

## COMMUNICATION

### COMPLEXES OF COPPER AND SILVER WITH TETRACYANOBIIMIDAZOLE

Paul G. Rasmussen\* and James E. Anderson  
Department of Chemistry  
The University of Michigan  
Ann Arbor, Michigan 48109

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We have recently reported the synthesis and properties of a remarkable new ligand 4,4',5,5'-tetracyano-2,2'-biimidazole ( $H_2Tcbiim$ ).<sup>1</sup> This acidic ligand readily binds metal ions in its dianionic form and appears to act as a strong pi acceptor. Its use as a quadridentate bridging ligand allows study of metal-metal interactions through a planar conjugated system and extends earlier work by us<sup>2</sup> and by Hendrickson and coworkers<sup>3</sup> on 2,2'-biimidazole. In this communication we report on the reactions of  $H_2Tcbiim$  with Ag(I), Cu(I) and Cu(II) salts.

The silver(I) and copper(I) complexes have the general formulae  $(Mpy)_2Tcbiim$  and  $[M(bpy)]_2Tcbiim$  where py = pyridine and bpy 2,2'-bipyridine and M = Cu, Ag. The compound  $[Cu(P\phi_3)_2]_2Tcbiim$  has also been prepared where  $P\phi_3$  is triphenyl phosphine. The Cu(II) compounds are  $Cu(py)_2Tcbiim$ ,  $Cu(bpy)Tcbiim$  and  $[(Cu - diene)_2Tcbiim](NO_3)_2$  where diene = diethylenetriamine. All of these compounds can be made in high yield; they have been characterized by analytical, spectroscopic and magnetic techniques.

The syntheses of these compounds are straightforward. To a solution of the metal nitrate salt in acetonitrile an excess of L is added, L = bpy, py for Cu and Ag and L =  $P\phi_3$  for Cu only. A stoichiometric amount of  $H_2Tcbiim$  dissolved in acetonitrile is then added, the solution is stirred for 2 hours and the resulting complexes precipitate. The Cu(I) nitrate is

\* Author for correspondence

formed in situ in acetonitrile by the reduction of  $\text{Cu}(\text{NO}_3)_2$  with Cu metal. Attempts to synthesize Ag(II) complexes containing  $\text{Tcbim}^{2-}$  resulted in the formation of the corresponding Ag(I) complex. In a typical reaction a silver(II) salt, such as  $\text{Ag}(\text{bpy})_2\text{S}_2\text{O}_8$  would react with  $\text{H}_2\text{Tcbim}$  in a 1:1 mole ratio to form  $\text{Ag}_2(\text{bpy})_2\text{Tcbim}$  and unidentified oxidation products.

The copper(II) compounds are made in a similar way.

Copper(II) nitrate was dissolved in methanol, a excess of L is added, where L = bpy, py and diene. A stoichiometric amount of  $\text{H}_2\text{Tcbim}$ , dissolved in methanol, is then added and after two hours the green product is collected.

The structural evidence for the dimers is clearest in the case of the  $[(\text{P}\phi_3)_4\text{Cu}_2]\text{Tcbim}$  (Figure 1).  $^{13}\text{C}$  NMR shows three

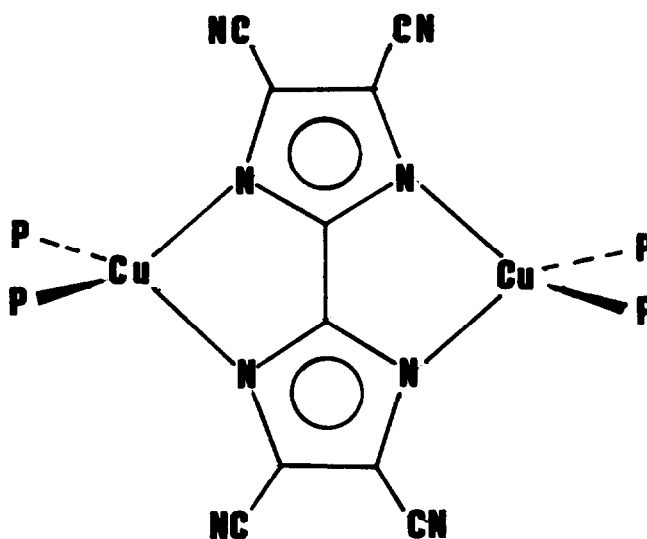
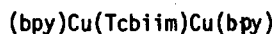


Figure 1. Proposed structure of  $[(\text{P}\phi_3)_4\text{Cu}_2]\text{Tcbim}$ , phenyl rings omitted for clarity.

signals at 151.2, 119.6, and 113.4 ppm relative to  $\text{Me}_4\text{Si}$  indicating a symmetrically bridged tetracyanobiimidazole.  $^{31}\text{P}$  NMR gives only one signal showing equivalent phosphines. The IR spectrum shows a sharp singlet due to nitrile at  $2220\text{ cm}^{-1}$ . The low solubility of the other Cu(I) compounds precludes good NMR.



I



II

Compound I appears from stoichiometry to contain three coordinate copper. Furthermore, the nitrile stretch in the IR at  $2220\text{ cm}^{-1}$  is unsplit. Compound II could be three coordinate in two ways, a) monodentate bpy and symmetrically bonded to  $\text{Tcbiim}^{2-}$  or b) bidentate to bpy and coordinated to  $\text{Tcbiim}^{2-}$  only once. We favor case b) since the nitrile peak at  $2220\text{ cm}^{-1}$  shows a reasonable splitting ( $\sim 10\text{ cm}^{-1}$ ) suggesting inequivalent nitrile groups. It appears that univalent copper is satisfied with three coordination when the strongly pi accepting phosphines are absent but increases to four when they are present. We are pursuing this model of behavior by trying to effect further syntheses. Polymeric structures cannot be ruled out however at this time.

The Cu(II) dimer is directly analogous to those synthesized by Hendrickson.<sup>3</sup> Since biimidazole was found to give weak magnetic coupling between the copper ions, it was of interest to see if the tetracyanobiimidazole bridge enhances the interaction. Room temperature magnetic moment measurements were used to give a preliminary assay, and the value of  $\mu = 1.58 \pm .05\text{ BM}$  per mole of Cu, is indication of significant interaction. A more definitive study is underway.

The fact that  $\text{Tcbim}^{2-}$  will act as a bridging group in both Cu(I) and Cu(II) systems is noteworthy. It suggests the possibility of preparing mixed valence dimers which, if the coordination geometry is properly contrived, can sustain substantial interaction through the bridge. Pairs of Cu(II) ions bridged by imidazoles have been extensively reported on as models for active sites in enzymes.<sup>4</sup> The compounds described here offer further examples of such model systems, which can be synthesized under significantly less basic conditions than those previously observed. Work on both these aspects is continuing.

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