Relation between Metal Environment and Antiferromagnetic Interactions in Binuclear Copper Complexes, and Crystal Structures of $Cu_2Cl_2O_4N_2C_{20}H_{20}$, $Cu_2O_8N_4C_{20}H_{20}$, and $Cu_2O_4N_2C_{28}H_{26}$

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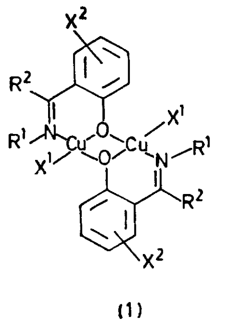
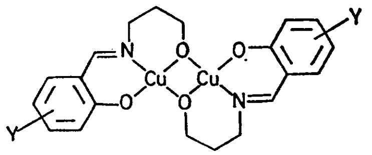
Summary For copper(II) dimers, a correlation between antiferromagnetic interaction and metal environment is demonstrated, and this correlation is strong enough to be used in the solution of three crystal structures.

In binuclear copper(II) complexes of type (**1**), the Cu_2O_2 bridge produces pair-wise antiferromagnetic exchange interactions which increase as the copper(II) stereochemistry approaches square planar.[1-3] This dependence on metal environment outweighs the effect of varying the nature of the ligand X. The same relationship should therefore be applicable in complexes of type (**2**),[4] whose structural formulae were established from magnetic and i.r. spectroscopic data.[5] A series of such complexes have been prepared and investigated by magnetic susceptibility and *X*-ray diffraction methods. The experimental techniques used for the magnetic measurements[1-3] and diffraction intensity collection[6] are described elsewhere.



(1)



(2)

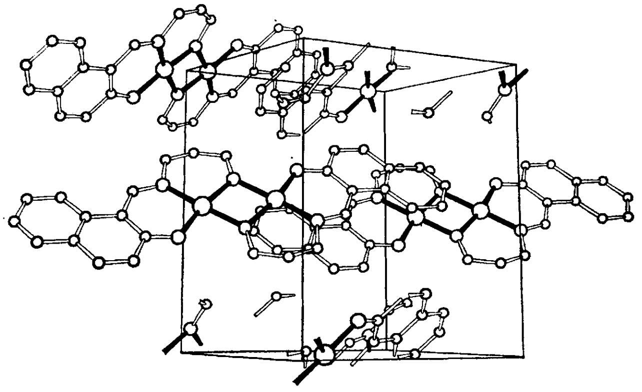


Figure. Molecular packing in (**2c**).

The antiferromagnetic interaction is very strong in compounds (**2**) (singlet–triplet separation, $-2J > 800\ cm^{-1}$).

TABLE. Some magnetic and structural features

						For type (1) complexes			
	Complex	$-J$/cm^{-1}	τ/°	Cu-O-Cu′	Ref.	R	R′	X	X′
(**2a**)	$Cu_2C_{20}H_{20}N_2O_4Cl_2$	$\geqslant$ 400	13·7	103·7	a				
(**2b**)	$Cu_2C_{20}H_{20}N_4O_8$		9·6	103·5	a				
(**2c**)	$Cu_2C_{28}H_{26}N_2O_4$		10·4	104·0	a				
(**1a**)	$Cu_2C_{18}H_{20}N_2O_2Cl_2$	240	33·1	103·3	1	Et	H	Cl	H
(**1b**)	$Cu_2C_{34}H_{34}N_2O_2Br_2Cl_2$	220	35·5	101·2	2	Bu	Ph	Br	5-Cl
(**1c**)	$Cu_2C_{18}H_{20}N_2O_2Br_2$	205	35·7	104·6	1	Et	H	Br	H
(**1d**)	$Cu_2C_{16}H_{16}N_2O_2Cl_2$	146	39·3	102·2	1	Me	H	Cl	H

[a] Present work.

This requires a copper(II) environment very close to square planar, which in turn requires the entire molecule to be approximately flat because of ligand conjugation. Therefore the entire molecule must be visible in each case as an approximate reciprocal image in a photograph of the diffraction pattern, for a suitable crystal orientation.[7] This method was used successfully for three complexes of type (**2**) (**a**) Y = 5-Cl,† R 2·4%, (**b**) Y = 3-NO_2, R 4·7%, (**c**) Y = 5-6-benzo, R 3·9%, each belonging to the same space group $P2_1/c$. From the unit cell volumes, the molecular formulae and an assumed atomic volume of 19 ± 2 Å^3 for non-hydrogen atoms, $Z = 2$ in each case, and a centre of inversion is required in each of the molecules. The procedure is described below.

In each case the approximate orientation of the molecular plane, as viewed on a precession photograph, defined the Cu_2O_2 plane. Cu–Cu and Cu–O were taken as 3 and 2 Å respectively.[1,2] This phased the diffractometer data well enough to permit location of the remaining atoms by difference Fourier syntheses, clearly illustrating the power of the correlation between structure and magnetism. The Figure illustrates this for (**2c**) with molecular orientations as expected from the initial location of the reciprocal image of the molecules on film in the plane defined by the a^* axis and the $0kl$ vector.

A convenient, albeit somewhat crude, way to parameterise the degree of distortion from planarity is the angle τ between the Cu_2O_2 plane and the plane of the remaining ligands. The Table gives τ and $|J|$ values, which demonstrate generality of the correlation between the copper geometry and strength of antiferromagnetic interaction, and support the hypothesis that the strength of interaction is determined by the efficiency of Cu–O–Cu superexchange overlap; on this basis the $-2J$ values for the complexes (**2**) should be large, as observed.

No systematic relation is observed between $|J|$ and the Cu–O–Cu′ angle, *i.e.* this variable has fortuitously been held approximately fixed over the range of complexes in the Table, enabling the effect of the metal environment to be examined closely. In addition, no significant inductive effects are observed upon varying substituents directly on the metal atoms (O,Cl,Br) as well as at other sites. Clearly the environments of the metal atoms and the bridging oxygen atoms have the greatest effect on J and substituents are relatively unimportant except for any structural modifications they produce in the Cu_2O_2 bridge.

Financial support for instrumentation from the National Science Foundation is gratefully acknowledged.

(*Received*, 28*th May* 1975; *Com.* 584.)

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† Reported in unrefined form at March 1974 meeting of the A.C.A. at Berkeley, California.

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