as 2.[18] The ionic association of butylpyridinium cation with chloride ion has been indicated by NMR[19–21] and FTIR[22] studies of $AlCl_3$:BuPyCl melts.

For solutions of iodine and (TEA)I_3 in basic $AlCl_3$–BuPyCl ionic liquids the spectrophotometric studies confirmed polyhalogen equilibria deduced from the electrochemical results.[2] In particular, the formation of I_3^- in iodine solution, expected from the values of eqilibrium constant for reactions 1 and 2 estimated in the electrochemical studies,[2] was directly observed. Attempts to obtain more accurate estimates of the equilibrium constants for reaction 1 and 2 from the spectral data were unfortunately unsuccessful. Spectra recorded for I_2 and (TEA)I_3 solutions in basic $AlCl_3$–BuPyCl mixtures were limited to a narrow range of wavelengths and consisted of overlapping bands of all ions involved in the polyhalogen equation, i.e., ICl_2^-, I_2Cl^-, I_3^-, and I^-. Additionally, a spectrum of I_2Cl^- ion could not be obtained separately; thus molar absorptivity values for this ion were uncertain. However, the spectra obtained for iodine and triiodide solutions at low chloride concentration (Figures 4 and 5) confirmed the approximate values of the equilibrium constants for reactions 1 and 2. Concentrations of I_3^- ions calculated from these equilibria agreed reasonably well with the I_3^- concentrations estimated from the absorbance measured at 365 nm.

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Registry No. $AlCl_3$, 7446-70-0; BuPyCl, 1124-64-7; ICl, 7790-99-0; ICl_2^-, 14522-79-3; I_2, 7553-56-2; I_2Cl^-, 17705-05-4; $AlCl_3I^-$, 23606-63-5; $Al_2Cl_6I^-$, 93426-73-4.

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Proton Exchange of $Co(NH_3)_6^{3+}$ Ion with Cosolvent Water in Me_2SO Solutions: A ^{59}Co NMR Study

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^{59}Co NMR spectra are reported for the hexaamminecobalt(III) ion in dimethyl sulfoxide solutions containing small amounts of deuterium oxide and triethylamine. The spectra show the time dependence of the isotopomer distribution which requires that the base-catalyzed exchange process proceed by two paths: one involves a single hydrogen-exchange event while the other requires equilibration of the complex with the isotopic composition of the proton-exchangeable solvent at each activation event by the base.

Introduction

Conjugate base formation may be an important step in reactions of transition-metal amine complexes leading to racemization and ligand substitution.[1,2] Several groups have examined conjugate base participation by following the base-catalyzed proton-exchange reactions in complexes of cobalt(III),[3,4] platinum(II),[5,6] and platinum(IV)[7] using proton NMR spectroscopy. In contrast to the proton NMR spectra, the cobalt-59 NMR spectrum permits observation of each H/D isotopomer. There is a 5.6 ppm isotope shift experienced at the cobalt nucleus for every deuterium atom substituted for a proton at the nitrogen in the hexaamminecobalt(III) ion.[8–10] Similar shifts are found with the tris(ethylenediamine)cobalt(III) ion.[9] The ^{59}Co NMR spectrum thus provides an efficient means for following the H/D exchange reactions in detail as it approaches equilibrium: The final isotopomer distribution will be dependent on the number of exchangeable positions in the metal complex and the H/D ratio in the solvent.

Figure 1 shows representative spectra for hexaamminecobalt(III) chloride recorded as a function of time in an aqueous solution containing 75% deuterium oxide at pH 4.00. A plot of the H_{18} isotopomer resonance amplitude against time gives a linear plot with a pseudo-first-order rate constant of 2.1×10^{-3} min^{-1} for the decrease in the H_{18} isotopomer concentration. The mechanism expected,[1,2] involving base catalysis with a rate law first order in cobalt(III) and in hydroxide ion, is consistent with our data. An ion-pair mechanism for proton exchange has also been proposed,[11] but questioned.[12,13] Block and Gold[14] maintain that the acidity of the hexaamminecobalt(III) complex is consistent with a rapid hydroxide association process, conjugate base formation, rapid proton interchange, and regeneration of the hydroxide ion. The cobalt NMR spectrum provides a sensitive method for probing such reaction mechanisms further because the spectral resolution provides the isotopomer distribution as a function of time. We report here results for proton exchange in a nonaqueous solvent that was partly motivated by applications to analytical methodologies.[9] These data also provide a striking example of the detailed mechanistic information sometimes available from high-field multinuclear NMR spectrometers.

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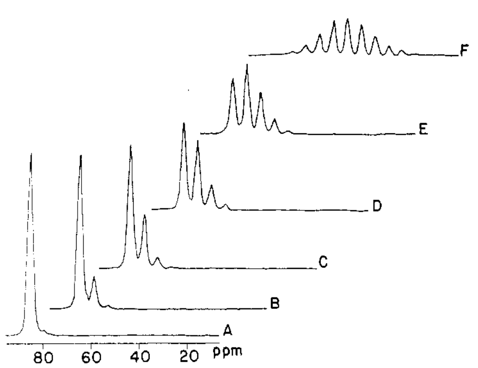

Figure 1. ^{59}Co NMR spectra obtained at 71.7 MHz and 298 K for 0.050 M hexaamminecobalt(III) chloride as a function of time in a 75% deuterium oxide and 25% water solution at pH 4.0: (A) 1.7 min; (B) 18 min; (C) 38 min; (D) 68 min; (E) 109 min; (F) 140 min.

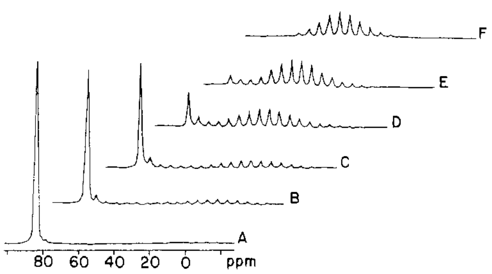

Figure 2. ^{59}Co NMR spectra obtained at 71.7 MHz and 298 K for solutions containing 0.050 M hexaamminecobalt(III) perchlorate, 0.50 mM triethylamine, and 0.225 M deuterium oxide in Me_2SO as a function of time: (A) 3 min; (B) 22 min; (C) 42 min; (D) 143 min; (E) 265 min after solution preparation. Spectrum F was obtained approximately 12 h after preparation and does not change further with time.

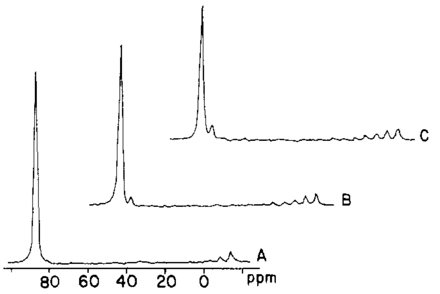

Figure 3. ^{59}Co NMR spectra obtained at 71.7 MHz and 298 K for solutions containing 0.010 M hexaamminecobalt(III) perchlorate, 0.010 mM potassium hydroxide, and 0.225 M deuterium oxide in Me_2SO as a function of time: (A) 3.3 min; (B) 59 min; (C) 122 min after solution preparation.

Experimental Section

Hexaamminecobalt(III) perchlorate was prepared by adding concentrated perchloric acid dropwise to a saturated aqueous solution of hexaamminecobalt(III) chloride until no further precipitation occurred. The solid was collected by filtration, washed with cold water, recrystallized twice from hot water, and dried overnight under vacuum.

Dimethyl sulfoxide, triethylamine, and pyridine were dried over 4A molecular sieves for at least 2 days. The 12-mm NMR tubes and other glassware used were allowed to stand overnight with 0.1 N HCl and then rinsed several times with deionized water and placed in a drying oven overnight. While the NMR tubes and glassware were still warm, they were capped with rubber septa and allowed to cool to room temperature. A stock solution of Me_2SO containing the appropriate concentration of triethylamine or pyridine was prepared by weight. The hexaamminecobalt(III) perchlorate was weighed and dissolved in a weighed aliquot (9 mL) of the Me_2SO–amine solution, then a weighed amount of deuterium oxide was added, and the solution was quickly mixed. The solution was then divided into three equal aliquots, placed in NMR tubes, and a ^{59}Co NMR spectrum of each aliquot was immediately obtained. The ^{59}Co NMR spectra were determined at intervals over a several-hour period. Spectra of equilibrated solutions were checked for further changes as a function of time. The samples in which potassium hydroxide was used as the base catalyst were prepared similarly except the appropriate amount of potassium hydroxide was dissolved in the deuterium oxide that was added to the Me_2SO–hexaamminecobalt(III) perchlorate solution.

The aqueous sample of the cobalt complex was prepared from a 0.2 M aqueous solution of hexaamminecobalt(III) chloride adjusted to pH 4.00. A 1-mL aliquot of this solution was mixed with 3.00 mL of deuterium oxide at pH 4.00 to give a solution 0.05 M in cobalt complex. The pH reported was read directly from a pH meter operating with a glass electrode and adjusted with a dilute solution of HCl and KOH in deuterium oxide or water as appropriate.

The cobalt-59 NMR spectra were determined at 71.1 MHz with a Nicolet NT-300 wide-bore multinuclear spectrometer. The acquisition conditions used were a 90° pulse (24 μs), a pulse repetition time of 200 ms, a 20-kHz spectral width, and a data table of 2K data points which was zero filled to 8K points. Depending on the cobalt complex concentration, 40–800 transients were collected in order to obtain a suitable signal to noise ratio. The spectra were collected without field-frequency lock.

Results and Discussion

The cobalt-59 NMR spectrum shows that no proton exchange occurs in a solution made to contain 0.1 M hexaamminecobalt(III) perchlorate and 0.9 M deuterium oxide in Me_2SO after 10 h. Addition of a base like triethylamine at millimolar concentration, however, leads to a readily monitored exchange reaction as shown by the spectra in Figure 2. Several features of these data are notable: (1) Unlike the data shown in Figure 1 for aqueous solutions, the proton exchange in Me_2SO containing a trace of water does not proceed directly to the equilibrium isotope distribution from the H_{18} spectrum through the D_1, D_2 isotopomers but the D_{18} isotopomer is populated almost immediately in the exchange process. In contrast the D_{18} isotopomer is never detectable in the data of Figure 1 when the exchange proceeds in water as solvent. (2) The H_{17} isotopomer is populated to a small, but significant, extent early in the time course of the exchange reaction. (3) At equilibrium the isotopomer ratio is given by the binomial distribution as expected after correction for isotope fractionation effects.[9] (4) We find that the exchange rate is linear in both cobalt complex and base concentration. Points 1 and 2 are shown more clearly in Figure 3.

These results require two parallel channels for the base-catalyzed reaction. One path leads to exchange of just one hydrogen on the complex, the other leads to equilibration of all the hydrogen in the metal complex with the solvent at each incidence of reaction. A reasonable suggestion for the second path involves formation of the metal complex conjugate base, $(NH_3)_5Co(NH_2)^{2+}$. This conjugate base may react in a series of exchange and proton-transfer reactions like that shown in Scheme I, which causes very rapid equilibration of the metal complex composition with that of the solvent. The first

Scheme I

$$[(NH_3)_5Co\mathit{N}H_2\cdots HOD]^{2+} \rightleftharpoons [(NH_3)_5Co\mathit{N}H_2\cdots DOH]^{2+}$$

$$[(NH_3)_5Co\mathit{N}H_2\cdots DOH]^{2+} \rightleftharpoons [(NH_3)_5Co\mathit{N}H_2D\cdots OH]^{2+}$$

$$[(NH_3)_5Co\mathit{N}H_2D\cdots OH]^{2+} \rightleftharpoons [(NH_3)_4(\mathit{N}H_2D)CoNH_3\cdots OH]^{2+}$$

$$[(NH_3)_4(\mathit{N}H_2D)CoNH_3\cdots OH]^{2+} \rightleftharpoons [(NH_3)_4(\mathit{N}H_2D)CoNH_2\cdots HOH]^{2+}$$

$$[(NH_3)_4(\mathit{N}H_2D)CoNH_2\cdots HOH]^{2+} + D_2O \rightleftharpoons [(NH_3)_4(\mathit{N}H_2D)CoNH_2\cdots HOD]^{2+} + HOD$$

$$[(NH_3)_4(\mathit{N}H_2D)CoNH_2\cdots HOD]^{2+} \rightleftharpoons [(NH_3)_4(\mathit{N}H_2D)CoNH_2\cdots DOH]^{2+}$$

etc.

pathway requires immediate termination of the proton-exchange process, and the present experiments do not provide detailed further constraints on the mechanistic detail. The mechanism for the rapid scrambling is similar to one that has been suggested for platinum(IV) complexes by Grunwald,[7] wherein the water solvating the cation interacts simultaneously with the proton-deficient nitrogen atom and an adjacent coordinated ammonia molecule. The very rapid exchange kinetics, implied by this earlier result, appears to be consistent with our present findings.

In summary, this series of ^{59}Co spectra shows very clearly the requirement of two different proton-exchange paths for this complex. Though this study shows the power of ^{59}Co NMR to elucidate mechanistic details of proton-exchange processes, it falls far short of the potential development in this area because it lies beyond the primary interest of the laboratory.

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Registry No. Hexaamminecobalt(III), 14695-95-5; water, 7732-18-5; triethylamine, 121-44-8.

Contribution from the Departments of Chemistry, Purdue University,
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Redox Chemistry of Multiply Bonded Diosmium Complexes: Preparation and Characterization of Complexes Containing Osmium–Osmium Bonds of Order 2.5

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The complexes $Os_2(O_2CR)_4Cl_2$ ($R = C_2H_5$ or C_3H_7) and $Os_2(hp)_4Cl_2$ (hp is the monoanion of 2-hydroxypyridine) each possess a reversible one-electron reduction at $E_{1/2} \simeq +0.3$ V (for the carboxylates) or +0.1 V (for the hp derivative) vs. SCE. These reductions can be accomplished chemically by using cobaltocene as the reducing agent to produce $[(\eta\text{-}C_5H_5)_2Co][Os_2(O_2CR)_4Cl_2]$ and $[(\eta\text{-}C_5H_5)_2Co][Os_2(hp)_4Cl_2]$. These complexes are the first derivatives of the Os_2^{5+} core to have been isolated and have been characterized by cyclic voltammetry, electronic absorption spectroscopy, ESR spectroscopy, and magnetic susceptibility measurements. They are believed to contain Os–Os multiple bonds of order 2.5 with the configurations $\sigma^2\pi^4\delta^2\delta^{*1}\pi^{*2}$ ($S = {}^3/_2$) and $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*1}$ and/or $\sigma^2\pi^4\delta^2\pi^{*3}$ ($S = {}^1/_2$) being the principal contributors to the ground state at room temperature.

Introduction

Recently, various strategies have been explored for the synthesis of diosmium carboxylates, especially with a view to the isolation of compounds that might contain osmium–osmium multiple bonds. One such approach involved the use of the complexes *trans*-$OsO_2X_2(PR'_3)_2$ as synthetic starting materials,[2] and this led to the isolation and structural characterization of the novel, diamagnetic diosmium(IV) species $Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR'_3)_2$.[3,4] Among the properties of note for this class of complexes ($R = CH_3$ or C_2H_5; X = Cl or Br; $PR'_3 = PPh_3$ or PEt_2Ph) is the occurrence of a very accessible one-electron reduction ($E_{1/2}$ values in the range +0.09 to +0.23 V vs. SCE) to give the paramagnetic $Os^{III}Os^{IV}$ monoanions.[4] On the other hand, when recourse was made to a different osmium starting material, namely, the hexachloroosmate(IV) ion, then reaction with acetic acid–acetic anhydride was found to give the diosmium(III) acetate $Os_2(O_2CCH_3)_4Cl_2$.[5] Subsequently, other diosmium(III) carboxylates $Os_2(O_2CR)_4Cl_2$ (R = Et, *n*-Pr, or CH_2Cl) were discovered[6,7] and the crystal structures of the acetate, propionate and butyrate were determined,[6-8] thereby establishing that these complexes are derivatives of the multiply bonded Os_2^{6+} core.[9]

We have explored the redox chemistry of these diosmium(III) complexes with a view to understanding their relationship to the well-established class of diruthenium carboxylates[10] and various derivatives that contain the isoelectronic triply bonded Re_2^{4+} core.[11,12] We provide in this report details of the redox chemistry of these diosmium(III) species which establish quite clearly that they undergo a facile one-electron reduction to give compounds that contain the hitherto unknown Os_2^{5+} core.

Experimental Section

Materials. All solvents were dried over molecular sieves, distilled, and purged with nitrogen gas for 30 min prior to use. Cobaltocene was purchased from Strem Chemicals, Inc., and was used as received. The *n*-propionate and *n*-butyrate complexes of the type $Os_2(O_2CR)_4Cl_2$ were prepared from $[OsCl_6]^{2-}$ solutions by using the procedure described previously.[7]

Reaction Procedures. All syntheses were carried out under an atmosphere of nitrogen.

$Os_2(hp)_4Cl_2 \cdot 2H_2O$. This complex, where Hhp = 2-hydroxypyridine, was prepared by a modification of the existing procedure.[7] A mixture of $Os_2(O_2CC_3H_7)_4Cl_2$ (112.7 mg, 0.141 mmol) and Hhp (116.7 mg, 1.23 mmol) was refluxed in 10 mL of ethanol for 45 min. The deep red solution was cooled to room temperature, and the solvent was removed by evaporation in an N_2 stream. Dichloromethane was then added to dissolve the dark red residue, and this solution was filtered through a medium-porosity frit. The volume of this solution was reduced to approximately 5 mL, and 5 mL of diethyl ether was added to initiate precipitation of the product. This mixture was refrigerated

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