that of the product of the in situ reaction of $[Pt(PPh_3)_3]$ and butadiene at low temperatures. The proposed "monodentate" structure (1) is supported by the infrared spectrum of $[Pt(PPh_3)_2(C_4H_6)]$ (Nujol mull), which contains a sharp band at 1605 cm^{-1}, consistent with the expected stretching frequency of an uncoordinated C=C bond. A similarly assigned band at 1608 cm^{-1} has previously been reported for the platinum(II) compound $[PtCl_2(C_4H_6)]_2$.[15]

By analogy with the case of cyclohexene, no displacement of PPh_3 from $[Pt(PPh_3)_3]$ by 1,5-cyclooctadiene could be detected at −100 °C.

Other Reactions. O_2 did not react with $[Pt(PPh_3)_3]$ in toluene solution below −70 °C. At −70 °C, a reaction analogous to that with C_2H_4 was observed (eq 4). At somewhat

$$2[Pt(PPh_3)_3] + O_2 \rightarrow [Pt(PPh_3)_4] + [Pt(PPh_3)_2(O_2)] \quad (4)$$

higher temperatures (ca. −45 °C), O_2 also reacted with $[Pt(PPh_3)_4]$ in toluene solution according to eq 5. The formation

$$[Pt(PPh_3)_4] + O_2 \rightarrow [Pt(PPh_3)_2(O_2)] + 2PPh_3 \quad (5)$$

of $[Pt(PPh_3)_2(O_2)]$ by O_2 displacement of PPh_3 from $[Pt(PPh_3)_3]$ has previously been postulated as a step in the $[Pt(PPh_3)_3]$-catalyzed oxidation of PPh_3 by O_2.[9,16]

Passing CO through a toluene solution of $[Pt(PPh_3)_3]$ at −80 °C resulted in the formation of $[Pt(PPh_3)_3(CO)]$[4] according to eq 6. Warming to −65 °C resulted in further

$$[Pt(PPh_3)_3] + CO \rightarrow [Pt(PPh_3)_3(CO)] \quad (6)$$

reaction to form $[Pt(PPh_3)_2(CO)_2]$[4] with displacement of PPh_3 (eq 7). The higher temperature required for the latter reaction

$$[Pt(PPh_3)_3(CO)] + CO \rightarrow [Pt(PPh_3)_2(CO)_2] + PPh_3 \quad (7)$$

presumably reflects the fact that $[Pt(PPh_3)_3(CO)]$ is an 18-electron complex and therefore undergoes substitution by a dissociative mechanism.

Experimental Section

$[Pt(PPh_3)_3]$,[17] $[Pt(PPh_3)_4]$,[17] $[Pt(PPh_3)_2(C_2H_4)]$,[18] $[Pt(PPh_3)_3(CO)]$,[19] and $[Pt(PPh_3)_2(O_2)]$[20] were prepared by the literature procedures cited.

$[Pt(PPh_3)_2(C_4H_6)]$. $[Pt(PPh_3)_2(O_2)]$ (0.3 g) was dissolved in ethanol (10 mL), and the resulting solution was saturated with 1,3-butadiene. A solution of $NaBH_4$ (0.02 g) in ethanol (5 mL) was then added dropwise with stirring, while butadiene was passed through the solution. After a few minutes a pale yellow solid precipitated. This was collected by filtration, washed with water and ethanol, and dried under vacuum: yield 0.18 g (59%); mp 126–128 °C (uncor). Anal. Calcd for $[Pt(PPh_3)_2(C_4H_6)]$: C, 62.1; H, 4.7; P, 8.0. Found: C, 62.0; H, 4.8; P, 8.0.

Spectral Measurements. UV–visible spectra were recorded with a Cary 14 spectrophotometer and infrared spectra with a Beckman IR10 spectrophotometer. ^{31}P NMR spectra were determined with a Bruker HX-90E spectrometer interfaced with a Nicolet 1080 computer. A spectrometer frequency of 36.434 MHz was used. The spectra were determined in the pulsed FT mode and were broad-band proton decoupled. Concentrations of the platinum complexes were typically in the range from 1×10^{-2} to 5×10^{-2} M. Chemical shifts (δ) are reported relative to 85% H_3PO_4 at room temperature.

Elemental analyses were performed by Galbraith Laboratories.

Because most of the compounds encompassed by these studies are sensitive to oxygen, all manipulations and experiments were performed under a nitrogen atmosphere, using solvents which had been deoxygenated by purging with nitrogen.

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Registry No. $Pt(PPh_3)_3$, 13517-35-6; $Pt(PPh_3)_4$, 14221-02-4; $Pt(PPh_3)_2(O_2)$, 15614-67-2; $Pt(PPh_3)_2(C_2H_4)$, 12120-15-9; $Pt(PPh_3)_2(C_4H_6)$, 72347-07-0; $Pt(PPh_3)_3(CO)$, 15376-99-5; $Pt(PPh_3)_2(CO)_2$, 15377-00-1; PPh_3, 603-35-0.

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Assignment of the Elusive Metal–Ligand T_{1u} Stretching Vibration in Hexaammineruthenium(II) Salts

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Infrared and Raman spectra of octahedral hexaammine complexes constitute one of the most thoroughly investigated areas of vibrational spectroscopy in the realm of inorganic coordination complexes.[1] In view of the role of the vibrational contribution to the activation energy required for electron transfer in self-exchange reactions for species such as $M(NH_3)_6^{(n,n+1)}$[2] the absence of complete infrared data which has persisted in the literature for the hexaammineruthenium(II) cation is somewhat puzzling. A survey of infrared data listed by Nakamoto for fifteen octahedral hexaammine complexes with chloride as the counterion reveals that only for $[Ru(NH_3)_6]Cl_2$ is the infrared ν(M–N) frequency absent.[1] Recent infrared studies of $[Ru(py)_6](BF_4)_2$ in our laboratory revealed an extremely weak absorption in the low-frequency infrared region which was attributed to the infrared allowed T_{1u}(Ru–N) stretching mode.[3] The $Ru(py)_6^{2+}$ metal–ligand vibration was analyzed by treating the pyridine ligands as rigid groups in order to employ an MX_6 model for comparing the ratio of the ruthenium–nitrogen force constants in $Ru(py)_6^{2+}$ and $Ru(NH_3)_6^{3+}$. A desire to include the $Ru(NH_3)_6^{2+}$ cation in these studies led us to undertake the infrared characterization of a series of hexaammineruthenium(II) salts in order to unambiguously identify the elusive metal–ligand stretching frequency in these complexes. The results of our infrared studies are reported herein.

Experimental Section

Hexaammineruthenium(II) salts were prepared according to the procedure of Schreiner and Lin.[4] Following the zinc reduction step the aqueous solution containing $[Ru(NH_3)_6]^{2+}$ was carefully filtered under a nitrogen atmosphere into a saturated solution of the appropriate NH_4X salt, and the resultant two layers were allowed to diffuse together over a period of days to promote slow formation of crystalline $[Ru(NH_3)_6]X_2$. Purity of the samples was confirmed by potentiometric titration with standardized silver nitrate solution for the halide salts. The infrared spectra provided additional confirmation of sample purity since the most probable contaminants each display at least one characteristic infrared absorption which is evident at low concentrations and does not overlap any $[Ru(NH_3)_6]^{2+}$ band: NH_4X, ~1400 cm^{-1};

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Table I. $[Ru(NH_3)_6]X_2$ Infrared Data (cm^{-1})

complex	$\nu_a(NH_3)$	$\nu_s(NH_3)$	$\delta_a(HNH)$	$\delta_s(HNH)$	$\rho_r(NH_3)$	$\nu(Ru-N)$
$[Ru(NH_3)_6](BF_4)_2$	3365	3300	1623	1273	745	420
$[Ru(NH_3)_6](PF_6)_2$	3370	3295	1620	1272	735	423
$[Ru(NH_3)_6]Cl_2$	3315	3210	1612	1220	763	409
$[Ru(NH_3)_6]I_2$	3300		1604	1243	747	412
$[Ru(NH_3)_6]Br_2$	3295		1605	1230	758	403
$[Ru(ND_3)_6]Br_2$	2473		1144	942	590	378
$\nu(NH_3)/\nu(ND_3)$	1.33		1.40	1.31	1.28	1.066

$[Ru(NH_3)_6]^{3+}$, ~1320 cm^{-1}; $[Ru(NH_3)_5(N_2)]^{2+}$, ~2120 cm^{-1}. Anal. Calcd for X in $Ru(NH_3)_6X_2$: X = Cl, 25.79; X = Br, 43.91; X = I, 54.31. Found: X = Cl, 25.86; X = Br, 44.02; X = I, 55.53.

Isotopic substitution to form $[Ru(ND_3)_6]Br_2$ was effected by dissolving $[Ru(NH_3)_6]Br_2$ in D_2O and stirring overnight prior to recrystallization. Both the 3+ and 2+ hexaammineruthenium complexes are known to exchange deuterium for hydrogen on the ammine ligands under these conditions.[5]

Infrared spectra of each sample were recorded as KBr pellets for data in the range from 500 to 4000 cm^{-1} and as very thick Nujol mulls on CsI salt plates for measurements from 500 to 200 cm^{-1}. Spectra were recorded on a Beckman IR-4250 infrared spectrophotometer and calibrated with polystyrene.

Results and Discussion

Infrared data for the hexaammineruthenium(II) salts investigated are compiled in Table I. The vibrations above 700 cm^{-1} which are associated with coordinated ammine ligands are not controversial and have been assigned in accord with extensive data for ammine complexes as summarized in a recent review article.[6] The values listed are in substantial agreement with previous reports characterizing these infrared frequencies of $[Ru(NH_3)_6]X_2$.[7,8]

As noted by Nakamoto[1] it is the metal-nitrogen T_{1u} stretching mode which is of particular interest since it provides direct information about the metal-ligand bond. Although a weak band at 437 cm^{-1} was assigned as the infrared-allowed Ru-N stretching vibration for $[Ru(NH_3)_6]Cl_2$ in an early report by Fairey and Irving,[7] this result has not been confirmed by later studies[8] and has not been generally accepted as suitable for calculations requiring knowledge of ruthenium(II)-ammine force constants.[2,9,10]

In view of our experience in locating the allowed T_{1u} skeletal stretching mode of $[Ru(py)_6][BF_4]_2$[3] we anticipated that an extremely concentrated Nujol mull sample would be required for observation of the Ru-N stretching mode in $[Ru(NH_3)_6]X_2$ salts. In Figure 1 two spectra of the hexaammineruthenium(II) bromide salt are illustrated which emphasize the sample density necessary for an accurate assessment of vibrations occurring in the low-frequency region. The sharp absorption at 403 cm^{-1} is the only well-resolved band in this range for X = Br and leads to the proposed T_{1u}(Ru-N) assignment. For each complex investigated an absorption in the range of 400-425 cm^{-1} was readily apparent in the thick samples utilized to obtain the low-frequency spectra. These have been assigned as the elusive metal-ligand stretch on the basis of the frequency and intensity exhibited by this band for all five $[Ru(NH_3)_6]^{2+}$ salts examined.

The most definitive experimental evidence in support of the proposed Ru-N infrared stretching frequency assignment stems from the infrared spectrum of the deuterated bromide salt. In addition to the observation of the expected isotope shifts for $\nu(NH_3)$, $\delta_a(NH_3)$, $\delta_s(NH_3)$, and $\rho_r(NH_3)$[8] the weak 403-cm^{-1} absorption assigned as ν(Ru-N) is replaced by a weak band at 378 cm^{-1} (see Table I). Simple harmonic oscillator theory predicts $\nu(M-NH_3)/\nu(M-ND_3) = 1.085$ on the basis of the ratio of the ligand masses. Assuming that the bond stretching force constant is large relative to the remaining terms justifies approximating the solution of the second-order T_{1u} vibrational secular equation for the MX_6 model[11] as in eq 1

$$\lambda_3 = 4\pi^2c^2\nu_3^2 = (1/m_x + 2/m_M)(f_d - \delta) \qquad (1)$$

for the Ru-NH_3 stretch (ν_3) and predicts that $\nu_3(M-NH_3)/\nu_3(M-ND_3) = 1.061$. The observed frequency ratio of 1.066 for this low-energy absorption provides confirmation of the proposed metal-ligand stretching vibration assignment. Furthermore the proximity of the deuterated absorption energy to that predicted by the rigid-ligand MX_6 model supports the validity of treating the ammine as a point mass (m_x) for analysis of the skeletal vibrations.

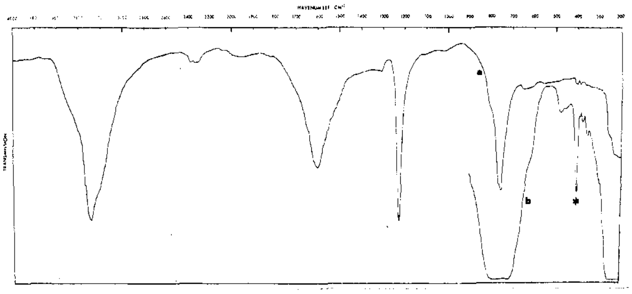

Figure 1. Infrared spectra of $[Ru(NH_3)_6]Br_2$: (a) regular KBr pellet sample spectrum; (b) very thick Nujol mull sample spectrum displaying the 403-cm^{-1} absorption band (*).

Estimates of the ruthenium(II)-nitrogen force constant for $Ru(NH_3)_6^{2+}$ have been based on a range of frequencies from those characteristic of divalent first-row transition-metal ammine complexes near 300 cm^{-1}[9] to values similar to those of Ru(III) complexes which approach 500 cm^{-1}.[2] Schmidt and Müller noted that the 437 cm^{-1} ν_{as}(RuN) assignment of Fairey and Irving[7] seemed anomalously high for a divalent metal ion, but several additional factors need to be considered when ruthenium(II) complexes are compared with both 2+ and 3+ first-row metal hexaammine salts or with second- and third-row trivalent metal complexes.

Crystallographic data for $Ru(NH_3)_6^{3+/2+}$ provides evidence that the variation of bond distance with oxidation state is far less than the difference which arises when a spin change also occurs (Δ(M-N) for $Co(NH_3)_6^{3+/2+}$ = 0.178 (17) Å; Δ(M-N) for $Ru(NH_3)_6^{3+/2+}$ = 0.040 (6) Å).[9] The small difference between the metal-ligand bond distances for $[Ru(NH_3)_6]I_2$ (2.144 (4) Å) and $[Ru(NH_3)_6][BF_4]_3$ (2.104 (4) Å) suggests that while a Ru(II)-N infrared stretching frequency below the 463-cm^{-1} band of $Ru(NH_3)_6^{3+}$ [12,13] would be expected, a large shift into the low-energy region near 300 cm^{-1} typical of high-spin $M(NH_3)_6^{2+}$ complexes would be incompatible with the similar Ru-N distances present in the two ruthenium complexes. In retrospect the experimentally determined T_{1u}

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frequency of 409 cm^{-1} for $[Ru(NH_3)_6]\ Cl_2$ is a very rational compromise between the two extremes which have been considered plausible for this vibration. Some precedent for this range of frequencies for ruthenium(II) ammines exists in the reported Ru–NH_3 stretching modes assigned from ~390 to 450 cm^{-1} for a series of $[Ru(NH_3)_5(N_2)]^{2+}$ salts.[14]

The factors which determine the intensity of the T_{1u} metal–ligand vibration in the infrared spectrum are not well understood. The controversy which persisted for years regarding assignment of the T_{1u} stretching vibration in $[Co(NH_3)_6]Cl_3$ was a direct result of the low intensity exhibited by this symmetry allowed T_{1u} vibrational mode. Shimanouchi and Nakagawa[15] have suggested a correlation between the ionicity of the M–N bond and the intensity of the infrared T_{1u} absorption which seems applicable in the case of the two hexaamminecobalt complexes. The Co(II)–N bond is more ionic than the Co(III)–N bond, and a lower frequency, more intense T_{1u} mode is observed for hexaamminecobalt(II) than for $[Co(NH_3)_6]^{3+}$. However, this intensity pattern is reversed for hexaammineruthenium complexes where the $[Ru(NH_3)_6]^{3+}$ T_{1u} vibration is sufficiently intense to be observed at 463 cm^{-1} in routine spectra while the $[Ru(NH_3)_6]^{2+}$ Ru–N stretching mode is extremely weak and therefore difficult to locate. It may be that a more valid correlation between infrared intensity and metal properties lies in the electronic structure since both of the hexaammines with very weak M–N infrared absorptions are low-spin d^6 metal ions. It should be noted, however, that Griffith's vibrational study of the low-spin d^6 $[M(NH_3)_6]^{3+}$ (M = Rh, Ir) ions does not indicate an anomalously low intensity for ν_3 (T_{1u}) in these complexes.[12]

The original goal of comparing Ru(II)–N force constants for the octahedral pyridine and ammine complexes of ruthenium(II) is now accessible. Utilizing the rigid-ligand MX_6 model leads to eq 2.[3] Insertion of 326 cm^{-1} for $\tilde{\nu}_3$(py) and

$$\frac{(f_d - \delta)_{py}}{(f_d - \delta)_{NH_3}} = \left[\frac{m_{py}(m_{Ru} + 2m_{NH_3})}{m_{NH_3}(m_{Ru} + 2m_{py})}\right]\frac{[\tilde{\nu}_3(py)]^2}{[\tilde{\nu}_3(NH_3)]^2} \qquad (2)$$

409 cm^{-1} for $\tilde{\nu}_3(NH_3)$ as measured for $[Ru(NH_3)_6]Cl_2$ leads to a ratio of 1.54 for the force constants characterizing pyridine and ammonia bound to ruthenium(II). As discussed previously, the interaction force constant for trans M–X bonds, δ, is expected to be small compared to the bond-stretching force constants, f_d.[3] To the extent that the δ term is not negligible it would only serve to reinforce the conclusion that the ruthenium–pyridine bond has a substantially larger force constant than the ammine analogue since coupling in the ammine complex is through σ-only bonds and is likely to be small.[12]

Identification of the T_{1u} (Ru–N) stretching frequency in $[Ru(NH_3)_6]Cl_2$ allows one to calculate a ratio of Ru(III)/Ru(II) force constants on the basis of the square of the observed frequencies since the mass factors are identical and thus cancel. A ratio of $f_3(\text{Ru(III)–N})/f_2(\text{Ru(II)–N}) = (463\ \text{cm}^{-1}/409\ \text{cm}^{-1})^2 = 1.28$ results for the $Ru(NH_3)_6^{3+/2+}$ complexes.

Calculation of the inner-sphere rearrangement energy for the rate of electron transfer in the $Ru(NH_3)_6^{3+/2+}$ exchange reaction can be accomplished in terms of eq 3[2] where the force

$$\Delta G_{in}^* = 6f_2f_3(\Delta a)^2/2(f_2 + f_3) \qquad (3)$$

constants, f_i, refer to the Ru–N bonds for the divalent and trivalent metal centers and Δa is the 0.04-Å difference between the equilibrium Ru–N bond distances.[9] Brown and Sutin calculated ΔG_{in}^* to be 0.9 kcal mol^{-1} on the basis of the assumption that $f_3 = f_2 = 2.5$ mdyn/Å. Employing the f_3/f_2 ratio of 1.28 reported here and retaining the f_3 value of 2.5 mdyn/Å imply that f_2 is approximately 2.0 mdyn/Å and ΔG_{in}^* for $Ru(NH_3)_6^{3+/2+}$ is then 0.8 kcal mol^{-1}. It is clear that the inner-sphere reorganizational energy is indeed very small for the hexaammineruthenium redox couple regardless, but the quantitative basis provided by the $Ru(NH_3)_6^{2+}$ infrared data reported here supplies the final piece of experimental information required to eliminate discrepancies in the input for such calculations.[2,9]

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Registry No. $[Ru(NH_3)_6](BF_4)_2$, 16446-60-9; $[Ru(NH_3)_6](PF_6)_2$, 72496-76-5; $[Ru(NH_3)_6]Cl_2$, 15305-72-3; $[Ru(NH_3)_6]I_2$, 16446-59-6; $[Ru(NH_3)_6]Br_2$, 16446-58-5; $[Ru(ND_3)_6]Br_2$, 72496-75-4.

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Functional Dependence upon Ligand Composition of the Reaction Entropies for Some Transition-Metal Redox Couples Containing Mixed Ligands

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Although a knowledge of the entropies and enthalpies of reaction $\Delta S°$ and $\Delta H°$ is important for unraveling the factors influencing the kinetics of electron-transfer processes,[1] such information has been surprisingly scarce for transition-metal redox couples. We have recently pointed out that measurements of the temperature dependence of formal potentials using a nonisothermal cell arrangement provide a simple method of evaluating the difference $\Delta S°_{rc}$ $(=\bar{S}°_{red} - \bar{S}°_{ox})$ between the absolute ionic entropies $\bar{S}°$ of the reduced and oxidized halves of the redox couple.[2] Besides furnishing a direct route to the determination of $\Delta S°$ and $\Delta H°$ for appropriate pairs of redox couples, these "reaction entropies" $\Delta S°_{rc}$ are of particular interest since they provide a sensitive monitor of the changes in solvent polarization that are necessary in order for electron transfer to occur.[2,3] An approximately linear correlation has also been found between $\Delta S°_{rc}$ and the activation free energies of corresponding outer-sphere self-exchange processes.[3] The experimental values of $\Delta S°_{rc}$ for simple octahedral M(III/II) couples in aqueous media have been found to be dependent upon the nature of the ligands to a much greater extent than predicted by the dielectric-continuum Born model.[2] These latter results suggest that specific interactions between individual ligands and surrounding water molecules play an important role by influencing the extent of overall solvent polarization induced by changes in the metal oxidation state.[2]

Of interest in this connection is the effect of stepwise alterations in the ratio of the number of the ligands L′ and L″ upon $\Delta S°_{rc}$ for redox couples such as $M^{III}L'_mL''_n + e^- \rightleftarrows M^{II}L'_mL''_n$. Fundamental studies of electron-transfer kinetics typically employ such "mixed-ligand" complexes. It is therefore desirable to understand the functional dependences of $\Delta S°_{rc}$ upon m and n both to yield further insight into the various ligand influences upon the solvent polarization and to

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