Reactions of Deprotonated Ligands. IV. Tris(ethylenediamine)cobalt(III) Ion[1]

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Abstract. Treatment of $[Co(en)_3]I_3$ with potassium amide in liquid ammonia at $-33.5°$ has led to the isolation and characterization of $[Co(en\text{-}H)_2(en)]I$; other anticipated deprotonation products either did not form or could not be isolated pure owing to high solubility. Reactions of $[Co(en\text{-}H)_2(en)]I$ with CH_3I, $SOCl_2$, SO_2Cl_2, and CH_3COCl are described and discussed in relation to the infrared spectra of the parent complex and the reaction products.

Although deprotonation of en ligands associated with transitional metal ions of the 4d and 5d series has been reported[2] in several cases, and methylation of en-*x*H complexes demonstrated in two instances,[3] analogous reactions involving 3d series ions have not been observed. The only earlier attempt failed because of the lability of the en complex of Mn(II) and the resultant ligand substitution by ammonia, the deprotonation reaction medium.[4]

Selection of Co(III) for further studies was influenced by other considerations. Since $[Co(en)_3]^{3+}$ is spin-paired,[5] it might permit an assessment of the effect of deprotonation upon ligand field strength. Thus, if the effect of deprotonation is to decrease field strength and if sufficiently extensive deprotonation could be accomplished, a change in paramagnetic susceptibility might be observed.

Throughout the present studies, efforts to isolate the products of deprotonation by means of amide ion in liquid ammonia were commonly thwarted by the exceptionally high solubility of the deprotonated species in ammonia. Efforts to precipitate these products by dilution with anhydrous ether or toluene, or incorporation of heavy anions such as $[Ni(CN)_4]^{2-}$ or $[HgI_4]^{2-}$, were unsuccessful. A product of satisfactory purity was obtained only by operating at low temperatures and high concentrations of reactants and minimizing the washing of the ammonia-insoluble fraction.

Experimental Section

Methods and Materials. Unless otherwise indicated, (1) reactions in liquid ammonia and all physical measurements were performed as described earlier,[2] (2) standard analytical procedures were employed, and (3) all chemicals were reagent grade and used without further purification, except as described below.

Tris(ethylenediamine)cobalt(III) iodide (A) was prepared in 82% yield by the method of Fernelius.[6] The product was diamagnetic.

Anal. Calcd for $[Co(en)_3]I_3$: Co, 9.50; I, 61.4. Found: Co, 9.44; I, 61.3.

The infrared spectrum is included in Figure 1 and Table I. The most intense lines in the X-ray diffraction pattern (*d* spacings in angstroms; relative intensities in parentheses) were 6.91 (0.5) 4.92 (0.4), 4.29 (1.0), 3.52 (0.4), 3.34 (0.3), 3.02 (0.3).

Deprotonation of $[Co(en)_3]I_3$. To determine whether the iodide undergoes either solvolysis or ligand substitution, a 0.25-g sample was exposed to 40 ml of liquid ammonia at $-33.5°$ for 3 hr. The solvent was evaporated and an X-ray diffraction pattern of the residual solid was identical with that of the starting material; there were no lines attributable to NH_4I.

In a preliminary experiment designed only to detect evidence of successive deprotonation, 0.0980 g of $[Co(en)_3]I_3$ in 50 ml of ammonia was titrated potentiometrically at $-33.5°$ with the potassium amide formed from 0.0447 g of potassium in 28 ml of ammonia (*i.e.*, relatively dilute solutions) using procedures described elsewhere.[2] Initially most of the iodide was undissolved, but during dropwise addition of the first 4 ml of amide solution (*ca.* 1 molar equiv) there was a gradual increase in potential amounting to only 100 mv while all of the iodide reacted to form a deep red solution. As the second equivalent of amide solution was added, a small quantity of red solid separated and the potential increased by about 225 mv, but again gradually. The precipitate dissolved as more amide solution was added and addition of 7 ml of amide solution resulted in an increase in potential of about 700 mv. Addition of the remainder of the amide solution led to neither further change in potential nor other evidence of reaction.

In a typical experiment designed to isolate $[Co(en\text{-}H)(en)_2]I_2$, 1.621 g of $[Co(en)_3]I_3$ in 50 ml of ammonia was treated with the potassium amide formed from 0.102 g of potassium in 20 ml of ammonia. Evaporation of the resulting red solution did not result in separation of solid products until virtually all of the solvent had been removed. A variety of efforts to isolate the *pure* deprotonated complex in useful quantities were unsuccessful. Accordingly, attention was directed to the study of the somewhat less soluble $[Co(en\text{-}H)_2(en)]I$, as follows.

Treatment of a *ca.* 0.1 *M* solution of $[Co(en)_3]I_3$ in ammonia at $-33.5°$ with 2 molar equiv of KNH_2 resulted in the separation of a rose-red solid in quantities too small to permit purification. The solubility of this product was not significantly less at $-70°$. Dilution of the red solutions with dry ether or toluene resulted in the separation of black solids having compositions that were not reproducible. Addition of an ammonia solution of $K_2Ni(CN)_4$ failed to produce an insoluble tetracyanonickelate(II) of $[Co(en\text{-}H)_2(en)]^+$; similar experiments designed to precipitate a tetraiodomercurate(II) were unsuccessful because K_2HgI_4 reacts with liquid ammonia.[7] The desired complex was finally obtained pure and in useful quantities as follows. A 4.30-g sample of $[Co(en)_3]I_3$ (6.94 mmoles) was dissolved and (mostly) suspended in 30 ml of ammonia at $-33.5°$ and treated dropwise with 15.0 ml of 0.924 *M* KNH_2 solution (13.9 mmoles) over 1 hr. After digestion for 2 hr, the rose-red solid was washed three times with 50-ml portions of ammonia, dried *in vacuo* for 24 hr, and transferred to a drybox for storage and sampling.

Anal. Calcd for $[Co(en\text{-}H)_2(en)]I$ (B): Co, 16.2; C, 19.8; H, 6.05. Found: Co, 16.1; C, 19.0; H, 6.25.

This product was diamagnetic at 25°. Infrared spectral data are given in Table I and Figure 1. X-Ray diffraction data are 7.19 (0.5), 6.15 (0.3), 5.18 (1.0), 4.23 (0.4), 3.98 (0.4), 3.67 (0.4).

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(1) Abbreviations: en, ethylenediamine; en-*x*H, an en ligand from which *x* protons have been removed.

(2) G. W. Watt and J. K. Crum, *J. Am. Chem. Soc.*, **87**, 5366 (1965), and references therein.

(3) G. W. Watt and D. G. Upchurch, *ibid.*, **87**, 4212 (1965); **89**, 177 (1967).

(4) G. W. Watt and B. S. Manhas, *J. Inorg. Nucl. Chem.*, **28**, 1945 (1966).

(5) C. J. Ballhausen and R. W. Asmussen, *Acta Chem. Scand.*, **11**, 479 (1957).

(6) W. C. Fernelius, *Inorg. Syn.*, **2**, 221 (1946).

(7) G. W. Watt and B. S. Manhas, *J. Inorg. Nucl. Chem.*, **29**, 1820 (1967).

Table I. Infrared Spectral Data[a]

A	B	C	D	E	F
3180 vs	3240 m	3210 vs	3200 vs	3200 vs	3190 vs
3090 vs	3140 m	3135 vs	3120 vs	3100 vs	3095 vs
2977 sh	2960 s	3010 m	2940 s	2985 sh	2980 sh
2955 sh	2840 s	2980 m	2860 s	2900 sh	2900 sh
2890 sh	1595 m	2880 m	1570 s, br	1580 s, br	1675 m, br
1623 w	1460 s	1575 m, br	1495 sh	1520 vw	1570 s, br
1578 m	1370 m	1488 m, sp	1462 ms	1461 ms	1495 m, sp
1564 m	1326 w	1472 m	1395 m	1400 m	1461 m
1546 s	1300 m	1455 m	1369 w	1369 m	1395 m
1462 s	1255 w	1405 w, sp	1326 m	1325 m	1370 m
1458 m	1150 sh	1397 vw	1297 w	1300 sh	1326 m
1379 m	1123 m	1374 m	1265 m	1265 s	1315 sh
1366 m	1052 s	1347 sh	1197 sh	1220 w	1296 w
1325 m	1030 sh	1320 w	1129 vs, br	1155 s	1275 sh
1299 m	897 m	1298 w	1054 s	1102 s, br	1200 w
1277 m	850 w, br	1285 sh	1030 sh	1056 s	1149 m
1235 w	735 sh	1262 w	1000 sh	1030 sh, br	1114 m
1210 w	725 m	1225 vw	985 m, sp	894 w	1052 s
1154 m	611 w, sh	1124 m	968 sh	879 w	1027 m
1145 sh	571 m	1051 s	890 w	805 s	1000 m
1120 sh	536 w, sh	1025 w	875 vw	622 ms	965 w
1112 m	515 vw	1008 w	795 m	580 m	890 w
1054 s	485 vw	955 ms	746 m	570 sh	875 sh
1025 w	465 vw	924 m	631 sh	555 vw	795 w
1000 w	300 sh	898 vw	620 s	502 w	745 w
892 w	245 s, br	880 vw	577 m	464 w	580 m
876 w		853 w	566 sh	392 w	565 sh
794 m		816 w	556 sh	371 w	557 sh
778 m		738 w	494 sh	270 s, br	506 m
741 w		615 w	464 m, br		473 w
728 sh		568 m	442 sh		370 w
579 s, sp		534 w, sh	400 vw		280 s, br
563 s, sp		500 vw	374 vw		
556 s, sp		455 w			
493 s		402 vw			
466 w		380 vw			
456 w		280 m, br			
437 w					
429 m					
363 s					
269 sh					
257 vs					

[a] Symbols: vs, very strong; s, strong; m, medium; ms, medium strong; w, weak; vw, very weak; sh, shoulder; sp, sharp; br, broad.

Several efforts were made to produce [Co(en-H)$_3$] by treating [Co(en)$_3$]I$_3$ with 3 or 3.5 molar equiv of potassium amide in ammonia. The composition of the ammonia-insoluble products, however, did not correspond to the anticipated product, but indicated displacement of en ligand. This was confirmed by evaporating the solvent from the combined filtrate and washings, extracting the residue with ethanol, and treating this solution with HCl. The resulting white solid gave an infrared spectrum identical with that of an authentic specimen of ethylenediamine hydrochloride.

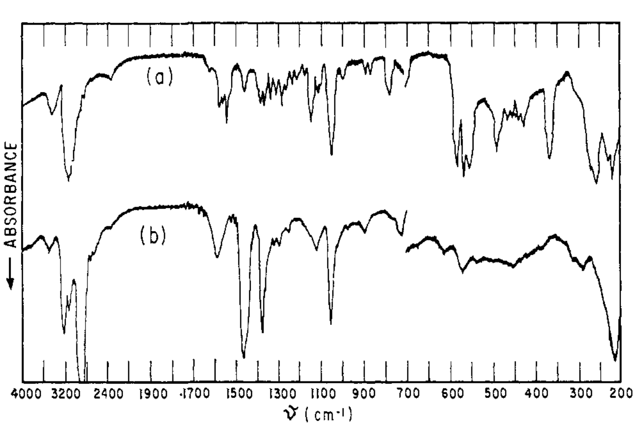

Figure 1. The infrared spectra of (a) [Co(en)$_3$]I$_3$, (b) [Co(en-H)$_2$(en)]I.

Reactions of [Co(en-H)$_2$(en)]I. (a) With Methyl Iodide. Approximately 20 ml of doubly distilled CH$_3$I was added to 0.50 g of [Co(en-H)$_2$(en)]I by distillation under reduced pressure into a reaction vessel containing a magnetic stirring bar. The vessel was sealed and its contents stirred for 10 days at 25° during which the color of the solid changed from rose-red to brown. After removing excess CH$_3$I by distillation and drying *in vacuo* for 2 hr, the brown solid (0.60 g) was recrystallized from warm water (about 0.1 g of yellow-brown solid remained undissolved and was filtered off). The filtrate was concentrated at 50°, and the resulting red-brown crystals were filtered, washed with acetone, and dried in air.

Anal. Calcd for [Co(NH$_2$CH$_2$CH$_2$NHCH$_3$)$_2$(en)]I$_3$ (C): Co, 9.10; C, 14.8; H, 4.32. Found: Co, 9.35; C, 15.0; H, 4.26.

Infrared spectral data are included in Table I. X-Ray diffraction data are 7.34 (0.9), 5.88 (0.2), 5.27 (0.1), 4.82 (0.1), 4.20 (1.0), 1.94 (0.8).

(b) With Sulfuryl Chloride. In an experiment strictly analogous to that described above, [Co(en-H)$_2$(en)]I was treated with excess SO$_2$Cl$_2$ whereupon the red solid became green. After 2 days the SO$_2$Cl$_2$ was removed by filtration and the solid product was dried *in vacuo* for 24 hr.

Anal. Calcd for [Co(en){(en-H)$_2$SO$_2$}]ICl$_2$ (D): C, 14.4; H, 4.41; N, 16.8. Found: C, 14.1; H, 4.89; N, 16.5.

Infrared spectral data are given in Table I. X-Ray diffraction data are 5.84 (1.0), 5.24 (0.8), 4.94 (0.8), 4.41 (0.2), 3.86 (0.6), 3.57 (0.7). This product is stable in air and did not change color over several days; after 2 weeks, however, the color had changed to a darker green.

(c) With Thionyl Chloride. Similarly, 1.0 g of [Co(en-H)$_2$(en)]I was treated with excess SOCl$_2$; the red solid changed at once to a greenish brown color which appeared to darken slowly over 7 days. The orange-red supernatant solution was removed by filtration and the yellow-green solid product was dried *in vacuo* for 24 hr and transferred to a drybox for storage and sampling.

Anal. Calcd for $[\mathrm{Co(en)\{(en\text{-}H)_2SO\}}]\mathrm{ICl_2}$ (E): Co, 12.2; C, 15.0; H, 4.55. Found: Co, 12.7; C, 15.7; H, 4.87.

Infrared spectral data are given in Table I. X-Ray diffraction data are 6.10 (0.4), 5.05 (0.6), 3.98 (0.2), 3.16 (1.0), 2.23 (0.4), 1.95 (0.5). This product was unstable in air and turned dark green when exposed for 2 days.

(d) **With Acetyl Chloride.** In analogous experiments, 0.8 g of $[\mathrm{Co(en\text{-}H)_2(en)}]\mathrm{I}$ was treated with $\mathrm{CH_3COCl}$ for 2 days; the color of the solid changed from red to green. The product was isolated as described above.

Anal. Calcd for $[\mathrm{Co(NH_2CH_2CH_2NHCOCH_3)(NH_2CH_2CH_2NH_3Cl)Cl_2}]\mathrm{I}$ (F): Co, 12.9; C, 15.7; H, 4.17. Found: Co, 12.8; C, 15.0; H, 4.75.

Infrared spectral data are given in Table I. X-Ray diffraction data are 5.37 (0.5), 3.26 (1.0), 3.20 (0.4), 3.09 (0.4), 2.41 (0.4), 2.27 (0.4). This complex also turned dark green on exposure to air, but without change in its infrared spectrum. An aqueous solution of the complex was orange-red, but evaporation and recrystallization resulted in recovery of the original dark green solid. Since the composition given above was not anticipated (*i.e.*, loss of one en ligand), a total halogen determination was attempted after boiling an aqueous solution of the complex for 30 min. The result (49.4%) was somewhat lower than the 51.2% calculated on the basis of three Cl and one I per mole of complex.

Discussion

It has been established that $[\mathrm{Co(en)_3}]\mathrm{I_3}$ reacts in liquid ammonia with 2 molar equiv of amide ion in a manner exactly analogous to the reaction described previously[2] for $[\mathrm{Rh(en)_3}]\mathrm{I_3}$

$$[\mathrm{Co(en)_3}]\mathrm{I_3} + 2\mathrm{KNH_2} \longrightarrow [\mathrm{Co(en\text{-}H)_2(en)}]\mathrm{I} + 2\mathrm{KI} + 2\mathrm{NH_3}$$

As expected, the infrared spectrum of the product is similar in every respect to that of $[\mathrm{Rh(en\text{-}H)_2(en)}]\mathrm{I_3}$, differing only slightly in the band positions. As observed[2] in this latter case, the N–H vibrations decrease in intensity on deprotonation and are poorly resolved. The effect on the Co–N stretching modes is not as clear as was found for the Rh complex. For $[\mathrm{Rh(en)_3}]\mathrm{I_3}$ the doublet at 570 and 558 $\mathrm{cm^{-1}}$ attributed to ν(Rh–N) was observed to change to a single band on deprotonation with a small but definite increase in bond order with each successive step. For $[\mathrm{Co(en)_3}]\mathrm{I_3}$, we assign the strong, sharp triplet at 579, 563, and 556 $\mathrm{cm^{-1}}$ to ν(Co–N) which degrades to a singlet at 571 $\mathrm{cm^{-1}}$ on deprotonation.

It is of interest to note that $[\mathrm{Co(en\text{-}H)_2(en)}]\mathrm{I}$ remained diamagnetic as was the case for the analogous Rh(III) complex. The effect of deprotonation on the ligand field strength is apparently no greater in the Co(III) system than for Rh(III) in which it was required that four protons be removed before a change in paramagnetic susceptibility was observed.[2]

However, attempts to prepare the Co complex analogous to $[\mathrm{Rh(en\text{-}H)_3}]$ failed. This can evidently be attributed to the instability of the Co–en system in the more highly basic solution obtained with the addition of 3 or more equiv of amide ion. A similar result has been observed[8] in strong *aqueous* NaOH solution (15%) in which the characteristic orange color of $[\mathrm{Co(en)_3}]\mathrm{I_3}$ in water slowly changes to a dark red on gentle warming and, if evaporated almost to dryness, a blue Co(II) salt is obtained. The loss of en in liquid ammonia at high amide ion concentrations is therefore not unexpected, and the brown solids obtained were probably mixtures of decomposition products.

It has been stated[9] that the conjugate base of a coordinated amino group might be expected to exhibit a significant tendency to act as a nucleophile toward many different types of reagents. The reactions of the complex, $[\mathrm{Co(en\text{-}H)_2(en)}]\mathrm{I}$, described here are of the general type

$$\mathrm{Co\bar{N}HR} + \mathrm{R'X} \longrightarrow \mathrm{CoNHRR'} + \mathrm{X^-}$$

where X represents a halogen atom and the cobalt complex acts as a nucleophile. The reactants used were $\mathrm{CH_3I}$, $\mathrm{SO_2Cl_2}$, $\mathrm{SOCl_2}$, and $\mathrm{CH_3COCl}$; the reactions involved are shown in eq 1–4.

$$\mathrm{Co(en\text{-}H)_2(en)]I} + 2\mathrm{CH_3I} \longrightarrow [\mathrm{Co(NH_2CH_2CH_2NHCH_3)_2(en)}]\mathrm{I_3} \tag{1}$$

$$[\mathrm{Co(en\text{-}H)_2(en)}]\mathrm{I} + \mathrm{SO_2Cl_2} \longrightarrow [\mathrm{Co\{(en\text{-}H)_2SO_2\}(en)}]\mathrm{ICl_2} \tag{2}$$

$$[\mathrm{Co(en\text{-}H)_2(en)}]\mathrm{I} + \mathrm{SOCl_2} \longrightarrow [\mathrm{Co\{(en\text{-}H)_2SO\}(en)}]\mathrm{ICl_2} \tag{3}$$

$$\mathrm{Co(en\text{-}H)_2(en)]I} + 2\mathrm{CH_3COCl} \longrightarrow [\mathrm{Co(CH_3CONHCH_2CH_2NH_2)(NH_2CH_2CH_2NH_3Cl)Cl_2}]\mathrm{I} + \text{decomposition products} \tag{4}$$

Reaction 1 follows the normal path for the type of nucleophilic reaction expected, with methylation presumably occurring at the coordinated imino groups. Reactions 2 and 3 with sulfuryl chloride and thionyl chloride proceed differently; only 1 mole of reactant adds to the complex with two reactive sites. Reaction 4 is different again, and analytical data for the product suggest loss of one bidentate ligand. The 1 mole of HCl necessarily included to rationalize the analytical data is quite arbitrarily shown in association with the unacetylated en ligand.

The observed infrared absorption bands are listed in Table I and provide evidence for the structural changes expected in the reaction products.

The complex $[\mathrm{Co(NH_2CH_2CH_2NHCH_3)_2(en)}]\mathrm{I_3}$ exhibits a number of bands in the NaCl region of the infrared not present in either $[\mathrm{Co(en)_3}]\mathrm{I_3}$ or $[\mathrm{Co(en\text{-}H)_2(en)}]\mathrm{I}$. The well-defined, medium bands at 3010 and 2960 $\mathrm{cm^{-1}}$ are assigned as the antisymmetric and symmetric stretching modes of $\mathrm{CH_3}$ by comparison with the assignments for $\mathrm{(CH_3)_2NH_2^+I^-}$ made by Ebsworth and Sheppard.[10] Similarly, the medium bands at 1488 and 1405 $\mathrm{cm^{-1}}$ are assigned as the antisymmetric and symmetric bending motions, respectively, and the $\mathrm{CH_3}$ rocking deformation appears at 955 $\mathrm{cm^{-1}}$. The previously unobserved band at 924 $\mathrm{cm^{-1}}$ is attributed to a C–N stretching vibration.[11]

Comparison of the spectra of $[\mathrm{Co(en)_3}]\mathrm{I_3}$ and $[\mathrm{Co\{(en\text{-}H)_2SO_2\}(en)}]\mathrm{ICl_2}$ reveals four main regions of difference near 1500, 1265, 1120, and 620 $\mathrm{cm^{-1}}$; these are attributed to the presence of the $\mathrm{SO_2}$ group. A sharp shoulder appears at 1495 $\mathrm{cm^{-1}}$ which we assign to the NH bending vibration on the basis of assignments made by Watt and Klett[11] at 1460 $\mathrm{cm^{-1}}$ for [Pt(dien)Cl]Cl and by Kraihanzel and Grenda[12] for a series of diacetamide complexes at 1496 to 1508 $\mathrm{cm^{-1}}$. This NH bending vibration could also contribute to some extent

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(8) R. N. Keller and L. J. Edwards, *J. Am. Chem. Soc.*, **74**, 215 (1952).

(9) D. H. Busch, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 11.

(10) E. A. V. Ebsworth and N. Sheppard, *Spectrochim. Acta*, 13, 261 (1959).

(11) G. W. Watt and D. S. Klett, *ibid.*, 20, 1053 (1964).

(12) C. S. Kraihanzel and S. C. Grenda, *Inorg. Chem.*, 4, 1037 (1965).

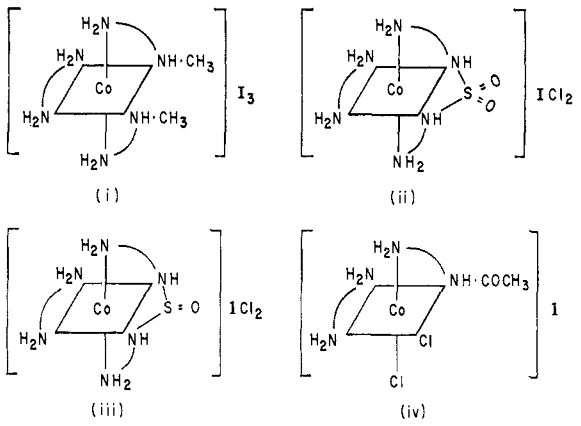
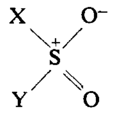


Figure 2. Possible structures for products of reactions of [Co(en-H)$_2$(en)]I.

to the bands at 1488 cm^{-1} observed in the spectrum of the methylated complex. The bands at 1265 and 1129 cm^{-1}, which are extremely intense, are associated with the asymmetric and symmetric stretching vibrations of SO$_2$. These modes have been assigned by Robinson[13] for SO$_2$Cl$_2$ at 1414 and 1182 cm^{-1} and for sulfamide, SO$_2$(NH$_2$)$_2$, at 1350 and 1163 cm^{-1}. A linear correlation was found between $\nu_{\mathrm{asym}}(\mathrm{SO_2})$ and $\nu_{\mathrm{sym}}(\mathrm{SO_2})$ which were found to increase with increasing electronegativities of the groups X and Y in SO$_2$XY. It is seen that $\nu_{\mathrm{asym}}\mathrm{SO_2}$ is considerably lower for the complex than for either SO$_2$Cl$_2$ or SO$_2$(NH$_2$)$_2$, indicating a decrease in the electronegativity of the coordinated imino group with respect to an amino group and a corresponding increase in the N—S bond strength. In the same instance, the S=O bond strength would be expected to decrease and, in the simple cases of SO$_2$XY, this has been attributed[13] partly to an increase in the importance of structures such as



with decreased double-bond character when X and Y are of low electronegativities.

Evidence for the formation of S–N bonds is provided by the very characteristic strong band at 620 cm^{-1} in the spectrum of [Co{(en-H)$_2$SO$_2$}(en)]ICl$_2$ which is tentatively assigned as the ν(S–N) on the basis of assignments made for NH$_3$SO$_3$[14] at 688 cm^{-1} and for SO$_2$(NH$_2$)$_2$[15] at 555 cm^{-1}. However, the assignment of ν(S–N) is often a complex problem as indicated by Lippincott and Tobin[16] for S$_4$N$_4$, since S–N vibrations occur as band combinations over the range 460–790 cm^{-1}. With regard to the Co–N stretching frequencies, there are three bands at 577, 566, and 556 assigned, and these are very close to the same modes of [Co(en)$_3$]I$_3$.

In most respects the spectral characteristics of [Co{(en-H)$_2$SO}(en)]ICl$_2$ are similar to those of the sulfuryl chloride product. The NH bending vibration is observed only as a weak shoulder at 1520 cm^{-1}. A strong band at 1265 cm^{-1} is assigned as the S–O stretching vibration and a medium-strong band at 622 cm^{-1} as ν(S–N). For SOCl$_2$, ν(S–O) has been reported[17] at 1229 cm^{-1}, considerably lower than the observed frequency in the complex. This seems to indicate an increase in S–O bond strength when the two chloride ions are replaced by the deprotonated N atoms of the complex.

The infrared spectrum of [Co(CH$_3$CONHCH$_2$CH$_2$NH$_2$)(NH$_2$CH$_2$CH$_2$NH$_3$Cl)Cl$_2$]I is similar in general to those previously discussed. The important differences occur in the acyl stretching region at 1675 cm^{-1} and in the NH bending region at 1495 cm^{-1}. The bonding of the carbonyl group to a secondary amino group is known[18] to involve a decrease in the acyl stretching frequency with respect to its position for CH$_3$COCl at 1790 cm^{-1}. For comparison, ν(C=O) for acetamide occurs at 1675 cm^{-1} so that there is no doubt that an amide link has been formed in the reaction. The sharp, strong band at 1495 cm^{-1} is assigned to the NH bending mode in agreement with assignments made[18] for secondary amides. It would be expected that Co–Cl stretching vibrations should appear in the region 300–400 cm^{-1}. However, the spectrum was poorly resolved in this region, and no assignments could reasonably be made.

Although direct evidence bearing upon the structures of these products is not yet available, suggested structures are shown in Figure 2. The sulfur-containing products are of interest since the observed stoichiometry appears to require bridged structures such as ii and iii. It follows that the deprotonated N atoms in [Co(en-H)$_2$(en)]I must be *cis* to each other during the final step of the reaction with, for example, SOCl$_2$. However, such a reaction need not occur as a single step in which the anionic sites are initially in *cis* positions. Reaction at one of the deprotonated sites may occur first and then, since basic deprotonation and thus exchange is rapid, a second site may be generated *cis* to the first position of attachment of the sulfur species.

The situation concerning the structures of the CH$_3$I and CH$_3$COCl reaction products is even less clear because there is no possibility of bridging reactions affecting the anionic site positions. The assumption of *cis*-N-methyl groups in structure i is therefore purely speculative.

However, some basis for this postulate is found by considering the acetyl chloride reaction. The apparent loss of en during this reaction seems to indicate a *cis* configuration of anionic sites in the final reaction step where steric interaction between the bulky acetyl groups could account to some extent for loss of one of the en molecules. Inductive factors should also have some effect in this loss, and it has been shown[19] that a reaction of the type

$$\mathrm{Pd(NH_2CH_2CH_2S)_2 + 2CH_3I \longrightarrow Pd(NH_2CH_2CH_2SCH_3)I_2}$$

occurs with the Pd(II) mercaptoamine complexes. Here the donor ability of the S atom is impaired to such an extent by formation of the thioether that 1 mole of ligand is replaced by iodide ions. Similarly, the forma-

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(13) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).

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(16) E. R. Lippincott and M. C. Tobin, *J. Chem. Phys.*, **31**, 1559 (1953).

(17) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **39**, 2171 (1961).

(18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 205.

(19) D. H. Busch, J. A. Burke, D. C. Jicha, M. C. Thompson, and M. L. Morris, ref 9, p 125.

tion of the amide grouping, $-NHCOCH_3$, should decrease the donor ability of the N atom resulting in loss of 1 mole of en to give structure iv. The presence of an extra HCl indicated by the analytical data could then be accounted for by association through H bonding to one of the donor N atoms or by formation of an adduct as in the well-known complex *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl$.

There appears, therefore, to be some support for structures i and iv in the formation of which reactions are assumed to occur at two anionic sites in *cis* positions which could be initially present in $[Co(en\text{-}H)_2(en)]I$ or might be formed by anionic site migration during the reactions.

Acknowledgments. This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

The Oxidation of *p*-Hydroxymethylbenzoatopentaamminecobalt(III) by One-Electron Oxidizing Agents

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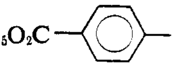
Abstract: In the oxidation of *p*-hydroxymethylbenzoatopentaamminecobalt(III) by Ce(IV) in perchloric acid medium and by Co^{3+} in perchloric and sulfuric acid media both $[Co(NH_3)_5O_2C$—  —$CHO]^{2+}$ and Co^{2+} are formed (with free *p*-formylbenzoic acid accompanying the latter product). The ratio of the Co(III) product to Co^{2+} ("product ratio") increases with the concentration of Ce(IV) when this is low but reaches a limiting value of about 1.2 at 25° when the Ce(IV) concentration is increased. The product ratio is not affected by the presence of O_2 when "saturation" with respect to Ce(IV) is reached, but it is increased by O_2 at low Ce(IV) concentration. The observations are interpreted on the basis that two radical intermediates are formed. For one of these, the external oxidant can interfere with internal electron transfer (the latter process gives rise to Co^{2+}), but for the other, internal electron transfer is so rapid that reaction with external oxidants does not compete effectively with it.

Other work[1-3] has shown that when the ligand L^- in a complex of the type $Co^{III}(NH_3)_5L^-$ is oxidized by an external one-electron oxidizing agent, the Co(III) center may be reduced. When reduction of the Co(III) center does take place, it is of interest to learn whether the internal oxidizing agent Co(III) and the external oxidizing agent act in concert, or whether rate-determining attack by the external oxidizing agent takes place followed then by internal electron transfer. In the latter event an intermediate $Co^{III}(NH_3)_5L\cdot$ would be formed, and competition between the processes 1 and 2 might be expected.

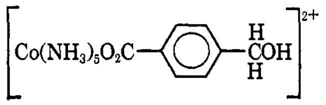
$$Co^{III}(NH_3)_5L\cdot \longrightarrow Co^{2+} + L^+ + NH_4^+ \tag{1}$$

$$Co^{III}(NH_3)_5L\cdot \longrightarrow Co^{III}(NH_3)_5L^+ + e^- \tag{2}$$

Equation 2 represents attack on the intermediate by an external oxidizing agent (which may but need not be the oxidizing agent used to generate the intermediate) preserving the oxidation state of Co(III). No evidence for successful competition of a process such as 2 against process 1 was found in the oxidation of coordinated oxalate[2] by Ce(IV), but the competition studies[3] on the reaction of MnO_4^- with $Co(NH_3)_5O_2CH^{2+}$ provided clear-cut evidence for the formation of an intermediate in this case.

These reactions become particularly interesting when the ligand L^- bears an oxidizable group located at some distance from the carboxyl coordinated to Co(III). If a radical intermediate is formed, the ratio k_2/k_1 can be measured for a particular external oxidizing agent. It is of interest to compare these ratios for various locations of the oxidizing group. Measurements of this type can be considered to be complementary to those which have been done with reducing agents, attempting to reduce the Co(III) center by "remote attack." They can in principle be carried a step further so as to yield the actual value of k_1, which is of course of interest in itself as measuring the rate of internal electron transfer. When the ratio k_2/k_1 is determined for a particular external oxidizing agent, and k_2 can be measured or estimated, k_1 can then be calculated. The strategy would be to use for the determination of k_2/k_1 not necessarily the one-electron oxidizing agent used for primary attack on the oxidizable ligand but one for which k_2 has been independently estimated.

We turned to the one-electron oxidation of



$$\left[Co(NH_3)_5O_2C-C_6H_4-\overset{H}{\underset{H}{C}}OH\right]^{2+}$$

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(1) P. Saffir and H. Taube, *J. Am. Chem. Soc.*, 82, 13 (1960).

(2) R. T. M. Fraser and H Taube, *ibid.*, 82, 4152 (1960).

(3) J. P. Candlin and J Halpern, *ibid.*, 85, 2518 (1963).