are, however, known for other metal centers.[32] It should be noted that eq 3 is written as it is because the new spectral features (bands at 420 and 960 nm) grow at low $[Rh(I)]_{tot}$ as $[Rh(I)]_{tot}^2$ and $[H^+]$. Because of the ambiguities associated with water as solvent, the overall reaction eq 1 + eq 3 could equally well be written as eq 13 or eq 14, in which OH^- is a

$$2Rh(bpy)_2(OH)_2^- + H^+ \rightleftharpoons [Rh(bpy)_2(OH)]_2OH^- + H_2O \tag{13}$$

$$2Rh(bpy)_2OH + H^+ \rightleftharpoons [Rh(bpy)_2]_2OH^+ + H_2O \tag{14}$$

bridging ligand. These would, however, require six- and five-coordinate hydroxy complexes as the dominant form of mononuclear Rh(I), a possibility we reject[20] since the spectrum of Rh(I) at very low concentrations is $[OH^-]$ independent above pH 7 (an exceptionally large affinity of $Rh(bpy)_2^+$ for OH^- or acidity for $Rh(bpy)_2(H_2O)^+$ or $Rh(bpy)_2(H_2O)_2^+$ would be required). Furthermore, the IR spectra of brown solids isolated from neutral solutions of $[Rh(bpy)_2]Cl$ show no absorption in the O–H stretching region. No M–H stretch is observed for these solids either, but none would be expected in the 2000-cm^{-1} region for the bridged structure postulated. Presumably the true nature of this dimer may be resolved through X-ray crystallographic methods, and efforts to grow crystals of this species are ongoing.

Conclusions

The nature of aqueous $Rh(bpy)_2^+$ solutions is a function of the hydrogen ion and rhodium(I) concentrations, with four species formulated as $Rh(bpy)_2^+$, $[Rh(bpy)_2]_2^{2+}$, $[Rh(bpy)_2]_2H^{3+}$, and $Rh(bpy)_2(H)(H_2O)^{2+}$ being required to account for the spectral changes that accompany acidification and/or dilution of the solutions. Equilibration between the species is achieved rapidly, but strongly acid solutions of $Rh(bpy)_2(H)(H_2O)^{2+}$ are much less reactive toward ligand exchange and oxidation, as expected for rhodium(III), than are the basic solutions containing rhodium(I).

Acknowledgment. Helpful comments from Drs. G. M. Brown, H. B. Gray, and J. Halpern are gratefully acknowledged. We thank Dr. M. Andrews for his comments and for running the NMR spectra. This research was carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and supported by its Office of Basic Energy Sciences.

Registry No. $[Rh(bpy)_2]Cl$, 17633-22-6; $[Rh(phen)_2]Cl$, 82752-94-1; $[Rh(bpy)(H)Cl_2]_2$, 82752-95-2; $[Rh(bpy)_2(H)Cl]Cl$, 82752-96-3; $[Rh(phen)_2(H)Cl]Cl$, 82752-97-4; $[Rh(bpy)_2(D)Cl]Cl$, 82752-98-5; $[RhCl(C_8H_{14})_2]$, 12279-09-3.

Supplementary Material Available: Tables of absorbance data for various concentrations of $Rh(bpy)_2^+$ in 0.05 and 0.1 M NaOH (2 pages). Ordering information is given on any current masthead page.

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[32] See: Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176 and references cited therein.

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Isocyanide as a Ligand on Ruthenium(II) Ammines

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A pentaammine–isocyanide complex of Ru(II) is readily prepared by the reaction of $Ru(NH_3)_5H_2O^{2+}$ with the ligand, but if the contact time is long, a *trans*-bis(isocyanide) complex results. Measurement of the rate of aquation of the benzyl isocyanide complex $Ru(NH_3)_5C_7H_7NC^{2+}$ compared with earlier measurements for $Ru(NH_3)_6^{2+}$ shows that C_7H_7NC (as compared to ammonia) labilizes a trans ammonia by a factor of 40. A similar comparison between $Ru(NH_3)_4(H_2O)C_7H_7NC^{2+}$, now following the replacement of H_2O by isn (isonicotinamide), shows that the trans isocyanide (compared to trans ammonia) is slightly delabilizing. The rate of aquation of isn in a trans position is enormously enhanced by isocyanide as compared to ammonia, and the affinity of Ru(II) for isn is much reduced. As determined by cyclic voltammetry, the values of E_f for the couples $Ru(NH_3)_5C_7H_7NC^{3+/2+}$, $Ru(NH_3)_4(H_2O)C_7H_7NC^{3+/2+}$, *trans*-$Ru(NH_3)_4(C_7H_7NC)_2^{3+/2+}$, and *trans*-$Ru(NH_3)_4(c\text{-}HxNC)_2^{3+/2+}$ are 0.79, 0.92, 0.99, and 0.93 V vs. NHE at 25 °C.

The specific rates for substitution in pentaammineaquoruthenium(II) by neutral ligands at 25 °C lie in the range[1] 0.02–0.3 M^{-1} s^{-1}. The species $Ru(NH_3)_5H_2O^{2+}$ however is a rather strong reducing agent ($E_f = 0.051$ V);[2] for some applications, namely, in certain catalytic processes, it is desirable to have a couple that has a much higher value of E_f, but with the Ru(II) form substitutionally labile so that a high turnover number is realized in reaction with dioxygen or another oxidant.[3] While E_f for the Ru(III)/Ru(II) couple is readily increased by replacing saturated ligands with π acids, for many of the π acids commonly used this is at the expense of substitution lability.[4] Thus, while substitution of H_2O on $Ru(NH_3)_5H_2O^{2+}$ by isn (isonicotinamide) takes place at a specific rate of 1.0×10^{-1} M^{-1} s^{-1} at 25 °C, when the trans or cis ammonias are replaced by isn, the specific rates fall to 3.5×10^{-3} or 5.0×10^{-3} m^{-1} s^{-1}, respectively.[4] There are some ligands however, among them SO_3^{2-}, which in replacing NH_3 on Ru(II) cause an increase in E_f yet labilize the trans ligand.[5] These ligands seem to constitute a distinct class,[6] but just what features of electronic structure distinguish them from saturated or π-acid ligands such as pyridine are not understood. The existence of ligands such as SO_3^{2-} however does offer some hope that a high substitution lability in Ru(II) is not incompatible with a high value of E_f for the Ru(III)/Ru(II) couple. Preliminary preparative work with an isocyanide acting on $Ru(NH_3)_5H_2O^{2+}$ showed that the reaction readily yields a *trans*-bis(isocyanide) complex, thus suggesting trans labilization by a ligand ordinarily considered a strong π acid.[7] This finding is described in this paper, as are the results of the more complete study prompted by it.

A large number of isocyanide complexes of ruthenium(II) have been reported,[8,9] but in most cases more than one π-acid

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(1) Taube, H. *Comments Inorg. Chem.* **1981**, *1*, 17.
(2) Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107.
(3) A metal complex to be useful as a catalyst for the O_2 electrode should have a value of $E_f \sim 1.0$ V and a turnover number of 10^2–10^3 s^{-1} for oxygen in a saturated solution in equilibrium with the atmosphere.
(4) Isied, S. S.; Taube, H. *Inorg. Chem.* **1976**, *15*, 3070.
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ligand is contained in the unit. We were particularly interested in the mono(isocyanide)aquotetraammine series. Here, all the ligands complementary to the isocyanide are saturated and H_2O is the group being replaced. The single report of an ammine–isocyanide complex was made by Clarke and Ford,[10] who cited a stretching frequency for the bound isocyanide but gave no further details.

Experimental Section

Chemicals and Reagents. House-line distilled water was purified by redistillation from alkaline permanganate.

Benzyl isocyanide (C_7H_7NC) and cyclohexyl isocyanide ($C_6H_{11}NC$) were purchased (Aldrich) and used without further purification. Ethanol solutions of isocyanides were prepared by dissolving 1 g of the pure isocyanide in 20 mL of ethanol.

Trifluoromethanesulfonic acid was purified by distillation under an inert atmosphere at reduced pressure. Its sodium salt was prepared by neutralizing the acid with Na_2CO_3. The precipitate was recrystallized from hot water.

The compound $[Ru(NH_3)_5Cl]Cl_2$ was prepared from $[Ru(NH_3)_6]Cl_3$ (Matthey Bishop) by standard methods.[11]

The description of the preparation of the isocyanide complexes follows.

(Benzyl isocyanide)pentaammineruthenium(II) Hexafluorophosphate. A 100-mg amount of finely ground $[Ru(NH_3)_5Cl]Cl_2$ was suspended in 5 mL of water; the mixture was degassed and then reduced over zinc amalgam for 1 h. One milliliter of an ethanolic solution of benzyl isocyanide was added, and after 5 min the reaction mixture was filtered and a solid precipitated by adding solid ammonium hexafluorophosphate. The precipitate was collected, dissolved in 5 mL of acetone, and reprecipitated by adding it to 75 mL of rapidly stirred ether. The air-dried solid was dissolved in a minimum amount of hot water; the resulting solution yielded a crystalline material upon cooling to 0 °C. The final product was collected, washed with water, and vacuum-dried. Anal. Calcd for $[Ru(NH_3)_5(C_7H_7NC)](PF_6)_2$: C, 16.19; H, 3.74; N, 14.17. Found: C, 16.30; H, 3.82; N, 13.96.

***trans*-Bis(benzyl isocyanide)tetraammineruthenium(II) Hexafluorophosphate.** The procedure used to prepare the corresponding pentaammine complex of this ligand was repeated, but the reaction time was increased to 18 h. The product was recrystallized from boiling water. Anal. Calcd for $[Ru(NH_3)_4(C_7H_7NC)_2](PF_6)_2$: C, 27.71; H, 3.78; N, 12.12. found: C, 27.68; H, 3.78; N, 12.02.

***trans*-Bis(cyclohexyl isocyanide)tetraammineruthenium(II) Perchlorate.** The same procedure was followed as outlined above for the corresponding benzyl isocyanide derivative except for the method of purification.

The crude hexafluorophosphate salt was air-dried, dissolved in a minimum amount of acetone, and precipitated as a chloride salt by addition of tetrabutylammonium chloride. The chloride salt was filtered, washed with acetone and ether, and air-dried. The solid was then dissolved in water and precipitated by adding a saturated aqueous solution of sodium perchlorate. The perchlorate salt was collected and recrystallized from hot water. Anal. Calcd for $[Ru(NH_3)_4(C_6H_{11}NC)_2](ClO_4)_2$: C, 28.67; H, 5.84; N, 14.33. Found: C, 28.41; H, 5.78; N, 14.35.

***trans*-(Benzyl isocyanide)aquotetraammineruthenium(II) Hexafluorophosphate.** Twenty milligrams of finely ground $[Ru(NH_3)_5C_7H_7NC](PF_6)_2$ was dissolved in 20 mL of water, and argon was bubbled through the solution for 46 h to expel NH_3. The solution was kept in the dark. The product solution was evaporated in vacuo at room temperature, whereupon a white solid was obtained. Anal. Calcd for $[Ru(NH_3)_4(H_2O)C_7H_7NC](PF_6)_2$: C, 16.19; H, 3.57; N, 11.80. Found: C, 16.44; H, 3.60; N, 12.05.

Table I. Isocyanide and Related Stretching Frequencies[a]

complex	$\nu_{complex}$, cm^{-1}	$\nu_{free\ ligand}$, cm^{-1}	ref
$Ru(NH_3)_5C_7H_7NC^{2+\,b}$	2058	2146	
trans-$Ru(NH_3)_4(H_2O)C_7H_7NC^{2+\,b}$	2060		
trans-$Ru(NH_3)_4(C_7H_7NC)_2{}^{2+\,b}$	2138	2146	
trans-$Ru(NH_3)_4(c\text{-}HxNC)_2{}^{2+\,c}$	2115	2138	
$R(NH_3)_5CH_3NC^{2+\,c}$	2095	2095	12
cis-$Ru(bpy)_2(C_7H_7NC)_2{}^{2+\,b}$	2193, 2153	2146	13
$Ru(NH_3)_5CO^{2+\,d}$	1955	2143	23
$Ru(NH_3)_5N_2{}^{2+\,d}$	2129	2330	24

[a] Measured in KBr. [b] PF_6^- salt. [c] ClO_4^- salt. [d] I^- salt.

Table II. NMR Resonances of Isocyanide Complexes[a]

compd	NH_3	$-CH_2-$	phenyl
free ligand[b]		4.28	7.20
$Ru(NH_3)_5C_6H_5NC^{2+}$	2.50, 3.50[c]	5.20	7.50
trans-$Ru(NH_3)_4(H_2O)C_6H_5NC^{2+}$	2.75	5.20	7.40
trans-$Ru(NH_3)_4(C_6H_5NC)_2{}^{2+}$	2.75	5.63	7.80

[a] Measured in acetone-d_6 as the PF_6 salt. Values are in ppm referred to tetramethylsilane. [b] Reference 12. [c] The ratio between the integrals of the two peaks is (3.7–4.0):1.

$Ru(NH_3)_5C_7H_7NC^{3+}$ in Solution. Two milligrams of $Ru(NH_3)_5C_7H_7NC^{2+}$ was dissolved in 6 mL of a solution containing 10^{-3} M trifluoromethanesulfonic acid and 0.2 M sodium trifluoromethanesulfonate. The solution was electrolyzed at 0 °C in a coulometric cell between Pt electrodes, with a potential drop of 0.75 V for the anode as measured against a SCE. The number of coulombs passed was found to be approximately equivalent to (1.05) the amount of Ru; electrolysis time 15 min.

Kinetic Experiments. The aquation of $Ru(NH_3)_5C_7H_7NC^{2+}$ was studied spectrophotometrically by measuring the change of the absorbance at 240 nm (not a maximum). The finely ground solid was dissolved with vigorous stirring and the resulting solution transferred into an absorption cell.

The formation of isonicotinamide complex was also followed spectrophotometrically. The reactant $Ru(NH_3)_4(H_2O)C_7H_7NC^{2+}$ was formed in situ by aquation of the pentaammine, after which isonicotinamide was added and the absorption at 358 nm was measured as a function of time.

The absorption vs. time curves were treated with the assumption of pseudo-first-order behavior. The rate constants were calculated by applying a least-squares iteration computer program. The calculated and experimental curves agreed over at least 3 half-lives. The ionic strength was maintained with trifluoromethanesulfonic acid and its sodium salt. Control experiments showed that the light of the spectrophotometer lamp does not affect the reaction rates.

Instruments. Beckman UV 5270 and Cary 15 spectrophotometers were used for spectrophotometric measurements. The electrochemical experiments were carried out with PAR electrochemical instrumentation. The pH of the solutions were measured by a Brinkman Instruments (Metrohm) pH 101 meter. A Varian T-60 instrument was used for NMR and a Perkin-Elmer 621 IR spectrophotometer for IR measurements.

Results

Constitution of the Bis Complexes. The preparative work shows that both the mono- and bis(isocyanide) complexes can be prepared from $Ru(NH_3)_5H_2O^{2+}$, a result which suggests a labilizing influence of isocyanide. Both IR and NMR methods were used to determine whether a cis or trans ammonia is lost from the pentaammine–isocyanide complex in the second stage of the substitution.

The results of the IR measurements are summarized in Table I. It can be seen that for all of the bis(isocyanide) complexes prepared by us only a single $-N{\equiv}C$ stretching frequency is observed, a result which is consistent with a trans geometry for the complex. In this context, the fact that a

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(8) (a) Malatesta, A. L. *Prog. Inorg. Chem.* **1959**, *1*, 283. (b) Malatesta, L.; Bonati, F. "Isocyanide Complexes of Metals"; Wiley-Interscience: New York, 1969. (c) Doonan, D. J.; Balch, A. L. *Inorg. Chem.* **1974**, *13*, 921. (d) Baker, G. K.; Galas, A. M. R.; Green, M.; Howard, J. A. K.; Stone, F. G. A.; Turney, T. W.; Welch, A. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1977**, 256. (e) Chatt, J.; Richards, R. L.; Royston, G. H. D. *J. Chem. Soc., Dalton Trans.* **1973**, 1433. (f) Prater, B. E. *J. Organomet. Chem.* **1972**, *34*, 379. (g) Christian, D. F.; Roper, W. R. *Ibid.* **1974**, *80*, C35. (h) Christian, D. F.; Roper, W. R. *Chem. Commun.* **1971**, 1251. (i) McCleverty, J. A.; Seddon, D.; Whitley, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 832.

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(10) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 227.

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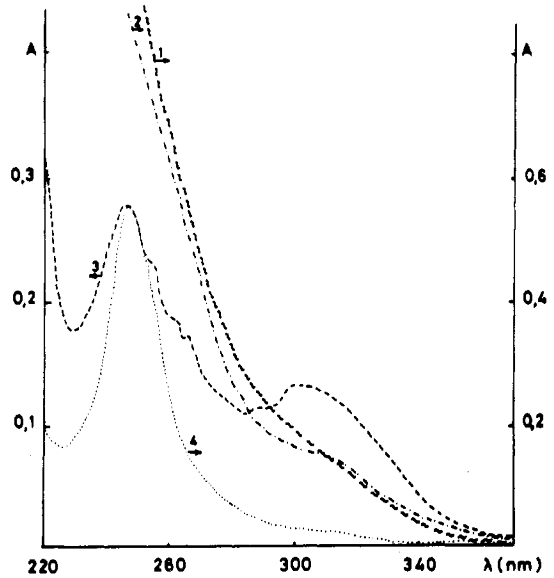

Figure 1. Absorbance profiles for (1) $Ru(NH_3)_5C_7H_7NC^{2+}$, (2) $Ru(NH_3)_4(H_2O)C_7H_7NC^{2+}$, (3) $Ru(NH_3)_5C_7H_7NC^{3+}$, and (4) $Ru(NH_3)_4(C_7H_7NC)_2{}^{2+}$ (measured in 0.1 M HCl at room temperature; cell length 1 cm; concentrations 2.9 × 10^{-4} M for 1,2, and 3 and 2.1 × 10^{-5} M for 4.

bis(isocyanide) known to have the cis configuration shows two IR frequencies in the $-N{\equiv}C$ stretching region is significant.[12]

The NMR results for the isocyanide complexes are summarized in Table II. For the pentaammine, two signals attributable to the protons of coordinated ammonia are observed, in the ratio of ca. 4:1, as expected for the cis and trans ammonias, respectively. In the case of the bis complex, a single peak is observed in the ammonia proton region, a result that is in harmony with the trans structural assignment. The bis complexes will hereinafter be designated as trans. In all cases, the ratios of the integrated intensities for the different peaks are in agreement with the compositions as specified.

UV-Visible Absorption. The absorption spectra for certain of the complexes in the UV-vis region are shown in Figure 1. The absorption properties for $Ru(NH_3)_5C_7H_7NC^{2+}$ and $Ru(NH_3)_4(H_2O)C_7H_7NC^{2+}$ are featureless over the spectral range covered (down to 200 nm) except for weak shoulders at just above 300 nm ($\epsilon \sim 5 \times 10^2$ M^{-1} cm^{-1}). In the bis(benzyl isocyanide) complex, a well-defined maximum is observed at 247 nm (ϵ 2.6 × 10^4) and a shoulder at ~300 nm (ϵ 1.7 × 10^3); for the bis(cyclohexyl isocyanide), λ_{max} = 244 nm (ϵ 2.7 × 10^4). For *trans*-$Ru(NH_3)_4(isn)C_7H_7NC^{2+}$ only the $\pi^*(isn) \leftarrow \pi d$ transition was identified, appearing at 358 nm with $\epsilon = 7.0 \times 10^3$ M^{-1} s^{-1}. The shift to higher energies compared to $Ru(NH_3)_5isn^{2+}$ (λ_{max} 479 nm)[13] is expected and is attributable to the fact that the isocyanide as a strong π acid is electron withdrawing. The absorption for $Ru(NH_3)_4(C_7H_7NC)_2{}^{3+}$ shows considerable structure; the major maxima occur at 246 nm (ϵ 9.9 × 10^2) and 302 nm (ϵ 4.7 × 10^2).

Electrochemistry. The redox potentials were determined by cyclic voltammetry. The measurements were made at 25 °C at an ionic strength of 0.20 (sodium trifluoromethanesulfonate) with use of a carbon paste electrode. In acidic solution (pH <4) the couples showed reversible behavior as judged by the equality of the integrated cathodic and anodic currents and by the peak-to-peak separations, 60–70 mV at a scan rate of 0.10 V s^{-1}. The values of E_f vs. NHE for our conditions are as follows: $Ru(NH_3)_5C_7H_7NC^{3+/2+}$, 0.79 V; $Ru(NH_3)_4(H_2O)C_7H_7NC^{3+/2+}$, 0.92 V; *trans*-$Ru(NH_3)_4(C_7H_7NC)_2{}^{3+/2+}$, 0.99V; *trans*-$Ru(NH_3)_4(c\text{-}HxNC)_2{}^{3+/2+}$, 0.93 V. The values of E_f for the first named couple were shown to be independent of acidity over a wide range, but above pH 7, irreversible behavior was observed. That for the second couple was found to be independent of acidity in the range 0.10–0.0010 M H^+.

Table III. Aquation of $Ru(NH_3)_5C_7H_7NC^{2+a}$

$-\log [H^+]$	T, °C	10^5k_{obsd}, s^{-1}	$-\log [H^+]$	T, °C	10^5k_{obsd}, s^{-1}
2	25	6.0[b]	3	20	3.3
2	25	6.2	3	30	12.1
3	25	5.8	3	35	23.3
3	25	5.8[c]	1	25	5.9
3	15	1.74	1	25	5.9

[a] $[Ru(II)]_0 = (2\text{–}3) \times 10^{-4}$ M. [b] Under Ar; others in air. [c] $[NH_4PF_6]_0 = 1.3 \times 10^{-4}$ M. [d] In 0.1 M HCl.

Aquation of $Ru(NH_3)_5C_7H_7NC^{2+}$. The rate of reaction 1

$$Ru(NH_3)_5C_7H_7NC^{2+} + H^+ + H_2O = Ru(NH_3)_5(H_2O)C_7H_7NC^{2+} + NH_4{}^+ \quad (1)$$

was studied in acidic media over the temperature range 15–35 °C; the results are shown in Table III. The reverse reaction in negligible under our experimental conditions, as was demonstrated by a run in which $[NH_4{}^+]$ was added without effect on the rate. The reaction rate is unaffected by atmospheric O_2, and it is independent of $[H^+]$ over the range 0.001–0.1 M.

The activation parameters as determined from the temperature dependence of the rates are $\Delta H^{\ddagger} = 22.9 \pm 1.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.5 \pm 3$ cal mol^{-1} K^{-1}.

Reaction of *trans*-$Ru(NH_3)_4(H_2O)C_7H_7NC^{2+}$ with Isonicotinamide (isn). The data bearing on the dynamics of this system as a function of acidity, [isn], and [Ru(II)] are summarized in Table IV. In principle, in treatment of the data, not only the reaction

$$Ru(NH_3)_4(H_2O)C_7H_7NC^{2+} + isn \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} Ru(NH_3)_4(isn)C_7H_7NC^{2+} + H_2O \quad (2)$$

but also the forward and reverse processes for $isnH^+$ acting in place of isn need to be considered:

$$Ru^{II}H_2O + isnH^+ \underset{k_{-h}}{\overset{k_h}{\rightleftharpoons}} Ru^{II}isn + H^+ + H_2O$$

The latter path has been shown[14] to be significant in the reaction of pyridine or isonicotinamide with $Ru(NH_3)_5H_2O^{2+}$. On treating our data for the purpose of evaluating four parameters, namely, k_i, k_{-i}, k_h, and k_{-h}, we find that the path involving $isnH^+$ accounts at most for 3% of the reaction, so that k_h is not fixed by our data. Accordingly, the data were treated graphically as shown in Figure 2, where k_{obsd} is plotted against [isn]. When [isn] is low, $[H^+]$ is high, and it is evident that the proton-dependent term is unimportant. The graph shows that the data are correlated reasonably well by $k_{obsd} = k[isn] + k'$, where $k = 1.45$ ($\pm 0.004 \times 10^{-2}$ M^{-1} s^{-1} can be identified with k_i and $k' = 1.7$ (± 0.2) × 10^{-4} s^{-1} with k_{-i}.

The value of the equilibrium quotient, K, as calculated from the graphical treatment of the data is 85 ± 10, but owing to the inaccuracy in fixing the intercept, it was considered desirable to obtain K by a more direct method, namely, one that depends on determining the composition of equilibrated samples. Accordingly, the values of the absorbance, A, after completion of the reaction, as a function of the concentration of isonicotinamide were analyzed by using data at 358 nm,

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Table IV. Reaction of *trans*-$Ru(NH_3)_4H_2OC_7H_7NCN^{2+}$ with Isonicotinamide[a]

$[isn]_t$, M	pH	[isn], M	$[isnH^+]$, M	10^3k_{obsd}, s^{-1}	$10^4[Ru(II)]_t$, M	A_∞	$10^{-3}\bar{\epsilon}$
0.20	1.48	0.0019	0.1981	0.213	0.779	0.093	1.19
0.133	1.68	0.002	0.1310	0.220	0.779	0.088	1.13
0.005	4.67	0.0047	0.0003	0.259	0.689	0.150	2.18
0.10	2.68	0.0131	0.0869	0.300	1.21	0.509	4.21
0.02	4.40	0.0178	0.0022	0.489	0.689	0.298	4.33
0.267	2.75	0.0403	0.2267	0.795	0.779	0.404	5.19
0.10	5.88	0.0996	0.0004	1.93	0.689	0.433	6.28
0.333	3.15	0.1031	0.2302	1.78	0.779	0.480	6.19
0.20	3.67	0.1193	0.0807	1.86	1.21	0.777	6.42
0.20	6.15	0.2000	0.0000	3.38	0.689	0.460	6.68
0.30	3.92	0.2174	0.0826	3.24	1.21	0.847	7.00
0.40	3.73	0.2249	0.1751	3.2	1.12	0.732	6.53
0.40	3.75	0.2355	0.1645	3.7	1.12	0.730	6.51
0.40	6.19	0.4		5.37	1.08	0.731	6.76
0.40	6.20	0.4		5.04	1.08	0.741	6.86

[a] $\bar{\epsilon} = A_\infty/[Ru(II)]_t$; [isn] and $[isnH^+]$ were calculated from the p*K* value of isn (3.5) and pH.

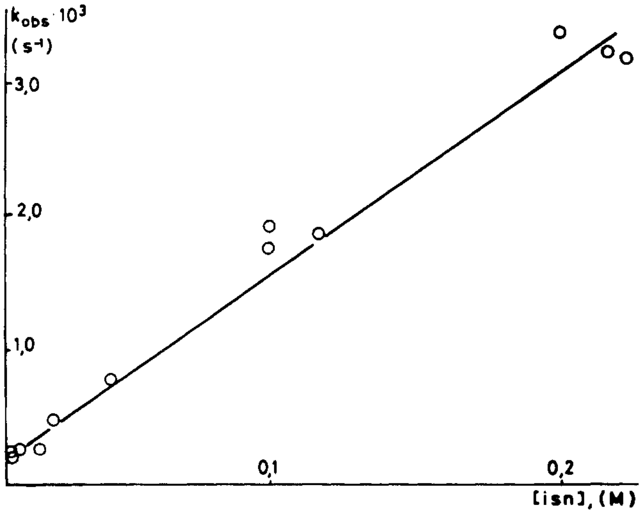

Figure 2. Variations of k_{obsd} with [isn] (data of Table IV).

where only the isn complex (ML) and the aquo ion (M) contribute to the optical density:

$$A = \epsilon_{ML}[ML] + \epsilon_M[M]$$

At equilibrium

$$A_\infty = \epsilon_{ML}\frac{[Ru(II)][L]K}{1 + K[L]} + \epsilon_M\frac{[Ru(II)]}{1 + K[L]}$$

([Ru(II)] = [ML] + [M]; [L] = [isn], always in great excess over Ru(II)). The extinction coefficient ϵ_M is known (76.7 M^{-1} cm^{-1} at 380 nm), and the data can then be treated to obtain K and ϵ_{ML}. The resulting values are 96 ± 5 and 6.94 (±0.09) × 10^3 M^{-1} cm^{-1}.

In the respect that it is specifically trans labilizing, benzyl isocyanide resembles SO_3^{2-},[5] $P(OR)_3$,[15] and C-bound imidazole.[4] In the case of SO_3^{2-} as a substituent on ruthenium(II), it has been shown that this ligand is in fact also cis delabilizing.[5] Whether the other members of the group share this property is not known.

The sense in which the isocyanide is labilizing must be considered with some care. Ammonia is lost from the trans position of the pentaammine–isocyanide complex at a specific rate of 6 × 10^{-5} s^{-1} at 25 °C, but from $Ru(NH_3)_6^{2+}$ at a specific rate[14] of 9 × 10^{-6} s^{-1}. When account is taken of the statistical factor, the labilization attending replacing ammonia by isocyanide amounts to a factor of 40. The situation is different however when the substitution of water is considered. The specific rate of replacement of water by isn in $Ru(NH_3)_4(H_2O)C_7H_7NC^{2+}$ has been measured as 1.45 × 10^{-2} M^{-1} s^{-1} as compared to 0.10 M^{-1} s^{-1} in $Ru(NH_3)_5H_2O^{2+}$; i.e., the isocyanide in this instance is delabilizing in comparison to ammonia. The lability of the isocyanide however is quite high for a complex with E_f at 0.92 V; from the graph of E_f vs. specific rate shown in ref 4, a specific rate of less than 10^{-5} M^{-1} s^{-1} would have been predicted. An astonishing aspect of the observations is that the labilizing effects of isocyanide are different for two such similar ligands.

An important difference between aquation of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5C_7H_7NC^{2+}$ is that the replacement of NH_3 by H_2O in the former case is markedly enhanced by acid,[16] and at 0.10 M acid, 97% of the aquation reaction proceeds by the proton-dependent path.[14] In the case of the isocyanide complex, this path can at most account for a few percent of the reaction. The results are consistent with the view that the protons in the case of the hexaammine participate by protonating the πd electrons but by no means prove this hypothesis (the basicity of these protons would be markedly decreased when a saturated ligand is replaced by a π acid).

Because of the slow substitution in $Ru(NH_3)_4(H_2O)C_7H_7NC^{2+}$, and its insensitivity to the atmosphere, no special effort was devoted to measuring the rate of reaction with O_2. Even if the oxidation of the complex were governed by the rate of substitution, the pseudo-first-order rate for reaction with atmospheric O_2 would be 1.45 × 10^{-2} × 2.4 × 10^{-4} = 3.6 × 10^{-6} s^{-1} (here it is assumed that the specific rate for substitution by O_2 is the same as it is by isn; the factor 2.4 × 10^{-4} is the concentration of O_2 in an aqueous solution in equilibrium with the atmosphere). Since the complex $Ru(NH_3)_4(H_2O)C_7H_7NC^{2+}$ is durable in air, the actual rate of reaction with O_2 is probably even slower than that calculated for oxidation controlled by substitution. The turnover number of 3.6 × 10^{-6} s^{-1} is very far removed from a desirable value such as 10^2 s. At this point, it is not clear what measures would need to be adopted to retain a value of E_f ~ 0.9 V and keep a turnover number very much greater than what we find for $Ru(NH_3)_4(H_2O)C_7H_7NC^{2+}$ in reaction with O_2.

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Registry No. $[Ru(NH_3)_5(C_7H_7NC)](PF_6)_2$, 82741-97-7; *trans*-$[Ru(NH_3)_4(C_7H_7NC)_2](PF_6)_2$, 82741-99-9; *trans*-$[Ru(NH_3)_4(C_6H_{11}NC)_2](ClO_4)_2$, 82742-01-6; *trans*-$[Ru(NH_3)_4(H_2O)C_7H_7NC](PF_6)_2$, 82742-03-8; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1.

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