

imidazolate-bridged complexes can be prepared as models for the bimetallic active sites of metalloproteins such as superoxide dismutase.

## REFERENCES

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THOMAS N. SORRELL  
A.S. BOROVNIK  
DEBORA J. ELLIS  
CHIEN-CHANG SHEN  
Department of Chemistry  
University of North Carolina  
Chapel Hill, NC 27514  
U.S.A.

## MODELS FOR COPPER PROTEINS

Copper proteins are widespread in biology, performing many functions related to oxygen metabolism; and binding and activation of dioxygen by hemocyanin and tyrosinase have attracted much recent attention [1]. In many respects, this focussed interest has largely ignored the rich inorganic chemistry of the binuclear active-site in hemocyanin which encompasses reactions of the reduced form of the protein with carbon monoxide, nitric oxide, and other small ligands; generation of mixed-valence derivatives; and reactions of the oxidized form of the protein with small anionic ligands.

We have pursued studies in several directions with the aim of exploring the chemistry, spectroscopy, and physical properties of mono- and binuclear copper complexes. Much of this work involves the synthesis of multidentate ligands that are able to chelate the copper ion in an environment that mi-

mics the structural features of the hemocyanin active site.

We prepared the binucleating ligand bpeac (2,6-bis{bis[2-(1-pyrazolyl)ethyl]amino}-*p*-cresol) and both its copper(II) [2] and copper(I) [3] derivatives. The copper(II) complex thus formed contains two Cu(II) ions bridged by a phenolate group and bound by three nitrogen donors each. In addition, another anionic ligand (acetate or azide) bridges the two copper ions, completing the coordination sphere. The azide derivative is especially interesting since the two copper(II) ions are antiferromagnetically coupled, and the singlet-triplet splitting,  $2J$ , is equal to  $-1800 \text{ cm}^{-1}$ , rendering the complex diamagnetic at room temperature. Other spectroscopic properties of this azido-bridged dimer are similar to those for the azido derivative of hemocyanin, strengthening the proposals for the structure of its active site. The copper(I) derivative of bpeac represents one of only two phenolato-bridged copper(I) dimers having no other bridging group. However, the reaction of this compound with  $\text{O}_2$ , even at low temperature, results in irreversible oxidation of the copper(I) ions and illustrates the possible importance for isolation of the active site by the protein in hemocyanin in order to eliminate intermolecular interactions. Studies of the copper(I) derivatives of more hindered analogs of bpeac will be reported.

The unusual luminescence of the carbonyl derivative of hemocyanin has provided us with another interesting lead to follow to understand the structure of the hemocyanin active site [4]. We have prepared a number of mononuclear copper(I) complexes and examined their absorption spectra and luminescence properties both in the absence and presence of carbon monoxide. The results of these investigations will be reported, and their implications discussed.

## REFERENCES

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PS4.22 — TH

STEPHEN A. KOCH

RONALD FIKAR

DOUGLAS CORWIN

Department of Chemistry

State University of New York at Stony Brook

Stony Brook, New York

U.S.A.

MICHELLE MILLAR

Department of Chemistry

New York University

New York, NY 10003

U.S.A.

### COBALT THIOLATE COMPLEXES: MODELS FOR THE ACTIVE SITES OF METAL-CYSTEINE PROTEINS

Cobalt has been extensively substituted for native metals in metalloproteins to serve as a spectral probe. A series of cobalt thiolate complexes have been prepared to serve as models for the cobalt-cysteine coordination found in cobalt-substituted proteins, including alcohol dehydrogenase, blue copper proteins, and metallothionein. We have used the steric capacity of the thiolate ligands to control the coordination number and the molecularity of the cobalt thiolate complexes. The reaction of three equivalent of 2,3,5,6-tetramethylbenzenethiolate with  $\text{CoCl}_2$  gives a monomeric, four-coordinate complex  $[\text{Co}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_3(\text{CH}_3\text{CN})]^-$  (Fig. 1); with less sterically encumbered thiolate ligands, the  $[\text{Co}_4(\text{SR})_{10}]^{2-}$  adamantane cluster is obtained. We have found that  $\text{Co}(\text{SR})_2\text{L}_2$  complexes have a strong tendency to become five-coordinate by adding another ligand. For the case of  $[\text{Co}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H})_2(\text{bipy})]$ , this is achieved by dimerization to give a structure with an unsymmetric  $\mu$ -di-thiolate bridge (Fig. 2). In the case where the thiolate is 2,4,6-triisopropylbenzenethiolate, the coordination shell is expanded by the addition of an  $\text{CH}_3\text{CN}$  to give the five coordinate monomeric complex  $[\text{Co}(\text{SR})_2(\text{L}_2)(\text{CH}_3\text{CN})]$  ( $\text{L}_2 = \text{bipy}, \text{phen}$ ). The analogous zinc compound,  $[\text{Zn}(\text{S}-2,4,6\text{-i-Pr}_3\text{C}_6\text{H}_2)_2(\text{bipy})]$ , does not add an

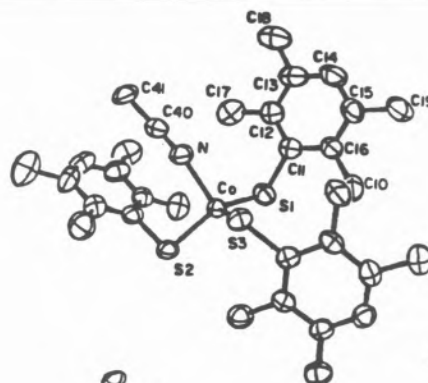


Fig. 1

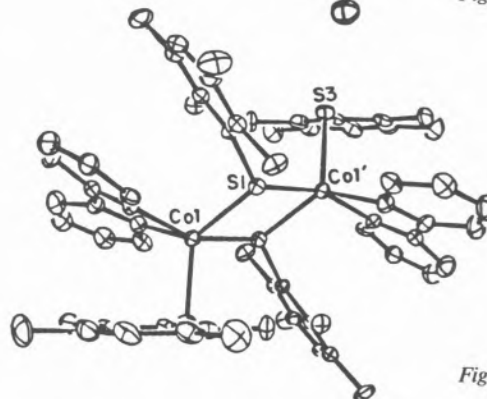


Fig. 2

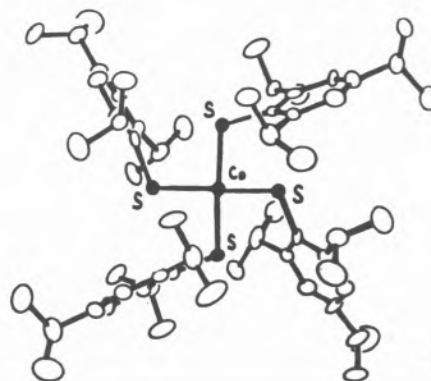


Fig. 3

$\text{CH}_3\text{CN}$  ligand and remains four coordinate. The possible relevance of these findings to the question of the occurrence of five coordinate intermediates in alcohol dehydrogenase will be presented. EXAFS and ESR studies of the newly discovered nickel center in certain hydrogenase enzymes suggest that this center contains  $\text{Ni(III)}$  in a tetragonal ligand environment with four sulfur ligands. We have been studying nickel and related cobalt thiolate complexes to serve as models for this novel biological active site. With these objectives in mind, we have synthesized a quite interesting  $\text{Co(III)}$  tetrathiolate anion (Fig. 3) which is a rare example of a square planar  $\text{Co(III)}$  complex.