

477. *The Colour Isomerism and Structure of Some Copper Co-ordination Compounds. Part VI.* The Visible Absorption Spectra of Copper Complexes.*

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The visible absorption spectra of a number of copper(II) complexes of salicylaldehyde and 2-hydroxy-1-naphthaldehyde derivatives have been measured in chloroform and pyridine solution. They provide further evidence that the main spectral features are determined by the co-ordination symmetry. The presence of a band near 385 m μ in some spectra and the possibility of four *d-d* transitions with bis(salicylaldehydato)copper(II) are discussed.

THE increasing attention given to the interpretation of the visible absorption in copper(II) co-ordination complexes has not yet produced an agreed assignment for the *d-d* transitions and a more detailed treatment has been called for.¹ However, in spite of one or two discrepancies in the literature, a qualitative correspondence between absorption and co-ordination seems evident in some compounds. Those which are *cis*-planar show high absorption near 550 m μ ; strongly co-ordinating solvents appear to emphasise a trough near 520 m μ in *trans*-planar complexes; those with four oxygen donor atoms are characterised by a low-intensity spectrum of two very broad bands. We have determined further spectra and checked existing anomalies to extend this qualitative correlation.

EXPERIMENTAL

We have measured the spectra of the copper complexes of salicylaldehyde (I), salicylaldimine (II), *N*-methylsalicylaldimine (III), *NN'*-disalicylidene-ethylenediamine (IV), *NN'*-disalicylidenepropane-1,2-diamine (V), *NN'*-disalicylidene-*o*-phenylenediamine (VI), 2-hydroxy-1-naphthaldehyde (VII), 2-hydroxy-1-naphthaldimine (VIII), 2-hydroxy-*N*-methyl-1-naphthaldimine (IX), *NN'*-di-(2-hydroxy-1-naphthylidene)ethylenediamine (X), *NN'*-di-(2-hydroxy-1-naphthylidene)propane-1,2-diamine (XI), and *NN'*-di-(2-hydroxy-1-naphthylidene)-*o*-phenylenediamine (XII) in chloroform and pyridine. The solvents were of analytical grade, dried, and distilled. The complexes were prepared by standard methods and recrystallised.

The spectra of the complexes (I), (II), (IV), (VII), (VIII), (X), and (XII), in chloroform (A) and pyridine (B), which we believe to be unpublished or which help resolve previous disagreements are shown in the Figures.

DISCUSSION

The spectra accord with generalisations on the visible absorption of copper complexes which can now be made.^{1,2} The following comments seem pertinent.

Pyridine solutions of compounds with a *trans*-ligand configuration show enhanced absorption in the 550–650 m μ region^{1,3,4} and our results support this (Figs. 1 and 2) although the effect is not very obvious with compound (VIII) (Fig. 2). (In pyridine this complex does show a small increase in absorption in the expected region but the overall higher values for the chloroform solution seem unusual. However its low solubility makes quantitative measurement difficult and somewhat suspect.) In general a trough, whose exact position and depth depends on the enhancement, falls at approx. 500–580 m μ between it and the tail of the u.v. absorption. This u.v. tail is itself influenced by a peak,¹

* Part V, Hall, Rae, and Waters, *J.*, 1963, 5897.

¹ Piper and Belford, *Mol. Phys.*, 1962, **5**, 169.

² Belford and Piper, *Mol. Phys.*, 1962, **5**, 251.

³ Graddon, *J. Inorg. Nuclear Chem.*, 1960, **14**, 161.

⁴ Ferguson, *J. Chem. Phys.*, 1961, **35**, 1612.

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sometimes solvent-dependent,⁴ in the 370–450 $m\mu$ region. Thus what appears to be a trough may be a region of lower but significant absorption overshadowed by the flanking bands and easily overlooked in any assignment scheme. The spectrum of crystals of (III), for example, is reported to resemble that of its pyridine solution⁴ but the band near 500 $m\mu$ in the former is not obvious in this solvent. Indeed, if solvation by pyridine enhances the intensity by making some of the $d-d$ transitions more probable¹ the implied

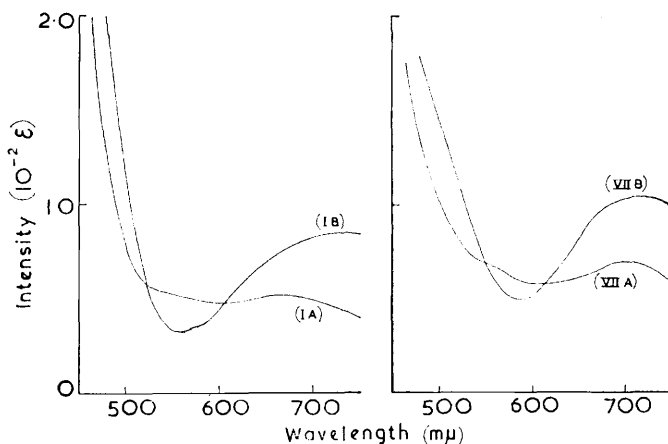


FIG. 1.

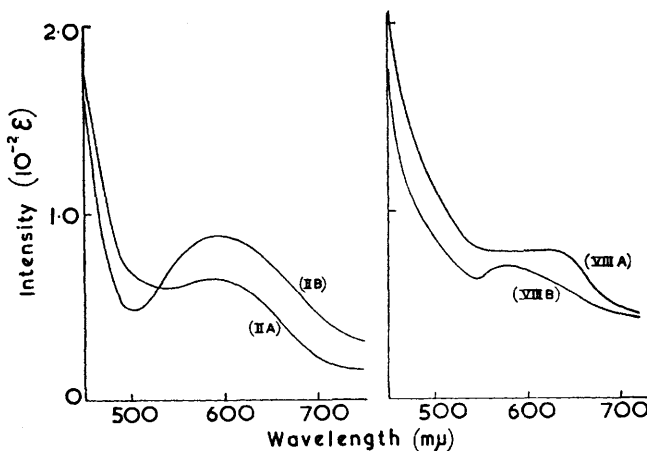


FIG. 2.

lowering of molecular symmetry, apart from the introduction of a trough, suggests that assignment by solvent shift is difficult.

cis-Quadridentate complexes, being acentric, are said to be characterised by a high intensity ($\epsilon = 400$) band in the 550 $m\mu$ region.² This seems to be true. In chloroform solution this band occurs at 560 $m\mu$ in compounds (IV)^{5,6} (Fig. 3), (V),⁶ (X) (Fig. 3), (XI)⁶ and in this region in compound (VI)⁷ and possibly (XII) (Fig. 4)—allowance here being made for the free-ligand absorption between 400 and 500 $m\mu$. This suggests a similar

⁵ Ferguson, *J. Chem. Phys.*, 1961, **34**, 2206.

⁶ Waters and Hall, *J.*, 1959, 1200.

⁷ Kiss, Backsai, and Csokan, *Z. prakt. Chem.*, 1942, **160**, 1.

ligand field in these complexes, but one weaker than that of *NN'*-ethylenebis(acetylacetoniminato)copper(II), where the maximum occurs at 545 $m\mu$.⁸ The maxima shift about 40 $m\mu$ in pyridine solutions of compounds (IV), (V), (X), and (XI) to 600 $m\mu$ [the extent of the shift is not clear in (VI) and (XII)], but we have found only a 5 $m\mu$ increase to 550 $m\mu$ in the acetylaceton complex. That the general features of the visible absorption spectra are the same in all these compounds [excluding (XII) where absorption involving

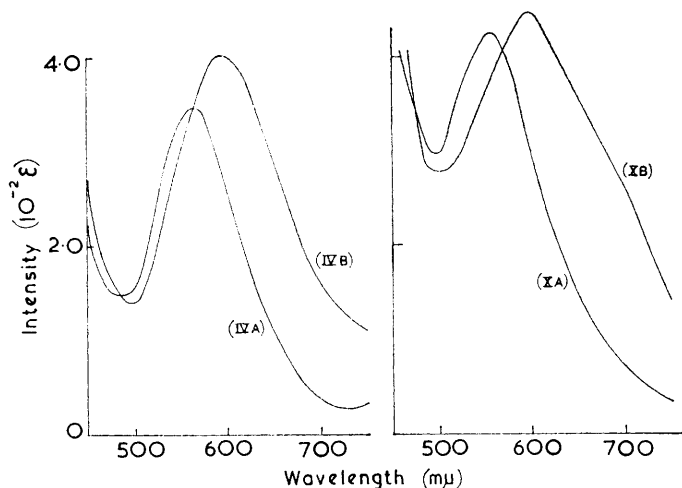


FIG. 3.

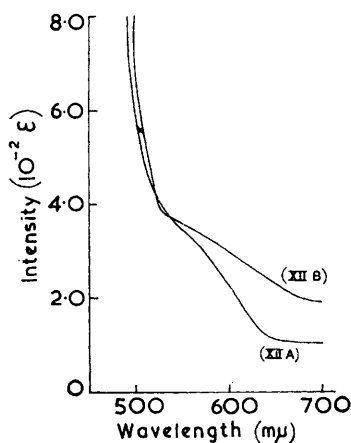


FIG. 4.

the ligand extends well into the visible region] strengthens the conclusion that a simple crystal-field picture is a useful one¹ but the correlation between structure and band position is not obvious, and probably demands, at least, an assessment of the σ - and π -bonding involved. Disregarding the high intensity band at 440 $m\mu$ in compound (VI)⁷ as a transition involving the ligand its spectral similarity with the ethylene and isopropylene bridged complexes (IV, V, X, and XI) suggests that the distortion expected in these latter^{9,10} has little effect on the ligand field—supporting a similar conclusion for complexes with a *trans*-configuration.²

⁸ Chakravorty and Basu, *Nature*, 1959, **184**, 50.

⁹ Llewellyn and Waters, *J.*, 1960, 2639.

¹⁰ Hall and Waters, *J.*, 1960, 2644.

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Attention has been drawn to a band near 385 $m\mu$ in bis(acetylacetonato)copper(II)¹ and its derivatives³ which has been variously ascribed to a $d-d$ transition or a ligand transition.¹ We note that a similar band is a feature of a number of other spectra—it can be seen in the spectra of crystals of bis-(3-phenylacetylacetonato)copper(II) at 420 $m\mu$ ¹¹ and of (IV) at 475 $m\mu$ ^{2,5} and in the chloroform spectra of compounds (I) and (II) at 470 $m\mu$ ⁷ and (III) at 430 $m\mu$.⁴ We found that these bands can be easily overlooked and need to be emphasised by plotting $\log \epsilon$ on the absorption axis.⁷ We were not able to detect it in solutions of complex (IV) in agreement with an earlier report⁷ although it is possibly obscured by the heavy absorption in the 350–450 $m\mu$ region. Other observations have shown that the band decreases in pyridine, leading to the assertion that as it is not intensified the band cannot be a $d-d$ transition¹—a conclusion probably supported by its wide range in position. It is worth noting that this band is more common in these complexes than has probably been recognised and it might therefore be possible to distinguish between a $d-d$ or a ligand (spin forbidden $n-\pi^*$ or $\pi-\pi^*$)¹ transition by observing it in a suitable series of compounds.

We find the chloroform spectrum of complex (I) (Fig. 1) to be very like that reported for bis(acetylacetonato)copper(II) in this solvent^{12,13} and not unlike the crystal spectrum of bis-(3-phenylacetylacetonato)copper(II).¹¹ Thus it shows two low broad bands at 550 and 670 $m\mu$ with an indication of further resolution into bands at approx. 540, 570, 630, and 680 $m\mu$. Such a claim is difficult to substantiate and we can merely point out that as both the obvious bands are low and very broad further resolution as found in the crystal is not at all inconsistent. Bis(acetylacetonato)copper(II) shows two very broad bands at 535 and 660 $m\mu$ in chloroform and at 555, 640, and 690 $m\mu$ in the crystal.¹² The 3-phenyl derivative gives a crystal spectrum with four bands at approx. 480, 530, 590, and 660 $m\mu$.¹¹ The solution bands are also seen in bis(ethylacetoacetato)copper(II) at 550 and 700 $m\mu$ ³ and in complex (VII) at approx. 550 and 710 $m\mu$ (Fig. 1). This latter spectrum is now found to be similar in the visible region to those of other complexes with four planar oxygen donor atoms, contrary to earlier evidence,⁶ and we suggest that they are all showing $d-d$ transitions characteristic of this co-ordination arrangement. The reported resolution of the chloroform spectrum of complex (I) into three bands at 615, 675, and 790 $m\mu$ ¹⁴ would appear doubtful in view of the above agreement.

The band positions in solution suggest that the ligand field of bis(acetylacetonato)copper(II) is stronger than those of complex (I), (VII), or bis(ethylacetoacetato)copper(II). Once the $d-d$ transitions have been unequivocally assigned these compounds should provide more detailed information; *e.g.*, the extent of the metal-ligand bonding and the effect of small changes in molecular symmetry.

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¹¹ Basu, Belford, and Dickerson, *Inorg. Chem.*, 1962, **1**, 438.

¹² Ferguson, *J. Chem. Phys.*, 1961, **34**, 1609.

¹³ Belford, Calvin, and Belford, *J. Chem. Phys.*, 1957, **26**, 1165.

¹⁴ Basu and Basu, *Z. phys. Chem.*, 1960, *A*, **215**, 308.