Crystal Structure of the Copper(I) Iodide–Pyridine (1/1) Tetramer

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The crystal structure of the copper(I) iodide pyridine adduct has been determined by *X*-ray diffraction at 295 K and refined by least squares to *R* 0.057 for 2 710 ' observed ' reflections. Crystals are orthorhombic, space group $P2_12_12_1$, with $a = 16.032(6)$, $b = 15.510(2)$, and $c = 11.756(3)$ Å. The asymmetric unit is $Cu_4I_4py_4$, based on the well-known tetrahedral tetrameric Cu_4I_4 unit, with Cu–N 2.04, Cu–I 2.70, and Cu–Cu 2.69 Å; the latter distance is much shorter than in the analogous complexes formed with phosphine and arsine ligands.

INTEREST in the adducts CuXL formed by the copper(I) halides CuX, with ' soft ' phosphine and arsine ligands L, has centred around their tetrameric nature, $(CuXL)_4$, and been accompanied by neglect of the adducts formed with L = nitrogenous base. The present paper describes the structure of the pyridine (py) adduct, prepared as described in the literature,[1] and also shown to be tetrameric $\{CuX(py)\}_4$; during the course of the present work, the structure of the morpholine analogue has been reported briefly and independently.[2]

TABLE 1

Atomic fractional cell and thermal parameters (non-hydrogen atoms only), with least-squares estimated standard deviations in the final digit in parentheses [(*x*,*y*,*z*); Cu, I, × 10^4; N, C, × 10^3: *U*; Cu, I, × 10^3, N, C, × 10^2 Å^2]

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
i = 1									
I	−1 546(1)	2 656(1)	2 270(2)	58(2)	51(2)	60(2)	−10(1)	11(1)	2(1)
Cu	0 591(2)	4 124(2)	0 950(3)	58(3)	56(3)	67(3)	−11(2)	16(2)	−2(2)
N	153(1)	481(1)	024(2)	5(1)	3(1)	6(1)	0(1)	2(1)	0(1)
C(a)	167(2)	563(2)	048(3)	7(2)	5(2)	9(2)	−2(2)	0(2)	0(2)
C(b)	232(2)	610(2)	−006(2)	9(2)	5(2)	8(2)	−3(2)	2(2)	−3(2)
C(c)	281(2)	568(2)	−092(2)	7(2)	9(2)	6(2)	−4(2)	−2(2)	2(2)
C(d)	266(2)	482(2)	−112(2)	9(2)	5(2)	5(2)	−1(2)	−1(2)	0(1)
C(e)	207(2)	440(2)	−049(2)	7(2)	7(2)	7(2)	−2(2)	−1(2)	4(2)
i = 2									
I	−0 489(1)	3 980(1)	−0 803(2)	77(2)	60(2)	41(20)	−6(1)	−1(1)	5(1)
Cu	−0 015(3)	3 302(2)	2 787(3)	81(3)	59(3)	48(3)	−1(2)	−3(2)	6(2)
N	031(1)	284(1)	436(2)	6(1)	8(2)	3(1)	−2(1)	0(1)	−2(1)
C(a)	042(3)	198(2)	456(3)	18(4)	5(2)	7(2)	−2(2)	0(3)	1(2)
C(b)	069(2)	169(2)	554(3)	14(3)	5(2)	9(2)	−2(2)	−2(3)	5(2)
C(c)	081(3)	220(2)	644(2)	21(4)	8(2)	4(2)	−2(3)	0(2)	0(2)
C(d)	068(2)	312(2)	629(3)	17(4)	9(2)	7(2)	−6(3)	−3(3)	0(2)
C(e)	042(2)	339(2)	524(2)	8(2)	10(2)	6(2)	−2(2)	−3(2)	4(2)
i = 3									
I	1 259(1)	2 583(1)	1 478(2)	53(2)	48(2)	64(2)	6(1)	0(1)	−1(1)
Cu	−1 058(2)	4 150(2)	1 344(3)	61(3)	56(3)	68(3)	5(2)	−3(2)	2(2)
N	−206(1)	496(2)	116(2)	5(1)	9(2)	6(2)	2(1)	0(1)	3(1)
C(a)	−220(2)	563(2)	180(2)	5(2)	13(3)	7(2)	5(2)	2(2)	1(2)
C(b)	−278(2)	626(2)	160(3)	6(2)	9(2)	11(3)	1(2)	−1(2)	−2(2)
C(c)	−325(2)	619(2)	064(3)	12(3)	4(2)	14(3)	0(2)	−8(2)	0(2)
C(d)	−314(2)	549(3)	−003(3)	8(3)	16(4)	13(3)	1(3)	−3(2)	−7(3)
C(e)	−251(2)	488(3)	022(3)	6(2)	21(4)	6(2)	6(2)	−3(2)	−3(3)
i = 4									
I	0 023(1)	5 019(1)	2 729(1)	50(2)	44(2)	46(2)	1(1)	−1(1)	−6(1)
Cu	−0 296(2)	2 645(2)	0 771(3)	62(3)	65(3)	65(3)	−2(2)	1(2)	−21(2)
N	−050(2)	168(1)	−037(2)	9(2)	6(1)	4(1)	−0(1)	3(1)	−1(1)
C(a)	007(1)	114(2)	−070(2)	5(2)	7(2)	3(1)	2(1)	−1(1)	−1(1)
C(b)	−007(2)	057(2)	−163(2)	10(2)	6(2)	8(2)	0(2)	−1(2)	−5(2)
C(c)	−084(2)	053(2)	−208(3)	10(3)	10(3)	9(2)	−5(2)	−2(2)	−3(2)
C(d)	−144(2)	106(2)	−165(3)	7(2)	13(3)	13(3)	−3(2)	2(2)	−6(3)
C(e)	−127(2)	162(2)	−085(3)	8(2)	6(2)	11(3)	0(2)	−2(2)	−5(2)

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[1] A. V. Malik, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2106.

[2] V. Schramm and K. F. Fischer, *Naturwiss.*, 1974, **61**, 500.

RESULTS

A crystal 0.12 × 0.12 × 0.12 mm mounted up b was used for the crystallographic work. Cell dimensions were obtained from a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 25° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer, and a unique set of data in the range $2\theta < 50°$ gathered by a conventional 2θ—θ scan, yielding 2 906 independent reflections; of these 2 710 with $I > 2\sigma(I)$ were considered 'observed' and used in the structure solution and refinement after application of an analytical absorption correction.

Crystal Data.—$(C_5H_5CuIN)_4 \equiv C_{20}H_{20}Cu_4I_4N_4$, M = 1 078, Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), a = 16.032(6), b = 15.510(2), c = 11.756(3) Å, U = 2 923(2) Å^3, D_m = 2.44 g cm^{-3}, Z = 4, D_c = 2.45$_4$ g cm^{-3}, $F(000)$ = 1 984, Mo-K_α radiation (monochromatic), λ = 0.710 69 Å, μ(Mo-K_α) = 72.8 cm^{-1}, T = 295(1) K, neutral atom scattering factors, non-hydrogen atoms being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[3–5]

The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least squares, the parameters of the $Cu_4I_4N_4$ molecular core being refined as a single block in order to approximate a full matrix procedure. Anisotropic thermal parameters were of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{23}klb^*c^*)]$; parameters of the hydrogen atoms were included as invariants (*i.e.* r_{C-H} fixed at 1.1 Å^2, U at 0.10 Å^2). Refinement converged with all parameter shifts $< 0.2\sigma$, R being 0.057 and R' =

TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in the final digit in parentheses

(*a*) The pyridine rings; values are given for rings i = 1—4 in order

N–C(a)	1.32(3)	1.38(4)	1.30(3)	1.29(3)	C(e)–N–C(a)	119(2)	118(2)	118(3)	118(2)
C(a)–C(b)	1.43(3)	1.31(5)	1.36(4)	1.42(4)	N–C(a)–C(b)	121(3)	122(3)	126(3)	122(2)
C(b)–C(c)	1.43(4)	1.25(4)	1.36(5)	1.34(4)	C(a)–C(b)–C(c)	119(2)	123(3)	118(3)	118(3)
C(c)–C(d)	1.38(4)	1.45(5)	1.35(5)	1.37(5)	C(b)–C(c)–C(d)	118(3)	117(3)	118(3)	118(3)
C(d)–C(e)	1.37(4)	1.37(4)	1.41(5)	1.31(5)	C(c)–C(d)–C(e)	119(3)	118(3)	121(3)	122(3)
C(e)–N	1.37(3)	1.35(4)	1.33(4)	1.37(4)	C(d)–C(e)–N	123(2)	122(3)	120(4)	121(3)
Cu–N	2.02(2)	2.05(2)	2.06(2)	2.04(2)	Cu–N–C(a)	122(2)	122(2)	124(2)	124(2)
					Cu–N–C(e)	119(2)	121(2)	117(2)	117(2)

(*b*) Core geometries; (1) values are given for I(i − 1, i + 1, i + 2) in that order

Cu(1)–I	2.670(4)	2.700(4)	2.692(4)	N(1)–Cu(1)–I	107.8(6)	101.8(6)	105.4(6)
Cu(2)–I	2.720(5)	2.790(4)	2.665(4)	N(2)–Cu(2)–I	107.6(6)	100.0(6)	111.4(6)
Cu(3)–I	2.678(4)	2.696(4)	2.734(4)	N(3)–Cu(3)–I	103.2(6)	104.8(6)	110.1(6)
Cu(4)–I	2.669(4)	2.794(4)	2.629(4)	N(4)–Cu(4)–I	109.3(7)	108.8(7)	95.2(6)

(2) values for I(i − 1)–Cu(i)–I(i + 1, i+ 2); I(i + 1)–Cu(i)–I(i + 2) and Cu(i − 1)–I(i)–Cu(i + 1, i + 2); Cu(i + 1)–I(i)–Cu(i + 2) in that order

I–Cu(1)–I	115.0(1)	114.6(1)	110.9(1)	Cu–I(1)–Cu	58.1(1)	61.1(1)	60.6(1)
I–Cu(2)–I	113.0(1)	112.5(1)	111.6(1)	Cu–I(2)–Cu	59.7(1)	59.0(1)	59.4(1)
I–Cu(3)–I	113.0(1)	113.3(1)	111.7(1)	Cu–I(3)–Cu	57.7(1)	58.7(1)	61.1(1)
I–Cu(4)–I	120.2(1)	110.9(1)	110.4(1)	Cu–I(4)–Cu	59.6(1)	60.5(1)	60.6(1)

(*c*) Cu–Cu distances

1—2	1—3	1—4	2—3	2—4	3—4
2.690(5)	2.684(5)	2.707(5)	2.722(5)	2.722(5)	2.619(5)

(*d*) I–I distances (similarly)

4.488(3)	4.594(3)	4.479(3)	4.442(3)	4.529(3)	4.513(3)

(*e*) I · · · H contacts <3.5 Å (intermolecular)

I(1) · · · H(1a^{I})	3.3	I(2) · · · H(2b^{II})	3.2
I(2) · · · H(4b^{III})	3.2	I(2) · · · H(4c^{III})	3.3
I(3) · · · H(1c^{IV})	3.4	I(3) · · · H(4e^{V})	3.4
I(3) · · · H(3a^{I})	3.2	I(3) · · · H(3b^{I})	3.2
I(4) · · · H(1c^{IV})	3.3	I(4) · · · H(1d^{IV})	3.4
I(4) · · · H(3d^{VI})	3.0	I(4) · · · H(2a^{II})	3.1

Roman superscripts refer to the following transformations of the asymmetric unit (x, y, z):

I $(\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z)$ II $(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z)$
III $(\bar{x}, \frac{1}{2} + y, -\frac{1}{2} - z)$ IV $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$
V $(\frac{1}{2} + x, \frac{1}{2} - y, \bar{z})$ VI $(-\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$

TABLE 3

Comparison of molecular parameters for other $(CuXL)_4$ systems containing Cu_4 tetrahedra with X = halogen

Compound	Cu–Cu	Cu–L	X · · · X	Cu–X	L–Cu–X	X–Cu–X	Cu–X–Cu
$\{CuCl(Ph_3P)\}_4$ [a]	3.1_1	2.19_2	3.5	2.44_4	122	94	85
$\{CuCl(Et_3P)\}_4$ [b]	3.21_1	2.17_6	3.65_7	2.43_8	120.0	97.2	82.4
$\{CuBr(Et_3P)\}_4$ [b]	3.18_4	2.19_9	3.93_2	2.54_4	116.8	101.3	77.5
$\{CuI(Et_3P)\}_4$ [c]	2.92_7	2.25_4	4.38_0	2.68_4	109.6	109.4	66.1
$\{CuI(Et_3As)\}_4$ [c]	2.78_3	2.36_1	4.42_4	2.67_7	107.4	111.5	62.6
$\{CuI(py)\}_4$ [d]	2.6_9	2.0_4	4.5_1	2.7_0	105.5	113.0	59.7
$\{CuI(morph)\}_4$ [e]	2.6_5	2.0_3		2.7_5			

[a] M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1065. [b] M. R. Churchill, B. G. DeBoer, and S. J. Mendak, *Inorg. Chem.*, 1975, **14**, 2041. [c] M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 1974, **13**, 1899. [d] This work. [e] Ref. 2.

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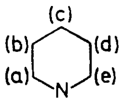
[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

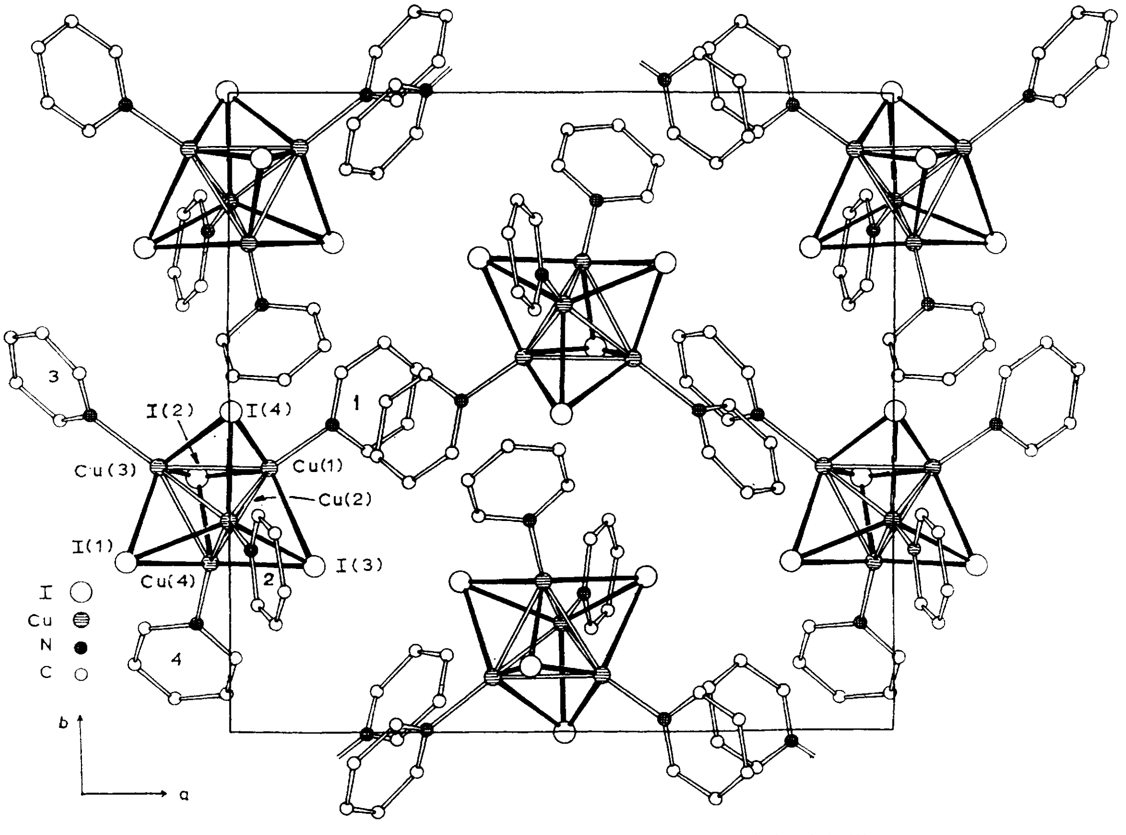
[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

$(\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}} = 0.059$; in a weighting scheme of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$ the appropriate value of n was found to be 2. Change of parity of the structure produced no significant change in R when refined and only trivial changes in geometry; the large variations found within the $N_4Cu_4I_4$ geometry do not appear to be an artefact of a wrong choice of parity.

Results are given in the Tables and Figure. Structure amplitude tables and a table of least-squares planes are deposited as Supplementary Publication No. SUP 21832 (12 pp., 1 microfiche).[*] Within the pyridine rings, carbon atoms are labelled as follows:



being prefixed by i, the number of the associated CuN grouping where necessary; for each iodine, i is defined so that I(i) is bonded to the three Cu atoms numbered Cu-($i-1$, $i+1$, and $i+2$) in the cyclic array {1 2 3 4} (*i.e.* when $i = 4$, $i + 1 = 1$). Hydrogen atoms are given the number of their parent carbon. Computation was carried out using an adaptation of the '*X*-Ray '72' program system [6] implemented on a CDC 6200 machine.



Unit cell contents, projected down c, showing Cu, I, and ring labelling

DISCUSSION

The structure contains the familiar Cu_4I_4 tetrameric unit based on a tetrahedral array of copper atoms with an interpenetrating tetrahedron of iodine atoms triply bridging at the midpoints of the faces. The ligand nitrogen atoms are directed outward from the copper atoms and along the tetrahedral threefold axes. Unlike a number of derivatives of this type, the tetramer contains no crystallographically imposed symmetry elements, and a number of small but significant deviations are found among the 'equivalent' distances within the Cu_4I_4 cluster (Table 2). The geometries of the pyridine rings are normal and will not be further discussed. A wide range of values varying between *ca.* 1.9 and 2.2 Å has been observed for Cu(I)–N distances, broadly correlating with both co-ordination number and the 'hardness' or 'softness' of the associated ligands; the present Cu–N distance of 2.0_4 Å lies at the shorter end of the spectrum for complexes of higher co-ordination number and 'soft' ligands.

Because of the proximity of the Cl–Cu–Cl angle to 90° (actually 94°) in $\{CuCl(Ph_3P)\}_4$, derivatives of the Cu_4X_4 cluster are sometimes referred to as 'cubane-like'; this tendency diminishes as X is changed successively from Cl to Br to I for a given L, X–Cu–X increasing correspondingly and Cu–X increasing while Cu–Cu diminishes (Table 3). The present derivative, together with the recently reported morpholine analogue, are the first examples of adducts with first-row ligands, and a

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[*] For details, see Notice to Authors, No. 7, *J.C.S. Dalton*, 1975, Index issue.

[6] '*X*-Ray System,' version of June, 1972, Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A.

second effect is revealed in that, within the series of group 5 donors, nitrogen is particularly conducive to enhancement of the Cu–Cu bond order with a corresponding diminution in the Cu–I bond order, so that the present examples with nitrogen donors represent the greatest deviations among the pseudo-cubane structures yet observed.

[6/423 *Received, 2nd March,* 1976]