CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305

The Preparation and Properties of Some Pentaamminecobalt(III) Complexes

BY R. B. JORDAN, A. M. SARGESON, AND H. TAUBE

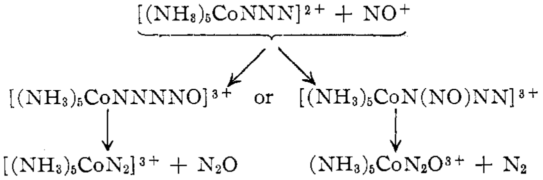
Received November 16, 1965

The nitrosation of the $Co(NH_3)_5N_3^{2+}$ ion leads to the preparation of some novel cobalt(III) pentaammine complexes, namely $[Co(NH_3)_5(py)]^{2+}$, $Co(NH_3)_5NCR^{3+}$, and $Co(NH_3)_5OCH_3^{2+}$. Some of these were prepared directly, others through $[Co(NH_3)_5OP(OC_2H_5)_3]^{3+}$ as an intermediate. The reactivity of the complexes in aqueous solution and reduction by Cr^{2+} ion are discussed, and some attempts to coordinate N_2 are also described.

Introduction

In a recent publication, Haim and Taube[1] proposed that the nitrosation of the $[Co(NH_3)_5N_3]^{2+}$ ion occurs by the addition of NO^+ to the terminal nitrogen leading to an intermediate of the form $[Co(NH_3)_5NNNNO]^{3+}$ (Scheme I), which immediately decomposes to yield N_2, N_2O, and $[Co(NH_3)_5OH_2]^{3+}$. This assumption receives some support from the fact that NNNNO[2] is formed when N_3^- reacts with NO^+.

SCHEME I
THE POSSIBLE MODES OF ADDITION OF NO^+ TO COORDINATED AZIDE ION



In the reaction of $[Co(NH_3)_5N_3]^{2+}$ with NO^+, there is the possibility that the N_2 formed when the coordinated N_4O decomposes remains coordinated to the metal ion for a finite length of time. It is also possible that NO^+ does not attack the terminal nitrogen of the azide, but the nitrogen coordinated to the metal ion. Since the Co–N–N angle (as determined[3] for $[Co(NH_3)_5N_3](N_3)_2$) is 125°, this mode of attack is not out of the question. The research which we are describing was initiated to check on these possibilities, by searching for a time lag in the liberation of N_2 compared to that of N_2O (see Scheme I). Though we have succeeded only in showing that an intermediate, if formed, does not persist longer than several seconds, we feel our research on this problem is nevertheless worth describing. The possibilities we considered deserve further exploration, and what we have done may guide others who become interested in the question.

A second theme which we pursued in our work was to exploit the fact that the reaction of NO^+ with coordinated azide does produce a good leaving group in preparing some novel complexes of the pentaamminecobalt(III) series. They are the complexes with triethyl phosphate, CH_3O^-, pyridine, or nitriles as the heteroligands. At the time of our work, the preparation of none of these complexes as pure solid phases had been described; since then, the pyridine complex has been prepared by direct reaction with aquopentaamminecobalt(III) in DMF as solvent.[4,5]

Experimental Section

(A) **Preparation of Starting Materials.**—$[Co(NH_3)_5N_3]Cl_2$[6] was converted to the perchlorate using silver acetate, then sodium perchlorate to crystallize the complex. The complex gave a sharp azide absorption at 2060 cm^{-1}. $[Pt(dtn)N_3]NO_3$ (dtn = diethylenetriamine) and $K_3[Co(CN)_5N_3]$ were prepared by the methods described in the literature.[7,8]

$[Ru(phen)_2(py)N_3]Cl$ (phen = 1,10-phenanthroline, py = pyridine) was prepared by bringing into reaction $[Ru(phen)_2(py)Cl]Cl$[9] (1.22 g) with NaN_3 (0.14 g) in water (20 ml) at 50° for 30 min. The cooled solution was filtered and the $[Ru(phen)_2(py)N_3]I$ complex precipitated with NaI. This salt was then treated with excess AgCl in warm water (20 ml), the solution was filtered and evaporated to ~5 ml at room temperature, and the $[Ru(phen)_2(py)N_3]Cl$ salt crystallized out with LiCl. The resulting complex was then recrystallized from alcohol with ether. The infrared spectrum showed a sharp azide absorption at 2020 cm^{-1}.

Anal. Calcd for $[RuC_{29}H_{21}N_8]Cl\cdot 3H_2O$: C, 51.82; H, 4.05; N, 16.67; Ru, 15.04. Found: C, 51.62; H, 4.00; N, 17.0; Ru, 15.1.

(B) **The Nitrosation Experiments.**—The azido complex (5×10^{-4} to 10^{-3} mole) was dissolved in water (50 ml) and the appropriate amount of solid $NaNO_2$ added. The mixture was deaerated with He and excess acid, usually 1 ml of 10 *N* $HClO_4$ or HCl, added with a syringe through a syringe cap. The gas evolved (10–25 cc) was repeatedly sampled (5 sec, 10–15 sec, 30 sec, 1 min) with a Hamilton gas syringe (5 cc) and the sample injected into a gas chromatograph at 25° containing a column (10 ft   0.25 in.) filled with *sec*-butyl phthalate absorbed on Chromosorb P (80–100 mesh) using He as the carrier gas. The experiments were carried out in a vessel with only a small space above the solution (~10 cc) and the helium flow rate varied from 0 to 200 cc/min. The gas escaped through a syringe needle which was varied in size depending on the He flow rate.

Since in most experiments the gases evolved were diluted with He, a 5-cc sample was collected. The He flushed both N_2 and N_2O out of the aqueous solution.

Several complexes, namely $[Co(NH_3)_5N_3]^{2+}$, $[Pt(dien)N_3]^+$, $[Ru(phen)_2(py)N_3]^+$, and $[Co(CN)_5N_3]^{3-}$, were used in the attempt to retain either N_2 or N_2O fixed in the first coordination sphere of a metal ion. In all cases, the gases N_2 and N_2O were observed to be liberated in equivalent amount except for the first

---

[1] A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).
[2] H. W. Lucien, *J. Am. Chem. Soc.*, **80**, 4458 (1958).
[3] G. J. Palenik, *Acta Cryst.*, **17**, 360 (1964).
[4] E. Gould, private communication.
[5] F. Nordmeyer, private communication.
[6] M. Linhard and H. Flygare, *Z. Anorg. Allgem. Chem.*, **262**, 328 (1950).
[7] F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).
[8] J. Fujita and Y. Shimura, *Bull. Chem. Soc. Japan*, **36**, 1281 (1963).
[9] F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Australian J. Chem.*, **16**, 544 (1963).

sample taken at 5 sec. For this sample, the concentration of N_2 was slightly greater than that of N_2O, but a small lag in this direction is expected because of the higher solubility of N_2O compared to N_2. Even when the experiment was carried out in a solvent less nucleophilic than water, namely CH_3CO_2H–$(CH_3CO)_2O$, both N_2 and N_2O were released together, except that N_2O again slightly trailed N_2.

The resolution time of our method is of course not short, and our experiments by no means prove that a complex containing N_2 bound for a finite time is not formed by the reactions we have tried. The failure to observe delay in the liberation of N_2 in the reaction of $[Ru(phen)_2(py)N_3]^+$ is especially noteworthy in the context of the report which has been made of the preparation of N_2 complexes of Ru(II) ammines.[10]

(C) Preparation and Characterization of Some Complexes of the Pentaamminecobalt(III) Class.—The success of the different preparative procedures to be described depends on keeping the water content of the systems low. Water is more nucleophilic than most of the ligands featured in this part of our work, and if it is present $[Co(NH_3)_5OH_2]^{3+}$ is the major product. Several preparative routes are open meeting the condition on water content and making use of the azide–NO^+ reaction to labilize the sixth coordination position.

(1) Nitrosyl perchlorate can be used in reaction with $[Co(NH_3)_5N_3]^{2+}$ in a solvent such as glacial acetic acid or methanol. When NOCl is used, the product is mainly $[Co(NH_3)_5Cl]^{2+}$.

(2) An alkyl nitrite together with a strong noncomplexing acid can be used in some instances in place of nitrosyl perchlorate. This is a possible method of preparing a variety of alcohol complexes. The success of the reactions in alcohols depends on the relative rate of reaction of NO^+ with the complex compared with the alcohol.

The details of the preparations of the complexes and some of their properties are herewith described.

$[Co(NH_3)_5OP(OC_2H_5)_3](ClO_4)_3$.—$[Co(NH_3)_5N_3](ClO_4)_2$ (0.4 g), dissolved in $OP(OC_2H_5)_3$ (3–4 ml of dry solvent) was treated with excess solid $NOClO_4$.[11] After about 10 min the clear solution was filtered and excess dry ether added to it with rapid stirring. The complex precipitated and crystallized and was filtered off and dried in a vacuum desiccator for 24 hr. The extinction coefficients of the product, ϵ 46 at 515 mμ and ϵ 39 at 350 mμ, are similar to those reported by Schmidt and Taube[12] for the trimethyl ester, ϵ 46.3 at 520 mμ and ϵ 39.2 at 350 mμ.

Anal. Calcd for $[Co(NH_3)_5PO_4C_6H_{15}](ClO_4)_3$: C, 11.54; H, 4.84; N, 11.21. Found: C, 10.8; H, 4.7; N, 11.4.

The proton nmr spectrum for the ion is presented in Figure 1. The pattern for the methylene protons is superimposed on the broad band arising from the ammonia protons. The pattern reveals splitting of the absorption for the methylene protons also by P ($I = {}^1/_2$) and can be understood as resulting from the superposition of two quartets, as shown in Figure 1.

The coordinated phosphate ester is more labile to substitution than is water in the same position, and the ester complex was used to prepare the methoxo, pyridine, and some nitrile complexes. We have evidence that CH_3NCS and CH_3SCN also replace the ester molecule from the coordination sphere, but the resulting products were not characterized.

The compound $[Co(NH_3)_5OP(OC_2H_5)_3](ClO_4)_3$ is soluble in acetone, methanol, and ethanol; the tri(*n*-butyl) derivative is even more soluble and sensitive to substitution.

$[Co(NH_3)_5OCH_3](ClO_4)_2$.—Triethylphosphatopentaamminecobalt perchlorate (0.3 g) was dissolved in dry methanol (5 ml) and excess solid $NaOCH_3$ was added. A pink crystalline solid formed which was filtered off, washed with dry ether, and dried in a vacuum desiccator.

Anal. Calcd for $[Co(NH_3)_5OCH_3](ClO_4)_2$: C, 3.21; H, 4.85; N, 18.73. Found: C, 3.1; H, 4.7; N, 18.7.

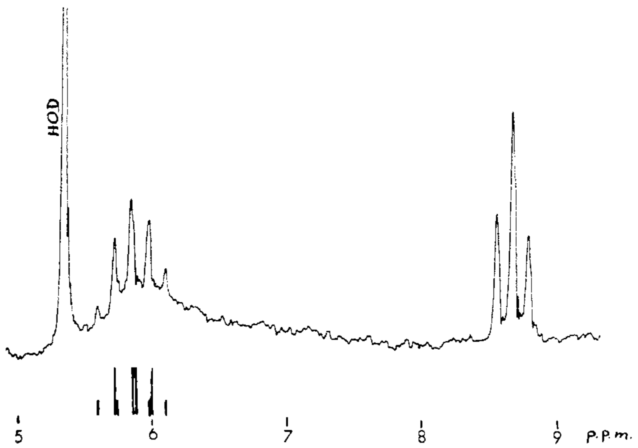


Figure 1.—The 60-Mc nmr spectrum of $[Co(NH_3)_5OP(OC_2H_5)_3](ClO_4)_3$ in D_2O, D_2SO_4 (0.1 *M*) relative to sodium trimethylsilylpropanesulfonate as internal standard (P.E.R. 10 spectrometer).

The proton nmr spectrum in D_2O shows a broad CH_3 peak at 3.05 ppm relative to tetramethylsilane (external) and the signal sharpens and moves downfield to 3.58 ppm on the addition of D^+. The broad signal further downfield is due to the coordinated NH_3 groups. As the solution is kept, a peak at 3.85 ppm develops at the expense of the 3.58 ppm peak. The absorption at 3.85 ppm is caused by free CH_3OH. The rate at which the coordinated methanol was replaced by D_2O was followed in the nmr spectrometer (A60) at 35° in 1.8 *M* D_2SO_4. Some of these results are given in Figure 2; they show the release of the coordinated CH_3OH and its appearance in the solvent. Under these conditions a first-order plot of log (peak height) against time is obtained both for the "appearance" and "disappearance" signals and the half-life of the process is 50 min at 35°. From a similar measurement in more dilute D^+ (pH $\sim$3) the half-life was $\sim$2 hr, so it would seem that the hydrolysis has an acid-dependent path. This reaction is now being examined in more detail. The rate at which the methoxide ion is replaced by water was not explored but the process is not rapid ($t_{1/2} >$ 30 min).

The acid dissociation constant for the methanol complex was measured. We found $pK_a^{20°} = 5.58 \pm 0.03$ at $\mu = 0.1$, a value not greatly different from that of the corresponding aquo complex. The extinction coefficients for both ions are also similar; for $[Co(NH_3)_5CH_3OH](ClO_4)_3$ at 494 mμ, ϵ is 49, at 345 mμ, ϵ is 50; for $[Co(NH_3)_5OH_2](ClO_4)_3$ in 0.1 *M* $HClO_4$ at 494 mμ, ϵ is 48.5, at 347 mμ, ϵ is 44; for $[Co(NH_3)_5OCH_3](ClO_4)_2$ in water ϵ is 75 at 510 mμ and 81 at 370 mμ.

Nitrilopentaamminecobalt(III) Perchlorates.—The nitrile compounds were made in two ways: by the nitrosation of the azido complex in the nitrile of choice as solvent, and by the reaction of the phosphate ester complex with the nitrile. All of the nitriles resemble $[Co(NH_3)_6](ClO_4)_3$ in appearance and the coordinated nitrile appears to undergo little replacement by water over several days time in both acid and dilute alkali. The malonodinitrile may be an exception. The methylene protons are quite acidic (pK $\sim 9 \pm 1$) compared to that for the free ligand[13] (pK = 11.2). A solution of the salt in water gives an intense red color when OH^- is added, but this changes rapidly to a yellow color, similar to that of the original solution. Corresponding to the development of the red color, the optical density at the maximum more than doubled and the band at 465 mμ moved to 530 mμ. Within 8 min this band had disappeared; though the colors are similar, the spectrum of the final solution is not identical with that of the solution before alkali was added. The secondary reaction interfered with the attempt to measure pK_a of the complex, but it was not investigated further.

$[Co(NH_3)_5NCCH_3](ClO_4)_3$.—$[Co(NH_3)_5N_3](ClO_4)_2$ (0.5 g) was

---

[10] A. D. Allen and C. V. Senoff, *Chem. Commun.*, **24**, 621 (1965).

[11] G. Brauer, "Handbuch der Preparativen Chemie," F. Enke Verlag, Stuttgart, 1954, p 253.

[12] W. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963). Note that S. and T. did not prepare a pure solid phase containing the complex.

[13] R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

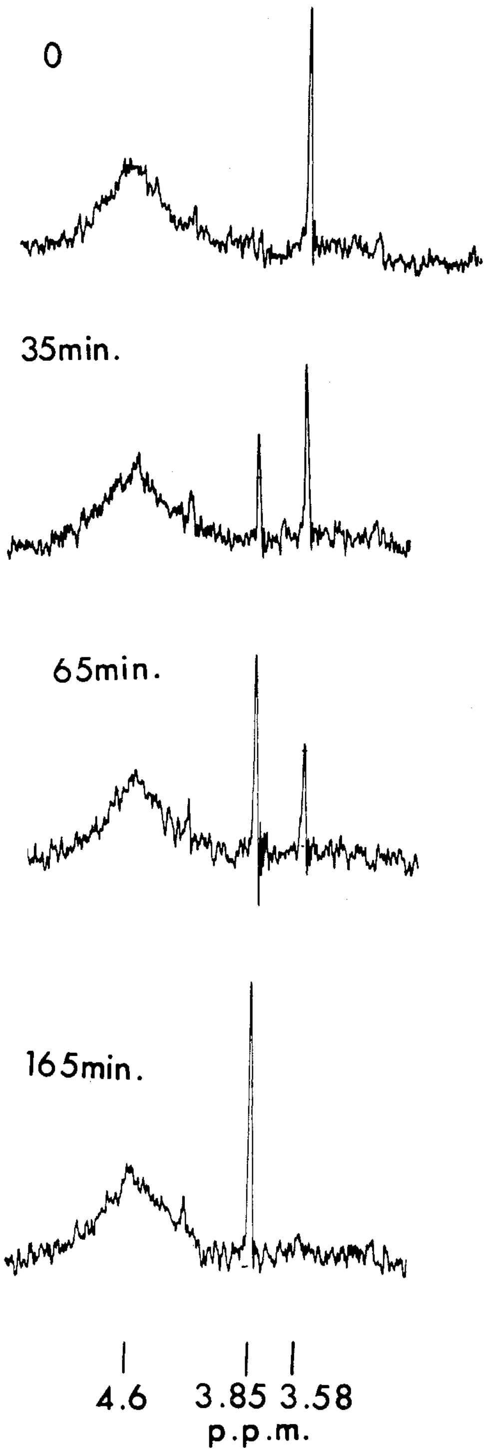


Figure 2.—The exchange of coordinated methanol with D_2O as shown by 60-Mc nmr spectra of $[Co(NH_3)_5OCH_3](ClO_4)_2$ in D_2O, D_2SO_4 (1.8 *M*) relative to tetramethylsilane as external standard (Varian A60 spectrometer, temperature 35°, times are measured from the first sample as zero).

suspended in CH_3CN (5 ml) and excess $NOClO_4$ added. There was a vigorous reaction following which the yellow-orange nitrile complex was precipitated with ether and then redissolved in water and recrystallized by adding concentrated $HClO_4$. The infrared spectrum showed a sharp absorption at 2320 cm^{-1} attributed to the C≡N stretching mode. The extinction coefficients in water are 57 at 465 mμ and 53 at 330 mμ and were unaltered in 0.1 *M* $HClO_4$.

Anal. Calcd for $[Co(NH_3)_5NCCH_3](ClO_4)_3$: C, 4.97; H, 3.75; N, 17.38. Found: C, 5.3; H, 3.8; N, 17.4.

$[Co(NH_3)_5NCCH{=}CH_2](ClO_4)_3$.—This compound was prepared by dissolving $[Co(NH_3)_5OP(OC_2H_5)_3](ClO_4)_3$ in acrylonitrile and heating the mixture at 50° until it turned yellow. The nitrile complex was isolated as above and the extinction coefficients were ϵ 69 at 470 mμ and ϵ 75 at 330 mμ.

Anal. Calcd for $[Co(NH_3)_5NCCH{=}CH_2](ClO_4)_3$: C, 7.27; H, 3.66; N, 16.96. Found: C, 7.4; H, 3.5; N, 17.1.

$[Co(NH_3)_5NCCH_2CH_2CH_2C(CH_3){=}CH_2](ClO_4)_3$.—This compound was prepared and isolated in the same manner as the acrylonitrile complex.

Anal. Calcd for $[Co(NH_3)_5C_7H_{11}N](ClO_4)_3$: C, 15.24; H, 4.75; N, 15.24. Found: C, 15.6; H, 4.8; N, 15.1.

$[Co(NH_3)_5NCCH_2CN](ClO_4)_3$.—The complex with malonodinitrile as ligand was also prepared by the method used for the acrylonitrile complex. The extinction coefficient is 84 at the first maximum in the long wavelength region of the spectrum appearing at 465 mμ.

Anal. Calcd for $[Co(NH_3)_5NCCH_2CN](ClO_4)_3$: C, 7.08; H, 3.37; N, 19.28. Found: C, 7.0; H, 3.4; N, 19.1.

$[Co(NH_3)_5NC_5H_5](ClO_4)_3$.—$[Co(NH_3)_5N_3](ClO_4)_2$ (0.3 g) in $OP(OC_2H_5)_3$ (5 ml) was mixed with excess $NOClO_4$. The reaction was allowed to continue until the azide was eliminated and then dry pyridine (1 ml) was added and the mixture warmed at 50–60° for 12 hr. Ether was added, whereupon the complex separated as an oil. The oil was washed with more ether and was finally redissolved in a minimum of water, and the pyridine complex was crystallized by adding concentrated $HClO_4$. The complex was recrystallized from NaOH (0.1 *M*) at 20° by adding $NaClO_4$. This procedure was used to eliminate pyridinium perchlorate from the product. The complex was finally washed with alcohol and ether and dried in a vacuum desiccator. The extinction coefficients were 46 at 480 mμ and 39 at 340 mμ. The pyridine absorption bands appear in the complex charge-transfer band region at 255, 260, and 265 mμ with $\epsilon \sim 5 \times 10^{-4}$.

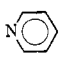
Anal. Calcd for $[(Co(NH_3)_5NC_5H_5](ClO_4)_3$: C, 11.51; H, 3.87; N, 16.12. Found: C, 11.3; H, 4.2; N, 16.0.

The Reaction with Cr^{2+} of the N-Coordinated Complexes.—As part of a search for ligands which lead to a slow rate of attack, a brief study was made of the rate at which Cr^{2+} reacts with some of the complexes which we prepared. In studying mediation in electron-transfer reactions by various bridging groups, it is an advantage to have ligands which limit the complex to a slow rate of reduction by adjacent attack. The method we used in this part of our work is substantially that described by Svatos and Taube.[14] The compound $[Co(NH_3)_5CN](ClO_4)_2$ was prepared as described by Siebert.[15]

The results of the experiments are shown in Table I. Our

TABLE I

THE RATE OF REACTION WITH Cr^{2+} OF NITRILO AND RELATED PENTAAMMINECOBALT(III) COMPLEXES
[$(HClO_4)$ = 1*M*; temperature 25°]

Heteroligand	$(Co(III))_0$ × 10^2, *M*	$(Cr^{2+})_0$ × 10^2, *M*	*k*, M^{-1} sec^{-1}
CN	0.08	0.08	100 ± 20 (2)[a]
$NCCH_3$	0.10	1.07	1.7×10^{-2} (1)[a]
$NC{-}CH{=}CH_2$	0.10	2.14	2.9×10^{-2} (1)[a]
$NC{-}CH_2{-}CN$	0.07	2.14	>10 sec^{-1}[b] (4)[a]
	0.10	3.22	4×10^{-3}

[a] Figures in parentheses indicate the number of rate measurements carried out. [b] The reaction in this case is complete; see text.

---

(14) G. Svatos and H. Taube, *J. Am. Chem. Soc.*, **83**, 4172 (1961).

(15) H. Siebert, *Z. Anorg. Allgem. Chem.*, **327**, 63 (1964). The compound was formulated by Siebert as having C coordinated to Co(III), but the evidence in support of this is by no means conclusive. The comparison of the spectrum observed for $Co(NH_3)_5CN^{2+}$ (ϵ 44 at the long wavelength maximum at 440 mμ) with that which we have observed for $Co(NH_3)_5NCCH_3^{3+}$ does not settle the matter, because the change expected in converting $-NC^-$ to $-NCCH_3$ as ligand cannot be predicted with confidence.

measurement for $[Co(NH_3)_5CN]^{2+}$ is consistent with that reported by Espenson and Birk[16] at 15°. Their value of 61 ± 6 M^{-1} sec^{-1} in combination with ours leads to $\Delta H^* \approx 9$ kcal mole^{-1} and $\Delta S^* \approx -30$ eu.

It is clear that acetonitrile, acrylonitrile, and pyridine as heteroligands lead to much lower rates of reduction than does a typical carboxylate, such as acetate. The nitrogen bound to the Co(III) center is less open to attack by Cr^{2+} than is at least one of the oxygens in the carboxylate complex. The spectra of the Cr(III) products in fact suggest that the ligand is not transferred in the case of the three nitrogen-containing ligands just mentioned. Though we are probably dealing there with an outer-sphere reaction, the rate is somewhat higher than it is for $[Co(NH_3)_6]^{3+}$. For the latter ion k has been reported[17] as 0.9×10^{-4} M^{-1} sec^{-1} at $\mu = 0.4$ and 25°.

The reduction of the complex with malonodinitrile as the ligand is very rapid, and the reduction phase is followed by at least two other processes, as judged by the changes in extinction with time. That the initial rapid phase corresponds to reduction was proven by quenching the reaction mixture with air quickly after mixing, whereupon analysis showed Co^{2+} to be present in substantial amounts. Ligand transfer does occur in this case. We do not understand the nature of the subsequent changes, but the system seems particularly interesting to us because there is the possibility of attack by Cr^{2+} at the carbon of the ligand.

Acknowledgment.—Support of this research by the Atomic Energy Commission, Contract No. AT(04-3)-326, is gratefully acknowledged.

---

[16] J. H. Espenson and J. P. Birk, *J. Am. Chem. Soc.*, **87**, 3280 (1965).

[17] A. Zwickel and H. Taube, *ibid.*, **83**, 793 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, STANFORD, CALIFORNIA 94305, AND THE BIOLOGICAL INORGANIC
CHEMISTRY UNIT, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA, AUSTRALIA

Oxygen Tracer Studies on the Reaction of Cyanate Ion with Aquo and Diaquo Cobalt Ammines, and on the Nitrosation of Carbamatopentaamminecobalt(III)

BY ALAN M. SARGESON AND HENRY TAUBE

Received January 17, 1966

The reaction of $Co(NH_3)_5OH_2^{3+}$ with NCO^- takes place to form the carbamato complex as an intermediate. Oxygen tracer studies on the reaction of the carbamato complex with nitrous acid prove that the Co–O bond remains intact in the reaction of the aquopentaammine complex with NCO^-. The mechanism of the nitrosation of the carbamato complex is such that it leads to 80% Co–O bond rupture. The competition of Cl^- and H_2O for the presumed intermediate $Co(NH_3)_5^{3+}$ is discussed. The reaction of NCO^- with $Co(en)_2(OH_2)_2^{3+}$ leads to $Co(en)_2CO_3^+$ as product. Oxygen tracer studies on the reaction of this product with acid show that one of the two oxygen atoms in the chelate ring is derived from NCO^-, the other from the aquo complex, and the remaining oxygen in the complex is derived from the solvent.

Introduction

The substitution of NCO^- in cobalt(III) ammine complexes has been examined previously by Linhard and Flygare[1] in the course of an extensive study of the spectral properties of the halo and pseudo-halo Co(III) ammine compounds. These authors noted that the spectra of the supposed cyanato compounds were not related to those of the halogen compounds and that NCO^- was not detected when the Co(III) complexes were decomposed. They suggested from these results and their analytical data that NCO^- substituted by addition to the coordinated water or more likely by the addition of HNCO to the hydroxo complex, giving the corresponding carbamato complex. In this way $Co(NH_3)_5O_2CNH_2^{2+}$ and $Co(NH_3)_4(OH_2)O_2CNH_2^{2+}$ were prepared; the latter ion, however, eventually hydrolyzes to the $Co(NH_3)_4CO_3^+$ ion.

The present investigation was carried out to test these proposals and to attempt to establish the mechanism of the reactions by means of tracer experiments. Nitrosation suggested itself as a convenient possibility for the workup of the carbamate complex. It proved to be well suited to our needs and the interest in the reaction itself grew so that it became the dominant theme of this part of our work.

The experiments divided naturally into two parts: (a) those concerning the pentaammine complex and (b) those dealing with a tetraammine system and its subsequent hydrolysis, and they will be dealt with in that order.

A. The Reaction of NCO^+ with $Co(NH_3)_5OH_2^{3+}$; Mechanism of Nitrosation of the Carbamato Complex

Experimental Section

Preparations.—$[Co(NH_3)_5O_2CNH_2](ClO_4)_2$ was prepared essentially by the method of Linhard and Flygare.[1] $[Co(NH_3)_5OH_2](ClO_4)_3$ (14 g) added to water (40 ml at 60°) was stirred rapidly until the complex dissolved.

NaNCO (2 g) was added and the mixture cooled to 25° over 30 min. The complex which formed was recrystallized rapidly from warm water with $NaClO_4$. The salt was collected and washed with methanol and dried in a vacuum desiccator for 12 hr. The extinction coefficient ϵ was 60 at 505 mμ. *Anal.* Calcd for $[Co(NH_3)_5O_2CNH_2](ClO_4)_2$: C, 2.98; H, 4.25; N, 20.85; ClO_4, 49.4. Found: C, 3.15; H, 4.16; N, 20.98; ClO_4, 50.5.

The sparingly soluble dithionate salt was prepared by dissolving the perchlorate in a minimum of water and adding excess

---

[1] M. Linhard and H. Flygare, *Z. Anorg. Chem.*, **251**, 25 (1943).