

Antiferromagnetism in Transition-metal Complexes. Part VI.¹ Low-lying Excited States of Dinuclear Copper(II) Complexes with Bridging Multidentate Schiff's Base Groups and Some Related Compounds

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Variable-temperature magnetic susceptibility data for a number of multidentate Schiff's-base complexes of copper(II) and related molecules are reinterpreted on a model which allows for the thermal population of excited states other than those predicted by the vector-coupling model. The mechanism of superexchange through the oxygen bridges is discussed and its magnitude is found to increase sensibly through the series quadridentate Schiff's base < terdentate Schiff's base < bidentate Schiff's base < aromatic *N*-oxide. This is also the reverse order of the overall, nephelauxetic effect of the ligands upon the metal *d*-orbitals, so that the additional direct interaction is of similar magnitude for the terdentate Schiff's base series as for copper carboxylates.

THE temperature-variation of the magnetic susceptibility of copper(II) acetate and related compounds containing proximate copper(II) ions has been commonly interpreted² by the Heisenberg, Dirac, and Van Vleck approach which leads to equation (1) for an exchange interaction of the form $-JS_1 \cdot S_2$. In this Series we have

$$\chi_M'(\text{dimer}) = \frac{2Ng^2\beta^2}{kT} \cdot \frac{1}{1 + 3 \exp(J/kT)} + 2N\alpha \quad (1)$$

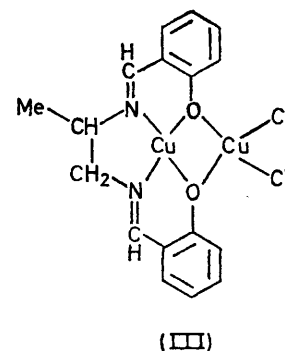
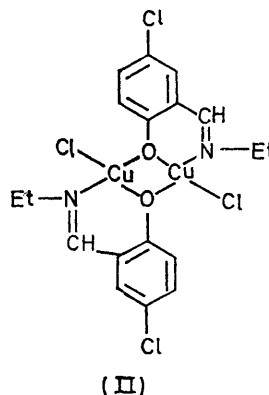
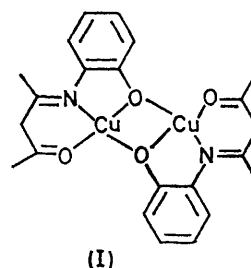
tested the applicability of equation (2) as an alternative, this being distinguished from equation (1) by the inclusion of an additional low-lying singlet state.³

$$\chi_M' = \frac{2Ng^2\beta^2}{kT} \cdot \frac{1}{1 + 3 \exp(J/kT) + \exp(-\Delta/kT)} + 2N\alpha \quad (2)$$

In the use of equation (2) it is desirable to use a fixed value for *g* as determined from the e.s.r. study of the compound concerned or one closely related to it. Similarly, *N* α should not be parameterized; we have preferred to use a constant value of 75×10^{-6} c.g.s.u. Cu^{-1} [0.92×10^{-9} m³ Cu^{-1}].¹

We now complete our survey of dinuclear copper(II) complexes by consideration of compounds containing bridging multidentate Schiff's bases and related species.^{4,5} The copper-copper distances reported for these compounds are, roughly, intermediate between those found in the copper carboxylates and the pyridine *N*-oxide complexes.⁶⁻¹⁹ Certain square-planar 'mono-

meric' bis(chelate) complexes of Schiff's bases also have weakly linked dimeric structures (4 + 1 coordination).²⁰⁻²⁵



As a background for our discussion we show in the Figure some representative dinuclear structures found in the Schiff's base series.

¹ Part V, R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J.C.S. Dalton*, 1972, 1133.

² P. O. Löwdin, *Rev. Modern Phys.*, 1962, **34**, 80.

³ R. W. Jotham and S. F. A. Kettle, *Inorg. Chem.*, 1970, **9**, 1390.

⁴ M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99.

⁵ E. Sinn, *Co-ordination Chem. Rev.*, 1970, **5**, 313.

⁶ G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1965, 1979.

⁷ J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, 1970, **4**, 203.

⁸ J. A. Bertrand, J. A. Kelley, and J. L. Breece, *Inorg. Chim. Acta*, 1970, **4**, 247.

⁹ R. D. Willett, C. Dwiggin, jun., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, 1963, **38**, 2429.

¹⁰ D. J. Hodgson, P. K. Hale, J. A. Barnes, and W. E. Hatfield, *Chem. Comm.*, 1970, 786.

¹¹ A. F. Cameron, K. P. Forrest, D. W. Taylor, and R. H. Nuttall, *J. Chem. Soc. (A)*, 1971, 2492.

¹² E. Sletten, *Chem. Comm.*, 1967, 1119.

¹³ M. Bonamico, G. Dessi, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 886.

¹⁴ P. de Meester and A. C. Skapski, *J. Chem. Soc. (A)*, 1971, 2167.

¹⁵ T. P. Mitchell, W. H. Bernard, and J. P. Wasson, *Acta Cryst.*, 1970, **B26**, 2096.

¹⁶ C. A. Bear, J. M. Waters, and T. N. Waters, *Chem. Comm.*, 1971, 703.

¹⁷ R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, 1970, **74**, 3497.

¹⁸ A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Comm.*, 1970, 904.

¹⁹ W. A. Franks and R. van der Helm, *Acta Cryst.*, 1971, **B27**, 1299.

²⁰ E. Fresson, R. Bardi, and S. Bezzi, *Acta Cryst.*, 1959, **12**, 201.

²¹ D. Hall and T. Waters, *J. Chem. Soc.*, 1960, 2644.

²² J. A. Bevan, D. P. Graddon, and J. F. McConnell, *Nature*, 1963, **199**, 573.

²³ V. F. Duckworth and N. C. Stephenson, *Acta Cryst.*, 1969, **25**, 1795.

²⁴ D. Hall, S. V. Sheat, and T. N. Waters, *Chem. Comm.*, 1966, 436.

²⁵ G. J. Palenik, *Acta Cryst.*, 1964, **17**, 687.

A complication arises because one cannot, in general, be certain that a given species is dinuclear. In particular, chain structures may occur. Such species would be expected to have a susceptibility given, at least approximately,²⁶ by equation (3). In practice we

$$\chi_M' = \frac{Ng^2\beta^2}{4kT} \exp\left(\frac{J}{2kT}\right) + N\alpha \quad (3)$$

found that it was often difficult to distinguish between linear and dinuclear models on the basis of the data available without structural evidence, even when we considered a number of compounds which were originally thought to have linear-chain polymeric structures. Conversely, we have found several other species which

than that adopted previously for the carboxylate and aromatic *N*-oxide series;^{1,31} the differences between series seem to be a reflection of the covalency of the metal-metal bonding. For some of the other related compounds we found it difficult to estimate \bar{g} reliably and we have tended to adopt a value of 2.16 in the absence of e.s.r. data on a closely related compound. It is clear that this value could well be very high for some of the more covalent systems. Such cases will be reflected in a tendency to overestimate $|J|$ and underestimate Δ when finding best fits to equations (1) and (2). For all compounds the value of $N\alpha$ was fixed at $0.92 \times 10^{-9} \text{ m}^3 \text{ Cu}^{-1}$ ($150 \times 10^{-6} \text{ c.g.s.}$ for one mole of dimer).

Summary of results

Type of copper(II) complex Class	No. of cases rejected	No. of acceptable cases ^b						Total cases considered
		Linear polymers			Dimers			
		Total	Pre- viously described as such	Average <i>J</i> value/cm ⁻¹	Total	% with infinite Δ	Average <i>J</i> value/cm ⁻¹	
Bidentate Schiff's base complexes	4	4	2	-38	29	59	-430	37
Terdentate Schiff's base complexes	10	5	1	-137	18	39	-281	33
Quadridentate Schiff's base complexes	4	0	0	—	6	33	-202	10
Miscellaneous complexes	15	4	3	-50	22	9	-203	41
Carboxylate complexes ^a	16(25)				125(116)	42(43)	-293(-296)	141
Aromatic <i>N</i> -oxide complexes ^a	8(13)				37(32)	81(81)	-350(-893)	45

^a Parenthesised figures give the published data (where the criteria of acceptability was $10^6\sigma \leq 50 \text{ c.g.s.u. Cu}^{-1}$). ^b Criterion of acceptability $10^6\sigma \leq 75 \text{ c.g.s.u. Cu}^{-1}$.

may be linear-chain molecular rather than dinuclear systems.

As in the previous Parts, we have found it necessary to consider the possible presence of diamagnetic or paramagnetic impurities in the compounds reported in the literature. It appears that the overall quality of the data used on the present paper is rather lower than that in earlier papers. We therefore divided the compounds into three sets, namely those for which the deviation between the experimental and the calculated susceptibility data for at least one of the equations (1)–(3) fell in the ranges 0–50, 50–75, and $>75 \times 10^{-6} \text{ c.g.s.u. Cu}^{-1}$. Compounds in the last set were rejected altogether but we found rather small differences between the overall pattern of results in the first two sets. From data in the literature it is apparent that, in the absence of a direct measurement, a convenient value of g for substitution in equations (1) and (2) varies considerably with the type of compound considered.²⁷ The \bar{g} values of the multidentate Schiff's base complexes and related compounds cluster around 2.13, and we have adopted this as the general value for complexes of bidentate, terdentate, and quadridentate Schiff's bases.^{28–30} This value is little lower

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

²⁶ R. W. Jotham, *Chem. Comm.*, 1973, 178.

²⁷ G. F. Kokoszka and G. Gordon, *Transition Metal Chem.*, 1969, 5, 181.

The results of our analysis of complexes of Schiff's bases and a number of related compounds are available together with the relevant bibliography in Supplementary Publication No. SUP 20816 (19 pp., 1 microfiche)* and are summarised for the various classes in the following sections and in the Table.

Bidentate Schiff's Bases and Related Ligands.—The compounds in this series are copper halide complexes with salicylaldimino-, 8-quinolinolato-, or β -aminoethanololigands. Few were found to have unacceptable susceptibility data and the average value of the singlet-triplet separation was the highest of any of the series considered herein. These compounds seem to be intermediate between the carboxylate and aromatic *N*-oxide series in this respect. In most cases the value of Δ was also found to be essentially consistent with the intermediate Cu–Cu distances expected in this series. The lack of structural data is particularly unfortunate in this context since knowledge of the molecular geometry would provide scope for a more detailed understanding of the antiferromagnetic coupling. Some indication of the planarity of the molecules is provided by the position of the *d*–*d* bands which are, as a whole,

²⁸ E. Sinn, *Inorg. Chem.*, 1970, 9, 2376.

²⁹ V. V. Zelentsov, *Zhuv. strukt. Khim.*, 1966, 7, 543.

³⁰ G. O. Carlisle, K. K. Ganguli, and L. J. Theriot, *Inorg. Nuclear Chem. Letters*, 1971, 7, 527.

³¹ R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J.C.S. Dalton*, 1972, 428.

at a much lower energy than those of corresponding tetrahedral bis(chelate) copper(II) complexes.^{32,33}

There is little evidence for linear polymeric structures among the salicylaldiminocopper halides, although the case of this structure for 8-quinolinolotocopper fluoride seems to be strong.³⁴ The complexes of the β -aminoethanololigands divide sharply into two groups. In three cases the data are of excellent quality and suggest a dinuclear complex, electronically akin to the aromatic *N*-oxide series, but in the other five compounds considered there seemed to be moderate to poor evidence for a more weakly interacting linear chain system.³⁵

Terdentate Schiff's Bases and Related Ligands.—Most compounds in this series are complexes of salicylaldiminoligands in which the nitrogen atom is substituted with an additional co-ordinating group. Almost one-third of the compounds were eventually rejected and several of the others are assigned to the class of linear polymers. The *J* and Δ values of the remaining, dinuclear, cases are similar to those found for the compounds with bridging carboxylate groups. A detailed study reveals a remarkably simple pattern, provided we distinguish nephelauxetic effects from specific effects on the superexchange interaction within the bridge. A comparison of aromatic *N*-oxide complexes with those of bidentate and terdentate Schiff's bases shows that, essentially, the terminal halogen atoms are successively replaced by ligand groups connected to the bridging oxygen atom by a substantially conjugated framework of carbon and nitrogen atoms. In each case we may envisage electron transfer from oxygen to copper of two types (which co-operate in superexchange *despite* promoting metal-metal overlap of different signs).¹ If $\sigma(n)$ and $\pi(n)$ refer to non-bonding electrons labelled with respect to the bond joining the bridging oxygen atom to the ligand framework, and the $d_{x^2-y^2}$ orbital is referred to the *local*, near-tetragonal symmetry axes, then these two mechanisms are $\sigma(n) \rightarrow d_{x^2-y^2}$ and $\pi(n) \rightarrow d_{x^2-y^2}$. The extent of transfer from the $\sigma(n)$ orbital will reflect the inductive effect of the ligand framework, leading to trends in *J* values which have already been recognised.^{33,36-38} In the aromatic *N*-oxide series, the $\pi(n)$ electrons appear to be conjugated to the electrons of the aromatic-ring* but in these Schiff's base ligands such conjugation seems much reduced, as would be expected on geometric grounds (Figure). If we accept this, the $\pi(n) \rightarrow d_{x^2-y^2}$ transfer will not be very sensitive to minor changes in ligand and will assume a characteristic magnitude for each type of complex. For most of the Schiff's base complexes studied the

groups which are substituted into the aromatic framework attached to the bridging oxygen atom are, first, a $-\text{CH}=\text{NR} \rightarrow \text{Cu}$ grouping and then R itself is replaced by an electron-withdrawing $\text{Cu}-\text{O}-\text{C}_6\text{H}_4^-$ group. These successive substitutions with groups that withdraw electrons both inductively and mesomerically presumably lead to a marked reduction in the extent of $\text{Cu}-\text{O}_\mu$ bonding as we move between these three different series (unfortunately, the available crystallographic data are not sufficient to test this hypothesis). It therefore seems reasonable that electron-density which promotes superexchange in the aromatic *N*-oxide series is successively dispersed over the conjugated framework of the ligand in the Schiff's base complexes. This provides an explanation for the observation that the average value of $|J|$ decreases sharply between these series of compounds.

Conversely, the pattern of values obtained for Δ suggest that any direct interaction between other suitable orbitals, such as the local d_{xy} orbitals, is negligible in the aromatic *N*-oxide series but increases when each terminal halogen atom is replaced by a Schiff's base ligand with an extra 'tooth'.

The overall nephelauxetic effect increases sharply as halogen atoms are replaced by oxygen atoms in a conjugated ligand framework, an effect manifest in the differing *g*-values obtained from e.s.r. measurements as well as in the magnetic susceptibility data.

Quadridentate Schiff's Bases as Ligands.—The low values of $|J|$ for these so-called *cis*-dimers has already been the subject of comment.^{36,39} It seems clear that the much weaker interaction in these complexes reflects the marked electronic asymmetry of the bridge system and also delocalisation of electron density over the single quadridentate ligand. On the basis of the limited number of acceptable cases, the Δ values also appear to be small, an observation which may be correlated with the nephelauxicity of the ligand itself. This is so high that the $\text{Cu}(\text{ligand})$ complexes may function as ligands towards numerous other systems apart from cupric halides.^{40,41} Within this series, the trend in $|J|$ values also appears to reflect the steric requirements of the unit which links the two salicylaldimino-sections together.

Concluding Remarks.—This paper and the associated supplementary publication completes the survey of the susceptibility data available for dinuclear copper(II) compounds. The results obtained indicate that there is a strong case for the replacement of equation (1) by

* It should be noted that Watson and his co-workers currently prefer a π -bond superexchange mechanism in these systems, and not the σ mechanisms (see *Inorg. Chem.*, 1969, 1879 and references therein).

³² L. Sacconi, M. Ciampolini, and U. Campigli, *Inorg. Chem.*, 1965, **4**, 407.

³³ C. M. Harris, J. M. James, P. J. Milham, and E. Sinn, *Inorg. Chim. Acta*, 1969, **3**, 81.

³⁴ M. J. Frazer, G. V. Robins, and F. B. Taylor, *J. Chem. Soc. (A)*, 1969, 2451.

³⁵ E. Uhlig and K. Staiger, *Z. anorg. Chem.*, 1968, **360**, 39.

³⁶ C. M. Harris and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2723.

³⁷ G. F. Kokoszka and R. W. Duerst, *Co-ordination Chem. Rev.*, 1970, **5**, 209.

³⁸ W. E. Hatfield and F. L. Bunger, *Inorg. Chem.*, 1966, **5**, 1161.

³⁹ S. J. Gruber, C. M. Harris, and E. Sinn, *Inorg. Chem.*, 1968, **7**, 268.

⁴⁰ M. Kato, U. Muto, H. B. Jonassen, K. Imai, and T. Tokii, *Bull. Chem. Soc. Japan*, 1970, **43**, 1066.

⁴¹ S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nuclear Chem.*, 1968, **30**, 1805.

an equation derived from a more detailed model whenever relatively short copper-copper separations or dinuclear complexes with highly nephelauxetic ligands are studied. In such cases, equation (2) represents a considerable improvement on equation (1) and has the advantage of reducing to equation (1) whenever these complicating factors are absent. It therefore offers

greater potential insight into the structure of a new compound. However, we believe that it is essential to use sensible values for g and $N\alpha$ and to limit discussion to those cases where the standard deviation between calculated and experimental susceptibilities is not excessive.

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