The molecular packing arrangement is shown in Fig. 3. No intermolecular hydrogen bonding is observed; instead the shortest intermolecular distances are between the iodine atom and the carbonyl oxygen (3·1 Å) and between each of the nitro-group oxygen atoms and its symmetry-related atom (3·0 Å and 3·1 Å). A number of contact distances less than 3·5 Å also occur between other atoms in the parallel nitrobenzoate groups. The shortest iodine–iodine contact distance is 4·4 Å; this seems short enough to account for the tendency of the crystals to turn yellow-brown in the X-ray beam.

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# The Crystal Structure of $CuCN . NH_3$*

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The compound $CuCN . NH_3$ is monoclinic, space group $P2_1/c$, with $a = 5{\cdot}814$, $b = 7{\cdot}977$ and $c = 8{\cdot}193$ Å, $\beta = 125{\cdot}8°$ and there are four formula units per unit cell. The structure consists of polymer sheets of composition $(CuCN)_\infty$ with $NH_3$ molecules, bonded to Cu, protruding from both sides of these sheets. There is ambiguity in the orientation of the cyanide group but the X-ray data appear to favor one arrangement over the other. The bonding about the Cu is particularly unusual, there being five close neighbors including a Cu atom 2·42 Å.

## Introduction

A number of years ago, during the course of an attempt to grow single crystals of CuCN†, it was observed that CuCN forms addition compounds with many nitrogen-containing compounds, *e.g.* ammonia, hydrazine, pyridine, aniline and pyrrole. Many of these same reactions are summarized in Gmelin (1961). Because of the unusual structures shown by $KCu(CN)_2$ (Cromer, 1957) and by $KCu_2(CN)_3 . H_2O$ (Cromer & Larson, 1962) it was decided to study the structure of some of these addition compounds. $CuCN . NH_3$ is the subject of the present paper; a report on $CuCN . N_2H_4$ will be presented in the near future.

## Experimental

Excess powdered CuCN was equilibrated with concentrated aqueous ammonia by shaking for a few minutes in a closed container. The supernatant liquid was de-

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

† Small single crystals of CuCN were eventually grown from water by a special technique (Cromer, Douglass & Staritzky, 1957).

canted and placed in a bell jar which was then evacuated. As excess ammonia was removed small crystals of CuCN . $NH_3$ were precipitated. The solution is readily oxidized in air, but if one works rapidly, excessive oxidation can be avoided. Alternatively, oxidation of the copper can be inhibited by adding a trace of hydrazine to the aqueous ammonia.

The crystals decompose in three or four days, presumably by loss of ammonia, but crystals coated with Krylon could be preserved for about two weeks.

Examination with a precession camera showed the crystals to be monoclinic, space group $P2_1/c$ (reflections $0k0$ with $k$ odd and $h0l$ with $l$ odd were systematically absent). Lattice constants were obtained from a least-squares fit of 27 lines measured with a carefully aligned single-crystal orienter on a General Electric XRD 5 using Mo $K\alpha_1$ radiation ($\lambda = 0{\cdot}70926$ Å). The cell constants are $a = 5{\cdot}814 \pm 0{\cdot}002$, $b = 7{\cdot}977 \pm 0{\cdot}003$, $c = 8{\cdot}193 \pm 0{\cdot}002$ Å and $\beta = 125{\cdot}80 \pm 0{\cdot}02°$. With 4 CuCN . $NH_3$ per unit cell, the calculated density is

Table 1. *Final least-squares parameters for orientation* I *of* CuCN. $NH_3$

| | $x$ | $y$ | $z$ | $B_{11} \times 10^4$ | $B_{22} \times 10^4$ | $B_{33} \times 10^4$ | $B_{12} \times 10^4$ | $B_{13} \times 10^4$ | $B_{23} \times 10^4$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 0·1605 ± 3 | 0·0748 ± 1 | 0·1557 ± 2 | 348 ± 8 | 83 ± 2 | 146 ± 4 | −12 ± 7 | 272 ± 9 | −42 ± 5 |
| C | 0·0830 ± 20 | 0·2487 ± 10 | 0·2826 ± 12 | 356 ± 54 | 6 ± 14 | 111 ± 24 | 51 ± 49 | 320 ± 62 | −80 ± 29 |
| N | 0·0457 ± 22 | 0·3442 ± 13 | 0·3607 ± 16 | 405 ± 64 | 180 ± 22 | 299 ± 36 | −53 ± 62 | 287 ± 80 | 167 ± 46 |
| $NH_3$ | 0·5950 ± 17 | 0·0400 ± 10 | 0·3285 ± 13 | 270 ± 46 | 110 ± 20 | 196 ± 26 | 6 ± 40 | 214 ± 59 | 23 ± 31 |

$g = 2{\cdot}62 \pm 0{\cdot}23 \times 10^{-6}$

Table 2. *Magnitudes and direction angles, relative to the crystallographic axes, of the principal axes of the thermal vibration ellipsoids. Orientation* I.

| | Axis $i$ | $B(Å^2{}_i)$ | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|---|
| Cu | 1 | 3·13 ± 0·07 | 23 ± 7° | 88 ± 6° | 103 ± 8° |
| | 2 | 1·76 ± 0·07 | 104 ± 2 | 35 ± 2 | 56 ± 2 |
| | 3 | 2·82 ± 0·08 | 108 ± 9 | 125 ± 2 | 37 ± 4 |
| C | 1 | 3·2 ± 0·5 | 37 ± 12 | 83 ± 11 | 89 ± 14 |
| | 2 | −0·8 ± 0·3 | 115 ± 5 | 36 ± 6 | 55 ± 6 |
| | 3 | 2·0 ± 0·4 | 116 ± 15 | 125 ± 7 | 35 ± 6 |
| N | 1 | 3·6 ± 0·6 | 48 ± 24 | 96 ± 31 | 79 ± 20 |
| | 2 | 2·9 ± 0·5 | 62 ± 28 | 34 ± 9 | 122 ± 10 |
| | 3 | 8·4 ± 0·8 | 125 ± 6 | 57 ± 5 | 34 ± 5 |
| $NH_3$ | 1 | 2·4 ± 0·4 | 40 ± 20 | 98 ± 46 | 86 ± 14 |
| | 2 | 2·8 ± 0·5 | 77 ± 37 | 14 ± 30 | 101 ± 15 |
| | 3 | 4·2 ± 0·5 | 127 ± 11 | 79 ± 14 | 11 ± 14 |

Table 3. *Final least-squares parameters for orientation* II *of* CuCN . $NH_3$

| | $x$ | $y$ | $z$ | $B_{11} \times 10^4$ | $B_{22} \times 10^4$ | $B_{33} \times 10^4$ | $B_{12} \times 10^4$ | $B_{13} \times 10^4$ | $B_{23} \times 10^4$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 0·1604 ± 3 | 0·0747 ± 1 | 0·1557 ± 2 | 349 ± 7 | 84 ± 2 | 147 ± 3 | −15 ± 7 | 273 ± 8 | −44 ± 5 |
| N | 0·0814 ± 16 | 0·2530 ± 10 | 0·2855 ± 10 | 422 ± 48 | 75 ± 14 | 153 ± 21 | 14 ± 45 | 329 ± 54 | −11 ± 28 |
| C | 0·0442 ± 21 | 0·3513 ± 12 | 0·3669 ± 15 | 337 ± 57 | 76 ± 15 | 182 ± 28 | −19 ± 49 | 316 ± 70 | −49 ± 35 |
| $NH_3$ | 0·5952 ± 15 | 0·0404 ± 9 | 0·3283 ± 12 | 264 ± 42 | 111 ± 18 | 190 ± 24 | 16 ± 37 | 205 ± 54 | 16 ± 28 |

$g = 2{\cdot}62 \pm 0{\cdot}22 \times 10^{-6}$

Table 4. *Magnitudes and direction angles, relative to the crystallographic axes, of the principal axes of the thermal vibration ellipsoids. Orientation* II

| | Axis $i$ | $B$ (Å$^2$) | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|---|
| Cu | 1 | 3·13 ± 0·06 | 24 ± 8° | 90 ± 6° | 102 ± 8° |
| | 2 | 1·77 ± 0·06 | 103 ± 2 | 35 ± 2 | 56 ± 2 |
| | 3 | 2·86 ± 0·07 | 109 ± 9 | 125 ± 2 | 37 ± 4 |
| N | 1 | 3·8 ± 0·4 | 29 ± 12 | 86 ± 11 | 97 ± 13 |
| | 2 | 1·8 ± 0·4 | 103 ± 15 | 20 ± 27 | 70 ± 27 |
| | 3 | 2·4 ± 0·4 | 115 ± 14 | 110 ± 27 | 22 ± 26 |
| C | 1 | 2·8 ± 0·5 | 13 ± 23 | 77 ± 23 | 125 ± 32 |
| | 2 | 1·7 ± 0·4 | 103 ± 21 | 23 ± 16 | 67 ± 16 |
| | 3 | 3·4 ± 0·5 | 86 ± 34 | 109 ± 14 | 44 ± 30 |
| $NH_3$ | 1 | 2·3 ± 0·4 | 42 ± 15 | 104 ± 31 | 86 ± 11 |
| | 2 | 2·8 ± 0·4 | 75 ± 25 | 15 ± 29 | 95 ± 15 |
| | 3 | 4·0 ± 0·4 | 129 ± 11 | 84 ± 15 | 6 ± 13 |

2·297 g.cm$^{-3}$; the measured density is 2·30 g.cm$^{-3}$. The linear absorption coefficient for Mo $K\alpha$ radiation is 67·5 cm$^{-1}$. Intensities from the entire hemisphere of the reciprocal lattice were measured out to $2\theta = 50°$ using Mo $K\alpha$ radiation and balanced filters. Thus most reflections were measured twice. The fixed-counter, fixed-crystal technique was used. The crystal was approximately $0·06 \times 0·06 \times 0·13$ mm in size and the longest dimension was approximately parallel to the rotation axis. Absorption corrections were very small and hence were not applied. Equivalent $F^2$ were averaged and the observed $F$ was the square root of this average. The average agreement of equivalent reflections was estimated by forming an index, $\Sigma|F^2-\overline{F^2}|/\Sigma\overline{F^2}$, where the summation was taken over all reflections which were observed more than once. This index was 0·038. A similar quantity, $\Sigma|F-\overline{F^2}^{\frac{1}{2}}|/\Sigma\overline{F^2}^{\frac{1}{2}}$, based on $F$, was 0·025.

## Determination and refinement of the structure

A three-dimensional Patterson map was computed. All atoms except hydrogen were easily located from this Patterson map, although the identity of the carbon and nitrogen in the cyanide group was uncertain. Assignment of the atoms in the cyanide group was made on what seemed to be logical structural grounds (we shall call this assignment orientation I) and a full-matrix least-squares refinement, including anisotropic thermal parameters, was made. The quantity minimized was $\Sigma w(F_o-F_c^*)^2$ where $w = w_E/(F_o+0·02\,F_o^2)$, $w_E$ is the weight based on counting statistics as given by Evans (1961),

$$F_c^* = KF_c/\{1+g\,\mathrm{Lp}\left[\frac{2(1+\cos^4 2\theta)}{(1+\cos^2 2\theta)^2}\right]F_c^2\}^{\frac{1}{2}},$$

$K$ = scale factor, $g$ = extinction parameter (Zachariasen, 1963), Lp = Lorentz and polarization factors and $F_c$ is the ordinary calculated structure factor. Anisotropic temperature factors were in the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$. Form factors which are given in *International Tables for X-ray Crystallography* (1962) were used. For unobserved reflections, $w=0$. At the end of the refinements, $\Delta\xi_i/\sigma(\xi_i)$ was $<10^{-2}$ for all parameters $\xi_i$ and $<10^{-4}$ for all positional parameters.

The parameters resulting from this least-squares refinement are given in Table 1. The thermal parameters of the carbon atom did not remain positive definite; hence, upon transformation to the thermal ellipsoids, given in Table 2, an ellipsoid with a negative axis results. Also, the thermal motion of the nitrogen atom is quite large. The behavior of these thermal parameters suggested that the cyanide group should be inverted.

The positions of the carbon and nitrogen atoms in the cyanide group were interchanged (orientation II) and a least-squares refinement made as before. The resulting parameters are given in Table 3 and the thermal ellipsoids in Table 4. The observed structure factors and those calculated with the parameters of Table 3 are given in Table 5.

Difference Fourier syntheses were computed after each of the above refinements but no indication of hydrogen atom positions was found.

Table 5. *Observed and calculated structure factors for* CuCN . NH$_3$, *orientation* II

The column headings are $l$, $|F_o|/K$ and $F_c^*/K$ (see text). A minus sign preceding $|F_o|/K$ means 'less than'.

| | | |
|---|---|---|
| H= 0 K= 0 | | |
| 2 | 60 | -64 |
| 4 | 44 | -49 |
| 6 | 36 | 36 |
| H= 0 K= 1 | | |
| 1 | 47 | 48 |
| 2 | 14 | -15 |
| 3 | 60 | -58 |
| 4 | 8 | 8 |
| 5 | -6 | 3 |
| 6 | 11 | 9 |
| 7 | 21 | 19 |
| H= 0 K= 2 | | |
| 0 | 55 | 59 |
| 1 | 63 | -59 |
| 2 | 15 | -13 |
| 3 | 9 | -8 |
| 4 | 30 | -30 |
| 5 | 35 | 34 |
| 6 | 24 | 23 |
| 7 | 11 | -12 |
| H= 0 K= 3 | | |
| 1 | 8 | -7 |
| 2 | 65 | -64 |
| 3 | -5 | 3 |
| 4 | 37 | 37 |
| 5 | -7 | 3 |
| 6 | 9 | 8 |
| 7 | -7 | 0 |
| H= 0 K= 4 | | |
| 0 | 12 | -11 |
| 1 | 71 | -70 |
| 2 | -6 | -7 |
| 3 | 11 | -12 |
| 4 | 20 | 20 |
| 5 | 40 | 38 |
| 6 | -8 | -7 |
| 7 | 10 | -12 |
| H= 0 K= 5 | | |
| 1 | 26 | -26 |
| 2 | 34 | -33 |
| 3 | 35 | 35 |
| 4 | 14 | 14 |
| 5 | -7 | -2 |
| 6 | 10 | 11 |
| H= 0 K= 6 | | |
| 0 | 51 | -51 |
| 1 | 22 | -22 |
| 2 | 21 | 21 |
| 3 | -6 | -1 |
| 4 | 18 | 17 |
| 5 | 11 | 12 |
| 6 | 16 | -16 |
| H= 0 K= 7 | | |
| 1 | 18 | -18 |
| 2 | -8 | 8 |
| 3 | 27 | 28 |
| 4 | -7 | 0 |
| 5 | -7 | -6 |
| H= 0 K= 8 | | |
| 0 | 22 | -21 |
| 1 | 14 | 13 |
| 2 | -8 | 6 |
| 3 | -8 | 8 |
| 4 | 14 | 13 |
| H= 0 K= 9 | | |
| 1 | -8 | -6 |
| 2 | 25 | 24 |
| H= 1 K= 0 | | |
| -8 | 25 | 25 |
| -6 | -6 | 1 |
| -4 | 64 | -68 |
| -2 | 50 | 49 |
| 0 | 63 | 69 |
| 2 | 73 | -79 |
| 4 | 11 | 11 |
| 6 | 19 | 19 |
| H= 1 K= 1 | | |
| -8 | -8 | 7 |
| -7 | 27 | 27 |
| -6 | 20 | -20 |
| -5 | 30 | -31 |
| -4 | 14 | 14 |
| -3 | 47 | -46 |
| -2 | 27 | 26 |
| -1 | 85 | 84 |
| 0 | 48 | -49 |
| 1 | 6 | -9 |
| 2 | 10 | 9 |
| 3 | 46 | -48 |
| 4 | 15 | 16 |
| 5 | 28 | 28 |
| 6 | -8 | -4 |
| H= 1 K= 2 | | |
| -8 | 12 | 11 |
| -7 | 15 | -13 |
| -6 | -7 | 6 |
| -5 | 22 | -22 |
| -4 | 49 | -49 |
| -3 | 61 | 61 |
| -2 | 66 | 62 |
| -1 | 29 | -27 |
| 0 | 9 | -6 |
| 1 | 49 | -51 |
| 2 | 34 | -35 |
| 3 | 40 | 39 |
| 4 | 12 | 12 |
| 5 | -7 | 6 |
| 6 | -8 | 8 |
| H= 1 K= 3 | | |
| -8 | -9 | 7 |
| -7 | -7 | 2 |
| -6 | 32 | -30 |
| -5 | -6 | 2 |
| -4 | 6 | 6 |
| -3 | -5 | -5 |
| -2 | 63 | 62 |
| -1 | 9 | 7 |
| 0 | 56 | -55 |
| 1 | 6 | -6 |
| 2 | 23 | -24 |
| 3 | -6 | -5 |
| 4 | 48 | 46 |
| 5 | -8 | 8 |
| 6 | 14 | -15 |
| H= 1 K= 4 | | |
| -7 | 14 | -13 |
| -6 | -7 | -5 |
| -5 | 30 | -29 |
| -4 | 27 | 26 |
| -3 | 61 | 60 |
| -2 | 17 | -17 |
| -1 | -6 | -6 |
| 0 | 13 | -14 |
| 1 | 55 | -54 |
| 2 | 10 | 11 |
| 3 | 32 | 32 |
| 4 | -7 | 7 |
| 5 | -9 | 7 |
| 6 | -8 | -7 |
| H= 1 K=. 5 | | |
| -7 | 15 | -14 |
| -6 | 25 | -24 |
| -5 | 22 | 22 |
| -4 | -6 | 0 |
| -3 | 10 | 10 |
| -2 | 44 | 44 |
| -1 | 43 | -43 |
| 0 | 33 | -33 |
| 1 | 16 | 17 |
| 2 | 10 | -10 |
| 3 | 20 | 19 |
| 4 | 19 | 19 |
| 5 | 14 | -14 |
| H= 1 K= 6 | | |
| -6 | -8 | 1 |
| -5 | 10 | 11 |
| -4 | 27 | 26 |
| -3 | 17 | 17 |
| -2 | 20 | -21 |
| -1 | -6 | -3 |
| 0 | 26 | -27 |
| 1 | 12 | -11 |
| 2 | 42 | 40 |
| 3 | 7 | 9 |
| 4 | -8 | -7 |
| 5 | -7 | -1 |
| H= 1 K= 7 | | |
| -6 | -9 | 8 |
| -5 | 18 | 17 |
| -4 | -8 | -9 |
| -3 | 9 | 9 |
| -2 | -7 | -3 |
| -1 | 35 | -36 |
| 0 | -7 | 9 |
| 1 | 16 | 17 |
| 2 | -7 | -4 |
| 3 | 17 | 17 |
| 4 | -7 | 1 |
| H= 1 K= 8 | | |
| -4 | 22 | 23 |
| -3 | 15 | -16 |
| -2 | 19 | -20 |
| -1 | -8 | -5 |
| 0 | -8 | -6 |
| 1 | 17 | 18 |
| 2 | 17 | 18 |
| 3 | -7 | -4 |
| H= 1 K= 9 | | |
| -3 | -9 | 8 |
| -2 | 18 | -18 |
| -1 | 11 | -12 |
| 0 | 15 | 16 |
| 1 | -7 | 2 |
| H= 2 K= 0 | | |
| -8 | 27 | 27 |
| -6 | 37 | -39 |
| -4 | 8 | -9 |
| -2 | 43 | 47 |
| 0 | 12 | -11 |
| 2 | 30 | -30 |
| 4 | 22 | 21 |
| H= 2 K= 1 | | |
| -9 | 16 | 15 |
| -8 | -8 | -5 |
| -7 | 9 | 10 |
| -6 | 15 | -15 |
| -5 | 57 | -59 |
| -4 | 36 | 37 |
| -3 | 39 | 41 |
| -2 | -5 | -1 |
| -1 | 54 | 50 |
| 0 | 51 | -52 |
| 1 | 63 | -64 |
| 2 | 31 | 32 |
| 3 | 11 | 11 |
| 4 | -8 | 3 |
| 5 | 16 | 17 |
| H= 2 K= 2 | | |
| -9 | -8 | 4 |
| -8 | 9 | 9 |
| -7 | 29 | -28 |
| -6 | 13 | -13 |
| -5 | 21 | 21 |
| -4 | 18 | -17 |
| -3 | 41 | 42 |
| -2 | 46 | 49 |
| -1 | 61 | -60 |
| 0 | 24 | -24 |
| 1 | -6 | -5 |
| 2 | 17 | -16 |
| 3 | 33 | 33 |
| 4 | 15 | 16 |
| 5 | 16 | -10 |
| H= 2 K= 3 | | |
| -8 | 14 | -14 |
| -7 | -7 | 2 |
| -6 | 29 | -28 |
| -5 | 12 | -13 |
| -4 | 65 | 64 |
| -3 | 15 | 15 |
| -2 | 12 | -12 |
| -1 | 10 | 11 |
| 0 | 56 | -57 |
| 1 | 23 | -23 |
| 2 | 33 | 33 |
| 3 | -7 | 7 |
| 4 | 12 | 14 |
| 5 | -7 | 5 |
| H= 2 K= 4 | | |
| -8 | -8 | -4 |
| -7 | 27 | -27 |
| -6 | -7 | 3 |
| -5 | 9 | 9 |
| -4 | 19 | 17 |
| -3 | 40 | 39 |
| -2 | 28 | -28 |
| -1 | 38 | -40 |
| 0 | 8 | 8 |
| 1 | 7 | -7 |
| 2 | 9 | 9 |
| 3 | 25 | 25 |
| 4 | -8 | -7 |
| 5 | -9 | -9 |
| H= 2 K= 5 | | |
| -7 | -7 | 1 |
| -6 | 23 | -24 |
| -5 | 25 | 24 |
| -4 | 28 | 29 |
| -3 | 22 | -22 |
| -2 | 9 | 10 |
| -1 | 18 | -18 |
| 0 | 41 | -40 |
| 1 | 28 | 28 |
| 2 | 24 | 25 |
| 3 | -7 | -2 |
| 4 | -7 | 0 |
| H= 2 K= 6 | | |
| -7 | -8 | -4 |
| -6 | 28 | 26 |
| -5 | -7 | -3 |
| -4 | -6 | 2 |
| -3 | -7 | 8 |
| -2 | 38 | -38 |
| -1 | -6 | -4 |
| 0 | 16 | 17 |
| 1 | -6 | 0 |
| 2 | 21 | 21 |
| 3 | -7 | 2 |
| 4 | 17 | -18 |
| H= 2 K= 7 | | |
| -6 | -8 | -1 |
| -5 | 29 | 27 |
| -4 | -7 | -2 |
| -3 | 23 | -25 |
| -2 | -7 | -1 |
| -1 | 17 | -17 |
| 0 | -7 | 4 |
| 1 | 32 | 32 |
| 2 | -8 | -2 |
| 3 | -8 | -6 |
| H= 2 K= 8 | | |
| -5 | -8 | -2 |
| -4 | 10 | 10 |
| -3 | 13 | -15 |
| -2 | 26 | -26 |
| -1 | 12 | 13 |
| 0 | 11 | 12 |
| 1 | -7 | 4 |
| H= 2 K= 9 | | |
| -2 | -7 | 2 |
| -1 | -7 | -7 |
| H= 3 K= 0 | | |
| -8 | 11 | 10 |
| -6 | 44 | -46 |
| -4 | 35 | 35 |
| -2 | 29 | 29 |
| 0 | 47 | -48 |
| 2 | -7 | 9 |
| 4 | 16 | 15 |
| H= 3 K= 1 | | |
| -9 | 17 | 18 |
| -8 | 16 | -16 |
| -7 | 29 | -28 |
| -6 | 13 | 12 |
| -5 | 10 | -10 |
| -4 | 22 | 21 |
| -3 | 56 | 58 |
| -2 | 23 | -23 |
| -1 | 36 | -36 |
| 0 | 12 | -13 |
| 1 | 18 | -18 |
| 2 | 22 | 22 |
| 3 | 23 | 24 |
| 4 | -8 | -6 |
| H= 3 K= 2 | | |
| -9 | 12 | -10 |
| -8 | -7 | 0 |
| -7 | 20 | -20 |
| -6 | 20 | -19 |
| -5 | 45 | 45 |
| -4 | 8 | 7 |
| -3 | -6 | 1 |
| -2 | 31 | 31 |
| -1 | 49 | -50 |
| 0 | 29 | -30 |
| 1 | 24 | 24 |
| 2 | -7 | -1 |
| 3 | 11 | 12 |
| 4 | 12 | 13 |
| H= 3 K= 3 | | |
| -9 | -8 | 6 |
| -8 | 31 | -30 |
| -7 | -8 | -9 |
| -6 | 15 | 15 |
| -5 | -6 | -3 |
| -4 | 47 | 48 |
| -3 | 17 | 18 |
| -2 | 63 | -62 |
| -1 | 9 | -9 |
| 0 | -6 | 5 |
| 1 | -7 | -5 |
| 2 | 26 | 26 |
| 3 | -8 | 5 |
| 4 | -9 | -10 |
| H= 3 K= 4 | | |
| -8 | -8 | 6 |
| -7 | 18 | -19 |
| -6 | -7 | 2 |
| -5 | 34 | 33 |
| -4 | -7 | -6 |
| -3 | -6 | 1 |
| -2 | -6 | -3 |
| -1 | 39 | -38 |
| 0 | 10 | 10 |
| 1 | 23 | 23 |
| 2 | -7 | -3 |
| 3 | -8 | 7 |
| H= 3 K= 5 | | |
| -8 | 12 | -13 |
| -7 | 14 | 16 |
| -6 | 8 | 7 |
| -5 | -7 | 5 |
| -4 | 17 | 15 |
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| 0 | -6 | 1 |
| 1 | 16 | 16 |
| 2 | 17 | 16 |
| 3 | 11 | -12 |
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| -6 | 22 | 22 |
| -5 | 27 | 28 |
| -4 | -6 | -6 |
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| -2 | 12 | -12 |
| -1 | 33 | -32 |
| 0 | -8 | 4 |
| 1 | -8 | 8 |
| 2 | -8 | 6 |
| 3 | -10 | 10 |
| H= 4 K= 2 | | |
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| -8 | 15 | -16 |
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| -6 | -7 | -8 |
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| -3 | 33 | -34 |
| -2 | 12 | -12 |
| -1 | -7 | -8 |
| 0 | 15 | -14 |
| 1 | 22 | 22 |
| 2 | 12 | 12 |
| H= 4 K= 3 | | |
| -9 | -7 | 3 |
| -8 | 13 | -13 |
| -7 | -7 | -7 |
| -6 | 31 | 30 |
| -5 | -6 | 0 |
| -4 | -6 | 0 |
| -3 | -6 | 5 |
| -2 | 39 | -37 |
| -1 | -7 | 0 |
| 0 | 25 | 24 |
| 1 | -7 | -2 |
| 2 | -8 | 4 |
| H= 4 K= 4 | | |
| -8 | 12 | 11 |
| -7 | -8 | 7 |
| -6 | -8 | -8 |
| -5 | 29 | 28 |
| -4 | -7 | -6 |
| -3 | 37 | -36 |
| -2 | -7 | 9 |
| -1 | -7 | -2 |
| 0 | -8 | 1 |
| 1 | 24 | 24 |
| 2 | -9 | -3 |
| H= 4 K= 5 | | |
| -8 | -8 | -7 |
| -7 | 17 | 17 |
| -6 | 20 | 19 |
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| -4 | 10 | -11 |
| -3 | 11 | -10 |
| -2 | 10 | -10 |
| -1 | 20 | 20 |
| 0 | 11 | 11 |
| 1 | -8 | -4 |
| H= 4 K= 6 | | |
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| -1 | -7 | 1 |
| 0 | 14 | 14 |
| H= 4 K= 7 | | |
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| -4 | -8 | 5 |
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| -2 | -8 | 2 |
| -1 | 18 | 18 |
| H= 5 K= 0 | | |
| -8 | 24 | -24 |
| -6 | 27 | 29 |
| -4 | 14 | 12 |
| -2 | 37 | -34 |
| 0 | -8 | 9 |
| H= 5 K= 1 | | |
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| -8 | -8 | -1 |
| -7 | -7 | -7 |
| -6 | 15 | 14 |
| -5 | 30 | 30 |
| -4 | 15 | -14 |
| -3 | 13 | -12 |
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| -1 | 16 | -18 |
| 0 | -8 | 6 |
| 1 | 16 | 15 |
| H= 5 K= 2 | | |
| -9 | 11 | -10 |
| -8 | 18 | -17 |
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| -6 | 16 | 15 |
| -5 | -7 | -4 |
| -4 | 10 | 7 |
| -3 | 21 | -19 |
| -2 | 21 | -19 |
| -1 | 15 | 15 |
| 0 | 9 | 9 |
| 1 | -8 | 1 |
| H= 5 K= 3 | | |
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| -7 | -9 | -6 |
| -6 | 17 | 17 |
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| -4 | 20 | -19 |
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| 0 | 19 | 18 |
| H= 5 K= 4 | | |
| -8 | -8 | 7 |
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| -1 | 19 | 19 |
| 0 | -8 | -2 |
| H= 5 K= 5 | | |
| -7 | -8 | 2 |
| -6 | 17 | 16 |
| -5 | 17 | -17 |
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| H= 5 K= 6 | | |
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| -3 | -8 | -7 |
| -2 | 12 | 14 |
| H= 6 K= 0 | | |
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| -6 | 23 | 24 |
| -4 | 13 | -13 |
| -2 | -8 | -8 |
| H= 6 K= 1 | | |
| -8 | -8 | 4 |
| -7 | 14 | 14 |
| -6 | -8 | 0 |
| -5 | 12 | 13 |
| -4 | -10 | -9 |
| -3 | 22 | -22 |
| -2 | -9 | 8 |
| H= 6 K= 2 | | |
| -8 | -8 | -2 |
| -7 | -8 | 8 |
| -6 | 10 | 10 |
| -5 | 13 | -15 |
| -4 | -8 | -5 |
| -3 | -8 | 3 |
| -2 | -9 | -5 |
| H= 6 K= 3 | | |
| -7 | -8 | 0 |
| -6 | -8 | -6 |
| -5 | -8 | 2 |
| -4 | 15 | -16 |
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| -2 | 16 | 13 |
| H= 6 K= 4 | | |
| -6 | -9 | -8 |
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| -3 | -8 | 0 |

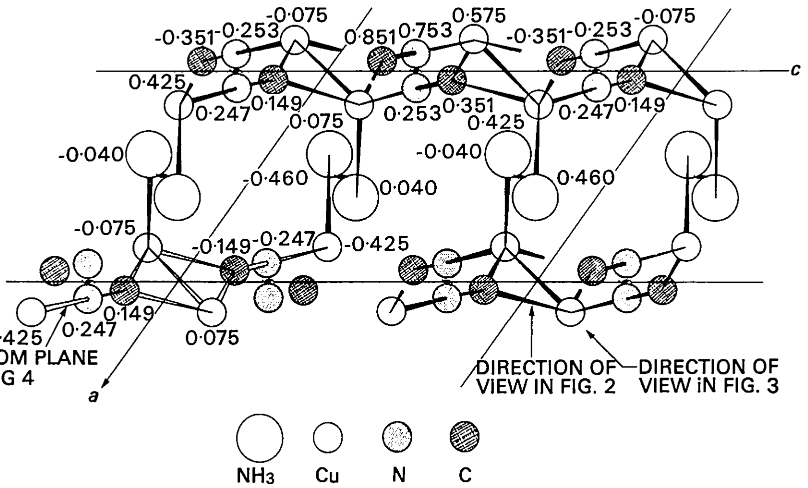

Fig. 1. CuCN . $NH_3$, orientation II, projected on (010). The numerals are the fractional *y* coordinates.

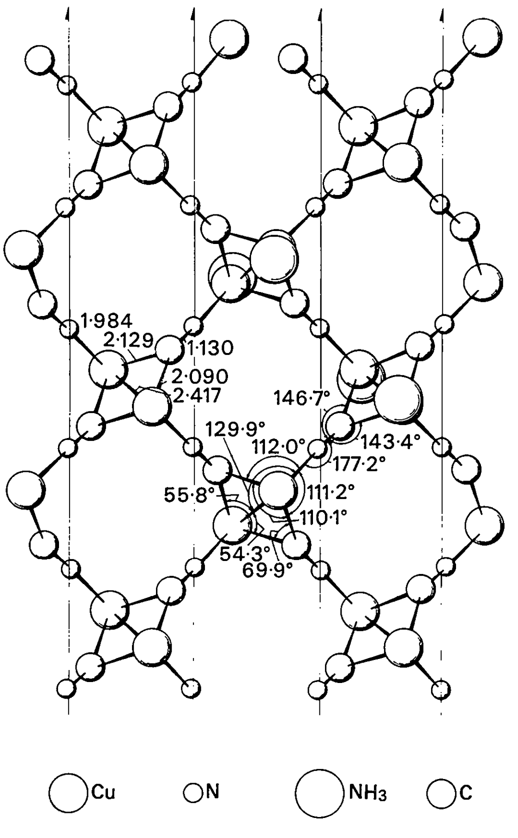

Fig. 2. A view of CuCN . $NH_3$, orientation II, as seen along $a^*$. The $NH_3$ molecules are shown attached to only four Cu atoms.

## Discussion of the structure

The orientation of the cyanide group in this compound is somewhat uncertain. Table 6 compares the *R* index and other quantities for the two cases. Orientation II is slightly favored. Also, the thermal parameters of

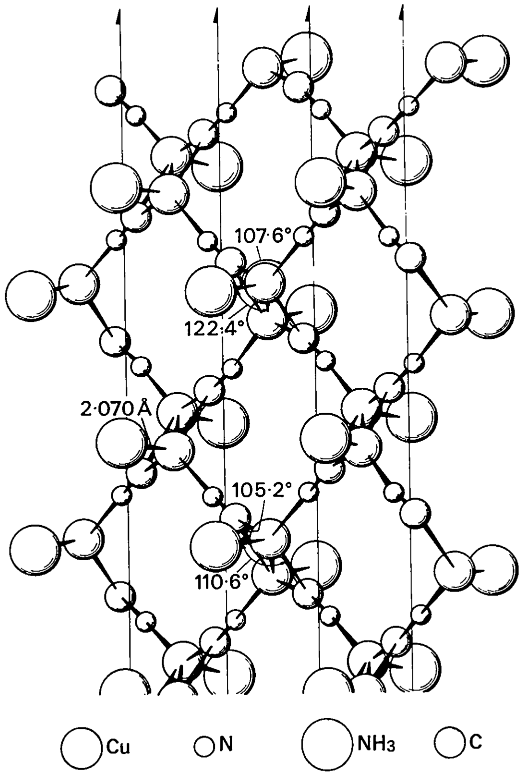

Fig. 3. A view of CuCN . $NH_3$, orientation II, as seen along [101].

Table 6. *Comparison of residuals for the two orientations*

| Orientation | $\Sigma \lvert F_o\rvert - \lvert F_c\rvert^* /\Sigma\lvert F_o\rvert$ | $\Sigma w \lvert F_o\rvert - \lvert F_c^*\rvert /\Sigma w\lvert F_o\rvert$ | $\Sigma w(F_o - F_c^*)^2$ | $\sigma(\varrho)$ |
|---|---|---|---|---|
| I | 0·0436 | 0·0486 | 53·701 | 0·188 e.Å$^{-3}$ |
| II | 0·0397 | 0·0450 | 45·379 | 0·173 |

the cyanide group are clearly more sensible for orientation II. On the other hand, orientation I seems intuitively more reasonable because in this case the Cu–C–N group is essentially linear. In the other complex cyanides we have studied, [$KCu(CN)_2$ and $KCu_2(CN)_3$ . $H_2O$], there have been linear Cu–C–N groups within the polymeric structures. For orientation II there are non-linear Cu · · · C–N groupings although the Cu–C distances are long (2·13 and 2·09 Å) for a single bond. In the compounds mentioned above, the Cu–C distances ranged from 1·89 to 1·92 Å. Because the direct X-ray evidence favors orientation II, the assumption will be made that this is correct. The evidence is not overwhelming so we present rather complete data for both cases.

Fig. 1 shows the atom positions projected along the *b* axis. There are infinite –Cu–C–N–Cu–C–N– spiral chains surrounding the screw axes. These chains are linked together to form sheets by Cu–Cu bonds of 2·42 Å and by 2·13 Å Cu–C bonds which are similar in character to the 2·09 Å Cu–C bonds in the chains. This is a rather short Cu–Cu distance, 0·13 Å shorter than in the metal. The ammonia molecules are bonded to the copper and the Cu–$NH_3$ bonds are nearly normal to the $(CuCN)_\infty$ sheets. The ammonia molecules protrude from both sides of the $(CuCN)_\infty$ sheets and those from one sheet fit in between those of an adjacent sheet. A view of one of these sheets as seen along $a^*$ is shown in Fig. 2 and a view as seen along [101] is shown in Fig. 3. For clarity, only a few of the ammonia molecules are shown in Fig. 2.

The copper atoms have five close neighbors. The nitrogen of the cyanide group, the nitrogen of the ammonia molecule and the copper related by a symmetry center form a nearly planar grouping around the copper. Also, the copper and the carbon atoms are required to form a plane with their neighbors related by the symmetry center. The dihedral angle between these two planes is 87°40′. Data on these planes are given in Table 7. The ammonia molecule, the cyanide nitrogen atom and two carbon atoms from nearby cyanide groups form a somewhat distorted tetrahedron about the copper atom. These tetrahedra occur in pairs formed by sharing a common C–C edge. The pairs of tetrahedra are then linked to other pairs by the bond in the cyanide group. If the cyanide groups are thought of as one atom, the tetrahedron pairs are linked by having a common vertex (the cyanide group).

Interatomic distances are given in Table 8. Both orientations are shown and analogous distances and

Table 7. *Least-squares planes of interest in* CuCN . $NH_3$

Equations are in the form $aX+bY+cZ=d$ where *a*, *b*, and *c* are direction cosines in a right handed orthogonal coordinate system such that *X* and *Y* are coincident with *x* and *y* of the crystallographic system.

| Atoms in plane | Coefficients *a* | *b* | *c* | *d* | Distance of atom from plane |
|---|---|---|---|---|---|
| Cu, Cu′<br>C, C′ | 0·83976 | −0·52194 | 0·14958 | 0·0 | 0·0 Å<br>0·0 |
| Cu<br>Cu′<br>N<br>$NH_3$ | 0·48362 | 0·70827 | −0·51426 | 0·00992 | −0·030<br>0·010<br>0·011<br>0·009 |
| Cu, Cu′<br>C, C′,<br>N, N′<br>Cu″, Cu‴ | 0·83576 | −0·52749 | 0·15248 | 0·0 | ±0·001<br>±0·013<br>±0·002<br>±0·006 |

Table 8. *Interatomic distances and bond angles in* CuCN . $NH_3$

| Orientation I | | Orientation II | |
|---|---|---|---|
| Cu–Cu | 2·418 ± 0·002 Å | Cu–Cu | 2·417 ± 0·002 Å |
| Cu–C | 1·938 ± 0·008 | Cu–N | 1·984 ± 0·008 |
| Cu–N | 2·157 ± 0·012 | Cu–C | 2·090 ± 0·010 |
| Cu–N | 2·195 ± 0·012 | Cu–C | 2·129 ± 0·010 |
| Cu–$NH_3$ | 2·068 ± 0·008 | Cu–$NH_3$ | 2·070 ± 0·007 |
| C–N | 1·096 ± 0·012 | N–C | 1·130 ± 0·011 |
| ∠Cu–C–N | 177·5 ± 0·9° | ∠Cu–N–C | 177·2 ± 0·8° |
| ∠Cu–Cu–C | 129·9 ± 0·3 | ∠Cu–Cu–N | 129·9 ± 0·2 |
| ∠Cu–Cu–$NH_3$ | 122·4 ± 0·3 | ∠Cu–Cu–$NH_3$ | 122·4 ± 0·2 |
| ∠C–Cu–$NH_3$ | 107·6 ± 0·4 | ∠N–Cu–$NH_3$ | 107·6 ± 0·3 |
| ∠C–Cu–N | 110·4 ± 0·4 | ∠N–Cu–C | 111·2 ± 0·4 |
| ∠C–Cu–N | 111·3 ± 0·4 | ∠N–Cu–C | 112·0 ± 0·4 |
| ∠N–Cu–N | 112·5 ± 0·4 | ∠C–Cu–C | 110·1 ± 0·3 |
| ∠N–Cu–$NH_3$ | 109·9 ± 0·3 | ∠C–Cu–$NH_3$ | 110·6 ± 0·3 |
| ∠N–Cu–$NH_3$ | 104·8 ± 0·4 | ∠C–Cu–$NH_3$ | 105·2 ± 0·4 |
| ∠Cu–N–Cu | 67·5 ± 0·4 | ∠Cu–C–Cu | 69·9 ± 0·3 |
| ∠Cu–N–C | 148·2 ± 0·9 | ∠Cu–C–N | 146·7 ± 0·8 |
| ∠Cu–N–C | 144·3 ± 0·9 | ∠Cu–C–N | 143·4 ± 0·8 |

angles are in the same row. Standard deviations were computed using the entire variance-covariance matrix and include lattice constant errors. The first three angles with copper as the central atom are formed by the three ligands that are nearly coplanar. These angles are similar to those formed by the three coplanar ligands in $KCu(CN)_2$ and $KCu_2(CN)_3 . H_2O$. The last six angles with copper as the central atom are formed by the tetrahedral neighbors. The Cu–$NH_3$ bond is 0·07 Å longer than the average of 2·00 Å observed for the Cu–N bonds in $KCu(CN)_2$ and $KC_2(CN)_3 . H_2O$; the Cu–$NH_3$ bond is essentially the same as the Cu–$NH_3$ (2·04, 2·06 Å) bonds found in $Cu(NH_3)_4SO_4 . H_2O$ (Mazzi, 1955).

The ammonia molecule ought to rotate fairly easily in this environment. Perhaps this is why hydrogen was not found. However, with a heavy atom such as copper, it would be difficult to find hydrogen in any case.

No calculations involving a disordered cyanide group were made. In this structure, the two ends of the cyanide group have such different surroundings that one orientation, whichever it is, must be highly favored.

Essentially planar groups of eight atoms occur in the structure. These planes are formed by two copper atoms, the cyanide group and the four atoms related to these by a symmetry center. The least-squares plane is given in Table 7 and the arrangement is diagrammed in Fig. 4.

Current theories of bonding seem inadequate to account for the structures of these complex cyanides. In $KCu(CN)_2$ and $KCu_2(CN)_3 . H_2O$ the copper atom is perhaps in an $sp^2$ hybridized state. The three ligands are approximately planar but the bond angles vary considerably from 120°. This also may be the case for the present compound, as far as the N, $NH_3$ and Cu ligands are concerned. In the present compound it is not clear how the Cu–C bonds are formed from the standpoint of either the copper atom or the carbon atom.

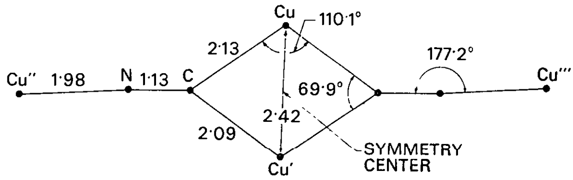

Fig. 4. Eight atom plane occurring in $CuCN . NH_3$.

All calculations were performed with an IBM-7094 computer using programs written by the authors.

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# Structures Involving Unshared Electron Pairs: Coordination of Antimony in Racemic Potassium Antimonyl Tartrate.*

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The structure of racemic potassium antimonyl tartrate has been determined by X-ray diffraction methods. The space group is $Pca2_1$ (No. 29) and the unit cell has dimensions $a = 8·79$, $b = 16·32$, $c = 12·19$ Å. The chemical formula is established as $C_4H_4O_7KSb . \frac{1}{2}H_2O$, eight of which are contained in the unit cell. The compound is shown to be based upon the antimonite ion, $[Sb(OH)_4]^-$.

There is an uncertainty about the structural formula of 'tartar emetic' in the chemical literature, but nevertheless the formulation of the compound as potassium antimonyl tartrate in still commonly used. Reihlen & Hezel (1931) proposed another structural formula with the antimony atom coordinated by one carboxylic and two hydroxylic oxygen atoms completed to a tetrahedron by one oxygen atom of a water molecule. On the basis of such a formula, these authors were able to explain why only D- or L-tartaric acid was able to form tartar emetic, while *meso*-tartaric acid was devoid of this property. The chemical behaviour of tartar emetic

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[*] Reported at the Sixth Congress of the International Union of Crystallography, Rome, September 1963 (Grdenić & Kamenar, 1963).