

reaction 2 with $P(n-C_4H_9)_3$, reactions at 73.9 °C at various $P(n-C_4H_9)_3$ concentrations were studied. The k_{obsd} values obtained at the phosphine concentrations given in parentheses were 5.84×10^{-4} (0.181 M), 6.14×10^{-4} (0.502 M), 6.33×10^{-4} (0.903 M), and $8.05 \times 10^{-4} \text{ s}^{-1}$ (1.33 M). However, plots from which these k_{obsd} values were obtained deviated from linearity especially at the lowest phosphine concentrations. In addition, a precipitate formed during these reactions. While the rate of the reaction does show a substantial $P(n-C_4H_9)_3$ concentration dependence, it is doubtful that the calculated k_1 and k_2 values ($5.28 \times 10^{-4} \text{ s}^{-1}$ and $1.87 \times 10^{-4} \text{ s}^{-1} \text{ M}^{-1}$) are reliable in view of the above-mentioned complications.

Discussion

The two terms in the rate law (eq 3) suggest that reaction 2 proceeds by both dissociative and associative pathways. The dissociative mechanism presumably involves rate-determining dissociation of one of the two mutually trans CO groups, as was observed previously for $Cr(CO)_4(o\text{-phen})$.⁴ The associative pathway with $P(OCH_3)_3$ is negligible at the highest temperature studied (83.8 °C) but becomes measurable at the lower temperatures. Although the k_2 rate constants are too small to give accurate activation parameters, the decreasing contribution of the associative mechanism at higher temperatures indicates that the activation energy for the associative mechanism is less than that of the dissociative pathway, as was found for reaction 1.¹

A direct comparison of the rates of the dissociative pathways for reactions 1 and 2 may be made by extrapolating the rate constant for the thiocarbonyl reaction to 114 °C. This yields a k_1 value of $2.3 \times 10^{-2} \text{ s}^{-1}$ for reaction 2 which is approximately 140 times larger than that ($1.63 \times 10^{-4} \text{ s}^{-1}$) for reaction 1 under the same conditions (114 °C, in chlorobenzene solvent).¹ Thus, the thiocarbonyl ligand has clearly increased the rate of CO dissociation as compared to the carbonyl analogue.

Activation parameters for the dissociative pathways of reactions 1 and 2 are given in Table II. These results show that the increased rate for the thiocarbonyl complex is pri-

marily due to a decrease of 7.6 kcal/mol in the activation energy. A decrease (8.4 kcal/mol, Table II) in ΔH^\ddagger was also observed for the dissociation of the trans CO from $W(CO)_5(CS)_2$ as compared to $W(CO)_6$.⁵ This result could be interpreted as indicating that the CS group weakens the W-CO bond thereby reducing the activation energy. The kinetic results support other evidence⁶⁻⁹ which suggests that CS is a better π^* -bonding ligand than CO. Its stronger π^* -bonding ability would reduce π bonding to the CO groups, hence weakening the W-CO bonds and facilitating CO dissociation.

To our knowledge only one other kinetic comparison of CO and CS has been reported. In that case the rate of cyclooctene dissociation from $(C_8H_{14})Mn(CO)(CS)(C_8H_{14})$ ¹⁰ was found to be approximately 4 times faster than from $(C_8H_{14})Mn(CO)_2(C_8H_{14})$,¹¹ and the activation energy was also lower for the thiocarbonyl complex. The increased lability of the cyclooctene group was also attributed to the greater π^* -bonding ability of the CS ligand.

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Registry No. $W(CO)_3(CS)(o\text{-phen})$, 66523-88-4; $P(OCH_3)_3$, 121-45-9; $P(OCH_2CH_3)_3$, 122-52-1; $P(C_6H_5)_3$, 603-35-0; $P(n-C_4H_9)_3$, 998-40-3; $W(CO)_2[P(OCH_3)_3](CS)(o\text{-phen})$, 66523-89-5; $Bu_4N-[W(CO)_4(CS)]$, 56031-00-6.

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Metal Ion Specificity in the Oxidation of the Coordinated Mercapto Group

Sir:

There are many examples of metalloproteins which contain a coordinated sulfur.^{1,2} A large fraction of these metalloproteins are involved in electron-transfer reactions. Because of these biological implications there have been many studies on suitable model systems.³⁻¹⁰

All the systems previously studied are cobalt(III)-mercapto complexes. The cobalt(III) can be reduced via electron transfer through the coordinated mercapto group or by direct electron transfer.³⁻¹¹ However, the coordinated mercapto group is a good electron donor and it can be oxidized to either a disulfide group,¹² a sulfinato,^{3,4,8-10} or a sulfenato group.³ The mole ratio of oxidizing agent per mercapto group and the type of oxidizing agent employed determine in part the nature of the oxidized product.

All the complexes employed in the above studies, except one,⁸⁻¹⁰ contained only one mercapto group bonded to the cobalt(III). We have been studying the reactions of various metal ions with tris(2-mercaptoethylamine)cobalt(III) (CoL_3).¹¹ CoL_3 is slightly soluble in water and insoluble in

other solvents. This complex, CoL_3 , can function as a tridentate ligand and coordinate to such metal ions as Ni^{2+} , Co^{3+} , Fe^{3+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} using the coordinated mercapto groups as the donor atoms.¹³⁻¹⁵ However, the reactions of CoL_3 in the presence of reducing metal ions such as chromium(II) or iron(II) or oxidizing metal ions such as chromium(III) or UO_2^{2+} resulted in the isolation of the product $Co(CoL_3)_2X_3$. A mechanism involving several oxidation-reduction reactions has been suggested.¹¹ In these previous studies we have not been able to isolate the oxidized sulfur ligand coordinated to the cobalt(III).

The reactions of $[Ni(CoL_3)_2]Br_2$ ¹³ or $[Pb(CoL_3)_2](NO_3)_2$ with large excesses of H_2O_2 resulted in the formation of a yellow precipitate which analyzed for $Co(NH_2CH_2CH_2S-O)_3(CoL_3O_6)$. This yellow precipitate is slightly soluble in water. Evidence that CoL_3O_6 contains three coordinated sulfinato groups includes the observation of bands at 1173 and 1187 cm^{-1} in the infrared spectra which did not appear in the complex CoL_3 and also a sharp band at 1098 cm^{-1} . (The S-coordinated sulfenato group usually has one asymmetric stretch in the 1250-1100- cm^{-1} range and another symmetric stretch at 1100-1000 cm^{-1} .^{3,4,16}) Since two bands instead of one were observed in the 1250-1100- cm^{-1} region of the in-

frared spectra, it is possible that all three sulfonato groups are not coordinated on one face of an octahedron. If all the sulfonato groups were not in identical environments, more than one absorption would be expected.

No absorption bands were observed in the visible region of the electronic spectrum for $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_2)_3$. However, a band was observed at $306\text{ m}\mu$ (ϵ 11 700) and a shoulder at $365\text{ m}\mu$ (ϵ 3850). The diffuse transmittance spectrum of CoL_3 has a band at $600\text{ m}\mu$ and shoulders at 460 and $365\text{ m}\mu$. Since the coordinated sulfonato group is a stronger ligand than the coordinated mercapto group,⁴ the ligand field bands of CoL_3O_6 should be at higher energies than the ligand field bands of CoL_3 . The lowest energy band for a cobalt(III) complex containing only one sulfonato group, $(\text{en})_2\text{Co}[\text{S}(\text{O})_2\text{CH}_2\text{CH}_2\text{NH}_2]^{2+}$, is at $432\text{ m}\mu$. Therefore it is likely that a complex containing three sulfonato groups should have its lowest energy band maximum in the charge-transfer region of the electronic spectrum.

The $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_2)_3$ is air stable and acid stable. Even in concentrated acid the electronic spectrum is not altered from that observed in distilled water. This complex is also stable to further oxidation. The addition of large excesses of H_2O_2 to an aqueous solution of $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_2)_3$ does not result in either the formation of the sulfonato complex or decomposition. However, in 5 M NaOH, CoL_3O_6 appears to decompose.

Although, $\text{Ni}(\text{CoL}_3)_2^{2+}$ and $\text{Pb}(\text{CoL}_3)_2^{2+}$ cations are highly reactive toward H_2O_2 when reacted in a 1 to 12 mole ratio at 80°C , the opposite is true for the cation $\text{Co}(\text{CoL}_3)_2^{3+}$. The reaction of $\text{Co}(\text{CoL}_3)_2\text{Br}_3$ with H_2O_2 (in a 1 to 500 mole ratio) at 80°C did not result in an observable reaction. However, upon boiling a mixture of $\text{Co}(\text{CoL}_3)_2\text{Br}_3$ and H_2O_2 (in a 1 to 500 mole ratio), gas is evolved and the slightly soluble yellow CoL_3O_6 precipitates out of solution. Since $\text{Co}(\text{CoL}_3)_2\text{Br}_3$ appears to be more stable in the presence of H_2O_2 than $\text{Ni}(\text{CoL}_3)_2\text{Br}_2$ or $\text{Pb}(\text{CoL}_3)_2(\text{NO}_3)_2$, the reactivities of the mercapto groups are more effectively masked by bonding to two cobalt(III) ions rather than bonding to a cobalt(III) and a nickel(II) or to a cobalt(III) and a lead(II). There are several reasons why the central nickel(II) or lead(II) does not mask the reactivity of the coordinated mercapto group to the same degree as does the central cobalt(III). Since $\text{Co}(\text{CoL}_3)_2\text{Br}_3$ is a more inert complex than $\text{Ni}(\text{CoL}_3)_2\text{Br}_2$ or $\text{Pb}(\text{CoL}_3)_2(\text{NO}_3)_2$, then more free CoL_3 may be available in solution in the latter cases. Therefore a possible function of the central metal ion is to control the concentration of free CoL_3 via an equilibrium: $\text{M}(\text{CoL}_3)_2^{n+} \rightleftharpoons \text{M}^{n+} + 2\text{CoL}_3$. This assumes that the CoL_3 and not $\text{M}(\text{CoL}_3)_2\text{X}_n$ is the compound that reacts with H_2O_2 . However, it is also possible to explain the above data assuming that only the trinuclear cations are reacting with H_2O_2 . Since the central cobalt(III) is more electronegative than nickel(II) or lead(II), the bridging sulfur groups bonded to these metal ions should be less oxidizable in the cation $\text{Co}(\text{CoL}_3)_2^{3+}$ than in the cations $\text{Ni}(\text{CoL}_3)_2^{2+}$ or $\text{Pb}(\text{CoL}_3)_2^{2+}$.

Attempts have been made to oxidize $\text{Fe}(\text{CoL}_3)_2\text{Cl}_3$, $[\text{Zn}(\text{CoL}_3)_2]\text{ZnBr}_4$, and $[\text{Cd}(\text{CoL}_3)_2]\text{CdBr}_4$ with H_2O_2 . The reaction of $\text{Fe}(\text{CoL}_3)_2\text{Cl}_3$ with H_2O_2 resulted in the isolation of an unidentified light brown powder containing iron. In the reactions of H_2O_2 with $[\text{Zn}(\text{CoL}_3)_2]\text{ZnBr}_4$ and $[\text{Cd}(\text{CoL}_3)_2]\text{CdBr}_4$, CoL_3O_6 was formed but in much smaller yields than was obtained with $\text{Ni}(\text{CoL}_3)_2\text{Cl}_2$ or $\text{Pb}(\text{CoL}_3)_2(\text{NO}_3)_2$. If the only reactive species was CoL_3 , we would expect the largest yield for the thermodynamically least stable complex, $[\text{Zn}(\text{CoL}_3)_2]\text{ZnBr}_4$ vs. $\text{Ni}(\text{CoL}_3)_2\text{Cl}_2$, and we would expect to isolate the same product in all the above reactions. Since this is not the case, it seems unlikely that CoL_3 is the only reactive species in solution.

Further proof that CoL_3 is not the only reactive species in these reactions was observed in the repetitive spectral scans of all the reactions of $\text{M}(\text{CoL}_3)_2^{n+}$ with H_2O_2 taken as a function of time. All these repetitive scans were run under the same experimental conditions. In the reaction of $[\text{Ni}(\text{CoL}_3)_2]^{2+}$ with H_2O_2 a band appeared at $355\text{ m}\mu$ as the reaction proceeds while another band at $275\text{ m}\mu$ loses intensity. An isosbestic point was observed at 323 nm . In contrast the repetitive spectral scans of the reaction of $\text{Co}(\text{CoL}_3)_2^{3+}$ with H_2O_2 resulted in a gain in intensity at all wavelengths as a function of time including the band at $275\text{ m}\mu$. There was no isosbestic point observed. For the reaction of $[\text{Zn}(\text{CoL}_3)_2]\text{ZnBr}_4$ with H_2O_2 a peak appears at $340\text{ m}\mu$ within 1 min and the height of this peak remains unchanged as a function of time. There appears to be an isosbestic point at $330\text{ m}\mu$. The original band at $265\text{ m}\mu$ shifts slightly to $260\text{ m}\mu$, but the intensity of this band did not change. Although all the above reactions were carried out under similar conditions, the repetitive spectral scans look different for each reaction. It appears that all these reactions have a different mechanism and therefore it is unlikely that CoL_3 is the only reactive species.

In order to further prove that CoL_3 could not be the only species that reacts with H_2O_2 in solution, an attempt was made to oxidize free CoL_3 . The reaction of CoL_3 (6.69×10^{-3} mol) with H_2O_2 (40×10^{-3} mol) resulted in the isolation of a water-soluble yellow compound and a red compound. Besides this new yellow compound having different solubility properties than the CoL_3O_6 , it also analyzed for $\text{CoL}_3\text{O}_5\text{H}_x$, where $x = 0, 2, \text{ or } 4$ (CoL_3O_5 , $\text{CoL}_3\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{CoL}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). There seems to be little doubt that the $\text{CoL}_3\text{O}_5\text{H}_x$ contains a sulfenato group and possibly a sulfonato group. Although the infrared spectrum of this compound is difficult to interpret unambiguously, an intense band was observed at $370\text{ m}\mu$ (ϵ 8350) in the electronic spectra. Upon reaction of $\text{CoL}_3\text{O}_5\text{H}_x$ with acid, the band at $370\text{ m}\mu$ disappeared. Deutsch has shown that this is a good criterion for a coordinated sulfenato group.¹⁷ The red compound has not been characterized; however, it also contains the sulfenato group. Both the isolated red and soluble yellow compounds can be further oxidized with H_2O_2 in a 1 to 1 mole ratio to form $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_2)_3$. (The approximate yield of CoL_3O_6 from CoL_3 is estimated to be less than 10%.) However, using a large excess of H_2O_2 resulted in decomposition of both the red compound and the soluble yellow compound. Since CoL_3O_6 is stable in large excesses of H_2O_2 it is not likely that the bulk of the CoL_3O_6 was formed by the reaction of H_2O_2 with CoL_3 in equilibrium with $\text{M}(\text{CoL}_3)_2^{n+}$. CoL_3 will decompose in large excesses of H_2O_2 . In conclusion the data suggest that the central metal ion plays a role in controlling these oxidation reactions.

Physical Measurements. The physical methods employed in the study have been reported¹⁸ except that a Beckman Acta 4 spectrophotometer was used to record electronic spectra.

Synthesis of $\text{Pb}[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_3]_2(\text{NO}_3)_2$. Lead nitrate (0.87, 0.0026 mol) was dissolved in 100 mL of H_2O . A slurry of CoL_3 (1.50 g, 0.0052 mol) dissolved in 100 mL of H_2O was added to the lead nitrate solution. The mixture was rapidly stirred for 30 min at room temperature. The solution (dark brown) was then filtered. The brown solution was concentrated until a precipitate began to form. At this point the solution was cooled for several days. Filtration yielded a green noncrystalline product which was washed with one 10-mL portion of cold water and then transferred to a flask where it was shaken with 50 mL of absolute ethanol and filtered again. The product was then dried in vacuo.

Anal. Calcd for $\text{Pb}[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_3]_2(\text{NO}_3)_2$: C, 15.90; H, 4.02; N, 12.38. Found: C, 16.06; H, 4.06; N, 12.27.

Heating the dissolved product precipitates the CoL_3 starting material. After the product stands in solution for several hours, a shiny silver solid, Pb, begins to fall from solution.

Synthesis of $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_2)_3$. Hexaaquonickel(II) chloride and CoL_3 (1.78 g, 0.0062 mol) were mixed in 150 mL of H_2O . This suspension was stirred and heated gently for 1 h in which time the CoL_3 solubilized. The deep brown solution was filtered hot and then again at room temperature to remove unreacted CoL_3 . Hydrogen peroxide (10 mL of 30% H_2O_2) was added slowly to the solution. Stirring and gentle heating were continued as a vigorous reaction took place. Gas was evolved as the reaction mixture lightened from brown to yellow-orange over a period of several minutes. Gentle heating and stirring were continued for about 1 h. The precipitate which formed in this time was then collected by filtration, washed with water and then absolute ethanol, and dried in vacuo. The product was bright yellow.

Anal. Calcd for $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_2)_3$: C, 18.80; H, 4.70; N, 10.97; Cl, 0.00. Found: C, 18.74; H, 4.69; N, 10.87; Cl, 0.44.

The same product was obtained by dissolving solid $\text{Ni}[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_3]\text{Cl}_2$ or $\text{Pb}[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_3](\text{NO}_3)_3$ in 150 mL of water and then adding excess H_2O_2 .

Reactions of CoL_3 with H_2O_2 . CoL_3 (1.92 g, 6.69×10^{-3} mol) was mixed in 150 mL of H_2O at 0 °C. H_2O_2 (4.00×10^{-3} mol) was then added. The CoL_3 dissolved to form a deep red solution. After 20 min of being stirred the reaction mixture was filtered. A saturated solution of NaClO_4 (1.38 g, 2.01×10^{-2} mol) was added to the deep red solution. The solution was refrigerated 2 days in which time a yellow precipitate formed. The precipitate was noncrystalline and seemed to form in paper-thin sheets. The precipitate was collected by filtration and washed with about 2 mL of absolute ethanol.

Anal. Calcd for $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_2)_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO})$: C, 19.63; H, 4.95; N, 11.44. Found: C, 20.20; H, 5.30; N, 11.37.

To isolate the red compound, CoL_3 and H_2O_2 are mixed in the same manner as described above except that the solution is concentrated by vacuum evaporation to 30 mL, and 200 mL of acetone rather than NaClO_4 is then added. The red compound precipitates out of solution.

Anal. Calcd¹⁹ for $[\text{NH}_3\text{CH}_2\text{CH}_2\text{SH}]_2[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{S})_2\text{O}]_2$: C, 19.57; H, 5.21; N, 11.41. Found: C, 19.81; H, 5.32; N, 10.9.

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Registry No. $[\text{Pb}(\text{CoL}_3)_2](\text{NO}_3)_2$, 66551-69-7; CoL_3O_6 , 66482-82-4; $\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO}_2)_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{SO})$, 66482-83-5; CoL_3 , 18703-22-5; $[\text{Ni}(\text{CoL}_3)_2]\text{Cl}_2$, 66454-93-1; H_2O_2 , 7722-84-1.

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Model for Carbonate Apatite

Sir:

Recently Santos and González-Díaz¹ have assigned parameters to the CO_3 group of carbonate apatite on the basis of highly improbable interpretations of infrared data and correlations of certain ratios with quantitative determinations of constituents. Our primary objection to their model is that for every CO_3 group substituted for a PO_4 group, there is no provision for the fourth oxygen. What happens to it? Does it exist as a large hole? If so, it should markedly affect the density, unit-cell dimensions, and optical properties in ways which they completely failed to explain.

They completely disregarded the proposal by McConnell² that $3\text{PO}_4 \rightarrow 4\text{CO}_3$, thus preserving the "oxygen lattice" essentially intact. In fact, Santos and González-Díaz consider merely the model of Elliott³ and thus disregard all other models that are to be found in the mineralogical literature on apatite (including carbonate apatite) which are summarized in 1973 in book form.⁴ The types of substitution in apatite appear to be very complex—in addition to the mechanism for replacement of phosphate ions by carbonate. For example, it has been postulated⁵ that combined water can enter the structure in several ways: (i) H_2O can replace (OH) at (0, 0, $1/4$), (ii) vacancy of a tetrahedral P can result in (H_4O_4), and/or (iii) calcium can be replaced by H_3O^+ .

Although Santos and González-Díaz appear to accept (i) they completely disregard (ii) and (iii), following Elliott in this respect. Nevertheless, Simpson⁶ has greatly augmented the arguments of McConnell⁵ by obtaining evidence in partial confirmation and has suggested what modifications of the unit-cell dimension (a) would be probable for each configuration. It is known, for example, from Foreman's⁷ study (by neutron diffraction) of $\text{Ca}_3\text{Al}_2(\text{D}_4\text{O}_4)_3$, that the volume of the unit cell increases significantly with (ZO_4) \rightarrow (H_4O_4) and, despite Elliott's disparaging remarks, this type of substitution is now recognized among many silicate and phosphate minerals.⁸

With respect to the infrared absorption spectra, the interpretations of Santos and González-Díaz are highly speculative for reasons stated in 1966,⁹ as well as a recent study: "The fact that the doublet is not observed at first with high CO_2 content (Fig. 4A), and appears only at low CO_2 content, supports, in our opinion, McConnell's (1952b) hypothesis that CO_3^{2-} groups in the apatite are in two different orientations "perpendicular" and "parallel" to the c axis (both groups are, in fact, tilted at $\sim 32^\circ\text{C}$)."¹⁰ In connection with their consideration of quantitative relationships of constituents, the following remarks seem pertinent: "In the present study the line of best fit is having a slope of -0.5328 , therefore [the] more probable mode of substitution was 4CO_3 for 3PO_4 as suggested by McConnell (1952)."¹¹

Finally, if there is such a substance as "B carbonate apatite"—which we seriously doubt, believing that both