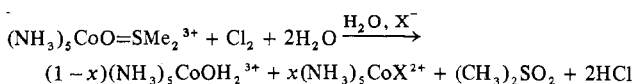## Trapping of Labile Cobalt(III) Complexes. Characterization of the Perchloratopentaamminecobalt(III) Ion

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and J. C. Sullivan

Treatment of the complex ion $(NH_3)_5CoO=SMe_2{}^{3+}$ with aqueous Cl_2 results in the very rapid substitution of the dimethyl sulfoxide ligand by water and anions present in solution. The reaction stoichiometry is

$$(NH_3)_5CoO=SMe_2{}^{3+} + Cl_2 + 2H_2O \xrightarrow{H_2O,\ X^-}$$

$$(1-x)(NH_3)_5CoOH_2{}^{3+} + x(NH_3)_5CoX^{2+} + (CH_3)_2SO_2 + 2HCl$$

Dimethyl sulfone was the sole organic product (established by ^1H NMR spectroscopy on the reaction mixture and isolation with gravimetric quantitation and physical characterization: analysis, ir, ^1H NMR, melting point, and mixture melting point comparisons with authentic material). The Co(III)-containing products were characterized by ion-exchange chromatographic separation and visible spectroscopy.

In the presence of acids HX ($X^- = Cl^-$, NO_3^-, HSO_4^-) containing anions which form slowly aquating $(NH_3)_5CoX^{2+}$ complexes the oxidation was observed as a simple first-order process (in the presence of excess Cl_2), with the observed rate constant showing a linear dependence on Cl_2 concentration (Table I). In the presence of other acids ($X^- = CF_3SO_3^-$, ClO_4^-) known or expected to form relatively labile $(NH_3)_5CoX^{2+}$ complexes, consecutive first-order reactions were observed, one rate then being independent of Cl_2 concentration and the other still showing a first-order dependence (Table I). In neither system were the rates dependent on acidity when allowance was made for the dependence of the Cl_2 hydrolysis equilibrium on H^+ concentration. In constant ionic strength mixtures of, for example, HCl and $HClO_4$ a change from a single- to a double-rate process was detected as the $HClO_4$ concentration increased. An obvious rationalization of these data was inferred when it was recognized that the chlorine-independent rate in CF_3SO_3H solutions corresponded to the independently measured rate constant for $(NH_3)_5CoO_3SCF_3{}^{2+}$ aquation.[2] Thus it was concluded that oxidation in $HClO_4$ yielded some rapidly aquated $(NH_3)_5CoOClO_3{}^{2+}$ ($k \simeq 0.1$ sec^{-1}, 25°, $\mu = 1.0$).

To support this interpretation, efforts were made to detect the perchlorato complex in other systems where its transient presence might be anticipated. By choice of conditions (0.8 M $HClO_4$, 0.1 M $Hg(ClO_4)_2$) such that mercury(II)-catalyzed removal of halide from $(NH_3)_5CoBr^{2+}$ and $(NH_3)_5CoI^{2+}$ was complete in <1 sec, a subsequent reaction was indeed detected. This had a first-order rate process with a half-life of 7 ± 1 sec; i.e., $k = 0.1$ sec^{-1} for both reactants. Attempts to observe the reaction after nitrosation of $(NH_3)_5CoN_3{}^{2+}$ were frustrated by the vigorous effervescence occurring under conditions required for very rapid nitrosation. Nonetheless, the apparent detection of $(NH_3)_5CoOClO_3{}^{2+}$ and its moderate stability provoked an attack upon its synthesis.[3]

The synthesis was accomplished via nitrosation of $[(NH_3)_5CoN_3](ClO_4)_2$ in concentrated $HClO_4$. NO and NO_2, generated from HNO_3 + $NaNO_2$, were passed intermittently with dry N_2 into a stirred suspension of $[(NH_3)_5CoN_3](ClO_4)_2$ in 70% $HClO_4$ for 2 hr. The product mixture of pink crystals and acid plus excess $NOClO_4$ was then kept for 12 hr at 25° before being poured onto ice and the insoluble complex was

Medium	$[Cl_2]_T,$ M	$[Cl_2],$[a] M	$k_1,$[b] sec^{-1}	$k_2,$[b] sec^{-1}	$k_{Cl_2},$[c] M^{-1} sec^{-1}	$\lambda,$[d] nm
1 M $HClO_4$	0.0433	0.0404	0.100	0.420	10	535
	0.4040	0.0380		0.385	10	270
	0.0300	0.0280	0.100	0.270	9.6	535
	0.0250	0.0230	0.093	0.220	9.5	535
	0.0230	0.0210		0.217	10	270
	0.0166	0.0150		0.152	10	270
0.2 M HCl– 0.8 M $HClO_4$	0.0435	0.0405	0.080	0.380	8.3	535
0.5 M HCl– 0.5 M $HClO_4$	0.0435	0.0405	0.100	0.270	6.7	535
0.75 M HCl– 0.25 M $HClO_4$	0.0435	0.0405	e	0.173	4.3	535
1 M HCl	0.0435	0.0405		0.154	3.8	535
1 M HNO_3	0.0428	0.0398		0.630	15.8	535
1 M H_2SO_4	0.0411	0.0384		0.578	15.1	535
1 M HO_3SCF_3	0.0400	0.0373	0.0320	0.324	8.7	535

[a] Actual free Cl_2 concentration calculated from the measured total oxidizing power of the solution and the independently measured equilibrium constant for chlorine hydrolysis ($K = 1.96 \times 10^{-4}$ M^2, 25°, $I = 1.0$ ($NaClO_4$)). [b] Rate constants for consecutive reactions evaluated by the nonlinear least-squares fitting procedure of Osborne.[1] [c] $k_{Cl_2} = k_2/[Cl_2]$. [d] At 270 nm, $[Co^{III}] = 10^{-4}$ M. Spectral changes at this wavelength are determined by but one of the two processes in $HClO_4$. At 535 nm, $[Co^{III}] = 2.5 \times 10^{-3}$ M. [e] The slower process makes too small a contribution to the total absorbance change under these conditions to be detected.

filtered off. The complex was recrystallized as lustrous pink flakes by washing the crude material through the filter with ice water (pH 3) straight into $HClO_4$ (70%)–ice slush. It was washed with ethanol and ether and dried in vacuo. Anal. Calcd for $CoH_{15}N_5Cl_3O_{12}$: H, 3.42; N, 15.83; Cl, 24.04. Found: H, 3.5; N, 15.9; Cl, 24.5. The nitrate salt was obtained by a similar crystallization using an HNO_3–ice mixture. Anal. Calcd for $CoH_{15}N_7ClO_{10}$: H, 4.11; N, 26.58; Cl, 9.65. Found: H, 4.5; N, 27.0; Cl, 8.8. This material presumably contains a little $[(NH_3)_5CoONO_2](NO_3)_2$. No water was detected in either compound by ir spectroscopy and both showed characteristic bands for a unidentate ClO_4^- ligand (ν_4 triplet 620, 640, 658 cm^{-1}; ν_3 triplet 1190, 1115, 1035 cm^{-1}) consistent with C_s symmetry.[4]

The aquation of the recrystallized $[(NH_3)_5CoClO_3](ClO_4)_2$ complex was followed by leaching the solid with dilute (10^{-3} M) acid into an equal volume of 2 M $HClO_4$ and examining spectral changes at 535 nm. The last half of the reaction was detected in this way, giving a first-order rate constant of 0.1 sec^{-1} at 25°. Although of low solubility in almost all solvents, the complex reacted rapidly with, for example, CH_3CN and DMSO to give the corresponding solvento complexes. This property is not shared by $[(NH_3)_5CoOH_2](ClO_4)_3$. In aqueous media substitution of the perchlorato ligand by nucleophiles other than H_2O is readily detected. Thus in 1 M HCl the complex reacted to give 3% $(NH_3)_5CoCl^{2+}$ and 97% $(NH_3)_5CoOH_2{}^{3+}$.

Another unexpected observation made in the study of the chlorine oxidation of $(NH_3)_5CoDMSO^{3+}$ was that in 1 M HBF_4 the reaction produced 11% $(NH_3)_5CoF^{2+}$. A similar result was obtained in nitrosation of $(NH_3)_5CoN_3{}^{2+}$ in HBF_4. The amount of fluoropentaammine complex is approximately the same as that produced by nitrosation in 1 M HF and cannot be ascribed to the very small amount of HF present in HBF_4 (<2%). The implication is that BF_4^- is captured by Co(III) to give a transient $(NH_3)_5CoF$–$BF_3{}^{2+}$ species from which BF_3 is rapidly extruded. In HPF_6, $(NH_3)_5CoF^{2+}$ was again produced, presumably by an analogous mechanism. The

general implication of all the present results for cobalt-(III)–amine substitution reactions is now being explored.

Registry No. (NH₃)₅CoO═SMe₂³⁺, 44915-85-7; Cl₂, 7782-50-5; [(NH₃)₅CoOClO₃](ClO₄)₂, 18042-14-3; [(NH₃)₅CoOClO₃](NO₃)₂, 56335-61-6; [(NH₃)₅CoN₃](ClO₄)₂, 14283-04-6.

References and Notes

(1) M. R. Osborne "A Method for Fitting Exponentials to Data", Technical Report No. 31, Australian National University Computer Centre, 1969.

(2) P. J. Cresswell, Ph.D. Thesis, Australian National University 1974. The value there obtained for the rate constant was 2.7×10^{-2} sec⁻¹ (25°, $I = 1.0$, NaClO₄).

(3) The synthesis of the perchlorato complex has been reported previously by R. Duval, *Ann. Chim. (Paris)*, **18**, 241 (1932), but the properties given (see also R. Duval, C. Duval, and J. Lecomte, *Bull. Soc. Chim. Fr.*, 1048 (1947)) do not coincide with those presently described. We have been unable to obtain any solid other than [(NH₃)₅CoOH₂](ClO₄)₃ by Duval's synthetic procedure.

(4) Similar, though less well resolved, ir absorptions are seen for the complex Co(DTH)₂(ClO₄)₂ (DTH = 2,5-dithiahexane): F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.*, **87**, 4189 (1965).

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Metal Ion Selectivity on the Products of a Cyclic Condensation Reaction

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It has been demonstrated that metal ions can control the course of organic reactions by either a kinetic or a thermodynamic template effect.[1-3] The role of the specific metal ion employed in determining the nature of products must be related to electronic factors and the size of the metal ion. Presently, there have been only a few studies made on the products of a given organic reaction in which only the specific metal ion is systematically varied. One example of such a study is the self-condensation reaction of *o*-aminobenzaldehyde in the presence of various metal ions. In the presence of copper(II),[4] iron(II),[5] and cobalt(II)[5] the *o*-aminobenzaldehyde will condense forming only the coordinated tetradentate macrocyclic Schiff base tetrabenzo[*b,f,j,n*][1,5,9,-13]tetraazacyclohexadecane (TAAB) (I). However, *o*-aminobenzaldehyde in the presence of Ni(II)[6] will produce a mixture of coordinated TAAB (I) and the coordinated

I   II
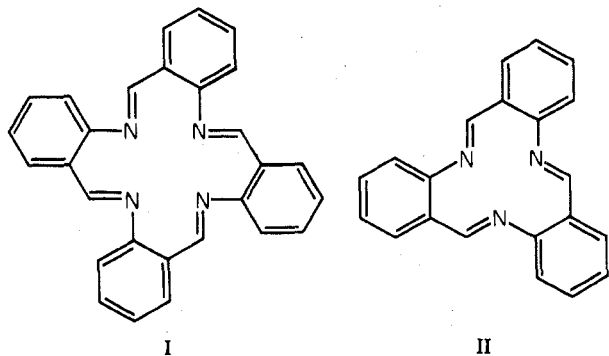
tridentate macrocyclic Schiff base tribenzo[*b,f,j*][1,5,9]-triazacycloduodecane (TRI) (II). Cobalt(III) complexes of both TRI and TAAB have been isolated.[7,8]

At present, there is no information concerning how the size of the transition metal ion controls the degree of cyclic condensation of *o*-aminobenzaldehyde or how a transition metal ion containing less than five d electrons affects this reaction. We have begun such a study of the condensation

of *o*-aminobenzaldehyde in the presence of the oxovanadium(IV) ion. There are several reasons for using the oxovanadium(IV) ion in this study. Vanadium(IV) in oxovanadium(IV) is much smaller than the ions that have been previously studied. This ion contains only one 3d electron and therefore it should function as an obvious contrast to the previously studied metal ions employed in the cyclic condensation of *o*-aminobenzaldehyde. Finally, extensive research has already been conducted on oxovanadium(IV) and oxovanadium(V)[9,10] chemistry that aided us in this research.

Experimental Section

Materials. *o*-Nitrobenzaldehyde was purchased from Matheson Coleman and Bell. *o*-Aminobenzaldehyde, 13-hydroxy-6,12-benzo-6*H*-quinazolino[3,4-*a*]quinazoline, (oab)₃, and the various salts (TAAB)(HX)₂[11] were prepared according to established procedures. Vanadyl sulfate pentahydrate was purchased from Alfa Inorganics and vanadyl dichloride was prepared by an established procedure.[12]

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 337. Mass spectral data were obtained using a Varian MAT CH7 mass spectrometer. The ion source heater was approximately 240°C. All samples were solids and run using the direct-inlet system. Inlet temperature ranged from 150 to 200°C. Proton magnetic resonance spectra were recorded using a Varian Associates Model A-60. Spectra were run in deuterated acetone with TMS as an internal standard. Visible spectra were recorded using a Beckman Model DK-IIA recording spectrophotometer. Magnetic moments were determined using an Alfa Scientific Model 4600 4-in. adjustable gap electromagnet in conjunction with an Alfa Scientific Model 3002-1 current power supply. Hg[Co(SCN)₄] was used as the standard and diamagnetic corrections were made using published Pascal's constants.[13] All carbon, hydrogen, and halogen and some nitrogen analyses were performed by Galbraith Microanalytical Laboratories. Most nitrogen analyses were done in this laboratory using a Coleman Model 29A nitrogen analyzer.

Syntheses. Reaction of *o*-Aminobenzaldehyde with Oxovanadium(IV) Dichloride (Compound A). Freshly prepared *o*-aminobenzaldehyde (4.7×10^{-2} mol) was dissolved in 30 ml of absolute ethanol, which had previously been degassed by bubbling oxygen-free nitrogen through it for about 0.5 hr. This mixture was then brought to reflux in a 50-ml three-necked flask which was kept under a positive pressure of nitrogen. After several minutes of refluxing, approximately 1.4×10^{-2} mol of VOCl₂ dissolved in 20 ml of degassed absolute ethanol was added to the reaction vessel. The reaction mixture changed from yellow to light green and after about 1 hr became a deep olive green. The reaction mixture was then refluxed for 12 hr and allowed to cool to room temperature. Upon 24 hr of standing, a green precipitate formed which was collected by centrifugation, washed several times with absolute alcohol by decantation, and then dried under vacuum for 48 hr. Anal. Calcd for C₂₅H₂₇N₃V₄O₈Cl₂: C, 38.95; H, 3.36; N, 5.23; Cl, 8.84. Found: C, 39.21; H, 3.57; N, 6.08; Cl, 8.97.

Reaction of (oab)₃ or (TAAB)(HClO₄)₂ with Oxovanadium(IV) Dichloride. The bisanhydro trimer (oab)₃ described by McGeachin[11] was allowed to react in a 3:1 molar ratio with VOCl₂ in absolute ethanol. The reaction mixture was refluxed for 12 hr under nitrogen and then allowed to cool to room temperature. Upon 2 days of standing, a dark green precipitate formed and was collected by centrifugation. The product was washed by decantation with absolute ethanol until the solvent remained clear. The product was then dried for several days under vacuum. The reaction of (TAAB)(HClO₄)₂ with VOCl₂ was carried out in an identical manner. (The infrared spectra of both compounds were identical with that of compound A.)

Isolation of [(VO)₂(TRI)₂(OH)₂]Cl₄·(CH₃)₂CO. One gram of compound A was dissolved in 1 l. of water which was strongly acidified with 20 ml of concentrated hydrochloric acid. The solution was stirred overnight, after which the color had changed from pale green to pale brown. The volume was then reduced by rotoevaporation to near dryness resulting in a dark brown viscous solution. Acetone (approximately 20 ml) was then added, followed by the addition of 100 ml of water. The solution was then rotoevaporated to 50 ml and allowed to stand several days. A dark brown precipitate formed which was collected by suction filtration in a Buchner funnel and dried overnight under vacuum. Anal. Calcd for C₄₅H₃₈N₆O₅V₂Cl₄: C, 54.7; H, 3.86; N, 8.52. Found: C, 54.6; H, 4.62; N, 8.36.