than 0.01,[15] while in the uv photolysis all three types of ligands are labilized with ϕ_{NH_3} rising to 0.2,[35] or to the same value as found here for ϕ_{eq} at 254 nm.

As a last comment, our preparative experiences suggest that considerable caution should be exercised in making assumptions about the stereospecificity of a substitution reaction. Reactions 1 and 2, both run in liquid ammonia, behaved quite differently in this respect; in particular, we did not expect reaction 1 to be so poorly stereospecific. Cr(III) substitutions are generally thought to be stereospecific in aqueous media,

(35) P. Riccieri and E. Zinato, unpublished results.

yet it appears that in reaction 12 the displaced ammonia is not primarily the one originally cis to the chloride.

Nitrogen-Bound and Carbon-Bound Imidazole Complexes of Ruthenium Ammines[1]

Richard J. Sundberg,* Robert F. Bryan,* Ivan F. Taylor, Jr., and Henry Taube*

Contribution from the Departments of Chemistry, Stanford University, Stanford, California 94305, and University of Virginia, Charlottesville, Virginia 22901. Received July 24, 1973

Abstract: Complexes of a series of imidazoles including imidazole, 1-methylimidazole, 4-methylimidazole, 4,5-dimethylimidazole, and benzimidazole with pentaammineruthenium in the II and III oxidation states are described. Except for 4,5-dimethylimidazole, good yields of complexes having imidazole bound to ruthenium through the N-3 nitrogen are obtained by reaction of the imidazole with aquopentaammineruthenium(II) followed by air oxidation. Electronic and pmr spectral features of the Ru(II) and Ru(III) states of these complexes are described. The Ru(II) complexes are not stable below pH ~2, largely reverting to the aquopentaammine species. Kinetic data on this aquation reaction are given for the imidazole complex. The aquation leads to low conversion to derivatives of tetraammineruthenium(II) in which an imidazole ligand is bound to ruthenium through atom C-2. 4-Methylimidazole and benzimidazole give similar carbon-bound species. An analogous carbon-bound complex is the principal product of the reaction of 4,5-dimethylimidazole with pentaammineruthenium(II). The Ru(III) trichloride complexes have been isolated as crystalline solids. Carbonylated derivatives of the Ru(II) complexes of imidazole and 4,5-dimethylimidazole have been prepared and characterized. Spectral data indicating the novel carbon-bound structures are discussed. . The results of an X-ray structure determination of the carbonylated derivative of the carbon-bound dimethylimidazole complex as the hexafluorophosphate salt which confirm the carbon-bound structure are presented.

I midazole and its derivatives have been of substantial interest as ligands because the imidazole ring of histidine plays a prominent role in the biological chemistry of transition metal ions.[3] This study was undertaken to gain further insight into the properties of the imidazole ring as a ligand by extending earlier studies of pyridine complexes of ruthenium ammines.[4-6] In particular, many of the unique properties of the ruthenium(II) complexes of pyridine-type bases can be related to strong metal–ligand π bonding. The imidazole ring contains a pyridine-type nitrogen but its ability to act as a π-acceptor is expected to be attenuated by the π-donor characteristics of the pyrrole-type nitrogen which serves as an internal electron donor substituent.[7] In this paper we describe the preparation and characterization of a number of pentaammineruthenium complexes of imidazole and its derivatives which are bound through N-3, the pyridine nitrogen, of the imidazole ring. In addition, the isolation of novel complexes in which the ligand is the imidazolium ylide, bound to ruthenium at C-2 of the ring, is described. Structural assignments based largely on nmr evidence and a structure determination by X-ray diffraction methods for one of these compounds are reported.

Experimental Section[8]

General Procedure for Pentaammineimidazoleruthenium(III) Trichlorides. The preparation of pentaammine-4-methylimidazole-

(1) Isolation, characterization, and spectral studies were carried out at Stanford University with the support of NSF Grant GP 24726X, NIH Grant GM 13638-07, and NIH Special Research Fellowship GM 50833-01. Structural conclusions based on these studies have been published in a preliminary communication.[2] Determination of the crystal structure of compound **8d** was carried out at the University of Virginia.

(2) R. J. Sundberg, R. E. Shepherd, and H. Taube, *J. Amer. Chem. Soc.*, **94**, 6558 (1972).

(3) R. J. Sundberg and R. B. Martin, *Chem. Rev.*, in press.

(4) R. G. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).

(5) P. C. Ford, J. R. Kuempel, and H. Taube, *Inorg. Chem.*, **7**, 1976 (1968).

(6) P. Ford, De F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

(7) K. Schofield, "Hetero-Aromatic Nitrogen Compounds. Pyrroles and Pyridines," Plenum Press, New York, N. Y., 1967, Chapters 2 and 3.

(8) Abbreviations: Im = imidazole; 1-MeIm = 1-methylimidazole; 4-MeIm = 4-methylimidazole; DMIm = 4,5-dimethylimidazole; BzIm = benzimidazole.

ruthenium (2c) is typical. 4-MeIm (216 mg, 2.64 mmol) was dissolved in 40 ml of 0.05 N HCl. Solid [(NH₃)₅RuCl]Cl₂ (145 mg, 0.50 mmol) was added and the resulting suspension was reduced over zinc amalgam for a period of 4 hr, during which time the [(NH₃)₅RuCl]Cl₂ dissolved completely. Alternatively, the ruthenium could be added as a solution of [(NH₃)₅RuCl](CF₃-CO₂)₂.[6] A stream of deoxygenated argon was bubbled through the mixture throughout the course of the reaction. At the end of the reaction period the solution was removed from the zinc, diluted with 100 ml of water and subjected to an air stream for 1 hr. The pH of the resulting solution was adjusted to 1–2 with dilute HCl. Ion exchange was carried out using the H⁺ form AG50W-X2 resin supplied by Bio-Rad Laboratories and subsequently purified.[9] Column size was approximately 2.5 × 10 cm. HCl (3 N) eluted the major product which was isolated by rotary evaporation to dryness and crystallized from water–ethanol. Yields were 50–80% for 2a, 2b, 2c, and 2e. The course of the reaction with DMIm was different and is described separately below.

Pentaammineimidazoleruthenium(II) Tetrafluoroborate (1a). A suspension of [(NH₃)₅RuCl]Cl₂ (0.200 g) in water (8 ml) containing Im (0.136 g) and 0.5 N HCl (2 ml) was purged with argon, and zinc amalgam was added. The solution was kept over the zinc with continuous argon bubbling until all the solid had dissolved and the color was light yellow. The solution takes on a brownish purple color during intermediate stages of the reduction. When reaction was complete (3–4 hr) the solution was transferred under argon pressure through a glass wool filter plug to a receiver containing 1.0 g of NaBF₄ in water (2 ml). Precipitation began almost immediately. The product was isolated by filtration, washed with a small amount of methanol and dried, yield 0.245 g, 83%. See analytical data in Table I. The solid was stable to extended storage under vacuum.

Table I. Analytical Data

Compound	Composition[a]		C	H	N	Cl
2a	(NH₃)₅ImRuCl₃	Calcd	9.08	5.84	24.72	26.81
		Found	8.94	5.69	25.05	26.32
2b	(NH₃)₅-1-MeImRuCl₃	Calcd	12.82	5.65	26.17	28.38
		Found	12.55	5.66	25.78	28.15
2c	(NH₃)₅-4-MeImRuCl₃	Calcd	11.70	6.14	23.87	25.89
		Found	11.43	5.94	24.03	25.92
2d	(NH₃)₅DMImRuCl₃	Calcd	14.76	6.19	24.10	26.14
		Found	14.35	5.79	24.35	25.84
2e	(NH₃)₅BzImRuCl₃	Calcd	18.82	5.64	21.95	23.81
		Found	18.96	5.08	22.78	23.95
			18.78	5.17	22.37	23.00
1a	(NH₃)₅ImRu(BF₄)₂	Calcd	8.42	4.48	22.91	
		Found	8.47	4.29	23.09	
4a	(NH₃)₄(Im)₂RuCl₃	Calcd	17.52	4.90	27.25	25.74
		Found	17.49	4.76	27.44	25.42
4c	(NH₃)₄(4-MeIm)₂RuCl₃	Calcd	21.84	5.50	25.48	24.08
		Found	20.50	5.55	25.90	24.05
6a	(NH₃)₄Im'RuCl₃	Calcd	10.48	4.69	24.46	30.95
		Found	10.75	4.60	24.04	29.82
			10.26	4.72	24.83	30.15
6c	(NH₃)₄-4-MeIm'RuCl₃	Calcd	13.43	5.07	23.50	29.74
		Found	13.39	4.90	23.93	29.82
6d	(NH₃)₄DMIm'RuCl₃	Calcd	16.16	5.42	22.61	28.61
		Found	16.11	5.31	22.77	27.06
			15.69	5.14	23.19	28.64
6e	(NH₃)₄BzIm'RuCl₃	Calcd	21.35	4.61	21.35	
		Found	21.11	4.51	21.20	
8a	(NH₃)₄COIm'Ru(PF₆)₂	Calcd	8.65	2.90	15.14	
		Found	8.61	2.96	15.72	
8c	(NH₃)₄CODMIm'Ru-(PF₆)₂	Calcd	12.35	3.46	14.41	
		Found	12.33	3.20	14.82	

[a] The abbreviations Im, DMI, etc., refer to nitrogen-bound ligands. For carbon-bound ligands, Im', DMI', etc., are used.

Spectrophotometric Titrations. Solutions of the salts having appropriate concentrations to give absorbances of 0.5–1.5 near 300

nm were prepared. After incremental addition of standard NaOH, pH and spectra were recorded. Back-titration with acid revealed that no irreversible change occurred up to pH 10.5. pK_a values were estimated by calculating the extent of deprotonation as measured by the development of the absorbance characteristic of the conjugate base at several pH values near the pK_a. The results are given in Table III.

Tetraammine(2-imidazolium)ruthenium(III) Trichloride (6a). Solid [(NH₃)₅RuCl]Cl₂ (200 mg) was suspended in a solution of Im (136 mg) in 20 ml of 0.05 N HCl. The mixture was subjected to an argon stream, and zinc amalgam was added. When reduction was complete (2–4 hr) the solution was transferred using a gas-tight syringe to 0.020 N HCl (200 ml) which had been thoroughly deoxygenated using argon. The resulting solution was kept for 6.5 hr at room temperature and then subjected to oxidation with a stream of air for 1 hr. The solution was brought to 0.5–1.0 M in Cl⁻ by addition of HCl and refrigerated overnight to precipitate some [(NH₃)₅RuCl]Cl₂. The orange filtrate was subjected to ion-exchange chromatography using a 2.5 × 10 cm column of purified AG50W-X2 resin. HCl (1–1.5 N) elutes [(NH₃)₅RuCl]Cl₂. The orange product 6a was eluted by 2–2.5 N HCl and isolated by rotary evaporation. Rechromatography is necessary if a band at 330 nm ([(NH₃)₅RuCl]Cl₂) is prominent. The product can be isolated as a microcrystalline orange solid by dissolving the evaporation residue in a minimum amount of water and adding ethanol or acetone to induce precipitation, yield 20–30 mg.

Compounds 6c and 6e were prepared by analogous procedures except that the starting materials were isolated samples of 2c and 2e which were reduced over zinc amalgam prior to addition of acid. The yield of 6c was usually about 10% but the yield of 6e was less than 5%.

Tetraammine(4,5-dimethyl-2-imidazolium)ruthenium(III) Trichloride (6d) and Pentaammine-4,5-dimethylimidazoleruthenium(III) Trichloride (2d). A solution of DMIm[10] (0.576 g, 6.00 mmol) and trifluoroacetic acid (0.570 g, 5.00 mmol) in water (20 ml) was prepared. [(NH₃)₅RuCl]Cl₂ (292 mg, 1.00 mmol) was dissolved in water (≈10 ml) containing CF₃CO₂Ag prepared by dissolving Ag₂O (0.231 g) by addition of a minimum amount trifluoroacetic acid. These solutions were mixed, and the precipitated AgCl was removed by filtration. The filtrate was added to the DMIm solution. The pH was adjusted to 5 with 0.1 N NaOH, and the solution was transferred to a flask equipped with an argon inlet and reduced over zinc amalgam for 8–10 hr. The solution was removed from the zinc, diluted with water (100 ml), subjected to an air stream for 1 hr and then brought to pH 1–2 with dilute HCl, and refrigerated overnight. The deep purple solution was divided into equal portions and chromatographed on two 2.5 × 10 cm columns of purified AG50W-X2 resin. The carbon bound species 6d was eluted rapidly by 3 N HCl and was followed by an overlapping band containing 2d which could be recognized by the appearance of a prominent absorbance at 310 nm. The fractions containing mainly 6d were combined and evaporated to dryness. The residue was dissolved in a minimum amount of water, diluted with acetone, and refrigerated. Yields on the basis of absorbance at 600 nm were 20–30% and the crystalline material amounted to 100–120 mg. The fractions containing 2d were combined and evaporated to dryness. Recrystallization from water–ethanol gave 2d. The yields were usually low, <10%, and quite variable, in part, at least, because of variable efficiency in the separation from 6d.

An unidentified product which was lavender in color, λ_{max} 560 nm, was eluted prior to the principal products. Some [(NH₃)₅-RuCl]Cl₂ was also eluted from the column prior to 6d and 2d.

Bis-Imidazole Complexes of Tetraammineruthenium(III). Small amounts of by-products having two imidazole ligands were isolated in the case of Im and 4-MeIm. The compound 4a was most conveniently isolated by oxidizing the crystallization mother liquors from preparation of 1a with a stream of air and subjecting the resulting solution to ion-exchange chromatography using 3 N HCl as the eluent. Compound 4a is eluted as an orange band absorbing strongly near 310 nm. The presence of the species could also be recognized from the nmr of reduced ion-exchange fractions containing the total 3+ ion fraction eluted in the course of preparation of 2a. In addition to the large peaks characteristic of 1a a series of smaller peaks at 7.54, 7.24, and 6.87 was present. An authentic sample of 4a was prepared as follows. A suspension of cis-[(NH₃)₄-RuCl₂]Cl in water (4 ml) containing Im–ImH⁺ buffer at [Im] = [ImH⁺] = 0.25 M was deoxygenated and subjected to zinc amalgam

(9) E. Deutsch and H. Taube, Inorg. Chem., 7, 1532 (1968).

(10) H. Bredereck and G. Theilig, Chem. Ber., 86, 88 (1953).

reduction under an argon atmosphere. After an intermediate stage during which it was deep purple, the solution became orange (1.5 hr). The solution was transferred from the zinc, diluted, and oxidized with an air stream. The oxidized solution was subjected to ion-exchange chromatography and the product was eluted by 3 N HCl. The combined orange fractions were evaporated to dryness and triturated with methanol–acetone to give 4a as the trichloride salt in 60% yield. A reduced solution showed aromatic protons at 6.87, 7.25, and 7.54 and two ammine signals of equal intensity at 2.20 and 2.43 ppm.

The bis-4-MeIm analog, 4c, was isolated from the crystallization mother liquors from a large scale preparation of 2c. It was purified by several recrystallizations from water–ethanol.

Kinetics of Acid-Catalyzed Aquation of 1a. A solution (47.50 ml) containing the appropriate quantity of LiCl for ionic strength adjustment was thermostated and deoxygenated by an argon stream. A weighed sample of 1a (8.5 ± 0.2 mg) was dissolved in the thermostated solution. Reaction was initiated by injection of 2.50 ml of argon purged HCl of the appropriate concentration. One-centimeter quartz cells were filled via an all glass connection and sealed by closing the stopcocks of the cell filler. The cell was transferred to the thermostated cell compartment of the spectrophotometer and the course of the reaction followed by monitoring absorbance decrease at 285 or 255 nm. The treatment of the data is discussed in the text. No change in the observed rate was evident in runs at which the initial concentration of 1a was from one-half to two times that quoted above.

Product Analysis on Aquation Reactions. Reaction product studies were conducted at $[H^+] = 0.10\ M$, $\mu = 0.10$, and at $[H^+] = 0.025\ M$, $\mu = 0.10$. The concentration of $[(NH_3)_5ImRu]^{2+}$ was about twice that used in the majority of the kinetic experiments but within the range which was demonstrated to show identical kinetics. Deoxygenated solutions containing 1a (21.4 mg, 5×10^{-6} mol) and LiCl were treated with the appropriate amount of HCl to give a total volume of 70 ± 1 ml and the desired acidity and ionic strength. After three and seven half-lives, 25-ml aliquots were removed and immediately subjected to a stream of air to quench the reaction by oxidation of ruthenium to the +3 state. The oxidized aliquots were then subjected to ion-exchange separation on purified H^+-form AG50W-X2 resin. See the Results section for description of the fractions which were characterized.

Nmr Spectra. Spectra were normally recorded in water using a Varian HA 100 instrument with water as a lock signal. Spectra of dilute solutions ($<5 \times 10^{-2}\ M$) were recorded over a 250-Hz sweep range in the δ 6.0–10.0 region depending upon the particular system under investigation. Repetitive scans were obtained with the aid of a Varian C-1024 time-averaging computer. The number of scans recorded varied from about ten for solutions around $4.0 \times 10^{-2}\ M$ in Ru(II) to 35 for those near $1.0 \times 10^{-2}\ M$ in Ru(II). When crystalline Ru(III) salts were available, a solution $\sim 0.1\ M$ was prepared and reduced over Zn/Hg. The resulting solution was then transferred by gas-tight syringe to an nmr tube which had been well flushed with argon and contained a small amount of sodium 3-trimethylsilylpropionate for internal reference. The chemical shift data are recorded in Table VIII which is included in the microfilm edition. See paragraph at end of paper regarding supplementary material.

Nmr Studies of Reactions of 1a with Acid. a. Excess Acid. A solution [1a] = $2.7 \times 10^{-2}\ M$ in 0.1 M LiCl was treated with 0.2 N HCl to give final concentrations of [Ru(II)] = $2.2 \times 10^{-2}\ M$, $[H^+] = 4 \times 10^{-2}\ M$, and $[Cl^-] \approx 0.12\ M$. The resulting spectrum (28 scans, $\sim$15–70 min after addition of acid) is dominated by peaks at 7.5 and 8.7 ppm attributable to the ImH$^+$ ion. Weak peaks due to 1a are present as well as a weak series of peaks having chemical shifts of $\sim$7.6, 7.1, and 6.5 ppm.

b. Stoichiometric Amount of Acid. A solution of [1a] = $4.0 \times 10^{-2}\ M$, $[H^+] = 4 \times 10^{-2}\ M$, and $[Cl^-] \approx 0.12\ M$ was prepared by addition of 0.20 ml of 0.2 N HCl to a solution of 1a (17.1 mg) in 0.8 ml of 0.1 N LiCl. The time-dependent nmr spectrum was observed during the period 5–350 min after addition of acid. The changes in the spectrum during the initial phase of the observation period involved the decrease of the 1a peaks at δ 7.75, 7.29, and 7.04 and appearance of the ImH$^+$ ion peaks at 7.5 and 8.7 ppm. At a probe temperature of 35° the maximum concentration of imidazolium ion was reached at 35–40 min. Throughout the observation period a set of peaks at 7.6, 7.1, and 6.6 ppm grew in size. This set of peaks is assigned to the ion $[(NH_3)_4ImRuOH_2]^{2+}$ on the basis of the following observations. Addition of NH$_3$–NH$_4^+$ buffer such that [NH$_3$] = [NH$_4^+$] $\approx$ 0.1 M caused disappear-

ance within minutes of these peaks and the reappearance of the peaks characteristic of 1a. Addition to a similar solution of Im–ImH$^+$ buffer such that [Im] = [ImH$^+$] $\approx$ 0.03 M followed by oxidation and separation of the reaction products by ion-exchange chromatography led to isolation of a $\sim$40% yield of 4a, as identified by its nmr spectrum.

trans-**Tetraamminecarbonyl-2-imidazoliumruthenium(II) Hexafluorophosphate (8d).** A solution of 6d (90 mg) in 3 ml of water was reduced over zinc amalgam in an argon atmosphere. When reduction was complete carbon monoxide was bubbled through the solution for 3 hr. The solution was then removed from the zinc, filtered, and treated with a solution of 140 mg of ammonium hexafluorophosphate in 1 ml of water. The product (80 mg) was isolated by filtration after the solution had been refrigerated for about 2 hr.

The crystals used for X-ray diffraction were recovered after use in recording an nmr spectrum in DMSO-d_6 by diluting the solution with water. These crystals were then dissolved in acetone and the solution was diluted with ethanol. Satisfactory crystals formed on slow evaporation under a nitrogen flow in a desiccator. When X-ray data revealed the presence of a pyramidal molecule as well as 8d in the unit cell, evidence for the presence of DMSO-d_6 was obtained. The crystals sinter above 180° on a hot stage melting point apparatus, suggesting desolvation. In the mass spectrometer three prominent peaks were observed at 84, 68, and 66 amu from the crystals before but not after heating to 180°. Accurate mass determination of these ions as $[CD_3SOCD_3]^+$ (calcd 84.0516, found 84.0518), $[CD_3SCD_3]^+$ (calcd 68.0567, found 68.0571), and $[CD_3SO]^+$ (calcd 66.0093, found 66.007) was in agreement with expectation for DMSO-d_6. Qualitative analysis by spark source mass spectrometry and quantitative analysis for sulfur (calcd 4.75, found 5.66) confirmed the presence of sulfur in these crystals.

Crystal Structure Determination. A single-crystal fragment, $0.5 \times 0.5 \times 0.3$ mm³, was used for the X-ray study. From precession photographs, taken with Mo Kα radiation, the crystal was shown to have monoclinic symmetry and systematic absences (hkl) with $h + k$ odd. The possible space groups are $C2$, Cm, or $C2/m$.

The unit cell dimensions, found from a least-squares fit of preliminary values from precession photographs to the carefully measured diffractometer values of $\pm 2\theta$ for 24 strong general reflections, are $a = 22.725\ (5)$, $b = 8.500\ (2)$, $c = 12.307\ (3)$ Å, and $\beta = 94.22$ $(3)°$, giving a unit cell volume of 2371 Å³. The observed density, 1.88 (1) g cm^{-3}, suggests $Z = 4$ for $[(NH_3)_4(CO)(C_5H_8N_2)Ru]^{2+}$ $2(PF_6)^-$ but requires the presence of an additional moiety per formula unit of mass ca. 80 amu. This additional unit was identified as deuterated dimethyl sulfoxide. The calculated density when solvent is included is 1.87 g cm^{-3}, in good agreement with the observed value.

We chose the space group of highest symmetry, $C2/m$, as a starting point, and the results of the analysis show this to be correct. With $Z = 4$ in this space group the cation must have crystallographically imposed C_s or C_2 symmetry, but there are no constraints on the symmetry of the anion formally required. From the length of the b axis it is clear that C_2 symmetry is ruled out so that the cations must lie in the mirror planes at $y = 0$ and $^1/_2$.

Intensity measurements were made from the same crystal by standard diffractometric methods.[11] With monochromatic Mo Kα radiation 3565 reciprocal lattice points to $2\theta = 60°$ were surveyed within a single quadrant, and scattered intensity significantly above background was recorded at 2426 of them by use of $\theta/2\theta$ scans. Structure amplitudes were derived in the usual way. The absorption coefficient for the radiation used is small, 9.85 cm^{-1}, and no corrections for absorption were applied.

The positions of the Ru atom, the imidazole group, and the ammine residues were found from the three-dimensional Patterson function, and the C_s symmetry of the cation was confirmed. Successive cycles of structure factor calculation and Fourier evaluation of the electron density led to the location of all the remaining non-hydrogen atoms ($R = 0.35$).

The atomic parameters were refined by block-diagonal least-squares methods. With unit weights and individual isotropic thermal parameters assumed, $R = 0.10$, and with a conventional weighting scheme[12] and anisotropic thermal parameters $R = 0.06$.

---

(11) For a detailed description of the experimental methods used in our laboratory, see R. F. Bryan, P. T. Greene, P. F. Stokely, and E. W. Wilson, Jr., *Inorg. Chem.*, 10, 1468 (1971).

(12) D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Crystallogr., Sect. B*, 25, 374 (1969).

Table II. Ultraviolet–Visible Spectral Data[a]

Ligand	1	2	3	4	5	6	8
a	255 (2800)	299 (1880)	362 (2990)	311 (2490)	262 (8350)	224 (5700)	220 (15,600)
	280s (2700)	430 (250)	555 (~350)	435 (347)		480 (1630)	
b	258 (2880)	312 (2310)					
	287 (2640)	425 (186)					
c		303 (2020)	370 (3000)	290s (2080)	264 (10,000)	227 (6200)	224 (18,000)
		470 (267)	600 (472)	313 (2880)		545 (2860)	
				475 (480)			
d	280 (2820)	312 (2190)	392 (2830)		265 (8300)	230 (5000)	229 (15,500)
		520 (168)	~750 (?)			250s (4050)	
						600 (4700)	
e		255 (5400)	270–300 (?)				
		262 (5950)	505 (270)				
		269 (7000)					
		275 (6300)					
		443 (1370)					

[a] In water or 0.1 N LiCl. No variation of spectra between these media were noted.

Fine details of the structure were now revealed by a three-dimensional difference electron-density map. One of the $(PF_6)^-$ ions was found to be disordered by rotation about an axis passing through the P atom and perpendicular to the mirror plane. From peak-height measurements the occupancy ratio at the two sites was taken to be 2:1. A second difference electron-density map showed the positions of all the hydrogen atoms in the structure, including a clear indication of disordering of one ammine group by rotation about the Ru–N axis. With the hydrogen atoms fixed at their observed sites and assigned isotropic thermal parameters, $B = 4.0$ Å^2, the refinement was continued and convergence was reached with $R = 0.032$, $R_w = 0.038$.

The scattering functions for the hydrogen atoms were taken from Stewart, et al.,[13] and those for the other atom types were derived by empirical calculation.[14] Since the charges are not localized the functions for the neutral atoms were used. Anomalous dispersion terms were included for Ru, S, and P.[15]

All programs used were written in this laboratory for the XDS Sigma 2 computer also used to control the diffractometer.

Results

Preparation and Characterization of N-Bound Species 1 and 2.

Reactions of $[(NH_3)_5RuOH_2]^{2+}$ with imidazole and its derivatives were carried out in the presence of excess ligand at pH such that 50–80% of the ligand was protonated, as described in detail in the Experimental Section. The kinetics of the substitution reaction with imidazole have been studied previously by Shepherd,[16] but the reaction product was not isolated in the earlier study. In the case of imidazole, the Ru(II) complex **1a** was isolated as the fluoroborate salt, but the substituted imidazoles were isolated only in the air-stable Ru(III) state as trichloride salts. Studies on the Ru(II) species were carried out on solutions prepared by reduction of the Ru(III) ion over zinc amalgam (Scheme I).

Proton magnetic resonance spectra of **1a, 1b, 1c,** and **1d** are consistent with formulating these ions as involving bonding with the metal using the sp^2 pair of electrons of the "pyridine" nitrogen atom of the imidazole ring. This is the only bonding mode of neutral imidazole molecules to transition metal ions which had been established prior to this study, although it has been implied from time to time that the "pyrrole"

Scheme I

	R_1	R_2	R_4	R_5
a	H	H	H	H
b	CH_3	H	H	H
c	H	H	CH_3	H
d	H	H	CH_3	CH_3
e	H	H	benzo	
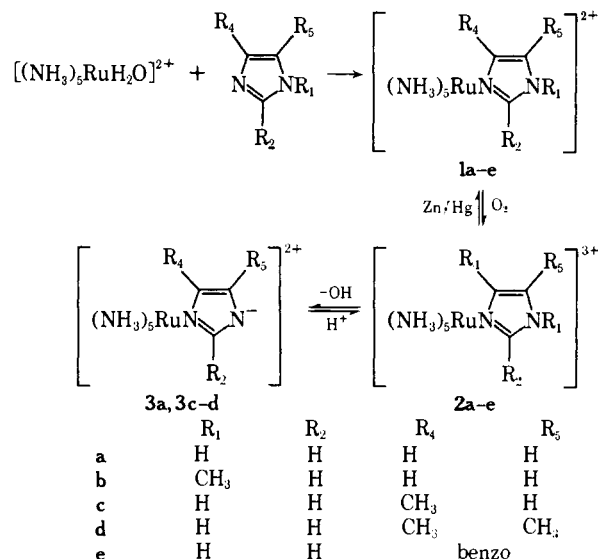
nitrogen might also be utilized for bonding.[17] Arguments against this possibility can be brought forward based on the electronic structure of the imidazole ring and on accumulated structural data.[18] The nmr spectra of **1a, 1b,** and **1d** show distinct signals for the protons or methyl groups attached to C-4 and C-5, ruling out any possibility of rapid equilibration between the two nitrogen sites in aqueous solution at 35° or below.[19] The proton at C-2 is also evident in the spectrum of each ion.

Table II records the electronic spectra of the various ions. The Ru(III) ions were characterized by a band near 300 nm and a weaker band in the visible region. The latter band is clearly quite sensitive to the imidazole substituents. The absorption maximum shifts toward longer wavelength on addition of methyl groups, suggesting that the band may be a ligand to metal charge transfer band although extinction coefficients are only

(13) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.,* **42,** 3175 (1965).

(14) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A,* **24,** 321 (1968).

(15) D. T. Cromer, *Acta Crystallogr.,* **18,** 17 (1965); D. T. Cromer and D. Liberman, *J. Chem. Phys.,* **53,** 1891 (1970).

(16) R. E. Shepherd and H. Taube, *Inorg. Chem.,* **12,** 1392 (1973).

(17) G. R. Lenz and A. E. Martell, *Biochemistry,* **3,** 750 (1964); J. E. Letter, Jr., and R. B. Jordan, *Inorg. Chem.,* **10,** 2692 (1971); A. D. Mighell and A. Santoro, *Acta Crystallogr. Sect. B,* **27,** 2089 (1971); L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.,* **11,** 457 (1972).

(18) H. C. Freeman and J. T. Szymanski, *Acta Crystallogr.,* **22,** 406 (1967).

(19) (a) M. Tsutsui, D. Ostfeld, and L. M. Hoffman, *J. Amer. Chem. Soc.,* **93,** 1820 (1971); M. Tsutsui, D. Ostfeld, J. N. Francis, and L. M. Hoffman, *J. Coord. Chem.,* **1,** 115 (1971); (b) cf. S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometal. Chem.,* **32,** C52 (1971); **39,** 179 (1972).

in the range 150–300. Certain of the spectral properties of the Ru(II) and Ru(III) complexes of imidazole and its derivatives stand in sharp contrast with the pyridine analogs and seem to reflect the greatly diminished acceptor characteristics of the imidazole ring. Thus, pyridinepentaammineruthenium complexes are colored in the II state but colorless in the III state. The visible region of the spectra of Ru(II)–pyridine complexes is dominated by bands which have metal to ligand charge transfer character and are shifted to longer wavelength by electron-withdrawing substituents.[6] In contrast, the imidazole–Ru(II) complexes show strong absorption only in the region 250–280 nm. It is not clear that this band is analogous to the bands near 400 nm in the pyridine complexes. The band position does not appear to be sensitive to the introduction of methyl groups on the ring. The only prominent absorptions of Ru(III)–pyridine systems appear to be essentially ligand transitions, whereas a strong absorption appears at 300–310 nm in the Ru(III) imidazole compounds, as well as the weak bands in the visible region. The imidazole ring itself does not have absorption bands above 240 nm.

The Ru(III) ions containing coordinated imidazoles are titrated by hydroxide ion with a pronounced shift of both absorption maxima. This is attributed to deprotonation at the "pyrrole nitrogen." Consistent with this assignment is the fact that the N-methyl ion 2b undergoes no analogous color change. Spectrophotometric titration has provided the pK_a values shown in Table III. Compared with the uncomplexed

Table III. pK_a for Deprotonation

Compound	pK_a^{a}	Compound	pK_a^{a}
2a	8.9	2d	9.5
2b	None below 11	2e	7.2
2c	9.0		

^{a} ±0.1 at $\mu < 3 \times 10^{-3}$.

imidazole which deprotonates with a pK_a of around 14.2,[20,21] it is seen that complexation with the pentaammineruthenium(III) moiety leads to an increase in the acidity constant by about 5 orders of magnitude. This is a somewhat stronger effect than for imidazole complexed to Fe(III) porphyrin systems for which pK_a values of 10.3[21] and 10.45[22] have been recorded or to values >10 which characterize pyrrole deprotonations of imidazole ligands in complexes of divalent metal ions of the first transition series.[3]

Small amounts of the bis complexes 4a and 4c were isolated as by-products of the preparation of 2a and 2c and may have been present in other cases also. The cis orientation of the imidazole groups is deduced from the ammine region of the nmr spectra of the Ru(II) species prepared from 4a and 4c. Both ions show two broad signals in the ammine region of approximately equal intensity which is consistent only with cis stereochemistry. A sample of the Ru(II) derivative of 4a showing identical nmr properties was also prepared from

(20) G. Yagil, *Tetrahedron*, 23, 2855 (1967); H. Walba and R. W. Isensee, *J. Org. Chem.*, 21, 702 (1956).

(21) P. George, G. I. Hanania, D. H. Irvine, and I. Abu-Issa, *J. Chem. Soc.*, 5689 (1964).

(22) P. Mohr, W. Scheler, H. Schumann, and K. Muller, *Eur. J. Biochem.*, 3, 158 (1967).

4a, R = H
4c, R = CH$_3$
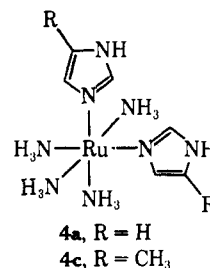
cis-[(NH$_3$)$_4$RuCl$_2$]Cl by reduction followed by imidazole substitution.

Acid-Mediated Aquation and Rearrangement of 1a. Kinetic and Thermodynamic Stability of 1a. The rate of acid-catalyzed aquation of 1a is of interest for two reasons. First, direct comparison with previously recorded rates for hexaammineruthenium(II)[5] and pentaamminepyridineruthenium(II)[5,16] would provide additional information on the sensitivity of the aquation reaction to ligand structure. Secondly, since the rate of the reverse reaction, substitution by imidazolium ion on aquopentaammineruthenium(II), is available, measurement of the rate of aquation would permit calculation of the formation constant for 1a and comparison with analogous data for hexaammineruthenium(II) and pentaamminepyridineruthenium(II).[16] Such comparisons promise further insight into the effect of ruthenium(II) back-donation on the kinetic and thermodynamic properties of complexes with ligands of varying π-acceptor capacity.

The reaction of pentaammineimidazoleruthenium(II) in media of [H$^+$] = 0.01–0.10 M, ionic strength 0.10, was followed by measuring the decrease of absorbance at 285 and 255 nm. Pseudo-first-order rate plots linear through about three half-lives and two half-lives, respectively, were obtained at these wavelengths and rate constants were extracted from the data by the method of Guggenheim. The data are recorded in Table IV and reveal the following salient features.

Table IV. Aquation Rate Data^a for Compound 1a

[H$^+$] × 10^2	μ	k_{obsd}, sec^{-1} × 10^4	$k = k_{obsd}/$ [H$^+$], sec^{-1} M^{-1} × 10^2	k_{corr}, sec^{-1} × 10^4	k_{aq}, sec^{-1} M^{-1} × 10^2
2.5	0.10	3.84	1.54	2.80	1.12
5.0	0.10	7.47	1.49		
9.0	0.10	12.7	1.41		
10.0	0.10	14.0	1.40	11.8	1.18
5.0^b	1.0	16.9	3.38		

Comparison with Other Systems

	μ	k, sec^{-1} M^{-1}
(NH$_3$)$_5$ImRu^{II}	1.0	3.38 × 10^{-2}
(NH$_3$)$_6$Ru^{II}	1.0	2.1 × 10^{-4} ^{c}
(NH$_3$)$_5$PyRu^{II}	1.0	5.42 × 10^{-5} ^{d}

^{a} As measured by absorbance decrease at 285 nm. $T = 25.0°$. Reproducibility of the individual pseudo-first-order rate constants was ±3%. ^{b} Limited data at other [H$^+$] for $\mu = 1.0$ confirm the trend. ^{c} Reference 5; corrected by a statistical factor of 6. ^{d} Reference 16.

(1) Like the reaction of pentaamminepyridineruthenium(II), the rate of aquation is proportional to [H$^+$], with a small positive intercept, as shown in Figure 1. (2) The reaction is ionic strength dependent, increasing by a factor of 2.2 on increase of μ from 0.1 to 1.0 at constant [H$^+$]. (3) The reaction is significantly more rapid
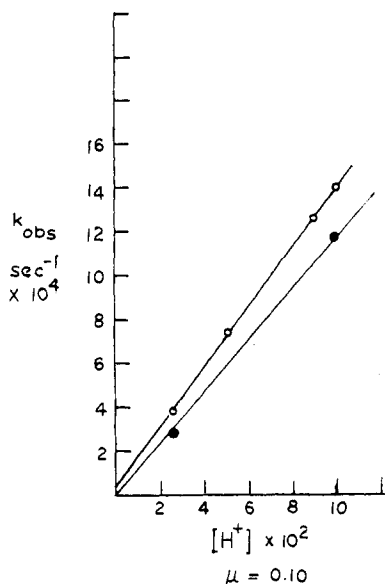
Figure 1. Hydrogen ion dependence of first-order rate constants at $\mu = 0.10$: $O = k_{\text{obsd}}$; $\bullet = k_{\text{corr}}$.

Table V. Products of Acid-Catalyzed Aquation of **1a**.
Moles ($\times 10^5$) of Product from 5×10^{-5} mol of $[A_5RuIm]^{2+}$

Fraction	$[H^+] =$ (0.025 M) $\mu = 0.10$ $3t_{1/2}$	$\mu = 0.10$ $7t_{1/2}$	$[H^+] =$ (0.100 M) $\mu = 0.10$ $3t_{1/2}$	$\mu = 0.10$ $7t_{1/2}$
NH_4^+	1.9, 1.7	..., 2.3	..., 1.3, 1.2	..., 1.9, 1.7
$[A_4RuCl_2]^+$	0.1, 0.1	0.1, 0.1	..., ~0.1, ...	..., ~0.1, ...
$[A_5RuCl]^{2+}$	3.2, 3.0	3.7, 3.6	3.5, 3.9, 3.7	4.1, 4.3, 4.2
$6a^a$	0.1	0.1	0.1	0.04

^{a} Because of the small amount of **6a** formed on this scale these values are not of high accuracy. An identical run on a larger scale gave a value of 0.19 after seven half-lives at $[H^+] = 0.025\ M$, $\mu = 0.10$.

than either the acid-catalyzed aquation of the hexaammine or pentaamminepyridineruthenium species.

It was clear from the absorbance data that another reaction competed with aquation of the complex. A run at $[H^+] = 0.025$, $[1a] = 4.0 \times 10^{-4}\ M$, after 7.5 half-lives showed an absorbance at 262 nm of 0.68 whereas the calculated value for quantitative formation of aquopentaammineruthenium(II) would be 0.22.[23] The discrepancy in "final" absorbance was even greater at $[H^+] = 0.010\ M$ but less ($A_s \approx 0.50$) at $[H^+] = 0.090\ M$. The absorbance at 262 nm subsequently decreased at a rate much slower than the initial reaction. This slower secondary absorbance change causes a more serious curvature of rate plots based on absorbance data taken at 255 nm than from those taken at 285 nm because the change in absorbance at 285 during the slow secondary reaction is not large. The rate data included in Table IV are, therefore, derived from measurements at 285 nm only.

These absorbance anomalies prompted a detailed product analysis.[24] Aquation reactions were quenched by air oxidation after three and seven half-lives and separated into several fractions by ion-exchange chromatography. Fraction 1 was analyzed for NH_4^+ by addition of base, distillation, and development of the indophenol color.[25] Fraction 2 was assumed to contain trace amounts of $[(NH_3)_4RuCl_2]^+$ on the basis of a weak broad absorption at 310–350 nm. Fraction 3 was analyzed for $[(NH_3)_5RuCl]^{2+}$ by measuring the intensity of the sharp band at 327 nm. Fraction 4 was analyzed for **6a** using the absorbance at 480 nm (ϵ 1630 for the pure compound). The results are summarized in Table V.

The product data in Table V show that the major reaction product is aquopentaammineruthenium(II) which is isolated as chloropentaammineruthenium(III) dichlo-

ride after the oxidation procedure. At seven half-lives this accounts for 72–74% of the initial ruthenium at $[H^+] = 0.025\ M$ and 82–86% of the initial complex at $[H^+] = 0.10\ M$.

Some $[(NH_3)_5ImRu]^{3+}$ was recovered from the runs quenched after three half-lives. The only other ruthenium species which could be identified among the products was **6a**, which has the composition $(NH_3)_4$-$ImRuCl_3$. The characterization of this material is considered in the next section. For the present purposes it is necessary to note that the Ru(II) state, **5a**, of this substance absorbs strongly at 262 nm (ϵ 8350). It can account for at least part of "excess" absorbance at 262.

The amount of ammonia found is too large to be accounted for on the basis of the ruthenium species which were characterized. This suggests extensive deammination of a small portion of the starting complex to unidentified products.

Since the measured reaction rate is not cleanly that of substitution of imidazole by water on pentaammineruthenium(II), the observed rate must be dissected to provide a rate constant for the aquation reaction. The product data in Table V indicate that at the two acidities studied 73 ± 1 and 84 ± 2%, respectively, of the initial complex undergoe aquation. Corrected aquation rate constants obtained by multiplying the observed rate constants by the fraction undergoing simple aquation are included in Table IV. When plotted in Figure 1, they give an approximately zero intercept.

Shepherd and Taube[16] have reported the forward rate constant as 2.7×10^{-3} at $\mu = 0.1$, 25°.

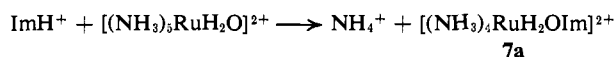$$(NH_3)_5RuH_2O + ImH^+ \underset{k_{aq}}{\overset{k_f}{\rightleftharpoons}} (NH_3)_5RuIm + H_3O^+$$
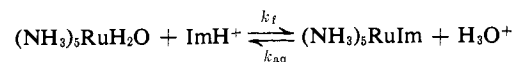
Using the corrected rate constant from our highest acidity, $[H^+] = 0.100\ M$, where the competing reaction(s) is minimized, gives $k_{aq} = 1.18 \times 10^{-2}$ at $\mu = 0.1$, 25°. In conjunction with the recorded[26] equilibrium constant for protonation of imidazole, log $K_a = 7.09$ at $\mu = 0.135$, 25°, these rates permit calculation of the equilibrium constant, K_{Im}, for formation pentaammineimidazoleruthenium(II) from imidazole and aquopentaammineruthenium(II) as 2.8×10^6. For comparison, Shepherd and Taube[16] give formation constants of 3.5×10^4 for hexaammineruthenium(II) and 2.4×10^7 for pentaamminepyridineruthenium(II) at $\mu = 0.50$, 25°. The order of increasing affinity to $[(NH_3)_5Ru(OH_2)]^{2+}$ of the ligands can be understood in terms of the π-acceptor capacity of the three bases and the assumption

(23) Calculated from a reported ϵ 550: J. N. Armor, Ph.D. Thesis, Stanford University, 1970, p 86.

(24) Slower loss of ammonia was considered a possible factor since this process has been shown to occur in the hexaammineruthenium(II) and pentaamminepyridineruthenium(II) systems, ref 5.

(25) W. T. Bolleter, C. J. Bushman, and P. W. Tidwell, *Anal. Chem.*, **33**, 592 (1961).

(26) L. G. Sillén and A. S. Martell, *Chem. Soc., Spec. Publ.*, No. 17, 387 (1964).

that metal to ligand π-bonding constitutes a stabilizing factor. Thus, ammonia which is not a π-acid forms the weakest of the three complexes. Imidazole is expected to be a poorer π-acceptor than pyridine because the pyrrole nitrogen acts as an electron donor toward the pyridine nitrogen and conveys π-excessive character to the imidazole molecule.[7] There is a striking contrast between this order of thermodynamic stability and the observed reactivity toward acid-catalyzed aquation which falls in the order Im > NH₃ > Py (Table IV).

Certain additional aspects of the reactivity of ion **1a** in aqueous acid were evident from nmr studies. Addition of sufficient acid to bring the pH of solutions 1–5 × 10⁻² M in **1a** to pH 2.0 and below resulted in rapid disappearance of the signals due to **1a** and appearance of two signals attributed to the imidazolium ion over a period of minutes. Such solutions underwent further changes observable in the nmr, especially when the original concentration of acid and **1a** were approximately equal. A series of three new peaks appeared, suggesting the formation of a nitrogen-bound imidazole complex different from **1a**. This secondary process is believed to be substitution of ammonia by imidazole leading to the formation of *cis*-aquotetraammine-imidazoleruthenium(II) (**7a**). The evidence for assignment

$$\text{ImH}^+ + [(\text{NH}_3)_5\text{RuH}_2\text{O}]^{2+} \longrightarrow \text{NH}_4^+ + [(\text{NH}_3)_4\text{RuH}_2\text{OIm}]^{2+}$$

7a

ment of this structure to the species responsible for the new series of peaks is derived from subsequent substitution reactions on the species. Addition of buffered ammonia solution results in the disappearance of the set of signals assigned to **7a** and the reappearance of peaks characteristic of **1a**. Addition of Im–ImH⁺ buffer to solutions containing ion **7a** generated in the same manner on a preparative scale, followed by oxidation and ion exchange isolation of 3+ ions gives a substance in 40% yield which is mainly the bisimidazole ion **4a**. This identification is made on the basis of the electronic spectra of the Ru(III) salt and the nmr of the reduced material. These nmr studies did not provide any unequivocal evidence concerning the structure or yield of the imidazole containing ion **5a** which is the side product in the kinetic experiments. This is not surprising since the maximum yields calculated from absorbance data would put the concentration of the ion at about the limit for reliable detection by the nmr methods used.

Structural Characterization of Carbon-Bound Imidazole Complexes. As indicated in the previous section a side product, **6a**, of acid-catalyzed aquation was isolated by ion-exchange chromatography, and structural studies were undertaken, initially using principally proton magnetic resonance spectroscopy. A solution of **6a**, reduced over zinc amalgam to the II state, **5a**, showed two peaks in the nmr, a relatively sharp singlet at 7.2, and a broad but symmetric peak at 1.92 ppm. The appearance of a single type of aromatic proton and the elemental composition which was consistent with the presence of an imidazole ring suggested the C-2 bound structure **5a**. Several substituted analogs were prepared. Treatment of **1c** under conditions like those used in the aquation studies on **1a** provided a 7% yield of **6c**. This material showed electronic spectral characteristics similar to **6a** except that the visible band was shifted to 545 nm and enhanced in intensity (Table II).
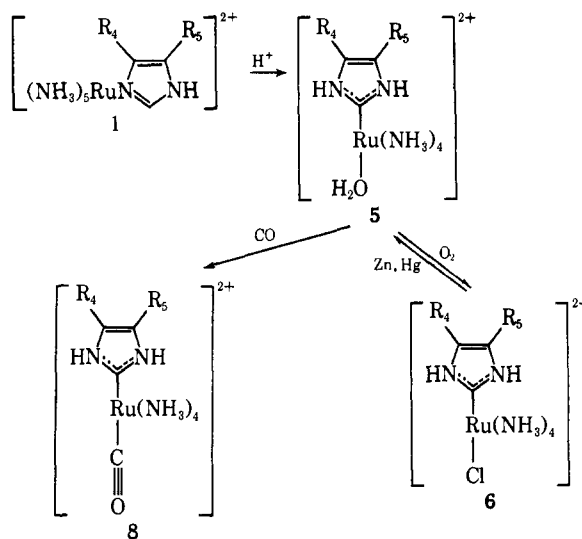
The 4,5-dimethyl analog **6d** proved to be much more accessible than **6a** or **6c**. Reaction of aquopenta-ammineruthenium(II) with a solution of excess DMIm–DMImH⁺ buffer near pH 5, followed by air oxidation, afforded in 20–30% yield a purple solid which was concluded to be structurally analogous to **6a** and **6c**. The electronic spectrum continues the pattern set by **6a** and **6c** with a further shift of the visible band to 600 nm. The nmr of **5d** shows the 4 and 5 positions of the imidazole ring to be equivalent since there is a single methyl signal at 2.1 ppm. A broad but symmetric ammine peak appears at 1.9 ppm. The solid Ru(III) compound also analyzes as a tetraammine complex analogous to **6a** and **6c**. The carbon-13 nuclear magnetic resonance spectrum of **5d** was recorded. Only two peaks could be observed in the region 0–600 ppm downfield of TMS. One peak appeared at 13.4 ppm, *i.e.*, in the methyl region, and the second in the aromatic region at 128 ppm. These two features of the cmr spectrum are in agreement with expectation for **5d**. In addition a third peak corresponding to the ruthenium-bound carbon would be expected. No very good model for this type of carbon exists among compounds for which cmr spectra have been recorded but limited data on other types of metal-bound carbons suggested 200–400 ppm as the most likely range.[27] The failure to observe this peak may stem from some inadvertent oxidation of the sample during transfer operations. Traces of Ru(III) could be expected to broaden this peak by electron transfer processes. The intensity of the signal may also be decreased by long relaxation times and by the fact that about one-third of Ru consists of isotopes having ⁵/₂ nuclear spin which will broaden about one-third of the total signal.

The carbon-bound benzimidazole ion **6e** was also isolated by acid treatment of **1e** followed by oxidation. The nmr spectrum of the reduction product **5e** consists of an ammine peak at 2.0 ppm and AA'BB' multiplets centered at 7.14 and 7.34 ppm. The nmr multiplets are characteristic of a symmetrically ortho-disubstituted benzene and are thus in agreement with structure **5e**.

(27) (a) C. G. Kreiter and V. Formacek, *Angew. Chem., Int. Ed. Engl.*, 11, 141 (1972); (b) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Commun.*, 1078 (1971); (c) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, 94, 2550 (1972); G. M. Bodner, S. B. Kahl, K. Bork, B. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, 12, 1071 (1973).
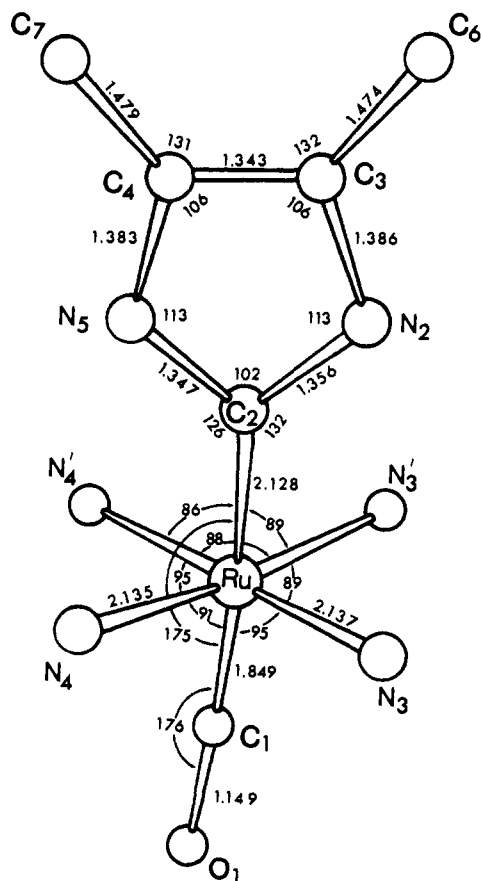
Figure 2. Bond lengths (Å) and angles in the *trans*-tetraammine-carbonyl-2-(4,5-dimethylimidazolium)ruthenium(II) cation.

Two features of the nmr data support the carbon-bound structure **5**. The absence in any of the series of compounds of a signal attributable to a proton at C-2 is consistent with structure **5** and rules out π-bonded structures such as A, B, and C. Each of these structures
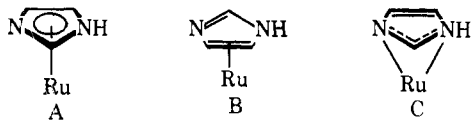
would be expected to show a signal for the C-2 proton in the aromatic region. Secondly, the pmr spectra of **5a**, **5d**, and **5e** and the cmr spectra of **5d** demand that, on the nmr time scale, C-4 and C-5 of the imidazole ring be equivalent.

The proton nmr spectra of **5a**, **5d**, and **5e** suggest that the four ammine groups are all equivalent and thus cis to the imidazolium ligand. A single broad, but symmetrical, peak appears near 2.0 ppm suggesting a single type of ammine group in each complex. In contrast, the pentaammine complexes of the **1** series show two peaks assigned to ammine resonances. The peak areas are in the approximate intensity ratio of 1:4 in agreement with expectation for the two types of co-ordinated ammonia in the pentaammines.

Spectral data for the ions of the **5** and **6** series are included in Table II. From the intensity and sensitivity to alkyl substitution of the visible band observed in the **6** series, it appears that this is a ligand-to-metal charge transfer band. The ultraviolet absorption near 262 nm which characterizes the **5** series is quite insensitive to the imidazole substituents. Its position is similar to the

band characteristic of the **1** series but the intensity of the band is about three times as great.

The more substantial amounts of **6d** which were available permitted conductivity measurements that were not practical for **6a** and **6c**. Table VI reports the

Table VI. Molar Conductivities[a]

	Δ_m
[(NH$_3$)$_5$RuCl]Cl$_2$	290
2f	400
5d	367

[a] The recorded values in water were approximately constant (±3%) in the range 5×10^{-5} to 2×10^{-4} M but became lower at concentrations near 1×10^{-3} M.

observed molar conductivities for **2e** and **6d** as well as for [(NH$_3$)$_5$RuCl]Cl$_2$. From these data we conclude that **6d** is a 1:3 electrolyte in aqueous solution and that any chloride bound to ruthenium in the solid is largely dissociated in solution, presumably by aquo substitution. These data, together with the qualitative ion exchange behavior of **6a**, **6c**, and **6d**, which indicated that the ions were not more highly charged than the tripositive ions of the **2** series, provide evidence that **6a**, **6c**, and **6d** are mononuclear species.

The tetraammine (2-imidazolium)ruthenium(II) ions **5a**, **5c**, and **5d** react with carbon monoxide to give carbonyl derivatives **8a**, **8c**, and **8d**, respectively. Solid samples of **8a** and **8d** have been isolated as hexafluorophosphate salts. The infrared spectra show strong carbonyl absorption bands near 2000 and 1950 cm^{-1}, respectively. The nmr spectra indicate that the imidazole ligands in these complexes remain carbon bound since protons or methyl groups at C-4 and C-5 are equivalent. Unlike the other Ru(II) complexes examined in this study, the carbonyl derivatives are not subject to air oxidation. The cmr spectrum of **8d** was recorded. It consists of lines at 6.5, 121.5, 180.5, and 200.3 ppm downfield of TMS. The high field signals are somewhat more than twice as intense as the low field pair. This spectrum is in accord with the assigned structure of **8d**. The single peaks in the aromatic and methyl regions again demand a symmetrical orientation of the ligand. One of the low field peaks can be assigned to the metal bound C-2 carbon and the other to the carbonyl carbon but there is no firm evidence for distinguishing between the two possible assignments. Metal-bound carbonyls are expected in this region,[27] and, though a close model for the C-2 imidazolium carbon is lacking, it would be expected to be well downfield of a normal aromatic carbon. For example, the metal-bound carbon in σ-diphenyl-π-cyclopentadienyltitanium is found at 193 ppm downfield of TMS with the remainder of the aromatic carbons in the range 124–136 ppm.[27b]

Description of the Structure of 8d. The structural conclusions based on spectral data have been confirmed by an X-ray crystal structure analysis of the hexafluorophosphate salt of **8d**. The crystal structure consists of discrete [(C$_5$H$_8$N$_2$)Ru(NH$_3$)$_4$(CO)]$^{2+}$ and PF$_6^-$ ions, with deuterated dimethyl sulfoxide as solvent of crystallization. The constituent ions and solvent are held together by a three-dimensional network of hydrogen bonds and electrostatic interactions.

Table VII. Bond Lengths (Å) and Angles (deg)[a]

(PF)₆⁻ Groups

P-1-F-1	1.605 (3)		F-2-P-1-F-3	89.8 (3)	
P-1-F-2	1.569 (4)				
P-1-F-3	1.569 (4)				
	Mean 1.581				
P-2-F-4	1.582 (3)		F-4-P-2-F-5	89.8 (2)	
P-2-F-5	1.582 (4)		F-4-P-2-F-4'	91.9 (2)	
	Mean 1.582		F-4-P-2-F-4''	88.1 (2)	

		Fa group			Fa group
P-3-F-6	1.588 (4)	1.498 (12)	F-6-P-3-F-7	87.1 (2)	92.4 (7)
P-3-F-7	1.576 (5)	1.492 (14)	F-6-P-3-F-6'	88.3 (2)	86.2 (6)
P-3-F-8	1.540 (4)	1.547 (10)	F-6-P-3-F-8	91.7 (2)	93.8 (6)
P-3-F-9	1.551 (5)	1.525 (14)	F-6-P-3-F-9	91.0 (2)	89.8 (7)
			F-7-P-3-F-8	91.1 (2)	87.2 (6)
	Mean 1.564	1.516	F-7-P-3-F-9	177.4 (3)	176.9 (8)
Av P-F 1.556, rms 0.12			F-8-P-3-F-8'	90.7 (2)	83.0 (5)
			F-8-P-3-F-9	90.7 (3)	90.5 (6)

DMSO

S-C-8	1.771 (5)		C-8-S-O-2	105.0 (2)
S-O-2	1.499 (4)		C-8-S-C-8'	100.2 (2)

Distances Involving Hydrogen

N-2-H-2	1.00	N-4-H-4b	1.06			
N-3-H-3	0.88	N-5-H-5	0.93			
N-3-H-3a	0.95	Mean N-H 0.96, rms 0.06				
N-3-H-3b	1.02					
N-3-H-3c	0.98	C-6-H-6a	1.01		C-8-D	1.01
N-3-H-3d	0.92	C-6-H-6b	0.93		C-8-Da	1.04
N-3-H-3e	0.88	C-7-H-7a	0.99		C-8-Db	0.97
N-4-H-4	0.95	C-7-H-7b	0.98		Mean C-H 0.99, rms 0.04	
N-4-H-4a	0.99					

[a] Standard deviations, in parentheses, include contributions from errors in the cell dimensions, and correlations between the positional parameters for an individual atom, but do not include possible correlations between parameters of different atoms.
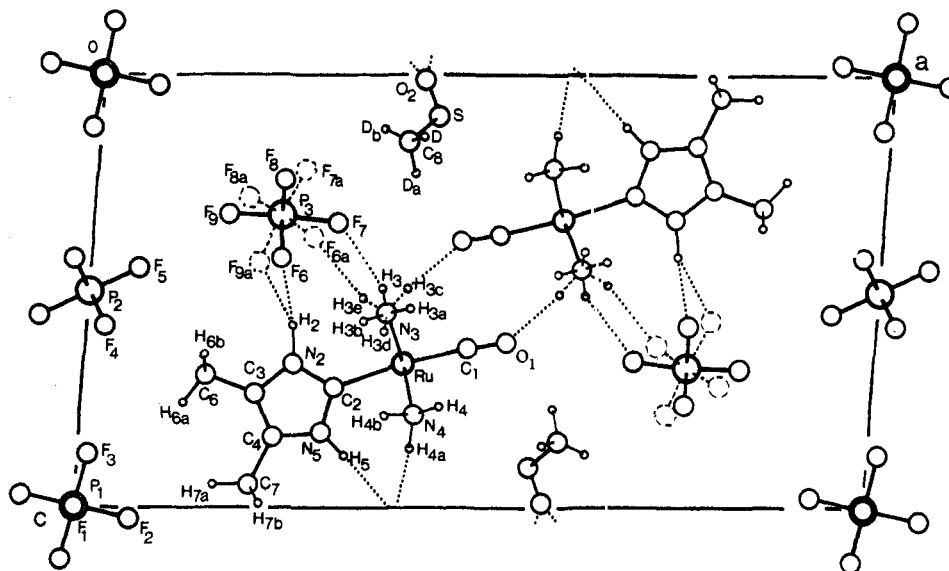

Figure 3. View of the packing arrangement in the plane at $y = \frac{1}{2}$. Hydrogen bonds are indicated by the broken lines.

The principal bond lengths and angles in the cation are shown in Figure 2. Other bond lengths and angles are given in Table VII, and a view of the structural arrangement in the crystal in the plane at $y = \frac{1}{2}$ is shown in Figure 3. The atomic parameters and structure factors are given in the microfilm edition.

Geometry of the Cation. The attachment of the imidazolium moiety to the metal atom through the central carbon atom of the ring is clearly established, with Ru–C 2.128 (4) Å. The complex is analogous, in this respect, to tetracarbonyl-1,3-dimethyl-2-imidazo-

liumiron(0)[28] and bis(N,N-diphenyl-2-imidazolium)mercury perchlorate.[29]

Ru–C$_{sp}$₂ σ-bonded distances in the range 2.04–2.19 Å have been reported[30] for a variety of irregularly co-

(28) G. Huttner and W. Gartzke, Chem. Ber., 105, 2714 (1972).

(29) P. Luger and G. Ruban, Acta Crystallogr., Sect. B, 27, 2276 (1971).

(30) (a) M. 1. Bruce, M. A. Cairns, A. Cox, M. Green, M. D. H. Smith, and F. Woodward, Chem. Commun., 735 (1970); (b) R. Belford, M. 1. Bruce, M. A. Cairns, M. Green, H. P. Taylor, and P. Woodward, ibid., 1159 (1970); (c) T. Blackmore, M. 1. Bruce, F. G. A. Stone, R. E. Davis, and A. Garza, ibid., 852 (1971); (d) F. A. Cotton and W. T. Edwards, J. Amer. Chem. Soc., 90, 5412 (1968); (e) F. A. Cotton and R. Eiss, ibid., 91, 6593 (1969).
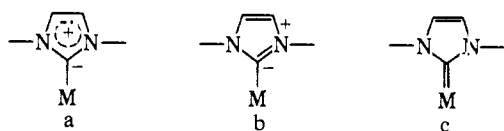
ordinated Ru(II) complexes involving polyhapto organic ligands, and the values at the lower end of this range certainly reflect substantial metal to carbon conjugation. However, in the only recorded analysis[31] of a regular octahedral complex of Ru(II) involving a metal to sp^2 carbon bond, hydridobis[1,2-bis(dimethylphosphino)-ethane]naphthylruthenium(II), Ru–C is 2.16 (1) Å, so that any bond shortening in the present case is very slight. This view is confirmed by noting that the Ru–NH_3 bonds lengths, 2.135 and 2.137 (3) Å, are only very slightly longer than the Ru–C_{sp^2} bond length. The Ru–N distances agree well with those found in the azidodinitrogenbis(ethylenediamine)ruthenium(II) ion,[32] 2.125 (19) Å, in [Ru(NH$_3$)$_6$]I$_2$,[33] 2.144 (5) Å, [Ru(NH$_3$)$_4$-Cl(SO$_2$)]Cl,[34] 2.127 (6) Å, and [Ru(NH$_3$)$_5$N$_2$Ru(NH$_3$)$_5$]-(BF$_4$)$_4$,[35] 2.12 (1) Å.

If the covalent radius of sp^3-hybridized nitrogen is assumed, conservatively, to be 0.75 Å, a value of 0.74 Å is obtained for the radius of the sp^2-hybridized carbon atom, exactly what would be expected in a bond of unit order. We conclude, then, that the Ru–C bond to the ring is a bond of unit order and that in contrast to the proposed interpretation[28] for the related Fe(0) complex there is no significant metal–carbon multiple bonding.

The imidazolium ring itself is planar by crystallo-graphic requirement, and the close agreement between corresponding bond lengths and angles shows the ring to have C_{2v} symmetry within the limits of error. Indeed, but for small deformations in the bond angles at Ru and C-2 the cation as a whole has the same symmetry. The pattern of bond distances and angles in the ring is closely similar to that found in (C$_5$H$_8$N$_2$)Fe-(CO)$_4$,[28] in the mercury perchlorate complex,[29] in 1,3-dimethyl-2(3H)-imidazolethione,[36] and the cation of histidine hydrochloride.[37] It differs, naturally, from that found in nitrogen-bound metal imidazole complexes in the equivalence of the two central C–N bond lengths.

There is excellent agreement between the individual bond lengths and angles in our analysis and the averaged values for corresponding bond types and angles in the Fe(0) complex. As in that complex, we find the internal angles at the ring nitrogens to be opened and at the central carbon atom to be reduced from the values found in the histidine cation (113 and 103° vs. 109 and 109°), the C–C bond to be shorter (1.343 vs. 1.358 Å), and the difference in length of the two sets of C–N bonds to be less pronounced (1.385 and 1.352 Å vs. 1.373 and 1.317 Å).

Three different types of structure, a–c, may be

written to describe the system. Structure b was favored

for 1,3-dimethyl-2(3H)-imidazolethione based on the absence of any significant lengthening of the olefinic double bond or shortening of the two adjacent C–N bonds (1.31 and 1.41 Å, respectively). However, in our complex and in (C$_5$H$_8$N$_2$)Fe(CO)$_4$ the two sets of C–N bonds are more nearly equivalent, and an explanation of the very short C=C bond distance may be suggested by the extra-ring C–Me distances, 1.474 and 1.479 (7) Å. These are some 0.03 Å shorter than would be expected for a C_{sp^2}–C_{sp^2} bond and this may reflect an overall reduction in the size of these atoms due to charge redistribution within the ring. If this is so then a substantial contribution from structure a is indicated. It is clear from our results that structure c makes no significant contribution.

The Ru–C-1 distance is in the normal range for such bond lengths in Ru(II) complexes.[30] The C≡O distance is longer than is usually encountered, but is in agreement with the low observed stretching frequency for this group, 1950 cm^{-1}.[30e]

The PF$_6^-$ Anions. There are *three* crystallographically independent PF$_6^-$ anions in the asymmetric unit, corresponding to the *two* chemical units required to maintain electrical neutrality. They occupy Wyckoff sited b, d, and i, of multiplicity 2, 2, and 4, in space group C2/m. The range of raw P–F distances observed, 1.50–1.61 Å, is typical of that found for these anions where precise definition of the bond lengths is made difficult by the strong influence of thermal motion of the fluorine atoms.[32,38] In our case this problem is compounded by the disordering of the P-3 anion, discussed in more detail in the description of the crystal packing. While simple "riding" models are normally not very useful in correcting for the effects of thermal motion, the P–F distances corrected in this way are, with one exception, within 0.01 Å of the mean corrected value of 1.625 Å.

Solvent of Crystallization. Dimethyl sulfoxide has been studied by both X-ray and neutron diffraction methods and at low temperatures.[39] We find a C–S distance of 1.771 (5) Å, significantly shorter than that found in any of the previous studies. This may be an isotope effect associated with the substitution of deuterium for hydrogen. The S=O distance is in the range previously established as is the C–S–C angle, but the C–S–O angle, 105.0 (2)°, is about 1.5° lower than previously noted.

Crystal Packing. As is expected for a salt of this kind, the crystal packing is dominated by electrostatic and hydrogen-bonded interactions. The locations of the cations and anions disposed about the mirror planes at y = 0 and $^1/_2$ lead to a layer type structure but with strong interactions between the layers.

Of particular interest is the disordering of the P-3 anion, by rotation about an axis through P-3 and perpendicular to the mirror, and the accompanying disordering of the N-3 ammine group by rotation about the Ru–N bond. This takes place to accommodate energetically closely equivalent but spatially different patterns of hydrogen bonding and electrostatic attraction. In the less-favored orientation (as judged by

(31) U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, J. Chem. Soc. A, 1118 (1971).

(32) B. R. Davis and J. A. Ibers, Inorg. Chem., 9, 2768 (1970).

(33) H. Stynes and J. A. Ibers, quoted in ref 32.

(34) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, Inorg. Chem., 4, 1157 (1965).

(35) I. M. Treitel, M. T. Flood, R. E. Marsh, and H. B. Gray, J. Amer. Chem. Soc., 91, 6512 (1969).

(36) G. B. Ansell, D. M. Forkey, and D. W. Moore, Chem. Commun., 56 (1970).

(37) J. Donohue and A. Caron, Acta Crystallogr., 17, 1178 (1964).

(38) (a) H. Bode and H. Clausen, Z. Anorg. Chem., 265, 229 (1951); (b) F. C. Marsh and G. Ferguson, Can. J. Chem., 49, 3590 (1971).

(39) O. Bastiansen and H. Viervoll, Acta Chem. Scand., 2, 702 (1948); E. Tommila and M.-L. Murto, ibid., 17, 1947 (1963); M. A. Viswamitra and K. K. Kannan, Nature (London), 209, 1016 (1966); R. Thomas, C. B. Shoemaker, and K. Eriks, Acta Crystallogr., 21, 12 (1966).

occupancy) strong hydrogen bonds are formed between F-9a and H-2, 2.08 Å, and between F-8a and H-4b of a neighboring cation, 2.13 Å. No such strong interactions are present in the predominant orientation of the anion, the shortest F···H distance being 2.19 Å. However, a larger number of weaker F···N interactions, both hydrogen bonded and electrostatic, is possible leading to what is presumably an energetically equivalent arrangement.

Though hydrogen bonding is certainly not involved, the orientation of the methyl groups with respect to the P-1 anion suggests some form of interaction. There is an asymmetry of external angles at C-3 and C-4 arising from the disposition of H-6a and H-7a in the mirror plane. A minor perturbation of the structure by rotation about the C–C bond would relieve this stress, and one must conclude that there is a compensating stability in the particular arrangement found where these hydrogen atoms are directed at F-3 and F-2.

Discussion

The properties of the nitrogen-bound complexes of the **1** and **2** series are generally in agreement with the expectation that imidazole would be a poorer π-acceptor than pyridine. The order of increasing affinity for $(NH_3)_5Ru^{II}$ of $NH_3 < Im < Py$ is the most direct evidence for diminished back-bonding in the imidazole complex. The lack of a metal-to-ligand charge transfer band analogous to that found in the Ru(II)–pyridine compounds also attests to the poorer acceptor properties of the imidazole ring. A redox potential of $+0.11$ V has been measured for **1a**[40] and comparison with a corresponding value of $+0.305$ V for pentaammine-pyridineruthenium(II)[41] again indicates less stabilization of Ru(II) oxidation state by imidazole.

The carbon-bound coordination of the imidazole ring found in the ions of the **5** and **6** series is novel. The formal ligand in this bonding mode is the imidazolium ylide, a neutral, dipolar tautomer of imidazole. In qualitative terms, the molecule possesses an unshared pair of σ electrons on carbon-2. The compensating
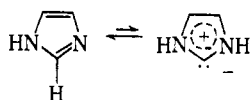
positive charge is, as in the imidazolium ion, delocalized over the aromatic ring but presumably primarily centered on the equivalent nitrogen atoms. The ylide is of sufficiently high energy that only an undetectable amount exists at equilibrium with imidazole. Nevertheless, the relatively rapid hydrogen–deuterium exchange which takes place at C-2 of imidazole in protic solvents is believed to occur *via* this intermediate on the basis of the pH–rate profile of the exchange reaction.[42] The adjacent nitrogen atoms are important to the stabilization of the ylide and additional nitrogens in the ring further enhance the acidity of the C-2 proton. The chemistry of such species has largely been developed by studies of derivatives having alkyl substitution at

nitrogen.[43] The previous examples of carbon-bound imidazole ligands have involved 1,3-disubstituted imidazole derivatives.[28,29,44-46] The 1,3 disubstitution prevents competitive formation of nitrogen-bound species. The carbon-bound imidazolium ylide ligands bear some structural relationship to the carbon-bound *anion* of tetrazole derivatives[47] and the rapidly growing family of metal–carbene complexes.[48]

It is of interest to consider if the release of the trans ammonia is an intimate part of the mechanism of formation of the carbon-bound species or if it occurs after the formation of **5**. We tend to favor the latter possibility. In analogy with studies of the trans-effect of carbon ligands in the cobalt(III) series, the carbon-bound imidazole could be expected to have a significant labilizing effect on the trans position.[49] Some support for this expectation comes from preliminary data which indicate that ions of the **5** series react at extraordinarily rapid rates with pyridine bases.[50] If such a labilizing effect exists, the loss of ammonia in the acidic media utilized for preparation of the carbon-bound ions can be considered to be a rapid aquation reaction mechanistically independent of the actual formation of the **5** species.

The relationship of our work to that of Tsutsui, *et al.*,[19a] on imidazole complexes of ruthenium porphyrins bears brief mention. Tsutsui, on the basis of observations involving puzzling chemical shifts of imidazole protons as a function of temperature, proposed that the imidazole underwent a dynamic reorientation relative to the ruthenium porphyrin, which these workers defined as "metal shuttling." The work, as it relates to imidazole, has been called into question.[19b] On the basis of peak reassignments Faller and Sibert[51] have concluded that the features of the ruthenium porphyrin imidazole spectrum can be satisfactorily understood in terms of exchange of complexed imidazole with free imidazole in the solution. In the case of 4,5-dimethylimidazole, Tsutsui and coworkers have presented evidence against the occurrence of intermolecular exchange.[19a] Further, they were unable to observe the C-2 proton under certain experimental conditions. This feature and the coalescence of the methyl signals are, of course, to be expected if the carbon-bound form of the 4,5-dimethylimidazoleruthenium porphyrin complex were present under some conditions. We have not studied this compound and, because of the uncertainties associated with the work, it would be premature to conclude that the carbon-bound ligand is present, but the possibility should be considered in any future examination of the compound.

(40) Measured by cyclic voltametry at ionic strength 0.1 by Mr. Glen Tom, Stanford University, 1972.

(41) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, 11, 1460 (1972).

(42) T. M. Harris and J. C. Randall, *Chem. Ind. (London)*, 1728 (1965); J. D. Vaughan, Z. Mughrabi, and E. C. Wu, *J. Org. Chem.*, 35, 1141 (1970).

(43) R. A. Olofson, W. R. Thompson, and J. S. Michelman, *J. Amer. Chem. Soc.*, 86, 1865 (1964); P. Haake, L. P. Bausher, and J. P. McNeal, *ibid.*, 93, 7045 (1971); R. A. Olofson, J. M. Landesberg, K. N. Houk, and J. S. Michelman, *ibid.*, 88, 4265 (1966).

(44) K. Öfele, *Angew. Chem., Int. Ed. Engl.*, 8, 916 (1969); K. Ofele and C. G. Kreiter, *Chem. Ber.*, 105, 529 (1972).

(45) H. J. Schönherr and H.-W. Wanzlick, *Chem. Ber.*, 103, 1037 (1970).

(46) K. Öfele, *J. Organometal. Chem.*, 12, P42 (1968).

(47) W. P. Fehlhammer and L. F. Dahl, *J. Amer. Chem. Soc.*, 94, 3370 (1972), and references therein.

(48) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 72, 545 (1972).

(49) G. C. Hayward, H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *J. Chem. Soc. A*, 196 (1971); J. M. Pratt and R. G. Thorp, *Advan. Inorg. Chem. Radiochem.*, 12, 375 (1969); H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Chem. Brit.*, 5, 156 (1969).

(50) S. Isied, unpublished work, Stanford University.

(51) J. W. Faller and J. W. Sibert, *J. Organometal. Chem.*, 31, C5 (1971).

The observation that the imidazole ring in aqueous solution in the pH range 1–5 can adopt the carbon-bound arrangement and that this form has considerable stability, at least in a kinetic sense, is of substantial interest to considerations of metalloenzyme structure and function. The implication is that histidine residues might be capable of carbon bonding at metal ions in biological media. In terms of similarity in electronic structure to the Ru(II) and Ru(III) systems we have studied, low spin iron(II) and iron(III) in porphyrins could be suggested as potential sites for such binding. It is conceivable that a change in conformation near the metal site or the changes in ligand characteristics that would accompany a nitrogen to carbon bonding re-organization could play a role in the function of metalloenzymes. These possiblities are entirely speculative at this time, but it will be of interest to learn, as detailed mechanisms of action of metalloenzymes are developed, if carbon-bound histidines play any biological role.

Oxygen Carrier and Redox Properties of Some Neutral Cobalt Chelates. Axial and In-Plane Ligand Effects

Mark J. Carter, D. Paul Rillema, and Fred Basolo*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received August 17, 1973

Abstract: Thermodynamic data are reported for the reversible oxygen uptake of several cobalt(II) complexes. A linear correlation was found between the equilibrium constants for oxygen adduct formation and the ease of oxidation of cobalt(II) to cobalt(III), as measured by cyclic voltammetry. It is suggested that this correlation exists because the redox potential of the cobalt chelate is a measure of the electron density on the cobalt, which in turn is the most important parameter in determining the oxygen affinity of the substrates.

The reversible oxygenation of cobalt complexes has posed some striking challenges in our attempt to understand the chemical behavior of heme in myoglobin and hemoglobin. One of the most significant recent achievements was that reported by Hoffman and Petering[1] who reconstituted globin with Co(Pp IX), cobalt(II) protoporphyrin IX, the analog of heme, and found that the resulting coboglobin has oxygen carrier properties similar to hemoglobin.

Since the initial discovery of Tsumaki[2] that Schiff base complexes of cobalt(II) are oxygen carriers, there has been a continued interest in this property of cobalt complexes.[3] However, the recent resurgence of research activity on these systems can be traced to the isolation of one-to-one adducts[4,5] of the type Co–O_2 and to the use of esr to investigate these systems.[6–8] Considerable effort has been made to determine the oxygen uptake ability of Co(L)B complexes, where L is a quadridentate chelate group which occupies the equatorial position in the complex and B is a unidentate ligand in the axial position. Investigations include the effect of the axial base,[5,9,10] of the equatorial chelate group,[11–13] and the role of the solvent.[14]

From esr results,[7] approximately 90% of the spin density of the unpaired electron on cobalt(II) is calculated to transfer to oxygen upon formation of the Co-(L)B·O_2 adduct. This suggests that the system can be viewed as a superoxide ion attached to cobalt(III), Co^{III}–O_2^-. On this basis, the reaction of Co(L)B with O_2 may be described as an electron transfer from cobalt(II) to the oxygen molecules. Thus, the ability of these complexes to react reversibly with oxygen should be very closely related to the redox potentials of the systems.[15]

This paper reports data which show that there is a direct correlation between the redox potentials of neutral cobalt chelates and their ability to behave as oxygen carriers.

(1) B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Sci. U. S.*, 67, 637 (1970).

(2) T. Tsumaki, *Bull. Chem. Soc. Jap.*, 13, 252 (1938).

(3) R. G. Wilkins, *Advan. Chem. Ser.*, No. 100, 111 (1971).

(4) C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 946 (1969).

(5) A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 92, 55 (1970).

(6) J. H. Bayston, N. K. King, F. D. Looney, and M. E. Winfield, *J. Amer. Chem. Soc.*, 91, 2775 (1969).

(7) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, 92, 61 (1970).

(8) F. A. Walker, *J. Amer. Chem. Soc.*, 92, 4235 (1970).

(9) F. A. Walker, *J. Amer. Chem. Soc.*, 95, 1154 (1973).

(10) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Amer. Chem. Soc.*, 95, 1796 (1973).

(11) H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, 94, 1559 (1972).

(12) G. Tauzher, G. Amiconi, E. Antonini, M. Brunori, and G. Costa, *Nature (London)*, 241, 222 (1973).

(13) A preliminary account of the work reported in this paper is given in M. J. Carter, L. M. Engelhardt, D. P. Rillema, and F. Basolo, *Chem. Commun.*, 810 (1973).

(14) H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, 94, 5125 (1972).

(15) L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberly, *Chem. Rev.*, 63, 269 (1963).