The Uptake of Oxygen by Ammoniacal Cobalt(II) Solutions

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Abstract: The rapid and reversible uptake of O_2 by ammoniacal cobalt(II) solutions has been examined. Equilibrium constants for the oxygenation process have been determined in aqueous ammonia solution containing 2 M NH_4NO_3. The pentaammine reacts rapidly with O_2, and second-order rate constants and associated activation parameters have been measured for this process. In high ammonia concentrations there is evidence for lower reactivity of the hexaammine, but this is not unambiguous. The tetraammine and lower species do not pick up O_2 over relatively long periods of time. The decomposition (using EDTA in ammonia solution) of the oxygenated species generated *in situ* yields identical rates and activation parameters to those exhibited by the well-characterized solid $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_4$, dissolved in concentrated aqueous ammonia.

Aqueous ammonia solutions containing cobalt (II) salts have been long known to turn brown on exposure to oxygen.[1] Certain thermodynamic[2] and kinetic[3] studies on cobalt(II) ammines have therefore been carried out in an inert atmosphere. From oxygen-saturated solutions can be isolated a diamagnetic salt of a binuclear cobalt complex ion, $(NH_3)_5CoO_2Co(NH_3)_5^{4+}$ (I) whose structure has recently been determined.[4] The bridging O–O group is considered a peroxide ion, with an O–O distance of 1.47 Å and a torsion angle of 146° about the O–O bond. The five NH_3 and one O form a nearly regular octahedron about the cobalt atoms. The solid is relatively unstable, releasing oxygen at 100° under vacuum.[5] In aqueous solution it acts as an oxygen carrier, easily giving up O_2 by a variety of treatments including nitrogen purging and acidification. The bridging oxygen in I originates entirely from the gaseous oxygen used in its preparation, as shown by the results of ^{18}O experiments.[5] Certain characteristics of the oxygenation step in aqueous solution have been examined.[6] Previous workers have shown the reversibility of the $Co(II)–NH_3–O_2$ system with only slow transformation to mononuclear cobalt(III) complexes. In addition, Jouan attempted to measure the rate of O_2 uptake by a special manometric technique. The major part of the O_2 was said to be absorbed in 20–30 sec with some solutions (0.2 M NH_3) which we know now interact with O_2 in the order of milliseconds. In addition, Bjerrum's data[2] were ignored as a basis for the calculation of the species present, and a completely speculative mechanism was proposed, involving improbably slow $Co(II)–NH_3$ formation steps. No equilibrium or rate constants were determined. We have therefore examined the equilibria between cobalt(II) ammines and oxygen in aqueous solution directly using an oxygen probe, as well as studied the kinetics of formation and decomposition of the O_2 adduct initially (and rapidly) obtained. We hoped therefore to show its relation to the peroxo compound (I) which is usually isolated from solution after a period of oxygen passage through cobalt(II) ammine solutions. In addition, the cobalt(II)–ammonia system offers an excellent opportunity to observe the stage of ammine formation (*i.e.*, value of n in $Co(NH_3)_n(H_2O)_{6-n}^{2+}$) at which reactivity toward O_2 ceases. Oxidation of $(NH_3)_5CoO_2Co(NH_3)_5^{4+}$ to the more stable green ion $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$ occurs only easily with strong oxidants, and formation of $(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4^{3+}$ is very slow,[5] so that there are no reactions immediately following the rapid O_2 uptake.

Experimental Section

Materials. The μ-peroxo solid $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_4$ was prepared as described in the literature.[5] Decomposition by dilute H_2SO_4 apparently produces a variety of products and releases only about 50% of the available O_2.[7] We have found, however, that ~90% of the theoretical oxygen is evolved on addition of the solid to ~0.01 M hydrochloric acid or by decomposition by EDTA in 15 M NH_3 solution. The deficiency is probably accounted for by a paramagnetic impurity in the original solid, which shows an esr signal attributable to the well-known green $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ ion. The material is difficult to purify by recrystallization.[4] All other chemicals used were reagent grade. Solutions of cobalt(II) nitrate and ammonia were standardized by conventional methods.

Oxygen Uptake. The measurement of the amount of dissolved O_2 in solutions containing Co(II), NH_3, and 2 M NH_4NO_3 was effected with a Beckman Oxygen Analyser 96260. Data on the solubility of oxygen in water are available.[8] The solubility in aqueous ammonia was determined by adding a known volume of an air-saturated solution of NH_3-2 M NH_4NO_3 to a larger volume of pre-nitrogen flushed distilled water and determining the oxygen content of the combination. At 25° the concentration of O_2 in a saturated solution of 15 M NH_3-2 M NH_4NO_3 was $1.5 \pm 0.2 \times 10^{-4}$ M, and in a 3.9 M NH_3-2 M NH_4NO_3 solution was $2.1 \pm 0.2 \times 10^{-4}$ M. In aqueous solution it is $2.5 \pm 0.2 \times 10^{-4}$ M.[8] Separate experiments showed that the oxygen probe measured the amount of physically dissolved oxygen in solution and that the response was not affected by the presence of the large amounts of ammonia. A freshly cleaned and charged sensor probe was used for each separate experimental determination of K_{O_2}.[5]

Kinetic Experiments. These were carried out in a glass Lucite stopped-flow apparatus. The formation and decomposition of the

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[1] E. Fremy, *Ann. Chim. Phys.*, [3] **25**, 257 (1852); G. Vortmann, *Monatsh.*, **6**, 404 (1885); A. Werner and Mylius, *Z. Anorg. Chem.*, **16**, 245 (1898).

[2] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[3] Traces of oxygen markedly catalyze the cobalt(II)–(III) ammine electron transfer: W. B. Lewis, C. D. Coryell, and J. W. Irvine, Jr., *J. Chem. Soc.*, S386 (1949); N. S. Biradar, D. R. Stranks, and M. S. Vaidya, *Trans. Faraday Soc.*, **58**, 2421 (1962).

[4] W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968).

[5] M. Mori, J. A. Weil, and M. Ishiguro, *J. Amer. Chem. Soc.*, **90**, 615 (1968).

[6] R. Jouan, *J. Chim. Phys.*, **56**, 277 (1959), and references therein.

[7] R. G. Charles and S. Barnartt, *J. Inorg. Nucl. Chem.*, **22**, 69 (1961).

[8] G. A. Truesdale and A. L. Downing, *Nature*, **173**, 1236 (1954); R. Battino and H. L. Clever, *Chem. Rev.*, **66**, 395 (1966); tables supplied by Beckman Instruments.

Table I. Uptake of O_2 by Cobalt(II) Ammines ($I = 2\ M\ NH_4NO_3$, 25.0°)

$[Co]_T$, mM	$[NH_3]_T$, M	$[O_2]$, μM	$[A_5O_2A_5]$, μM	$[A_5]$, mM	$[A_6]$, mM	(a_{H_2O})	(f_{NH_3})	$10^{-6}K_{O_2}{}^5$
0.0	2.8	225	0.0	0.0	0.0	0.94	1.1	...
1.1	2.8	160	65	0.46	0.34	0.94	1.1	1.8
2.1	2.8	85	140	0.91	0.68	0.94	1.1	1.9
2.6	2.8	60	165	1.2	0.85	0.94	1.1	2.0
3.2	2.8	44	180	1.4	1.04	0.94	1.1	2.0
0.0	3.9	210	0.0	0.0	0.0	0.93	1.2	...
2.0	3.9	140	70	0.81	1.05	0.93	1.2	0.7
4.0	3.9	59	150	1.6	2.1	0.93	1.2	0.8
6.0	3.9	23	190	2.4	3.2	0.93	1.2	1.2
0.0	6.3	150	0.0	0.0	0.0	0.86	1.4	...
2.0	6.3	92	58	0.53	1.35	0.86	1.4	1.6
3.0	6.3	62	88	0.82	2.0	0.86	1.4	1.6
4.0	6.3	38	112	1.1	2.7	0.86	1.4	1.8
5.0	6.3	30	120	1.4	3.4	0.86	1.4	1.6
6.0	6.3	23	127	1.6	4.1	0.86	1.4	1.6
0.0	10.0	96	0.0	0.0	0.0	0.76	1.9	...
1.0	10.0	85	11	0.16	0.83	0.76	1.9	3.8
2.0	10.0	66	30	0.32	1.66	0.76	1.9	3.4
3.0	10.0	48	48	0.48	2.49	0.76	1.9	3.3
4.0	10.0	35	61	0.64	3.32	0.76	1.9	3.2
0.0	15.0	147	0.0	0.0	0.0	0.58	2.9	...
2.0	15.0	122	25	*a*	1.95	0.58	2.9	5.8
4.0	15.0	80	67	*a*	3.9	0.58	2.9	6.1
6.0	15.0	50	97	*a*	5.81	0.58	2.9	6.3
8.0	15.0	32	115	*a*	7.77	0.58	2.9	6.5
10.0	15.0	23	125	*a*	9.75	0.58	2.9	6.3
12.0	15.0	16	131	*a*	11.7	0.58	2.9	6.3
0.0	15.0[b]	146	0.0	0.0	0.0	0.58	2.9	...
2.0	15.0[b]	81	65	0.08[a]	1.80	0.58	2.9	40
4.0	15.0[b]	38	108	0.17[a]	3.61	0.58	2.9	36

[a] Mole fraction is 0.03 ± 0.005. [b] 15°.

brown oxygenated species were usually followed in the region of the absorption band at 360 mμ (ε 2.9 ± 0.3 × 10^3). Observation at other wavelengths gave similar results. In the formation experiments, a deaerated Co(II), NH_3, and $2\ M\ NH_4NO_3$ solution was mixed with a NH_3, $2\ M\ NH_4NO_3$, and O_2 solution. In the decomposition studies, freshly prepared Co(II), NH_3, $2\ M\ NH_4NO_3$, and O_2 solutions were mixed with NH_3, $2\ M\ NH_4NO_3$, and EDTA solutions. Single, first-order rate plots (rate constant, k_{obsd}) were linear, over at least three half-lives, for all the kinetic experiments. The high ammonia concentrations used in some of the experiments apparently did not impede measurements. Temperature control was ±0.1°.

Results

Equilibria. We focus attention initially on the penta- and hexaammine and assume formation of a binuclear oxygenated adduct. The various equilibria which may be considered present in ammoniacal cobalt(II) solutions containing O_2 are shown in eq 1–3.

$$2Co(NH_3)_5(H_2O)^{2+} + O_2 \rightleftarrows (NH_3)_5CoO_2Co(NH_3)_5{}^{4+} + 2H_2O \quad (1)$$

$$K_{O_2}{}^5 = [(NH_3)_5CoO_2Co(NH_3)_5{}^{4+}]a_{H_2O}{}^2/[Co(NH_3)_5(H_2O)^{2+}]^2[O_2]$$

$$K_{O_2}{}^5 = [(NH_3)_5CoO_2Co(NH_3)_5{}^{4+}][NH_3]^2f_{NH_3}{}^2 \times (K_6)^2/[Co(NH_3)_6{}^{2+}]^2[O_2]$$

$$2Co(NH_3)_6{}^{2+} + O_2 \rightleftarrows (NH_3)_5CoO_2Co(NH_3)_5{}^{4+} + 2NH_3 \quad (2)$$

$$K_{O_2}{}^6 = [(NH_3)_5CoO_2Co(NH_3)_5{}^{4+}][NH_3]^2 \times f_{NH_3}{}^2/[Co(NH_3)_6{}^{2+}]^2[O_2]$$

$$Co(NH_3)_5(H_2O)^{2+} + NH_3 \rightleftarrows Co(NH_3)_6{}^{2+} + H_2O \quad (3)$$

$$K_6 = [Co(NH_3)_6{}^{2+}]a_{H_2O}/[Co(NH_3)_5(H_2O)^{2+}][NH_3]f_{NH_3}$$

Bjerrum[2] has characterized the cobalt(II)–ammonia system in $2\ M\ NH_4NO_3$, which are also the conditions of all our experiments. In various concentrations of ammonia therefore we know the concentrations of the penta- and hexaammine governed by the relationship in (3) where a_{H_2O} and f_{NH_3} are the active mass of water and the activity coefficient of ammonia, respectively.[2] These latter, assumed unity in $2\ M\ NH_4NO_3$ solution,[2] will deviate in the high ammonia concentrations used in this study. The values can be estimated.[2,9] By measuring the amount of oxygen taken up by cobalt(II) solutions in NH_3–H_2O, we can calculate the value of $K_{O_2}{}^5$ or $K_{O_2}{}^6$, which are interrelated by the expression $K_{O_2}{}^5 = K_{O_2}{}^6(K_6)^2$. All equilibria are established within the time of measurement, and addition of EDTA reliberates all the combined O_2. The results are shown in Table I. With cobalt(II) ammine solutions of lower $\bar{n}$, containing predominantly tetra- and trisammines, only 2–3% of the dissolved O_2 was taken up over a period of at least 20 min. These results

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[9] E. P. Perman, *J. Chem. Soc.*, 1168 (1903).

Table II. Kinetics of Formation of Oxygen Adduct from Cobalt(II) Ammines ($I = 2\,M\,NH_4NO_3$)

Temp, °C	$[Co]_T$, mM	$[NH_3]_T$, M	$[A_4]$,[a] mM	$[A_5]$,[a] mM	$[A_6]$,[a] mM	k_{obsd}, sec^{-1}	$k_{obsd}/[A_5]$, M^{-1} sec^{-1}
5.0	80	0.2	30.2	9.2	0.44	126	14×10^3
5.0	8	1.9	1.1	4.3	2.6	69	16×10^3
5.0	8	3.9	<0.2	3.2	4.8	37	11×10^3
5.0	8	4.7	<0.2	2.8	5.2	41	14×10^3
5.0	8	5.5	<0.2	2.2	5.8	37	16×10^3
5.0	8	6.3	<0.2	2.2	5.8	25	11×10^3
5.0	8	9.0	<0.2	1.1	6.9	17	16×10^3
5.0	8	11.0	<0.2	0.94	7.1	16	17×10^3
5.0	8	12.0	<0.2	0.58	7.4	13	23×10^3
15.0	8	1.9	1.1	4.3	2.6	92	21×10^3
15.0	8	3.9	<0.2	3.3	4.7	57	17×10^3
15.0	8	4.7	<0.2	2.9	5.1	69	24×10^3
15.0	8	5.5	<0.2	2.3	5.7	58	25×10^3
15.0	8	6.3	<0.2	2.0	6.0	43	21×10^3
15.0	8	9.0	<0.2	1.2	6.8	30	25×10^3
15.0	8	11.0	<0.2	0.9	7.1	25	31×10^3
15.0	8	12.0	<0.2	0.64	7.4	25	40×10^3
15.0	13	15.0	<0.2	0.39	12.6	31	79×10^3
30.0	8	1.9	1.5	4.3	2.2	126	29×10^3
30.0	8	3.9	0.45	3.4	4.1	99	25×10^3
30.0	8	4.7	<0.2	3.1	4.9	99	32×10^3
30.0	8	5.5	<0.2	2.5	5.5	77	31×10^3
30.0	8	6.3	<0.2	2.3	5.7	69	30×10^3
30.0	8	9.0	<0.2	1.3	6.7	69	52×10^3
30.0	8	11.0	<0.02	0.93	7.07	61	65×10^3
30.0	8	12.0	<0.02	0.76	7.24	77	100×10^3
5.0[b]	25	15.0	<0.02	1.0	24[c]	38	38×10^3
5.0[b]	15	15.0	<0.02	0.6	14.4[c]	25	42×10^3
5.0[b]	10	15.0	<0.02	0.4	9.6[c]	18	22×10^3
5.0[b]	5	15.0	<0.02	0.2	4.8[c]	7	35×10^3
5.0[b]	3.5	15.0	<0.02	0.14	3.4[c]	5	36×10^3
30.0	5.0	0.074	3.5	0.4	...	V. small	

[a] These represent the concentrations of tetra-, penta-, and hexaammine species, respectively. The values were calculated from the stability constants (ref 2) and activities of H_2O and NH_3 (ref 9). [b] This set of runs shows first-order dependence on $[Co]_T$ in $[NH_3]$ region where $A_5 \propto [Co]_T$. Subscript T represents total. [c] $(f'/a')_{15M}{}^{5°} \approx 5$, $K_6{}^{5°} = 0.32$, $A_6/A_5 = 24$.

allowed choice of conditions for the kinetics measurements.

Kinetics. The sum of the concentrations of penta- and hexaammine greatly exceeded the O_2 concentration used in the formation studies, and their relative concentrations were continuously maintained because of their rapid interconversion.[10] The reactions proceeded to completion and gave pseudo-first-order plots. At 5°, in the region 0.2–9.0 M total ammonia concentration, $[NH_3]_T$, the values of $k_{obsd}/[Co(NH_3)_5(H_2O)^{2+}]$ (see Table II and Figure 1) are constant within an appreciable experimental error occasioned by the short half-lives ~5 (±20%) to 40 (±15%) msec for the formation reactions. Over this range of $[NH_3]_T$ the pentaammine decreases and the hexaammine increases some tenfold in concentration. Thus the data can be well described by the rate law

$$(d/dt)[\text{oxygenated species}] = k_{obsd}[O_2] = k_1{}^5[Co(NH_3)_5(H_2O)^{2+}][O_2]$$

At 15 and 30°, a similar behavior is observed, but now there are indications at high ammonia concentrations ($\geqslant 9.0\,M$), and particularly at the highest temperature, that $[Co(NH_3)_6{}^{2+}]$ contributes directly to the formation rate. Plots of

$$k_{obsd} = k_1{}^5[Co(NH_3)_5(H_2O)^{2+}] + k_1{}^6[Co(NH_3)_6{}^{2+}]$$

or

$$k_{obsd}/[Co(NH_3)_5(H_2O)^{2+}] = k_1{}^5 + k_1{}^6K_6[NH_3]f_{NH_3}/a_{H_2O}$$

$k_{obsd}/[Co(NH_3)_5(H_2O)^{2+}]$ against $[NH_3]f_{NH_3}/a_{H_2O}$ are shown in Figure 1. The slopes of the best straight lines drawn through the points from ~11 to ~0 M NH_3 at 30 and 15° represent $k_1{}^6K_6$, from which $k_1{}^6 \sim 1.7 \times 10^3$ M^{-1} sec^{-1} at 30° and $k_1{}^6 \sim 0.7 \times 10^3$ M^{-1} sec^{-1} at 15°.

The decomposition of the freshly produced oxygenated species was first order with a rate constant independent of the concentrations of EDTA or NH_3 used or whether it was produced *in situ* or generated from the solid peroxo preparation. The results are shown in Table III.

Discussion

In $[NH_3] < 6.3\,M$ and over a wide range of Co(II) concentration, the value of $K_{O_2}{}^5$ is fairly constant and has

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(10) There is little doubt about this point although no direct exchange data exist. For example, the $Co(NH_3)_6{}^{2+}$–NH_3 exchange in liquid ammonia is rapid (H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 1061 (1965)) as is the $Co(en)_3{}^{2+}$–en exchange in water (R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, **86**, 765 (1964)).

Table III. Kinetics of Decomposition of Oxygen Adduct from Cobalt(II) Ammines ($I = 2\,M\,NH_4NO_3$)

Temp, °C	$[Co]_T$, mM	$[NH_3]_T$, M	[EDTA], mM	$k_{obsd}\,(=k_{-2})$, sec^{-1}
6.5	1.0	15.0	5.0	4.2[a]
7.0	5.0	15.0	25.0	6.9
15.0	1.0	15.0	6.0	15
15.0	1.0	15.0	10.0	16
15.0	1.0	15.0	15.0	16
15.0	5.0	15.0	25.0	12
15.0	1.0	15.0	5.0	12[a]
25.0	1.0	15.0	5.0	58[a]
25.0	4.0	15.0	20.0	58
25.0	8.0	8.0	32.0	69
30.0	4.0	4.3	16.0	69

[a] Solid dimer added to 15 M NH_3 solution and decomposed with EDTA.

no particular trend. The increase in its value at higher $[NH_3]$ may not necessarily be significant since it may simply reflect the different solvent characteristics of this medium which are only partly offset by assigning values of f_{NH_3} and a_{H_2O} to such solutions. Furthermore the computed value of $K_{O_2}{}^5$ is sensitive to the chosen values of f_{NH_3}, and there is the additional difficulty of calculating the concentration of species present in high ammonia concentrations from thermodynamic data obtained in lower ones.[2] We consider then that the equilibria 1–3 are the *important* ones, and this is supported by the decomposition experiments which indicated that the same *one* species was present in freshly oxygenated solutions prepared in high and low ammonia concentrations. An adduct such as $(NH_3)_4(H_2O)CoO_2Co(H_2O)(NH_3)_4{}^{4+}$ formed by replacement of NH_3 of the pentaammine by O_2 is therefore relatively unimportant, and this is consistent with the inability of $Co(NH_3)_4(H_2O)_2{}^{2+}$ (and lower species) to take up O_2 to form, for example, the tetraammine μ-peroxo species.

It is apparent from Figure 1 and Table II that the pentaammine is the major carrier (kinetically) of O_2 at the lower $[NH_3]$. The second-order rate constant $k_1{}^5$ refers to the first step of a mechanism for oxygen uptake which has been previously proposed[5] and which we suggest by analogy with other systems we have studied,[11] *e.g.*

$$Co(NH_3)_5(H_2O)^{2+} + O_2 \underset{k_{-1}{}^5}{\overset{k_1{}^5}{\rightleftharpoons}} Co(NH_3)_5O_2{}^{2+} + H_2O$$

$$Co(NH_3)_5O_2{}^{2+} + Co(NH_3)_5(H_2O)^{2+} \underset{k_{-2}{}^5}{\overset{k_2{}^5}{\rightleftharpoons}} (NH_3)_5CoO_2Co(NH_3)_5{}^{4+} + H_2O$$

The second-order rate law holds when $k_2{}^5[Co(NH_3)_5(H_2O)] \gg k_{-1}{}^5$. Only at high ammonia concentrations ($\geqslant 9.0\,M$) and the higher temperatures is there indication of curvature in the plots of Figure 1. Here it is difficult to assess accurately the contributions of the hexaammine to the rate because (a) the solvent characteristics are markedly different, considerations discussed above, and (b) the value of $k_1{}^5$ estimated at low $[NH_3]$ may itself be different in this change of medium. Only approximate (and possibly incorrect) values for $k_1{}^6$ at 15 and 30° can be obtained, but in any case it is clear that the pentaammine is by far the more reactive species, with a rate constant for reaction at least 20 times that of the hexaammine. We cannot compare its reactivity with the lower ammines since the latter may react rapidly with O_2, but an enhanced value of k_{-2} or k_{-1}/k_2 may ensure that the equilibrium lies well over to the cobalt(II) side. This at least appears possible in view of the marked kinetic reactivity ($k_1 = 4.7 \times 10^5\,M^{-1}\,sec^{-1}$ at 25°)[11] of $Co(en)_2(H_2O)_2{}^{2+}$ toward O_2. Fallab[12] has suggested that at least three N donor atoms must be present in the coordination compound if the binding of O_2 is to be possible. The inability of the tetraammine and lower species to pick up O_2 shows that this is obviously only a minimum requirement.

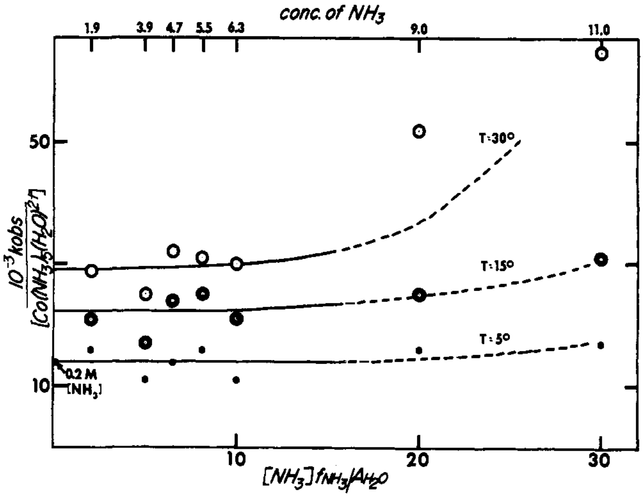

Figure 1. Plot of $10^{-3}k_{obsd}/[Co(NH_3)_5(H_2O)^{2+}]$ against $[NH_3]\cdot f_{NH_3}/a_{H_2O}$ for reaction of cobalt(II) ammines with O_2.

Two of the methods used to decompose the bis(histidinato)cobalt(II)–O_2 adduct[11] could not be employed here. It was obviously impractical to use $[H^+]$ to decompose the adduct present in the high ammonia concentrations, and the addition of $S_2O_4{}^{2-}$ to remove O_2 resulted in the formation of dark red species. In order to measure $k_{-2}{}^5$ we used decomposition by EDTA in alkaline solution. This was shown to regenerate the O_2 completely, the EDTA reacting with Co(II) ammines and forming a mixed species which is O_2 insensitive. The dissociative lability of the cobalt(II) ammines will ensure that these will react *rapidly* with a decomposing ligand such as EDTA, and this was confirmed by independent experiments. The first-order decomposition rate constant was substantially independent of the concentration of decomposing agent and almost certainly represented $k_{-2}{}^5$. Freshly oxygenated solutions and the μ-peroxo solid dissolved in various concentrations of NH_3 (Table III) gave the same decomposition behavior, establishing that the solid and the oxygenated species in solution have identical structures, unless there is an unlikely structural change on dissolving the solid. This has been implied previously and certainly is supported by the observation of high efficiency (~90%) in the preparation of the peroxo-bridged complex from aerated solutions of cobalt(II) in 10 M ammonia.[5] All the kinetic data are collected in Table IV and will be com-

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[11] J. Simplicio and R. G. Wilkins, *J. Amer. Chem. Soc.*, **89**, 6092 (1967); F. Miller, J. Simplicio, and R. G. Wilkins, submitted for publication.

[12] S. Fallab, *Angew. Chem. Intern. Ed. Engl.*, **6**, 496 (1967).

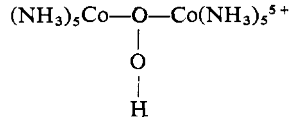
Table IV. Data for Cobalt(II)–Ammonia–O_2 System at 25°

$k_1{}^5 = 2.5 \times 10^4\ M^{-1}\ \text{sec}^{-1}$	$k_{-2}{}^5 = 56\ \text{sec}^{-1}$	$K_{O_2}{}^{5a} = 6.3 \times 10^6\ M^{-2}$
$\Delta H_1{}^* = 4$ kcal mole^{-1}	$\Delta H_{-2}{}^* = 18$ kcal mole^{-1}	$\Delta H^a = 30$ kcal mole^{-1}
$\Delta S_1{}^* = -25$ eu	$\Delta S_{-2}{}^* = +9$ eu	

[a] In 15 M NH_3.

pared with that for cobalt(II) chelates in another paper.[11]

Our observations on the reactivity of $(NH_3)_5CoO_2Co(NH_3)_5{}^{4+}$ are consistent with two studies made of the reduction of $(NH_3)_5CoO_2Co(NH_3)_5{}^{5+}$ in acid medium. Sykes[13] observed the production of oxygen bubbles within a few seconds of completion of reduction by Fe^{2+}, which can be ascribed to decomposition of the 4+ cation. Hoffman and Taube[14] in reductions carried out with Cr^{2+}, V^{2+}, and Eu^{2+} detected a common intermediate which was assigned the structure



$$(NH_3)_5Co{-}\underset{\underset{H}{|}}{\underset{O}{|}}{O}{-}Co(NH_3)_5{}^{5+}$$

Its decomposition rate constant (k = 5.0 sec^{-1} at 25° and $[H^+] = 1.0\ M$) is smaller than that observed by us for $(NH_3)_5CoO_2Co(NH_3)_5{}^{4+}$ in alkaline solution, in agreement with the observation[14] that the protonated form decomposes more slowly than the nonprotonated. It has been observed[15] that the decomposition of (histidine-H)$_2CoO_2Co$(histidine-H)$_2{}^{4+}$ is also retarded in strong acid due presumably to the formation of a more stable species, protonated at the bridge. The pK of this species was determined kinetically and spectrally as 1.2 ± 0.2 and is interestingly similar to that of the dibridged (en)$_2$Co(NH$_2$)(O$_2$H)Co(en)$_2{}^{4+}$ (pK = 0.8).[16]

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The Charge-Transfer Spectra of Pyridine N-Oxide Metal Complexes. Determination of Optical Electronegativities

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Abstract: The metal-to-ligand charge-transfer spectra of octahedral Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) complexes of pyridine N-oxide and various methyl-, nitro-, and carboxyl-substituted derivatives are presented. The data are analyzed in terms of the concept of optical electronegativity. The charge-transfer bands are assigned as $t_{2g} \rightarrow \pi^*$ transitions in the complexes of Fe(II), Co(II), and Ni(II), and as $e_g \rightarrow \pi^*$ transitions in complexes of Mn(II) and Cu(II). A general method of assigning such spectra is discussed. The optical electronegativities of the octahedral Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) ions and the acceptor π^* orbitals of the ligand are calculated and discussed.

In one of the earliest studies of pyridine N-oxide metal complexes,[2] the unusual color, yellow, of the manganese(II) complex was pointed out and ascribed to the presence of a low-lying charge-transfer band. Since then there has been extensive activity in the investigation of pyridine N-oxide complexes,[3,4] but no detailed discussion of the charge-transfer spectra of these complexes has appeared. Many pyridine N-oxide complexes exhibit a broad and fairly intense band near 400 mμ which we attribute to a charge-transfer transition. In this paper, preliminary details of which appeared earlier,[5] we present evidence supporting this contention and attempt to rationalize the variation of the band position with metal ion and ligand in terms of the concept of optical electronegativity.

Experimental Section

Electronic spectra were recorded with an Optika CF4NI double-beam grating spectrophotometer with a diffuse reflectance

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