(11) All calculations were carried out on a CDC-6400 computer. The programs DATCO3, ABSORB, and DATRON from the X-Ray 71 package were used for preliminary treatment of data. The full-matrix least-squares program, CUDLS, group least-squares program, GROUPLS, Fourier programs, SYMFOU, and least-squares program, PALS, were written locally by J. S. Stephens, J. S. Stephens, J. S. Rutherford, and P. G. Ashmore, respectively. Diagrams were prepared using the program ORTEP by C. K. Johnson, U.S. Atomic Energy Commission Report ORNL 3794, Revised June 1965.
(12) $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$.
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Existence of the Monomeric $Cu(CN)_3^{2-}$ Anion in the Solid State. Molecular Structure and Disorder of Sodium Tricyanocuprate(I) Trihydrate

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The crystal and molecular structure of sodium tricyanocuprate(I) trihydrate, $Na_2Cu(CN)_3 \cdot 3H_2O$, has been determined by a three-dimensional X-ray crystallographic analysis. The crystal system is hexagonal with $a = 25.256$ (5) Å, $c = 7.188$ (3) Å, $d = 1.81$ g cm^{-3}, and $Z = 18$, but an abnormal distribution of the intensities (very weak for $h - k \neq 3n$ or $l \neq 2n$) reveals a disorder along the z axis. Thus the structure was solved by Patterson and Fourier methods in a subcell which is considered to be ideally disordered over one part of the atomic positions ($a = 14.582$ Å, $c = 3.594$ Å, and $Z = 3$; space group $P6_3/m$). The least-squares refinements led to the final discrepancy factors $R = 0.044$ and $R_w = 0.052$ for 669 independent reflections ($I \geq 2\sigma(I)$) collected with a CAD 4 Nonius diffractometer. The main characteristic of this structure is the existence in the solid state of the simple mononuclear planar tricoordinated species $Cu(CN)_3^{2-}$ (point group D_{3h}). One set (2/3) of these ions forms a three-dimensional ordered network (Cu–C = 1.929 (3) Å; C–N = 1.133 (5) Å) with the sodium cations in which channels appear parallel to the ternary axes; anions of the second type (1/3) occur in a disordered manner (Cu–C = 1.946 (13) Å; C–N = 1.160 (19) Å) in these channels. The nitrogen atoms of the ordered species are in contact with three sodium cations and these sodium cations are octahedrally surrounded by nitrogen and oxygen (water) atoms. The water molecules are also of two types, ordered and disordered, and exhibit a hydrogen bond (O···O = 2.732 (14) Å). Raman and infrared spectra show also the presence of two types of $Cu(CN)_3^{2-}$ anion and are interpreted on the basis of these results.

Introduction

In a preceding paper[1] we have described the structure of sodium dicyanocuprate(I) dihydrate, $NaCu(CN)_2 \cdot 2H_2O$, and the main characteristic of this compound was the absence of the $Cu(CN)_2^-$ ion but the presence of a polymeric anionic chain with a planar three-coordinated copper(I). Thus it can be noted that up to now all cyanocuprates with ratios CN/Cu ≤ 2 are polymeric.

The species corresponding to a ratio CN/Cu = 3, viz., the complex ion $Cu(CN)_3^{2-}$, displays a higher thermodynamic stability, in aqueous solution, than the two other known ions.[2]

$$Cu(CN)_2^- + Cu(CN)_4^{3-} \rightleftarrows 2Cu(CN)_3^{2-} \qquad \log K = 3.82$$

The structure of this ion may be planar (D_{3h})[3] or pyramidal (C_{3v}) with or without a coordinated water molecule.[4] As pointed out by Wicholas and Wolford,[5] the isolation of $Cu(CN)_3^{2-}$ in the solid state would be of particular significance in that it would represent sterically the simplest example of three-coordinated copper(I). These authors have isolated a mixed-valence compound $[Cu(en)_3][Cu(CN)_3]$ but did not yet report the structure. We have prepared the sodium salt $Na_2Cu(CN)_3 \cdot 3H_2O$ for which we describe the structure and discuss the vibrational spectra herein.

Experimental Section

Preparation. Copper cyanide (2.25 g, 25 mmol) was dissolved in 50 mL of water containing sodium cyanide (2.5 g, 50 mmol) and the solution was evaporated to 15 mL. After several days in a desiccator white shaggy needles appeared and were dried on filter paper. To obtain single crystals suitable for an X-ray study, the same solution was slowly evaporated at room temperature. Anal. Calcd for $Na_2Cu(CN)_3 \cdot 3H_2O$: Cu, 26.30; Na, 19.03; H_2O, 22.4. Found: Cu, 25.9; Na, 18.6; H_2O, 23.3.

Table I. Experimental Data for $Na_2Cu(CN)_3 \cdot 3H_2O$

(A) Crystal Data

Laue symmetry group 6/*m*	
$a = 25.256$ (5) A	$d_{exptl} = 1.81$ g cm^{-3}
$c = 7.188$ (3) A	$d_{calcd} = 1.818$ g cm^{-3}
$V = 3970.7$ A	$Z = 18$
Mol wt 241.62	$\mu(\lambda_{Mo}) = 26$ cm^{-1}

(B) Measurement of Intensity Data

Radiation: Mo Kα (λ 0.710 69 A)
Monochromator: graphite
Scan technique: θ–2θ
Scan length: $1 + 0.2 \tan\theta$
Reflections measd: $+h$, $+k$, $+l$ for $2\theta < 66°$
Takeoff angle: $3 + 0.5 \tan\theta$
Max scanning time: 1 min
Prescan speed: 20°/min
Check reflections: three, remeasured after every 50 reflections ($00\bar{4}$, $\overline{142}$, $\overline{662}$) with a standard deviation less than 2% for the intensities

The thermogravimetric analysis showed the loss of two water molecules at 46 °C and a third at 91 °C.

Spectra. See ref 1.

Crystal Data and Collection of Intensities. Examination under a polarizing microscope revealed extinction in the direction of the spindle axis of the hexagonal prismatic needle. A preliminary study with the de Jong and Bouman method showed that the crystal belongs to the hexagonal system and revealed an abnormal distribution of the intensities with all tested crystals. Accurate unit cell parameters (Table IA) as well as reflection intensities (Table IB) were measured at room temperature with a Nonius CAD 4 automated diffractometer. The

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Table II. Distribution of the Square of the Mean Structure Factor

	Sum per level			$h-k=3n$			$h-k\neq 3n$		
level	n[a]	n'[b]	$\overline{F^2}$[c]	n[a]	n'[b]	$\overline{F^2}$[c]	n[a]	n'[b]	$\overline{F^2}$[c]
*hk*0	680	167	16.4	227	162	*144.6*	453	5	0.0006
*hk*1	671	125	0.3	224	75	1.4	447	50	0.08
*hk*2	654	364	31.4	218	171	*128.2*	436	193	7.5
*hk*3	631	195	1.6	210	89	4.5	421	106	0.67
*hk*4	592	267	14.7	197	161	*81*	395	106	1.6
*hk*5	541	161	1.3	180	69	2.8	361	92	0.78
*hk*6	477	188	5.1	159	112	*23.5*	318	76	0.94
*hk*7	402	54	0.17	134	29	0.5	268	25	0.06
*hk*8	319	89	1.2	106	61	*5.8*	213	28	0.21
*hk*9	227	5	0.003	76	2	0.005	151	3	0.003
*hk*10	119	10	0.059	40	3	*0.05*	79	7	0.06

[a] n: number of reflections in each part of reciprocal space. [b] n': number of reflections with intensities $I > 2\sigma(I)$. [c] The structure factors of the rejected reflections were taken equal to 0. Italicized values correspond to the reciprocal supercell.

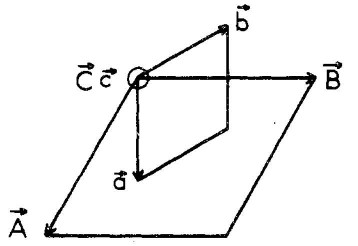

Figure 1. Correspondence between the small cell ($\vec{a}$, $\vec{b}$, $\vec{c}$) and the big cell ($\vec{A}$, $\vec{B}$, $\vec{C}$): $\vec{a} = {}^2/_3\vec{A} + {}^1/_3\vec{B}$, $\vec{b} = -{}^1/_3\vec{A} + {}^1/_3\vec{B}$, $\vec{c} = {}^1/_2\vec{C}$.

crystal (0.4 × 0.2 × 0.2 mm) was mounted in a Lindeman tube with the c axis (elongated axis) coincident with the ϕ axis.

From 5313 independent reflections measured, 1625 had intensities $I \geq 2\sigma(I)$ where I is the net intensity and $\sigma(I)$ the standard deviation. Lorentz and polarization corrections were applied but absorption corrections were not made. The high number of rejected reflections (70%) is due to the abnormal intensity distribution.

Distribution of Intensity Data and Disorder. The photographic studies as well as the diffractometer data show that the hkn levels with n odd are systematically weak; moreover each level also has an abnormal intensity distribution. The details of this distribution are given in Table II and it appears that the weak reflections correspond to $h - k \neq 3n$ *or* $l \neq 2n$. Moreover, for the $hk0$ level, the reflections with $h - k \neq 3n$ are systematically absent. These facts can be explained by a disorder in the crystal and the weak reflections correspond to a *partial ordering* giving a superstructure with the unit cell given above; this unit cell will be called the big cell.

On the $hk0$ level, the superstructure reflections are absent; so the projection of the structure on the xy plane remains ordered; the disorder takes place only along the z axis.

The 670 strong reflections ($h - k = 3n$ *and* $l = 2n$)—viz., 70% of the explored reciprocal space—determine a superreciprocal space with the same symmetry and, consequently, a subcell (called small cell) with the following parameters: $a = 14.582$ Å, $c = 3.594$ Å, $Z = 3$.

This small cell represents a completely disordered structure. The correspondence between the small and the big cell is given on Figure 1. Thus the translations defining the small cell are pseudotranslations of the lattice.

Structure Determination

Patterson Map. A three-dimensional Patterson map was calculated with all the reflections (viz. in the big cell) and showed clearly that the translations ($\vec{a}$, $\vec{b}$, $\vec{c}$) of the small cell are consistent for more than 80% of the unit cell content (89% for the translation $\vec{c}$). Besides these particular peaks, the section $z = {}^1/_4$ of the Patterson map shows several peaks (Cu–Cu, Cu–C, and Cu–N) which can correspond to a trigonally planar $Cu(CN)_3^{2-}$ species (Figure 2). This can be interpreted by a particular arrangement of the copper atoms, in a model consistent with the small cell. Thus we can see that already at this stage, the structure of the $Cu(CN)_3^{2-}$ ion is practically resolved.

In a first step we have resolved the structure only in the small cell,[6] this supposes that a part of the asymmetric unit must be completely or ideally disordered.

Choice of Space Group. The model deduced from the Patterson function is consistent with the space groups $P6_3$, $P\bar{6}$, and $P6_3/m$. The

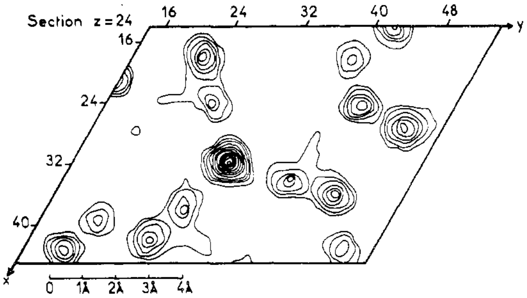

Figure 2. Section $z = {}^1/_4$ of the Patterson map (the quotas are given in ${}^1/_{96}$th of the cell parameters).

systematic absences ($00l'$, $l' \neq 2n$)[7] led to a 6_3 axis and the centrosymmetric statistical tests favor a centric structure.[8] These facts and the planarity of the $Cu(CN)_3^{2-}$ ion are in agreement with the $P6_3/m$ space group.

Refinements of the Structure. The structure was solved by classical 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]

A first Fourier synthesis calculated with the preceding model (2 Cu of 3, $R = 0.44$) revealed the positions of the cyanide groups, the sodium atoms, and a part of the water oxygen atoms; all these atoms are completely ordered and located on the mirror planes (special position h) ($R = 0.34$). The third copper atom was found on a subsequent Fourier map, in special position e; this position corresponds to an ideal disorder over four equivalent sites ($R = 0.20$). After the last atoms had been found in disordered positions, successive cycles of block-diagonal least-squares refinements with isotropic thermal parameters and with unit weights, converged at $R = 0.14$, $R_w = 0.13$, and $R_F = 2.6$[11] (669 reflections and 27 parameters). The same computations made for the space groups $P\bar{6}$ and $P6_3$ led to less satisfactory results.[12]

Then the following weighting scheme was used: $w = 1$ for $|F_o| \leq 30$ and $w = (30/|F_o|)^2$ for $|F_o| > 30$, and by allowing anisotropic thermal parameters for all atoms, further cycles of full-matrix least-squares refinements converged at $R = 0.044$, $R_w = 0.052$, and $R_F = 0.78$ (54 parameters). No reflection was rejected and we considered the cyanide group bonded by the carbon atom to the copper.[1] The ratio of the largest shift to standard deviation in the last refinement was 0.20 for the position parameters and 0.22 for the thermal parameters (z and β_{33} of the C(2) atom). The highest positive peaks in the final difference synthesis (0.44 and 0.42 e/Å^3) may be interpreted as hydrogen atoms bonded to the ordered water oxygen atom O(1), but refinements of these two positions led to very short oxygen–hydrogen bond lengths[13] and were not taken into consideration; the highest negative peaks (−0.71 e/Å^3) are near the ordered copper atoms (above and below). Such a strong lowering of the agreement indices between the isotropic and anisotropic models shows an important anisotropy of vibration along the z axis (Table IV), but it may

Table III. Final Atomic Coordinates and Equivalent Isotropic Temperature Factors[a]

Atom	x	y	z	B, Å^2
Cu(1)	0.3333	0.6667	0.2500	2.46
Na	0.3730 (2)	0.9799 (2)	0.2500	4.20
O(1)	0.8646 (3)	0.5944 (3)	0.2500	3.95
N(1)	0.5066 (3)	0.9002 (3)	0.2500	4.32
C(1)	0.4430 (3)	0.8136 (3)	0.2500	3.05
Cu(2)	0.0	0.0	0.4145 (8)	2.89
O(2)	0.2703 (7)	0.0563 (8)	0.2500	4.18
N(2)	0.2310 (9)	0.0429 (11)	0.3914 (48)	3.48
C(2)	0.1448 (9)	0.0268 (9)	0.4169 (46)	3.40

[a] Here and in the other tables standard deviations of the last significant digits are given in parentheses.

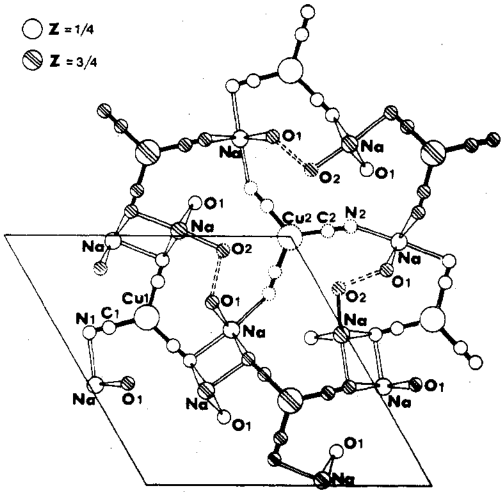

Figure 3. Small cell showing the two types of $Cu(CN)_3^{2-}$ ions: full lines, covalent bonding; hollowed lines, electrostatic bonding; dotted lines, hydrogen bonding. For clarity the disordered atoms are pictured in only one of their possible positions.

be also a consequence of the disorder or of absorption.

A listing of the observed and calculated structure factors, the indexed powder diffraction data, and a listing of all the observed structure factors in the big cell are available as supplementary material. Tables III and IV list the final positional and thermal parameters and the root-mean-squared displacements (RMSD).

Interpretation of the Weak Reflections. Several attempts to localize the atoms in an ordered fashion in the big cell have failed, probably because the order is only partial. A Patterson map was computed using only the weak reflections; the interatomic peaks appearing on this map correspond only to the atoms that contribute to these weak reflections. The results show that the disordered atoms of the small cell are responsible for the weak reflections through a partial ordering.

By careful examination of the two Patterson maps, we observe a small disorder of the sodium atoms (on the z axis), but the computations including this disorder do not converge toward a best model.

Recently another disordered structure has been published[14] and the authors define, as we, two cells, a big cell ideally ordered (with $Z = 4$) and a small cell completely disordered over four positions ($Z = 2$) and the structure is resolved in the small cell.

Description of the Structure and Discussion

Bond distances and bond angles are given in Table V. The content of unit cell is illustrated in Figure 3, and Figure 4 shows a stereoview of the packing with the same orientation.[15]

Coordination around the Copper Atoms. Figure 3 shows the existence of trigonally planar monomeric $Cu(CN)_3^{2-}$ anions with practically D_{3h} symmetry (the site symmetry is C_{3h} for the $Cu(1)(C(1)N(1))_3$ group and C_3 for the $Cu(2)(C(2)N(2))_3$ group). There are three complex anions per cell and these ions are of two types.

Two $Cu(1)(C(1)N(1))_3^{2-}$ totally ordered and lying in the mirror planes ($z = {}^1/_4$ and ${}^3/_4$); these ions are strongly bonded to the sodium cations by electrostatic forces. Each nitrogen atom N(1) is bonded to three sodiums (see Figure 5), one in the plane, one over the plane, and one under the plane (which is not pictured in Figure 3); thus each complex ion is surrounded by nine sodium cations and these bondings shape up

Table IV. Final Anisotropic Thermal Parameters[a] and Root-Mean-Square Displacements (Å)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\langle u \rangle$[b]
Cu(1)	0.00272 (2)	0.00272	0.0756 (8)	0.00136	0.0	0.0	0.148, 0.148, 0.222[c]
Na	0.0040 (1)	0.0041 (1)	0.132 (3)	0.0013 (1)	0.0	0.0	0.170, 0.210, 0.293
O(1)	0.0034 (2)	0.0056 (2)	0.117 (4)	0.0023 (2)	0.0	0.0	0.162, 0.216, 0.277
N(1)	0.0042 (2)	0.0038 (2)	0.143 (6)	0.0015 (2)	0.0	0.0	0.171, 0.204, 0.306
C(1)	0.0031 (2)	0.0034 (2)	0.099 (5)	0.0017 (2)	0.0	0.0	0.151, 0.167, 0.255
Cu(2)	0.00378 (7)	0.00378	0.074 (3)	0.00189	0.0	0.0	0.175, 0.175, 0.221
O(2)	0.0042 (6)	0.0049 (6)	0.138 (13)	0.0028 (5)	0.0	0.0	0.167, 0.202, 0.300
N(2)	0.0033 (7)	0.0046 (7)	0.108 (14)	0.0022 (6)	−0.003 (2)	0.001 (2)	0.152, 0.192, 0.269
C(2)	0.0042 (7)	0.0031 (6)	0.107 (14)	0.0018 (5)	−0.002 (3)	0.001 (2)	0.154, 0.183, 0.268

[a] The anisotropic thermal parameters enter the expression for the structure factor in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] These values correspond to the root-mean-square displacements of the atom along the three principal axes of its vibration ellipsoid (minor, median, and major, respectively). [c] The major principal axis is parallel to the $\vec{c}$ translation for all the atoms.

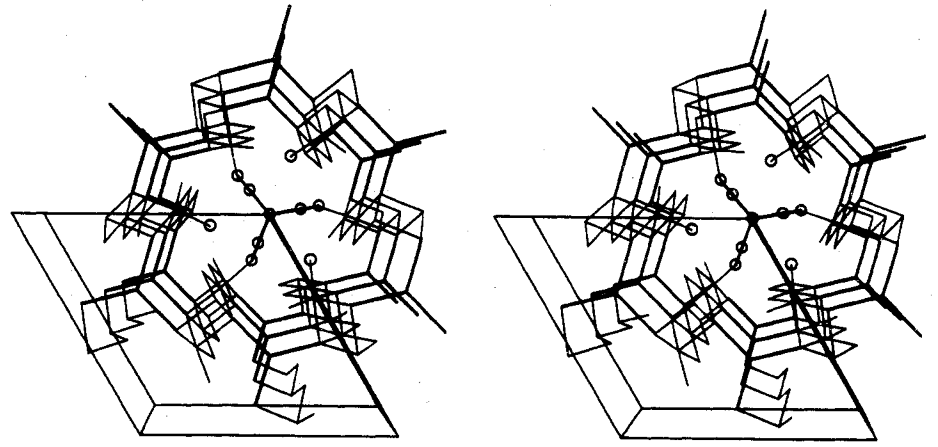

Figure 4. Stereoview of the packing showing one channel along the $\vec{c}$ axis. Thick lines correspond to covalent bonds and thin lines to electrostatic ones. Circles represent only the disordered atoms in one of the possible positions. For labels see Figure 3.

Table V. Selected Interatomic Distances (Å) and Bond Angles (deg) for $Na_2Cu(CN)_3 \cdot 3H_2O$

(A) Copper Coordination			
Cu(1)-C(1)	1.929 (3)	Cu(2)-C(2)	1.946 (13)
C(1)-N(1)	1.133 (5)	C(2)-N(2)	1.160 (19)
Cu(1)-C(1)-N(1)	179.2 (3)	Cu(2)-C(2)-N(2)	175.2 (9)
		C(2)-Cu(2)-C(2)	120.0 (6)
(B) Nitrogen Coordination			
N(1)-Na	2.723 (6)	N(2)-Na	2.700 (16)
N(1)-Na′	2.510 (2)	Na′-N(1)-Na′	91.5 (2)
C(1)-N(1)-Na	96.6 (3)	C(2)-N(2)-Na	151.9 (9)
C(1)-N(1)-Na′	132.4 (3)		
Na-N(1)-Na′	96.0 (2)		
(C) Sodium Coordination			
Na-N(1)	2.723 (6)	Na-O(2)	2.268 (14)
Na-N′(1)	2.510 (2)	Na-N(2)	2.700 (16)
Na-O(1)	2.405 (2)	O(1)-Na-N′(1)	85.8 (1) cis
O(2)-Na-O(1)	90.6 (3)	O(1)-Na-N′(1)	175.2 (2) trans
O(2)-Na-N′(1)	93.6 (3)	N′(1)-Na-N′(1)	91.5 (2)
O(2)-Na-N(1)	176.6 (3)	N′(1)-Na-N(1)	84.1 (2)
O(1)-Na-O(1)	96.7 (2)	N(2)-Na-O(1)	77.4 (3)
O(1)-Na-N(1)	91.7 (2)	N(2)-Na-N(1)	168.4 (4)
(D) Water Coordination			
O(1)-Na	2.405 (3)	O(1)· · ·O(2)	2.732 (14)
O(2)-Na	2.268 (14)	Na-O(2)-O(1)	106.5 (3)
Na-O(1)-Na	96.7 (1)		
Na-O(1)-O(2)	118.4 (3)		

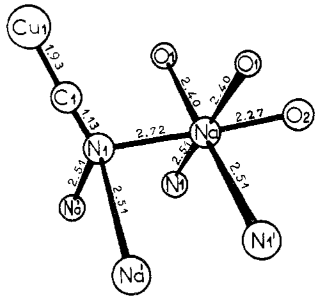

Figure 5. Coordination around nitrogen N(1) and sodium. For half of the sodium cations, the oxygen atoms O(2) are substituted by the nitrogen atoms N(2) (Na–N(2) = 2.70 Å).

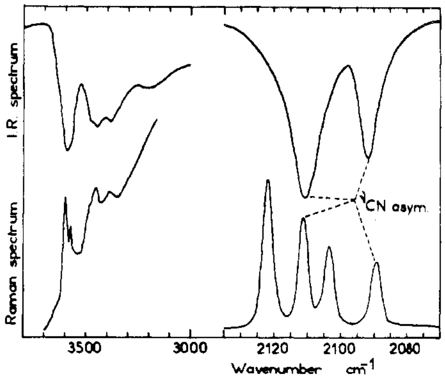

Figure 6. Infrared and Raman spectra of $Na_2Cu(CN)_3 \cdot 3H_2O$.

Table VI. Vibrational Spectra of $Na_2Cu(CN)_3 \cdot 3H_2O$ Frequency in cm^{-1} (relative intensity)

Infrared	Raman	Assignment
3590, 3450	3600, 3580	OH str
3380, 3200	3470, 3400	
2110	2122, 2111	CN str
2090	2103, 2090	
1640, 1630		Very weak H_2O bend
1615		
	400 (6), 380 (3), 364 (40), 330 (6), 250 (65), 232 (55), 165 (100), 116 (12), 90 (25), 70 (65)	

Table VII. Assignment of the CN Stretching

	$Cu(CN)_3^{2-}$ ordered	$Cu(CN)_3^{2-}$ disordered	$Cu(CN)_3^{2-}$ in aqueous solution
ν_{CN}(sym), cm^{-1}	2122 (R)	2103 (R)	2108 (R)
ν_{CN}(asym), cm^{-1}	2111 (R, IR)	2090 (R, IR)	2094 (R, IR)

Intensity Ratio: ν_{CN}(ordered)/ν_{CN}(disordered)

Raman	Infrared
1.9 ± 0.1	2.0 ± 0.1

a three-dimensional network in which channels appear parallel to the ternary axes. This network is clearly illustrated in Figure 4 with one of such channel.

In the second type, anions pile up in these channels in a disordered fashion over four positions; there is one such anion per cell and this anion is bonded to only three sodium ions.

As we can see, the estimated standard deviations for the ordered atoms are smaller than for the disordered ones and were best refined. The ordered CuCN group is linear (CuCN angle 179.2 (3)°) and thus the $Cu(CN)_3^{2-}$ anion point group is D_{3h}. We note a slight distortion of the CuCN group for the disordered anion (CuCN angle = 175.2 (9)°).

This planar trigonal coordination of copper(I) in solid state is quite rare for mononuclear complexes and appears most frequently in polynuclear complexes such as $KCu(CN)_2$ or $NaCu(CN)_2 \cdot 2H_2O$. The other known examples of such a coordination number for copper(I) show the planar CuS_3 group[16] and the CuN_3 group[17] for identical coordinated ligands; for monodentate ligands we can also cite the CuP_2Br group[18] (monomeric) and the Cu‖Br_2 group[19] (polymeric) where ‖ denotes an ethylenic bond.

Nitrogen and Sodium Coordination. Each ordered nitrogen atom N(1) is bonded to three sodium cations in a tetrahedral geometry (N(1)–Na = 2.51 and 2.72 Å); on the other hand, the nitrogen atoms N(2) are bonded only to one sodium (N(2)–Na = 2.70 Å). The sodium cation shows a classical octahedral structure (Figure 5) similar to the one found in $NaCu(CN)_2 \cdot 2H_2O$,[1] with the three nitrogens N(1) and the three water molecules in cis configuration. Because of the disorder, half of the sodium cations are bonded to the nitrogen N(2) in place of the atom O(2). It can be noted that the longest sodium–nitrogen distance corresponds to the smallest sodium–oxygen distance in the trans position.

Water Molecules. The water molecules are also of two types. The first one O(1) is ordered and bonded to two sodium atoms, and the second one O(2), disordered, is bonded most strongly to one sodium cation. There is a hydrogen bond between these two oxygen atoms, as can be seen by the O(1)–O(2) bond length (2.73 Å). These hydrogen bonds are pictured in dotted lines in Figure 3.

Spectral Studies. Figure 6 gives the infrared and Raman spectra for the high frequency range and Table VI lists the band frequencies. In the range over 3000 cm^{-1}, and characteristic of the water molecules (O–H stretching band), the bands at 3200 and 3400 cm^{-1} show well the existence of "hydrogen bonds" between the water molecules. In the range 2000–2200 cm^{-1} corresponding to the stretching vibrations of the cyano groups, we find four bands in the Raman spectrum and two bands in the infrared one. But for a $Cu(CN)_3^{2-}$ complex ion with a D_{3h} symmetry, there are two stretching vibrations of the cyano groups: the first, symmetric (A'_1) is active only in Raman and the second, asymmetric (E′) is active in Raman as well as in infrared. Thus these spectra show the existence of two types of $Cu(CN)_3^{2-}$ ions, each type being characterized by two Raman bands and one infrared band. Moreover, the ratio of these two anion types, deduced from the intensities of the bands, is near 2 (Table VII), and these

Table VIII. Cu–C and C–N Bond Lengths for Some Cyanocuprates

Compound	Bonding around copper	Cu–C, Å	C–N, Å
$K_3Cu(CN)_4$[a] monomeric	4 Cu–C	1.99 and 2.01	1.13
$Na_2Cu(CN)_3 \cdot 3H_2O$ monomeric	3 Cu–C ordered	1.93	1.13
	3 Cu–C disordered	1.95	1.16
$NaCu(CN)_2 \cdot 2H_2O$[b] polymeric	2 Cu–C and 1 Cu–N	1.90	1.15 and 1.17
$KCu(CN)_2$[a] polymeric	2 Cu–C and 1 Cu–N	1.92	1.13 and 1.15
$KCu_2(CN)_3 \cdot H_2O$[a] polymeric	2 Cu–C and 1 Cu–N	1.89	1.14 and 1.15
	1 Cu–C and 2 Cu–N	1.87	1.17

[a] Reference 21. [b] Reference 1.

data agree very well with the structural results. Thus we can attribute unambiguously, the two highest frequencies to the ordered anion and the two lowest frequencies to the disordered one. For the disordered species, that is for the species which are more free in the network, we observe that the ν_{CN} frequencies are near the corresponding values for the same ion in aqueous solution. The transition from the disordered anion to the ordered one corresponds to an increase of nearly 20 cm^{-1} of the stretching vibrations ν_{CN}.

The reflectance spectrum shows the following bands (in nm): 323, 308 (shoulder), 277, 247, and 226.

Conclusion

This compound is a new example of the coordination number three which is fairly uncommon in monomeric species. It is also the second example of mononuclear cyanocuprate(I) ions known in the solid state, the first one being the classical tetrahedral tetracyanocuprate(I) $K_3Cu(CN)_4$. Another example of a three-coordinated cyanide complex is provided by the mercuric complex $Hg(CN)_3^{2-}$ which was found to be trigonal planar in the cesium compound $CsHg(CN)_3$.[20]

We can make a comparison between Cu–C and C–N bond distances in the known cyanocuprate salts; their values (Table VIII) show that the C–N distance remains constant, but for the Cu–C bond length we observe that this length decreases in a normal fashion as the number of copper–carbon linkages decreases: the $Cu(CN)_3^{2-}$ ion occupies an intermediate position between $Cu(CN)_4^{3-}$ and the polymeric anions.

If we consider now an isoelectronic metal, planar three-coordination has only been observed with nickel(0) in the presence of neutral "soft" ligands like phosphines, phosphites, and olefins,[22] but to our knowledge no anionic species has ever been reported.

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Registry No. $Na_2Cu(CN)_3 \cdot 3H_2O$, 66358-72-3.

Supplementary Material Available: Indexed powder diffraction data, observed and calculated structure factors, and listing of all the observed structure factors in the big cell (18 pages). Ordering information is given on any current masthead page.

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(7) There remains an ambiguity for the 001 reflection which is very weak, but not totally absent (21 in intensity vs. 7260 for the 002 reflection) like the reflections 003 and 005.

(8) The results of the statistical tests are the following: Wilson ratio: centric, 0.637; acentric, 0.785; result, 0.497. Variance test: centric, 2; acentric, 1; result, 1.89. The $N(z)$ test of Howels, Philipps, and Rogers is not very conclusive and shows an acentric distribution for $z < 0.5$ and a hypercentric one for $z > 1$.

(9) Patterson, Fourier, and block-diagonal least-squares computations were carried out on an IBM 1130 computer with local modified programs derived from those of M. Laing. Full-matrix least-squares refinements were computed on an IBM 370-168 computer with a personal program by C.K.

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(12) For $P\bar{6}$, $R = 0.16$ and $R_w = 0.168$ and for the space group $P6_3$, $R = 0.17$ and $R_w = 0.16$.

(13) Refinements of the two possible hydrogen positions led to the discrepancy factors $R = 0.041$, $R_w = 0.047$ with the following results (x, y, z, B): H1 (0.443 (6), 0.267 (6), 0.250, 5.0) and H2 (0.366 (6), 0.225 (6), 0.250, 5.0). The oxygen–hydrogen bond lengths are O1–H1 = 0.57 Å and O1–H2 = 0.63 Å.

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