cu.[10]

The position of the copper atom was determined unambiguously from a three-dimensional Patterson function ($R = 0.40$) and all of the remaining nonhydrogen atoms were found in a subsequent Fourier synthesis; successive cycles of block-diagonal least-squares refinements with isotropic thermal parameters converged at $R = 0.082$. The computations were made initially with unit weights and at this stage we used the following weighting scheme for which the quantity $\sum w(|F_o| - |F_c|)^2$ showed nondependance on $|F_o|$: $w = 1$ for $|F_o| < 50$ (647 reflections) and $w = (2500F_o^{-2})^2$ for $|F_o| > 50$.

The Fourier synthesis did not permit us to distinguish between the carbon and nitrogen atoms and for the preceding computations we used the most likely hypothesis in considering the two nearest atoms from the copper as carbon atoms. In reversing this hypothesis, after four cycles of refinement R became 0.088 and appreciable changes for the isotropic thermal parameters of these two atoms were observed.[11] Thus, the first identification of the atoms was the good one.

By allowing anisotropic thermal parameters for all nonhydrogen atoms, further cycles of full-matrix least-squares refinements converged to $R = 0.067$ and $R_w = 0.100$. A difference synthesis showed three of the four hydrogen atoms and two cycles of refinement of the hydrogen positions with isotropic thermal factors of 5.0 decreased the R to 0.065 and R_w to 0.087. After rejection of seven reflections, which did not satisfy the criterion $w^{1/2}(|F_o| - |F_c|) \leq 10$, the final R was 0.058 and $R_w = 0.064$. The estimated standard deviation of an observation of unit weight, calculated from $|\sum w(|F_o| - |F_c|)^2/(m - n)|^{1/2}$, was 1.80 for 707 reflections (m) and 81 variables (n). The ratio of the largest shift to standard deviation in the last refinement was 0.065 for the nonhydrogen atoms and 0.5 for the hydrogen atoms. The highest peak in the final difference Fourier synthesis has a height of 0.5 e Å^{-3}. A listing of the observed and calculated structure factors, as well as the indexed powder diffraction data, is available as supplementary material. Tables I and II list the final positional and thermal parameters.

Description of the Structure and Discussion

The bond distances and bond angles are given in Table III and the coordination around copper and sodium is illustrated in Figures 1 and 2. The unit cell is shown in Figure 3.

Coordination of Copper. The first characteristic of this structure is the absence of the monomeric $Cu(CN)_2^-$ ion and the existence of polymeric chains $[Cu(CN)_2^-]_\infty$ as in the potassium salt. Here the symmetry of the chain is that of the glide plane c; the chains are parallel to the c axis. The trigonal coordination of the copper atom (Figure 1) is exactly planar; the sum of the three angles is 360.0°. Two kind of cyano groups exist—bridging and terminal—but the C–N and Cu–C bond distances are not significantly different. The bond angles CuCN are almost linear.

Table II. Final Anisotropic Thermal Parameters (β_{ij})[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.052 (1)	0.001 17 (3)	0.0075 (2)	0.0004 (2)	0.0066 (4)	0.000 36 (8)
Na	0.021 (2)	0.001 44 (8)	0.0086 (5)	−0.0009 (3)	0.004 (1)	−0.000 3 (2)
O(1)	0.231 (15)	0.002 9 (3)	0.008 (1)	0.002 (2)	0.001 (4)	−0.001 2 (5)
O(2)	0.031 (5)	0.001 38 (15)	0.011 (1)	0.0011 (7)	0.003 (2)	−0.000 6 (3)
N(1)	0.023 (6)	0.001 4 (2)	0.010 (1)	−0.0002 (8)	0.002 (2)	−0.000 1 (4)
C(1)	0.018 (6)	0.001 3 (2)	0.007 (1)	−0.0007 (9)	0.008 (2)	−0.000 7 (4)
N(2)	0.070 (8)	0.001 5 (1)	0.009 (1)	0.002 (1)	0.009 (3)	0.000 2 (4)
C(2)	0.062 (8)	0.001 3 (2)	0.008 (1)	−0.001 (1)	0.007 (3)	0.000 2 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

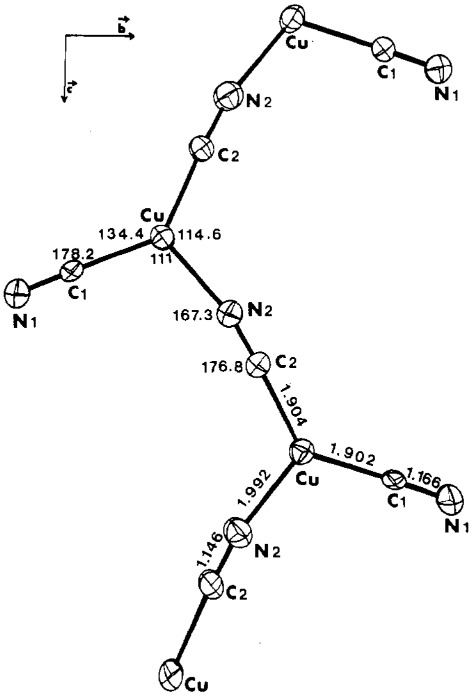


Figure 1. The polymeric chain $[Cu(CN)_2^-]_\infty$ and the coordination around copper.

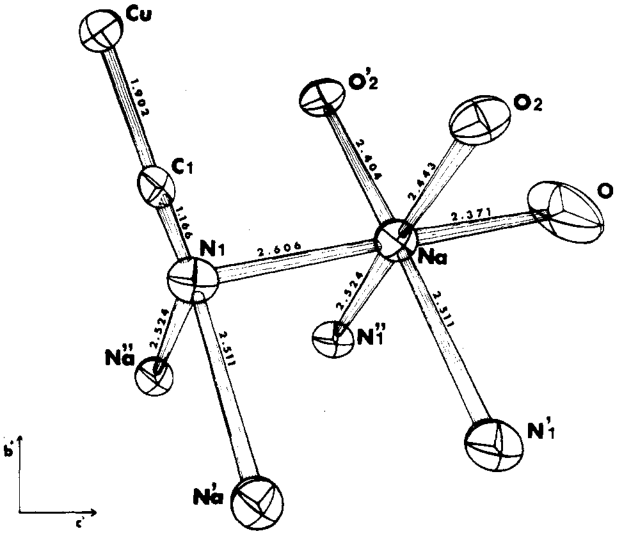


Figure 2. Coordination around sodium and nitrogen.

Table III. Interatomic Distances (Å) and Bond Angles (deg)

Distances

Cu–C(1)	1.902 (7)	Na–N′(1)	2.511 (7)
Cu–C(2)	1.904 (9)	Na–N″(1)	2.524 (7)
Cu–N(2)	1.992 (8)	N(1)–C(1)	1.166 (10)
C(1)–N(1)	1.166 (10)	N(1)–Na′	2.511 (7)
C(2)–N(2)	1.146 (12)	N(1)–Na″	2.524 (7)
Na–O(1)	2.371 (8)	O(1)· · ·O(1)	2.801 (12)
Na–O(2)	2.443 (6)	O(1)–H(3)	1.135
Na–O′(2)	2.404 (6)	O(2)–H(1)	0.956
Na–N(1)	2.606 (8)	O(2)–H(2)	1.101

Relations between Equivalent Atoms

$$\left.\begin{array}{l} O(2) \rightarrow O'(2) \\ N'(1) \rightarrow N''(1) \\ Na' \rightarrow Na'' \\ Na \rightarrow Na''' \end{array}\right\} \text{translation } \vec{a}$$

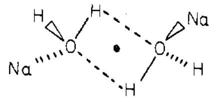
$$\left.\begin{array}{l} N(1) \rightarrow N'(1) \\ Na \rightarrow Na' \end{array}\right\} \text{inversion and translation } \vec{a}$$

Angles

C(1)–Cu–C(2)	134.4 (4)	O(1)–Na–O(2)	88.7 (3)
C(1)–Cu–N(2)	111.0 (4)	O(1)–Na–O′(2)	88.6 (3)
C(2)–Cu–N(2)	114.6 (4)	O(2)–Na–O′(2)	95.9 (2)
Cu–C(1)–N(1)	178.2 (5)	C(1)–N(1)–Na	103.5 (5)
Cu–C(2)–N(2)	176.8 (6)	C(1)–N(1)–Na′	134.6 (5)
Cu–N(2)–C(2)	167.3 (6)	C(1)–N(1)–Na″	128.3 (5)
N(1)–Na–O(2)	93.5 (3)	Na–N(1)–Na′	92.6 (2)
N(1)–Na–O′(2)	91.0 (3)	Na–N(1)–Na″	95.0 (2)
N(1)–Na–N′(1)	87.5 (3)	Na′–N(1)–Na″	91.2 (2)
N(1)–Na–N″(1)	85.0 (3)	Na–O(1)–H(3)	147.2
N(1)–Na–O(1)	177.8 (4)	Na–O(1)–O(1)	105.9 (4)
N′(1)–Na–N″(1)	91.2 (3)	H(3)–O(1)–O(1)	89.0
N′(1)–Na–O(2)	86.2 (3)	Na–O(2)–Na‴	95.9 (2)
N′(1)–Na–O(1)	92.9 (3)	Na–O(2)–H(1)	120.9
N′(1)–Na–O′(2)	177.5 (3)	Na–O(2)–H(2)	109.5
N″(1)–Na–O(1)	92.8 (3)	Na‴–O(2)–H(1)	114.3
N″(1)–Na–O′(2)	86.7 (3)	Na‴–O(2)–H(2)	119.4
N″(1)–Na–O(2)	177.1 (3)	H(1)–O(2)–H(2)	98.4

Coordination of Sodium. Figure 2 shows the classical octahedral coordination[12] around the sodium atom, with a cis geometry for the three nitrogens and the three oxygens. The nitrogens come only from the terminal cyano groups; the bridging CN groups have only a very weak interaction with the sodium atom (distance >3.5 Å). The sodium atoms are the links between the polymeric chains and realize the cohesion of the crystal in addition with the electrostatic forces.

Water Molecules and Hydrogen Bonds. There is a notable difference between the two water molecules. One of these molecules O(2) is bonded to the two sodium atoms and the two hydrogen atoms (H(1) and H(2)) show no peculiarity (Figure 3). The other water molecule O(1), for which only one hydrogen atom (H(3)) was found, is bonded to one sodium atom and by hydrogen bonds to the equivalent water molecule as shown in Figure 3 (distance 2.801 Å). We have two symmetrically equivalent molecules which are hydrogen bonded, and this is unusual. The two unlocalized hydrogen atoms between the two water molecules can present two extreme possibilities of bonding. One is a disordered hydrogen bond for which the inversion center is destroyed; the other is a twofold bridging hydrogen bond keeping the H atoms related by the inversion center as shown by



Comparison with $KCu(CN)_2$.[3] Although the two compounds exhibit polymeric chains with three-coordinated copper, the structures are nevertheless very different. In the $KCu(CN)_2$ structure several differences appear: the polymeric chain is along a twofold screw axis; the three-coordination of copper is not planar; the bond distance Cu–N in the chain is longer (2.05 vs. 1.99 Å) and the bond angle CuNC is quite distorted from linearity (139°); the coordination around the potassium ion is not simple and it is the whole cyano group which is coordinated rather than only the nitrogen atom.

Spectral Studies

The infrared spectrum, given in Figure 4, confirms well the presence of two different water molecules. The first molecule O(2) has the OH stretching frequencies at 3600 and 3530 cm^{-1} and for the other molecule O(1), the hydrogen bond is clearly apparent (3390 and 3190 cm^{-1}). The CN stretching vibrations show two bands in the infrared (2126 and 2113 cm^{-1}) and in the Raman spectra (2124 and 2112 cm^{-1}) (Table IV) but this is not conclusive for two different cyano groups. Indeed, if we neglect the interactions between the CN stretching vibrations and the vibration in the polymeric chain in considering only the $Cu(CN)_2^-$ group, with a C_{2v} symmetry we can apply the intensity relationship given by Cotton:[13] $I_{sym}/I_{asym} = \cot^2(\theta/2)$, where I denotes the integrated intensity of the band and θ the angle between the two cyano groups. A value of 133.5

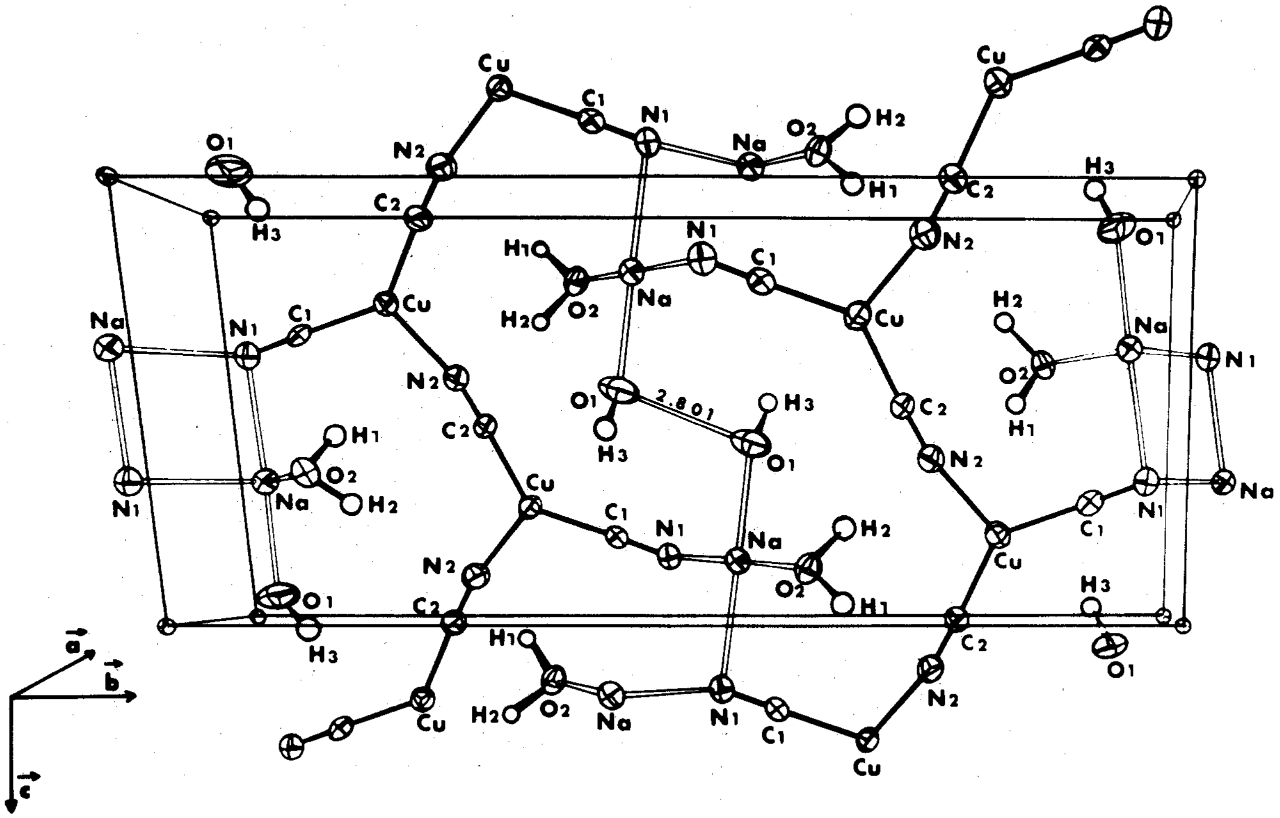


Figure 3. Perspective view of the unit cell showing the packing of the polymeric chains and the "hydrogen bond", indicated by bond distance (2.801 Å).

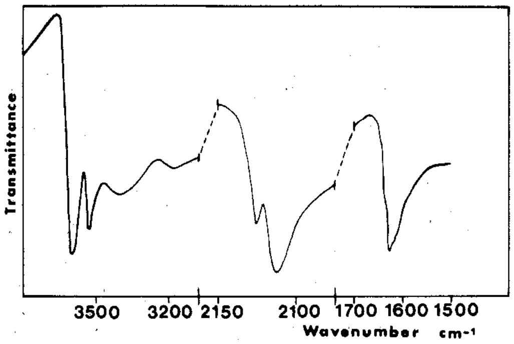


Figure 4. Infrared spectrum of $NaCu(CN)_2{\cdot}2H_2O$.

Table IV. Raman Spectrum of $NaCu(CN)_2{\cdot}2H_2O$

Freq, cm^{-1} (rel intens)	Assignment
3601 (2.7), 3533 (3.5)	OH str of O(2)
2124 (100), 2112 (43)	Sym and asym CN str
2070 (1.2)	Isotopic ^{13}C CN str
1628 (0.6)	H_2O bend
450 (1.8), 394 (1), 336 (0.8), 323 (3.5), 304 (0.5)	
297 (0.4), 260 (11.8), 190 (1.5), 176 (12.3), 143 (8.7)	
100 (0.8), 84 (20.4), 46 (5.4)	

± 4.5° for θ is found, which is in agreement with the crystallographic angle.

The reflectance spectrum (Figure 5) shows three bands at 320, 255, and 205 nm and differs from the $KCu(CN)_2$ spectrum (330, 280, and 210 nm) and from the aqueous solution spectrum of the sodium compound with the typical bands of the monomeric ion $Cu(CN)_2^-$.[14]

Conclusion

The structure is a new example of trigonal copper(I) coordination, but like most three-coordinated copper(I) compounds the metal is in a polymeric network with bridging ligands. The problem of the existence of the monomeric ion $Cu(CN)_2^-$ in the solid state then remains open.

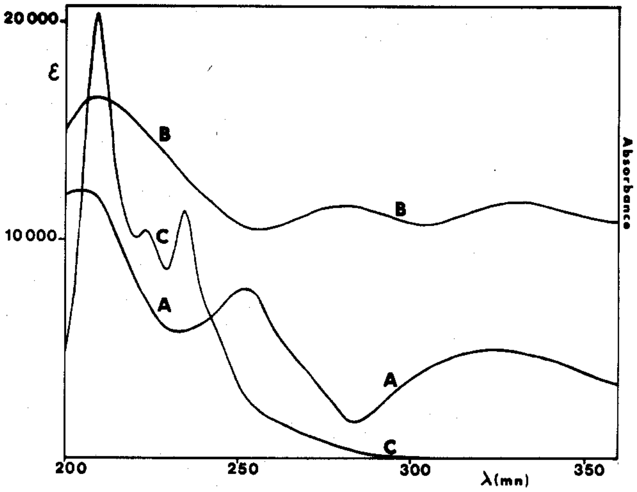


Figure 5. Absorbance spectra of $NaCu(CN)_2{\cdot}2H_2O$ (A), of $KCu(CN)_2$ (B), and of an aqueous solution of $NaCu(CN)_2{\cdot}2H_2O$ (C). The molar absorbance scale is only for spectrum C.

Registry No. $NaCu(CN)_2{\cdot}2H_2O$, 60949-74-8.

Supplementary Material Available: Indexed powder diffraction data and a listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

References and Notes

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(8) The structure of the compound $Na_2Cu(CN)_3{\cdot}3H_2O$ is under investigation in our laboratory.

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Synthesis and Properties of Bis[*N*-R-(5-chloro-α-phenyl-2-hydroxybenzylidene)aminato]copper(II) Complexes and Crystal and Molecular Structures of the Derivatives with R = *n*-Butyl and R = Isobutyl (Two Structural Isomers)

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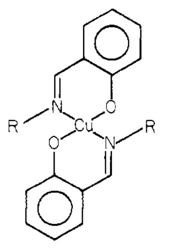
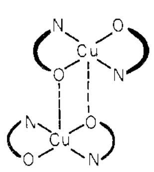
A series of bis[*N*-R-(5-chloro-α-phenyl-2-hydroxybenzylidene)aminato]copper(II) complexes, with R = alkyl (or benzyl), has been prepared and studied using magnetic, spectroscopic, and crystallographic techniques. Unlike the *N*-methyl derivative, the compounds are magnetically normal and are presumed to consist of monomeric distorted planar (R = H, ethyl, *n*-propyl, isobutyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, benzyl) or distorted tetrahedral (R = isopropyl, *sec*-butyl, cyclohexyl) species, usually having the alkyl groups pointing to *opposite* sides of the approximate O_2N_2 ligand plane ("trans"). The *n*-butyl and isobutyl complexes are exceptional and their crystal structures were determined by single-crystal x-ray diffraction using counter techniques. The isobutyl complex exists in two distinct crystalline forms, green and red. The green isomer has the isobutyl groups pointing to the *same* side of the approximate CuO_2N_2 plane ("cis"). The *n*-butyl complex, which is dark green, has the same arrangement of the *n*-butyl groups. The red isomer of the isobutyl complex contains two crystallographically independent molecules, each having the isobutyl groups trans. The metal environment of the *n*-butyl complex (cis) is much closer to tetrahedral (dihedral angle 31°) than the green isobutyl (also cis) complex (14.5°). Crystal data for the *n*-butyl complex: space group $P2_1/c$, $Z = 4$, $a = 9.026$ (4) Å, $b = 19.52$ (3) Å, $c = 17.88$ (2) Å, $\beta = 94.46$ (7)°, $V = 3142$ Å^3, $R = 3.6\%$, 2624 reflections. Crystal data for the green isomer of the isobutyl complex: space group $P\bar{1}$, $Z = 2$, $a = 10.964$ (5) Å, $b = 11.490$ (5) Å, $c = 12.861$ (7) Å, $\alpha = 99.52$ (5)°, $\beta = 97.07$ (5)°, $\gamma = 97.59$ (6)°, $V = 1566$ Å^3, $R = 3.8\%$, 2309 reflections. Crystal data for red isomer of isobutyl complex: space group $P1$, $Z = 2$, $a = 8.900$ (2) Å, $b = 9.991$ (2) Å, $c = 17.998$ (3) Å, $\alpha = 102.54$ (4)°, $\beta = 94.61$ (4)°, $\gamma = 92.49$ (2)°, $V = 1554$ Å^3, $R = 4.8\%$, 5194 reflections.

Introduction

Copper(II) complexes with bidentate Schiff base ligands such as salicylaldimines can vary from four-coordinated distorted planar[2-10] and distorted tetrahedral[2-4,11,12] monomers, **1**, to square-pyramidal weakly linked dimers,[13] **2**. In all of the four-coordinated species for which definitive studies have been made, the nitrogen substituents have been observed to be on opposite sides of the approximate O_2N_2 plane formed by the four ligand donor atoms.



1



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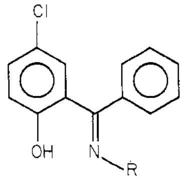

3

The complexes of *N*-R-(5-chloro-α-phenyl-2-hydroxybenzylidene) ligands (5-chloro-2-hydroxybenzophenone imines, cbp, **3**) are expected to have similar structures, but with greater steric constraints in the ligands, as in the bidentate salicylaldimine and related complexes. Structural features should be elucidated by the same physical techniques, such as spectroscopy in the ligand field region for the gross metal geometry and low-temperature magnetic moments for the oxygen-bridged metal dimers. More detailed structural information, such as a new type of isomerism in which both alkyl groups point to the same side of the O_2N_2 plane, are best obtained by x-ray studies. Thus x-ray structural data are given here for the red and green isomers of the (*i*-Bu)cbp complex and of the one form of its closest chemical relative, the *n*-butyl complex. This isomerism is of interest to compare with the monomer–dimer isomerism of the *N*-methylsalicylaldimine complex,[13] the green (known dimeric[14])–red (presumed monomeric) isomerism of the *N*-Me-cbp complex, and the diamagnetic (known planar monomeric)–paramagnetic (presumed polymeric) *N*-Me-cbp complex of nickel(II).[14] The isomerism in the other complexes implies molecular association and hence a change in the magnetic properties, while the