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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 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 μ -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 CH_3CN 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

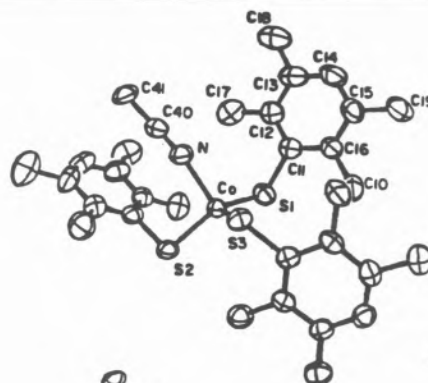


Fig. 1

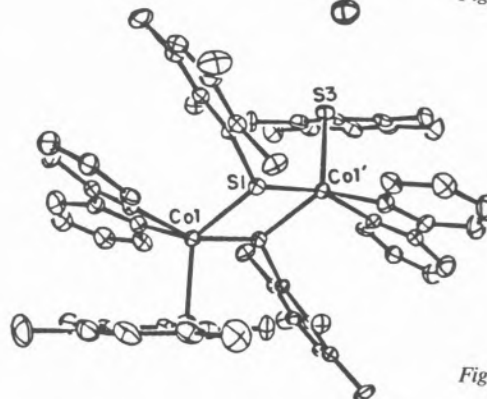


Fig. 2

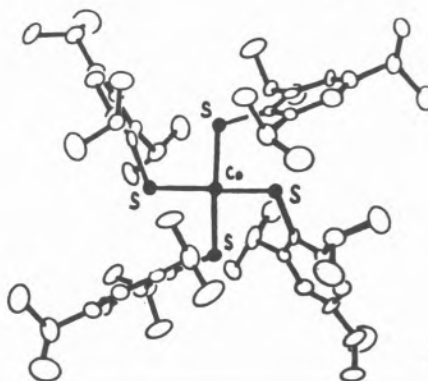


Fig. 3

CH_3CN 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 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 Co(III) tetrathiolate anion (Fig. 3) which is a rare example of a square planar Co(III) complex.

5. Complexes of Biochemical Interest



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METAL COMPLEXES OF SULFUR-CONTAINING LIGANDS OF BIOLOGICAL INTEREST:

S-METHYL-L-CYSTEINE, α -LIPOIC ACID AND GLUTATHIONE

S-methyl-L-cysteine (SMC) offers three possible binding sites for metal atoms: The carboxylate group, the amino nitrogen atom and the thioether linkage. Since sulfur atoms are soft bases, they are expected to interact most favorably with soft acids as Hg(II), Pt(II), Ag(I) or Cu(I), but to a less extent with borderline acids as *e.g.* Cu(II).

We have grown single crystals of a copper(II) complex $Cu(SMC)_2$ from solution on the surface of solid copper(II) hydroxy salts. The crystal structure determination ($R=0.045$, $R_w=0.052$) confirms spectroscopic evidence that the thioether sulfur is not coordinated to copper(II), even though there is a potentially favorable five-membered chelate ring with sulfur and nitrogen as coordinating atoms. Bridging of the copper centers by carboxylate groups leads to a two-dimensional polymeric structure approximately isostructural with its cadmium analogue [1]. The copper(II) atom exhibits a (4+2) tetragonally elongated CuN_2O_4 coordination octahedron.

α -Lipoic acid (LIP, DL-6,8-thiooctic acid) is a biomolecule widely distributed in animals and plants. Obviously there are two binding sites for metal

atoms: The carboxylate group and the disulfide moiety.

Single crystals of a zinc complex, $Zn(LIP)_2 \cdot 2H_2O$, were grown on the surface of solid zinc hydroxy salts. The crystal structure determination ($R=0.068$, $R_w=0.084$) proofs the occurrence of isolated molecules $[Zn(LIP)_2(H_2O)_2]$ with the carboxylate groups acting as bidentate ligands. As suggested [2] there is no interaction of the disulfide moiety of α -lipoic acid with the metal atom. The coordination geometry of the zinc(II) atom is a ZnO_6 octahedron with pronounced distortion. This is the first crystal structure reported of a metal complex of lipoic acid.

Glutathione (GSH): A copper(II) complex with the formula $Cu(II)_2GSSG \cdot 6H_2O$ could be isolated. From the interpretation of UV- and EPR-spectra it seems plausible that this complex exhibits a dimeric structure with the disulfide moiety linking two copper(II) atoms as it is found in $Cu(II)_2GSSGNa_4 \cdot 6H_2O$ [3].

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