Sulfone and Ester Ligands in Pentaamminecobalt(III) Complexes

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Abstract: Preparation and characterization of (tetramethylene sulfone)pentaamminecobalt(III) and (methyl acetate)pentaamminecobalt(III) perchlorates are described. Both complexes undergo rapid aquation reactions; for the methyl acetate complex, $k \geq 2 \times 10^{-2}$ sec^{-1} at 23°, and the aquation rate of the sulfolane complex is comparable. Aquation of the methyl acetate complex proceeds without ester hydrolysis and largely by cobalt–oxygen bond rupture.

Only a very few coordination complexes of tetramethylene sulfone, $(CH_2)_4SO_2$, with transition metal ions have been prepared, and the coordinative ability of sulfolane is generally regarded as quite low.[2a] Sulfolane complexes should therefore serve as excellent precursors of coordination compounds containing other weakly nucleophilic ligands. In the present study a complex of methyl acetate with the pentaamminecobalt(III) (Ro) group has been prepared by replacement of sulfolane in the Ro–sulfolane perchlorate. The substitution properties of the Ro–methyl acetate complex, of interest in connection with other studies,[2b] have been investigated.

Experimental Section

Reagents. Commercially available tetramethylene sulfone was purified by vacuum distillation from molecular sieve using a nitrogen bleeder to minimize bumping. Methyl acetate was purified by refluxing it with acetic anhydride and by fractional distillation.[3] These and other solvents used in the study were stored over molecular sieve.

Rigorous exclusion of moisture from the reaction mixtures proved necessary as water is a much better nucleophile than the organic ligands used and substitutes rapidly for sulfolane and methyl acetate in these complexes. Preparation of Ro–sulfolane perchlorate was therefore carried out in a glove box maintained dry by P_2O_5. Manipulative procedures required that the Ro complexes be taken occasionally from the glove box. To protect them from atmospheric moisture, a special apparatus was designed. A test tube containing a 28/15-O-ring joint on the open end was constructed; the companion joint was fitted to a ground-glass vacuum stopcock, the other end of the stopcock being provided with a standard taper joint of suitable size to fit the vacuum line used in the preparation. To facilitate closure of the tube, a constriction was placed between the O ring and the stopcock. A second tube containing an O-ring joint and a joint to fit the vacuum line on opposite ends was also constructed. A standard taper cap was provided for this tube.

The test tube, joined to the stopcock with an O-ring clamp, was flamed out under vacuum, the stopcock closed, and the tube transferred to the glove box. All other glassware and reagents used in the preparation were also placed in the box, and sufficient time (24 hr) was given to remove residual water. The Ro–sulfolane complex was prepared by the reaction of Ro–azido perchlorate with nitrosyl perchlorate in sulfolane.[4] Both reagents are soluble in sulfolane; $NOClO_4$ reacts only slowly with the solvent and the reaction with coordinated azide proceeds smoothly, the solution undergoing a color change from intense purple to cherry red during reaction. Successive extractions of the product solution with anhydrous ether removed the solvent and a powdery pink solid was eventually isolated. The solid was suspended in ether and transferred to the test tube, made accessible by breaking the O-ring seal. The apparatus was reassembled and removed to the vacuum line where residual ether and solvent were distilled off.

The Ro–methyl acetate complex was prepared by equilibrating Ro–sulfolane perchlorate as a suspension in methyl acetate. (Direct preparation of the methyl acetate complex by the reaction used to form Ro–sulfolane is unfeasible because reactants and products are insoluble in this solvent.) Methyl acetate was added to Ro–sulfolane perchlorate in the O-ring test tube in the glove box and, after reassembling the apparatus and transferring it to the vacuum line, the contents of the tube was frozen in liquid N_2, a vacuum applied to the system, and the reaction tube sealed at the constriction. The sealed tube was heated in an oven at 70° for *ca.* 3 hr. Yellowing of the solvent was noticed at the end of this time, indicating that some decomposition had occurred. The reaction vessel was transferred again to the glove box where the solid was washed with methyl acetate and the sealed joint replaced by the capped tube. The apparatus was then returned to the vacuum line where excess methyl acetate was removed under vacuum and the solid pumped on to remove any residual volatile material. Some water-insoluble material was present in the complex although the quantity did not appear to be large. No means of purifying the complex was devised. Solution of the product in solvents sufficiently polar to dissolve the complex resulted in immediate substitution of the solvent for methyl acetate. Attempted preparations using Ro–acetone or Ro–trimethyl phosphate perchlorates as starting materials were unsatisfactory.

O^{18}-Isotope Labeling Experiments. Approximately 1 g of material from the Ro–methyl acetate preparation was dissolved in a Urey tube in 7 ml of 1.53 atom % (eightfold) O^{18}-enriched water, which was also 10^{-2} *M* in $HClO_4$. Noncondensable gases were removed from solution in three freeze–pump–thaw cycles on the vacuum line, using liquid N_2 as coolant. The solution was then cooled to −18° in a salt–ice bath and methyl acetate fractionally distilled into a second Urey tube cooled with liquid N_2. Fractional distillation from the second to a third Urey tube effectively removed water from the methyl acetate sample. The solution of Ro–aquo ion (formed by aquation of Ro–methyl acetate ion) in the original Urey tube was filtered to remove insoluble material and the complex precipitated from solution as the bromide salt by cooling and adding concentrated HBr. The solid obtained was isolated by filtration, recrystallized from acidic (HBr) solution, washed with methanol, and dried in a vacuum desiccator. Coordinated water was removed from Ro–aquo bromide by heating the complex to 110° for several hours. The accumulated moisture was then transferred to a Urey tube and its isotopic composition determined by equilibration with CO_2.[5] The procedures and apparatus employed have been given detailed descriptions.[6] Mass ratios of equilibrated CO_2 samples determined both by direct reading from the instrument using a double collecter and by calculation from the relative peak heights in the spectrum from 44 to 48 amu were in good agreement.

Instrumentation. Infrared and electronic spectra were obtained using Perkin-Elmer Model 421 and Cary Model 14 and 15 recording spectrophotometers, respectively. Solid reflectance spectra were determined with a Cary 14 spectrophotometer equipped with an iodine vapor lamp using a tungsten filament and Model 1411750 and 1511000 cell-space total diffuse reflectance accessories. Varian Associates Model A-60 and Atlas Model M-86 spectrometers were used to obtain proton nmr and mass spectra, respectively.

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[1] Allied Chemical Corporation Fellow, 1963–1964.

[2] (a) C. H. Langford and P. O. Langford, *Inorg. Chem.*, 1, 184 (1962); (b) H. Taube and J. Hurst, to be published.

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Results and Discussion

The electronic absorption spectrum of the Ro–sulfolane perchlorate preparation in sulfolane showed a maximum at 522 mμ with a pronounced shoulder at *ca.* 470 mμ; such band splittings are expected for ligands well-separated from ammonia in the spectrochemical series.[7] Addition of a few drops of water to the sulfolane solution caused an immediate color change from red to orange, the visible spectrum changing to a symmetrical peak centered at 491 mμ, characteristic of the Ro–aquo ion. The proton nmr resonance spectrum of the complex in D_2O was identical with that of free sulfolane, confirming that aquation of Ro–sulfolane is rapid and complete. This facile conversion of Ro–sulfolane to Ro–aquo illustrates that sulfolane is a "good" leaving group.

Nmr analyses in D_2O of the reaction products from the sealed tube reactions showed two strong peaks of equal intensities at δ 4.1 and 2.5 (relative to external TMS) characteristic of the CH_3O and CH_3C protons, respectively, of noncoordinated methyl acetate. Proton absorptions ascribable to coordinated methyl acetate were absent, as were absorptions due to sulfolane (δ 2.2, 3.0). Measurement of the increase in peak heights when a known amount of methyl acetate was added to a D_2O solution containing a known weight of reaction product led to a semiquantitative measure of the amount of Ro–methyl acetate complex formed. In the best preparations examined in this way the quantity of methyl acetate giving rise to signal was only *ca.* 40% of that expected on the basis of weight for pure complex. It appears that there is no noncoordinated methyl acetate in the preparations; continued pumping of the reaction product under vacuum for periods up to 48 hr caused no decrease in the intensities of the methyl acetate resonances, whereas Ro–aquo perchlorate, precipitated from methyl acetate, lost all traces of ester when placed under vacuum for only *ca.* 0.5 hr.

Comparison of the visible reflectance spectrum of the solid with other Ro complex perchlorates indicates the formation of a new species (Figure 1). In particular, the absorption maximum which appears at 502 mμ for carboxylate complexes is expected to shift to lower energies when the negative charge on the carboxylate is decreased.

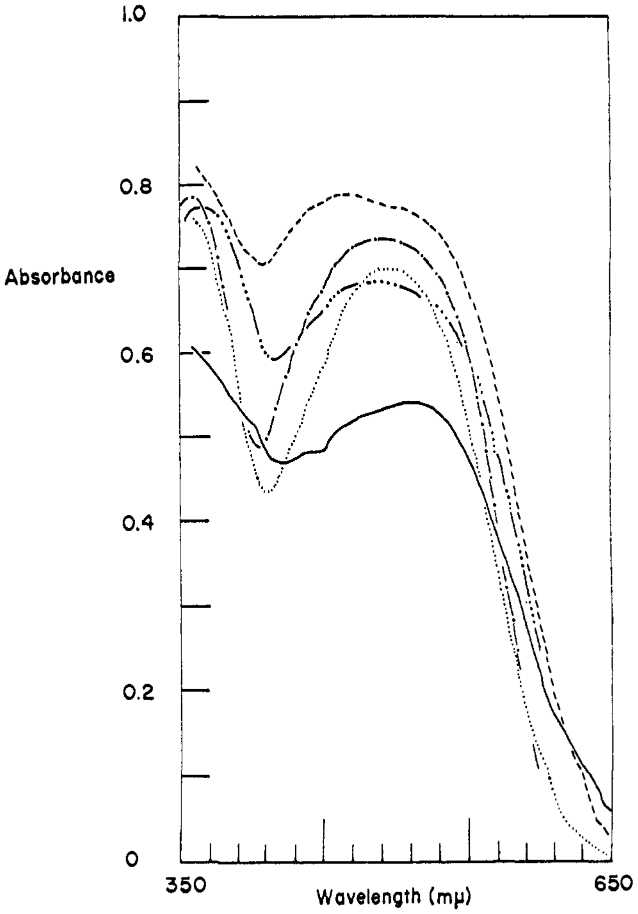

Figure 1. Diffuse reflectance spectra of Ro complexes: Ro–methyl acetate perchlorate, ———; Ro–aquo perchlorate, - - - -; Ro–methyl fumarato perchlorate, ...; Ro–acetato perchlorate, -·-·-·; Ro–maleato perchlorate, —····—.

The infrared spectrum of the complex in a Nujol mull was compared to that obtained for Ro–aquo perchlorate. Bands not corresponding to the Ro–aquo spectrum are listed in Table I; they are of medium to weak intensity. For comparison, the strong absorptions observed for methyl acetate and their tentative assignments are listed also.[8] Notable in the reaction product spectrum is the absence of a well-defined carbonyl absorption frequency. Possibly the band has been shifted by coordination so far that it is hidden under the broad degenerate ammonia deformation mode centered at 1610 cm^{-1},[9] or perhaps the broad ill-defined band at 1690 cm^{-1} is actually the carbonyl mode. At any rate, the absence of absorption at 1748 cm^{-1} indicates that the methyl acetate in the reaction product is coordinated. Also, no splitting of the degenerate perchlorate absorption bands was observed, thus probably eliminating a perchlorate complex as a component of the product mixture.[10]

Table I. Infrared Spectrum of Ro–Methyl Acetate Perchlorate

Infrared, cm^{-1}		Assignment for
Ro complex[a]	Methyl acetate[b]	methyl acetate
1690	1748	Carbonyl stretch
1320	1435	Symmetrical C–H
1290	1369	bending modes
1250	1243	Skeletal vibration
1200		
1010	1047	Skeletal vibration
870		

[a] Nujol suspension; only absorptions not present in the Ro–aquo perchlorate spectrum are listed. [b] In CCl_4.

The behavior of the Ro–methyl acetate preparation in a variety of solvents is given in Table II. The solubility of the complex in several solvents differs greatly from that of Ro–aquo perchlorate. Comparison of the spectrum of the complex in the solvents with the spectra of Ro–solvent complexes suggests rapid substitution of a solvent molecule for methyl acetate in the primary coordination sphere of the cobalt ion. The po-

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Table II. Behavior of Ro–Methyl Acetate in Various Solvents[a]

Solvent	Ro–methyl acetate λ_{max}, mμ	 Aquation rate	Ro–aquo λ_{max}, mμ	Ro–solvent λ_{max}, mμ	 Aquation rate
DMSO	514 (sym)	Slow ($t_{1/2}$ = hours)	492 (sym)	514 (sym)	Slow ($t_{1/2}$ = hours)[b]
Sulfolane	519 (asym)	Instantaneous	sl sol, dec	522 (asym)	Instantaneous[b]
Acetone	511 (sym)	Instantaneous	491 (sym) sl sol	515 (sym)	Instantaneous[c]
DMF	510 (sym)	Very slow	491 (sym)	506 (sym)	Very slow[b]
TMP	510 (sym) (ppt formed)	Slow	481 (?) (very broad)	520	$t_{1/2}$ = 47 min[d]
Methanol	499 (sym)	...	499 (very broad) sl sol	494	$t_{1/2} \simeq$ 1 hr[e]
Water	491 (sym)	...	491 (sym)	...	...

[a] Symbols and abbreviations: sym = symmetrical; asym = asymmetrical; $t_{1/2}$ = half-time; λ_{max} = wavelength at maximum; dec = decomposes; sl sol = slightly soluble. [b] This work. [c] F. Nordmeyer, private communication; also observed in this work. [d] W. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963). [e] Reference 4.

sition of the low-energy maxima observed for the solutions of the complex (water > methanol > DMF $\simeq$ TMP > acetone > DMSO > sulfolane) compares well with the order observed for the Ro–solvent complexes (water > methanol > DMF > acetone $\simeq$ DMSO > TMP > sulfolane). The small discrepancies in the relative orders which appear can probably be ascribed to differences in moisture content of the solvents. The presence of some aquo impurity in the Ro–methyl acetate preparation is the probable cause of the shift to higher energies of the maxima of the spectra of Ro–methyl acetate dissolved in the various solvents relative to the corresponding Ro–solvent spectra. The interpretation of spectral behavior in terms of rapid solvolysis of Ro–methyl acetate is given credence by qualitative measurements of aquation rates of the complex made up in various solvents which showed that these rates parallel the aquation rates of the corresponding Ro–solvent complexes.

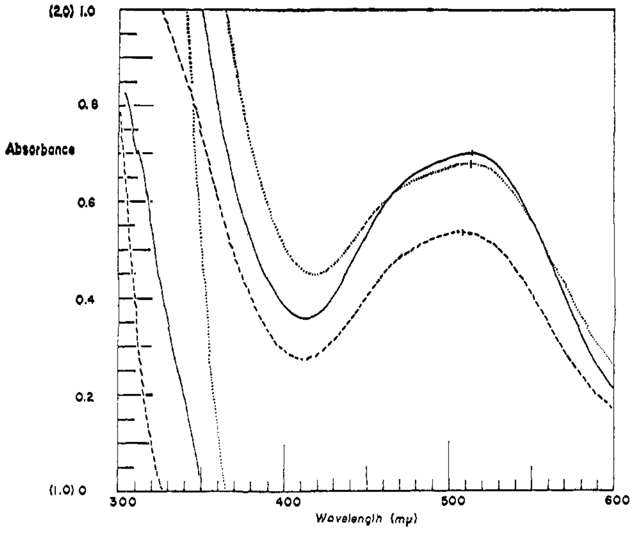

Figure 2. Competition of sulfolane and methyl acetate for the sixth ligand position: Ro–methyl acetate in sulfolane, ———; added methyl acetate, - - - -; added sulfolane, ...

Experiments with solutions of the reaction product in sulfolane suggest that there is a rather labile equilibrium between the sulfolane and methyl acetate complexes. The electronic absorption spectrum of the reaction product dissolved in sulfolane showed an asymmetrical peak with a maximum at 513 mμ (Figure 2). Addition of approximately one-third volume of methyl acetate caused an immediate shift in the position of the maximum to 508 mμ. Accompanying the shift was a loss in peak asymmetry. Addition of enough sulfolane to increase the volume threefold caused an immediate shift in maximum back to 512 mμ. Addition of water caused an instantaneous collapse of the spectrum to that of Ro–aquo. These results are interpreted in terms of a labile equilibrium of the type

$$\text{Ro–sulfolane}^{3+} + \text{methyl acetate} = (\text{Ro–methyl acetate})^{3+} + \text{sulfolane}$$

in which methyl acetate and sulfolane are competing for the sixth ligand position in the first coordination shell of the Ro complex. The effect of solvent changes upon the electronic absorption spectra of a complex of fixed composition can be expected to be considerably less than that observed. The fact that methyl acetate substitutes readily for sulfolane in the complex in solution implies that it will substitute readily in the heterogeneous reaction. The weight of evidence accumulated thus strongly suggests that methyl acetate is bound to the Ro moiety in the first coordination sphere. The point of attachment, whether to the acyl or alkoxy oxygen, is, however, not known.

A solution of Ro–methyl acetate in water immediately shows the Ro–aquo spectrum and aquation is complete in the time of dissolution which was about 2 min. Thus the half-time for the aquation is less than *ca.* 30 sec, and the specific rate[11] is greater than 2 × 10^{-2} sec. Ester hydrolysis does not accompany aquation. Addition of methyl acetate to a solution of the complex in D_2O only increases the intensities of peaks present in the nmr spectrum of the complex, but addition of acetic acid and methanol cause the appearance of new peaks in the CH_3C and CH_3O regions. (The CH_3C-proton resonance of acetic acid nearly overlaps that of methyl

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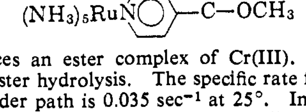
(11) Working in these laboratories, R. G. Gaunder finds that the reaction of

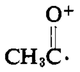


with Cr^{2+} produces an ester complex of Cr(III). This intermediate aquates without ester hydrolysis. The specific rate for this reaction by the simple first-order path is 0.035 sec^{-1} at 25°. In many cases, complexes of $(H_2O)_5Cr^{3+}$ and $(NH_3)_5Co^{3+}$ show similar labilities.

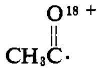
acetate but the CH_3O absorption of methanol is shifted significantly (*ca.* 0.33 ppm upfield from methyl acetate).)

Aquation of the complex proceeding by attack of water at the acyl carbon atom of the ligand is plausible and, in fact, the rapid reaction rate suggests this mechanism.[12] To distinguish between this mechanism and the alternative attack by water at the cobalt center, aquations were studied in O^{18}-enriched water. Attack at the acyl carbon will lead to incorporation of O^{18} into methyl acetate, while attack at the metal center causes metal–oxygen rupture and enrichment of the Ro–aquo product.

The mass spectra of methyl acetate isolated from reaction mixtures of Ro–methyl acetate perchlorate in normal and O^{18}-enriched water were compared to a reference spectrum of methyl acetate of normal isotopic composition. The spectra were complex, but major peaks appeared only at 15, 43, and 74 amu. The relative peak heights of the spectra of methyl acetate from the various sources were nearly identical. Particularly significant were the mass ratios 76/74 and 45/43, mass numbers 74, 76 corresponding to the parent ion peaks and 43, 45 undoubtedly being predominantly the fragments



$$CH_3\overset{\overset{O^{+}}{\|}}{C}\cdot$$



$$CH_3\overset{\overset{O^{18\,+}}{\|}}{C}\cdot$$

The relative peak heights $(\times 10^3)$ for isotopically normal CH_3OAc and for CH_3OAc recovered when the complex is brought into contact with normal water and with O^{18}-enriched water (eightfold) are as follows: (76/74) 6.5, 6.5, 6.7, (45/43) 8.4, 21.5, 10.2. These ratios show that there is negligible incorporation of O^{18} into the organic product.

The isotopic composition of the water in $RoOH_2^{3+}$ recovered from the aquation of the isotopically normal ester complex in solvent 7.77-fold enriched in O^{18} showed it to be 6.36-fold enriched. Thus, of the aquo ion which is formed, 85% derives its oxygen from the solvent. Because the preparation of Ro–methyl acetate undoubtedly contained some Ro–aquo (of normal isotopic composition), the value of 85% indicates largely Co–O bond breaking. On the basis of weight, nmr measurements had indicated only *ca.* 40% Ro–methyl acetate in the preparation. The apparent discrepancy between this value and the minimum index of purity, 85%, suggested by the isotope-labeling experiments can be resolved in part by the presence of water-insoluble impurities in the preparation, although the quantity of water-insoluble material did not appear to be sufficiently large to account for all of this difference. Exchange by the reaction $Ro\text{–}H_2O^{3+} + H_2O^{18} = (Ro\text{–}H_2O^{18})^{3+} + H_2O$, unless catalyzed in some unknown fashion, is negligible under the experimental conditions[13] and cannot account for the discrepancy. Although the limited purity of the preparation renders it impossible to make a quantitative statement about the position of bond breaking, it is clear that aquation of the Ro–methyl acetate complex proceeds predominantly by cobalt–oxygen bond rupture.

It should be noted that the tracer experiments described by themselves prove that a pentaamminecobalt(III) species which aquates rapidly is present in the preparations. Since the solid does not contain sulfolane, nor does ClO_4^- appear to be coordinated to Co(III) (see above), while it does contain methyl acetate, the conclusion that we are dealing with a methyl acetate complex of Co(III) receives additional support.

The conclusion that ester hydrolysis does not take place when the ester complex of $(NH_3)_5Co^{3+}$ aquates is particularly interesting in the context of the observations reported for ester complexes in which the ester group is known[14] to be bound to a substitution-inert center in a chelate configuration, and in which this kind of binding can reasonably be inferred.[15] In the latter cases, the ester function is largely hydrolyzed rather than simply being released. The difference between the monodentate case we report on here and the chelated may only be that the rate of release of the ester function by substitution at the metal ion is decreased in the chelate case compared to the monodentate. A difference of this kind has been documented for release of one end of ethylenediamine compared to release of NH_3.[16,17]

Acknowledgments. Financial support for this research by the National Institutes of Health, Grant No. 13638-01, is gratefully acknowledged. Acknowledgment is also made to the National Science Foundation, Grant G-22611, for purchase of the spectrophotometer.

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