461. *The Crystal Structure of Cuprous Iodide–Methyl Isocyanide.*

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The structure of cuprous iodide–methyl isocyanide, $CuI,CH_3·NC$, has been determined by *X*-ray methods. The crystals are monoclinic, space-group $C2/c$, with $a = 13·88$, $b = 13·20$, $c = 5·765$ Å, $\beta = 105°$. The atomic positions have been determined from *b*- and *c*-axis electron-density projections and from the components C_1 and S_1 of the generalised Fourier projection calculated with the data $F(hk1)$. There are double chains of copper and iodine atoms running parallel to the *c*-axis. Cu(1), at the centre of the chain, is bonded tetrahedrally to four iodine atoms at 2·64 and 2·67 Å. Cu(2), on alternate sides of the chain, is bonded tetrahedrally to two iodine atoms [shared with Cu(1)] at 2·73 Å and to two $CH_3·NC$ groups which are at the sides of the chain. There are also short Cu · · · · Cu distances, indicating bonds, 2·89 and 3·42 Å.

Cuprous iodide–methyl isocyanide, a stable crystalline complex, was first prepared by Hartley[1] from cuprous cyanide and methyl iodide. Decomposition yielded methyl isocyanide, but never methyl iodide; later, the compound was prepared from methyl isocyanide and cuprous iodide and is further described by Irving and Jonason.[2] Attempts at molecular-weight determination in acetonitrile solution suggested that the complex is not monomeric; a similarity to Wells's[3] tetrameric $CuI,As(C_2H_5)_3$ seemed possible and the structure determination was undertaken.

Crysta Data.—$CuI,CH_3·NC$, $M = 231·6$, monoclinic, $a = 13·88$, $b = 13·20$, $c = 5·765$ Å, $\beta = 105°$, $U = 1020$ Å^3, $D_m = 2·94$ (by flotation), $Z = 8$, $D_c = 3·02$, $F(000) = 832$. Space-group $C2/c$ (No. 15), Cu-K_α radiation, $\mu = 575$ cm.$^{-1}$. Single-crystal oscillation and Weissenberg photographs.

Experimental

The crystals are colourless needles, elongated along *c*. Oscillation and Weissenberg photographs were taken about the *c* and *b* axes. The intensities of the *hk*0 and *h*0*l* reflections, and later *hk*1 reflections were measured visually, and Lorentz and polarisation corrections applied. Approximate scale and temperature factors were determined from a " Wilson plot "; more accurate values were later derived by comparison of $|F_c|$ with $|F_o|$, and from difference syntheses.

The crystal used to record the *hk*0 data was nearly square in cross section, of thickness 0·06 mm., and the needle axis was parallel to the oscillation axis. The linear absorption coefficient is 575 cm.$^{-1}$. Absorption corrections $A(hk0)$ were estimated by a method based on that of Albrecht[4] for all inner, and a selection of outer reciprocal lattice points. Apart from 6 inner reflections, the correction is equivalent to an additional temperature factor, $\Delta B \sim 0·4$ Å^2; in the 6 inner reflections the correction to F may differ by 10% from the mean correction. The corrections were not applied, for they did not improve the agreement appreciably on the inner reflections and are compensated for by the temperature factor on the others.

Absorption corrections for the *h*0*l* intensities, recorded with the needle axis perpendicular to the oscillation axis, would be much larger. However, this projection has not been refined as far as the *hk*0 projection and no corrections have been applied.

Earlier Fourier summations and calculations of the structure factors were carried out on punched-card equipment supplied by British Tabulating Machines Ltd., later ones on the Ferranti Mercury Computer, using the programmes of J. S. Rollett. The programme, General Fourier Series, by O. S. Mills, was used to calculate the components of the generalised projection. In the structure-factor calculations, Thomas and Umeda's atomic scattering factors[5] have been used for copper and iodine, and those of Berghuis *et al.*[6] for carbon and nitrogen.

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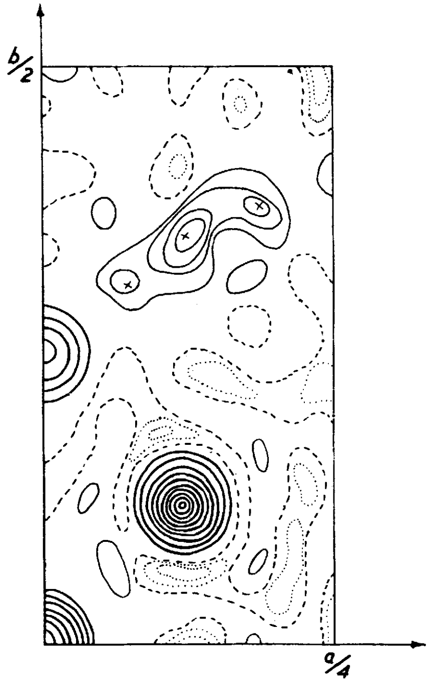
[1] Hartley, *J.*, 1928, 780.
[2] Irving and Jonason *J.*, 1960, 2095.
[3] Wells, *Z. Krist.*, 1936, **94**, 447.
[4] Albrecht, *Rev. Sci. Instr.*, 1939, **10**, 221.
[5] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.
[6] Berghuis, Haanappel, Potters, Loopska, MacGillavry, and Veenendaae, *Acta Cryst.*, 1955, **8**, 478.

STRUCTURE ANALYSIS.

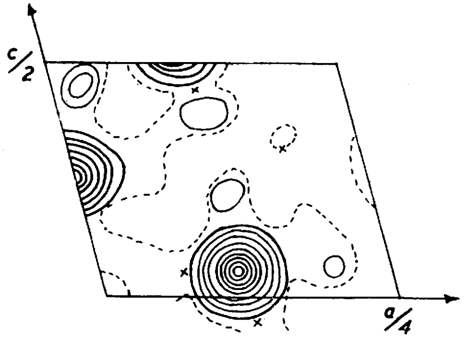
Patterson Projections.—Approximate (x,y) parameters for the iodine and copper atoms were derived from the c-axis Patterson projection. There were four possible arrangements of these atoms which could account for the positions of the Patterson peaks but, of these, only one was

FIG. 1. *c-Axis electron-density projection; compare with Fig. 5 for atomic positions.*



Contour interval 10 e Å^{-2} *on* Cu *and* I, 2 e Å^{-2} *elsewhere.*
Zero contour, broken line; negative contours, dotted lines.

FIG. 2. *b-Axis electron-density projection; showing* Cu's *(at* $x = 0$, $z = 0{\cdot}25$), I *(at* $x = 0{\cdot}1175$, $z = 0{\cdot}057$); *the light-atom positions found by other means are marked* ×.



Contours, etc., as in Fig. 1.

TABLE 1(*a*). *Atomic parameters.*

	x	y	z		x	y	z
Cu(1)	0	0·005	0·25	C(1)	0·072	0·314	0·567
Cu(2)	0	0·254	0·75	N	0·124	0·351	0·444
I	0·1175	0·119	0·056	C(2)	0·184	0·381	0·317

TABLE 1(*b*). *Summary of parameters and method of determination.*

(Origin of co-ordinates and axes as in International Tables for Crystallography.)

	I ($hk0$)			II ($h0l$)	III (hkl)				IV
Atom	x	y	B	z	th.*	C_1†	S_1‡	deduce §	final z
Cu(1)	0	±0·005	3·9	0·25	31	0	+	($y = +0{\cdot}005$)	0·250
Cu(2)	0	0·254	3·9	0·75	31	0	−45		0·750
I	0·1175	0·119	1·8	0·057	93	102	38		0·056
C(1)	0·072	0·314	(3·9)	—	4·7	−4·4	−2·2	$z = \frac{1}{2} - \frac{3}{4}$	0·567
N	0·124	0·351	(3·9)	—	5·5	−9·3	0	$z \sim \frac{1}{2}$	0·444
C(2)	0·184	0·381	(3·9)	—	4·7	0	6·5	$z \sim \frac{1}{4}$	0·317
R factor ...		10%		21%			25%		

(I) From c-axis Fourier projection.
(II) From b-axis Fourier projection.
(III) From generalised projection using $(hk1)$ data: * th. = theoretical peak height of atom at $z = 0$ in C_1 or $\frac{1}{4}$ in S_1; † C_1 = peak height in C_1; ‡ S_1 = peak height in S_1 (electrons Å^{-2}); § deduction from C_1 and S_1.
(IV) z Parameter chosen.

TABLE 2. *Bond lengths and angles.*

(For numbering of atoms, see Figs. 4 and 5.)

Bond	Length (Å)	Bond	Angle
Cu(1)–I	2·668	I–Cu(1)–I$^{\mathrm{I}}$	114°
Cu(1)–I$^{\mathrm{I}}$	2·638	I–Cu(1)–I$^{\mathrm{III}}$	111°
Cu(1)–Cu(1)$^{\mathrm{I}}$	2·885	I–Cu(1)–I$^{\mathrm{IV}}$	107°
Cu(1)$^{\mathrm{I}}$–Cu(2)	3·419	I$^{\mathrm{I}}$–Cu(1)–I$^{\mathrm{IV}}$	103°
Cu(2)–I$^{\mathrm{I}}$	2·731	I$^{\mathrm{I}}$–Cu(2)–I$^{\mathrm{II}}$	99°
Cu(2)–C(1)	1·81	C(1)–Cu(2)–C(1)	128°
C(1)–N	1·24	I$^{\mathrm{I}}$–Cu(2)–C(1)	110°
N–C(2)	1·30	I$^{\mathrm{II}}$–Cu(2)–C(1)	104°
		Cu(1)–I$^{\mathrm{I}}$–Cu(1)$^{\mathrm{I}}$	66°
		Cu(1)–I$^{\mathrm{I}}$–Cu(2)	108°
		Cu(1)$^{\mathrm{I}}$–I$^{\mathrm{I}}$–Cu(2)	79°

Estimated accuracy of bond lengths involving Cu and I, ±0·02 Å; of angles ±2°; of Cu(2)–C(1) bond length ±0·15 Å.

TABLE 3. *Observed and calculated F's (half absolute values).*

*h*00	F_o	F_c
2	123	126
4	127	−111
6	33	26
8	171	167
10	88	88
12	46	−46
14	19	−24
16	49	55
*h*10		
1	131	140
3	13	−15
5	73	−62
7	81	74
9	108	102
13	39	−43
17	35	38
*h*20		
0	8	−6
2	11	−8
*h*30		
1	13	0
3	88	93
5	117	109
7	13	−8
9	45	−42
11	30	31
13	55	55
*h*40		
0	141	−120
2	77	76
4	248	236
6	105	90
8	68	−62
10	12	−13
12	90	92
14	52	57
16	27	−29
*h*50		
1	78	−71
3	104	95
5	150	134
7	21	−19
9	66	−63
11	30	32
13	60	61
*h*60		
0	19	−18
4	19	20
*h*60	F_o	F_c
6	10	2
8	20	−19
*h*70		
1	82	78
3	13	3
5	28	−22
7	42	40
9	55	56
13	5	−19
*h*80		
0	184	173
2	57	51
4	71	−67
6	19	17
8	117	112
10	62	58
12	35	−39
14	16	−23
*h*90		
1	102	95
3	41	−42
5	74	−72
7	50	47
9	77	77
13	34	−44
h,10,0		
0	31	37
4	32	−31
8	18	21
h,11,0		
3	31	33
5	44	42
13	14	20
h,12,0		
0	43	−53
2	18	19
4	93	90
6	32	35
8	35	−37
12	32	44
h,13,0		
1	36	−46
3	43	48
5	54	63
7	21	−25
9	39	−48
11	12	16
h,14,0		
0	29	−35
h,14,0	F_o	F_c
4	22	30
8	16	−22
h,15,0		
1	10	18
h,16,0		
0	49	55
2	11	14
4	24	−31
*h*11		
1	64	−45
3	20	12
5	151	106
7	113	78
9	34	−30
11	39	−35
13	29	34
15	31	39
−1	51	71
−3	210	156
−5	13	11
−7	80	−65
−9	25	24
−11	79	82
−13	16	26
−15	18	−32
*h*21		
0	73	−51
2	302	−219
4	24	13
6	211	144
10	127	−93
12	22	−18
14	54	57
−2	172	181
−4	105	80
−6	149	−120
−8	115	−90
−10	73	73
−12	50	66
−14	21	−44
−16	17	−48
*h*31		
1	242	−171
3	141	−103
5	63	42
7	50	40
9	95	−69
11	81	−68
13	14	18
15	22	30
*h*31	F_o	F_c
−1	25	−12
−3	108	95
−5	74	−60
−7	160	−134
−9	26	−22
−11	40	50
−15	22	−54
*h*41		
2	15	−5
4	14	13
6	9	14
8	15	−6
10	17	−14
−6	14	−17
*h*51		
1	109	97
3	67	52
5	38	−27
7	23	−20
9	52	47
11	43	44
13	7	−11
15	10	−20
−1	9	16
−3	50	−48
−5	39	37
−7	98	86
−9	22	17
−11	26	−34
*h*61		
0	35	24
2	141	129
4	37	−33
6	163	−123
10	91	75
14	44	−52
−2	155	−138
−4	77	−66
−6	101	89
−8	68	65
−10	54	−70
−12	39	−64
*h*71		
1	73	74
3	27	32
5	131	−95
7	103	−85
9	26	28
11	34	38
13	31	−34
−1	93	−75
*h*71	F_o	F_c
−3	154	−153
−5	13	−9
−7	58	67
−9	23	−22
−11	51	−77
*h*81		
2	19	27
6	27	−26
10	11	18
−2	23	−25
−4	20	−20
−8	11	20
−10	12	−14
*h*91		
1	22	−29
5	35	38
7	29	33
9	11	−10
11	10	−14
−1	22	26
−3	52	62
−7	23	−26
−11	15	32
h,10,1		
0	32	−37
2	77	−97
6	62	70
8	11	−8
10	53	−71
12	10	−14
−2	57	71
−4	25	31
−6	57	−73
−8	37	−57
−10	22	40
−12	12	41
h,11,1		
1	75	−94
3	52	−61
5	28	40
7	25	35
9	36	−48
11	35	−49
−3	41	64
−5	26	−37
−7	57	−87
h,12,1		
0	16	−14
2	23	−35
6	11	27
h,12,1	F_o	F_c
10	15	−19
−2	16	28
−6	16	−20
h,14,1		
2	29	48
6	34	−52
−2	32	−55
−4	15	−34
h,15,1		
1	20	39
5	32	−46
−1	14	−31
−3	36	−63
*h*02		
0	75	59
2	157	−143
4	148	−204
8	77	67
10	57	−44
12	89	−84
−2	74	40
−4	156	−171
−6	151	−188
−10	58	53
−12	74	−61
−14	84	−85
*h*04		
0	77	58
2	72	−64
6	56	90
8	47	55
10	31	−29
−2	166	157
−4	70	44
−6	56	−56
−10	84	99
−12	58	50
*h*06		
0	49	−51
2	45	−69
4	4	6
6	24	37
−2	45	33
−4	14	32
−6	55	−59
−8	62	−69
−10	3	17
−12	22	35
−14	36	−25

found to be consistent with the peak heights. This placed the iodine atom in a general position at approximately 1/8,1/8 and the copper atoms at two 4-fold special positions; for Cu(2) the position was of type $0,y,1/4$ with $y \sim 1/4$, while Cu(1) was located either at a centre of symmetry at 0,0,0 or at a position of type $0,y,1/4$ with $y \sim 0$. The *b*-axis Patterson projection showed that both Cu(1) and Cu(2) were, in fact, at positions of type $0,y,1/4$ and gave an approximate z co-ordinate for the iodine atom.

Electron-density Projections.—The first c-axis electron-density projection, phased by the odine-atom contributions alone, confirmed the chosen copper positions; further confirmation was given by calculation of $F(h20)$ and $F(h60)$ whose observed values are very low. Refinement of this projection by difference Fourier syntheses (copper and iodine subtracted) indicated small adjustments in the copper and iodine positions and different temperature factors for copper and iodine; (x,y) parameters could also be derived for the $CH_3{\cdot}NC$ group. The atomic positions and temperature factors are listed in Table 1 (the temperature factor for carbon and nitrogen was assumed to be the same as for copper). The R factor for this projection (excluding non-observed reflections) is 10%. The observed and calculated structure amplitudes are compared in Table 3, and the final electron-density projection is shown in Fig. 1.

The b-axis electron-density projection (Fig. 2) was calculated and indicated a small adjustment of the iodine z co-ordinate. From the two projections the character of the CuI structure was clear, *i.e.*, double chains of copper and iodine atoms running parallel to the c-axis, with the $CH_3{\cdot}NC$ groups attached at the sides of the chains. However, the z co-ordinates of the carbon and nitrogen atoms could not be determined from the b-axis electron-density projection, or from a difference Fourier synthesis with the copper and iodine contributions subtracted. Two sets of chemically reasonable positions for carbon and nitrogen could be postulated, but the agreement between the observed structure amplitudes and the values calculated for the two arrangements was not significantly different.

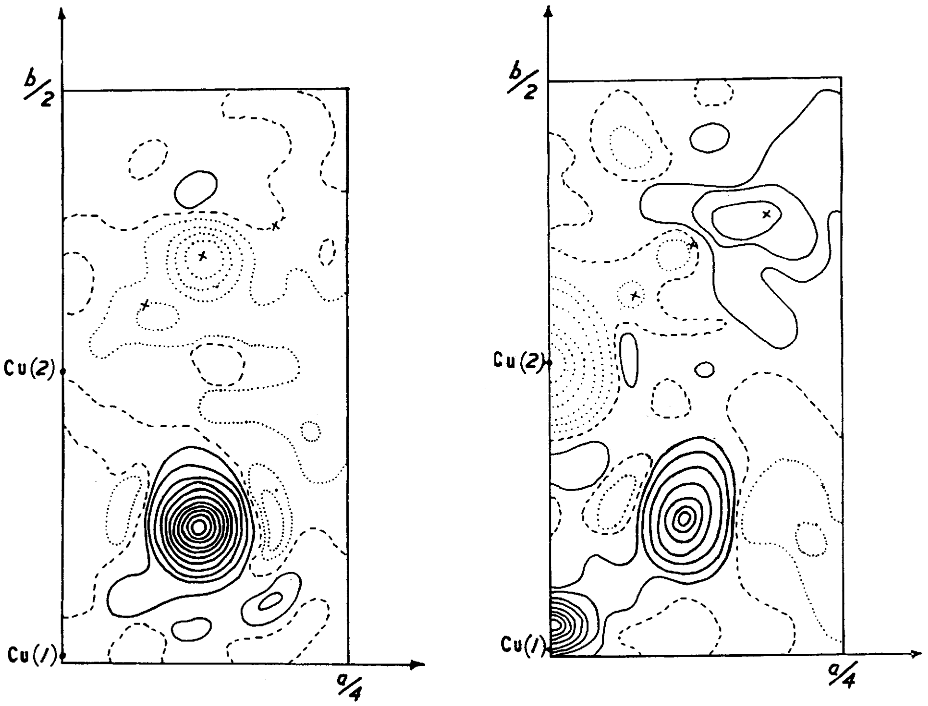


FIG. 3*a*. FIG. 3*b*.

FIG. 3. *The components C_1 (xy) (a), and S_1 (xy) (b) of the generalised electron-density projection. Contour interval* 2 e Å^{-2} *generally, but* 10 e Å^{-2} *on* I *in* (*a*) *and* 5 e Å^{-2} *on* Cu(2) *and* I *in* (*b*). *Zero contour, broken line; negative contours, dotted lines. Compare with Fig.* 5 *for atomic positions.*

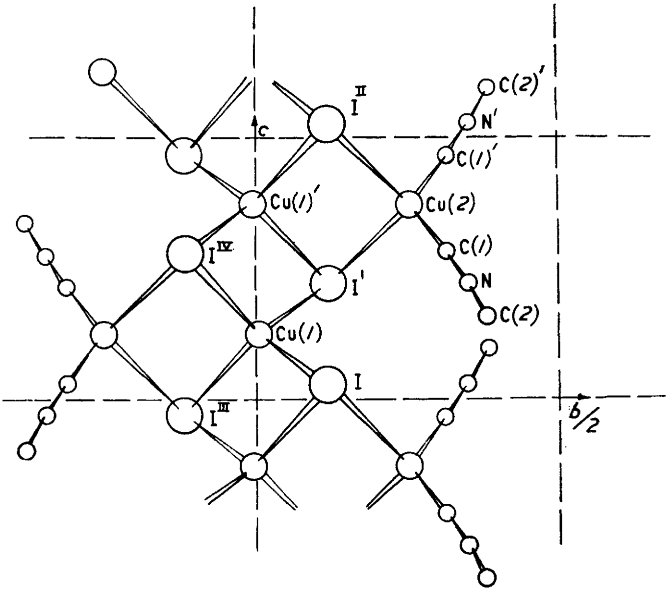
Further, the two projections leave an ambiguity in the position of Cu(1). Iodine and Cu(2) being taken as fixed, Cu(1) at $z = 1/4$ may have $y = \pm 0{\cdot}005$. Generalised projections using the data $F(hkl)$ were able to resolve this ambiguity and to give a good indication of the z parameters of the carbon and nitrogen.

Generalised Electron-density Projections.—The contributions of the copper and iodine atoms to $F(hkl)$ were calculated, it being assumed that, for Cu(1), $y = 0$. These agreed well with the observed $|F(hkl)|$ and were used to derive a scaling constant. By using the calculated signs and observed structure amplitudes, the components $C_1(x,y)$ and $S_1(x,y)$ of the generalised projection $\rho_1(x,y)$ [7] were computed. The component projections are shown in Fig. 3. The peak heights and deductions made are listed in Table 1. Theoretical peak heights were calculated, but it seemed better to estimate z parameters from

$$\tan 2\pi lz = \frac{\sin 2\pi lz}{\cos 2\pi lz} = \frac{\text{height of peak in } S_L}{\text{height of peak in } C_L}$$

Differences between the theoretical and the observed peak heights could be due, in part, to residual errors in the scaling and temperature factors. No refinement of the generalised projection was attempted. The final z-parameters for the carbon and nitrogen atoms are a compromise between those derived from the generalised projection, those which fit the b-axis electron-density projection, and those which give chemically reasonable bond lengths.

FIG. 4. *Projection of structure along a-axis.*



DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Table 1 summarises the co-ordinates of the atoms, and Figs. 4 and 5 show the structure. Table 2 gives bond lengths and angles, which were calculated from the co-ordinates on " Mercury," with a programme written by R. A. Sparks.

Both copper atoms are in nearly regular tetrahedral co-ordination, Cu(1) by four iodine atoms, and Cu(2) by two iodine atoms and two light atoms, presumably carbon atoms, of isocyanide groups. Each pair of copper atoms shares two iodine atoms. The Cu–I bonds around Cu(2) are slightly longer than those around Cu(1). Each iodine atom is co-ordinated to three copper atoms, two Cu(1) and one Cu(2); two of the angles Cu–I–Cu are much smaller than tetrahedral.

There are also short, presumably bonded, distances ($2{\cdot}88_5$ Å) between successive Cu(1) atoms along the chain. The Cu(1)–Cu(2) distance is 3·42 Å, not more than a very weak bond; this suggests that the copper atom cannot readily take part in two metal–metal bonds at right angles.

The closest van der Waals contacts between chains are between iodine and the methyl group, with I • • • • C(2) equal to 3·91 and 3·94 Å.

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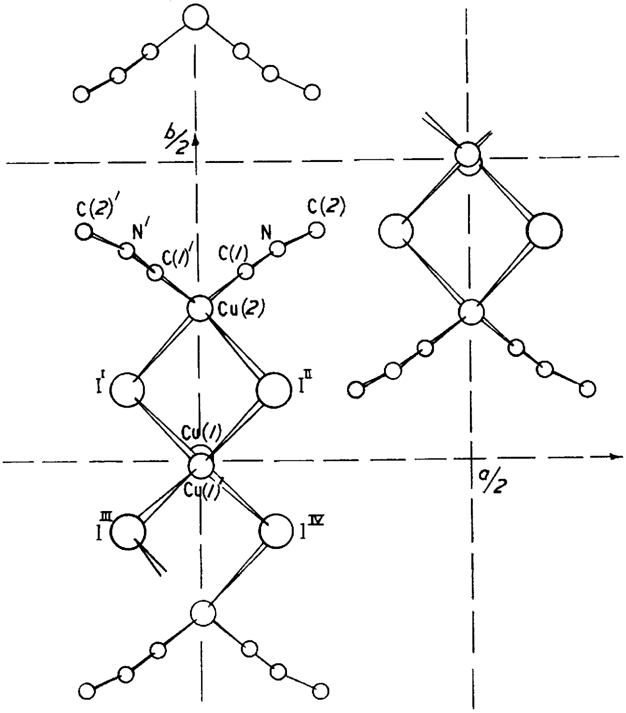
[7] Lipson and Cochran, " The Crystalline State," Vol. III, p. 221, 1953.

Two copper atoms sharing two iodine atoms can be regarded as a four-membered ring, in which, if all the atoms were alike, all the angles would be approximately 90°. But here, the angles at copper are expanded to nearer the tetrahedral angle whereas those at iodine are reduced, thus shortening appreciably the Cu · · · Cu distance. The fact that Cu is four-co-ordinated whereas iodine is only three-co-ordinated might account for this, but Cu · · · Cu bond formation will be very much in its favour. Cu · · · Cu bonds of various lengths have been reported, from 2·60 Å in $CuI,As(C_2H_5)_3$ [3] and in copper diazoaminobenzene,[8] 2·64 Å in cupric acetate dihydrate,[9] and 3·27 Å and 3·82 Å in cuprous chloride–azomethane;[10] the last is presumably very weak.

Single- or double-chain structures are common in cuprous halide complexes (for examples, see Brink *et al.*[11]) but no structure reported has quite the same copper–halogen relationships as $CuI,CH_3{\cdot}NC$. In cuprous iodide the Cu · · · I distance is 2·62 Å, and in $CuI,As(C_2H_5)_3$ it is 2·66 Å.

Fig. 5. *Projection of structure along c-axis.*



That the ligand is methyl isocyanide rather than methyl cyanide, is not proved by this structure analysis. It has been assumed from the chemical work that it is the isocyanide, and the peak heights in the (001) electron-density projection are in agreement with this. This projection does suggest that the $CH_3{\cdot}NC$ group is not linear; in the (010) projection the accuracy is not sufficient to indicate non-linearity. The angle CNC calculated from the final co-ordinates is 174°, only possibly significantly different from 180°.

We thank Mrs. D. C. Hodgkin for much advice and help and Dr. J. S. Rollett for his help with computations on "Mercury." One of us (N. E. T.) is indebted to the Commonwealth

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[8] Brown and Dunitz, Internat. Conf. on Co-ordination Chem., *Chem. Soc. Special Publ.* No. **13**, London, 1959.

[9] van Niekirk and Schoening, *Acta Cryst.*, 1953, **6**, 227.

[10] Brown and Dunitz, *Acta Cryst.*, 1960, **13**, 28.

[11] Brink *et al.*, *Acta Cryst.*, 1949, **2**, 158; 1952, **5**, 433, 506; 1954, **7**, 176.

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