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Zinc, Cobalt and Cadmium Thiolate Complexes: Models for the Zn(S-cys)$_3$(his) Center in the Gene 32 Protein

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In the past two years, a new class of zinc metalloproteins has been established [1–6]. A number of DNA and RNA binding proteins have been shown to contain zinc and to be characterized by Zn(S-cys)$_x$ coordination. In particular, it has recently been shown that the gene 32 protein (g32P) isolated from bacteriophage T4 contains a mole of tightly bound zinc. Inspection of the amino-acid sequence of the protein and the spectroscopic properties of the Co(II) and Cd(II) substituted protein led Coleman to propose a [Zn(S-cys)$_3$(his)] coordination unit for this protein [4, 5]. The coordination of three cysteines to a monomeric zinc center has also been suggested to occur in the enzyme aminolevulinate dehydratase [7]. We wish to report the synthesis, structure, and spectroscopic properties of a series of Zn, Co, and Cd complexes that reproduce this proposed coordination unit.

The reactions of MCl$_2$ (M = Zn, Co, Cd) with 3 equivalents of LiS-2,3,5,6-Me$_4$C$_6$H, 1 equivalent of 1-methylimidazole and 1 equivalent of [(*n*-Pr)$_4$N]Br gives [(*n*-Pr)$_4$N][M(S-2,3,5,6-Me$_4$C$_6$H)$_3$(1-Me-imid)] in 60–70% yields. The complexes are recrystallized from CH$_3$CN to give large blue green crystals for Co (**1**) and colorless crystals for Zn (**2**) and Cd (**3**). X-ray crystallographic studies have shown that the [(*n*-Pr)$_4$N][M(S-2,3,5,6-Me$_4$C$_6$H)$_3$(1-Me-imid)] complexes of cobalt and cadmium are isomorphous. The X-ray structure of the Co complex was determined (Fig. 1). Crystal data: triclinic, space group $P\bar{1}$, $a = 12.321(5)$, $b = 18.038(4)$, $c = 11.852(3)$ Å, $\alpha = 97.95(2)$, $\beta = 113.36(2)$, $\gamma = 76.44(2)^\circ$, $V = 2348(2)$ Å^3, $Z = 2$. $R(R_w) = 0.051(0.063)$ for 2599 unit reflections with $I > 3\sigma I$. The cobalt is coordinated by three thiolate ligands and the nitrogen of the 1-Me-imid. The average Co–S distance of 2.300(6) Å is similar to that in the related [Co(S-2,3,5,6-Me$_4$C$_6$H)$_3$(CH$_3$CN)]$^-$ anion [8]; the Co–N distance is 2.051(5) Å. The [CoS$_3$N] core shows small distortions for tetrahedral coordination with the L–M–L angles lying in the range of 105 to 114°.

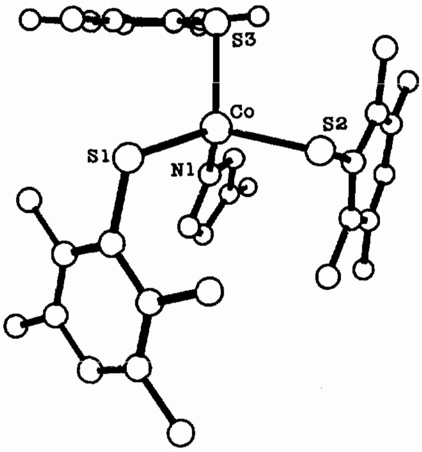

Fig. 1. A ROTOCHEM diagram of the anion of [(*n*-Pr)$_4$N]-[Co(S-2,3,5,6-Me$_4$C$_6$H)$_3$(1-Me-imid)]. Bond distances (Å): Co–S1 2.299(2); Co–S2 2.307(2); Co–S3 2.294(2); Co–N1 2.051(5). Bond angles (deg): S1–Co–S2 112.75(7); S1–Co–S3 114.51(7); S1–Co–N1 110.5(2); S2–Co–S3 107.41(8); S2–Co–N1 105.4(1); S3–Co–N1 105.6(2).

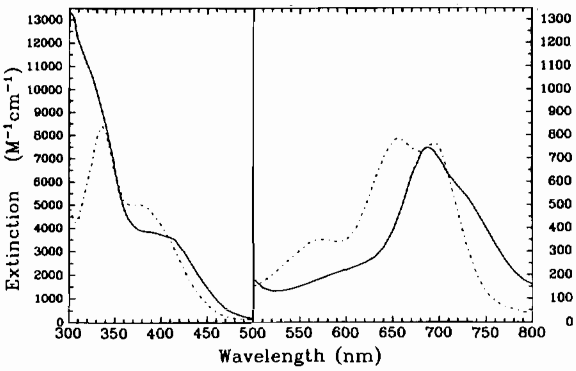

Fig. 2. The electronic spectra (CH$_3$CN) of [(*n*-Pr)$_4$N][Co(S-2,3,5,6-Me$_4$C$_6$H)$_3$(1-Me-imid)] (——) and [Co(S-2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$(1-Me-imid)$_2$] (–·–).

The electronic spectrum of [Co(S-2,3,5,6-Me$_4$C$_6$H)$_3$(1-Me-imid)]$^-$ (Fig. 2) is consistent with a tetrahedral Co(II) center with thiolate coordination [9, 10]. The intense transitions at 390(sh) nm [ϵ = 3830 M^{-1} cm^{-1}]; 322(sh), [10900] and 301, [13400] are characteristic of RS to Co(II) charge transfer transitions. The ligand field transitions occur at 730(sh) nm, [ϵ = 535]; 687, [745]; and 590(sh), [210]. Although the spectrum of **1** is quite similar to that of Co substituted g32P, this does not definitively imply a congruence in the coordination units of model and the protein. The visible spectrum of **1**, although differing in detail, is similar to the spectrum of the corresponding [Co(SR)$_2$(1-Me-imid)$_2$] complexes [11]. The ^{1}H NMR spectra of the Zn and the

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Cd complexes are consistent with their formulation. The ^{1}H NMR spectrum (CD_3CN) of **1** shows paramagnetically shifted resonances in the region of +40 to −40 ppm; all of the individual resonances can be assigned by comparison to related compounds. The resonances of the 1-methylimidazole ligand occur at 38.4 δ (1H), 5-H; 4.02 (3H), 1-CH_3; and two broad resonances at 36.7 and 34.2 which are assigned to the 2 and 4 protons. The chemical shifts of the thiolate ligands occur at 28.9 (18H), 2- and 6-CH_3; −9.9 (18H), 3- and 5-CH_3; −30.7 (3H), 4-H. The ^{113}Cd NMR resonance of the Cd complex occurs at 533 ppm; a chemical shift which is consistent with the Cd(S_3N) coordination. The ^{113}Cd spectra of the gene 32 protein has not been reported.

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