Antiferromagnetism in Transition-metal Complexes. Part V.[1] Binuclear Copper(II) Complexes with Bridging Aromatic *N*-Oxide Groups

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Variable-temperature magnetic susceptibility data for a number of 1:1 aromatic *N*-oxide complexes of cupric halides 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 is found to be dominated by two paths which promote an effective metal–metal overlap in opposite senses, yet co-operate in the antiferromagnetic exchange process. Analogous data on the 2:1 series is more limited but the relationship between structure and magnetic properties is reaffirmed for these more diverse compounds.

A LARGE number of binuclear copper(II) complexes with abnormal, usually subnormal, magnetic moments are known,[1,2] the vector coupling model of Bleaney and Bowers having been commonly used in the discussion of their e.s.r. and magnetic susceptibility data.[3] In the first four parts of this series we have established, for the binuclear copper(II) carboxylates, a *prima facie* case for the consideration of certain low-lying excited states in addition to the singlet and triplet levels required on the earlier model.[1,4-6] These carboxylate compounds generally have structures like that of copper acetate monohydrate so that the main contributions to the singlet and triplet levels of the vector-coupling model come from unpaired electrons in orbitals with an $(x^2 - y^2)$ angular form.[7,8] In the revised model we have adopted the energy-level diagram shown in Figure 1 for the binuclear cupric carboxylates, where the additional singlet considered arises similarly from partially occupied $|z^2\rangle$ orbitals.[1] This energy-level pattern leads to the following expression for the molar susceptibility of the dimer (using conventional symbols) [9]

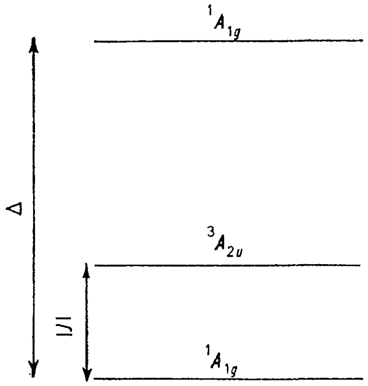

FIGURE 1 Energy-level diagram for binuclear copper(II) complexes which was found to be appropriate for the carboxylates (D_{4h} symmetry labels)

$$\chi_M' = \frac{Ng^2\beta^2}{3kT} \cdot \frac{6 \exp(J/kT)}{1 + 3\exp(J/kT) + \exp(-\Delta/kT)} + N\alpha \quad (1)$$

We have always chosen to adopt constant values for g and α in this expression, being those which are derived from measurements of e.s.r. spectra and electronic-absorption spectra respectively,[1,5] and have then optimised the values of J and Δ to obtain the best fit to the observed susceptibility.[1] In a study of the binuclear carboxylates we concluded that the upper singlet is at a sufficiently low energy to be thermally populated in more than half the compounds considered. A detailed discussion of the data for these compounds led us to conclude that the component of σ-bonding is of a direct nature but we could draw no firm conclusion as to the nature of the δ-interaction, although it seems likely that it must involve a large proportion of 'superexchange'. This latter component may be studied in more detail by attempting to apply equation (1) to a class of compounds in which the direct overlap may reasonably be regarded as negligible, and we now present the results of such an analysis of the available data for binuclear copper(II) complexes with aromatic *N*-oxide bridges, for which the Cu–Cu distances lie in the range 3·2—3·5 Å.

This application of equation (1) is of additional interest in that a negligible σ-overlap should result in Δ assuming a value indistinguishable from infinity. If this value of Δ is, indeed, commonly obtained then the significance of the Δ value previously found for binuclear copper carboxylates is reinforced.

The large variety of compounds between aromatic *N*-oxides and copper(II) compounds has been discussed by Watson.[10] We shall be principally concerned with low-magnetic-moment 1 : 1 complexes and with a few low- and normal-magnetic-moment 2 : 1 dimeric complexes. In Figure 2 we illustrate, as representative examples, the

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structures of (A) pyridine N-oxide cupric chloride,[11–13] (B) bis(pyridine N-oxide)–cupric chloride,[10,14] (C) bis(pyridine N-oxide)–cupric bromide,[14] and (D) bis(pyridine N-oxide)–cupric nitrate.[15] The latter is of particular interest in view of its structural similarity with the halogen-bridge system of pyridine N-oxide–cupric chloride, in which each copper atom is bridged in different ways to two other coppers. Unlike most of the other known copper(II) complexes of aromatic N-oxides, bis(pyridine N-oxide)–copper(II) nitrate apparently exhibits very weak coupling with a triplet ground state.[16] It therefore seems safe to assume that the dominant copper–copper coupling in molecules such as that shown in Figure 2(A) is between those copper atoms linked as shown in Figure 2(B). This assumption finds support in some ^{35}Cl n.q.r. data which similarly suggests that the inter-dimer interaction is very small.[17] It is also in accord with Goodenough's classical cases of a 90 or a 180° geometry.[18]

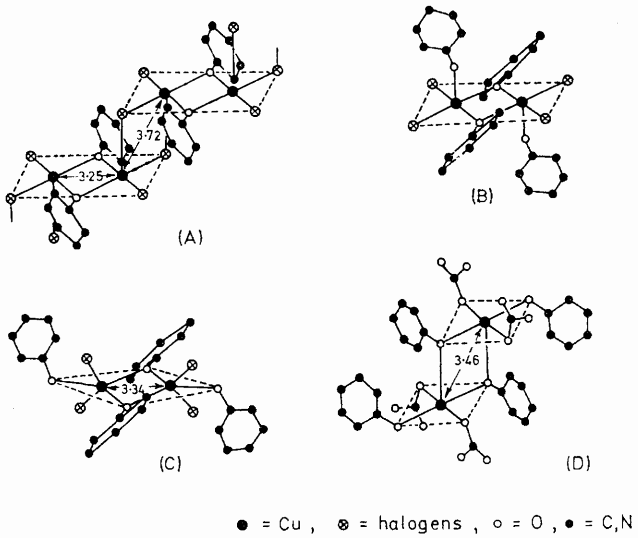

FIGURE 2 Some pyridine N-oxide complexes of copper(II) salts. Reported Cu–Cu distances in Å. Dotted lines define idealised planes of co-ordination

The variation in the room-temperature moment and the spectroscopic properties of both the 1 : 1 and the 2 : 1 series is much greater than that found for the copper(II) carboxylates,[2,10,19] and the different series exhibit characteristic metal–halogen and metal–oxygen stretching frequencies in their i.r. spectra.[20] Similar differences in ^{35}Cl and ^{79}Br n.q.r. spectra have been noted.[17] Some e.s.r. data for binuclear aromatic N-oxide complexes [18,21,22] are given in Table 1, where the g values are compared with typical data of related systems.[23–25] The average g values are a little lower than those found for typical binuclear copper carboxylates. This is because the $g_{\parallel}$ component is slightly reduced by admixture of the d_{z^2} orbital into the ground state when the Cu–Cu axis is reduced from an effectively 4- to a 2-fold rotational symmetry;[21] the g values of very low symmetry complexes such as those of Schiffs bases are even lower.[25] The e.s.r. data of the aromatic N-oxide complexes have been interpreted in terms of relatively strong metal-ligand bonding.[22]

TABLE 1

E.s.r. values of g for binuclear copper(II) complexes of aromatic N-oxides and some comparative data

Compound	Ref.	g_x	g_y	$g_{\perp}$	g_z	$\bar{g}$
$[Cu(CH_3COO)_2,H_2O]_2$	23	2·053	2·093		2·344	2·17
$[Cu(PhCOO)_2$,-$PhCOOH]_2$	24	2·048	2·074		2·345	2·16
$[CuCl_2(pno)_2]_2$	21	2·06	2·08		2·32	$2{\cdot}15_6$
$[Cu,ZnCl_2(pno)_2]$	22	2·056	2·080		2·323	$2{\cdot}15_6$
$[CuCl_2(pno),H_2O]_2$	21	2·06	2·08		2·31	$2{\cdot}15_3$
$[Cu,ZnCl_2(pno),H_2O]_2$	22	2·056	2·083		2·306	$2{\cdot}15_1$
$[Cu(o\text{-hydroxyanil})]_2$	25			2·07	2·25	2·13
$[Cu(NO_3)_2(pno)_2]_2$	16			2·05	2·23	2·11

Notes: $\bar{g} = [\frac{1}{3}(g_x{}^2 + g_y{}^2 + g_z{}^2)]^{\frac{1}{2}} = [\frac{1}{3}(2g_{\perp}{}^2 + g_{\parallel}{}^2)]^{\frac{1}{2}}$.

pno = Pyridine N-oxide, o-hydroxyanil = acetylacetone-(mono-o-hydroxyanil).

RESULTS

In Tables 2 and 3 we present the results of our analysis of the available bulk-susceptibility data [11,26–33] in terms of equation (1). Where a directly measured e.s.r. value was not available for $\bar{g}$ we adopted the constant value of 2·153.[21,22] The dominant contributions [5] to the value of $N\alpha$ do not vary very much for most copper(II) complexes and we therefore used the same constant value as before, namely 1·89 × 10^{-9} m^3 mol^{-1} (150 × 10^{-6} c.g.s.) for each

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TABLE 2

Magnetic data for 1 : 1 aromatic *N*-oxide complexes of copper(II) halides (and carboxylates)

				Published data (Δ = ∞)[b]			This work [equation (1)][b,c]			Electronic spectra	
Compound[a]	Ref. to χ/T data	Number of data used	g	$-J$ (cm^{-1})	$10^9N\alpha$ ($m^3\ mol^{-1}$)	$10^9\sigma$ ($m^3\ mol^{-1}$)	$-J$ (cm^{-1})	Δ (cm^{-1})	$10^9\sigma$ ($m^3\ mol^{-1}$)	d–d-Band max. ($cm^{-1} \times 10^3$)	Ref.
(4-Nitro-qno)$CuCl_2$	31	6[i]	2·20	−135	1·51	24·5	−148	∞	38·3[f]		
(4-Nitro-pno)$CuBr_2$	26	4	2·20	143	1·51	7·52	59	875	2·41[f]	12·0	18
(qno)$Cu(CH_3COO)_2$	33	14	2·13	323	1·51	0·26	334	886	0·20		
							335	821	0·21[h]		
(pno)$Cu(CH_3COO)_2$	33	15	2·18	345	1·51	0·54	348	∞	0·58		
							349	∞	0·57[h]		
(pno)$CuCl_2$	26	10	2·20	616	1·51	3·41	523	∞	1·74[f]	10·6	18, 30
(4-Nitro-pno)$CuCl_2$	30	23	2·20	529	1·51	0·06[e]	530	∞	0·20	10·3	30
(pno)$CuCl_2$	32	8	2·40	619	1·89	0·39[d]	575	∞	0·55	10·6	18, 30
(pno)$CuCl_2$	11	9	2·11	650	1·84	0·36	658	1095	3·62[f]	10·6	18, 30
(pno)$CuCl_2$	30	26	2·20	716	2·42	0·11	681	∞	0·14	10·6	18, 30
(3-Methyl-pno)$CuCl_2$	27	6	2·20	730	1·51	1·18	683	∞	0·43	11·8	18
(pno)$CuCl_2$	33	11	2·13	720	2·27	0·26	690	683	0·29		
							706	∞	0·34[g]		
(3-Methyl-pno)$CuBr_2$	27	6	2·20	990	1·51	2·55	796	∞	0·56	11·9	18
(4-Butyl-pno)$CuCl_2$	30	20	2·20	776	0·93	0·20	830	∞	0·50		
(4-Chloro-pno)$CuCl_2$	26	5	2·20	1090	1·51	2·41	842	∞	0·53	12·4	18, 30
(pno)$CuBr_2$	33	10	2·00	935	1·89	0·64[d]	868	182	0·53		
							974	∞	0·67[g]		
(4-Benzyl-pno)$CuCl_2$	30	21	2·20	838	1·36	0·10	873	∞	0·31		
(lno)$CuCl_2$	27	6	2·20	1010	1·51	0·34	942	213	0·19	13·2	18
							1033	∞	0·25[g]		
(4-Methyl-pno)$CuCl_2$	26	6	2·20	986	1·51	0·95	948	∞	0·86	12·0	18
(4-Methyl-pno)$CuCl_2$	30	32	2·20	829	0·35	0·18	976	∞	0·89	12·0	18
(lno)$CuBr_2$	27	7	2·20	1020	1·51	0·26	1004	590	0·07	13·5	18, 27
							1030	∞	0·09[g]		
(cno)$CuCl_2$	27	4	2·20	1020	1·51	0·25	1060	∞	0·25	13·3	18
(4-Pyridyl-carbno)$CuCl_2$	30	20	2·20	941	0·66	0·17[e]	1100	∞	0·75		
(cno)$CuBr_2$	27	7	2·20	1040	1·51	0·19	1123	∞	0·05		
(4-Cyano-pno)$CuCl_2$	30	20	2·20	966	0·88	0·08	1148	∞	0·65	11·9	30
(4-Methoxy-pno)$CuCl_2$	30	15	2·20	994	0·73	0·11	1202	∞	0·71	12·2	30
(4-Ethoxy-pno)$CuCl_2$	30	16	2·20	1027	0·93	0·09	1214	∞	0·62	12·1	30
(4-Chloro-pno)$CuCl_2$	30	24	2·20	1064	1·01	1·49	1224	∞	0·66	12·4	18
(4-Carbomethoxy-pno)$CuCl_2$	30	14	2·20	923	0·58	0·03[e]	1291	255	0·94		
							1291	∞	0·94[g]		
(4-Bromo-pno)$CuCl_2$	30	18	2·20	1050	0·91	0·04[e]	1309	∞	0·58		
(qno)$CuCl_2$	33	4	2·016	1400	1·89	0·40[d]	1368	∞	0·47		
(qno)$CuBr_2$	33	4	2·016	1400	1·89	0·41[d]	1368	∞	0·51		
(4-Phenyl-pno)$CuCl_2$	30	14	2·20	1027	1·21	0·03	1395	∞	0·50		
(4-Hydroxy-pno)$CuCl_2$	26	6	2·20	2150	1·51	0·93	2520	497	1·23[f]		

[a] pno = Pyridine *N*-oxide, lno = 2,6-lutidine *N*-oxide, cno = 2,4,6-collidine *N*-oxide, qno = quinoline *N*-oxide, carbno = carbinol *N*-oxide. [b] $\sigma = \left(\sum_{i=1}^{n} [\chi_i(\text{expt}) - \chi_i(\text{calc})]^2/n\right)^{\frac{1}{2}}$. [c] $\bar{g} = 2{\cdot}153$, $N\alpha = 1{\cdot}89 \times 10^{-9}\ m^3\ mol^{-1}$. [d] Best-fit g and J values determined in this work. [e] Published data allows for >1% paramagnetic impurity. [f] Large σ suggests that the data may be unreliable. [g] Δ fixed at ∞. [h] $g = 2{\cdot}160$, a value appropriate to copper carboxylates. [i] The susceptibility data collected below 15 K were not used.

TABLE 3[j]

Magnetic data for 2 : 1 aromatic *N*-oxide complexes of copper(II) halides and related-compounds

				Published data (Δ = ∞)			This work [equation (1)][b,c]		
Compound[a]	Ref. to to χ/T data	Number of data used	g	$-J$ (cm^{-1})	$10^9N\alpha$ ($m^3\ mol^{-1}$)	$10^9\sigma$ ($m^3\ mol^{-1}$)	$-J$ (cm^{-1})	Δ (cm^{-1})	$10^9\sigma$ ($m^3\ mol^{-1}$)
$(qno)_2Cu(NO_3)_2$	33	11	2·16	−64	1·89	1·41[d]	−72	∞	1·30[f]
$[(pno)_6Cu](ClO_4)_2$	33	12	2·02	−286	1·89	1·27[d]	−57	∞	2·24[f]
$(pno)_2Cu(SCN)_2$	33	12	2·07	−126	1·89	1·52[d]	−56	∞	1·81[f]
$(qno)_2CuBr_2$	33	11	2·01	−312	1·89	0·84[d]	−52	∞	1·86[f]
$(lno)_2CuCl_2$ (yellow)	28	5	2·26	23	1·89	3·59[d]	3	∞	5·66[f]
$[(pno)_4Cu](ClO_4)_2$	33	8	2·02	−38	1·89	1·44[d]	4	∞	2·17[f]
(2-Methyl-pno)$_2CuCl_2$	28	4	2·17	13	1·89	1·06[d]	10	∞	1·09
$(qno)_2CuCl_2$	33	10	2·16	19	1·89	0·65[d]	17	∞	0·48
$(lno)_2CuCl_2$ (green)	28	5	2·09	28	1·89	7·41[d]	34	∞	8·29[f]
$(pno)_2CuBr_2$	33	17	2·07	242	1·51	1·54	235	166	1·05
							258	∞	2·26[f,g]
$(pno)_2CuCl_2$	33	6	2·40	830	1·89	0·40[d]	779	∞	0·53
$(pno)_2CuCl_2$	29	17	2·153	550	1·51	4·26	805	∞	0·48

[j] Notes as for Table 2.

dimeric unit.[5,34] Adventitious factors such as the presence of impurities, which influence the values obtained for J and Δ from equation (1) have been discussed in Part IV of this series.[1]

DISCUSSION

In our discussion of the binuclear copper(II) carboxylates we omitted those cases where the standard deviation of the calculated and measured susceptibilities exceeded $1{\cdot}25 \times 10^{-9}$ m^3 mol^{-1} (10^{-4} c.g.s.) and we have applied the same criterion in this case. The present analysis appears to indicate that many of the results obtained with equation (1) are strikingly poorer than the published data. This is, in fact, not so, because a large proportion of the very low σ values in the published data originate from the use of $N\alpha$ as a parameter. As the susceptibilities of most of the compounds concerned are very small this procedure leads to deceptive results concerning the relative magnitudes of the exchange integrals. Pertinently, the best fit values of $N\alpha$ thus calculated are generally far too diverse to be regarded with any confidence.

The 1:1 *Series*.—It is clear from Table 2 that there is very little evidence of an additional thermally populated singlet in the 1:1 complexes of aromatic *N*-oxides with the cupric halides. The value of Δ was found to be finite in only 5 of the 27 cases considered to be acceptable and two of these involved a very limited quantity of data. As we would reasonably expect the occasional stray value of Δ to result from errors in the original data, we recalculated the values of J for these cases after setting Δ to ∞. As noted earlier the infinite values of Δ for most of the compounds considered reflect the weakness of any Cu–Cu σ-interaction and lend additional confidence to the general application of equation (1).

The mechanism of the superexchange in the 1:1 complexes has been the subject of speculation. Watson *et al.*, pointing out the normal length of the Cu–O bridge bonds, preferred a π-mechanism which might be influenced by the close proximity of the bridging oxygen atoms (2·4 Å).[12] Conversely, Muto *et al.* prefer a σ pathway because of the intrinsically larger metal-ligand overlap integrals and because of the clear correlation between magnetic moment and *d–d*-band maxima in these complexes.[19] (This general trend may also be traced in the data given in Table 2.) The latter approach is probably to be preferred, since it seems unlikely to be energetically feasible to promote the unpaired 'hole' into a metal orbital suitable for π-bonding in this geometry. All workers agree that the lower moments of the bromide series by comparison with their chloride counterparts reflect the nephelauxetic effect of the halogen ligands on the metal orbitals.

It is simple to demonstrate, qualitatively, the effect of overlap with a bridge orbital on the effective overlap between orbitals $\psi(\mathrm{Cu}_1)$ and $\psi(\mathrm{Cu}_2)$ on adjacent copper atoms. Suppose the copper atoms are sufficiently well separated that $\int\psi(\mathrm{Cu}_1)\,\psi(\mathrm{Cu}_2)\mathrm{d}\tau = 0$, but that each overlaps with an orbital of a single bridge atom, $\psi(\mathrm{BR})$, and $\int\psi(\mathrm{Cu}_1)\,\psi(\mathrm{BR}) = \int\psi(\mathrm{Cu}_2)\,\psi(\mathrm{BR}) = S$. It is appropriate therefore, to replace each copper orbital by a linear combination with $\psi(\mathrm{BR})$

$$\psi_1 = \frac{1}{N}\,[\psi(\mathrm{Cu}_1) + \lambda\psi(\mathrm{BR})]$$

$$\psi_2 = \frac{1}{N}\,[\psi(\mathrm{Cu}_2) + \lambda\psi(\mathrm{BR})]$$

where λ is a mixing coefficient and $N = 1 + 2\lambda S + \lambda^2$. It is trivial to show that

$$\int\psi_1\,\psi_2\mathrm{d}\tau = \frac{x}{1 + x}$$

where $$x = 2\lambda S + \lambda^2$$

so that for $\lambda = 0{\cdot}2$, $S = 0{\cdot}2$, $\int\psi_1\,\psi_2\mathrm{d}\tau \sim 0{\cdot}1$, which is to be compared with the value of the direct overlap integral between the two copper orbitals. Because of the larger number of intervening atoms in the binuclear copper carboxylate case one might expect to find a weaker coupling than in the molecules discussed in the present paper. For the carboxylates, however, the copper–copper overlap integrals are not entirely negligible and, furthermore, there is a geometric factor which enhances interaction in their case. Assuming constant Cu–O bond lengths and O–Cu–O angles of 90° then the group overlap integral between a copper $d_{x^2-y^2}$ orbital and σ orbitals of the four, coplanar, oxygen atoms of the carboxylate anions is $\sqrt{3}S_\sigma$. In the case shown in Figure 2(B) the corresponding overlap is $\sqrt{\tfrac{3}{2}}S_\sigma$. Deviations from the assumed geometry and increase in bond length will decrease S_σ but could be offset by changes of effective nuclear charge or hybridisation at the oxygen atoms. Experimentally, it is clear that whereas in the copper carboxylates the values of the singlet–triplet separation cluster around 300 cm^{-1} the characteristic value of $|J|$ for the 1 : 1 aromatic *N*-oxide series is *ca.* 1000 cm^{-1} (Table 2).

The bridge system in these compounds is one of the simplest found in binuclear copper(II) complexes. Nevertheless, certain structural features (Figure 2) pose difficulties for the interpretation of the bonding pathways. Fortunately, the structure is much closer to the C_{2v}-distorted square than to the C_{2v}-distorted tetrahedron and we shall consider the idealised geometry shown in Figure 3. The two unpaired electrons will be in antibonding orbitals of $\langle zx|$ symmetry on each copper atom. (These $\langle zx|$ orbitals are the $\langle x^2 - y^2|$ orbitals of the local square-planar environment).

The two $\langle zx|$ orbitals combine to give group orbitals which are symmetric and antisymmetric under reflection in the xy mirror plane, having symmetries of B_{3u} and B_{2g} respectively, in D_{2h}. In this model quite different orbitals of the pyridine *N*-oxide molecules are involved in the two interactions (Figure 4). In particular, only the B_{2g} orbital may be delocalised onto the aromatic ring and thus only this orbital is directly subject to perturbations resulting from the presence of substituent

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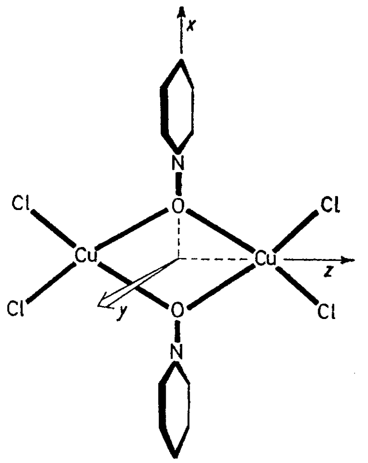

FIGURE 3 Idealised structure of [$CuCl_2$(pyridine *N*-oxide)]$_2$

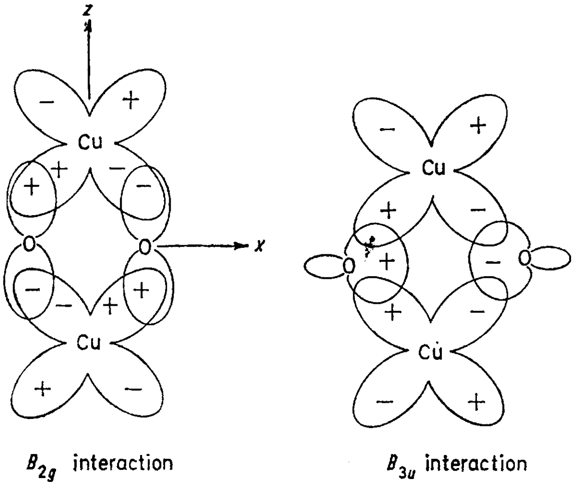

FIGURE 4 Superexchange paths involving Cu–O σ-bonding

groups. In practice, the local symmetry at each copper atom is C_1, not C_{2v}, and the plane of the aromatic *N*-oxide ring is inclined relative to that of the copper–oxygen bridge system. It thus becomes difficult, if not impossible, to entirely distinguish between Cu–Cu interactions transmitted by orbitals which are σ or π with respect to the O–N axes of the bridging ligands. Returning to the model system, it is not difficult to show (*cf.* Part III of this series) [6] that the lowest triplet and singlet are given approximately by

$$^3B_{1u}\,(S = 1 \text{ component}) = \langle\,|(zx)_a(zx)_b|\,|$$

$$^1A_{1g} = \frac{1}{\sqrt{2}}\langle(|(zx)_a(\overline{zx})_b| + |(zx)_b(\overline{zx})_a|)|$$

It may readily be shown that, within the model we have outlined, the $^3B_{1u}$ function is not significantly modified but the $^1A_{1g}$ function is mixed with two excited-state functions, which correspond to charge transfer between the two copper and oxygen molecular orbitals of B_{2g} and B_{3u} symmetry.

This is a striking result because it demonstrates that, although the B_{2g} and B_{3u} nodal patterns are such that they appear to lead to opposing overlap of the d_{zx} orbitals (Figure 4), the effect on the actual electronic states is co-operative.

Indeed, since these two interactions are of the same order of magnitude, this perception goes a considerable way towards explaining the relatively large overall antiferromagnetic interaction found in this series, whereas the normal Cu–O bond lengths may reflect the opposing metal-ligand overlaps. Furthermore, the synergistic double σ-pathway should also apply in principle to binuclear complexes, such as those of the Schiffs bases, which have, essentially the same type of ' dangling ' bridging oxygen atoms.

One compound, namely (4-nitroquinoline *N*-oxide)–cupric chloride, stands alone amongst those listed in Table 2 in having a ferromagnetic exchange integral.[31,35] The situation with respect to the molecule is by no means clear and it would be desirable to establish the structure before detailed discussion. The magnetic data give a very poor agreement with equation (1), with Bleaney and Bowers expression and also with the corresponding equation for a linear polymeric species.[31]

The 2:1 *Series*.—The complex variety of structures possible for this series makes it difficult to discuss the sparse data which we have collected in Table 3, and, unfortunately, many of these data led to unacceptably large standard deviations. It is convenient to divide the compounds into four groups, namely those represented by the molecules shown in Figure 2 (B, C, and D) and monomeric species. The case of the nitrates seems to be clear enough, for structure 2(D) suggests that there is no single orbital of the bridging ligands which will overlap with both of the local ($x^2 - y^2$) orbitals that contain the magnetic electrons thus leading to an indirect and ferromagnetic interaction.[18] We next notice in Table 3 that the *J* values of many of the 2 : 1 compounds are near zero and are similar to those calculated from data on the monomeric cationic species for which data were also available.[33] Most of these compounds are likely to be monomeric species also. Watson has subdivided these compounds in similar fashion by reference to the N–O stretching frequencies.[10] Of the compounds mentioned in Table 3, only the bis(pyridine *N*-oxide) complexes of cupric chloride and bromide can definitely be regarded as dimers with structures such as 2(B) or 2(C). In the case of the bromide complex the local geometry approaches trigonal rather than tetragonal and the Cu–O μ-bonds are slightly longer than those found in (pno)-$CuCl_2$.[14] The nephelauxetic effect of the halogen atoms on the local partially filled orbital is diminished by the overall removal of one ligand from the plane of the bridge system, and we therefore find that the singlet–triplet separation is smaller in this compound than in most 1 : 1 complexes. Conversely, the analogous chloride appears to favour structure 2(B) and, in this case, there seems to be just a slight increase in $|J|$ (by comparison with the

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[35] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1965, 1979.

1 : 1 complex) because of the nephelauxetic effect of the additional ligand. The unexpected order of the two magnetic moments of these compounds reflects this structural diversity, and it is clear that meaningful discussion of the dimeric species must await a significant increase in the available structural and magnetic data.[36] We do however record that, as with the 1 : 1 complexes of copper halides with aromatic *N*-oxides, there is little evidence for additional low-lying excited states in the corresponding 2 : 1 series.

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[36] D. R. Johnson and W. H. Watson, *Inorg. Chem.*, 1971, **10**, 1281.