

Table 6. *The least-squares plane through the palladium atom and the four coordinating atoms*

$-0.9001x - 0.0639y - 0.4311z + 1.6419 = 0$ where x , y and z are the coordinates in Å referred to the crystal axes a , b and c .

	Pd	Cl(1)	Cl(2)	N(1)	N(2)	C(1)	C(2)	C(3)	C(4)
Displacement (Å)	-0.01	0.00	0.01	0.01	-0.01	-0.20	0.20	-0.54	-2.05

Table 7. *Intermolecular distances less than 3.5 Å between non-hydrogen atoms*

		Molecule 1	x	y	z
		2	$\frac{1}{2} - x$	$-y$	$\frac{1}{2} + z$
		3	$-x$	$-y$	$-z$

From molecule 1	To atom	In molecule	Distance
Cl(1)	N(2)	2	3.28 Å
N(1)	Cl(2)	2	3.37
Pd	Pd	3	3.34
Cl(1)	N(2)	3	3.29
N(1)	Cl(2)	3	3.35

The computations for the structure analysis were carried out on the HITAC 5020E computer at the Computer Centre of the University of Tokyo using the programs of the UNICS system, and also on the electronic computer FACOM 270-30 at this Institute.

Fig. 1 was drawn with a plotter at the C. Ito Electronic Computing Service Co., Ltd. using ORTEP (Johnson, 1965).

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The Crystal Structure of a Mixed Valence Copper Cyanide Complex, $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4^*$

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The green compound $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$ contains Cu(I) and Cu(II) in a ratio of 2:1. The crystals are orthorhombic, space group *Cmca*, with $a = 12.273$ (6), $b = 13.646$ (8) and $c = 12.777$ (7) Å. There are eight formula units per unit cell. Through the use of counter data the structure was solved by the heavy-atom method and was refined by least-squares methods with anisotropic thermal parameters to a conventional R index of 0.055. Two of the three crystallographically different cyanide groups are disordered. If the NH_3 positions were fully occupied, the formula would have four NH_3 groups. However, a 16-fold set appears to be only 75% occupied by NH_3 and one of the 8-fold sets appears to be only 50% occupied by NH_3 . Furthermore, a better fit of the data was obtained with a model having freely rotating NH_3 molecules. Each Cu(II) atom is coordinated to three NH_3 molecules distributed over four positions, and to the nitrogen atoms of two cyanide groups in a distorted octahedral geometry. The Cu(I) atoms have a distorted trigonal planar coordination with the carbon atom of the ordered cyanide group and the ends of two disordered cyanide groups. The Cu(II) and four Cu(I) atoms form the apices of a nearly planar pentagon, with cyanide groups bridging the copper atoms. These rings share two edges with adjacent pentagons to form an infinite chain parallel to the a axis.

Introduction

Numerous studies of CuCN complexes have been conducted at this laboratory over the last few years (*e.g.*,

Roof, Larson & Cromer, 1968, and references contained therein). With the single exception of $\text{K}_3\text{Cu}(\text{CN})_4$, these complexes have exhibited unusual polymeric-type structures. Recently, there have been reports of the preparation and partial characterization of some mixed-valence CuCN complexes with additional nitrogen, phosphorus, and arsenic containing ligands

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(Cooper & Plane, 1966*a* & *b*). In one of these studies a compound with stoichiometry $\text{Cu}_3(\text{NH}_3)_4(\text{CN})_4$ was reported. In trying to prepare this complex by Cooper & Plane's (1966*a*) method, we obtained a compound with stoichiometry $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$. We now report the structural details of this compound.

Experimental

Dark green crystals of $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$ were prepared by the method used by Cooper & Plane (1966*a*) in their preparation of $\text{Cu}_3(\text{NH}_3)_4(\text{CN})_4$. Analysis: calculated for $\text{Cu}_3\text{C}_4\text{H}_9\text{N}_7$: Cu, 55.13; N, 28.36; C, 13.89; H, 2.62. Calculated for $\text{Cu}_3\text{C}_4\text{H}_{12}\text{N}_8$: Cu, 52.54; N, 30.89; C, 13.24; H, 3.33. Found: Cu, 55.35; N, 28.31; C, 13.72; H, 2.61.

Preliminary precession photographs showed the crystal system to be orthorhombic. Systematic absences hkl , $h+k=2n+1$; $h0l$, $l=2n+1$; and $hk0$, $h=2n+1$ are consistent either with space group $Cmca$ or with an appropriate transformation of axes, $Aba2$. Subsequent analysis showed the correct space group to be $Cmca$. Lattice constants were obtained from a least-squares analysis of the settings of 12 reflections measured with $\text{Mo K}\alpha_1$ radiation ($\lambda=0.70926 \text{ \AA}$) on an automated Picker diffractometer (Busing & Levy, 1967). Unit-cell dimensions are: $a=12.273$ (6), $b=13.646$ (8), and $c=12.777$ (7) \AA . The density was measured by the flotation method in a mixture of bromoform and 1,1,2-trichloroethane and found to be 2.072 g.cm^{-3} . The calculated density for $Z=8$ is 2.144 g.cm^{-3} . For four NH_3 molecules in the compound the calculated density is 2.250 g.cm^{-3} .

Intensities were measured by means of a Picker four-circle diffractometer interfaced with a Digital Equipment Corporation PDP-8 computer. The orientation least-squares, and data-collection programs used were modified versions of the Oak Ridge system (Busing, Ellison, Levy, King & Roseberry, 1968). A θ - 2θ scan technique was used with steps of 0.05° over a 2° range and a 2 sec count at each step. Reflections were measured for hkl and $\bar{h}\bar{k}l$ out to a 2θ maximum of 60° with zirconium-filtered molybdenum radiation. A total of 2588 reflections was measured. Equivalent reflections were compared and averaged to yield the final unique data set. A disagreement index for the averaged reflections, which is defined as $R_d = \frac{\sum_n \sum_i |F_{\text{ave}} - F_{i,n}|}{\sum_n \sum_i |F_{i,n}|}$, was 0.022, where $F_{\text{ave}} = \frac{\sum_i w_i F_i}{\sum_i w_i}$, the w_i 's are the individual weights of the F_i 's, and the summation is taken over all n sets of i equivalent F_i 's.

The crystal used for intensity measurements was a parallelepiped with approximate dimensions $0.24 \times 0.12 \times 0.10$ mm. Absorption corrections were applied according to the method of Busing & Levy (1957) through the use of a modified version of Burnham's (1962) program ($\mu=60 \text{ cm}^{-1}$). A total of 665 unique reflections, greater than zero, was observed according to the criterion:

$$(I-B) \geq 3\sigma(I) = 3 [I+B+(0.02 I)^2]^{1/2}, \quad (1)$$

where I is the integrated peak intensity, B is the normalized background intensity, and $\sigma(I)$ is the estimated standard deviation of I .

Structure determination

A three-dimensional Patterson function was calculated, and the positions of two independent copper ions in $Cmca$ were located. One, presumed to be the Cu(II) ion, is located in a special 8-fold $0yz$ position on the mirror, while the other, presumed to be the Cu(I) ion, is in a general position. This partial model, with isotropic thermal parameters, was submitted to three cycles of least-squares refinement. In this, and subsequent least-squares calculations, the minimized quantity was $\sum w(F_o - F_c^*)^2$, where w is the weight derived from equation (1) (Stout & Jensen, 1968), and $F_c^* = KF_c [1 + g\beta F_c^2]^{-1/2}$, where K is a scale factor, F_c is the usual calculated structure factor, g is an extinction parameter, and

$$\beta = \left(\frac{e^2 N}{mc^2} \right)^2 \frac{p_2}{p_1} \frac{AdA^*/d\mu}{\sin 2\theta},$$

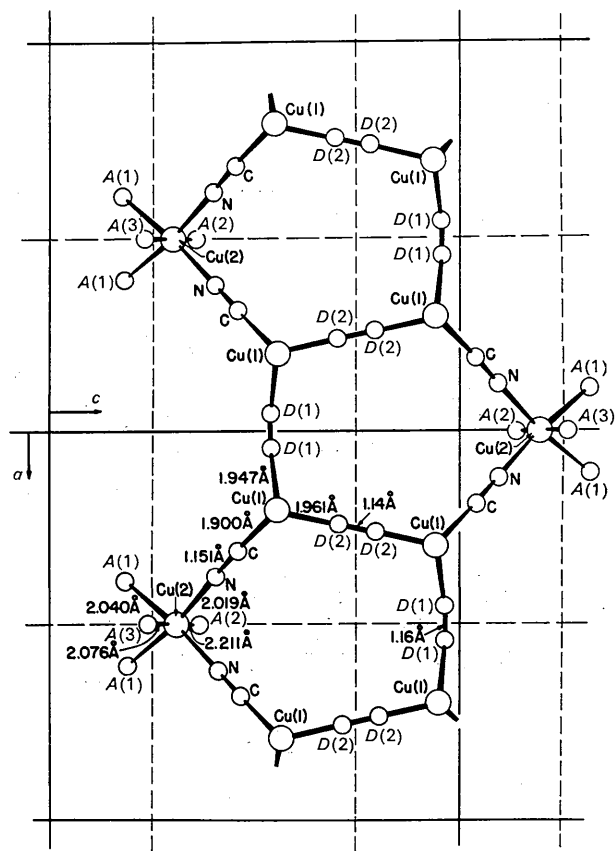


Fig. 1. Segment of the polymeric chains in $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$ as viewed along the b axis, including bond lengths.

(Zachariasen, 1963; Larson, 1967). Disagreement indices quoted are $R = \sum |AF| / \sum |F_o|$ and $R_w = [\sum w\Delta F^2 / \sum wF_o^2]^{1/2}$ (Hamilton, 1964).

This first partial model refined to $R = 0.24$ and $R_w = 0.22$. A three-dimensional electron density map was then calculated phased by the heavy atoms; the remaining atoms in the structure, except for the hydrogen atoms, were resolved. One ordered cyanide group exists and two which are required by symmetry to be disordered: one $[D(1)]$ by the mirror plane and one $[D(2)]$ by a twofold axis (see Fig. 1). Three independent ammonia molecules exist around the Cu(II) ion. One $[A(1)]$ is in a general position and two $[A(2)$ and $A(3)]$ are in special positions on the mirror. The orientation of the ordered cyanide group was fairly evident at this time from bond distances [Cu(1)–C, 1.95 (1); Cu(2)–N, 2.00 (1) Å] and peak electron density values (C, 7.8; N, 8.3 e.Å⁻³). The peak electron density values for all the cyanide atoms and one ammonia molecule, $A(2)$, ranged from 7.6 to 8.3 e.Å⁻³ while those for the other two ammonia positions, $A(1)$ and $A(3)$, were only 4.8 and 3.9 e.Å⁻³, respectively.

Refinement of this model by the least-squares method, first with isotropic and then with anisotropic thermal parameters, led to values of $R = 0.067$ and $R_w = 0.057$. Ammonia molecules $A(1)$ and $A(3)$ had quite large thermal parameters at this time, e.g., for $A(1)$ the B 's for the principal axes of vibration were 17 (1), 11 (1), and 3 (1) Å²; and for $A(3)$ they were 22 (2), 20 (3), and 14 (2) Å². Cooper & Plane (1966a) had reported that the compound had four ammonia molecules in the formula unit; although puzzled by the resulting discrepancy in density, we had until now assumed four ammonia molecules to be present, having followed their method of preparation. Chemical analysis of our own material now became available, however, and showed that only three molecules of NH₃ were present. The high apparent thermal motion of $A(1)$ and $A(3)$ suggested that these positions might be only partially occupied. Refinement of occupancy parameters, p , for these two atoms led to values of $p_{A(1)} = 0.991$ and $p_{A(3)} = 0.645$. Thermal parameters for principal axes of vibration were 5 (1), 9 (1), and

15 (1) Å² for $A(1)$; and 10 (2), 9 (2), and 6 (2) Å² for $A(3)$. For comparison those for $A(2)$ were 2.9 (6), 2.4 (6), and 4.2 (7) Å². For this second model $R = 0.058$ and $R_w = 0.049$. Because the stoichiometry determined by the least-squares method still did not agree with the chemical analysis and because of the still quite large thermal parameters of $A(1)$ and $A(3)$, a final model assuming freely rotating NH₃ molecules was calculated. Although the NH₃ molecule, if rotating, is most likely to rotate about the Cu–N bond, a freely rotating group is simpler to calculate. Whether rotating or not, this should be a better approximation to an ammonia molecule than just an isolated nitrogen atom. The rotating ammonia scattering factor was computed from equation (5.85) of James (1958), using Hartree–Fock scattering factors for N and H (Cromer & Mann, 1968), and an N–H distance of 1.0 Å. The ammonia form factor is given in Table 1. This model gave $p_{A(1)} = 0.75$ (1) and $p_{A(3)} = 0.51$ (2), leading to a formula with three NH₃ molecules within a standard deviation. The final R indices are $R = 0.055$ and $R_w = 0.044$. A difference Fourier calculated after the final refinement had only two significant peaks, of magnitudes 1.2 and 1.0 e.Å⁻¹, both located close to the two final copper-atom positions.

Table 1. Scattering factor for disordered ammonia group computed from Hartree–Fock wave functions for N and H.

The maximum value of $\sin \theta/\lambda$ for this function is 1.5 Å⁻¹.

$$f = \sum_{i=1}^4 a_i \exp(-b_i \sin^2 \theta/\lambda^2) + c$$

$a_1 = 4.96981$	$b_1 = 27.3056$
$a_2 = 1.75969$	$b_2 = 6.83120$
$a_3 = 1.67081$	$b_3 = 0.357098$
$a_4 = 1.50780$	$b_4 = 60.6853$
$c = 0.091797$	

Atomic scattering factors for copper and nitrogen were taken from Doyle & Turner (1968), and a Hartree–Fock valence-state scattering factor was used for carbon (Cromer, 1970). For the disordered cyanide groups, $(f_c + f_n)/2$ was used. Both real and imaginary

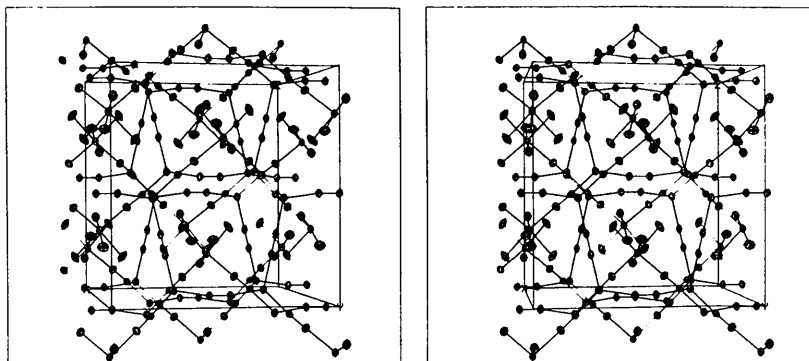


Fig. 2. Stereo view of $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$ along the (0-15, 1-0, 0) direction including thermal ellipsoids.

anomalous dispersion terms were used for all atoms (Cromer & Liberman, 1970). The largest secondary extinction correction, slightly less than 4% in F , was applied to the 202 reflection. The final least-squares parameters with their estimated standard deviations are given in Table 2, and the observed and calculated structure factors are presented in Table 3.

Discussion

The structure of this compound consists of infinite polymeric chains stretching in the a direction. A segment of one of these chains, including the important bond distances, is shown in Fig. 1. More complete lists of bond distances, intermolecular distances, and bond angles are given in Tables 4 and 5. The chains consist of one $\text{Cu}(2)$ and four $\text{Cu}(1)$ atoms bonded

together by cyanide ions to form a nearly planar pentagon. The greatest deviation from planarity involves the apex of the pentagon occupied by $\text{Cu}(2)$ which forms an angle of approximately 20° with the rest of the pentagon. Each pentagon shares two of its edges with adjacent pentagons which are reversed with respect to the first pentagon to form the infinite chains.

The geometry about $\text{Cu}(2)$ is distorted-octahedral, consisting of two nitrogen atoms *cis* to one another from the ordered cyanide groups and three ammonia molecules and a vacancy distributed over four positions. The $\text{Cu}(2)$ -N distance is 2.019 (8) Å, the two $\text{Cu}(2)$ - NH_3 distances are 2.04 (1) and 2.07 (2) Å, and a longer ammonia distance, with $A(2)$, is 2.21 (1) Å. Except for the last distance, these values are similar to those found in other Cu-NH_3 , Cu-CN complexes (Cromer, Larson & Roof, 1964).

Table 2. Position and thermal parameters with standard deviations

	x	y	z	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
$\text{Cu}(1)$	0.2032 (1)	0.3301 (1)	0.0570 (1)	36 (1)	88 (1)	47 (1)	-5 (2)	8 (2)	9 (2)
$\text{Cu}(2)$	0.0000 (0)	0.0712 (1)	0.1966 (1)	28 (1)	46 (1)	45 (1)	0 (0)	0 (0)	-4 (2)
C	0.1881 (7)	0.1374 (7)	0.0429 (7)	42 (7)	47 (7)	42 (7)	9 (11)	-20 (12)	19 (11)
N	0.1218 (6)	0.1061 (5)	0.0972 (5)	49 (6)	60 (6)	48 (6)	-7 (11)	20 (11)	1 (9)
$A(1)$	0.1092 (8)	0.0434 (8)	0.3133 (8)	68 (10)	100 (11)	100 (12)	49 (16)	-98 (20)	-63 (18)
$A(2)$	0.0000 (0)	0.4169 (7)	0.3561 (8)	53 (9)	32 (8)	68 (9)	0 (0)	0 (0)	-19 (15)
$A(3)$	0.0000 (0)	0.2098 (16)	0.2635 (17)	115 (26)	39 (17)	68 (22)	0 (0)	0 (0)	18 (30)
$D(1)$	0.0474 (5)	0.3479 (6)	0.0357 (6)	31 (5)	78 (7)	50 (6)	-6 (9)	-6 (10)	22 (10)
$D(2)$	0.2398 (7)	0.3288 (6)	0.2064 (5)	23 (5)	78 (7)	54 (6)	-2 (11)	2 (12)	-1 (12)

Table 3. Observed and calculated structure factors for $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$.

Column headings are l , $10F_o/K$, $10F_c^*/K$ (see text). A minus sign preceding F_o means 'less than'.

h	k	l	$10F_o/K$	$10F_c^*/K$	h	k	l	$10F_o/K$	$10F_c^*/K$	h	k	l	$10F_o/K$	$10F_c^*/K$
0	0	0	1000	1000	0	0	0	1000	1000	0	0	0	1000	1000
0	0	1	1000	1000	0	0	1	1000	1000	0	0	1	1000	1000
0	0	2	1000	1000	0	0	2	1000	1000	0	0	2	1000	1000
0	0	3	1000	1000	0	0	3	1000	1000	0	0	3	1000	1000
0	0	4	1000	1000	0	0	4	1000	1000	0	0	4	1000	1000
0	0	5	1000	1000	0	0	5	1000	1000	0	0	5	1000	1000
0	0	6	1000	1000	0	0	6	1000	1000	0	0	6	1000	1000
0	0	7	1000	1000	0	0	7	1000	1000	0	0	7	1000	1000
0	0	8	1000	1000	0	0	8	1000	1000	0	0	8	1000	1000
0	0	9	1000	1000	0	0	9	1000	1000	0	0	9	1000	1000
0	0	10	1000	1000	0	0	10	1000	1000	0	0	10	1000	1000
0	0	11	1000	1000	0	0	11	1000	1000	0	0	11	1000	1000
0	0	12	1000	1000	0	0	12	1000	1000	0	0	12	1000	1000
0	0	13	1000	1000	0	0	13	1000	1000	0	0	13	1000	1000
0	0	14	1000	1000	0	0	14	1000	1000	0	0	14	1000	1000
0	0	15	1000	1000	0	0	15	1000	1000	0	0	15	1000	1000
0	0	16	1000	1000	0	0	16	1000	1000	0	0	16	1000	1000
0	0	17	1000	1000	0	0	17	1000	1000	0	0	17	1000	1000
0	0	18	1000	1000	0	0	18	1000	1000	0	0	18	1000	1000
0	0	19	1000	1000	0	0	19	1000	1000	0	0	19	1000	1000
0	0	20	1000	1000	0	0	20	1000	1000	0	0	20	1000	1000
0	0	21	1000	1000	0	0	21	1000	1000	0	0	21	1000	1000
0	0	22	1000	1000	0	0	22	1000	1000	0	0	22	1000	1000
0	0	23	1000	1000	0	0	23	1000	1000	0	0	23	1000	1000
0	0	24	1000	1000	0	0	24	1000	1000	0	0	24	1000	1000
0	0	25	1000	1000	0	0	25	1000	1000	0	0	25	1000	1000
0	0	26	1000	1000	0	0	26	1000	1000	0	0	26	1000	1000
0	0	27	1000	1000	0	0	27	1000	1000	0	0	27	1000	1000
0	0	28	1000	1000	0	0	28	1000	1000	0	0	28	1000	1000
0	0	29	1000	1000	0	0	29	1000	1000	0	0	29	1000	1000
0	0	30	1000	1000	0	0	30	1000	1000	0	0	30	1000	1000
0	0	31	1000	1000	0	0	31	1000	1000	0	0	31	1000	1000
0	0	32	1000	1000	0	0	32	1000	1000	0	0	32	1000	1000
0	0	33	1000	1000	0	0	33	1000	1000	0	0	33	1000	1000
0	0	34	1000	1000	0	0	34	1000	1000	0	0	34	1000	1000
0	0	35	1000	1000	0	0	35	1000	1000	0	0	35	1000	1000
0	0	36	1000	1000	0	0	36	1000	1000	0	0	36	1000	1000
0	0	37	1000	1000	0	0	37	1000	1000	0	0	37	1000	1000
0	0	38	1000	1000	0	0	38	1000	1000	0	0	38	1000	1000
0	0	39	1000	1000	0	0	39	1000	1000	0	0	39	1000	1000
0	0	40	1000	1000	0	0	40	1000	1000	0	0	40	1000	1000
0	0	41	1000	1000	0	0	41	1000	1000	0	0	41	1000	1000
0	0	42	1000	1000	0	0	42	1000	1000	0	0	42	1000	1000
0	0	43	1000	1000	0	0	43	1000	1000	0	0	43	1000	1000
0	0	44	1000	1000	0	0	44	1000	1000	0	0	44	1000	1000
0	0	45	1000	1000	0	0	45	1000	1000	0	0	45	1000	1000
0	0	46	1000	1000	0	0	46	1000	1000	0	0	46	1000	1000
0	0	47	1000	1000	0	0	47	1000	1000	0	0	47	1000	1000
0	0	48	1000	1000	0	0	48	1000	1000	0	0	48	1000	1000
0	0	49	1000	1000	0	0	49	1000	1000	0	0	49	1000	1000
0	0	50	1000	1000	0	0	50	1000	1000	0	0	50	1000	1000
0	0	51	1000	1000	0	0	51	1000	1000	0	0	51	1000	1000
0	0	52	1000	1000	0	0	52	1000	1000	0	0	52	1000	1000
0	0	53	1000	1000	0	0	53	1000	1000	0	0	53	1000	1000
0	0	54	1000	1000	0	0	54	1000	1000	0	0	54	1000	1000
0	0	55	1000	1000	0	0	55	1000	1000	0	0	55	1000	1000
0	0	56	1000	1000	0	0	56	1000	1000	0	0	56	1000	1000
0	0	57	1000	1000	0	0	57	1000	1000	0	0	57	1000	1000
0	0	58	1000	1000	0	0	58	1000	1000	0	0	58	1000	1000
0	0	59	1000	1000	0	0	59	1000	1000	0	0	59	1000	1000
0	0	60	1000	1000	0	0	60	1000	1000	0	0	60	1000	1000
0	0	61	1000	1000	0	0	61	1000	1000	0	0	61	1000	1000
0	0	62	1000	1000	0	0	62	1000	1000	0	0	62	1000	1000
0	0	63	1000	1000	0	0	63	1000	1000	0	0	63	1000	1000
0	0	64	1000	1000	0	0	64	1000	1000	0	0	64	1000	1000
0	0	65	1000	1000	0	0	65	1000	1000	0	0	65	1000	1000
0	0	66	1000	1000	0	0	66	1000	1000	0	0	66	1000	1000
0	0	67	1000	1000	0	0	67	1000	1000	0	0	67	1000	1000
0	0	68	1000	1000	0	0	68	1000	1000	0	0	68	1000	1000
0	0	69	1000	1000	0	0	69	1000	1000	0	0	69	1000	1000
0	0	70	1000	1000	0	0	70	1000	1000	0	0	70	1000	1000
0	0	71	1000	1000	0	0	71	1000	1000	0	0	71	1000	1000
0	0	72	1000	1000	0	0	72	1000	1000	0	0	72	1000	1000
0	0	73	1000	1000	0	0	73	1000	1000	0	0	73	1000	1000
0	0	74	1000	1000	0	0	74	1000	1000	0	0	74	1000	1000
0	0	75	1000	1000	0	0	75	1000	1000	0	0	75	1000	1000
0	0	76	1000	1000	0	0	76	1000	1000	0	0	76	1000	1000
0	0	77	1000	1000	0	0	77	1000	1000	0	0	77	1000	1000
0	0	78	1000	1000	0	0	78	1000	1000	0	0	78	1000	1000
0	0	79	1000	1000	0	0	79	1000	1000	0	0	79	1000	1000
0	0	80	1000	1000	0	0	80	1000	1000	0	0	80	1000	1000
0	0	81	1000	1000	0	0	81	1000	1000	0	0	81	1000	1000
0	0	82	1000	1000	0	0	82	1000	1000	0	0	82	1000	1000
0	0	83	1000	1000	0	0	83	1000	1000	0	0	83	1000	1000
0	0	84	1000	1000	0	0	84	1000	1000	0	0	84	1000	1000
0														

Table 4. *Bond distances and intermolecular distances*

Bond lengths		Intermolecular distances	
Cu(1)–C	1·900 (9) Å	Cu(1)–Cu(1)	2·868 (3) Å
Cu(1)–D(1)	1·947 (7)	Cu(1)–C	2·642 (9)
Cu(1)–D(2)	1·961 (7)		
Cu(2)–N	2·019 (8)		
Cu(2)–A(1)	2·040 (10)		
Cu(2)–A(2)	2·211 (9)		
Cu(2)–A(3)	2·08 (2)		
N—C	1·151 (9)		
D(1)—D(1)	1·163 (13)		
D(2)—D(2)	1·142 (13)		

Table 5. *Bond angles (°)*

D(1)—Cu(1)—C	124·5 (3)
D(1)—Cu(1)—D(2)	111·3 (3)
C—Cu(1)—D(2)	119·7 (3)
N—Cu(2)—N	95·5 (4)
N—Cu(2)—A(1)	91·0 (4)
N—Cu(2)—A(2)	91·9 (3)
N—Cu(2)—A(3)	92·5 (5)
A(1)—Cu(2)—A(1)	82·1 (6)
A(1)—Cu(2)—A(2)	92·6 (4)
A(1)—Cu(2)—A(3)	82·5 (5)
A(2)—Cu(2)—A(3)	173·5 (7)
N—Cu(2)—A(1)	171·9 (4)
Cu(2)—N—C	171·9 (8)
Cu(1)—C—N	171·2 (9)
Cu(1)—D(1)—D(1)	169·2 (2)
Cu(1)—D(2)—D(2)	179·3 (8)

The coordination geometry about Cu(1) is approximately trigonal planar and consists of the carbon atom from the ordered cyanide group and two disordered cyanide groups. The Cu(1)–C distance is 1·900 (9) Å while the two Cu(1)–disordered-cyanide bond lengths are between a normal Cu–N and Cu–C bond length in complex copper (I) cyanides, *i.e.* Cu(1)–D(1), 1·947 (7) Å and Cu(1)–D(2), 1·961 (7) Å. A carbon atom from a chain above is at a distance of 2·642 (9) Å and is a fourth rather distant neighbor of Cu(1). There is also a moderately short Cu(1)–Cu(1) distance of 2·868 (3) Å between these chains. These interactions are shown in Fig. 2, and Fig. 3 reveals how the planar chains efficiently nest together with the ammonia molecules occupying the holes in the centers of the pentagons.

Table 6 lists the amplitudes and direction angles, relative to the crystallographic axes, of the principal axes of the thermal-vibration ellipsoids for each atomic-position set. The ellipsoids for the disordered cyanide groups D(1) and D(2) and possibly the ellipsoid for Cu(1) reflect positional disorder as well as thermal motion (Figs. 2 & 3). In the usual case, the direction of maximum vibrational freedom is perpendicular to the bond vector; but for D(2), the principal axis of the vibration ellipsoid (root-mean-square amplitude of 0·27 Å) parallels the Cu(1)–D(2) bond vector, indicat-

Table 6. *Magnitudes and direction angles, relative to the crystallographic axes, of the principal axes of the thermal-vibration ellipsoids*

	Axis <i>i</i>	R.m.s. amplitude	<i>B_i</i>	α	β	γ
Cu(1)	1	0·162 (2)	2·07 (5)	16 (3)°	87 (1)°	106 (3)°
	2	0·288 (2)	6·56 (8)	92 (1)	5 (1)	85 (1)
	3	0·198 (2)	3·11 (6)	74 (3)	94 (1)	17 (3)
Cu(2)	1	0·146 (3)	1·69 (6)	0 (0)	90 (0)	90 (0)
	2	0·209 (3)	3·45 (9)	90 (0)	16 (8)	106 (8)
	3	0·192 (3)	2·91 (8)	90 (0)	74 (8)	16 (8)
C	1	0·20 (2)	3·2 (5)	42 (14)	67 (29)	122 (23)
	2	0·22 (2)	3·9 (5)	94 (24)	33 (24)	57 (21)
	3	0·15 (2)	1·7 (4)	49 (14)	112 (11)	49 (12)
N	1	0·17 (1)	2·4 (4)	42 (13)	85 (10)	131 (14)
	2	0·24 (1)	4·5 (5)	101 (17)	11 (21)	94 (18)
	3	0·22 (1)	3·7 (4)	51 (15)	80 (23)	41 (14)
A(1)	1	0·16 (2)	2·0 (6)	34 (6)	92 (7)	57 (6)
	2	0·26 (2)	5·2 (8)	109 (8)	39 (7)	58 (7)
	3	0·37 (2)	10·8 (10)	116 (4)	129 (7)	50 (5)
A(2)	1	0·20 (2)	3·2 (5)	0 (0)	90 (0)	90 (0)
	2	0·17 (2)	2·2 (6)	90 (0)	16 (12)	74 (12)
	3	0·24 (2)	4·6 (6)	90 (0)	106 (12)	16 (12)
A(3)	1	0·30 (3)	6·9 (20)	0 (0)	90 (0)	90 (0)
	2	0·19 (5)	2·7 (13)	90 (0)	20 (30)	110 (30)
	3	0·24 (4)	4·7 (14)	90 (0)	71 (30)	20 (30)
D(1)	1	0·15 (1)	1·9 (3)	7 (12)	88 (6)	83 (14)
	2	0·28 (1)	6·1 (5)	94 (4)	16 (7)	75 (7)
	3	0·20 (1)	3·1 (4)	96 (14)	106 (7)	17 (9)
D(2)	1	0·13 (2)	1·4 (3)	2 (9)	89 (5)	91 (10)
	2	0·27 (1)	5·8 (5)	91 (5)	1 (7)	91 (10)
	3	0·21 (1)	3·5 (4)	89 (10)	89 (10)	1 (10)

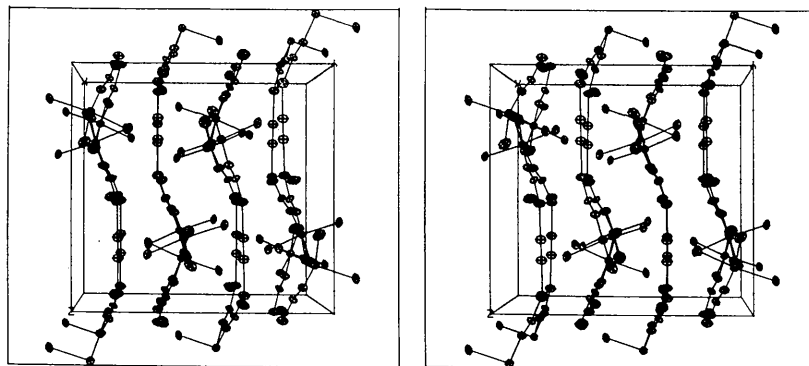


Fig. 3. Stereo view of $\text{Cu}_3(\text{NH}_3)_3(\text{CN})_4$ along the a axis including thermal ellipsoids.

ing that it represents, primarily, positional disorder in this direction. The principal axis of the vibration ellipsoid for $D(1)$ [r.m.s. amplitude of 0.28 \AA] is approximately perpendicular to the $\text{Cu}(1)-D(1)$ bond vector. It is reasonable that the positional disorder for this group is also in this direction since it allows the observed $\text{Cu}(1)-D(1)-D(1)$ angle of 169° to become approximately 180° on a local scale; also, it allows the locally ordered $\text{Cu}-\text{C}$ distance to be approximately 0.1 \AA shorter than the locally ordered $\text{Cu}-\text{N}$ distance. This is consistent with past structure results of copper(I) cyanide complexes, *i.e.* $\text{Cu}-\text{C}-\text{N}$ angles usually very close to 180° and $\text{Cu}-\text{C}$ distances around 1.9 \AA , while $\text{Cu}-\text{N}$ distances are usually about 2.0 \AA . The large r.m.s. amplitude of the vibration ellipsoid for the $\text{Cu}(1)$ atom of 0.28 \AA , which is perpendicular to the plane of the pentagons, might also be due to a slight positional disorder in this direction, although it would be difficult to separate positional and thermal contributions in this case. For the remaining atoms in the asymmetric unit, the ellipsoids appear to be mainly composed of vibrational contributions.

All calculations were performed on a CDC 6600 computer, and programs developed at this laboratory were used.

During the course of this investigation we discovered a report on this same or a very similar compound by Dunaj-Jurco & Poraj-Kosic (1967). They report a noncentrosymmetric space group, $Abm2$, and unit-cell dimensions $a=12.67$, $b=12.24$ and $c=14.57 \text{ \AA}$; these dimensions match ours reasonably well except for the c axis which is almost an ångström longer than our b axis. They used Weissenberg data and refined to a final R index of 17.9% . Although they did not report their atomic coordinates or give their structure factor list, they did publish a two-dimensional projection of their model with approximate atomic coordinates. Except for details of bond lengths and angles, this model appears to be the same as ours but is described in a different space group. An attempt to refine our model in $Cm2a$, the equivalent of their space group but with our orientation, was unsuccessful due to the near singularity of the system. The centrosymmetric space group $Cmma$ which has the same extinction con-

ditions as their space group, $Abm2$, is inconsistent with our observed Patterson function.

Assuming no error has been made either by us or Dunaj-Jurco & Poraj-Kosic, we can only speculate as to the reasons for the discrepancies between the two unit cells. One possibility is that their compound is slightly different from ours in stoichiometry. Also, it is possible that the partially vacant ammonia positions can be ordered in some way, which removes the center of symmetry and the c glide plane observed in our model.

To transform our (WCL) cell and atomic coordinates to theirs (DP):

$$\begin{aligned} a_{\text{WCL}} &= b_{\text{DP}} & x_{\text{WCL}} &= y_{\text{DP}} + 0.25 \\ b_{\text{WCL}} &= c_{\text{DP}} & y_{\text{WCL}} &= z_{\text{DP}} \\ c_{\text{WCL}} &= a_{\text{DP}} & z_{\text{WCL}} &= x_{\text{DP}} - 0.25 \end{aligned}$$

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