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(Acetato)pentaamminecobalt(III). Deacetoxylation and Linkage Isomerization of a Specifically Oxygen-18-Labeled Acetato Ligand[1]

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The acetato ligand of (acetato)pentaamminecobalt(III) can be removed by treatment with powerful methylating and acetylating agents. It has been shown that the reaction involves specific attack on the carbonyl atom of the ligand. The reaction has been used to prove that, in solvents of low polarity, acetylation of ^{18}O-labeled hydroxopentaamminecobalt(III) can produce the acetato complex without breaking the metal–oxygen bond. In more polar media linkage isomerization of the acetato ligand occurs. Deacetoxylation reactions provide a convenient means of generating pentaamminecobalt(III) complexes in which the sixth ligand is a very weak nucleophile such as tetramethylene sulfone.

Introduction

In the preceding paper,[2] experiments were reported which showed that treatment of (acetato)pentaamminecobalt(III) perchlorate with acetyl perchlorate in *N,N*-dimethylformamide (DMF) led to very rapid solvolytic replacement of the acetato ligand. An attractive mechanism for this reaction involves attack by the electrophile on the acetato group thus converting it to a much less nucleophilic ligand. Presumably this ligand departs yielding a five-coordinate species[3] which in turn would react rapidly with the solvent. These speculations have led us to consider the use of highly reactive methylating agents for generating the same five-coordinate species from the acetato complex. We now describe in detail deacetoxylation reactions using both acetyl perchlorate and methyl trifluoromethanesulfonate which achieve this purpose. We also report experiments with the ^{18}O-labeled acetato complex which permit certain conclusions concerning the mechanisms of these reactions to be drawn.

The deacetoxylation by methyl trifluoromethanesulfonate proves to be a useful tool for examining the scrambling of a specifically labeled ^{18}O (acetato)pentaamminecobalt(III) and we report a preliminary examination of this interesting example of linkage isomerization.

Experimental Section

The preparations of (acetato)pentaamminecobalt(III) perchlorate, (acetato)pentaamminecobalt(III) trifluoromethanesulfonate, and (benzoato)pentaamminecobalt(III) perchlorate have been described elsewhere.[2]

Solvents. DMF and tetramethylene sulfone were distilled at reduced pressure and stored over freshly heated (200 °C) Linde 4A molecular sieve. Triethyl and trimethyl phosphates were distilled over P_2O_5 and stored over the same molecular sieve.

^{18}O-Enriched (Acetato)pentaamminecobalt(III) Trifluoromethanesulfonate. Labeled aquapentaamminecobalt(III) trifluoromethanesulfonate (1.06 g, 1.74×10^{-3} mol; 4–4.5% ^{18}O in the aqua ligand) was dissolved in triethyl phosphate (5.5 mL) and treated with *N,N*-dimethylbenzylamine (0.51 mL, 3.4×10^{-3} mol). The solution was then cooled to 0 °C and acetic anhydride (0.50 mL, 5.2×10^{-3} mol) was added. After 2 min cold absolute ethanol (11 mL) was added and the solution was cooled in a liquid N_2 bath, but not to freezing. Cold ether (200 mL) was added followed by addition of room-temperature ether (200 mL) approximately 10 min later. The product was recovered by filtration, washed with ethyl acetate (3×10 mL) and ether (3×10 mL), and dried in vacuo. The yield was 0.79 g (91%).

Deacetoxylation of the ^{18}O-Enriched Acetato Complex by Methyl Trifluoromethanesulfonate. The reaction was carried out in a small vessel designed to permit sampling of the vapor above the reaction mixture. It consisted of a 10×1 cm tube with a 14/20 female joint into which fitted a short tube which terminated in a glass injection port fitted with a neoprene septum. The two halves of the vessel were securely fastened together with springs.

In the above apparatus was placed a solution of the labeled (acetato)pentaamminecobalt(III) trifluoromethanesulfonate (0.13 g, 2.6×10^{-4} mol) and triethyl phosphate (1.5 mL). Methyl trifluoromethanesulfonate (0.03 mL, 2.6×10^{-4} mol) was added and the vessel was closed immediately. Prior to sampling, the vessel was warmed in a water bath at 50 °C for 2 min to increase the vapor pressure of methyl acetate. For each ^{18}O analysis, 100-μL samples of vapor were injected into a GC/MS instrument.

^{18}O Analysis of Methyl Acetate. Optimum gas chromatography conditions were achieved by using a 6-ft. U-shaped column (2-mm i.d.), packed with Porapack N (80/100 mesh), operating at 180 °C with a flow rate of 25 mL/min.

Data were collected with a Finnigan Model 3200 quadrupole mass spectrometer equipped with a Model 9500 gas chromatograph and a Model 6000 data system. The system was used in the mass fragmentography mode which is a multiple ion monitoring technique which allows continuous observation of up to four ions by way of a continuous peak switching process.[4] The data are presented as a fragmentogram which is a plot of the intensity of a specific ion vs. elution time. In the present study the ions at m/e 76, 74, 45, and 43 were monitored, the last pair being associated with the fragment ion CH_3CO^+. Ion intensities were calculated as areas under the fragmentograms.

The total label in the acetato complex was calculated by comparing the ratios of parent ion intensities [(P + 2)/P] for standard unlabeled methyl acetate with the ratio for that obtained in the deacetoxylation reaction. The amount of label in the carbonyl position was determined from a similar analysis of the m/e 45 and 43 fragmentograms. The percent of unrearranged complex is given by $200[(I_{45}/I_{43})_s - (I_{45}/I_{43})_0]/[(I_{76}/I_{74})_s - (I_{76}/I_{74})_0] - 100$, where the subscripts s and 0 refer to the sample and standard, respectively. At least ten separate chromatograms were carried out for each reaction, and these were combined to give the mean values and precision indices used in the calculation of the percent (and its propagated precision index) of unrearranged complex.

A sample of carbonyl-labeled methyl acetate was prepared from the reaction of ^{18}O-labeled acetyl chloride with methanol and was used to verify the validity of the analytical technique.

Rearrangement of the ^{18}O-Labeled Acetato Complex. (a) Water. ^{18}O-enriched complex (0.18 g) was dissolved in distilled water (5 mL) and placed in a constant-temperature bath at 50 °C for a given length of time. The complex was recovered by rapid removal of the solvent under reduced pressure in a rotary evaporator. The complex was dried at 0.5-mm pressure overnight. Results of ^{18}O analyses are given in Table I.

(b) DMF. ^{18}O-enriched acetato complex (0.19 g) was dissolved in DMF (3 mL) and allowed to stand at 22 °C for 1 h. The complex was recovered by filtration after the addition of absolute ethanol (6 mL) and ether (200 mL). The product was dried overnight at 0.5 mm. Results of ^{18}O analysis are given in Table I.

(c) Triethyl Phosphate. ^{18}O-enriched acetato complex (0.13 g) was dissolved in triethyl phosphate (1.5 mL) and allowed to stand for 3 h at 23 °C before proceeding with the ^{18}O analysis. The results are shown in Table I.

Attempted Exchange of the Acetato Complex with CD_3COOK. (Acetato)pentaamminecobalt(III) trifluoromethanesulfonate (0.25 g, 5×10^{-4} mol) and potassium acetate-d_3 (0.055 g, 5.4×10^{-4} mol) were dissolved in water (5 mL). The solution was kept at 50 °C for 1 h at which time trifluoromethanesulfonic acid (0.5 g, 3.4×10^{-3} mol) in water (1 mL) was added. The water was removed under

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Table I

synthesis solvent[a]	rearrangement conditions[b]	age of sample, days	label, atom % total	label, atom % carbonyl	% unrearranged	% linkage isomerism[c]
TEP	none	1	4.00 ± 0.06	3.99 ± 0.12	100 ± 6	
TEP	TEP, 3 h, 23 °C	1	4.00 ± 0.06	3.95 ± 0.09	98 ± 5	2 ± 8
TEP	DMF, 1 h, 23 °C	3	3.60 ± 0.02	3.26 ± 0.06	81 ± 3	19 ± 7
TEP	solid state, 23 °C	90	3.78 ± 0.05	3.17 ± 0.06	68 ± 4	32 ± 5
DMF	none	1	4.61 ± 0.09	4.03 ± 0.05	75 ± 4	
DMF	H_2O, 15 min, 50 °C	1	4.61 ± 0.09	2.54 ± 0.09	10 ± 5	65 ± 6

[a] TEP = triethyl phosphate; DMF = *N,N*-dimethylformamide. [b] Solvent, time in solution, temperature. [c] % linkage isomerism = [% unrearranged (control)] − [% unrearranged (treated)].

reduced pressure, and the solid obtained was dissolved in ethanol and reprecipitated by the addition of ether. This precipitation process was repeated. The crystalline product was washed with ether and dried under reduced pressure. The product was submitted to the same analytical procedure as employed in the ^{18}O analyses. No increase in the intensity ratio of the peak with *m/e* 77 relative to that at *m/e* 74 compared with the same ratio of the standard unlabeled methyl acetate was observed. It was concluded that the exchange had not occurred (0 ± 1%).

(Tetramethylene sulfone)pentaamminecobalt(3+). (Acetato)-pentaamminecobalt(III) trifluoromethanesulfonate (0.14 g, 2.7×10^{-4} mol) was dissolved in tetramethylene sulfone (2 g). The solution was treated with methyl trifluoromethanesulfonate (0.1 mL, 8.3×10^{-4} mol). The excess methylating reagent and methyl acetate were removed by rotary evaporation under reduced pressure. The visible spectrum run at this time exhibited a maximum at 523 nm characteristic of the tetramethylene sulfone complex.[5]

$Co(NH_3)_5OP(OCH_3)_3^{3+}$. Trimethyloxonium tetrafluoroborate (0.5 g, 3.4×10^{-3} mol) was added to anhydrous trimethyl phosphate (10.0 g, 7.1×10^{-2} mol). The solution was placed under reduced pressure (0.5 mm) for 10 min. The resulting solution exhibited two doublets, one assignable to trimethyl phosphate (δ 3.75; J = 10.0 Hz) and the other to the tetramethoxyphosphonium ion (δ 4.27, J = 11.0 Hz). No absorption at δ 4.49 characteristic of the trimethyloxonium ion was observed.

This solution (3 mL) was added to (acetato)pentaamminecobalt(III) perchlorate (0.1 g, 2.5×10^{-4} mol) in trimethyl phosphate. The solution was placed under reduced pressure (0.5 mm) for 0.5 h to remove the methyl acetate produced. The resulting solution exhibited light absorption (λ_{max} 520 nm) characteristic of the trimethyl phosphate complex.[5]

Debenzoylation in Trimethyl Phosphate. A solution of (benzoato)pentaamminecobalt(III) (18 mg, 0.04 mmol) in anhydrous trimethyl phosphate (3 mL) was added to anhydrous silver perchlorate (0.04 g, 0.22 mmol), and benzoyl chloride (25 μL, 0.22 mmol) was added to the mixture. The supernatant had λ_{max} 343 (ϵ 63) and 520 (ϵ 63) nm. Acetic acid (0.63 mL, 11 mmol) was added and the light absorption observed at various time intervals. After 18 h the solution showed no further changes in light absorption and had λ_{max} 340 (ϵ 73) and 507 (ϵ 68) nm. The solution was evaporated in vacuo to an oil which was washed with ether (3 × 3 mL). The solid so obtained was triturated with ethanol–ether (1:1) (3 × 3 mL) and ether (3 × 3 mL) and then dried. The light absorption, NMR, and IR data were consistent with that expected for a sample of the acetato complex contaminated with approximately 10% of the aqua complex. No evidence for the presence of the benzoato complex was observed.

Formation of Acetic Anhydride. (Acetato)pentaamminecobalt(III) perchlorate (100 mg, 2.5×10^{-4} mol) and silver perchlorate (310 mg, 15×10^{-4} mol) in anhydrous DMF (2 mL) were treated with acetyl chloride (0.053 mL, 7.5×10^{-4} mol). The mixture was distilled at 0.05 mm and at ambient temperature. The distillate (1.5 mL) was reacted with β-naphthol under the conditions of Chattaway[6] to give β-naphthyl acetate (26 mg, 55%); mp and mmp with authentic β-naphthyl acetate 68.0–68.5 °C.

^{18}O-Enriched (Acetato)pentaamminecobalt(III) Perchlorate. ^{18}O-enriched aqua complex[2] (0.920 g, 2×10^{-3} mol) was treated with *p*-nitrophenyl acetate (0.72 g, 4×10^{-3} mol), *N,N*-dimethylbenzylamine (0.57 g, 4.2×10^{-3} mol), and DMF (3 mL). After 45 min it was evaporated to an oil, and ether was added (5 × 10 mL) to extract the yellow material. The aqueous solution (50 mL) of the complex was made just acid and evaporated to dryness, dissolution and evaporation being repeated twice. The total time in water was 1.5 h at 20 °C but an average of only 50% of the complex was in solution. It was washed with ethanol (3 × 8 mL) and ether (2 × 8 mL) and dried in vacuo. NMR showed the product (0.789, 98%) to be pure. This mode of preparation would have led to some rearrangement of the ^{18}O label.

Deacetoxylation of the ^{18}O-Enriched Acetato Complex by Acetyl Perchlorate. Labeled acetato complex (200 mg, 5×10^{-4} mol) and silver perchlorate (91 mg, 4.4×10^{-4} mol) in DMF (1.5 mL) were treated with acetyl chloride (3.7×10^{-4} mol) with rapid stirring. Within 10 min distillation of the DMF was commenced at 1 mm and 15 °C, with the aid of stirring. The distillate was collected in a liquid nitrogen trap containing aniline (0.5 mL). After 30 min the distillation flask contained a semisolid mass in which much solvent was still trapped. DMF (1 mL) was added with exclusion of moisture and the distillation completed (30 min). In this way nearly all the liquid initially present was transferred.

(a) Isotopic Analysis of the DMF Complex. The complex, which was largely crystalline and virtually free of DMF, was dissolved in water (3 mL). The supernatant and washings (2 × 1 mL) were combined and evaporated to dryness, dissolution and evaporation being repeated to remove DMF. Trituration with ethanol (2 × 3 mL) and ether (2 × 2 mL) gave a product (198 mg) whose NMR spectrum showed there was as much free DMF as DMF complex, so the complex was dissolved three times in water (10 mL) and evaporated to dryness before trituration with ethanol (5 × 3 mL) and ether (3 × 2 mL) and drying as before. The total time in water was 30 min. The product consisted of acetato (61%) and DMF complex (39%), but there was no free DMF (i.e., <4% of the DMF complex).

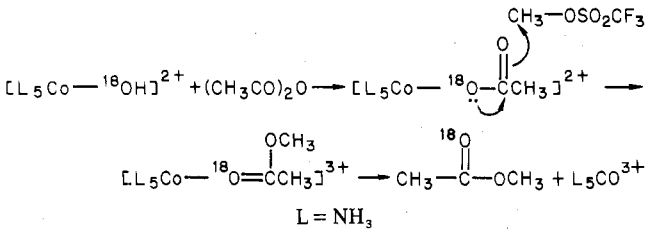
Virtually all the remaining complex (166 mg) was dissolved in water (7 mL), and KBr (230 mg) was added. After evaporation to ca. 5 mL and cooling, a white precipitate ($KClO_4$) was separated and discarded. The supernatant was then evaporated to dryness, and the solid (330 mg) was dried in vacuo. The (*N,N*-dimethylformamido)pentaammine tribromide was decomposed to give *N,N*-dimethylformamide as previously described.[2] The DMF was analyzed for ^{18}O and found to be ^{18}O enriched by −0.03 ± 0.02%.

(b) Isotopic Analysis of the Anhydride Produced. The distillate was heated on the steam bath for 2 h. The solid obtained on evaporation was rapidly extracted with cold HCl (3 × 1 mL) and recrystallized from water (pH 2), the conditions ensuring insignificant hydrolysis and, in particular, negligible exchange.[7] The yield of acetanilide was 5 mg (mp 112.5–113.0 °C) and it had a measured ^{18}O-enrichment of 0.50 ± 0.02%.

^{18}O Analysis of *N,N*-Dimethylformamide and Acetanilide. These analyses were performed with an Associated Electrical Industries MS 902 mass spectrometer.

The region to be studied was found from a calibration chart and the background was scanned from P + 6 to P − 2, at least five times at a multiplier setting (ca. 5.0) sufficiently high to give peaks which could be measured with accuracy. Heights were always used rather than areas because of the much greater speed of measurement. Accuracy was comparable. Settings of 70 eV and 50-Hz bandwidth were used at 2.7 min/decade and a chart speed of 3 cm/s. Under these conditions "square-topped" peaks were obtained. The resolving power was 1000. The sample was introduced (direct insertion probe for acetanilide, cold inlet for DMF), the quantities of fluids being sufficient to ensure that viscous flow predominated. Isotopic abundance was normally determined from the ratio (P + 2)/P, although with sufficient CO_2 the similarity of peak height permitted the determination of ratio (P + 2)/(P + 1) on the same attenuation scale. In each case

Scheme I



the compound with normal isotopic composition was studied analogously as a check on the error of the procedure. In all cases, these differed from calculated values[8] by less than the arbitrary estimates of error, but since these measurements were subject to variation in the same way as those on labeled samples, enrichment was calculated by subtraction of calculated values of peak heights[8] from the enriched-sample measurement.

The measurements depend on the ratios of the attenuation scales, in general ×1 and ×100. Direct measurement of these was not easy. A standard deviation of 1% for the ×10/×100 scales could be obtained from a large number of measurements of the same peak on both scales, although the maximum heights which could be obtained were only ca. 30 and 3 mm, respectively. Due to noise, the standard deviation for the corresponding ratios of ×1/×10 was 5%. Since the sum of these would contribute to the final calculation of enrichment, it was necessary to determine the ratio by standardization with CO_2 of normal enrichment. By this method the estimated error was only 1%.

Results and Discussion

Deacetoxylation of ^{18}O-Labeled (Acetato)pentaamminecobalt(III) Trifluoromethanesulfonate. An X-ray structure[9] for (acetato)pentaamminecobalt(III) chloride perchlorate reveals the two oxygen atoms to be nonequivalent, one of them being part of a typical carbonyl group and the other the point of attachment of the ligand to the metal. The reaction of ^{18}O-labeled hydroxo complex with acetic anhydride and base must therefore give, as the initial product, (acetato)pentaamminecobalt(III) with the labeled oxygen atom still attached to the cobalt atom. A preparation of labeled acetato complex was carried out in triethyl phosphate at 0 °C and the product was isolated and purified by precipitation with ether–ethanol followed by trituration with ethyl acetate–ether. When this material was treated with methyl trifluoromethanesulfonate in triethyl phosphate, it afforded methyl acetate in which *all* the labeled oxygen was in the carbonyl position. This result leads directly to two important conclusions. The first is that, under the conditions of preparation and deacetoxylation, *no linkage isomerization had occurred.* Secondly, *attack by the electrophile occurred exclusively at the carbonyl oxygen atom of the acetato ligand.* The mechanism is shown in Scheme I. It is, of course, conceivable that the attack by the electrophile and formation of the five-coordinate species occur concomitantly.

Linkage Isomerization. The preceding experiments showed that, by carrying out the acetylation of ^{18}O hydroxopentaamminecobalt(III) in triethyl phosphate, it is possible to generate the acetato ligand specifically labeled in the metal-bound oxygen position. Earlier experiments, in which DMF was employed as the solvent, had led to reduced specificity. We have therefore made a preliminary examination of the effect of solvent on the rate of rearrangement and the results are presented in Table I. It is apparent from these results that, in order to obtain specifically labeled acetato complex, it is necessary to use solvents of low polarity such as triethyl phosphate. Furthermore, purification procedures should avoid recrystallization from polar solvents, particularly water. The acetato complex slowly rearranges in the solid state. A sample of the solid was found to be 32% rearranged after 90 days of storage at room temperature.

We believe that the method described here, being based as it is on a direct comparison of the ^{18}O in the carbonyl position with the total ^{18}O in the ligand, is a particularly sound one for studying the rearrangement. Although in this paper we are not primarily interested in linkage isomerization itself, it is appropriate to consider the studies of analogous isomerizations reported by Andrade, Jordan, and Taube.[10] These investigators studied the incorporation of ^{18}O from enriched water into several (carboxylato)pentaamminecobalt(III) salts. If the rate of exchange of the carbonyl oxygen atom is slower or comparable with linkage isomerization, the latter process provides a pathway for the exchange of both oxygen atoms of the ligand with that of the solvent. Thus it was shown, for example, that the chelated complex binoxalatopentaamminecobalt(III) exchanged only two of its four oxygen atoms indicating that rearrangement of the carboxylato ligands was much slower than the exchange (half-life approximately 20 h at 25 °C in 1 M HCl). Unfortunately, data for the acetato ligand could not be obtained because aquation was faster than exchange. Data for several other complexes showed a wide range of rates of rearrangement with a half-life ranging from as long as 750 h to less than 7.5 h. Taube and his co-workers have carefully catalogued the erratic nature of these reactions but were unable to advance a convincing explanation for the observed behavior. In view of the comparatively rapid rearrangement we have observed for the acetato complex in water, it would appear that a detailed reinvestigation of these systems is desirable now that an alternative means of examining the reaction is available.

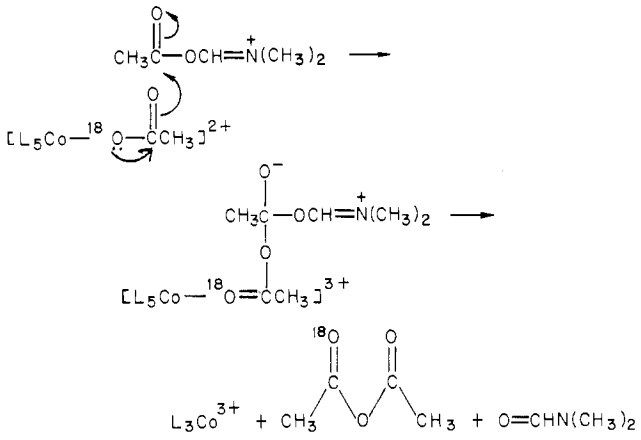
An experiment in which the rearrangement of the acetato ligand was carried out in the presence of acetate-d_3 in aqueous solution showed no incorporation of the deuterium-labeled acetate into the complex. The rearrangement is therefore an intramolecular process.

Complexation of Weak Ligands with the Pentaamminecobalt(III) Group. The introduction of the very weak ligand tetramethylene sulfone into the pentaamminecobalt(III) system was first achieved by Jordan, Sargeson, and Taube[11] through the reaction of azidopentaamminecobalt(III) with nitrosyl perchlorate in tetramethylene sulfone (sulfolane). It was subsequently shown[12] that the sulfolane ligand could be replaced reversibly by other weak ligands including methyl acetate. It is apparent that the deacetoxylation reaction provides a simple and alternative entry into the same class of compounds.

Powerful methylating agents, such as methyl trifluoromethanesulfonate and trimethyloxonium tetrafluoroborate, do not transfer a methyl group to sulfolane[13] but their solution in this solvent rapidly effects the deacetoxylation of (acetato)pentaamminecobalt(III). The initial product must be the methyl acetate complex but, as Hurst and Taube[12] have shown, there is a rapid competition between the ester and sulfolane for the sixth coordination site. Methyl acetate can therefore be removed by pumping under reduced pressure leaving a solution with the visible spectrum characteristic of the sulfolane complex. Similarly, solutions of tetramethoxyphosphonium salts in trimethyl phosphate rapidly lead to the formation of methyl acetate and the trimethyl phosphate complex, this reaction being analogous to that used for the ^{18}O analyses.

The conversion of the acetato complex to the *N,N*-dimethylformamido compound described in the preceding paper[2] can be regarded as a similar reaction. In an experiment with ^{18}O-labeled acetato complex, it was found that none of the label was retained in the dimethylformamido complex, and the reaction can thus be envisaged as a conversion of the acetato ligand to a much less nucleophilic ligand, such as acetic anhydride, which rapidly dissociates to yield the five-coordinate intermediate.[3] Attempts to achieve a similar reaction in sulfolane failed because the solution of acetyl chloride in this solvent became black on the addition of silver perchlorate.

Scheme II



Similar behavior was observed for trimethyl phosphate. In an analogous experiment in which a solution of (benzoato)-pentaammine and benzoyl chloride in trimethyl phosphate was treated with silver perchlorate, there was an immediate reaction and the resulting solutions had the characteristic light absorption of the trimethyl phosphate complex. Quenching of this solution with acetic acid afforded the acetato complex in 85% yield.

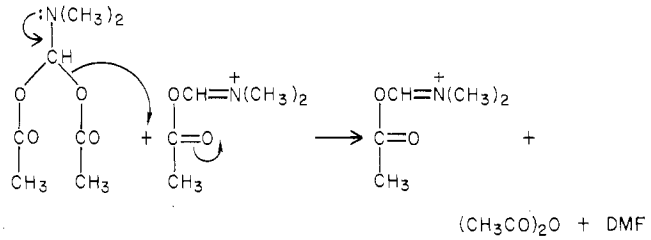
These experiments form the basis of a very simple method for generating the five-coordinate species and hence of introducing a variety of ligands into the pentaamminecobalt(III) system.[14]

Mechanism of the Deacetoxylation by CH_3CO^+/DMF. Consideration of the mechanism of the deacetoxylation of the acetato complex by acetyl perchlorate in DMF is complicated by the fact that the solvated acetylium ion $CH_3COOCH{=}N^+(CH_3)_2$ can react at either its carbonyl or imino carbon atoms. Furthermore, both reactive centers can attack either the carbonyl- or metal-bound oxygen atom of the acetato ligand. Again, ^{18}O-labeling studies have shed light on the nature of the process.

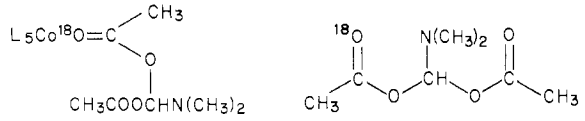
The reaction of the acetato complex with acetyl perchlorate in DMF yielded a volatile acetylating reagent presumed to be acetic anhydride since it reacted with β-naphthol and aniline to yield the corresponding *O*- and *N*-acetyl derivatives, respectively. The conversion to acetanilide was used to assay for ^{18}O in the carbonyl positions of acetic anhydride produced from the labeled acetato complex. It was found that greater than 42.5% of the original label was contained in the acetanilide. Since only one of the carbonyl oxygen atoms of the anhydride could have acquired the label, this result implies that 85% of the original label must have been present as carbonyl oxygen in acetic anhydride.[15] The sample of acetato complex used in this experiment was prepared and purified under conditions which would have resulted in as much as 10–15% rearrangement; we therefore conclude that in this deacetoxylation reaction, as in that employing powerful alkylating reagents, the electrophile reacts exclusively at the carbonyl oxygen atom of the ligand. Thus a plausible mechanism involving the carbonyl carbon atom of the electrophile is that shown in Scheme II.

Attack involving the imino carbon atom on the carbonyl oxygen atom of the ligand would give rise to **1** and thence to the free ligand **2**.

Scheme III



$(CH_3CO)_2O$ + DMF



1 **2**

Compound **2** has simple ester groups and is not expected to acetylate either β-naphthol or aniline under the conditions employed. It could, however, be converted by one of several mechanisms to acetic anhydride and DMF. Of these, only that shown in Scheme III can explain the result of the labeling experiment. This mechanism is assumed to involve catalysis by $CH_3COOCH{=}N^+(CH_3)_2$ and would lead to $CH_3C^{18}OOCOCH_3$ and an equimolecular mixture of dicarbonyl and unlabeled anhydride. The process, however, would require exclusive *O*-alkyl rather than *O*-acyl attack on **2**, which is highly unlikely. We therefore favor the mechanism in Scheme II.

Registry No. (Acetato)pentaamminecobalt(III) trifluoromethanesulfonate, 22239-79-8; aquapentaamminecobalt(III) trifluoromethanesulfonate, 69897-22-9; (tetramethylene sulfone)-pentaamminecobalt(3+), 46145-85-1; $Co(NH_3)_5OP(OCH_3)_3^{3+}$, 14970-17-3; (acetato)pentaamminecobalt(III) perchlorate, 14523-28-5; (benzoato)pentaamminecobalt(III) perchlorate, 30185-41-2; (*N*,*N*-dimethylformamido)pentaamminecobalt(III) perchlorate, 69897-24-1; (*N*,*N*-dimethylformamido)pentaamminecobalt(III) tribromide, 69897-25-2; acetic anhydride, 108-24-7; methyl trifluoromethanesulfonate, 333-27-7; acetyl perchlorate, 2889-74-9.

References and Notes

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(15) It is expected that any isotope effect in the conversion of the anhydride to acetanilide would have discriminated against the C=^{18}O group.