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I_4^{2-} Ions in the Structure of (2,6-Diacetylpyridine dihydrazone)diiodocopper(II).$\frac{1}{2}I_2$

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Abstract. $[Cu(C_9H_{13}N_5)I_2].\frac{1}{2}I_2$, $C_9H_{13}CuI_2N_5.\frac{1}{2}I_2$, monoclinic, $P2_1/c$, $a = 10{\cdot}705\ (2)$, $b = 7{\cdot}936\ (1)$, $c = 19{\cdot}472\ (3)$ Å, $\beta = 97{\cdot}23\ (2)°$, $V = 1641{\cdot}1$ Å^3, $Z = 4$, $\mu(Cu\ K\alpha) = 46{\cdot}6$ mm^{-1}. The structure was solved by heavy-atom methods and refined to $R = 0{\cdot}109$ for 2006 observed reflections. The Cu atom is coordinated to three N atoms of the organic ligand and to two I atoms in a distorted pyramidal arrangement. Chains of coordination polyhedra run parallel to [010]. The iodine molecule forms a bridge $^-I-I-I-I^-$ joining the chains of polyhedra.

Introduction. It is known that Cu^{II} can be reduced to Cu^I by several agents, such as thiourea, I^-, NCS^-, $S_2O_3^{2-}$, *etc.*, but when Cu^{II} is complexed with suitable ligands, reduction does not occur and mixed-ligand complexes with thiourea (Belicchi Ferrari, Calzolari Capacchi, Gasparri Fava, Montenero & Nardelli, 1972; Belicchi Ferrari, Bonamartini Corradi, Gasparri Fava, Grasselli Palmieri, Nardelli & Pelizzi, 1973; Belicchi Ferrari, Gasparri Fava & Pelizzi, 1976), NCS^- (Battaglia, Belicchi Ferrari, Bonamartini Corradi, Gasparri Fava, Pelizzi & Vidoni Tani, 1976) or $S_2O_3^{2-}$ (Belicchi Ferrari, Gasparri Fava & Pelizzi, 1977) can be observed. The crystal structure analysis of the title compound is part of our research on the stabilization of the oxidation state II for Cu and is in connection with an investigation of structural models involving the Cu^I–Cu^{II} redox couple in copper enzymes.

From the reaction of equimolar amounts of copper chloride and 2,6-diacetylpyridine dihydrazone (diap) in ethanol solution, green prisms of the complex $[Cu(diap)Cl_2]$ were isolated. This compound was then dissolved in ethanol and reacted with a large excess of potassium iodide. In this way, by slow evaporation of the solvent, brown needles were obtained, which showed C, H, N, Cu analytical data slightly lower than expected for the formula $[Cu(diap)I_2]$. The X-ray diffraction analysis subsequently defined the exact nature of the complex as $[Cu(diap)I_2].\frac{1}{2}I_2$, where the unexpected presence of the iodine molecule could be attributed to a redox involving Cu^{2+} and I^- ions.

X-ray intensity data were collected on a Siemens AED single-crystal computer-controlled diffractometer using the ω–2θ scan technique with $4° < 2\theta < 120°$ and Ni-filtered Cu $K\alpha$ radiation. 2432 reflections were measured; of these 2006 with intensities $>2\sigma(I)$ were considered as observed and used in the analysis. No absorption corrections were made for the rough crystal shape of the only untwinned sample available. This omission prevents an accurate discussion of the crystallographic parameters involving the lighter atoms.

A three-dimensional Patterson synthesis was used to obtain the coordinates for the heavy atoms [Cu, I(1), I(2), I(3)]. Successive Fourier syntheses gave the coordinates of all non-hydrogen atoms which were refined by means of isotropic and anisotropic least-squares calculations. Unit weights were used and the final value of R was 10·9% (R for observed reflections only). The *SHELX* 76 system of programs (Sheldrick, 1976) was used for the refinement.

The calculations were carried out on the Cyber 7600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Casalecchio, Bologna) with the financial support of the University of Parma.

Atomic coordinates are listed in Table 1 and bond lengths and angles in Table 2.*

Discussion. The projection of the structure of $[Cu(diap)I_2].\frac{1}{2}I_2$ in the plane (100) is shown in Fig. 1. There are two I atoms for each Cu^{II} in a distorted pyramidal pentacoordination. The basal corners of the pyramid are occupied by three N atoms [N(2), N(3), N(4)] of the organic ligand and by one iodine atom [I(1)], while the I(2) atom is located at the apex. The atoms forming the base of the pyramid are coplanar; the central Cu atom is displaced 0·20 Å from the equatorial plane towards I(2). The Cu–N basal distances lie in the middle of the range observed for other pentacoordinated Cu^{II} complexes (Duffin, 1968; Mangia, Nardelli, Pelizzi & Pelizzi, 1971, 1972, 1974; Mangia, Pelizzi & Pelizzi, 1974). A sixth coordination site is occupied by an amino N atom [$Cu-N(5^{ii}) = 3{\cdot}04$ Å], which gives rise to a distorted octahedral coordination around the metal atom; thus, there are

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35745 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* ($\times 10^4$), *with estimated standard deviations in parentheses, and equivalent isotropic thermal parameters* (Å^2)

	x	y	z	B_{eq}*
I(1)	2317 (3)	−352 (5)	3466 (2)	5·59
I(2)	2522 (2)	2328 (4)	1623 (1)	3·30
I(3)	4335 (3)	805 (4)	483 (1)	3·70
Cu	1715 (5)	−924 (9)	2186 (3)	3·42
N(1)	4386 (34)	−2419 (77)	2382 (24)	8·06
N(2)	3245 (27)	−2277 (53)	1935 (23)	5·28
N(3)	1139 (26)	−1763 (43)	1281 (14)	2·85
N(4)	−158 (29)	−211 (45)	2089 (15)	3·17
N(5)	−736 (32)	541 (48)	2598 (16)	4·12
C(1)	4218 (30)	−3789 (59)	1036 (24)	3·30
C(2)	3188 (37)	−2905 (60)	1315 (20)	3·70
C(3)	1932 (35)	−2585 (60)	913 (18)	3·42
C(4)	1601 (42)	−3161 (64)	244 (20)	8·06
C(5)	332 (45)	−2821 (75)	−44 (18)	5·28
C(6)	−523 (42)	−1975 (53)	334 (18)	2·85
C(7)	−94 (34)	−1513 (54)	1008 (18)	3·17
C(8)	−772 (32)	−710 (65)	1500 (19)	4·12
C(9)	−2183 (32)	−342 (64)	1285 (28)	4·87

* Defined according to Hamilton (1959).

Table 2. *Bond lengths* (Å) *and angles* (°)

Symmetry code: (i) $1-x, \bar{y}, \bar{z}$; (ii) $\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$.

Cu–I(1)	2·536 (7)	N(4)–N(5)	1·37 (5)
Cu–I(2)	2·974 (8)	N(4)–C(8)	1·31 (5)
I(3)–I(3^i)	2·806 (4)	C(1)–C(2)	1·47 (6)
Cu–N(2)	2·07 (4)	C(2)–C(3)	1·49 (5)
Cu–N(3)	1·91 (3)	C(3)–C(4)	1·38 (5)
Cu–N(4)	2·07 (3)	C(4)–C(5)	1·43 (6)
Cu–N(5^{ii})	3·04 (4)	C(5)–C(6)	1·41 (7)
N(1)–N(2)	1·41 (5)	C(6)–C(7)	1·38 (5)
N(2)–C(2)	1·30 (6)	C(7)–C(8)	1·42 (6)
N(3)–C(3)	1·35 (5)	C(8)–C(9)	1·54 (5)
N(3)–C(7)	1·37 (4)		

I(1)–Cu–I(2)	99·1 (2)	Cu–N(4)–N(5)	125·0 (2·3)
I(2)–Cu–N(4)	93·0 (1·0)	N(1)–N(2)–C(2)	118·5 (3·4)
I(2)–Cu–N(3)	92·1 (9)	C(3)–N(3)–C(7)	120·2 (3·0)
I(2)–Cu–N(2)	95·1 (9)	N(5)–N(4)–C(8)	122·9 (3·1)
I(1)–Cu–N(4)	99·5 (9)	N(2)–C(2)–C(1)	125·3 (3·5)
I(1)–Cu–N(3)	168·8 (1·0)	C(1)–C(2)–C(3)	123·9 (3·5)
I(1)–Cu–N(2)	102·4 (1·0)	N(2)–C(2)–C(3)	110·9 (3·4)
N(3)–Cu–N(4)	79·3 (1·2)	N(3)–C(3)–C(2)	113·0 (3·2)
N(2)–Cu–N(4)	155·2 (1·4)	C(2)–C(3)–C(4)	123·1 (3·7)
N(2)–Cu–N(3)	77·0 (1·4)	N(3)–C(3)–C(4)	123·9 (3·6)
N(2)–Cu–N(5^{ii})	82·7 (1·4)	C(3)–C(4)–C(5)	115·2 (3·7)
N(3)–Cu–N(5^{ii})	73·5 (1·4)	C(4)–C(5)–C(6)	122·1 (3·5)
N(4)–Cu–N(5^{ii})	84·3 (1·2)	C(5)–C(6)–C(7)	117·4 (3·8)
I(1)–Cu–N(5^{ii})	95·0 (9)	N(3)–C(7)–C(6)	121·1 (3·4)
I(2)–Cu–N(5^{ii})	166·0 (9)	C(6)–C(7)–C(8)	128·3 (3·5)
Cu–N(2)–N(1)	123·0 (3·1)	N(3)–C(7)–C(8)	110·5 (3·1)
Cu–N(2)–C(2)	118·2 (2·6)	N(4)–C(8)–C(7)	118·9 (3·3)
Cu–N(3)–C(7)	119·3 (2·4)	C(7)–C(8)–C(9)	117·8 (3·5)
Cu–N(3)–C(3)	120·5 (2·4)	N(4)–C(8)–C(9)	123·1 (3·5)
Cu–N(4)–C(8)	111·8 (2·5)		

chains of coordination polyhedra running parallel to [010]. The Cu–I distances for the two kinds of coordinated I atoms are significantly different: Cu–I(1) (2·536 Å) is slightly shorter than the sum of the covalent radii (2·68 Å), and Cu–I(2) (2·974 Å) is consistent with the sum of the ionic radii for Cu^{II} and I atoms.

The I_2 molecule forms a bridge, $^-$I(2)–I(3)–I(3)–I(2)$^-$ with two I(2)$^-$ belonging to two adjacent centrosymmetric complexes, joining the chains of polyhedra so that a layer in the (204) plane is formed (Fig. 2). The bond length in the I_2 molecule is 2·806 (4) Å, significantly longer than the 2·715 Å in crystalline I_2 (van Bolhuis, Koster & Migchelsen, 1967). The distance of 3·35 Å between neighbouring iodine atoms in I_2 and I^- units, in the centrosymmetric I_4^{2-} ion, indicates strong interaction between these units in view of the intermolecular distance of 3·50 Å in crystalline I_2. These distances are closely similar to those found in $C_5H_5IN^+.I_7^-$ (Hassel & Hope, 1961) and in the $I_3^-.I_2.I_3^-.I_3^-.I_2.I_3^-$ chains in $(\text{theobromine})_2.H_2I_8$ (Herbstein & Kapon, 1975). The I(2) atom of the $^-$I–I–I–I$^-$ bridge makes an angle of 98·7° with the iodine molecule and the Cu atom, a similar arrangement to that found in some polyiodide sheets (Schweikert & Meyers, 1968; Herbstein & Kapon,

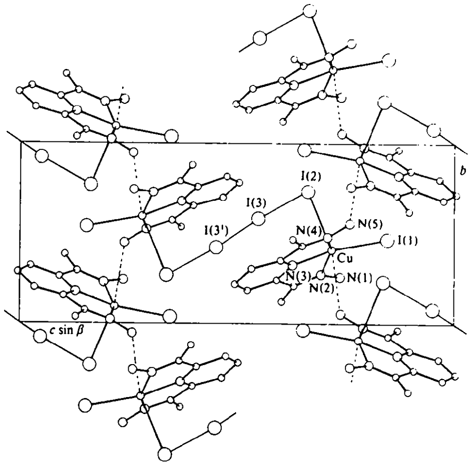

Fig. 1. Projection of the structure on the (100) plane.

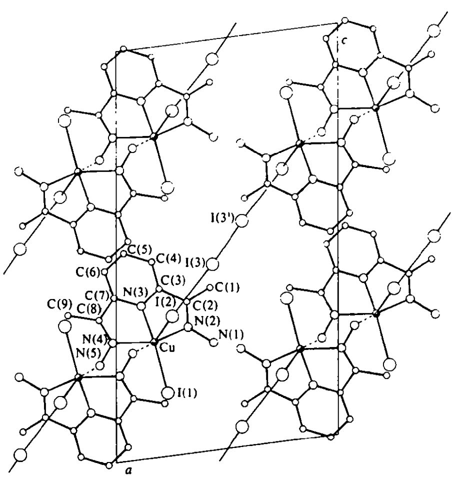

Fig. 2. Projection of the structure on the (010) plane.

Table 3. *Contacts less than* 4·0 Å

Symmetry code: (ii) $\bar{x}, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

N(5)···I(2^{ii})	3·63 (4) Å	I(1)···N(5)	3·56 (3) Å
N(1)···I(2^{iii})	3·62 (4)	I(2)···I(3)	3·353 (4)
I(1)···N(1)	3·64 (5)		

1975). The I(3)—I(3)—I(2) angle in the $^-$I(2)—I(3)—I(3)—I(2)$^-$ ion is 173·4°, similar to that in I_3^- ions.

The pyridine ring and the two five-membered chelate rings are planar, but not coplanar, within the limits of the accuracy.

The cohesion between the layers is due to N(1)···I(2^{iii}) bonds (3·62 Å). Contacts less than 4·0 Å are listed in Table 3.

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Structure of Bis(diallyldithiocarbamato)nickel(II)

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Abstract. $[Ni(C_7H_{10}NS_2)_2]$, $C_{14}H_{20}N_2NiS_4$, M_r = 403·3, monoclinic, $P2_1/n$, a = 7·980 (3), b = 9·069 (4), c = 13·076 (3) Å, β = 95·55 (3)°, U = 941·9 Å^3, Z = 2, D_m = 1·40, D_c = 1·42 Mg m^{-3}, Mo $K\alpha$ (λ = 0·71069 Å), μ = 1·44 mm^{-1}. Final R = 0·07 for 877 independent observed reflections. The Ni atom is coordinated by four S atoms in a plane. The ligand fragment S_2CNC_2 is nearly planar.

Introduction. As part of a study of dithiocarbamate complexes by X-ray diffraction (Kettmann, Garaj & Kúdela, 1977, 1978) we have examined bis(diallyldithiocarbamato)nickel(II).

The crystals are needles with approximate dimensions 0·225 × 0·27 × 0·15 mm. The diffraction intensities were collected on a Syntex $P2_1$ diffractometer by the θ–2θ scan technique with a take-off angle

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