solubilities combined with the fact that the solid phase is almost certainly $Pb(NO_3)_2$[21] suggests that even an undissociated soluble lead nitrate complex is improbable and that only the positively charged complex $Pb(NO_3)^+$ is formed. The extremely low adsorption of lead in both nitric acid and ammonium nitrate solutions thus almost surely is not due to the existence of appreciable concentrations of negatively charged complexes in the aqueous phase.

There appears to be little evidence for the formation of either neutral or negatively charged bismuth nitrate complexes. The solubility data on bismuth oxynitrate appear inconclusive since on the basis of these data formation of nitrate complexes has been postulated by Smith[22] and challenged by Swinehart and Garrett.[23] However, the anion-exchange results appear to be conclusive that negatively charged nitrate complexes of Bi(III) are formed to some extent ($Bi(NO_3)_4^-$?). However, the fraction of bismuth in the form of a negatively charged complex cannot be determined since an adsorption maximum does not exist in the ammonium nitrate solutions and since the meaning of the maximum in nitric acid solutions is in doubt.

In an earlier paper,[3] a striking parallel between solvent extraction by ethers and anion-exchange adsorbability was discussed and it was pointed out that solvent extraction from chloride solutions might occur most readily if the extracted species has the formula MCl_4^-. The postulated complexes for HCl solutions of Pb(II) and Bi(III) (with charge more negative than minus one) are in agreement with these earlier conclusions since negligible solvent extraction is found for these elements.[24] Moderate extraction of Bi(III) from nitric acid solutions has been found,[25] which would indicate that these considerations relating anion-exchange and solvent extraction are also applicable for nitrate solutions. However, in this extension caution appears indicated since slight extraction from nitric acid solutions has also been reported for Pb(II)[25] where solvent extraction apparently could not proceed by the same mechanism.

Acknowledgment.—The authors are greatly indebted to Mrs. L. W. Magnusson, Jr., for valuable technical assistance.

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OAK RIDGE, TENN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. VI. Formation of Nitrito- and Nitrocobalt(III) Complexes. O-Nitrosation[1, 2, 3]

BY RALPH G. PEARSON, PATRICK M. HENRY, JOHN G. BERGMANN AND FRED BASOLO

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The mechanism of formation of nitro derivatives in the case of aquopentamminecobalt(III) and *cis*-nitroaquobis-(ethylenediamine)-cobalt(III) ions in weakly acid solutions of nitrite ion is shown to involve first a nitrosation to the nitrito complex which then rearranges to the nitro complex in an intramolecular process. The nitrosation is generally rapid but may become rate determining at low nitrous acid concentrations. Nitrosation follows the rate law, rate = k[hydroxo complex] [nitrous acid]^2 similar to that found for amines. It is suggested that N_2O_3 is the active agent which forms the nitrito complex wihout breaking the cobalt–oxygen bond.

In an earlier paper[4] we reported the rates of formation of dinitro complexes from *cis*- and *trans*-nitroaquobis-(ethylenediamine)-cobalt(III) ions at 35° in aqueous solution with a ratio of nitrite ion to nitrous acid of 100 to 1 and with varying nitrite ion concentration. It was initially assumed that formation of the unknown nitrito (Co–ONO) complexes either did not occur or that they rearranged very rapidly to the nitro form ($Co–NO_2$). An interesting result was that the rate of the reaction increased with nitrite ion concentration for low concentrations but became independent of nitrite ion at high concentrations. This result was at one time thought to indicate an S_N1 mechanism in which the limiting rate was equal to the rate of dissociation of water from the aquo complex.[5]

A similar study was then undertaken with the aquopentamminecobalt(III) ion and nitrite ion. Very similar results were obtained except that the rate of formation of the nitro complex never quite leveled off at high nitrite ion concentrations (Fig. 1). The region of nearly constant rate, however, corresponded to a reaction some 5–10 times faster than the rate of isotopically labelled water exchange at the same temperature, *p*H and ionic strength.[6]

Furthermore the nitritopentammine ($[(NH_3)_5Co\text{-}ONO]^{+2}$) complex is known[7a] and its rate of rearrangement to the nitro form[7b] was approximately the same (within a factor of 2) as the rate of formation of nitro complex from the aquo complex as determined by us. Accordingly a study was made of the rate of formation of the nitrito complexes from the aquo complexes in the case of *cis*-$[Coen_2NO_2H_2O]^{+2}$ and $[Co(NH_3)_5H_2O]^{+3}$. This involved preparing *cis*-$[Coen_2NO_2ONO]NO_3$, the first time

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[1] Previous paper in this series, R. G. Pearson, C. Boston and F. Basolo, *J. Phys. Chem.*, in press.

[2] Investigation supported by U. S. Atomic Energy Commission under Contract AT (11-1)-89, Project No. 2.

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[4] F. Basolo, B. D. Stone, J. G. Bergmann and R. G. Pearson, THIS JOURNAL, **76**, 3079 (1954).

[5] F. Basolo, *Chem. Revs.*, **51**, 459 (1953).

[6] H. Taube and R. K. Murmann, personal communication.

[7] (a) S. M. Jorgensen, *Z. anorg. Chem.*, **5**, 169, 172 (1894); *ibid.*, **19**, 149 (1899); (b) B. Adell, *ibid.*, **252**, 232 (1944); *Svensk. Kem. Tids.*, **56**, 318 (1944); *ibid.*, **57**, 260 (1945); *Acta Chem. Scand.*, **5**, 941 (1951).

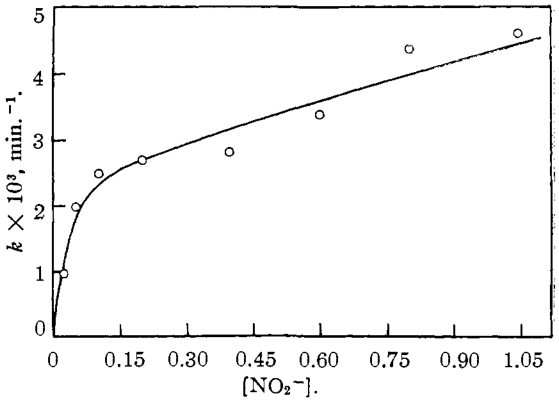

Fig. 1.—Variation of rate of formation of $[Co(NH_3)_5NO_2]^{+2}$ from $[Co(NH_3)_5H_2O]^{+3}$ with increasing concentration of NO_2^-.

that a nitritonitro complex has been isolated. Studies of the rearrangement of the nitrito complexes to the nitro under these same conditions were also made to supplement the data of Adell.[7b] The latter mentions the nitritonitro complexes only as probable intermediates in the rearrangements of *cis*- and *trans*-$[Coen_2(ONO)_2]^+$ to $[Coen_2(NO_2)_2]^+$, reactions studied by him in the solid state.

The reactions of the aquo complexes with nitrite ion in water were studied kinetically as a function of *p*H and nitrite ion concentration. As in the earlier work[4] on rates of formation of nitro complexes, spectrophotometric methods were used. However, wave lengths were selected at which the nitro and nitrito complexes have the same extinction coefficient, differing substantially from that of the aquo complex (Fig. 2). The rate of formation of the nitro complexes had been studied earlier at wave lengths where the nitro compound had a maximum. At these wave lengths it was later observed that the aquo complexes and the nitrito had similar (but not equal) extinctions, much lower than that of the nitro forms.

Experimental

Preparation of Compounds.—The synthesis of *cis*-$[Coen_2NO_2Cl]Cl$ and the preparation of a solution of *cis*-$[Coen_2H_2ONO_2]^{+2}$ were described previously.[4] The salts $[Co(NH_3)_5Cl]Cl_2$,[8a] $[Co(NH_3)_5H_2O]Cl_3$,[8b] $[Co(NH_3)_5ONO](NO_3)_2$[7a] and $[Co(NH_2)_5NO_2](NO_3)_2$[8c] were prepared by procedures given in the literature. The commercially available chemicals used in the kinetic studies were all of reagent grade.

***cis*-Nitritonitrobis-(ethylenediamine)-cobalt(III) Nitrate.**—Three grams of *cis*-$[Coen_2NO_2Cl]Cl$ was dissolved in 20 cc. of water and 3.4 g. of solid $AgNO_3$ was added to this solution. The mixture was continuously stirred at room temperature for approximately 5 hr. At the end of this time the AgCl was removed on a filter and the filtrate gave a faint test for chloride ion. This filtrate was then cooled to 0° and the *p*H adjusted to 4.5 by the dropwise addition of acetic acid. In a separate beaker 4 g. of $NaNO_2$ was dissolved in 15 cc. of water and acetic acid was added to a *p*H 4.5. The two solutions were then mixed and kept at 15° for approximately 20 min. At this point crystals began to appear and 2 g. of solid NH_4NO_3 was added. The orangish-tan product was in turn collected, washed with a minimum amount of ice-water followed by alcohol and ether. This salt was air-dried at room temperature by pulling air through the crystals contained on a small glass-sintered filter. The 1 g. of product was subjected to various studies immediately and the unused compound was stored in a cold (5°) room without noticeable change over a period of two weeks.

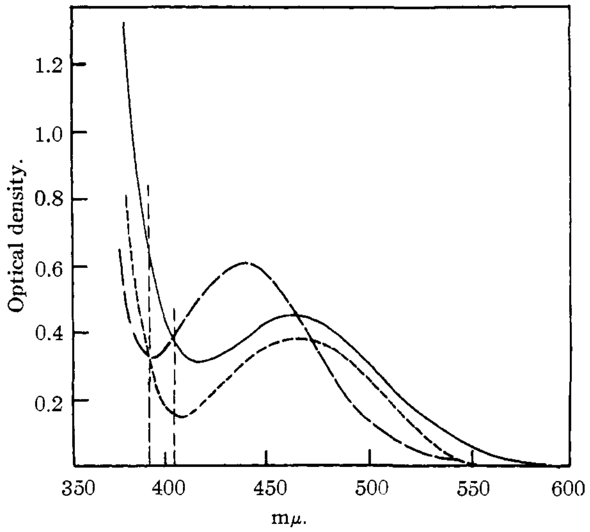

Fig. 2.—Absorption spectra of some cobalt(III) complexes. Measurements made with Cary recording spectrophotometer using Corex cells of 1-cm. light path and solutions of 0.00372 *M* concentration: *cis*-$[Coen_2NO_2ONO]NO_3$ ——; this same soln. after standing overnight or *cis*-$[Coen_2(NO_2)_2]NO_3$ — —; *cis*-$[Coen_2H_2ONO_2]Cl_2$ ------.

Anal. Calcd. for $[Coen_2NO_2(ONO)]NO_3$: N, 29.4. Found: N, 29.8.

That this is *cis*-$[Coen_2NO_2(ONO)]NO_3$ was verified by the fact that the absorption spectrum of this compound differs from either that of the corresponding aquonitro or dinitro complexes (Fig. 2). Furthermore after standing for several hours an aqueous solution of this salt has an absorption spectrum identical with that of *cis*-$[Coen_2(NO_2)_2]^+$. In addition the electrical conductivity of a freshly prepared solution of *cis*-$[Coen_2NO_2(ONO)]NO_3$ remains essentially unchanged upon standing and gradual conversion to the final yellow color of *cis*-$[Coen_2(NO_2)_2]^+$.

A preliminary attempt was made to isolate *trans*-$[Coen_2NO_2(ONO)]NO_3$ by this same method. The crystalline nitrate obtained was the dinitro complex, *trans*-$[Coen_2(NO_2)_2]NO_3$. This is perhaps due to the appreciable insolubility of the *trans*-dinitro nitrate and as the yield was not large it may be that the *trans*-nitritonitro complex remained behind in solution. Since it was not deemed necessary to have the *trans* isomer for this study, no great effort was made to obtain the complex.

Rate Measurements.—All kinetic studies were made by using the Beckman DU spectrophotometer as previously described[4] or in some cases by using a Cary Recording Spectrophotometer. Concentrations of the complex ions were in the range of 5×10^{-3} *M* and aqueous buffers of nitrite ion and nitrous acid prepared by adding perchloric acid to sodium nitrite were used as solvents. Under these conditions clean first-order kinetics were always observed if the wave lengths were chosen as described in the introduction.

(a) Aquopentamminecobalt(III) Ion.—The reactions of $[Co(NH_3)_5H_2O^+]^3$ were carried out at 25°. To study the rate of formation of $[Co(NH_3)_5NO_2]^{+2}$, a wave length of 460 mμ was used. The ratio of nitrite ion to nitrous acid was 8 to 1 corresponding to a *p*H of 4.1. Since the ionization constant of $[Co(NH_3)_5H_2O]^{+3}$ as an acid[9] is 2.0×10^{-6}, only a few percentage would be present as hydroxo complex at this *p*H. If perchloric acid is omitted and alkali added to form only the hydroxo complex, the rate drops by a factor of 100. Table I gives the results obtained at different nitrite ion concentrations.

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[8] (a) S. M. Jorgensen, *Z. anorg. Chem.*, **9**, 79 (1899); (b) A. Werner and A. Mylius, *ibid.*, **16**, 262 (1898); (c) S. M. Jorgensen, *ibid.*, **17**, 464 (1898).

[9] J. N. Brönsted and K. Volquartz, *Z. physik. Chem.*, **134**, 97 (1928).

Table I

Rate of Formation of Nitropentamminecobalt(III) Ion from Aquopentamminecobalt(III) at 25°[a]

Nitrite ion concn., M	$k \times 10^3$, min.$^{-1}$	Nitrite ion concn., M	$k \times 10^3$, min.$^{-1}$
1.00	4.6	0.10	2.5
0.80	4.4	.050	2.0
.60	3.4	.025	0.97
.40	2.8	1.12[b]	2.7×10^{-2}
.20	2.7		

[a] Nitrous acid concentration $^1/_8$ of nitrite ion, ionic strength adjusted with $NaClO_4$ to 1.125. While the measured pH of nitrous acid solutions is erratic owing to decomposition, it is about 4.1 for these solutions in agreement with a K_a of 6.3×10^{-4}, the literature value. [b] Contained no nitrous acid and added NaOH equal to concentration of complex (5×10^{-3} M).

A similar set of studies was made at 412 mμ where the nitro and nitrito complexes have the same extinction coefficient. Consequently the reaction studied is the net rate of disappearance of the aquo complex. The nitrite ion concentration was varied from 0.05 to 0.2 M and the nitrous acid varied from $^1/_8$ to $^1/_{32}$ of the nitrite ion. These results are given in Table II. Higher nitrite ion concentrations were not used because of decomposition of nitrous acid.

Table II

Rate of Disappearance of Aquopentamminecobalt(III) Ion in Presence of Nitrite Ion at 25°[a]

Nitrite ion, M	Nitrous acid	$k \times 10^3$, min.$^{-1}$
0.05	0.0063	16
.10	.0125	61
.20	.0250	250
.20	.0125	140
.20	.0063	59

[a] All runs made in duplicate, reproducibility 3%. Ionic strength held at 1.125 with $NaClO_4$.

Finally the rate of rearrangement of the nitrito complex was studied at 460 mμ. This was done in an environment of nitrite ion between 0.05 and 1.0 M and with again nitrous acid $^1/_8$ of the nitrite ion. The results are in Table III.

Table III

Rate of Rearrangement of Nitropentamminecobalt(III) Ion to Nitropentamminecobalt(III) Ion at 25° and pH of 4.1[a]

Nitrite ion	0.00	0.05	0.20	0.40	1.00
$k \times 10^3$, min.$^{-1}$	1.9[b]	2.5	2.5	2.9	4.6

[a] Ionic strength held constant at 1.125 with $NaClO_4$. [b] This value due to Adell[7b] who found the rate independent of pH in this region and independent of ionic strength up to 0.07 M $NaClO_4$.

(b) ***cis*-Nitroaquobis-(ethylenediamine)-cobalt(III) Ion.**—The rate of disappearance of *cis*-nitroaquobis-(ethylenediamine)-cobalt(III) ion in the presence of nitrite ion and nitrous acid of varying concentrations was studied at 25° using a wave length of 405 mμ where the nitrito and nitro complexes have the same absorption (Fig. 2). The reaction was also studied at 35° for 0.1 and 1 M nitrite ion to compare with the previously obtained[4] results of rate of formation of the dinitro complex from the aquo complex. These data are given in Table IV.

Table IV

Rate of Disappearance of *cis*-Nitroaquobis-(ethylenediamine)-cobalt(III) Ion in Presence of Nitrite Ion at 25°

Nitrite ion, M	Nitrous acid	$k \times 10^3$, min.$^{-1}$	Nitrite ion, M	Nitrous acid	$k \times 10^3$, min.$^{-1}$
0.40	0.0040	50.7[a]	0.80	0.0040	67
0.60	.0060	93.5	0.80	.0140	235
0.80	.0080	137[a]	0.10	.0010	8.0[b]
1.00	.0100	209[a]	1.00	.0100	338[b]

[a] Duplicate runs reproduce to 3%. [b] At 35°. Same ratio of nitrite ion to nitrous acid as in Table II, reference 4.

The rearrangement of the nitritonitro complex to dinitro was studied at 35° using a wave length of 440 mμ where the absorbancy of the nitritonitro and dinitro differ appreciably (Fig. 2). Runs were made in the absence of nitrite ion (complex only present) and in 1.0 M nitrite ion containing 0.01 M nitrous acid. Since virtually identical rates were obtained no further study of the effect of nitrite ion was made. Table V has the data.

Table V

Rate of Rearrangement of *cis*-Nitritonitrobis-(ethylenediamine)-cobalt(III) Ion to *cis*-Dinitrobis-(ethylenediamine)-cobalt(III) at 35°

Nitrite ion	0.00	1.00
$k \times 10^3$, min.$^{-1}$	45.3[a]	46.8[b]

[a] Duplicate run. [b] Containing also 0.01 M nitrous acid.

Discussion

It is clear that at high nitrite ion concentrations (and nitrous acid) the formation of the nitrito complex is much faster than the formation of nitro complex in the case of both the aquopentamminecobalt(III) and nitroaquobis-(ethylenediamine)-cobalt(III)ions. Thus the measured rates of formation of the nitro complex should be equal to the rates of rearrangement of the nitrito complex. This is confirmed by the data in Tables I, III and V. The value of the limiting rate of dinitro formation (above 0.8 M nitrite ion) had been found to be 45–50 $\times 10^{-3}$ min.$^{-1}$ for the *cis*-nitroaquobis-(ethylenediamine)-cobalt(III) ion.[4]

In the case of the aquopentamminecobalt(III) complex, rearrangement of the nitrito intermediate is the rate-determining step down to 0.05 M nitrite ion. Below this the rate of nitrito formation begins to be a factor which reduces the over-all rate of formation of nitro complex (Tables I and II).

With the nitroaquobis-(ethylenediamine)-cobalt(III) complex, rate of formation of the nitrito complex becomes rate determining in the range below 0.2 M nitrite ion. Thus the rate constant for formation of nitro complex at 0.1 M nitrite ion and 35° is 7.9×10^{-3} min.$^{-1}$ (reference 4) and the rate constant for formation of the nitrito complex is 8.0×10^{-3} min.$^{-1}$ (Table IV). The rearrangement step is rapid enough to be neglected in the over-all kinetics at these concentrations.

In each case the formation of the nitro complex can be accounted for by the two-step mechanism

$$\text{aquo complex} \xrightarrow{k_1} \text{nitrito complex} \xrightarrow{k_2} \text{nitro complex} \qquad (3)$$

The observed changes in optical density with time at several wave lengths can be accounted for completely on this basis. Thus at 395 mμ where the aquonitro bis-(ethylenediamine)-cobalt(III) complex has the same absorption as the dinitro and the nitritonitro is considerably higher, an initial rapid increase in optical density occurred with a maximum at 8 minutes. The density then decreased to the initial value. At the nitrite ion concentration used (1.0 M), the values of k_1 and k_2 in equation 3 predict a maximum concentration of nitrito complex at 7 minutes at which time 73% of the initial concentration will be nitrito. The observed concentration of nitrito complex from the optical density was 68%. Thus it appears that very little or none of the nitro complex is formed directly from the aquo complex.

The results of the rate of formation of nitrito complex are given exactly in the case of $[Co(NH_3)_5H_2O]^{+3}$ and very nearly for the *cis*-$[Coen_2H_2ONO_2]^{+2}$ by

$$\text{rate} = k[\text{aquo complex}][HNO_2][NO_2^-] \qquad (1)$$

From a mechanistic viewpoint, however, we prefer to use the kinetically indistinguishable form

$$\text{rate} = k[\text{hydroxo complex}][HNO_2]^2 \qquad (2)$$

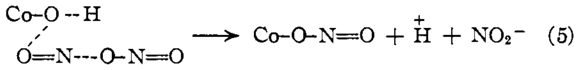
The form of the rate law (2) is of considerable interest. It is written in this manner because it is then completely analogous to the rate equation frequently found for the nitrosation of ammonia and the amines.[10]

$$\text{rate} = k[\text{amine}][HNO_2]^2 \qquad (4)$$

The interpretation of (4) is that the nitrosating agent in weakly acid solutions is N_2O_3 which then attacks the unshared pair of electrons in the amine[11] by splitting into NO^+ and NO_2^-.

It appears that the same mechanism applies to the nitrosation of hydroxyl groups.[12] Thus in our case the attack of N_2O_3 will be on the oxygen atom of the hydroxo complex (corresponding to the free amine).

$$CO{-}OH + O{=}\overset{+}{N}{\cdots}O{-}\overset{-}{N}{=}O \longrightarrow$$



$$\begin{matrix} Co{-}O{\cdots}H \\ \vdots \\ O{=}N{\cdots}O{-}N{=}O \end{matrix} \longrightarrow Co{-}O{-}N{=}O + \overset{+}{H} + NO_2^- \qquad (5)$$

If this view is correct then the cobalt–oxygen bond is not broken in forming the nitrito complex. This would account for the rapid rate of formation of this complex compared to the much slower replacement of water by other ligands including the replacement of water by itself.[4,5]

Furthermore the rearrangement of the nitrito complex to nitro is certainly an intramolecular one as was concluded by Adell.[7b] Thus the rate of rearrangement of nitrito complexes in solutions containing no excess nitrite ion is too great to be compatible with a dissociation–recombination mechanism. This can be seen by the extrapolation of the data of Table I in this work and of Table II in reference 4 to low nitrite ion concentrations. Accordingly the same oxygen atom bonded to cobalt in the aquo derivative should appear in the nitro derivative. The rate of formation of N_2O_3 (or whatever the active nitrosating agent may be) has been measured in nitrous acid solutions at 0°[11b] and in nitrous acid–acetate buffers at 25°.[13] The latter rates, calculated for the same total nitrite concentration and *p*H, are much faster than the rates shown in Table II. However they are only 2–3 times greater than some of the rates calculated from Table IV. This may account for the failure of the latter data to follow equation 2 exactly. The data in Table IV are first order in the complex ion, however, indicating that the complex is in the rate-determining step.

In conclusion it is worth commenting on the devious mechanism of what would appear to be a very simple reaction

$$[Co(NH_3)_5Cl]^{+2} + NO_2^- \longrightarrow [Co(NH_3)_5NO_2]^{+2} + Cl^- \qquad (6)$$

In aqueous solution this reaction is believed to go, first, by an acid hydrolysis[14]

$$[Co(NH_3)_5Cl]^{+2} + H_2O \longrightarrow [Co(NH_3)_5H_2O]^{+3} + Cl^- \qquad (7)$$

followed by an acid–base dissociation

$$[Co(NH_3)_5H_2O]^{+3} + H_2O \rightleftharpoons [Co(NH_3)_5OH]^{+2} + H_3O^+ \cdot \qquad (8)$$

The hydroxo complex is then nitrosated

$$[Co(NH_3)_5OH]^{+2} + N_2O_3 \longrightarrow [Co(NH_3)_5ONO]^{+2} + HNO_2 \cdot \qquad (9)$$

Finally the nitrito complex rearranges to the nitro product

$$[Co(NH_3)_5ONO]^{+2} \longrightarrow [Co(NH_3)_5NO_2]^{+2} \qquad (10)$$

It is of interest to point out that water is responsible for the complexities of reaction 6, since it appears from preliminary studies that in ethylene glycol (6) goes directly at least to the extent that the nitrito complex is not formed nor any stable intermediate. In methanol *cis*-dichlorobis-(ethylenediamine)-cobalt(III) ion also reacts with nitrite ion to give the chloronitro complex as the first observable product.[15]

Nitrito complexes of the type described here have as yet only been reported for cobalt(III). However in view of the results of this investigation it would appear that such a nitrosation reaction should permit the synthesis of nitrito complexes of certain metal ions other than cobalt(III).

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[10] For a list of references see A. T. Austin, E. D. Hughes, J. H. Ridd and C. K. Ingold, THIS JOURNAL, **74**, 555 (1952).

[11] (a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 294; (b) E. D. Hughes, C. K. Ingold and J. H. Ridd, *Nature*, **166**, 642 (1950); (c) N_2O_3 is not always the active agent in the case of amines since other rate expressions have been observed, particularly in buffered media. See J. H. Dusenberg and R. E. Powell, THIS JOURNAL, **73**, 3266, 3269 (1951); J. C. M. Li and D. M. Ritter, *ibid.*, **75**, 5828 (1953).

[12] E. Halfpenny and P. L. Robinson, *J. Chem. Soc.*, 928 (1952), report the rate of nitrosation of hydrogen peroxide to be given by rate = $k[H_2O_2][HNO_2][H^+]$. This corresponds to similar observations in the case of amines.[11c]

[13] J. C. M. Li and D. M. Ritter, THIS JOURNAL, **75**, 5823 (1953).

[14] The rate of appearance of chloride ion from $[Co(NH_3)_5Cl]^{+2}$ at 25° is 9×10^{-5} min.$^{-1}$ in water only and 12×10^{-5} min.$^{-1}$ in 1.0 *M* nitrite ion (P. M. Henry, unpublished data). This is the same general result as was found for *cis*- and *trans*-$[Coen_2NO_2Cl]^{+-}$ complexes.[4]

[15] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953).