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Dinuclear Copper(I) and Copper(II) Complexes with Dinucleating Ligands having Benzimidazole or Thioether Groups

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Dinuclear copper(I) and (II) complexes are of current interest as models for the active sites of type III coppers such as hemocyanin (Hc), tyrocynase, and multicopper oxidases. Various types of dinucleating ligands have been designed, and chemical and physicochemical properties of their complexes have been extensively studied [1–5].

A variety of chemical, spectrochemical and EXAFS studies [6–9] of hemocyanin (Hc) had indicated that in oxyHc, two tetragonal copper(II) ions are separated by *ca.* 3.6 Å and linked by two bridging groups, *viz.* exogeneous peroxo bridge and an endogeneous bridge, R^-, such as phenolate, alkoxide *etc.* For deoxyHc on the other hand it is uncertain whether the endogeneous (bridging) ligand, R^-, is still in the first coordination sphere.

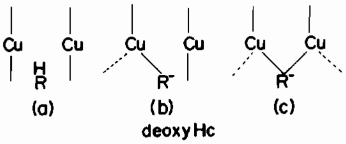

Fig. 1. Proposed structures of deoxyhemocyanin [9].

Three possible structures are proposed for deoxyHc (Fig. 1) [9]. Chemically modified hemocyanin (metHc) has provided valuable information on the nature of the active sites of Hc. Recently, Solomon and Spiro suggested that in met-N_3-Hc two copper(II) ions are linked by an endogeneous bridge, R^-, and an exogeneous N_3^- bridge in 1,3-bonding mode, and in met-H_2O-Hc two copper(II) ions are linked only by an endogeneous bridge, R^- [9]. It was also suggested that in metHc, exogeneous one-atom bridges such as OH^- or Cl^- are ruled out.

In the previous studies [10], it was found that some of the dinuclear cobalt(II) complexes with L-py react reversibly with molecular oxygen to form μ-peroxo complexes, where two cobalt ions are linked by endogeneous phenolate and exogeneous peroxo bridges. In this communication, we report various types of dinuclear copper(I) and copper(II) complexes with HL-Bzim and HL-SMe (Fig. 2).

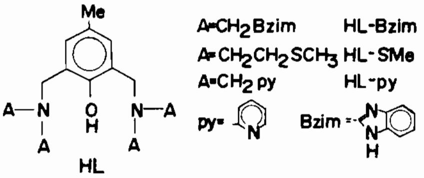

Fig. 2. Dinucleating ligands.

The preparation of HL-Bzim has been described elsewhere [10c]; HL-SMe was synthesized in the same way. The complexes were prepared as follows*. Reaction of HL with two equivalents of $[Cu(CH_3CN)_4]$-(ClO_4) in ethanol under nitrogen atmosphere gave a white powder, $[Cu_2(HL)](ClO_4)_2$ type complex. This white powder was air-sensitive in the solid state and exposure to air caused a rapid color change from white to brown. The elemental analyses of the complexes were carried out for the brown compounds. Reaction of HL with two equivalents of $Cu_2(ClO_4)_2 \cdot 6H_2O$ in methanol–ethanol mixture, followed by the addition of one equivalent of NaX (X = N_3^-, Cl^-, or CH_3COO^-) and CH_3ONa, gave $[Cu_2(L)X]^{2+}$ type complex. Treatment of HL-Bzim with two equivalents of $Cu(ClO_4)_2 \cdot 6H_2O$ in methanol–ethanol mixture, followed by the addition of Y (Y = OH_2 or py(pyridine)), afforded $[Cu_2(L\text{-}Bzim)Y_2]^{3+}$ type complex.

The elemental analyses of the copper(I) complexes are in agreement with the formula $[Cu_2(HL)](ClO_4)_2$, indicating that the dinucleating ligands are in the phenol form (HL) in those complexes. Molar conductivity of (2) in acetonitrile under nitrogen atmosphere was 245 Ω^{-1} cm^2 mol^{-1}, indicative of the presence of a 2:1 electrolyte. Since oxygen atoms are poor donors for copper(I) ions, the coordination of phenol oxygen to copper(I) ions seems to be unlikely. Recently, Karlin *et al.* [3] and Sorrel *et al.* [5] reported that the dinucleating ligands, m-XYLpy and m-XYLN$_6$, form discrete dinuclear complexes containing three-coordinate copper(I) ions. Since the structures of the present ligands resemble those of the above two ligands except for the presence of OH group in the benzene ring, it is likely that $[Cu_2(HL)]$-$(ClO_4)_2$ type complexes adopt a discrete dinuclear three-coordinate structure (Fig. 3a). It was attempted to prepare phenolate bridged copper(II) complexes. The addition of CH_3ONa to methanol solutions of $[Cu_2(HL)]^{2+}$ under nitrogen atmosphere resulted in a

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*The complexes prepared in this work: (1) $[Cu_2(HL\text{-}Bzim)](ClO_4)_2 \cdot 2.5H_2O$, (2) $[Cu_2(HL\text{-}SMe)](ClO_4)_2 \cdot 0.5C_2H_5OH$, (3) $[Cu_2(L\text{-}Bzim)N_3](ClO_4)_2 \cdot H_2O$, (4) $[Cu_2(L\text{-}Bzim)CH_3COO](ClO_4)_2 \cdot 3H_2O$, (5) $[Cu_2(L\text{-}Bzim)(OH_2)_2](ClO_4)_3 \cdot 1.5H_2O$, (6) $[Cu_2(L\text{-}Bzim)(py)_2](ClO_4)_3 \cdot 3H_2O$, (7) $[Cu_2(L\text{-}SMe)OH](ClO_4)_2 \cdot 1.5H_2O$, (8) $[Cu_2(L\text{-}SMe)N_3](ClO_4)_2$, and (9) $[Cu_2(L\text{-}SMe)Cl](ClO_4)_2 \cdot 1.5H_2O$. Analytical figures have been supplied to the referees.

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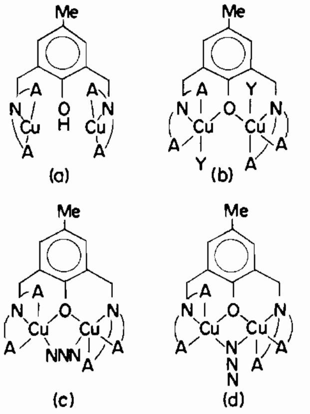

Fig. 3. Possible structures of $[Cu_2(HL)]^{2+}$, $[Cu_2(L\text{-}Bzim)Y_2]^{3+}$, and $[Cu_2(L)N_3]^{2+}$ type complexes.

disproportionation reaction to give copper metal and copper(II) complexes. In the case of (2), the complex (7) was isolated. These observations strongly suggest that the structure (a) in Fig. 1 is plausible for that of the active sites of deoxyHc.

L-Bzim formed two types of copper(II) complexes, $[Cu_2(L\text{-}Bzim)X]^{2+}$ ($X = N_3^-$ or CH_3COO^-) and $[Cu_2(L\text{-}bzim)Y_2]^{3+}$ ($Y = OH_2$ or py) as well as L-py [12, 13]. In $[Cu_2(L\text{-}bzim)Y_2]^{3+}$ type complexes, two copper(II) ions are linked only by a single phenolate bridge, as was found for the L-py complexes [10c, 11] (Fig. 3b). The structure of this type of complex is quite similar to that of met-aquo-Hc. It was attempted to prepare the complexes having exogeneous one-atom bridge such as OH^- or Cl^-. Such type of complexes, however, could not be isolated in this experiment. The infrared spectrum of the acetato complex showed that $\bar{\nu}(\bar{\nu}_{asymm}(CO_2^-) - \bar{\nu}_{symm}(CO_2^-))$ is $\sim 120\ cm^{-1}$, suggesting that the acetate ion acts as bridging ligand in syn–syn configuration. The above findings suggest that it is difficult for the binding sites available for linking two copper ions by one atom bridge such as OH^- or Cl^- to approach in close proximity. Therefore, in the azido complex, 1,3-N_3^- bridging seems to be reasonable (Fig. 3c). The presence of the 1,3-bridge of N_3^- is strongly suggested in met-N_3^--Hc [9]. Thus the L-Bzim complexes seem to be good structural models for deoxy and metHc.

In contrast to the above L-Bzim complexes, only $[Cu_2(L\text{-}SMe)X]^{2+}$ ($X = OH^-$, Cl^-, and N_3^-) type complexes were isolated. In the azido complex, 1,1-bridging of N_3^- appears to be preferable, since the L-SMe complexes tend to form one-atom bridges.

It is suggested that metHc contains antiferromagnetically coupled copper(II) ions with an endogeneous bridge which provides the superexchange pathway. All the L-Bzim complexes are essentially spin-free at room temperature*. These magnetic properties are in contrast with those of metHc. The L-SMe complexes have reduced magnetic moments at room temperature, indicating the presence of antiferromagnetic interactions between copper(II) ions.

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*Magnetic moments (μ_{eff}/BM) of the complexes at room temperature: (3), 1.89; (4), 1.88; (5), 1.86; (6), 1.82; (7), 0.85; (8), 1.41; (9), 1.71.