of protoporphyrin IX) bonded to 1-methylimidazole to that bonded to pyridine is 0.07.[23] Thus, the iron porphyrin with a 1-alkylimidazole tail of the Traylor type might be expected to have $P_{1/2}$ of about 28 Torr in toluene at −45°. If the same type of porphyrin and 1-alkylimidazole ligand were used in all of the iron porphyrin complexes, the values for $P_{1/2}$ would probably fall within a factor of 100 or ΔG would fall in a range of 2.0–2.5 kcal mol^{-1}. Considering the complications introduced by solvation and possible effects of protein upon the stability of the oxygen complex of myoglobin, the agreement is probably as good as one can expect.

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Synthesis and Properties of Osmium(II) and Osmium(III) Ammine Complexes of Aromatic Nitrogen Heterocyclics

Roy H. Magnuson and Henry Taube*

Contribution from Department of Chemistry, Stanford University, Stanford, California 94305. *Received December 28, 1974*

Abstract: Osmium(II) complexes of the type $[(NH_3)_4Os(N_2)(L)]^{n+}$, L = pyrazine, *N*-methylpyrazinium, isonicotinamide, isonicotinic acid, have been prepared by reaction of the appropriate nitrogen heterocycle with the bis(dinitrogen)tetraammineosmium(II) ion under argon. Heating of the dinitrogen(heterocycle)tetraammineosmium(II) ions in hydrohalic acids in air led to the isolation of osmium(III) compounds with the general formula $[(NH_3)_4Os(X)(L)]X_2$ for L = pyrazine, $X^- = Cl^-$, Br^-; and L = isonicotinic acid, $X^- = Cl^-$. Reduction of the osmium(III) ions resulted in the formation of the corresponding osmium(II) ions in solution. The pK_a of the chloro(pyrazinium)tetraammineosmium ion was found to be 7.6, seven orders of magnitude more basic than both the free ligand and the dinitrogen(pyrazine)tetraammineosmium(II) ion, and is indicative of very large back-bonding from the osmium(II) center to the nitrogen heterocycle. Anomalies in the charge transfer spectral bands of these ions are discussed in terms of a simple molecular orbital description and parameters of the back-bonding interaction, including the π-stabilization energy, are estimated. The ground state wave function of the pyrazinium osmium(II) π bond is found to possess greater ligand than metal character.

Complexes of ruthenium(III) and ruthenium(II) ammines with such ligands as pyridine and pyrazine have provided the basis for a wide variety of studies of substitution processes, electron transfer reactions, simple mixed-valence systems, and back-bonding interactions.[1-5] Displacement of a dinitrogen ligand has been used previously as a synthetic route to lower valence osmium ammine complexes.[6,7] In the course of our studies,[8] it was discovered that the *cis*-bis(dinitrogen)tetraammineosmium(II) ion[9] serves as a starting material for the introduction of an aromatic nitrogen heterocycle into the Os(II) coordination sphere. In this paper we report the preparation of a number of dinitrogen(N-heterocycle)tetraammineosmium(II) compounds, from which halogenotetraammineosmium(III) and chlorotetraammineosmium(II) complexes of pyrazine and isonicotinic acid are derived. A simple molecular orbital (MO) model has been applied to the π interaction in related Ru(II) compounds.[5] A similar approach is used here to discuss the unusual physical and spectral properties of the chlorotetraammineosmium(II) complexes in an effort to assess the back-bonding capability of this third-row transition metal.

Experimental Section

Materials and Reagents. Reagent grade chemicals were used throughout with the following exceptions: silver(I) *p*-toluenesulfonate, isonicotinic acid, pyrazine, chloroacetic acid, and hydrazine hydrate (99-100%). Deionized water was redistilled from alkaline potassium permanganate solution. Isonicotinamide was recrystallized from water. Trifluoromethylsulfonic acid was distilled before use. Deuterium chloride (38% solution in deuterium oxide at 99 atom %, International Chemical and Nuclear) was diluted 1:100 with deuterium oxide (99.8 mole %) for use in near-infrared measurements. Argon (99.99%) was passed through two bubbling towers containing 0.1 *M* chromium(II) perchlorate solution to remove traces of oxygen. Strongly acidic cation exchange resin (AG-50W-X2, 200-400 mesh), obtained from Bio-Rad in the hydrogen form, was pretreated as previously described.[10]

Standard europium(III) chloride solutions were prepared by dissolution of a known quantity of europic oxide (99.99%) in an excess of hydrochloric acid and dilution to a known volume. Europium(II) solutions were prepared by reduction of europium(III) chloride solutions with Zn(Hg) for 20 min under argon.

An iron(III) trifluoromethylsulfonate solution was prepared by dissolution of iron wire in an excess of 3 *M* trifluoromethylsulfonic acid with heating on a steam bath for 2 hr. After the solution was cooled and filtered, a fivefold excess of 30% hydrogen peroxide was added dropwise. The mixture was heated to drive off excess hydrogen peroxide, then cooled and diluted to ca. 0.01 *M*. The Fe(III) content was determined iodometrically using standard thiosulfate.

Syntheses. Ammonium hexachloroosmate(IV) was prepared from osmium tetroxide according to the procedure of Dwyer and Hogarth.[11]

Dinitrogenpentaammineosmium(II) chloride was synthesized by the method of Allen and Stevens.[12]

Chloropentaammineruthenium(III) chloride was prepared from hexaammineruthenium(III) chloride according to the procedure of Vogt et al.[13] and recrystallized from 0.1 *M* hydrochloric acid.

(*N*-Methylpyrazinium)pentaammineruthenium(II) chloride was prepared by the method of Creutz and Taube.[4]

***cis*-Bis(dinitrogen)tetraammineosmium(II) chloride** was synthesized using a modification of the procedure previously described.[9] Thus 2.00 g of dinitrogenpentaammineosmium(II) chloride (5.35 mmol) and 380 mg of sodium nitrite (5.50 mmol) were dissolved in 200 ml of water at 35-40°. With rapid stirring 90 ml of 0.25 *M* hydrochloric acid was added slowly over 1.5 hr. The solution was concentrated to near saturation by rotary evaporation and then filtered. The complex was precipitated by adding 20 g of solid sodium chloride. After cooling at 5° overnight, the off-white solid was collected by filtration, washed with a small volume of cold 0.1 *N* hydrochloric acid, followed by ethanol and ether, and dried in a vacuum desiccator overnight, yield 1.49 g, 72%.

***cis*-Dinitrogen(isonicotinamide)tetraammineosmium(II) Bromide Monohydrate.** A solution of 0.2 g (0.5 mmol) of *cis*-bis(dinitrogen)tetraammineosmium(II) chloride in 20 ml of water was deoxygenated for 15 min under a stream of argon. An excess of isonicotinamide (1.2 g, 10 mmol) was added and the mixture heated to 70-80° in a water bath for 12 hr with a slow argon flow passing through the solution. The mixture was cooled to room temperature and diluted about 1:2 with water in air. The components of the reaction mixture were separated by cation exchange on AG-50W-X2 resin using hydrochloric acid solutions as eluents. The orange 2 *M* fraction was collected and rotary evaporated to dryness to form the chloride salt. The complex was reprecipitated as the bromide salt by metathesis with sodium bromide. The bright orange solid was collected by filtration, washed with ethanol and ether, and recrystallized from 0.1 *M* hydrobromic acid. The yield before recrystallization was 0.15 g, 50%. Anal. Calcd for $[(NH_3)_4Os(N_2)(C_6H_6N_2O)]Br_2{\cdot}H_2O$: C, 12.3; N, 19.1; H, 3.4; Br, 27.3. Found: C, 12.2; N, 19.1; H, 3.3; Br, 27.3.[14] In no case was analysis for oxygen done, and water of crystallization was included in the formulas to improve the fit to the data of the analyses for the other elements.

***cis*-Dinitrogen(pyrazine)tetraammineosmium(II) Bromide.** This complex was prepared in a manner similar to that of the isonicotinamide analog. The ion of interest was eluted from the cation exchange resin as a virtually black band with 3 *M* HCl. After rotary evaporation to dryness, the solid was dissolved in a few milliliters of water and solid sodium bicarbonate was added carefully to the solution until the color just changed from black to red-orange. (If the pH became too high, decomposition occurred.) Solid sodium bromide was added until precipitation began. The mixture was cooled overnight at 5° and the red-orange solid was collected by filtration, yield 0.11 g, 42%. The complex could be recrystallized by dissolving 100 mg in 1 ml of 0.01 *M* lithium bromide with warming, filtering while hot, and cooling the filtrate overnight. Anal. Calcd for $[(NH_3)_4Os(N_2)(C_4H_4N_2)]Br_2$: C, 9.1; N, 21.3; H, 3.1; Br, 30.4. Found: C, 8.9; N, 21.3; H, 3.1; Br, 30.4.[15]

***cis*-Dinitrogen(isonicotinic acid)tetraammineosmium(II) Chloride.** This complex was prepared in a similar manner to the isonicotinamide analog, except that the reaction mixture was buffered at pH 5 with the addition of sodium hydroxide before heating. The product was isolated by cooling the red-orange 2 *M* acid ion exchange fraction overnight at 5° and collecting the red microcrystalline chloride salt by filtration, yield 0.16 g, 68%. Anal. Calcd for $[(NH_3)_4Os(N_2)(C_6H_5NO_2)]Cl_2{\cdot}\frac{1}{2}H_2O$: C, 14.7; N, 20.1; H, 3.7; Cl, 14.5. Found: C, 14.3; N, 20.2; H, 3.7; Cl, 14.5.

***cis*-Dinitrogen(*N*-methylpyrazinium)tetraammineosmium(II) Chloride.** This complex was prepared using the method for the isonicotinamide analog, substituting *N*-methylpyrazinium tosylate[4] for isonicotinamide in the reaction mixture. An impure chloride salt of this complex was formed by rotary evaporation of the virtually black 3 *M* ion exchange fraction. Although impurities in fresh samples of the solid were not detected spectrally (ir, uv-visible, and NMR), a satisfactory analysis was not obtained.[16]

Solutions of *cis*-dinitrogentetraammineosmium(II) complexes with 2,6-dimethylpyrazine and pyridine were obtained from the procedure described above for isonicotinamide, using the appropriate ligand. A nicotinic acid analog was prepared in the same manner as the isonicotinic acid complex. Solutions believed to contain these complexes were separated by ion exchange of the reaction mixtures. The dark yellow-green dimethylpyrazine complex was eluted from the column with 3 *M* HCl, while the yellow pyridine and nicotinic acid complexes moved off the column with 2 *M* acid. These solutions were found to have the spectral features of other compounds in the series (vide infra), but difficulty was encountered in isolating pure solids, in part due to the relatively high proton affinity of the dimethylpyrazine complex and the apparent low yield of the pyridine analog.

Bis(dinitrogen)(isonicotinamide)triammineosmium(II) Chloride. In a reaction analogous to the preparation of *cis*-bis(dinitrogen)-tetraammineosmium(II) chloride,[9] 39.1 mg of *cis*-dinitrogen(isonicotinamide)tetraammineosmium(II) chloride (0.079 mmol) was dissolved in 4 ml of water and mixed with 1.0 ml of 0.10 *M* sodium nitrite. With rapid stirring of the solution, 2.5 ml of 0.1 *M* HCl was added dropwise. The product was precipitated by adding solid sodium chloride. The yellow solid was collected by filtration, washed with ethanol and ether, and stored in the dark at −5°, yield 25 mg, 65%. Anal. Calcd for $[(NH_3)_3Os(N_2)_2(C_6H_6N_2O)]Cl_2$: C, 14.7; N, 25.7; H, 3.1. Found: C, 14.3; N, 26.0; H, 3.2.

***cis*-Chloro(pyrazine)tetraammineosmium(III) Chloride.** A solution of 103 mg of *cis*-dinitrogen(pyrazine)tetraammineosmium(II) bromide[17a] (0.195 mmol) in 10 ml of 5 *M* hydrochloric acid was heated with stirring at about 75° in air for 10 hr. The reaction mixture was cooled to room temperature and diluted to about 80 ml with water. Ion exchange of the mixture on AG-50W-X2 cation resin resulted in a brown band moving with 2-3 *M* HCl. This fraction was rotary evaporated to dryness and the dark greenish brown solid was slurried with 1:1 ethanol-ether and collected on a glass frit. The material was washed extensively with ethanol-ether until its color had changed to bright orange. It was then washed with ether and dried overnight in a vacuum desiccator, yield 75 mg, 85%. Anal. Calcd for $[(NH_3)_4ClOs(C_4H_4N_2)]Cl_2{\cdot}\frac{1}{2}H_2O$: C, 10.6; N, 18.5; H, 3.7; Cl, 23.6. Found: C, 10.6; N, 18.5; H, 3.8; Cl, 23.4.

***cis*-Bromo(pyrazine)tetraammineosmium(III) Bromide.** This complex was prepared in a manner similar to that of the chloro analog, replacing hydrochloric acid by 6 *M* hydrobromic acid in the reaction mixture. Anal. Calcd for $[(NH_3)_4BrOs(C_4H_4N_2)]Br_2{\cdot}\frac{1}{2}H_2O$: C, 8.2; N, 14.3; H, 2.9. Found: C, 8.1; N, 14.4; H, 3.0.

***cis*-Chloro(isonictonic acid)tetraammineosmium(III) Chloride.** A solution of *cis*-dinitrogen(isonicotinamide)tetraammineosmium(II) chloride in 5 *M* hydrochloric acid was heated with stirring at 80° for 16 hr in air. The reaction mixture was diluted and ion exchanged. The orange 2 *M* HCl fraction was rotary evaporated to dryness and the resultant orange solid was slurried in ethanol and collected by filtration. Anal. Calcd for $[(NH_3)_4ClOs(C_6H_5NO_2)]Cl_2{\cdot}H_2O$: C, 14.2; N, 13.9; N, 3.8. Found: C, 14.2; N, 14.0; H, 3.7.

Spectra. Ultraviolet (uv) and visible spectra were recorded on either a Cary 14 or Cary 15 spectrophotometer. Deuterium oxide or 0.12 M DCl in D_2O was used as solvent in a 1-cm quartz cell against a matched blank for near-infrared spectral measurements on a Cary 14 instrument. Spectra of air sensitive complexes were obtained by transferring a solution from a Zwickel flask[17b] through an all glass system under argon pressure into a 1-cm cell.

Ir spectra of complexes in potassium bromide pellets were recorded on a Perkin-Elmer Model 621 grating spectrophotometer in the 4000-250-cm^{-1} region. Proton nuclear magnetic resonance spectra were taken using a Varian T-60 instrument. NMR sample solutions were prepared in deuterium oxide at a concentration of 0.02-0.04 M (or less, when limited by solubility) and filtered before the NMR tube was filled.

Magnetic Susceptibility. Magnetic susceptibility measurements were made on a Faraday balance (Cahn Instruments) at ambient temperatures. Diamagnetic corrections for ligands and counterions were calculated from the tables of Earnshaw.[18]

Cyclic Voltammetry. Cyclic voltammetry scans at a sweep rate of about 100 mV/sec were made on conventional instrumentation built by Glenn Tom. The potential against current output was recorded by an omnigraphic recorder (Houston Instrument). Either a platinum or a hanging mercury drop indicator electrode was used against a saturated calomel reference electrode. Solutions were generally 2-5 mM in complex and at least 0.1 M in supporting electrolyte. Solutions were routinely deaerated with argon before scans were recorded.

Potentiometric Titrations under Argon. Potentiometric titrations of chloro(pyrazine)tetraammineosmium(III) chloride were carried out under argon. A sample cell of 15 ml capacity which could be deaerated from below was fitted with a hanging mercury drop indicator electrode. Titrant was delivered from a micrometer syringe of 1.500 ml capacity through a Teflon needle led through a dropper bulb. The syringe was initially filled and emptied six times with Ar before the deaerated titrant was drawn in. A potassium chloride-agar salt bridge was led from the sample cell into a 1 M KCl solution into which a saturated calomel reference electrode was dipped. The potential was monitored with a Beckman Expandomatic pH meter on the millivolt scale. The sample solution contained 5.3×10^{-3} mmol of the osmium complex in 10 ml of a solution 0.9 M in KCl and 0.1 M in HCl. It was deaerated for 30 min before titration.

Counterion Halide Analysis. The counterion halides of complexes with a readily oxidizable metal center were determined after an ion exchange separation. A bed of about 10 ml of AG-50W-X2 cation resin was washed with water until no cloudiness was observed in the effluent on addition of silver ion. A 5-ml solution of the complex containing ca. 10^{-2} mmol of halide was washed quantitatively onto the column with water and the bed washed with about 30 ml of water. The combined effluents were diluted to 50.00 ml. Aliquots were titrated potentiometrically with standard 0.01 M $AgNO_3$ solution. Quantitative recovery of counterion halide from the column was found for known amounts of sodium bromide and chloropentaammineruthenium(III) chloride. This procedure was also adopted for separations under argon.

Spectrophotometric pK_a Determinations. Six solutions containing identical quantities (1.2×10^{-4} M) of *cis*-dinitrogen(pyrazine)tetraammineosmium(II) bromide were prepared with various concentrations of HCl up to 0.500 M. The ionic strength was kept at 0.5 M with appropriate concentrations of NaCl. Spectra were then recorded from 800 to 200 nm. Since the complex could not be fully protonated at any reasonable acid concentration, a graphical method was adopted. The acid dissociation constant was determined as the slope of a plot of A_λ against $(A_\lambda^0 - A_\lambda)/[H^+]$, where A_λ^0 was the absorbance of the fully deprotonated species (0.5 M NaCl) at a particular wavelength and A_λ was the absorbance at that wavelength of a solution of known hydrogen ion concentration.

A similar method was employed to determine the acid dissociation constant of the chloro(pyrazine)tetraammineosmium(II) ion. Six solutions of chloro(pyrazine)tetraammineosmium(III) chloride (ca. 5×10^{-5} M) were reduced over Zn(Hg) under argon in a Zwickel flask for 2-6 hr and the spectra scanned after transfer of the air sensitive solutions into a 1-cm cell. The pH of the solutions was varied from 2.0 (10^{-2} M HCl) through 8.78 (NH_4Cl-NH_3 buffer), with intermediate acidities obtained with potassium phosphate buffers. The ionic strength was ca. 0.1 M, but was not carefully controlled. Difficulty was encountered in reaching complete reduction of solutions at pH ≥8 so that the data were normalized at an isosbestic point found at 440 nm (where the Os(III) species has insignificant absorption at these low concentrations). In this case only the spectrum of the fully protonated species was accessible. Thus the acid dissociation constant was determined as the reciprocal of the slope of a plot of A_λ against $(A_\lambda^0 - A_\lambda)[H^+]$, where A_λ^0 was the absorbance of the fully protonated species (10^{-2} M HCl) at a particular wavelength and A_λ the absorbance of a solution at higher pH.

Table I. Dinitrogen Stretching Frequencies of *cis*-$[(NH_3)_4(N_2)(L)Os]X_n$ Complexes (KBr)

L	X^-	n	ν_{NN} (cm^{-1})
Isonicotinamide	Br^-	2	2025
Isonicotinamide	Cl^-	2	2050 (sh), 2040
Pyrazine	Br^-	2	2040
Pyrazinium[a]	Cl^-	3	2095
N-Methylpyrazinium	Cl^-	3	2098

[a] Prepared by rotary evaporation of a solution of $[(NH_3)_4Os(pyrazine)_2]^{2+}$ in 3 M HCl.

Results

***cis*-Dinitrogentetraammineosmium(II) Complexes with Aromatic Nitrogen Heterocycles.** The ir spectra of complexes of the composition $[(NH_3)_4Os(N_2)(L)]^{n+}$, L = nitrogen heterocycle, all exhibited a strong peak in the 2000-2100-cm^{-1} region, as expected for complexes containing a terminal dinitrogen ligand. These frequencies are listed in Table I. In addition, peaks corresponding to ammonia coordinated to Os(II)[12] and to the particular heterocyclic ligand were observed.

Proton NMR spectra of D_2O solutions of the isonicotinamide (isn), pyrazine (pz), and *N*-methylpyrazinium (Me(pz)) complexes showed the expected aromatic ring protons in the δ 7.7-9.3 region and broad peaks around δ 4.0-4.7 associated with the ammine hydrogens. In the spectrum of the $[(NH_3)_4Os(N_2)(Me(pz))]^{3+}$ ion (I) a sharp resonance corresponding to the methyl group was found at δ 3.68 with ring protons at δ 9.33, 9.24 and 8.34, 8.25.

The electronic spectral properties of several *cis*-dinitrogentetraammineosmium(II) complexes with N-heterocyclic ligands are given in Table II and the spectrum of the *cis*-dinitrogen(pyrazine)tetraammineosmium(II) ion (II) is shown in Figure 1. The spectra of these complexes are characterized by three strong absorption maxima with extinction coefficients of 3×10^3 to 10^4 M^{-1} cm^{-1}. Each shows a peak in the ultraviolet region which is reasonably assigned to a $\pi^* \leftarrow \pi$ absorption of the ligand, such as observed in related pentaammineruthenium(II) complexes of these ligands.[5,20] The second pair of lower energy absorption maxima can be ascribed to $\pi^* \leftarrow d_\pi$ transitions from the asymmetric osmium(II) to a π^* level on the aromatic ligand. It can be seen from Table II that the energies of both absorptions decrease markedly with increasing electron acceptor properties of the ligand. For the para substituted pyridine derivatives the energies decrease in the order -H > -$CONH_2$ > -COOH, following the Hammett E substitution function which increases in the same series.[21]

While the spectra of $[(NH_3)_4Os(N_2)(isn)]^{2+}$ (III) and the Me(pz) analog, I, are insensitive to acidity changes from pH 0 to 7, the transitions observed in the spectrum of the pz complex, II, are found to shift dramatically to lower energies in strong acid. The spectrum of a 1:1 mixture of the protonated and unprotonated species (0.5 M HCl) is shown in Figure 1. Using this spectral change, the pK_a of the equilibrium in eq 1 was found to be 0.31 ± 0.05 at μ = 0.50, as described in the Experimental Section. Thus the coordinated pyrazine is slightly less basic than the first ni-

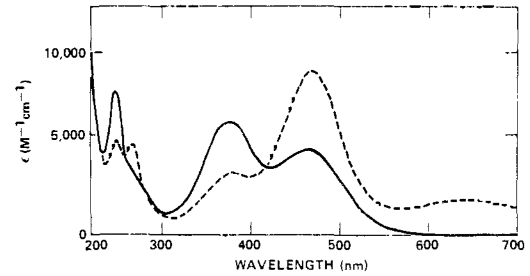
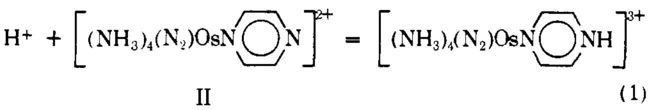


Figure 1. Spectra of $[(NH_3)_4N_2Os(pz)]^{2+}$(solid line) and of a 1:1 mixture with its protonated form.



II (1)

trogen to be protonated in the free ligand (pK_1 = 0.65).[22] A calculated spectrum of the fully protonated form was found to be very similar to that observed for the Me(pz) complex, I, both in peak position and relative absorbancies, as expected for protonation at the uncoordinated nitrogen of the pyrazine ring. In a similar manner the pK_a of the 3,5-dimethylpyrazine complex[23] was roughly estimated as 0.7 ± 0.3, which is to be compared with a pK_a of 1.9 for the free ligand.[22]

The dinitrogen(N-heterocycle)tetraammineosmium(II) compounds are irreversibly oxidized electrochemically or with ceric ion with loss of N_2. Using vacuum line techniques a noncondensable gas analysis was performed on the products of the oxidation of 9.7 mg (0.017 mmol) of the bromide salt of the isonicotinamide complex, III, with 0.5 ml of 0.5 *M* ceric perchlorate in 6 *M* $HClO_4$. It was found that 0.019 mmol of a gas not condensed in a liquid nitrogen trap was evolved, or 1.1 mol/mol complex.

Ceric ion destroys the orange color of III. A solution of Ce(IV) ion was added dropwise to a concentrated solution of III until the color had faded from deep orange to pale yellow. Addition of solid NaBr led to the precipitation of an unidentified pale yellow solid whose ir spectrum did not show the dinitrogen stretch, although the characteristics of the isn ligand remained.

Cyclic voltammetry measurements on $[(NH_3)_4Os(N_2)(isna)]^{2+}$, (isna = isonicotinic acid), buffered with NH_3-NH_4Cl at pH 9 (where the deprotonated form predominates) showed an irreversible oxidation wave at +0.62 V.[24] The irreversibility of this oxidation can be attributed to rapid loss of the dinitrogen ligand, as has been observed for $[(NH_3)_5Ru(N_2)]^{2+}$.[25]

The isn complex, III, was found to be susceptible to attack by NO^+ in a reaction directly analogous to Scheidegger's preparation of *cis*-bis(dinitrogen)tetraammineosmium(II).[9] The isolated product of the reaction, $[(NH_3)_3(N_2)_2Os(isn)]Cl_2$, exhibits two strong, sharp peaks at 2180 and 2125 cm^{-1} in the dinitrogen stretch region of its ir spectrum, indicating that the dinitrogen ligands occupy cis positions. Two uv-visible absorption maxima were found at 331 nm (ε 6.3 × 10^3 M^{-1} cm^{-1}) and 218 nm (2.2 × 10^4) with shoulders at 285 and 345 nm in spectra of fresh solutions of the compound in 0.1 *M* HCl. However, when the solution was heated to 70–80° for 15 min, its color changed from yellow to orange, and new peaks appeared at 450 and 344 nm. The similarity to the spectrum of III leads to the conclusion that one of the dinitrogen ligands is readily lost from the triammine complex.

Table II. Spectral Properties of *cis*-Dinitrogentetraammineosmium(II) Complexes of N-Heterocyclic Ligands

Ligand	Medium	λ_{max} (nm)	ε(M^{-1} cm^{-1})
Isonicotinamide	H_2O	441	4.7 × 10^3
		365	4.9 × 10^3
		240 (sh)	5.8 × 10^3
		~197 (sh)	~4 × 10^4
Isonicotinic acid	1 *M* HCl	457	5.2 × 10^3
		377	5.5 × 10^3
		252	4.5 × 10^3
Pyrazine	H_2O	463	4.3 × 10^3
		377	5.8 × 10^3
		249	6.7 × 10^3
Pyrazinium	HCl	640	3.0 × 10^3[a]
		468	9.8 × 10^3[a]
		268	6.4 × 10^3[a]
N-Methylpyrazinium[b]	0.1 *M* HCl	665	
		476	
		270	
		~200 (sh)	
3,5-Dimethylpyrazine[b]	10^{-4} *M* HCl	450	
		368	
		258	
3,5-Dimethylpyrazinium[b]	1 *M* HCl	613	
		457	
		281	
Nicotinic acid[b]	1 *M* HCl	407	
		340	
		251	
Pyridine[b]	1.5 *M* HCl	388	
		322	
		~245 (sh)	

[a] Estimated from pK_a measurements. [b] Species not isolated as pure solids.

***cis*-Halogenotetraammineosmium(III) Complexes with Aromatic Nitrogen Heterocycles.** When $[(NH_3)_4Os(N_2)(Hpz)]^{3+}$ (Hpz = pyrazinium) is heated in 4–6 *M* HCl or HBr at ca. 80° for 6–8 hr in air, the chloro- or bromo(pyrazine)tetraammineosmium(III) ion, IV and V, respectively, is obtained in good yield. A similar reaction of the dinitrogen isn analog, III, in 6 *M* HCl led to the isolation of chloro(isonicotinic acid)tetraammineosmium(III) chloride (VI) where hydrolysis of the amide linkage accompanied loss of dinitrogen and oxidation. In addition to elemental analysis, the -COOH functional group was identified by its characteristic strong peak at 1724 cm^{-1} in the ir and the pH dependence of its uv spectrum (vide infra). The ir spectra of these ions were quite similar to those of the Os(II) precursors, exhibiting peaks attributed to coordinated ammonia and the N-heterocyclic, but no peaks in the dinitrogen stretch region.

The counterions of the chloride salt of the chloropyrazine complex, IV, were analyzed by potentiometric titration with silver nitrate of the effluent of a solution of the complex passed through cation exchange resin. A sample of 5.41 mg (0.0119 mmol) required 0.0237 mequiv of $AgNO_3$ to reach the end point, corresponding to 1.99 Cl^-/molecule, demonstrating that one of the three chlorides is in the inner coordination sphere.

Magnetic susceptibility measurements carried out on the chloride salt of IV showed the compound to be paramagnetic with a susceptibility of 2705 × 10^{-6} cgs units/g at 23°, from which a value of 1.8 μ_B can be calculated. This is consistent with a low spin d^5 Os(III) species.

The spectral features of the complexes of several nitrogen heterocycles are given in Table III. The uv-visible spectra of these complexes consist of three principal absorption maxima with extinction of 2 × 10^3 to 5 × 10^3 M^{-1} cm^{-1}. The peaks around 250 nm are attributed to a ligand centered $\pi^* \leftarrow \pi$ transition. The peak at 286–287 nm in the spectra of the chlorotetraammine complexes of pyrazine, IV, isna, VI, and isonicotinate is assigned to a chloride to Os(III) transition by comparison with the absorption at 267

Table III. Spectral Features of Halogenotetraammineosmium(III) Complexes of N-Heterocycles, $[(NH_3)_4OsXL]^{n+}$

L	X^-	Medium	λ (nm)	ϵ(M^{-1} cm^{-1})
Pyrazine	Cl^-	0.1 *M* HCl	351 (br)	3.4×10^3
			286	3.6×10^3
			250	4.6×10^3
		0.1 *M* DCl–D_2O	2170	1×10^2
			1705	1×10^2
Pyrazine	Br^-	H_2O	354 (v br)	4.4×10^3
			287	2.7×10^3
			251	4.4×10^3
Isonicotinic acid	Cl^-	0.1 *M* HCl	338 (br)	4.0×10^3
			287	4.2×10^3
			255	4.0×10^3
			213 (sh)	6.9×10^3
Isonicotinate	Cl^-	pH ~6, HCO_3^-	305 (sh)	4.7×10^3
			286	4.9×10^3
			245 (sh)	4.6×10^3

Table IV. Spectral Properties of Chlorotetraammineosmium(II) Complexes with Pyrazine and Isonicotinic Acid

Complex	Medium	λ (nm)	ϵ (M^{-1} cm^{-1})
$[(NH_3)_4OsCl(Hpz)]^{2+}$	0.01 *M* HCl	430	1.1×10^4
		266	6×10^3
	0.12 *M* DCl–D_2O	1140 (br)	~5×10^2
$[(NH_3)_4OsCl(pz)]^+$	pH 8.8 (phosphate)	760 (br)	1×10^3
		465	1.4×10^4
		252	6×10^3
$[(NH_3)_4OsCl(isna)]^+$	0.1 *M* HCl	~800[a] (br)	
		523[a]	
		262[a]	
$[(NH_3)_4OsCl(isnate)]$	pH 9–10 (phosphate)	710[a] (br)	
		490[a]	

[a] New peaks appearing on partial (>50%) reduction of $[(NH_3)_4OsCl(isna)]Cl_2$.

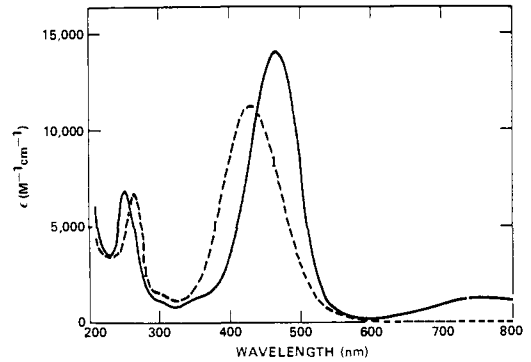


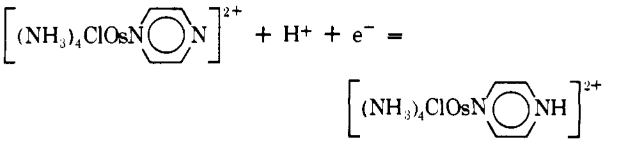
Figure 2. Spectra of $[Cl(NH_3)_4Os(pz)]^+$ and $[Cl(NH_3)_4Os(Hpz)]^{2+}$ (solid line).

nm in the spectrum of the less easily reduced $[(NH_3)_5OsCl]^{2+}$ ion.[26] In a similar manner the bromide to Os(III) transition in V is thought to be one of the components of the very broad absorption at 354 nm.[27] The lowest energy band of the isna analog, VI, was found to shift to higher energies on deprotonation of the carboxylic acid, behavior consistent with an assignment of a metal to ligand charge transfer to the peaks in the 300-400-nm region. A shoulder at about 445 nm was present in the spectrum of the chloropyrazine complex, IV, in strong acid and absent in neutral solution. A solution 2.5×10^{-4} *M* in the pyrazine complex showed absorbancies at 445 nm of 0.150, 0.178, and 0.205 in 0.9 *M* NaCl, 0.9 *M* HCl, and 1.8 *M* HCl, respectively, with an accompanying decrease in absorbance at 351 nm. It is believed that this behavior reflects partial protonation of the pyrazine ligand coordinated to Os(III).[28]

Chlorotetraammineosmium(II) Complexes with Pyrazine and Isonicotinic Acid. Reduction of chloro(pyrazine)tetraammineosmium(III) in acidic aqueous solution with strong reducing agents such as Zn(Hg) or Eu(II) afforded the air sensitive $[(NH_3)_4OsCl(Hpz)]^{2+}$ ion, VII, which has been characterized in solution. Solutions thought to contain the chloro(isna)tetraammineosmium(II) ion, VIII, were prepared by treating a solution of the corresponding Os(III) compound, VI, with Zn(Hg) under Ar, but the characterization of this ion was hindered by nonquantitative reductions and the extreme air sensitivity of the reduced solutions.

A solution, 0.9 *M* in KCl and 0.1 *M* in HCl and containing 0.0053 mmol of $[(NH_3)_4OsCl(pz)]Cl \cdot \frac{1}{2}H_2O$ was titrated potentiometrically under argon with a 0.0075 *M* solution of Eu(II). The end point was found at 0.81 ml of Eu(II) or 1.15 equiv/mol complex. A potential of +0.158 V was observed at half titration. After adding excess Eu(II), this solution was back-titrated with an argon purged solution of 0.0099 *M* iron(III) trifluoromethylsulfonate. Two breaks separated by 0.56 ml were found in a potential against volume plot, implying 1.06 equiv of Fe(III) were required to reoxidize 1 mol of the reduced Os complex. A potential of +0.154 V was observed at the midpoint between the two breaks. Thus the reduction of IV is a reversible, one-electron process.

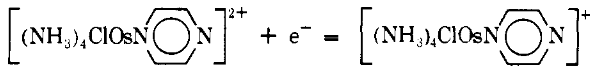
The dependence of the formal potential of the reduction on pH was determined by cyclic voltammetry measurements of solutions buffered in the pH 1-10 range. Between pH 2 and 5 the formal potential was found to fall off linearly with increasing pH with a slope of −57 mV/pH unit. This behavior is consistent with the process shown in eq 2,



(2)

VII

for which a theoretical slope of −59 mV/pH unit is predicted by the Nernst equation. Above pH 7.3 the potential was found to have a value of −0.21 V, independent of pH, as expected for the process shown in eq 3. Cyclic voltammetry



(3)

IX

scans of a solution of $[(NH_3)_4ClOs(isnate)]^+$ (isnate = isonicotinate) buffered at pH 10 with NH_3-NH_4Cl (where the anion of the ligand predominates) showed a nearly reversible couple at −0.44 V on a Pt electrode with a peak to peak separation of 70 mV.

Chloride is lost only slowly, if at all, from the $HpzOs^{II}$ ion, VII. A deaerated solution of 14.9 mg (0.0329 mmol) of the chloride salt of IV in ca. 5 ml of 0.1 *M* trifluoromethylsulfonic acid was treated with 0.6 ml of 0.1 *M* europium(II) trifluoromethylsulfonate under argon. After the solution stood for 30-40 min, it was passed through an inert atmosphere ion exchange column. Potentiometric titration of aliquots of the effluent with $AgNO_3$ showed 1.9 mol of Cl^-/mol complex, indicating that the chloride is retained in the coordination sphere of this Os(II) complex.

The uv-visible-near-ir spectral properties of the protonated and unprotonated forms of chlorotetraammineosmium(II) complexes of pz and isna are given in Table IV, and the spectra of VII and IX are shown in Figure 2. In addition to the expected ligand centered $\pi^* \leftarrow \pi$ transition in the uv region, two other maxima were found for each ion of the se-

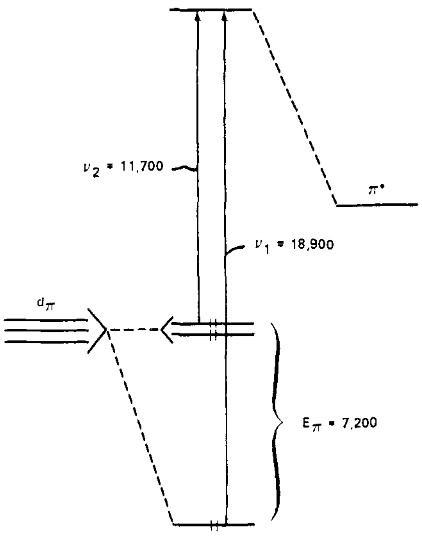
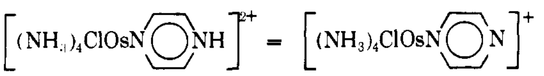


Figure 3. The π interaction in $[(NH_3)_5Ru(pyrazine)]^{2+}$ with assigned transitions (energies in cm^{-1}). ν_1 for both Ru(II) and Os(II) is defined as the transition from the occupied bonding level, to the corresponding antibonding one, and ν_2 as the transition from an occupied nonbonding level to the antibonding level referred to.

ries in the visible and near-ir spectra. Several pentaammineruthenium(II) complexes were examined for evidence of an unreported transition similar to the lowest energy peak of the Os(II) compounds. Weak broad peaks were observed at 855 nm (ϵ 220 M^{-1} cm^{-1}) and 880 nm for $[(NH_3)_5Ru(Hpz)]^{3+}$ and $[(NH_3)_5Ru(Mepz)]^{3+}$, respectively, in 0.12 M DCl-D_2O, while no indication of a similar peak appeared in the spectrum of the isn analog out to 1300 nm.

As noted above, reduction of the Os(III) isna complex, VI, with Zn(Hg) did not proceed smoothly, so that extinction coefficients could not be determined for the new peaks appearing on reduction. However, the ratios of the optical densities of the two visible peaks were similar to those observed in the pz system. A comparison of the spectral maxima of $[(NH_3)_4]OsCl(isna)]^+$, VIII, and $[(NH_3)_4OsCl(isnate)]$, X, shows a shift on protonation to lower energy for both peaks. Yet protonation of the pz complex, VII, led to a shift of the strong visible transition to ***higher*** energy (see Figure 2), that is, in a direction opposite to the shifts observed on protonation of pz coordinated to pentaammineruthenium(II)[20] anddinitrogentetraammineosmium(II) centers. On the other hand, the weaker far-visible absorption moved to much lower energy.

The visible spectral change associated with pH was used to determine a pK_a of 7.6 ± 0.3 for dissociation of a proton rom the Hpz complex (eq 4), in agreement with the break


(4)

at pH 7.3 observed in electrochemical measurements. Thus the pyrazine moleucle coordinated to the chlorotetraammineosmium(II) center is a full seven orders of magnitude more *basic* than free pyrazine.

Discussion

The synthetic utility of the *cis*-bis(dinitrogen)tetraammineosmium(II) ion has been exploited for the preparation of several osmium ammine complexes containing aromatic nitrogen heterocyclic ligands. This reaction has been reported previously for the preparation of dinitrogen bridged binuclear osmium complexes, where a terminal dinitrogen ligand served as the entering group.[8] The dinitrogen(ligand)tetraammineosmium(II) complexes retain the cis configuration of the starting material, as demonstrated by the presence of two metal to ligand charge transfer maxima in the visible spectra of these ions. The assignment of configuration for other complexes in this study is not as clear, but it is believed that the cis stereochemistry is found throughout. The conditions under which cis to trans isomerism of dichlorotetraammineosmium(III) chloride occurs[6] are much more strenuous (reflux for 3 days) than those employed here. Also no resolution of isomers was found during ion exchange isolation procedures.

As might be expected, the dinitrogen stretching frequencies of the *cis*-dinitrogen(N-heterocycle)tetraammineosmium(II) complexes lie intermediate to those reported[12] for chloride salts of dinitrogenpentaammineosmium(II) at 2022 and 2009 cm^{-1} and *cis*-carbonyldinitrogentetraammineosmium(II) at 2179 cm^{-1}. This is indicative of sharing of the back-bonding capability of the Os(II) center; that is, the more electron density is drawn off by the cis ligand, the higher the dinitrogen stretching frequency. In agreement, an inverse relationship exists between ν_{NN} and the energy of the visible charge transfer bands for various heterocyclic ligands.

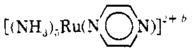
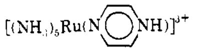
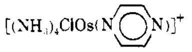
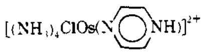
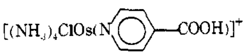
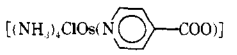
The saturation of back-bonding is reflected in the properties of the nitrogen heterocycle as well. The pK_a of a pyrazine ligand changes from 0.6 to 7.6 when dinitrogen is replaced by chloride in the coordination sphere. It is interesting to note the dinitrogentetraammine(pyrazinium)osmium(II) is somewhat more acidic than pentaammine(pyrazinium)ruthenium(II) (pK_a = 2.5). Similarly, the NMR methyl resonance of $[(NH_3)_5Ru(Me(pz))]^{3+}$ at δ 3.20 is at a somewhat higher field than the methyl resonance of the $[(NH_3)_4(N_2)Os(Me(pz))]^{3+}$ ion at δ 3.68, while both are at substantially higher fields than the free ligand (δ 4.58). A similar argument can be made for the ring protons.

Properties of Chlorotetraammineosmium(II) Complexes with Pyrazine and Isonicotinic Acid. The two visible maxima in the spectrum of $[(NH_3)_4ClOs(isna)]^+$ are both reasonably assigned to metal to ligand CT bands. Deprotonation of the ligand leads to shifts to higher energies of the transitions (from 19,100 and 12,500 cm^{-1} to 20,400 and 14,100 cm^{-1}), in accord with this assignment, to be compared to the similar change observed on deprotonation of $[(NH_3)_5Ru(isna)]^{2+}$ from 20,100 to 21,900 cm^{-1}.[20] The higher energy maximum of the Os(II) complexes can be attributed to the transition from the d_π orbital which is involved in the back-bonding interaction with the π^* level of the heterocyclic ligand.[29] The weak lower energy absorption appears to be a CT from one (or both) of the nearly nonbonding d_π orbitals of the Os center to the same π^* level of the ligand. Such a transition is symmetry allowed even for a pentaammine complex, but it is expected to have low intensity since the overlap of orbitals is poor, as noted by Zwickel.[5] The chloride ligand presents some difficulty in making a definite spectral assignment; however, strong support is found in the observation of similar weak low energy bands in the spectra of pyrazinium and N-methylpyrazinium complexes of pentaammineruthenium(II), which has no chloride ligand to reduce the symmetry.[30]

Anomalies appear in the spectral properties of the $[(NH_3)_4ClOs(pz)]^+$ ion (Figure 2). Protonation of the pyrazine led to a shift of the strong visible maximum from 465 nm (21,500 cm^{-1}) to 430 nm (23,300 cm^{-1}), that is, to *higher* energy,[31] behavior inconsistent with the assignment of a metal to ligand charge transfer transition. An acid dissociation constant for the CT state can be calculated from eq 5,[20]

$$pK_a^* = pK_a(gs) + (2.86(\nu_1 - \nu_2)/2.3RT) \qquad (5)$$

Table V. Observed Charge Transfer Energies and Calculated Energy Parameters of the π Interaction of Pentaammineruthenium(II) and Chlorotetraammineosmium(II) with Unsaturated N-Heterocyclic Ligands[a]

Complex ion	ν_1	ν_2	E_π	β	δ
$[(NH_3)_5Ru(isn)]^{2+}$ [b]	20.8		2.1	6.2	16.8
	21.3		2.3	6.6	16.7
	18.9	11.7	7.2	9.2	4.5
	21.5	13.2	8.3	10.5	4.9
	23.3	8.8	14.5	11.3	−5.7
	19.1	12.5	6.6	9.1	5.9
	20.4	14.1	6.3	9.4	7.8

[a] Energies are given in thousands of wave numbers (kK).
[b] Reference 5.

where $K_a{}^*$ is the acid dissociation constant of the excited state; pK_a (gs), the ground state value of 7.6; ν_1, the energy of the transition in the unprotonated form (21,500 cm^{-1}); and ν_2, the energy of the transition in the protonated form (23,300 cm^{-1}). This leads to a p$K_a{}^*$ of 3.9, such that charge transfer excitation causes the pyrazine ligand to become *less* basic than in the ground state, implying a net ligand to metal transfer of electron density during the transition. On the other hand, the weak lowest energy transition of the pyrazine complex, IX, shifted from 760 nm (13,200 cm^{-1}) to 1140 nm (8800 cm^{-1}) on protonation, that is, to lower energy, as was found in the isonicotinic acid system. This transition then must be classified as a metal to ligand CT.

Zwickel and Creutz[5] have used a simple molecular orbital approach to evaluate the π-stabilization energy, E_π, of several penta- and tetraammineruthenium(II) complexes. If their treatment is applied to the osmium complexes, energy parameters of the π-interaction can be readily calculated with the assumption that the lowest π^* level of the nitrogen heterocyclic ligand interacts strongly with one of the d_π orbitals of the metal center, and that the other two d_π orbitals are nonbonding to a to a first approximation. It must be emphasized that the chloride ligand (in a cis position) forces these two orbitals to be nondegenerate; however, the model does lead to an interesting and intuitively reasonable picture of the Os(II) pyrazine complexes. Following the definitions of Zwickel,[32] the visible charge transfer transition energy, ν_1, is equal to $(\delta^2 + 4\beta^2)^{1/2}$ and the energy of the weaker band, ν_2, is equal to $\frac{1}{2}\delta + \frac{1}{2}\nu_1$, from which values of δ and β can be determined. The so called π-stabilization energy, E_π, is simply the difference between ν_1 and ν_2. The π interaction in $[(NH_3)_5Ru(Hpz)]^{3+}$ (for which symmetry splitting of nonbonding levels is not a problem) is depicted in Figure 3.

Calculated MO energy parameters are given in Table IV for several Os(II) and Ru(II) complexes. It can be seen that the lower energy bands in the spectra of $[(NH_3)_5Ru(isn)]^{2+}$ and $[(NH_3)_5Ru(pz)]^{2+}$ would most likely be covered by the broad, intense ν_1 transition which has similar energy.

There is a very large interaction between the Os(II) metal center and the π-acid ligand, as is apparent from the high values of β and E_π, so that substantial delocalization of electron density onto the ligand is present. Strong supporting evidence of the delocalization is the very high pK_a of the pyrazine ligand (7.6), seven orders of magnitude more *basic* than free pyrazine despite coordination to a dipostive metal center. Examination of Table V shows that the chlorotetraammine(pyrazinium)osmium(II) ion is unique in that the value of δ was found to be negative, meaning that the π^* level of the pyrazinium ligand is initially *below* the d_π orbitals of the Os(II) center. Thus the resultant ground state MO has more ligand than metal character and the CT transition from this MO, ν_1, will have the properties of a ligand to metal transition, as observed. On the other hand, ν_2 is a transition from an orbital mostly metal in character (assumed purely metal in this naive treatment) to a MO possessing significant ligand character, and thus retains the metal to ligand CT behavior.

One check on the model is available from a comparison of the change in δ on protonation of pyrazine coordinated to pentaammineruthenium(II) and to chlorotetraammineosmium(II). The change in δ should be constant whether it is measured against α_{Ru} or α_{Os}. For the Ru(II) center, the change is 1.2×10^4 cm^{-1} and for Os(II), 1.1×10^4. Although the energy parameters calculated from this simple treatment are likely to be inaccurate, the picture which emerges does provide a satisfactory explanation of the observed properties of the Os(II) complexes.

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(15) Average of two preparations.
(16) The difficulty in obtaining analytically pure samples may be due to loss of dinitrogen accompanied by oxidation, since high chloride and low nitrogen contents were found.
(17) (a) This reaction may be carried out on the solid obtained from the 3 *M* ion exchange fraction in the preparation of the dinitrogen(pyrazine)tetraammineosmium(II) ion, with substantially higher overall yield. (b) A description of the device is given in the Ph.D. Thesis of A. M. Zwickel, University of Chicago, 1959, and will appear in a forthcoming publication by C. G. Kuehn and H. Taube.
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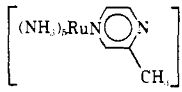
(23) It is assumed that the dimethylpyrazine ligand will coordinate through the least sterically hindered nitrogen of the ring. Compare the preferential formation of



over the ortho isomer. See ref 2.
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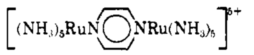
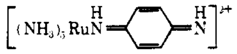
(27) The peak at 287 nm in the spectrum of this ion has much lower intensity when corrections are made for the overlapping peaks at 251 and 354 nm. It is possibly associated with a d–d transition.
(28) The pK_a can be roughly estimated as −2 to −1 from these data.
(29) This is the π^* with highest probability on the nitrogen atom(s) of the ring; cf. ref 5.

(30) The occurrence of this band in the spectra of Ru(II) pyrazinium complexes provides a satisfactory explanation, within the framework of the trapped-valence model, of the weak shoulder at ~850 nm in the spectrum of the mixed valence



ion (see ref 4). It has been pointed out to us by a referee that owing to the large magnitude of spin-orbit coupling constants for Ru and Os (G. A. Crosby, K. W. Hipps, and W. H. Elkins, Jr., *J. Am. Chem. Soc.*, **96**, 629 (1974)), there is some doubt in our assignment of the weak, long wavelength transitions. Our assignment does explain why the weak transitions are observed in Ru(II) complexes only when the interaction of π and π^* orbitals is large and is supported by the fact that the change in δ is the same whether calculated for Ru(II) or Os(II). For these reasons we prefer to retain our interpretation though admitting that we may have to revise it when more insight into the electronic spectra of these species is gained.

(31) Similar behavior is observed in the protonation of



K. Rieder, U. Hauser, H. Siegenthaler, E. Schmidt, A. Ludi, to be submitted to *Inorg. Chem.*

(32) $\alpha_L = (\pi^*|H|\pi^*)$, $\alpha_M = (t_{2g}|H|t_{2g})$, $\beta = (\pi^*|H|t_{2g})$, and $\delta = \alpha_L - \alpha_M$.

Stereochemistry of Eight-Coordinate Mixed-Ligand Complexes of Zirconium. I. Characterization and the Crystal and Molecular Structure of Dinitratobis(acetylacetonato)zirconium(IV)[1]

Victor W. Day*[2a] **and Robert C. Fay***[2b]

Contribution from the Departments of Chemistry, Cornell University, Ithaca, New York 14853, and University of Nebraska, Lincoln, Nebraska 68508.

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Abstract: The crystal and molecular structure of dinitratobis(acetylacetonato)zirconium(IV), $Zr(acac)_2(NO_3)_2$, has been determined by single-crystal X-ray diffraction and has been refined (anisotropically on Zr, O, N, and C; isotropically on H) by least-squares methods to $R_1 = 0.036$ and $R_2 = 0.032$ using 3891 independent diffractometer-recorded reflections having $2\theta_{MoK\bar{\alpha}} < 63.7°$ and $I > 2\sigma(I)$. The compound crystallizes in the monoclinic space group $C2/c$ with eight molecules in a unit cell of dimensions: $a = 29.247$ (3), $b = 7.870$ (1), $c = 14.257$ (1) Å; $\beta = 93.824$ (8)° ($\rho_{obsd} = 1.669$, $\rho_{calcd} = 1.677$ g/cm^3). The crystal contains discrete eight-coordinate molecules in which bidentate acetylacetonate and bidentate nitrate ligands span the *m* edges of a (necessarily distorted) D_{2d}-$\bar{4}2m$ dodecahedron; each BAAB trapezoid contains one acetylacetonate and one nitrate ligand. Averaged Zr-O bond distances are: Zr-O(acac) 2.096 Å and Zr-O(nitrate) 2.295 Å. Within a particular chelate ring, the Zr-O bond lengths involving dodecahedral A sites exceed those involving B sites by 0.015-0.051 Å (5σ-17σ) and these differences appear to be propagated in the N-O and C-O bond lengths in the ligands, N-O_A being shorter than N-O_B by 0.012-0.019 Å (3σ-5σ) and C-O_A being shorter than C-O_B by 0.017-0.023 Å (4σ-6σ). The ligands are planar, and the acetylacetonate methyl groups adopt a conformation in which one methyl hydrogen atom and the -CH= hydrogen atom are eclipsed. The relative merits of the observed C_2-*mmmm* stereoisomer and other possible stereoisomers are discussed in terms of ligand bite, polyhedral edge lengths, and nonbonded contacts. In solution, $Zr(acac)_2(NO_3)_2$ is a monomeric nonelectrolyte which is stereochemically nonrigid on the NMR time scale at temperatures above −130°. Below −144°, stereochemical rearrangement is slow, and ^{1}H NMR spectra are consistent with the C_2-*mmmm* structure found in the solid state. Retention of coordination number eight in solution is indicated by the similarity of solid-state and solution-state infrared spectra.

In 1958 Brainina and coworkers[3] reported syntheses of the interesting, mixed-ligand zirconium complexes, $Zr(dik)_2(NO_3)_2$ and $Zr(dik)_3(NO_3)$, where dik represents the anion of acetylacetone or benzoylacetone. More recently some analogous hafnium complexes have been prepared.[4] These compounds have not yet been fully characterized, and nothing is known about their structures.

Structural points of interest include (1) the denticity of the nitrate ligands and the coordination number (CN) of the zirconium atom and (2) the geometry of the coordination polyhedron. For the dinitrato complexes, possible structures are $Zr(dik)_2(ONO_2)_2$ (CN 6), $Zr(dik)_2(O_2NO)(ONO_2)$ (CN 7), and $Zr(dik)_2(O_2NO)_2$ (CN 8), depending on the mode of nitrate attachment.[5] In addition to analogous structures for the mononitrato complexes, viz., $Zr(dik)_3(ONO_2)$ (CN 7) and $Zr(dik)_3(O_2NO)$ (CN 8), one must also consider an ionic structure, $[Zr(dik)_3]^+[NO_3]^-$, in which the zirconium atom exhibits CN 6.

Structures of the nitrato complexes are of interest in relation to previous structural work on halo(acetylacetonato)zirconium complexes and the tetrakisacetylacetonate. $Zr(acac)_3Cl$ is a pentagonal bipyramidal molecule (CN 7),[6] while $Zr(acac)_4$ adopts a square antiprismatic geometry (CN 8).[7] The detailed geometry of $Zr(acac)_2Cl_2$ is not yet known; however, NMR, infrared, Raman, and dipole moment studies point to a cis octahedral structure in solution.[8]

In this paper we report the characterization and the crystal and molecular structure of dinitratobis(acetylacetonato)zirconium(IV), $Zr(acac)_2(NO_3)_2$. A following paper will deal with $Zr(acac)_3(NO_3)$.

Experimental Section

Preparation and Physical Data. Dinitratobis(2,4-pentanedionato)zirconium(IV), $Zr(acac)_2(NO_3)_2$, was prepared in 63% yield according to the procedure of Brainina et al.[3] by reaction of acetylacetone with $ZrO(NO_3)_2 \cdot 2H_2O$ in benzene solution. Recrystallization from hot benzene-hexane (~40:60 v/v), under a dry nitrogen atmosphere, gave colorless crystals which were washed with dry hexane and dried in vacuo for 12 hr at room temperature: mp 149-151°, lit.[3] 146-148°; mol wt 392 (cryoscopic, 0.0327 *m* nitro-