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Special Features of Some Dinuclear Copper (II) Complexes

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Abstract: This article describes synthesis, characterization and properties of some dinuclear copper complexes.

I. INTRODUCTION

The dinuclear copper(II) complexes have received a great deal of attention because of the role of dicopper centers in biological processes¹⁻⁸ and magnetic exchange interactions.^{9,10} Copper has been known as an essential bio-element for some time but its biological role(s) has been known only in the last decades due to the rapid development of bioinorganic chemistry.^{4,11-15} Copper-containing enzymes are involved in various processes in living systems. Hemocyanin (O₂ transport), tyrosinase (hydroxylation of monophenols) and catechol oxidase (oxidation of catechols) are classified as type 3 copper proteins (Fig.1) and have magnetically coupled dicopper(II) centers at their active sites. As a result, the biomimetic dinuclear copper(II) complexes have been extensively studied using several analytical techniques such as electronic absorption

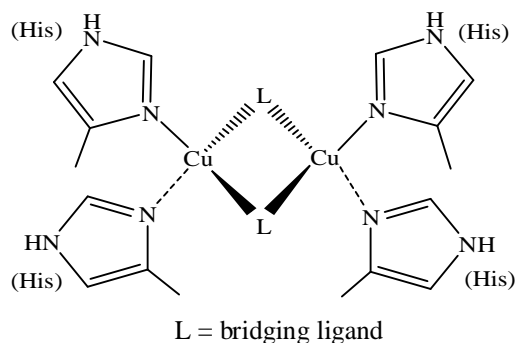
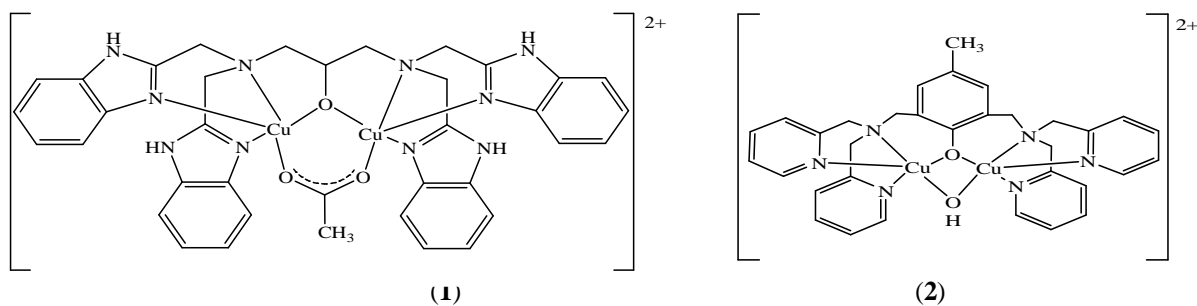


Fig. 1 General coordination modes in the type 3 copper proteins.

spectroscopy, EPR, X-ray crystallography and magnetic susceptibility measurements. ¹H NMR spectroscopy has also been emerged as a window for the investigation of structural and magnetic properties of dinuclear copper(II) complexes.

II. RESULTS AND DISCUSSION

Holz *et. al.*¹⁶ have reported one and two dimensional ¹H NMR studies on a series of magnetically diverse μ -alkoxo and μ -phenoxo bridged dinuclear copper(II) complexes. These complexes [Cu₂(L^{1a})(OAc)]²⁺ (1), [Cu₂(L^{2a})(OH)]²⁺ (2), [Cu₂(Me-L^{3a})(OH)]²⁻ (3) and [Cu₂(L^{4a})(OH)]²⁺ (4) (where, **HL**^{1a} = *N,N,N',N'*-tetrakis[(2-benzimidazolyl)-methyl]-2-hydroxy-1,3-diaminopropane; **HL**^{2a} = 2,6-bis[*bis*(2-pyridylmethyl)amino]methyl]-4-methylphenol; **H₅Me-L**^{3a} = *N,N'*-(2-Hydroxy-5-methyl-1,3-xylylene)bis(*N*-carboxymethylglycine) and **HL**^{4a} = 2,6-bis[*bis*(2-pyridylethyl)amino]methyl]phenol) (Fig.2) have been characterized by single crystal X-ray crystallography as well as several spectroscopic techniques.



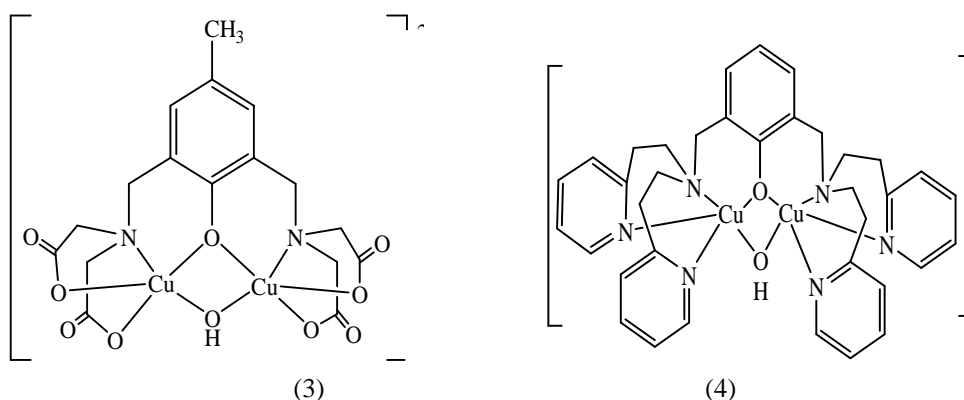


Fig. 2 Structures of $[\text{Cu}_2(\text{L}^{1a})(\text{OAc})]^{2+}$ (1), $[\text{Cu}_2(\text{L}^{2a})(\text{OH})]^{2+}$ (2), $[\text{Cu}_2(\text{Me-L}^{3a})(\text{OH})]^{2-}$ (3) and $[\text{Cu}_2(\text{L}^{4a})(\text{OH})]^{2+}$ (4).

In 2004, Powell *et. al.*¹⁷ have reported some dinuclear copper(II) complexes (Fig.3) with carboxylate rich dinucleating ligands ($\text{H}_5\text{Me-L}^{3a}$ and $\text{H}_5\text{MeO-L}^{3a}$) and studied their magnetic properties at low temperature. In these complexes, phenoxo oxygen atom of the ligand acts as a spacer-cum-bridging group to bind the two copper(II) centers. Low temperature magnetic susceptibility measurements have revealed that the copper(II) centers are antiferromagnetically coupled.

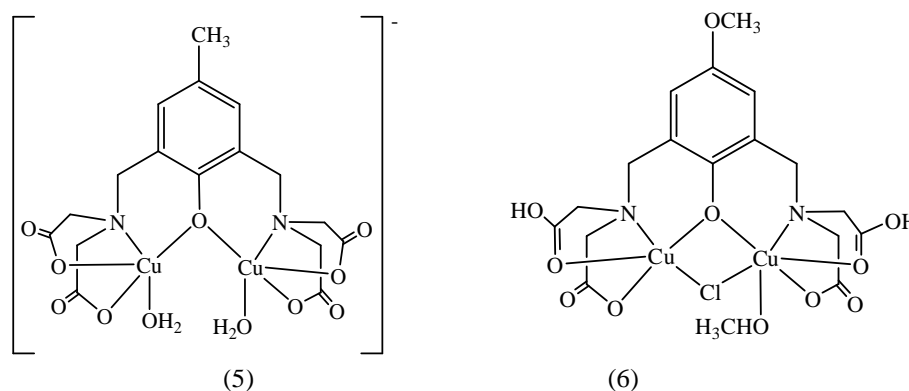
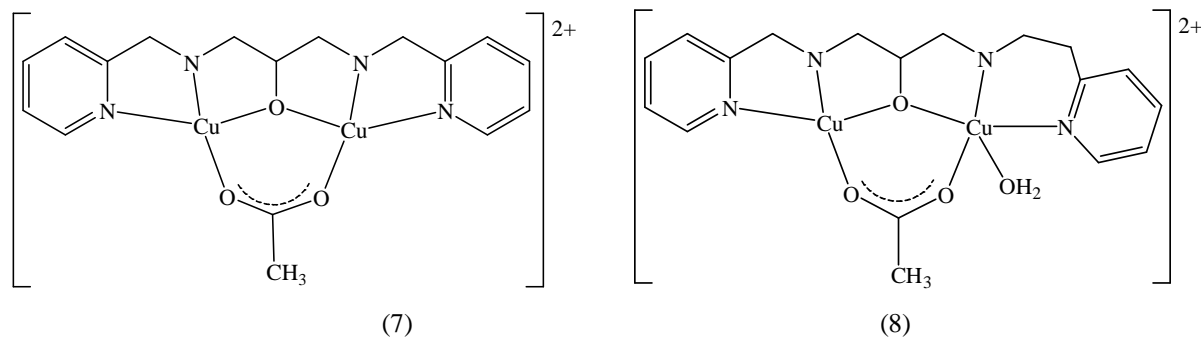


Fig. 3 Structures of $[\text{Cu}_2(\text{Me-L}^{3a})(\text{H}_2\text{O})_2]^-$ (5) and $[\text{Cu}_2(\text{H}_2\text{MeO-L}^{3a})(\mu\text{-Cl})(\text{CH}_3\text{OH})]$ (6).

Striegler *et. al.*¹⁸ have reported a sugar discriminating alkoxo bridged dinuclear copper(II) complex, $[\text{Cu}_2(\text{L}^{5a})(\text{OAc})](\text{ClO}_4)_2$ (7) (where, $\text{HL}^{5a} = 1,3\text{-bis}[(\text{pyridin-2-ylmethyl})\text{amino}]\text{propan-2-ol}$ (Fig. I.4). The reaction of complex 7 with different sugar substrates at $\text{pH} \sim 12.40$ gives 1:1 complex/substrate bound product, resulting in two-state systems. This complex shows a remarkable selectivity during coordination to the underivatized monosaccharides under strong binding conditions in alkaline solution. Recently, they have also studied the different dinuclear copper(II) complexes $[\text{Cu}_2(\text{L}^{5a})(\text{OAc})](\text{ClO}_4)_2$ (7), its unsymmetrical analogue complex (8) and $[\text{Cu}_2(\text{L}^{6a})(\text{OAc})]$ (9) (where, $\text{H}_3\text{L}^{6a} = N,N'\text{-}\{1,3\text{-bis}\{2\text{-hydroxy-4-[2-(2-methoxyethoxy)-ethoxy]\}-ethoxy\}\text{benzylideneamino}\}\text{propan-2-ol}$) (Fig.4) as new catalysts for the cleavage of glycosidic bonds to open a new direction towards the development of selective artificial glycosidase mimics.¹⁹



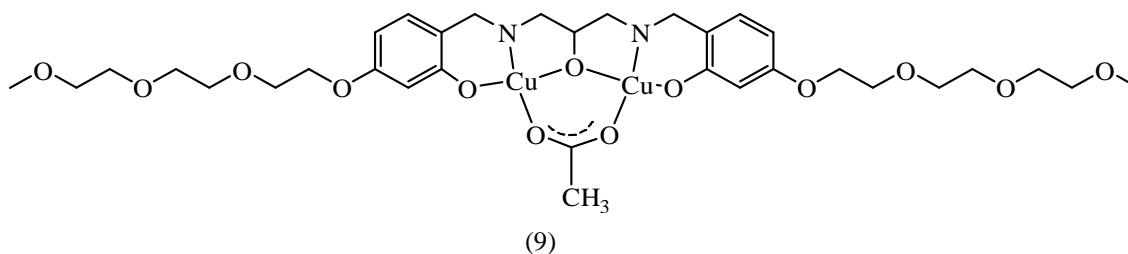


Fig. 4 Structures of $[\text{Cu}_2(\text{L}^{5a})(\text{OAc})]^{2+}$ (7), its unsymmetrical analogue (8) and $[\text{Cu}_2(\text{L}^{6a})(\text{OAc})]$ (9).

Recently, a series of three water-soluble dicopper(II) complexes of benzoic acid derivatives are reported.²⁰ All the three complexes induce oxidative DNA cleavage in the presence of H_2O_2 and noticeable DNA cleavage activity independent from the functional groups (F, Cl, NO_2) attached to the benzene ring. These complexes also display the selective cytotoxic effect against HepG2 cancer cells (2-fold higher) compared to that against the normal cells.

Buchanan and co-workers²¹ have reported the dinuclear copper(II) complexes $[\text{Cu}_2(\text{L}^{7a})(\text{pz})](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{CN}$ (10) and $[\text{Cu}_2(\text{L}^{7a})(\text{OAc})](\text{ClO}_4)_2 \cdot \text{CH}_3\text{CN}$ (11) where, $\text{HL}^{7a} = N,N,N',N'$ -tetrakis[(1-methylimidazol-2-yl)-methyl]-1,3-diaminopropan-2-ol (Fig.5) and pz is the pyrazolate anion. The single crystal X-ray structures reveal that both complexes 10 and 11 contain bridging alkoxide ligand including bridging pyrazolate and acetate ions, respectively. The magnetochemical characteristics of these complexes provide the evidences for “magnetic orbital switching”. Complex 10 shows strong antiferromagnetic coupling ($J = -130 \text{ cm}^{-1}$) between the two copper(II) centers, while complex 11 exhibits the ferromagnetic coupling ($J = +16.4 \text{ cm}^{-1}$) between the two copper(II) centers. They have rationalized the differences in the magnetic behavior of these two complexes using the “ligand orbital complementary” concept. The ground state magnetic orbital involved in spin coupling in complex 10 ($d_{x^2-y^2}$) is different from that in complex 11 (d_z^2).

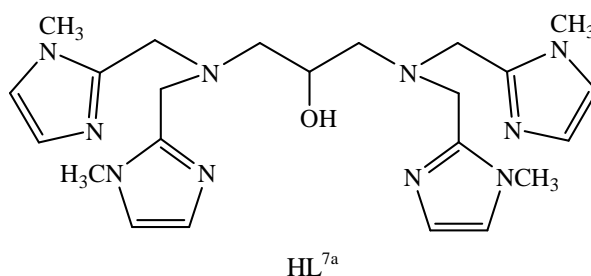


Fig. 5 Structure of N,N,N',N' -tetrakis[(1-methylimidazol-2-yl)-methyl]-1,3-diaminopropan-2-ol (HL^{7a}).

One of the well-characterized Cu/O_2 systems is based on the dinucleating ligand HL^{8a} (Fig.6).²² Oxygenation of its dicopper(I) complex (12) affords a species (12a)

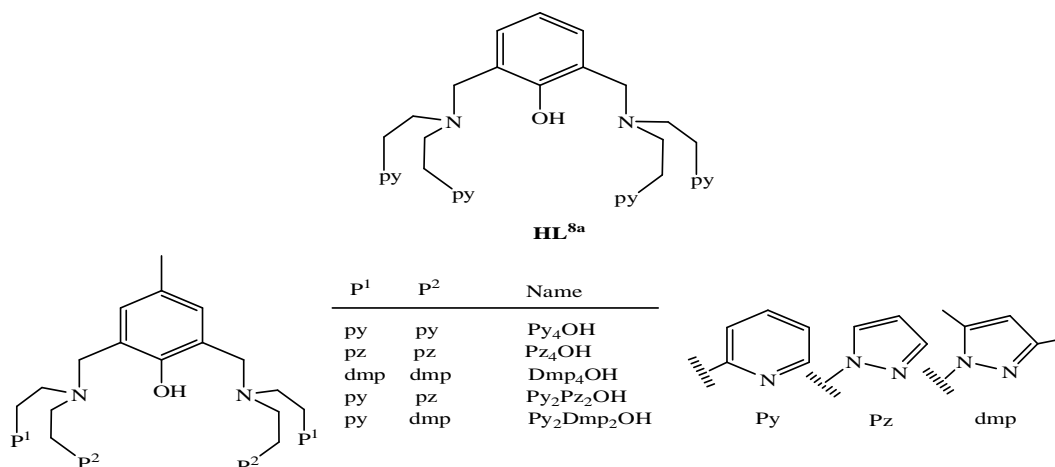


Fig. 6 Ligands derived from HL^{8a} .

with intense absorption bands at 505 nm ($\epsilon = 6300 \text{ M}^{-1}\text{cm}^{-1}$) and 610 nm ($\epsilon = 2400 \text{ M}^{-1}\text{cm}^{-1}$)^{sh}, attributed to peroxide to copper(II) charge transfer transitions. Oxygenation of the dicopper(I) complex (**13**) of the protonated ligand **HL**^{8a} produces a hydroperoxide species (**13a**) (Fig.7) exhibiting a charge transfer transition at 395 nm ($\epsilon = 8000 \text{ M}^{-1}\text{cm}^{-1}$) with a shoulder at 450 nm.²³ The Cu---Cu separation of $\sim 3.0 \text{ \AA}$ measured by EXAFS is most consistent with that between two copper(II) ions in a μ -1,1 hydroperoxide bridged dicopper(II) complex. This species can also be generated by protonating the peroxide complex derived from the ligand (**L**^{8a})⁻ (Fig. I.7, (**12a**) \rightarrow (**13a**)). Similar peroxy and/or hydroperoxy species can also be formed when the dinucleating ligands bearing pyrazoles or mixed pyrazole/pyridine subunits are used (Fig.I.6). The corresponding η^1 -peroxy complexes have characteristic charge transfer features in the regions of ~ 510 and ~ 620 nm, whereas the μ -1,1-hydroperoxy species has the charge transfer band at ~ 400 nm.²⁴

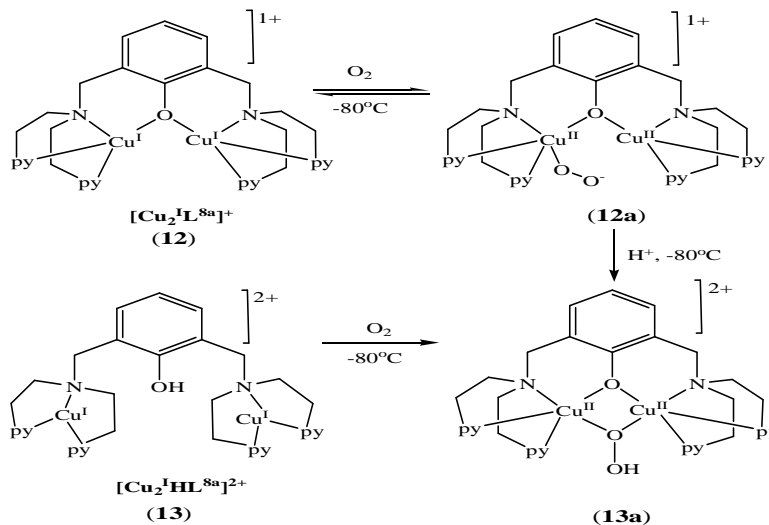


Fig. 7 Reactivity of copper(I) complexes of **HL**^{8a} and (**L**^{8a})⁻ ligands with O₂.

III. CONCLUSIONS

Properly designed di- and polynuclear metal complexes would provide new reactivity patterns and physical properties that could not be achieved with similar mononuclear complexes. Polynuclear complex systems are expected to have greater oxidizing and reducing power and the neighboring metal centers are expected to cooperate in promoting reactions and new electronic interactions leading to the distinct physical properties. The findings of this study will contribute towards designing the new polynuclear transition metal complexes.

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