236. *The Colour Isomerism and Structure of Some Copper Co-ordination Compounds. Part I. Absorption Spectra in Solution.*

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The absorption spectra of some copper(II) complexes of salicylaldehyde and 2-hydroxy-1-naphthaldehyde derivatives in pyridine, methanol, benzene, chloroform, and carbon tetrachloride have been obtained from 200 to 800 mμ. Measurements at 0°, 25°, and 43° gave no indication of a temperature effect, but significant differences were found on varying the solvents.

One of the unusual features of copper(II) co-ordination complexes is the existence of two differently coloured isomers of some compounds; *e.g.*, bis-(2-hydroxy-*N*-methyl-1-naphthaldimine)copper can be readily crystallised in either a green or a brown form.[1] Analysis and preliminary *X*-ray studies [2] have shown that the more obvious explanations involving solvent co-ordination, *cis–trans*-isomerism, and planar or tetrahedral ligand arrangements do not always apply. The suggestion that the isomers might arise from the use of inner and outer planar orbitals [3] can be criticised on the grounds that bonds involving two different orbital groups are unlikely in the same compound.[4] The results of a further investigation of some of these complexes by electronic absorption spectroscopy, magnetic susceptibility, and two *X*-ray diffraction analyses are presented in this and following papers.

Some qualitative observations gave the first indication of a possible explanation for the isomerism. It was noticed that both the green and the brown isomer of the above copper complex gave green solutions in pyridine and other co-ordinating solvents, and brown solutions in carbon tetrachloride. Similarly, *NN'*-disalicylidenepropane-1 : 2-diamine copper gave a green solution in pyridine and a violet solution in chloroform and methanol. Corresponding green and violet solids were isolated. The ethylenediamine analogue also gave green and violet solutions but could be prepared only as the green solid for reasons which became apparent after the *X*-ray studies had been completed. These similarities between the solutions and solids suggested that the colour of the green isomers

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[1] Pfeiffer and Glaser, *J. prakt. Chem.*, 1938, **151**, 134; 1939, **153**, 265.
[2] von Stackelberg, *Z. anorg. Chem.*, 1947, **253**, 136.
[3] Ray and Sen, *J. Indian Chem. Soc.*, 1948, **25**, 473.
[4] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, New York, 1939.

was due to a five- or six-fold co-ordination of the copper atom in contrast to the violet or brown isomers where only four-fold co-ordination was indicated. A more detailed study of this correspondence was made by absorption spectroscopy on the solid compounds and solutions.

EXPERIMENTAL

The spectra of the solutions were obtained with a Beckman D.U. spectrophotometer fitted with thermospacers and a photo-multiplier unit. They were determined in the 200—800 mμ region, the range from 300 to 440 mμ being repeated with a lower solute concentration. Measurements were made at 43°, 25°, and 0° (all ±2°) on the copper complexes of the following: (I) salicylaldehyde, (II) 2-hydroxy-1-naphthaldehyde, (III) *NN'*-disalicylidene-ethylenediamine and (IV) -propane-1 : 2-diamine, (V) *NN'*-(2-hydroxy-1-naphthylidene)propane-1 : 2-diamine, (VI) *N*-methylsalicylaldimine, and (VII) 2-hydroxy-*N*-methyl-1-naphthaldimine. The solvents used were pyridine and benzene (both " AnalaR " grade, dried over $CaCl_2$), chloroform and carbon tetrachloride (both washed with water and twice distilled from $NaHSO_3$), and methanol (fractionally distilled, and redistilled from magnesium amalgam).

The complexes were prepared by the same general method.[5] Both (I) and (II) were made by mixing the free aldehyde with copper acetate in 50% aqueous methanol, the green product being filtered off, washed, and dried. Addition of free amine to the appropriate aldehyde complex suspended in 50% aqueous methanol gave the Schiff's base compounds; these were warmed, filtered off, dissolved in chloroform, and precipitated with ether. 2-Hydroxy-1-naphthaldehyde was prepared by the method of *Organic Syntheses*.[6] The coloured isomers were obtained by crystallising the complexes from various solvents or heating them to 140°.[1] All compounds have been described in the literature [1,5] except the green *form* of (IV) which was found to be a monohydrate and not a true isomer. The anhydrous violet compound is well known. The monohydrate was prepared by recrystallising the violet complex from damp methanol or dioxan and hand separating the resulting mixture of green and violet crystals [Found: C, 56·5; H, 4·3; N, 7·5; Cu, 17·5; H_2O (loss at 150°), 5·2. $C_{17}H_{16}O_2N_2Cu,H_2O$ requires C, 56·4; H, 5·0; N, 7·75; Cu, 17·6; H_2O, 5·0%]. A similar green isomer of (V) was also prepared. This became violet and lost weight when heated and was assumed to be the monohydrate. None of the other complexes lost weight at 150°.

RESULTS AND DISCUSSION

A large number of spectra were obtained but only representative examples are shown to illustrate the conclusions drawn from them. It was found that the temperature effect, if any, was very small and less than the experimental errors arising from the slow evaporation of some solvents.

The spectra of the chloroform solution of each compound, obtained at 25°, are shown in Figs. 1—3. The heavy absorption in the 300—440 mμ region is ascribed to charge-transfer and free-ligand absorption, whereas the weak absorption in the visible region is ascribed to forbidden electronic transitions among the 3*d* levels of the copper atoms.[7,8] It is assumed that the absorption at *ca.* 570 mμ found in the complexes with an enforced *cis*-configuration arises from the unsymmetrical ligand fields expected in these compounds [cf. ligand-field calculations on *cis*- and *trans*-planar configurations in nickel(II) complexes [9]].

The effects of varying the solvents are shown in Figs. 4—6 for compounds (II), (V), and (VI). In the charge-transfer region these are best shown by (II), and in the visible region by (VI). Because of the possibility that evaporation of solvent had led to incorrect absorption coefficients, no account was taken of absolute peak heights; instead, their relative rise or fall was regarded as significant. In the charge-transfer region an increasing prominence of the absorption peak at approx. 380 mμ, relative to that at 310 mμ (probably

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[5] Pfeiffer, Breith, Lubbe, and Tsumaki, *Annalen*, 1933, **503**, 84.
[6] *Org. Synth.*, 1942, **22**, 63.
[7] Calloman, Simpson, and Sheppard, *Ann. Reports*, 1955, **52**, 79.
[8] Orgel, *Quart. Rev.*, 1954, **8**, 422.
[9] Maki, *J. Chem. Phys.*, 1958, **28**, 651.

FIGS. 1—3. *Spectra at 25° in chloroform.*

FIG. 1.

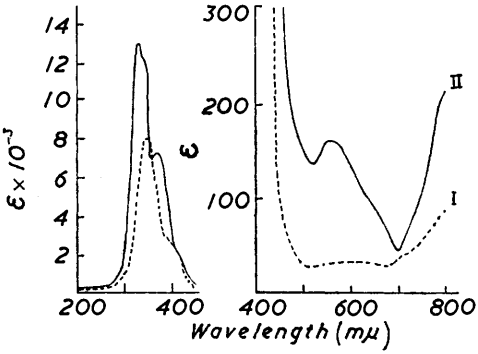


FIG. 2.

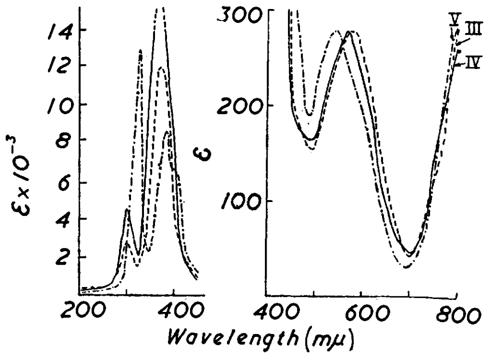


FIG. 3.

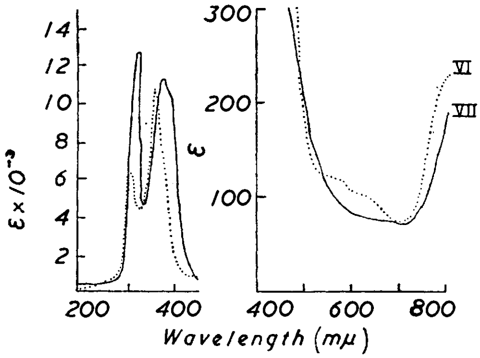
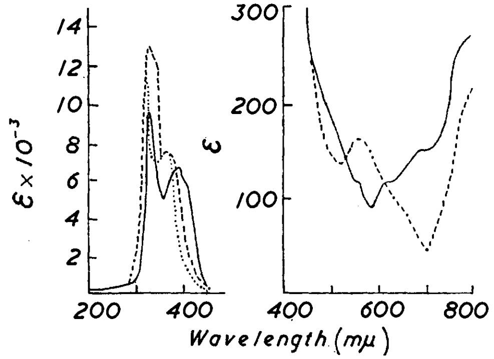
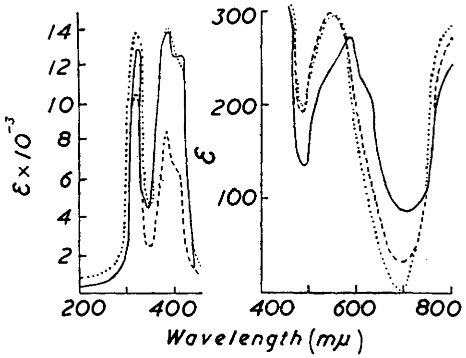


FIG. 4.



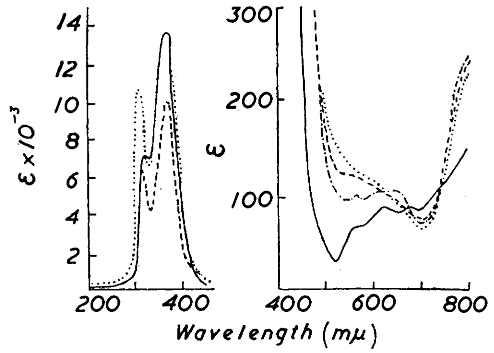
Compound (II): —— *in pyridine*, – – – – *in chloroform*, ... *in carbon tetrachloride.*

FIG. 5.



Compound (V): —— *in pyridine*, – – – – *in chloroform*, ... *in carbon tetrachloride.*

FIG. 6.



Compound (VI): —— *in pyridine*, – – – – *in chloroform*, ... *in carbon tetrachloride*, — · — · — *in methanol.*

due to free-ligand absorption [10]), resulted from an increase in the solvent co-ordinating power. This was taken as evidence of a new charge-transfer process arising from solvation to the metal. In the visible region a trough appeared at about 520 mμ and the existing one at 700 mμ was eliminated when the co-ordinating power of the solvent was increased. These spectral changes are consistent with the colour change from green in pyridine to violet or brown in carbon tetrachloride observed in solutions of these compounds. It is assumed that these effects are brought about by solvent co-ordination to the metal. It will be shown in Part II that a similar change in the visible region was found in the spectra of the solid compounds when two colour isomers were compared.

The variation of spectra with solvent follows the order, pyridine $>$ methanol $>$ chloroform $\approx$ benzene $>$ carbon tetrachloride, which is almost certainly the order of the solvent co-ordinating power. As can be seen, both chloroform and benzene have some effect on the spectra, presumably through weak co-ordination to the copper. This is not unexpected in view of recent reports,[11] and the observation that some of these copper complexes will dissolve in chloroform but not in carbon tetrachloride. It follows that magnetic and spectral data obtained in benzene and chloroform solutions should be interpreted with regard for the fact that solvation may occur.

Although complex (III) was found to undergo the spectral changes indicative of solvation, it is known that the nickel analogue, unlike most salicylaldehyde–nickel complexes, gives the same spectrum in both chloroform and pyridine.[10] The solvation in the copper complex lends some support to the suggestion [10] that the nickel compound is also solvated but has retained the diamagnetic electron configuration of the parent compound.

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[10] Clark and Odell, *J.*, 1955, 3431; 1955, 3435; 1956, 520.

[11] Reeves and Schneider, *Canad. J. Chem.*, 1957, **35**, 251; Fischer and Hafner, *Z. Naturforsch.*, 1955, **10**b, 665.