Inorganica Chimica Acta, 135 (1987) L1–L3

Observations on the Structure and Magnetic Properties of Dinuclear Copper(II) Complexes Derived from Flexible Dinucleating Schiff Base Ligands

HARRY ADAMS, NEIL A. BAILEY, DAVID E. FENTON*, RICHARD MOODY

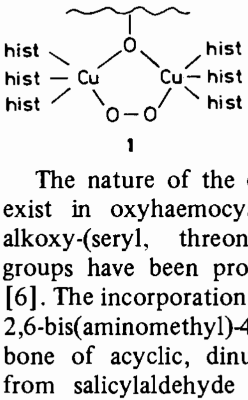
Department of Chemistry, The University, Sheffield S3 7HF, U.K.

and JEAN MARC LATOUR

DRF-CH (UA 321), C.E.N.G., F 38041, Grenoble, France

(Received July 22, 1986)

Subsequent to Robson's initial studies on binucleating Schiff base ligands derived from 2,6-diformyl-4-methylphenol [1] there has been much interest in the potential use of such compounds as small molecule models for dicopper(II)–biosites such as oxyhaemocyanin [2]. The relative rigidity of the ligand framework, imposed by the diiminophenolic head-unit, limits the copper–copper separation *ca.* 3.0 Å [3], as compared to 3.6 Å in the biosites [4], and so attempts to define more flexible systems have been made [5, 6].

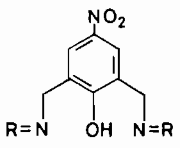


1

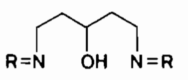
The nature of the endogenous bridge believed to exist in oxyhaemocyanin 1 is conjectural [2, 4]; alkoxy-(seryl, threonyl) and aryloxy-(tyrosinyl) groups have been proposed as plausible candidates [6]. The incorporation of 1,5-diaminopentan-3-ol and 2,6-bis(aminomethyl)-4-nitrophenol into the backbone of acyclic, dinucleating Schiff bases derived from salicylaldehyde (salH) and pentane-2,4-dione (acacH)[7], L_1–L_4, provides a means of comparing the nature of alkoxy- and aryloxy-endogenous bridges in closely related molecules.

Treatment of the Schiff bases with copper(II) ethanoate in the presence of a bridging ligand X, (X = OH^-, OCH_3^-, N_3^-, p-$NO_2C_6H_4O^-$, pyrazolate),

Treatment of the Schiff bases with copper(II) ethanoate in the presence of a bridging ligand X,

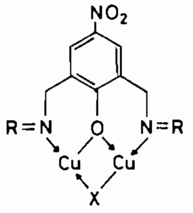


L_1, R = salH
L_2, R = acacH

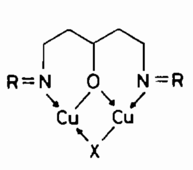


L_3, R = salH
L_4, R = acacH

(X = OH^-, OCH_3^-, N_3^-, p-$NO_2C_6H_4O^-$, pyrazolate), results in the formation of complexes of the type $[Cu_2(L)X]$ (2, 3) in which the Schiff base has been fully deprotonated thus providing an endogenous bridge between the copper(II) centres. The variation in X allows for the incorporation of μ-1,1-, μ-1,2- or μ-1,3- exogenous bridging units.



2



3

The complexes were characterised by elemental analysis, IR, UV–Vis, and, in the case of those derived from L_4, MS. Although it has been proposed that the azide stretching frequency (ν sym) *ca.* 1300 cm^{-1} can be used to differentiate between the μ-1,1- and μ-1,3- bridging modes of that anion [8] it has not been possible to do so in this study as the spectra are dominated, in this region, by absorptions common to the series $[Cu_2(L)X]$. The pyrazolate complexes exhibit absorptions at 1060 and 770 cm^{-1} ascribable to the CH out-of-plane deformation of the heterocyclic ring and implying a μ-1,2- coordination mode for this exogenous bridge [9]. A band at *ca.* 2800 cm^{-1} in the methoxy-bridged species has been ascribed to the νCH of the methoxy-group; this may be verified by comparison with the corresponding deuterated complex $[Cu_2(L)OCD_3]$ in which the band is shifted to *ca.* 2050 cm^{-1} (CH/CD = 1.37).

Magnetic parameters for the azido- and pyrazolato-complexes are given in Table I. The general features emerging are that the J values are more negative, *i.e.* greater antiferromagnetic coupling arises, when the exogenous μ-1,2- pyrazolate bridge is present, and

TABLE I. Magnetic Data

Compound[a]	$-2J$ (cm^{-1})	g	Monomer (%)	Reference
$Cu_2(L_1)N_3$	230	1.99	1.2	this work
$Cu_2(L_2)N_3$	246	2.04	3.5	this work
$Cu_2(L_4)N_3$	350 (81%) 49 (19%)	1.92 1.86		this work
$Cu_2(L_2)$pyz	394	2.10	1.6	this work
$Cu_2(L_4)$pyz	782	2.31		this work
$Cu_2(L_3)$pyz	diamag			12
$Cu_2(L_4)$pyz	716	2.00	1.3	12
$Cu_2(L_5)$pyz	457	2.20		5

[a] pyz = pyrazolate, L_5 = 2,6-bis(salicylideneamino)methyl)-4-methylphenol.

---

*Author to whom correspondence should be addressed.

also when the endogenous bridge contains the more flexible alkoxy-chain. One possible explanation for the latter is that the extent of anti-ferromagnetic coupling between metal centres via bridging ligands decreases as any electron density is removed from the bridging atoms [10]. Such a system would arise in complexes derived from L_1 and L_2 where the bridging phenolate contains an electron-withdrawing substituent in the para-position.

The flexible nature of the ligand, L_4, is demonstrated in the X-ray crystal structures of the compounds **3** (X = OH and X = pyrazolate) (Figs. 1 and 2). The ligand can accommodate both μ-1,1- and μ-1,2- bridges and the Cu–Cu separation increases from 3.00 Å in **3** (X = OH) to 3.35 Å in **3** (X = pyrazolate). In the pyrazolate complex there are two discrete molecules in the unit cell; the average Cu–O–Cu angle is 119°, the average folding angle (ϕ) [11] is 36.8° and the copper atoms have clear tetrahedral distortions. A recent communication concerning copper(II) complexes of binucleating ligands derived from 1,n-diamino-alcohols suggests that severe bending of the ligand with accompanying reduction of the Cu–O–Cu angle is noted where a trend towards ferromagnetism occurs [11]. Our results contrast with these observations but parallel those reported by Mazurek *et al.* [12] who, in related systems, have noted that it is a distortion from trigonal-planar towards pyramidal bonding around the endogenous-O that leads to a less negative J value. The sum of the three angles around the endogenous-O in **3** (X = pyrazolate) is 358°, indicative of a trigonally based geometry, and the high J value recorded for this compound is in accord with the above concept.

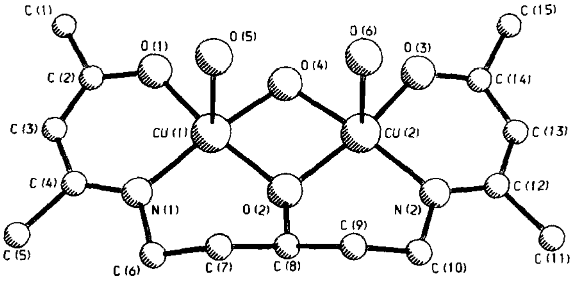


Fig. 1. Molecular structure of 3 (X = OH).

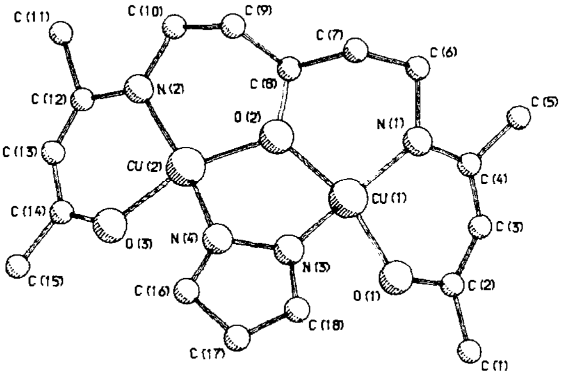
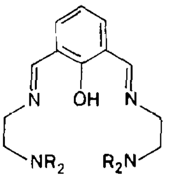


Fig. 2. Molecular structure of 3 (X = pyrazolate).

The best fit for the magnetic data concerning $Cu_2(L_4)N_3$ is obtained by considering the sample to be a mixture of two species; the reproducibility of the data was confirmed by using different samples. For the major component (~81%), $2J = -350\ cm^{-1}$ and $g = 1.92$; for the minor component (~19%), $2J = -49\ cm^{-1}$ and $g = 1.86$. Kahn *et al.* have established that in μ-azido complexes an azido-group which bridges two copper atoms in an end-on (μ-1,1-) fashion favours a triplet ground state (ferromagnetic interaction) whereas an end-to-end (μ-1,3-) mode leads to a singlet ground state (antiferromagnetic interaction) [13]. In a structurally defined binuclear copper(II) complex derived from **4**, and having endogenous phenoxo- and exogenous (μ-1,1-)-azido bridges an observed $2J$ value of $-34.8\ cm^{-1}$ has been interpreted to show a weakened antiferromagnetic coupling between the metal centres [14]. The μ-1,1-azido bridge is believed to exert a ferromagnetic stabilisation strong enough to lower the overall antiferromagnetic coupling to the value shown. Since no substantial lowering of $2J$ is noted for $Cu_2(L_1)N_3$, $Cu_2(L_2)N_3$ or the major component of $Cu_2(L_4)N_3$ a μ-1,3-azido bridge is proposed as present in these molecules. For the minor component of $Cu_2(L_4)N_3$ a μ-1,1-azido bridge would exert a ferromagnetic contribution producing the $2J$ value given in Table I. The ability of $[Cu_2(L_4)]$ to host either μ-1,1- or μ-1,3- bridges in the azide complex is a further indication of the enhanced flexibility of the systems.



4

Acknowledgements

We thank the SERC for a studentship to R.M., and the SERC and Royal Society for funds towards the purchase of a diffractometer.

References

1 R. Robson, *Aust. J. Chem., 23,* 2217 (1970).
2 D. E. Fenton, *Adv. Inorg. Bioinorg. Mech., 2,* 187 (1983).
3 N. A. Bailey, D. E. Fenton, J. Lay, P. B. Roberts, J. M. Latour and D. Limosin, *J. Chem. Soc., Dalton Trans.*, in press.

4 G. L. Woolery, L. Powers, M. Winkler, E. I. Solomon and T. G. Spiro, *J. Am. Chem. Soc., 106,* 86 (1984).

5 W. Mazurek, A. M. Bond, K. S. Murray, M. J. O'Connor and A. G. Wedd, *Inorg. Chem., 24,* 2484 (1985).

6 N. A. Bailey, D. E. Fenton, J. M. Latour, R. Moody and P. J. Scrimshire, *Inorg. Chim. Acta, 124,* L1 (1986).

7 R. Moody, *Ph.D. Thesis,* University of Sheffield, 1985.

8 J. Nelson and S. M. Nelson, *J. Chem. Soc. A.,* 1597 (1969).

9 W. D. McFadyen, R. Robson and H. Schaap, *Inorg. Chem., 11,* 1777 (1972).

10 P. J. Hay, J. C. Thibeault and R. S. Hoffman, *J. Am. Chem. Soc., 97,* 4884 (1975).

11 R. J. Butcher, G. Diven, G. Erickson, G. M. Mockler and E. Sinn, *Inorg. Chim. Acta, 123,* L17 (1986).

12 W. Mazurek. B. J. Kennedy, K. S. Murray, M. J. O'Connor, J. R. Rodgers, M. R. Snow, A. G. Wedd and P. R. Zwack, *Inorg. Chem., 24,* 3258 (1985).

13 O. Kahn, S. Sikorov, J. Gouteron, S. Jeannin and Y. Jeannin, *Inorg. Chem., 22,* 2877 (1983).

14 M. L. Boillot, O. Kahn, C. J. O'Connor, J. Gouteron, S. Jeannin and Y. Jeannin, *J. Chem. Soc., Chem. Commun.,* 178 (1985).