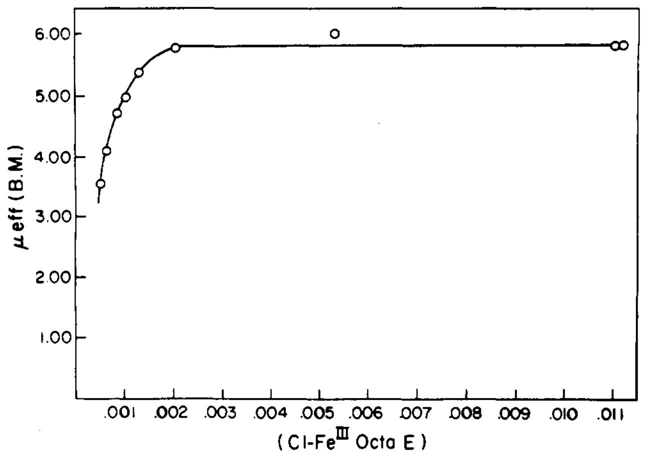

Figure 3. Magnetic moments of iron(III) porphyrin solutions as a function of concentration.

Table I. μ_{eff} of Chloroiron(III) Octaethylporphyrin in Pyridine–Effect of Salts and Water

[Fe^{III}Por], mol/L	anion	[anion], mol/L	μ_{eff}, μ_B	
			exptl	calcd
6.54×10^{-3}			5.87	5.60
	H_2O	0.10	5.17	5.11
2.9×10^{-3}	ClO_4^-	0.102	3.74	3.0
	BF_4^-	0.0822	3.34	3.20
5.23×10^{-3}	BPh_4^-	0.064	2.57	2.24
8.72×10^{-4}	Cl^-	0.13	5.11	5.92

However, a direct comparison of magnetic and spectral data was possible. The influence of water and added salts upon μ_{eff} is portrayed in Table I. The values of μ_{eff} in the final column are those calculated from visible spectra. For this purpose μ_{eff} for the low-spin bis(pyridinato) adduct was taken as 2.24 μ_B. The spin-only value (5.92 μ_B) was used for the chloroiron(III) adduct. The moment was calculated from the distribution of high-spin Fe-Cl and low-spin Fe-$(py)_2^+$ species derived from the optical density at 627 nm or determined from the equilirbium constant. The agreement is within the experimental error of our methodology.

Osmometric measurement of chloroiron(III) octaethylprophyrin in pyridine at 0.01 and 0.001 M indicate only a slightly greater concentration of particles than that observed for the benzil standard. A comparison of octaethylporphyrin at 0.001 M with the chloroiron(III) complex indicated both to be 0.001 M within experimental error.

In sum, chloroiron(III) octaethylporphyrin in pyridine solution exists predominantly as the undissociated adduct at concentrations greater than 10^{-3} M. Indeed, detectable quantities of the nondissociated species exist at 5×10^{-5} M. Water (0.1 M) does not markedly influence the degree of ionization. On the other hand salts not containing chloride increase the ionic strength of the solution and facilitate the dissociation of the complex to the low-spin bis(pyridinato) adduct.

Our results allow no quantitative assessment of the extent of pyridine solvation of the chloroiron(III) adduct. Qualitatively, however, they suggest the monopyridinato adduct is not a major species in these solutions. Thus, it is unlikely that the equilibrium constant for the affiliation of one pyridine with iron(III) would exceed that for two.[9-11] Moreover, the visible spectrum of the chloride salt in pyridine is remarkably similar to that observed in poor conditioning solvents. For example, the extinction coefficient at 627 nm in pyridine and chloroform are the same (±1%), and there is only a slight shift in the center of the broad change-transfer band (chloroform 633 nm; benzene, toluene 630 nm). In contrast, the visible spectrum of the monoimidazole adduct of chloroiron(III) tetraphenylporphyrin[11] differs substantially from that of the parent iron complex.

Acknowledgment. This work was supported in part by grants from the National Institute of Arthritis, Metabolism and Digestive Diseases (Grant AM-28271) and the National Institute of Environmental Health Sciences (Grant ES-01588).

Registry No. PFeCl, 28755-93-3; PFe(py)$_2$, 19496-63-0.

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A Reinvestigation of the Bonding in Bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV)

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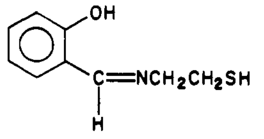
The vanadyl complex of *N*-(2-mercaptoethyl)salicylidineamine (I), a Schiff base ligand derived from the reaction of salicylaldehyde and 2-aminoethanethiol, was first prepared by Syamal.[1] It was reported to be a complex of the VOL_2 type (L = a bidentate, 1– anion) although the ligand has three potential donor atoms: O, N, and S. This is in contrast to the vanadyl complex of *N*-(2-hydroxyethyl)salicylidineamine (II), which is an ONO analogue of I. The latter vanadyl complex was reported to be of the VOL′ type[2] (L′ = a tridentate, 2– anion).



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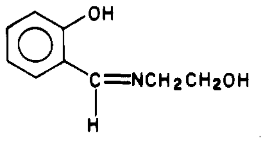
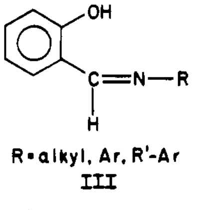


II

Specifically, Syamal[1] states that ligand I behaves as a bidentate monobasic ligand. This, he says, is supported by the IR spectrum, which shows a band at 3100 cm^{-1}. In another paper[3] on a series of vanadium complexes with similar Schiff base ligands, Syamal claims specifically that the 3100-cm^{-1} band is due to the O–H stretch of the ligands. This can only mean that the N and S atoms coordinate to the vanadyl group, leaving the hydroxyl group nonbonded.

We found this conclusion about the bonding in the complex rather unusual because for similar Schiff base ligands derived from salicylaldehyde or substituted salicylaldehyde and amines, the phenolic oxygens are always bonded to metals.[4] Pasquali et al.,[5] for example, showed that the Schiff base ligands III used their



III

phenolic oxygens in bonding to the vanadium atom. The ligand H_2salen [bis(salicylaldehyde) *N*,*N*′-ethylenediimine] has long been known to use both hydroxyl groups in bonding to metals.[4] It

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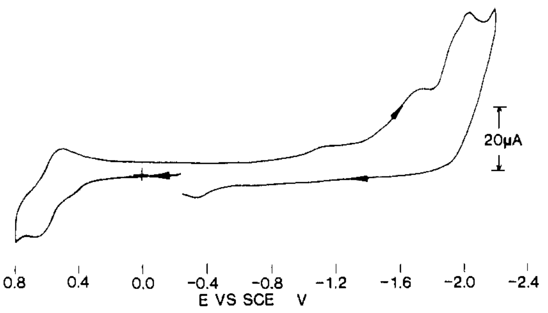

Figure 1. Cyclic voltammogram in 0.1 M TEAP/Me_2SO of 16 mM bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV) (scan rate 200 mV/s).

seemed to us that ligand I should behave similarly to H_2salen and the ligands studied by Pasquali; that is, it should coordinate to the vanadyl group through the N and O donor atoms instead of N and S donor atoms as reported. We report here a reinvestigation of the bonding of this ligand (I) in its oxovanadium(IV) complex.

Experimental Section

The electrochemical instrumentation used has been described previously.[6]

IR spectra were recorded on a Perkin-Elmer 683 IR spectrophotometer. The ^1H NMR spectrum of the ligand (I) in $CDCl_3$ was recorded on a Varian EM 360A NMR spectrometer. An NMR study of the vanadyl complex was carried out by electrolytically oxidizing the V(IV) complex, in Me_2SO-d_6 at 0.75 V vs. SCE with a platinum mesh electrode, until all V(IV) was converted to V(V). An FT ^1H NMR spectrum was then taken on a Bruker WH-90 DS NMR spectrophotometer.

Reagents. High-purity dimethyl sulfoxide (0.011% water) was obtained from Burdick and Jackson Laboratories and was deoxygenated before use. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium bromide (Aldrich) and perchloric acid as previously described[7] and used as the supporting electrolyte. $CDCl_3$ (99.8%) and Me_2SO-d_6 (99%) were obtained from Aldrich.

Preparation of Bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV). The green complex was prepared by the procedure as described by Syamal.[1] Anal. Calcd for $C_{18}H_{20}N_2S_2O_3V$: C, 50.59; H, 4.68; S, 14.99. Found: C, 50.54; H, 4.18; S, 14.11. When the complex was made without refluxing at the last step, the analysis was as follows. Found: C, 50.69; H, 4.58; S, 15.07.

Isolation of *N*-(2-Mercaptoethyl)salicylidineamine. This yellow precipitate was prepared by the in situ method used by Syamal for preparation of the above complex. (Syamal did not isolate the ligand.) After the yellow solution was obtained and stirred for at least $^1/_2$ h, the methanol solvent was stripped off until a yellow precipitate crystallized. The product was recrystallized in warm methanol. Anal. Calcd for $C_9H_{11}NSO$: C, 59.66; H, 6.07; S, 17.70. Found: C, 59.98; H, 5.62; S, 17.84.

Preparation of H_2salen and VO(salen). The H_2salen ligand and VO(salen) complex were prepared by the methods described by Selbin et al.[8] Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.65; H, 5.97. Found: C, 71.58; H, 6.05. Calcd for $C_{16}H_{14}N_2O_3V$: C, 57.68; H, 4.20. Found: C, 57.71; H, 4.26.

Results and Discussion

Obtaining the complex in pure form is not simple. When the reaction mixture of the vanadyl complex is refluxed for a few hours, the elemental analysis falls between the 1:1 (VOL′) and 1:2 (VOL_2) stoichiometric values (1:1 values: C, 43.90; H, 3.66; S, 13.01). The experimental data are much closer to the 1:2 values. The product is probably a mixture of a dominant VOL_2 complex and a trace of a VOL′ complex. A cyclic voltammogram of the complex (Figure 1) confirms this by showing a small shoulder at 0.45 V in addition to an oxidation peak at 0.65 V on an initial positive scan. This shoulder is believed to correspond to the VOL′ complex. The oxidation peak at 0.65 V is a one-electron-transfer process as shown by the controlled-potential coulometry. When heat was not applied to the reaction mixture, we obtained a pure product as indicated by elemental analysis and also by a cyclic voltammogram that showed the shoulder at 0.45 V to be even smaller.

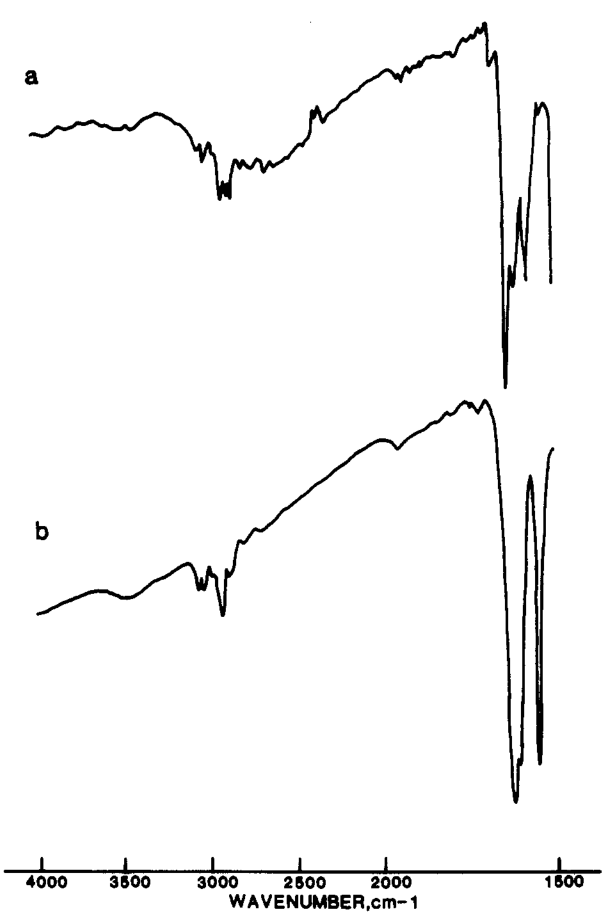

Figure 2. IR spectra in KBr of (a) *N*-(2-mercaptoethyl)salicylidineamine and (b) bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV).

Purity of the complex may also have been a problem for Syamal.[1] His calculated values for the complex are incorrect and his experimental values are of poor accuracy. For $C_{18}H_{20}N_2S_2O_3V$

	% V	% N
value calcd by Syamal	12.85	7.05
exptl value reported by Syamal	13.2	7.0
actual calcd value	11.94	6.56

IR studies in KBr of ligand I and its oxovanadium(IV) complex were made to reinvestigate the results observed by Syamal. Figure 2a shows the O–H band of the ligand as a broad envelope centered at ca. 2800 cm^{-1}. The shift of this hydroxyl stretch from the common range (3200–3600 cm^{-1}) to lower wavenumber is due to intramolecular hydrogen bonding to the imine nitrogen atom.[9] The small band at ca. 3500 cm^{-1} can be accounted for as a stretching mode of water in KBr. This is supported by the same observation in a spectrum of pure KBr. After complexation to the vanadyl group, the broad band at 2800 cm^{-1} completely disappears from the IR spectrum of the complex (Figure 2b). This spectrum shows more clearly the aliphatic and aromatic C–H stretches. We suspect that the band at 3100 cm^{-1}, due to aromatic C–H stretches, is the band Syamal believed was an O–H stretch.

Since the O–H band at 3500 cm^{-1} was always observed when KBr was used as the medium, we chose to do further IR studies in 1,3-hexachlorobutadiene (C_4Cl_6), which does not absorb from 4000 to 1600 cm^{-1}. The same results were obtained. The broad envelope at 2800 cm^{-1} of the ligand spectrum (Figure 3a) completely disappeared in the complex spectrum (Figure 3b) with no ambiguity concerning the band at 3500 cm^{-1}. Also present in Figure 3a is a series of peaks near 2000 cm^{-1}. (The sharp spike

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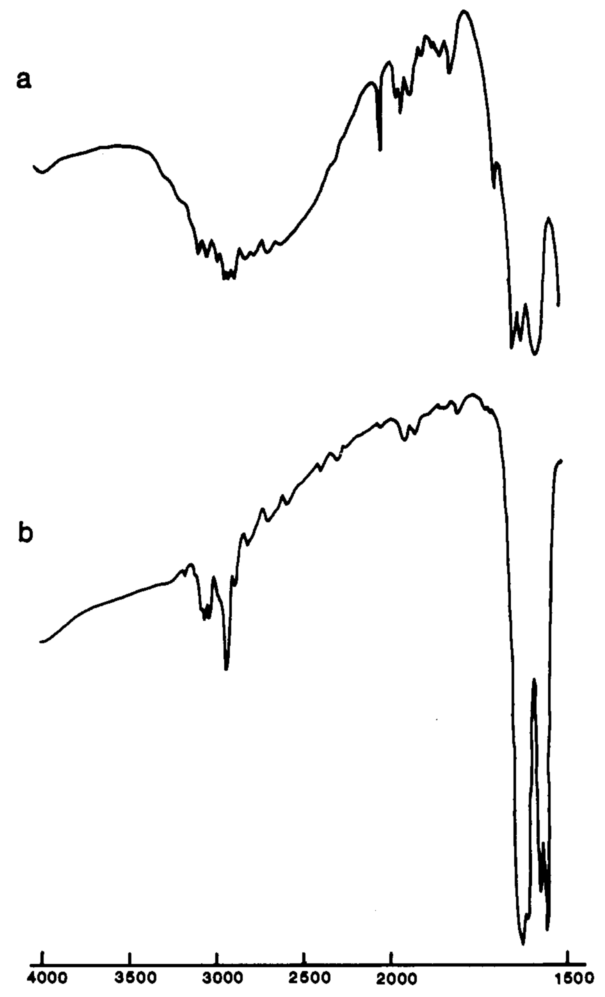

Figure 3. IR spectra in C_4Cl_6 of (a) *N*-(2-mercaptoethyl)salicylidineamine and (b) bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV).

occurs at 1995 cm^{-1}. This pattern of overtone bands is indicative of substituted aromatic compounds. Numerous examples of such compounds with peaks between 2000 and 1667 cm^{-1} are given in standard texts.[10] Figure 3b shows a similar pattern in this part of the spectrum.

Stretching bands for S–H usually occur in the 2600–2550-cm^{-1} range but may be shifted slightly to ~2400 cm^{-1} by hydrogen bonding, which is much weaker than for O–H and N–H groups. Also, S–H bands are often weak and not observable.[10] Such stretching bands cannot be clearly identified in either Figure 3a or Figure 3b.

To be certain of our interpretation, IR studies of the well-characterized H_2salen ligand and its vanadyl complex, VO(salen), were made for comparison. Similar behaviors for this ligand and complex were observed. Figure 4a shows the large envelope at about 2800 cm^{-1} for the ligand, while such a band is absent from the spectrum of the complex (Figure 4b). Finally, it should be noted that in a later paper[11] Syamal also assigns such a band (2700 cm^{-1}) as the O–H stretch in several similar ligands. We agree with this assignment.

NMR studies of ligand I and its vanadyl complex support the data obtained from the IR studies. Figure 5 shows a ^1H NMR spectrum of ligand I. The methylene protons appear at 3 and 3.9 ppm as triplets. The multiplets at ca. 7 ppm account for the aromatic protons. The singlet at 8.4 ppm is the proton of the azomethine group. The broad peak at ca. 13 ppm is assigned as the hydroxyl proton on the basis of its disappearance after addition

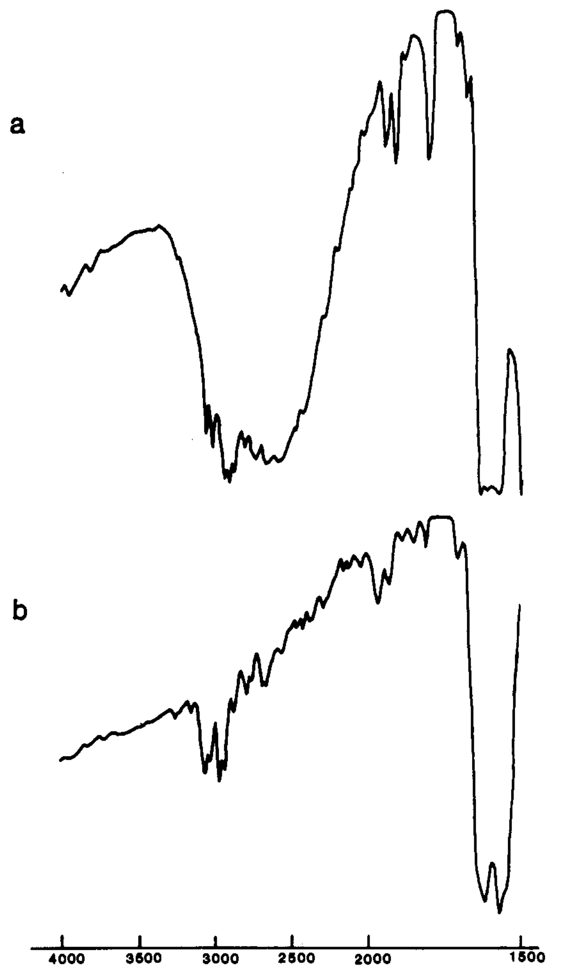

Figure 4. IR spectra in C_4Cl_6 of (a) [bis(salicylaldehyde) *N,N'*-ethylenediimine] and (b) [bis(salicylaldehyde) *N,N'*-ethylenediiminato]oxovanadium(IV).

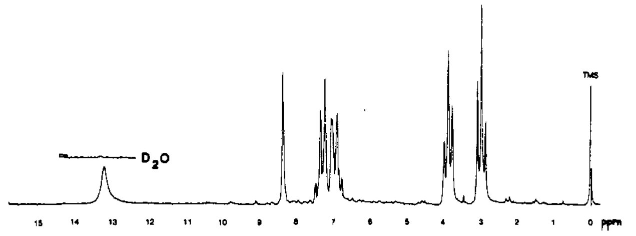

Figure 5. ^1H NMR spectrum in $CDCl_3$ of *N*-(2-mercaptoethyl)salicylidineamine.

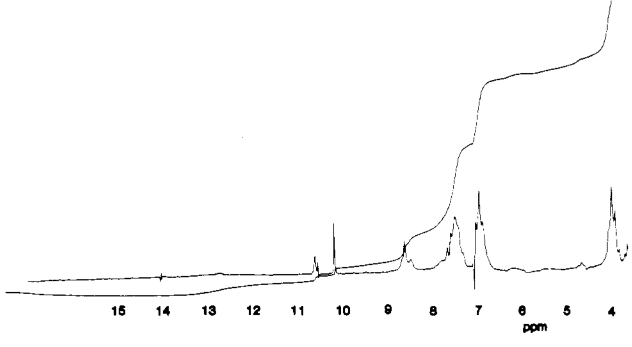

Figure 6. FT ^1H NMR spectrum in Me_2SO-d_6 (0.08 M TEAP) of the oxidation product (0.75 V) of bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV).

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of D_2O. The intramolecular hydrogen bonding discussed above is responsible for the downfield shift of the hydroxyl proton. Figure 6 shows the FT ^1H NMR spectrum of the V(V) complex. (The vanadium(IV) complex was oxidized to give a diamagnetic analogue.[12]) The upfield portion of the spectrum (not shown) contains peaks from the supporting electrolyte (TEAP). No band between 9 and 13 ppm that would integrate to 1 (relative to the azomethine proton peak) was observed. The flat, broad band at about 13 ppm is probably the hydroxyl proton of a trace of dissociated ligand. Although two peaks appear between 10 and 11 ppm, they are sharp, unlike the hydroxyl proton peaks, and their integrations are much smaller than 1. Their presence is probably due to artifacts of the electrolytic process. Neither the NMR spectrum of the ligand (Figure 5) nor the spectrum of the vanadium(V) complex (Figure 6) showed evidence of the SH proton. As with IR, such NMR signals are often not observed.

An attempt to synthesize a vanadyl complex with *N*-(2-mercaptoethyl)benzylideneamine (prepared from benzaldehyde and 2-aminoethanethiol) was unsuccessful. Since this ligand has only N and S donating atoms, this result suggests that N and S bonding is unlikely in the complex with ligand I.

Conclusion

The IR studies, in both KBr and C_4Cl_6, give conclusive evidence that the hydroxyl group is involved in bonding to the vanadyl group in bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV). The NMR data support this. Thus, although the protonated SH group cannot be confirmed by either IR or NMR, we are convinced that the complex bonds through N and O donors. We are now attempting to grow suitable crystals for an X-ray structure determination of this complex.

Acknowledgment. Financial support for this work was provided by a Sigma Xi grant to R.S. and by the Research Corp. We also wish to acknowledge preliminary work on this project by S. L. Bernard and assistance in obtaining the FT NMR data by J. F. Sebastian.

Registry No. Bis[*N*-(2-mercaptoethyl)salicylidineaminato]oxovanadium(IV), 68433-47-6.

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[12] The NMR spectrum of the vanadium(IV) complex was recorded, but as expected, paramagnetic broadening obliterated the spectrum.

Contribution from the Departments of Chemistry,
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Synthesis of $[Co(CoL_3)_2]^{3+}$ by HNO_3 Oxidation of CoL_3 (L = $^{-}SCH_2CH_2NH_2$) and Induced Electron Transfer. Crystal Structure of $[Co(CoL_3)_2]_2(SO_4)Cl_4$

Mary Jane Heeg,[1] E. L. Blinn,[2] and Edward Deutsch*[3]

Received August 8, 1984

The mechanisms governing oxidation of coordinated sulfur are diverse, and this diversity is of considerable relevance to catalytic and biological systems.[4] At least six different pathways exist for the oxidation of thiols coordinated to cobalt(III), and each of these paths leads to distinct reaction products. The mechanistic aspects of these systems have recently been reviewed.[4] In this context our observation that the HNO_3 oxidation of CoL_3 (where L represents $^{-}SCH_2CH_2NH_2$) leads to a product which can be formulated as "$CoL_2(NO_3)$" is of considerable interest. Since any mechanistic interpretation of this observation requires definitive knowledge of the identity of the "$CoL_2(NO_3)$" product, a single-crystal X-ray structural analysis of this material was undertaken. This paper presents the results of this analysis, which show that the "$CoL_2(NO_3)$" product is in fact the nitrate salt of the known trimeric complex $[Co(CoL_3)_2]^{3+}$.

The structure of the trimeric $[Co(CoL_3)_2]^{3+}$ complex is of interest in itself since it is dependent upon the ability of coordinated thiols to bridge metal centers. The single thiolato group of $[(en)_2CoL]^{2+}$ has been shown to effectively bridge the Co(III) center to Ag(I), Hg(II), Pt(II), Cu(I), and the iodonium ion.[5-7] While it has long been assumed that the bridging ability of coordinated thiols allows the facial isomer of CoL_3 to function as a tridentate, S-donating ligand to a variety of metal centers (Co(III), Ni(II), Fe(III), Ru(III), Zn(II), Cu(I), Cu(II), and Pb(II)),[8-12] none of these $[M(CoL_3)_n]^{m+}$adducts have been structurally characterized. The structural analysis presented in this work confirms the two tris(thiolato) bridges originating from the two terminal cobalt(III) ions and the octahedral arrangement of six sulfur atoms about the central cobalt(III) ion. This latter feature is in contrast to the trigonal-prismatic geometry of the central cobalt(II) ion found in the oxygen analogue $[Co(Co(OCH_2CH_2NH_2)_3)_2]^{2+}$.[13]

Experimental Section

HNO_3 Oxidation of CoL_3. $Co(SCH_2CH_2NH_2)_3$ was prepared by a published procedure.[8] Four grams of this material was slurried in 200 mL of water, and 52.5 mL of 0.16 M HNO_3 was added with stirring. On gentle heating for 30 min this stirred suspension changed from green to red-brown. Filtration of the reaction mixture and concentration of the filtrate yielded 0.70 g of brown crystalline product. Anal. Calcd for $Co(SCH_2CH_2NH_2)_2NO_3{\cdot}H_2O$: C, 16.50; H, 4.86; N, 14.59. Found: C, 16.33; H, 4.80; N, 14.56. An aqueous solution of this material was adsorbed onto SP-C25 cation-exchange resin and then eluted as a single band with 0.5 M LiCl. Addition of an equal volume of saturated $(NH_4)_2SO_4$ solution to this eluent, followed by slow cooling, yielded dark, red-brown, single crystals suitable for X-ray structural analysis.

Structural Analysis. A single crystal of dimensions 0.19 × 0.20 × 0.20 mm was selected and mounted on a CAD-4 automated diffractometer equipped with Mo Kα radiation and a graphite monochromator. A total of 11 098 reflections were collected at ambient temperature in the sphere $2.5° \le 2\theta \le 50°$. After averaging, 10 799 unique reflections were obtained; of these 7315 were observed reflections with $I_o \ge 3\sigma(I)$. Least-squares calculations on 25 high-angle reflections yielded a triclinic cell of dimensions $a = 11.803$ (3) Å, $b = 17.227$ (8) Å, $c = 17.239$ (4) Å; $\alpha = 83.24$ (2)°, $\beta = 69.98$ (2)°, $\gamma = 69.99$ (3)°, and $V = 3095$ (2) Å^3. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate, variable up to 45 s/scan; scan range, calculated by $0.80 + 0.20 \tan \theta$ with 25% extension on each side for backgrounds. Three intensity monitors were checked every 2 h of X-ray time, and they were observed to fluctuate randomly <2% over the entire data collection. Three orientation standards were centered after every 200 observations. Absorption corrections were applied with μ(Mo Kα) = 22.2 cm^{-1}; transmission coefficients varied from 0.66 to 0.71. The calculated density was 1.615 g cm^{-3} with $Z = 4$.

The centrosymmetric space group[14] $P\bar{1}$ was assumed and gave satisfactory refinement. The Co and S atoms were placed according to a

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