Mononuclear and Binuclear Complexes with Binucleating Ligands, Involving Pyrrole, Imidazole and Salicylaldehyde Derivatives

LONDA L. BORER

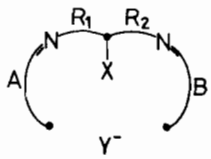
Department of Chemistry, California State University, Sacramento, Calif. 95819, U.S.A.

and EKK SINN

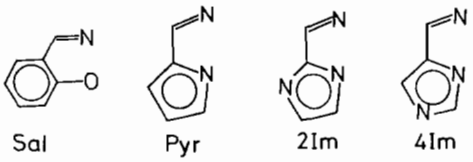
Department of Chemistry, University of Virginia, Charlottesville, Va. 22901, U.S.A.

(Received September 9, 1987)

Cu(II) complexes of ligands (**1**) can be mono- or binuclear with a variety of structures and the potential of reversible reduction to Cu(I) [1–6]. Sections of **1** can be varied at sites A, B, R_1, R_2 and X. We have used A = B = salicylaldimine (Sal), pyrrole-2-aldimine (Pyr), imidazole-2-aldimine (2Im) and imidazole-4-aldimine (4Im) [1–4].

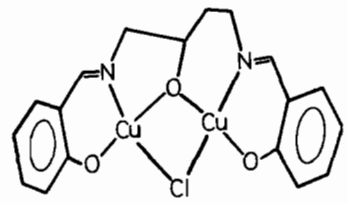


1

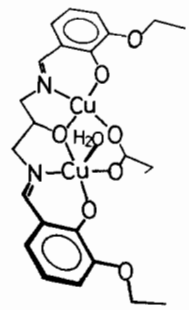


X can be O or S, allowing both X^--bridging or neutral X–H groups. The exogenous Y can be a one-atom bridge, such as OH^-, Cl^-, 1,1-N_3^-; a two-atom bridge, e.g. pyrazolate (pz), hydroxylamine, O_2^-; or a three-atom bridge, e.g. carboxylate, 1,3-N_3^-. Here we explore the effect of Sal, Pyr and 2Im on structures and properties when X = O.

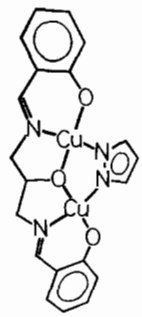
Independent variation of R_1 and R_2 is potentially useful as it could afford control over the metal geometries and make the two metal sites chemically distinguishable. We present evidence that this can be achieved. The crystal structure of complex **2**, with Cl^-, Sal and $R_1 = -CH_2-$, $R_2 = -CH_2CH_2-$ ($P2_1/n$, $a = 7.796$, $b = 19.044$, $c = 16.444$ Å, $\beta = 103.7°$) shows weak links between binuclear halves to form a tetranuclear aggregate. The R_1 and R_2 positions are distributed equally on both sides of the molecule, giving the Cu atoms similar environments. By contrast, several symmetric analogs of the ligand can produce different environments in binuclears like **3a** with one metal planar and one five-coordinated via solvent bonding [1, 6].



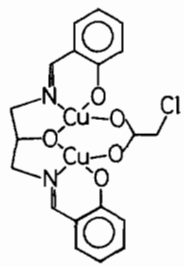
2 [Cu_2(Sal$_2$buO)Cl]



3a [$(H_2O)Cu_2$(3EtOSal$_2$prO)(C_2H_5COO)]



3b [Cu_2(Sal$_2$prO)pz]



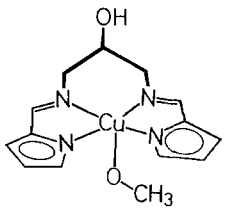
3c [Cu_2(Sal$_2$prO)($ClCH_2COO$)]

The Cu environments in **2** are distorted planar. The Cu–O distances to the bridging alkoxide (1.887, 1.893 Å) are slightly smaller than in **3a** (1.889, 1.949 Å) and **3b** (1.917, 1.905 Å), as is the Cu–O–Cu angle (114.4° in **2** *versus* 130.5° in **3a** and 122.5° in **3b**). As yet, there are no related structures with which to compare parameters involving Cl (Cu–Cl = 2.390, 2.391 Å and Cu–Cl–Cu = 83.3°). The magnitudes of the Cu–O–Cu and Cu–Cl–Cu angles in **2**

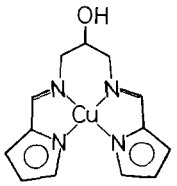
0020-1693/88/$3.50

predict moderate antiferromagnetic coupling [1, 4, 7, 8], which is observed, with singlet–triplet splitting, $-2J = 150$ cm^{-1}. How much of this is due to the O- and Cl-bridges themselves and how much to the effect of the metal geometry upon these bridges cannot be assessed until the comparison is expanded to complexes with wider ranges of different R_1 and R_2 groups. As expected, the longer alkyl chain pushes the metals closer together: Cu–Cu = 3.176 Å, compared with 3.473 Å in **3a** and 3.526 Å in **3c**.

A mononuclear complex, empirical formula $[Cu(Pyr_2prO)]_2 \cdot CH_3OH$, was obtained with Pyr and $R_1 = R_2 = -CH_2-$. The crystal structure ($P1$, a = 11.639, b = 11.059, c = 15.388 Å, α = 126.84, β = 114.82, γ = 126.84°), shows the asymmetric unit to contain two distinct molecular types, $Cu(Pyr_2prO) \cdot CH_3OH$ (**4**) and $Cu(Pyr_2prO)$ (**5**). The metal environment in **4** is a five-coordinated '4 + 1' square pyramid with the methanol molecule bound weakly (Cu–O = 2.601 Å) at the fifth position. Molecule **5** shows the differences expected when the fifth ligand is removed: it is closer to square planar and the N–Cu–N angles approach a little closer to 90 or 180°. The average pyrrole Cu–N separation decreases slightly on removal of the methanol ligand: 1.964 Å in **4** to 1.956 Å in **5**. The imine Cu–N distance also drops, from 1.993 Å in **5** to 2.000 Å in **4**. The methanol adduct presumably models the structure of the complex in coordinating solvents, while **5** shows the preferred structure in nondonor solvents. A mononuclear complex based on this Pyr ligand has been reported, but without a structure determination [9].



4

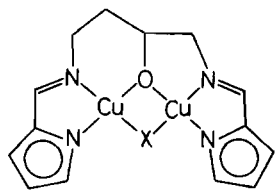


5

Some of the binuclear complexes which have been crystallographically characterized with symmetrical ligands can oxidize catechols to the corresponding quinones [1, 4, 6]. This models biological tyrosinase activity. Catalytic activity has also been suggested for the monomeric analogs: the well known Sal monomer with $R_1 = R_2 = -CH_2-$ [1, 2] is reported to catalyze oxidation of primary alcohols [10], analogous to the two-electron oxidation of D-galactose and of primary alcohols catalyzed by galactose oxidase [11]. This enzyme may contain two to four Im ligands and some oxygen ligands [12–14]. The observation of alcohol oxidation with the Sal monomer implies the same ability in the Pyr monomers, which would be more appropriate models for the enzyme than the Sal derivative, the Pyr nitrogens being better models for those of Im than would Sal oxygens. The facile adduction of methanol between **5** and **4** suggests Cu coordination as the first step in the mechanism for the oxidation process. However, when the oxidation is attempted in alcoholic KOH under literature conditions [10], no significant amounts of aldehyde form, nor is the metal fully reduced to Cu(I). Instead, complexes **4** and **5** form a deep red precipitate which displays ESR peaks characteristic of Cu(II) but which has not been further characterized. The cause of this discrepancy is of great interest and is under investigation.

The literature electrochemistry of the mononuclear Pyr derivative and analogous complexes highlights reversibility [9], but our study fails to confirm these findings. In our hands, the electrochemistry is consistently irreversible. In support of our finding, a recent review points out the difficulty of reproducible electrochemistry on such compounds [15]. There is marked solvent dependence which we attribute to the ready adduction of solvent molecules to the metal.

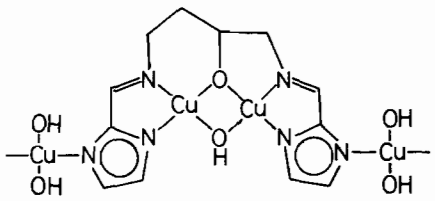
With $R_1 = -CH_2-$, $R_2 = -CH_2-CH_2-$ and A = B = Pyr, dimeric complexes **6** analogous to **2** form with $Y = CH_3COO^-$ and OCH_3^-. No crystal structure is available for either complex. The moment of the acetate complex rises from 1.05 BM at 11 K to 1.68 BM at 282 K, indicative of weak antiferromagnetic interactions. The OCH_3^- complex has a room temperature moment μ_{RT} of 1.97 BM.



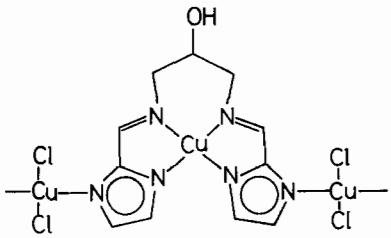
6

With A = B = 2Im and $R_1 = R_2 = -CH_2-$, and also with $R_1 = -CH_2-$, $R_2 = -CH_2CH_2-$, the complexes are highly insoluble, so that at present crystallography and solution studies are ruled out. The Pyr and Im ligands differ only in the external Im nitrogen atoms which must be responsible for large difference in properties of the complexes.

Reaction in basic solution produces a green magnetically coupled complex (μ_{RT} = 1.5 BM) which analyzes as an adduct of $Cu_2L(OH)$ and $Cu(OH)_2$ with a slight preponderance of the latter. The proposed structure **7** has Im and OH^- bridges, linkage types which are well known in multinuclear Cu(II) complexes [1–4]. The reaction with Cu(II) salts is different in the absence of base: structure **8** is proposed for the magnetically coupled (μ_{RT} = 1.6 BM)



7



8

CuLH-adduct of $CuCl_2$ which has a slight preponderance of $CuCl_2$. The slight excess of CuX_2 in each case is an indication that the chains in 7 and 8 terminate in CuX_2 end groups. These reactions and structures for 7 and 8 are analogous to those for Sal and Pyr, except for the bridges of CuX_2 to Im nitrogens.

Acknowledgement

Support under NSF grant CHE83-00516 is gratefully acknowledged.

References

1 L. L. Borer, G. Diven, G. R. Erickson, G. M. Mockler and E. Sinn, *ACS 192nd National Meeting*, Anaheim, Sept. 7–12, 1986, INOR199.
2 R. J. Butcher, G. Diven, G. R. Erickson, G. M. Mockler and E. Sinn, *Inorg. Chim. Acta, 111*, L55 (1986).
3 R. J. Butcher, G. Diven, G. R. Erickson, G. M. Mockler and E. Sinn, *Inorg. Chim. Acta, 123*, L17 (1986).
4 E. Sinn, Structures and properties of homo- and heterobinuclear and polynuclear complexes containing copper, in K. D. Karlin and J. Zubieta (eds.), 'Biochemical and Inorganic Copper Chemistry', Adenine Press, 1986, and refs. therein.
5 W. Mazurek, K. J. Berry, K. S. Murray, M. J. O'Connor, M. R. Snow and A. G. Wedd, *Inorg. Chem., 21*, 3071 (1981).
6 G. R. Erickson, G. M. Mockler and E. Sinn, unpublished results.
7 C. J. O'Connor, D. P. Freyberg and E. Sinn, *Inorg. Chem., 18*, 1077 (1979).
8 P. J. Hay, J. C. Thiebeault and R. Hoffman, *J. Am. Chem. Soc., 97*, 4884 (1975).
9 W. Mazurek, A. N. Bond, M. J. O'Connor and A. G. Wedd, *Inorg. Chem., 25*, 906 (1986).
10 N. Kitajima, K. Whang, Y. Moro-oka, A. Uchida and Y. Sasada, *J. Chem. Soc., Chem. Commun.*, 1504 (1986).
11 A. M. Kilbanov, B. N. Alberti and M. A. Marletta, *Biochem. Biophys. Res. Commun., 108*, 804 (1982).
12 L. Cleaveland, R. E. Coffman, P. Coon and L. Davis, *Biochemistry, 14*, 1108 (1975).
13 M. E. Winkler, R. D. Bereman and R. J. Kurland, *J. Inorg. Biochem., 14*, 223 (1981).
14 B. J. Marwedel, D. J. Kosman, R. D. Bereman and R. J. Kurland, *J. Am. Chem. Soc., 103*, 2842 (1981).
15 P. Zanello, S. Tamburini, P. A. Vigato and G. A. Mazzochin, *Coord. Chem. Rev., 77*, 165 (1987).