237. *The Colour Isomerism and Structure of Some Copper Co-ordination Compounds. Part II.*[1] *Absorption Spectra of Solids.*

By T. N. Waters and D. Hall.

The absorption spectra of some solid copper(II) complexes of salicylaldehyde and 2-hydroxy-1-naphthaldehyde derivatives have been obtained for potassium bromide discs. By analogy with the spectra in solution, it is suggested that the green complexes have a metal co-ordination number greater than the expected value of four.

In Part I [1] a description was given of the electronic absorption spectra of some copper salicylaldehyde and 2-hydroxy-1-naphthaldehyde complexes in solution. The spectra of the solid compounds are now given for comparison.

Experimental.—Spectra were determined with a Beckman D.U. spectrophotometer fitted with a photomultiplier unit. The samples were pressed in potassium bromide discs,[2] 1 mg. of complex being mixed with 100 mg. of bromide. The agreement between the solid spectra and those previously obtained in solution [1] indicated that the absorption was little changed by side reactions with the bromide. However, the clear discs containing the samples slowly became opaque when exposed to radiation in the spectrophotometer, but as this effect also occurred with pure potassium bromide it could not be ascribed to a breakdown of the compounds. Because this fogging increased the optical density, accurate absorption coefficients were not

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[1] Part I, Waters and Hall, preceding paper.
[2] Faust and Quagliano, *J. Amer. Chem. Soc.*, 1954, **76**, 5346.

obtained. The decrease in resolution available in the solid state also precluded the detection of the small changes in spectra found with the solutions. These difficulties were partially overcome as follows:

The effect of fogging, found by comparing the absorption of an opaque with a clear disc, of pure potassium bromide, added a constant value to the optical density throughout the measured range from 200 to 900 mμ. Discs judged to be equally fogged showed that all compounds had approximately the same optical density at 200 mμ—a result substantiated by measurements in solution—and this value was taken as an arbitrary zero. Because of the constant composition of the discs a comparison between spectra plotted in terms of optical density could then be made between compounds of similar molecular weight. To improve this comparison in the region of small absorption, and to counteract the lack of resolution, differential spectra were obtained by determining the optical density of one compound against another.

The preparation of the compounds has been described.[1]

RESULTS AND DISCUSSION

Spectra in the 200—900 mμ region are shown in Figs. 1—3 for the copper complexes of the following compounds: (I) salicylaldehyde, (II) 2-hydroxy-1-naphthaldehyde, (III) *NN'*-disalicylidene-ethanediamine, (IV) *NN'*-disalicylidenepropane-1 : 2-diamine (violet), (V) monohydrate of (IV) (green), (VI) *N*-methylsalicylaldimine (green and brown isomers), (VII) 2-hydroxy-*N*-methyl-1-naphthaldimine (green and brown isomers).

FIG. 1.

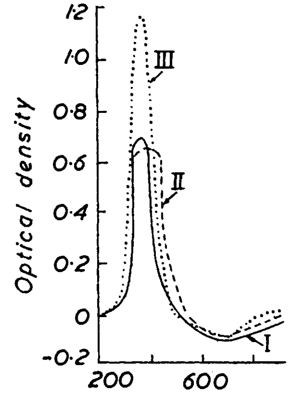


FIG. 2.

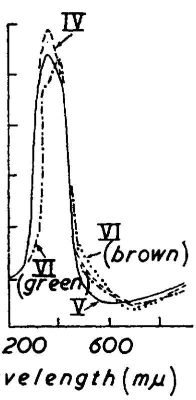


FIG. 3.

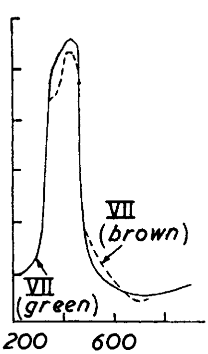


FIG. 4.

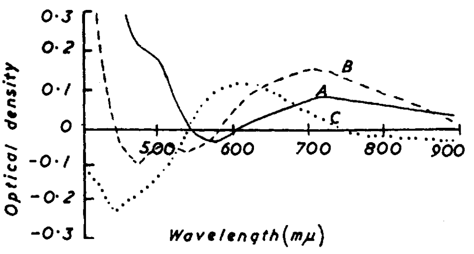
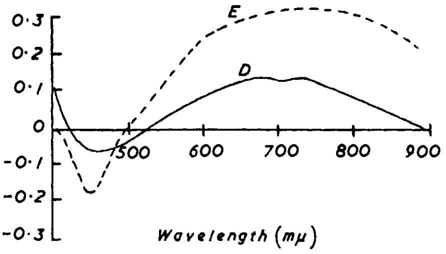


FIG. 5.



Differential spectra obtained from 400 to 900 mμ are shown in Figs. 4 and 5 for the following pairs: (*A*) (III), against (V) as blank; (*B*) (III), against (IV) as blank; (*C*) (V), against (IV) as blank; (*D*) green isomer of (VI), against brown isomer of (VI) as blank; (*E*) green isomer of (VII) against brown isomer of (VII) as blank.

It is realised that the difficulties outlined above make interpretation doubtful but the conclusions reached seem reasonable, and for the complexes of (III) and (V) have now been confirmed by *X*-ray diffraction studies.

In both solids and solutions there are large absorption peaks in the 300—450 mμ range and only small peaks elsewhere. These are respectively ascribed to charge-transfer and forbidden-transition processes. In the visible region there is a direct comparison between the solids, as shown by the differential spectra, and the solutions in various solvents. The green complexes absorb less at approx. 500 mμ and more at approx. 700 mμ than do the violet or brown compounds and in this respect correspond to the green solutions (solutions in co-ordinating solvents) which show a similar deviation from the violet or brown solutions (in non-co-ordinating solvents). The spectral change in solution has been ascribed to solvation,[1] giving five- or six-fold co-ordination of the copper atoms, and the above results suggest a similar effect in the solid state. If so, the green complexes have a co-ordination number greater than the four-covalency expected from the ligands, this value of four existing only in the violet or brown compounds.

The preliminary *X*-ray examination [3] of (VI), which shows that the green and the brown isomer have different crystal structures, supports this suggestion. The comparatively short copper–copper separation of 3·35 Å between the planar molecules of the green complex probably brings about the change in the spectrum by altering the ligand fields operating on the metal. Such an interaction between copper atoms must be weak, however, as the magnetic suceptibility is normal down to 81° K [4] (cf. anomalous magnetic susceptibility of copper acetate monohydrate,[5] where the copper–copper separation is only 2·64 Å [6]).

Chemistry Department, University of Auckland, New Zealand.
[Present address (T. N. W.): Chemistry Division,
Atomic Energy Research Establishment, Harwell,
Berks, England.]

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[3] von Stackelberg, *Z. anorg. Chem.*, 1947, **253**, 136.
[4] Calvin and Barkelew, *J. Amer. Chem. Soc.*, 1946, **68**, 2267.
[5] Figgis and Martin, *J.*, 1956, 3837.
[6] van Niekerk and Schoening, *Acta Cryst.*, 1953, **6**, 227.