

The Absorption Spectra of Copper Complexes of Intermediate Stereochemistry

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Absorption spectra are reported for three salicylaldiminato-complexes of copper(II) which have a distorted co-ordination geometry. Although this distortion varies between planar and tetrahedral extremes, the absorption maxima in the visible region do not show a gradual change but apparently reflect only the planar, or the tetrahedral, component of the co-ordination symmetry.

ALTHOUGH the study of absorption spectra in the ligand-field region can generally be used to determine the co-ordination stereochemistry of transition-metal complexes, we have recently found that this correspondence may not be definite in some circumstances. Structural and spectral studies on bis-(*N*-ethylsalicylaldiminato)-copper(II),¹ *NN'*-2,2'-biphenylbis(salicylaldiminato)-copper(II),² and bis-(*N*-*t*-butylsalicylaldiminato)-copper(II)³ illustrate this point.

X-Ray analyses show that these compounds exhibit a stereochemistry intermediate between planar and tetrahedral. In each, copper is chelated by substituted salicylaldiminato groups in a way conveniently described by the angle between the planes containing the co-ordinating atoms of each chelate group and the central copper atom. This angle is 36° in the *N*-ethyl, 37° in the biphenyl, and 54° in the *N*-*t*-butyl complex, whereas it should be 0° for a truly planar and 90° for a truly tetrahedral configuration.

We have measured the spectra of chloroform solutions of these three compounds, and the positions of the bands, together with those of two complexes known to be planar, are shown in the Table.

Absorption maxima (cm.⁻¹; ϵ in parentheses) for salicylaldiminato-complexes (sh = shoulder)

<i>N</i> -Methyl *	27,600, 33,100, 37,000
<i>N</i> -Ethyl	27,300 (9200), 32,800 (8900), 37,000sh (18,500)
<i>NN'</i> -Ethylene †	17,600, 26,700, 35,100
<i>NN'</i> -Biphenyl... ..	11,500sh (50), 15,200 (340), 20,800sh (790), 25,000 (15,000), 36,000 (39,000)
<i>N</i> - <i>t</i> -Butyl	13,400 (180), 20,000 (1100), 23,000sh (1100), 26,700 (5400), 31,300 (8700), 36,000sh (8700)

* S. V. Sheat and T. N. Waters, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1221. † A. von Kiss, G. Bacskaï, and P. Csokan, *J. prakt. Chem.*, 1942, **160**, 1.

None of the crystal structures shows evidence of significant intermolecular interactions which might be the cause of the configuration adopted, and it is reasonable to assume that the observed arrangements are maintained in solutions of non-polar solvents. Such a claim is difficult to substantiate, but the evidence available and a consideration of the compounds themselves suggest that it is reasonable. It seems unlikely that *NN'*-2,2'-biphenylbis(salicylaldiminato)copper or bis-(*N*-*t*-butylsalicylaldiminato)copper could assume a

more planar configuration in solution, since in the solid both molecules already show some distortion, or close intramolecular approaches, through the adoption of a stereochemistry considerably removed from the strain-free tetrahedral state. It is not so obvious that bis-(*N*-ethylsalicylaldiminato)copper must hold its intermediate geometry, but the detection of an appreciable dipole moment in benzene and dioxan solutions⁴ suggests that this is indeed what happens. The *N*-*t*-butyl complex also exhibits a dipole moment in solution,⁵ as expected. Solutions of this latter compound maintain the same violet colour as the solid. This colour is unusual for *trans*-planar bis(salicylaldiminato)copper complexes, which are generally green or brown, and is reflected in the two absorption maxima found in the visible region, contrasting with the almost featureless spectra normally associated with this type of compound.⁶ Since just these bands are present when measurements are made on crystals,⁵ it is apparent that the tetrahedral geometry present in the solid persists in solution. A somewhat reverse argument suggests that none of the complexes becomes significantly more tetrahedral on dissolution. As already stated, there are no indications that strong intermolecular forces, whose release would allow a more strain-free configuration, are responsible for the observed stereochemistry of the solids, and in agreement with this the *N*-ethyl and biphenyl complexes maintain their colour in solution. All the evidence suggests, in fact, that the intermediate stereochemistry observed in the solids reflects purely intramolecular factors involving the bonding requirements of the copper atom and the space occupancy of the ligand, and is independent, at least to a first approximation, of environment.

On considering the visible region of the spectra (roughly 11,000–22,000 cm.⁻¹), where the absorption bands reflect most strongly the stereochemistry, it can be seen that bis-(*N*-ethylsalicylaldiminato)copper shows the lack of absorption characteristic of the *trans*-planar complex bis-(*N*-methylsalicylaldehydeiminato)copper(II)⁷ and that *NN'*-2,2'-biphenylbis(salicylaldiminato)copper has the spectrum of a *cis*-planar complex⁶ as evidenced by *NN'*-ethylenebis(salicylaldiminato)-copper(II) which is known to have this configuration.⁸

⁴ L. Sacconi, M. Ciampolini, F. Maggio, and G. Del Re, *J. Amer. Chem. Soc.*, 1960, **82**, 815.

⁵ L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, 1964, 276.

⁶ J. M. Waters and T. N. Waters, *J. Chem. Soc.*, 1964, 2489.

⁷ E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Sheringer, and C. Freiburg, *Acta Cryst.*, 1961, **14**, 1222.

⁸ D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.

¹ E. N. Baker, G. R. Clark, D. Hall, and T. N. Waters, unpublished work.

² T. P. Cheeseman, D. Hall, and T. B. Waters, *Proc. Chem. Soc.*, 1963, 379.

³ T. P. Cheeseman, D. Hall, and T. N. Waters, preceding Paper.

We do not know of a purely tetrahedral complex of this type with which to compare bis-(*N*-*t*-butylsalicylaldiminato)copper, but its reflectance spectrum, the same as that from solution, has been associated with a tetrahedral configuration.⁵

Insofar as their spectra are concerned, therefore, these three complexes of intermediate stereochemistry are reasonably interpreted as exhibiting a *trans*-planar, a *cis*-planar, and a tetrahedral configuration. A spectrum thus responds markedly to one component of the symmetry at the expense of others, almost completely changing its characteristics as the angle between the planes containing the co-ordinating atoms alters by only 18°. Since in none of the complexes is an idealised stereochemical situation approached even approximately [cf. bis-(*N*-isopropylsalicylaldiminato)nickel(II)]⁹

where the interplanar angle is 81°], it is obviously not sufficient to interpret such spectra in terms of planar or tetrahedral extremes.

It is interesting to note that although the biphenyl complex shows a band at 15,200 cm.⁻¹ common to *cis*-planar complexes it also shows small shoulders at 11,500 and 20,800 cm.⁻¹ which roughly approximate to the positions of the two absorption bands shown in this region by the *N*-*t*-butyl compound. Neither of the other complexes obviously evidences such secondary absorptions.

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⁹ M. R. Fox, E. C. Lingafelter, P. L. Orioli, and L. Sacconi, *Nature*, 1963, **197**, 1104.