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Redox Comparisons of Pseudotetrahedral Copper(I) Complexes Containing Tripod Ligands

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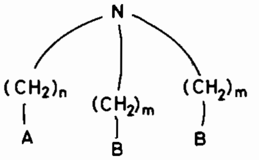
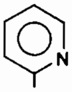
There is a paucity of structural and physicochemical information available on Cu(I) coordination complexes which relates to the copper ion sites of redox active copper proteins. Evidence pointing to low coordination numbers [1–4] sulfur ligands [4] and positive reduction potentials [1, 5, 6], supports the view that these protein sites contain copper ions in a 'Cu(I) like' environment. For tetra-coordination, a non-planar environment is favored and these considerations have led us to utilize tripodal tetradentate ligands to model protein copper sites.



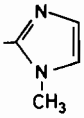
Tripod Ligands

peas A = 2-py =  = SEt, n = m = 2

pmas A = 2-py B = –SEt, n = 1, m = 2

tmpa A = B = 2-py, n = m = 1

tepa A = B = 2-py, n = m = 2

teSI A = B = -S-  n = m = 2

Synthetic variations in these ligands allow systematic investigations of the effect of donor atom type (N or S) and ligand constraints (n and m) on the structural and redox chemistry of Cu(I) ion centers [7].

We have previously reported X-ray structural studies of Cu(I) derivatives of thioether containing ligands peas and pmas. [Cu(peas)]BPh_4, *1* [8] and [Cu(pmas)]BPh_4, *2* [9] are pseudo-tetrahedral tetracoordinate complexes.

More recently, the structure of [Cu^I(tepa)]BPh_4 has been reported, showing similar coordination [10]. Here, we discuss observations of Cu(I) coordination to additional symmetric tripodal ligands tmpa and teSI as well as electrochemical studies on all of these compounds. The results show that there are considerable effects on the redox potentials due to both ligand donor group and chelate ring size.

Synthesis of the ligands and Cu(I) complexes of peas, pmas and tepa have been previously reported [8–10] while tmpa [11] was made by literature methods. The tripod ligand teSI was synthesized by refluxing in anhydrous methanol stoichiometric amounts of commerically available 2-mercapto-1-methylimidazole with tris (2-chloroethyl) amine in the presence of NaOH. Cu(I) complexes were stabilized as tetraphenyl boron salts except in the case of tmpa, whose cuprous derivative proved to be unstable. [Cu^I(tepa)]BPh_4, *3* was prepared by mixing equimolar amounts of $Cu^{II}(NO_3)_2 \cdot 3H_2O$ and tepa in methanol, which produced a blue solution. Addition of an excess of sodium tetraphenylborate in methanol gave the yellow-brown complex which was recrystallized from CH_2CH_2–MeOH (42%). [Cu^I(teSI)]BPh_4 *4*, was prepared by mixing equimolar amounts of teSI and $Cu^I(CH_3CN)PF_6$ in 1:1 methanol-acetone under argon. Addition of $NaBPh_4$ produced a white powder which was recrystallized from CH_2Cl_2–Et_2O. All complexes gave satisfactory C, H and N analyses.

Cyclic voltammetric measurements were carried out in order to explore the electrochemical behavior of these tetracoordinate (Cu(I) compounds (see Table I). Experiments were run in 0.11 *M* tetrabutylammonium hexafluorophosphate as supporting electrolyte in dimethyl-formamide. A standard three-electrode apparatus was employed with a glassy carbon working electrode, a non-aqueous reference electrode (0.1 *M* $AgNO_3$ in CH_3CN) separated by luggin capillary, and a Pt wire auxiliary electrode. The complexes all undergo quasi-reversible one-electron oxidations with current ratios i_c/i_a approaching unity.

As illustrated by the data for the thioether complexes *1* and *2*, there is a large increase of 0.27 V in the redox potential when the chain length between adjacent donor atom is increased from a methylene group (n = 1) to an ethylene group (n = 2). The greater chelate ring size (6, n = 2) of the peas complex favors the pseudotetrahedral structure of the Cu(I) form to a greater extent than does the five-membered chelate ring of the pmas complex. Crystallographic studies have shown that the N_{py}–Cu–

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TABLE I. Cyclic Voltammetric Data for the Complexes.

Compound	Chelate Ring Size[a]	$E_{1/2}$ (Volts *vs.* NHE)[b]
1 $Cu^I(pmas)BPh_4$	5–5–5	+0.24 ± 0.01
2 $Cu^I(peas)BPh_4$	6–5–5	+0.51
3 $Cu^I(tepa)BPh_4$	6–6–6	+0.29
4 $Cu^I(teSI)BPh_4$	5–5–5 (S coord.) 7–7–7 (N coord.)	+0.31

[a] The numbers correspond to chelate rings formed by Cu and the donors in A ~ N, B ~ N and B ~ N. (See Figure). [b] Potentials reported *versus* NHE by calibration with Ferrocene [13].

N_{amine} angle increases from 82.9° in *1* to 100.1 in *2* [8, 9]. It should be noted that this difference in potential parallels closely that found for five-coordinate analogs of peas and pmas, $[Cu^{II}LX]^{+1 \text{ or } 2}$, X = Cl^-, NO_3^-, 1-methylimidazole, demonstrating the dramatic effect of a change in one chelate ring of a complex [12].

In the tepa complex, *3* all chelate rings are six-membered. The relatively low redox potential found (compared to *1*) now reflects the strong preference of Cu(I) for 'soft' sulfur donors, compared to pyridyl nitrogen. Although no data for a Cu(I) compound containing tmpa is available, cyclic voltammetric measurements on Cu(II) analogs indicate that its oxidation potential would be considerably more negative than that of *3*. The $E_{1/2}$ value of $[Cu^{II}(tmpa)Cl]PF_6$ is −0.39 V compared to +0.17 V for $[Cu^{II}(tepa)Cl]PF_6$, a difference of 0.56 V [12]. Compared to compounds *1–3*, the redox potential observed for *4* seems too low to invoke all sulfur coordination for this compound and also too low for imidazole coordination with seven-membered chelate rings. Structural studies are required to settle this point.

In conclusion, a series of stable tetra co-ordinate (Cu(I) complexes containing tripodal tetradentate ligands have been synthesized. Studies of their redox behavior reveal substantial effects due to both donor atom-type and in particular the chelate ring size imposed by the ligand design. These results show that conformational constraints (in terms of chelate ring size or interligand bond angles) imposed by a protein environment could have substantial effects on the redox properties of copper ion centers.

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