The smaller frequency shift is explained on the basis of a change from intra-molecular hydrogen bonding V to intermolecular hydrogen bonding in which the NH (amide) and C=O (amide) participate. Absorption at 3,266, 3,083 and 3,035 cm.$^{-1}$ and characteristic of NH . . . O=C absorption in amides are observed in solid acetyl histamine (Fig. 1). An analogous structure to that proposed by Mizushima[8] for *N*-methylacetamide is suggested.

Several interesting consequences with respect to naturally occurring substances follow from these considerations. In so far as imidazole may participate in protein hydrogen bonding, two configurations would be possible (besides those which may involve bonding with other amino-acid residues).

Both structures contain seven-membered rings: however, structure (VIII) would be favoured. If such structures do exist in proteins, they might help provide an explanation for marked differences in reactivity of various histidine residues such as exist in ribonuclease[9].

Intramolecular hydrogen bonding in the dipeptide carnosine (β-alanyl-histidine) may exert an effect in facilitating the dissociation of the amide imino hydrogen atom during the formation of the copper carnosine chelate[10,11], also it may contribute to the base strength of the imidazole of carnosine ($pK\ (Im) = 6{\cdot}83$) which is a considerably stronger base than that in histidine ($pK\ (Im) = 6{\cdot}00$)[12].

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PROPERTIES OF SOME COPPER COMPLEXES

Five-Covalent Copper(II) Complexes containing 1,10-Phenanthroline and 2,2′-Bipyridyl

THIS preliminary communication reports the preparation and properties of an extensive series of five-covalent copper(II) complexes by the reaction of *bis*(1,10-phenanthroline)copper(II) and *bis*(2,2′-bipyridyl)copper(II) perchlorates with various neutral and negatively charged ligands.

The addition of halide ions (Cl^-, Br^- and I^-) to nitrobenzene or nitromethane solutions of $[Cu(phen)_2](ClO_4)_2$ leads to the formation of variously coloured solutions (blue, green and brown respectively) containing monohalogeno-*bis*(1,10-phenanthroline)-copper(II) ions due to the reaction:

$$[Cu(phen)_2]^{2+} + X^- \rightarrow [Cu(phen)_2X]^+$$

This 1 : 1 reaction has been confirmed both by conductometric titrations and spectrophotometric continuous variation studies. Also, by working in aqueous acetone solutions, a series of coloured crystalline compounds of the type $[Cu(phen)_2X]ClO_4$ (where $X = Cl^-, Br^-, I^-, SCN^-, NO_2^-, HCOO^-, CH_3COO^-$ and $C_6H_5COO^-$) has been isolated. These compounds possess molecular conductivities in the ranges 27–29 mho and 87–90 mho at 25° in 10^{-3} *M* nitrobenzene and nitromethane solutions respectively. These values are comparable with those of other uni-univalent electrolytes in these solvents[1] and practically half those of the diperchlorate $[Cu(phen)_2](ClO_4)_2$ (Table 1). The *bis*(2,2′-bipyridyl) compound $[Cu(bipy)_2](ClO_4)_2$ also reacts readily with halide ions in the above two solvents and compounds of the type $[Cu(bipy)_2X]ClO_4$ (where $X = Cl^-, Br^-, I^-$ and SCN^-) have also been isolated. These compounds possess similar conductivities to their phenanthroline analogues (see Table 1).

Table 1. Molecular Conductivities and Magnetic Moments of Various 1,10-Phenanthroline and 2,2′-Bipyridyl Complexes of Bivalent Copper

Compound	Molecular conductances (mho) in 10^{-3} *M* solutions at 25°		Magnetic moment per Cu atom in B.M.
	$C_6H_5NO_2$	CH_3NO_2	
$[Cu(phen)_3](ClO_4)_2$	43·1	176	1·94
$[Cu(phen)_2](ClO_4)_2$			1·91
$[Cu(phen)_2X]ClO_4$ ($X = Cl^-, Br^-, I^-, SCN^-$ $NO_2^-, HCOO^-, CH_3COO^-$ and $C_6H_5COO^-$)	27–29	87–91	1·83–1·96
$[Cu(phen)_2X]X$ ($Cl^-, Br^-, I^-, SCN^-, HCOO^-$ and CH_3COO^-)	24–27	82–93	1·86–1·97
$[Cu(phen)_2L](ClO_4)_2$ ($L = NH_3$ and C_5H_5N)		176–199	1·84–2·00
$[Cu(bipy)_3](ClO_4)_2$	54	186	2·03
$[Cu(bipy)_2](ClO_4)_2$	44·5	181	1·93
$[Cu(bipy)_2X]ClO_4$ ($X = Cl^-, Br^-, I^-$, and SCN^-)	28–31	89–91	1·89–1·97
$[Cu(bipy)_2X]X$ ($X = Cl^-, Br^-, I^-$, and SCN^-)	11–30	79–85	1·81–1·96
$[Cu(bipy)_2NH_3](ClO_4)_2$		199	1·92
$[Cu(bipy)Cl_2]$		~1	1·96

Attempts to prepare a monocyano-derivative of the $[Cu(phen)_2]^{2+}$ ion lead to the isolation of the cyano-bridged complex:

$$[(phen)_2Cu - C \equiv N - Cu(phen)_2](ClO_4)_3 . H_2O$$

in which the cyanide group is linking two $[Cu(phen)_2]^{2+}$ ions.

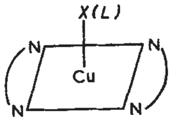
The *bis*-complexes $Cu(phen)_2X_2 . nH_2O$ ($X = Cl^-$, $n = 3{\cdot}5$; $X = Br^-$ and I^-, $n = 1$; $X = SCN^-$, $n = 0$; and $X = HCOO^-$ and CH_3COO^-, $n = 6$) and $Cu(bipy)_2X_2 . nH_2O$ ($X = Cl^-$, $n = 6$; $X = Br^-$, $n = 2$; $X = SCN^-$ or I^-, $n = 0$) were also prepared and their properties examined. These complexes are also uni-univalent electrolytes in nitromethane solution (Table 1) and contain the $[Cu(chelate)_2X]^+$ ion. In the more weakly polar solvent nitrobenzene they undergo some re-arrangement due to the reaction:

$$[Cu(chelate)_2X]^+ + X^- \rightleftharpoons [Cu(chelate)X_2] + \text{chelate}$$

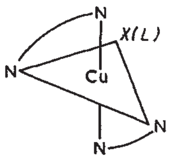
This equilibrium, which is independent of concentration, has been studied in detail by means of accurate conductivity measurements over a concentration range and will be reported later[2]. Mono-complexes of the type [Cu(bipy)X_2] (where X = Cl^-, Br^- and SCN^-) were prepared and examined during the course of this work. For example, the dichloro-complex [Cu(bipy)Cl_2], which is readily obtained by adding the ligand to excess copper(II) chloride in ethanol, is virtually a non-electrolyte in nitromethane solution (Table 1).

The reaction of neutral ligands with $[Cu(phen)_2]^{2+}$ and $[Cu(bipy)_2]^{2+}$ has also been studied and the stable mono-ammine complexes $[Cu(chelate)_2(NH_3)](ClO_4)_2$ were obtained from aqueous ammonia solutions. The *bis*(1,10-phenanthroline) complex also forms the mono-pyridine complex $[Cu(phen)_2(py)](ClO_4)_2$ as well as the aquo-derivative $[Cu(phen)_2(H_2O)](ClO_4)_2$. These compounds function as di-univalent electrolytes in nitromethane solution (see Table 1).

There is a number of possible structures for the five-covalent ions $[Cu(chelate)_2X]^+$ and $[Cu(chelate)_2L]^{2+}$ (where X is a negative ion and L is a neutral ligand). They could, for example, possess the square-pyramidal arrangement I, or the trigonal bipyramidal one represented in II.



(I)



(II)

In this regard it is of considerable interest that Barclay and Kennard (see following communication) have shown that the structure of iodo-*bis*(2,2′-bipyridyl)copper(II) iodide contains an approximately trigonal bipyramidal arrangement about the copper atom in the $[Cu(bipy)_2I]^+$ ion. This type of arrangement confers the possibility of mirror-image isomerism on the copper atom and the unit cell contains both isomers. The X-ray data reveal that the Cu – N and Cu – I distances correspond to normal covalent bond distances whereas the stereochemistry of bivalent copper is usually such that the copper atom is surrounded by four atoms at normal covalent bond distances in the plane with one or two more elongated bonds normal to the plane.

The magnetic moments of the 5-covalent complexes in the table all fall in the range 1·8–2·0 B.M. These values are similar to those of copper(II) complexes in general.

The magnetic moments of $[Cu(phen)_2Br]ClO_4$ and $[Cu(phen)_2Br]Br$ have been reported previously as being essentially independent of temperature over the range 90–300° K. (ref. 3).

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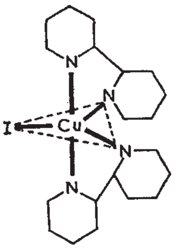
The Trigonal-Bipyramidal Configuration of the Iodo *Bis*(2-2′-Bipyridyl)Copper(II) Ion

The compounds $Cu(dipy)_2X_2$ and $Cu(phen)_2X_2$ formed between 2,2′-bipyridine or *o*-phenanthroline and copper(II) salts have been shown to have co-ordination numbers of five in non-aqueous solutions (see previous communication). The purpose of this communication is to record preliminary results of an X-ray structure determination of one of them, *bis*(2,2′-bipyridyl)copper(II) iodide.

The lustrous brown crystals are triclinic (a = 10·66 ± 0·01; b = 14·37 ± 0·01; c = 7·44 ± 0·01 Å.; α = 93 ± 1°; β = 101 ± 1°; γ = 108 ± 1°). There are two molecules of composition $Cu(C_{10}H_8N_2)_2I_2$ in the unit cell ($d_{meas.}$ = 1·99; $d_{calc.}$ = 1·98 gm. cm.$^{-3}$). The centro-symmetric space group, $P\bar{1}$, was assumed.

One-thousand-four-hundred independent intensities were estimated visually from equi-inclination Weissenberg photographs taken with copper radiation. The co-ordinates of the atoms were determined from three-dimensional Patterson and Fourier syntheses. With a disagreement index ($\Sigma||F_{obs.}| - |F_{calc.}||/\Sigma F_{obs.}|$) of 0·18, the estimated standard deviations of the atomic positions were I, 0·003; Cu, 0·005; N, 0·03; C, 0·05 Å. The structure is being refined further in an attempt to locate the light atoms more precisely. However, it is quite clear that the copper atom has an unusual stereochemistry.

The compound contains a positively charged iodo-*bis*(bipyridyl)copper(II) ion and a negatively charged iodide ion. The copper atom is surrounded by four nitrogen atoms (at a distance of 2·02 Å.) and an iodine atom (at 2·71 Å.) at the corners of a distorted trigonal bipyramid. The iodine atom and two nitrogen atoms (from different bipyridine molecules) are in the same plane as the copper atom. The other two nitrogen atoms lie on a line (passing through the copper atom) which makes an angle of about 9° with the normal to this plane. The arrangement is shown in III:



(III)

All five atoms are at normal covalent bond distances from the copper atom. The trigonal bipyramidal configuration for the copper atom differs in this respect from the usual stereochemistry of bivalent copper which involves four bonds of normal covalent lengths with a fifth, and sometimes a sixth, at a greater distance. As the iodo-*bis*(2,2′-bipyridyl)-copper(II) ion possesses neither a plane nor a centre of symmetry, the two ions in the unit cell are related to one another as optical isomers.

Terpyridylcopper(II) chloride dihydrate is isomorphous with terpyridylzinc chloride, which has a similar trigonal bipyramidal configuration about the metal atom[4].

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