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Preparation and Properties of Mixed-Valence (μ-Dinitrogen)bis(pentaammine) Complexes of Osmium and Ruthenium

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(μ-Dinitrogen)bis(pentaammineosmium(II)) is formed when a solution containing both $Os(NH_3)_5H_2O^{3+}$ and $Os(NH_3)_5N_2^{2+}$ is left in contact with amalgamated zinc and is readily oxidized to the mixed-valence form. Solids with a high content of the mixed-valence form of the ruthenium analogue can be prepared by rapid precipitation from a partially oxidized solution of the fully reduced state. The values of the reduction potentials for the stages 6+/5+ and 5+/4+ are 1.04 and −0.16 V for the osmium system and 1.2 and 0.73 V for the ruthenium system. The spectrum of the mixed-valence species at long wavelengths shows a succession of strong bands (700, 1175, 1740 (sh), 1840, 2090 nm), in general similar to those of mixed-valence μ-dinitrogen osmium species described earlier. The ruthenium mixed-valence species shows an absorption band at 1020 nm which is much narrower than that expected for a valence-trapped system. Both species appear to be delocalized, and the discussion of the absorption spectra is based on a delocalized valence orbital description of the electronic structure. Aquation specific rates for $[(Ru(NH_3)_5)_2N_2]^{5+}$, $[Ru(NH_3)_5N_2]^{3+}$ and $[(Ru(NH_3)_5)_2N_2]^{6+}$ at 25 °C are $(2.4 \pm 0.1) \times 10^{-2}$ s^{-1}, $(7 \pm 2) \times 10$ s^{-1}, and $\geq 10^3$ s^{-1}. The ion $[(Os(NH_3)_5)_2N_2]^{5+}$ is indefinitely stable in water.

A number of μ-dinitrogen osmium ammines in the [II, II], [III, II], and [III, III] oxidation states[1] (the latter quite unstable) have been prepared by replacing one dinitrogen molecule in $[(NH_3)_4Os(N_2)_2]^{2+}$ by the dinitrogen ligated to a pentaammine- or tetraammineosmium(II) species.[2,3] This approach yields molecules in which at most one of the osmium atoms contains five ammonia molecules as the auxiliary ligands. Earlier, numerous and diverse attempts[3] to convert a species such as $[(NH_3)_4ClOsN_2Os(NH_3)_5]^{4+}$ to the symmetrical decaammine have failed. The incentive for preparing the μ-dinitrogen decaammine was partly meeting the synthetic challenge but also in part the hope that the mixed-valence molecule based on it would also have a simpler absorption spectrum in the near-IR[2] region than the less symmetrical μ-dinitrogen species prepared thus far.

In contrast to the osmium system, $[(Ru(NH_3)_5)_2N_2]^{4+}$ is readily prepared and has been known for over a decade.[4,5] The ruthenium system contrasts with the osmium also in the relative stabilities of the possible oxidation states. For the former, the [II, II] state is the most stable, while the [III, II] undergoes rapid aquation, and the only prior measurements made on the mixed oxidation state were electrochemical.[6] For the osmium system, the most stable of the three states is the [III, II]; though the [II, II] is stable with respect to substitution, it is easily oxidized; the [III, III] state is strongly oxidizing and readily aquates with $Os^{III}–N_2$ bond rupture.

The mixed oxidation states for Os and Ru seem to be examples of strongly interacting systems. The remarkable stability of the [III, II] state for the osmium system is ascribable at least in part to electronic delocalization and, as a practical matter, facilitates its study by a variety of techniques. While the [III, II] state based on Ru lacks the chemical stability of the Os, the extent of delocalization is nevertheless great enough so that in many respects it resembles the μ-pyrazine complex.[7,8]

Experimental Section

Preparation of (μ-Dinitrogen)bis(pentaammineosmium) Pentabromide. Aquopentaammineosmium(III) was prepared by a controlled-potential electrolysis of $[(NH_3)_5OsN_2]Cl_2$[9] (100 mg) at a Pt anode at +0.40 V in about 3 mL of 0.1 N HCl. The electrolysis was done in an atmosphere of argon. Oxidation yielded the aquopentaammineosmium(III) species. The solution containing the aquo species was saturated with $[(NH_3)_5OsN_2]Cl_2$ and allowed to react in the presence of zinc amalgam under argon for about 12 h. On exposure to air, the solution changed from colorless to green (the latter is characteristic of the mixed oxidation state) and was charged onto an ion-exchange column of Bio-Rad AG50W-X2 resin in the acid form. The ion $[(NH_3)_5OsN_2Os(NH_3)_5]^{5+}$ was eluted with 4 M HCl, and the solution was evaporated to dryness by rotary evaporation. The solid was dissolved in 0.1 M LiBr and precipitated by adding solid LiBr. The complex was reprecipitated twice from hot 0.10 M HBr; yield 10%. Anal. Calcd for $[(NH_3)_{10}Os_2N_2]Br_5$: N, 17.18; H, 3.09; Br, 40.84. Found: N, 17.14; H, 2.96; Br, 39.42. The *p*-toluenesulfonate salt of the complex was prepared by dissolving the solid remaining after rotary evaporation in 0.10 M *p*-toluenesulfonic acid and then adding 3 M *p*-toluenesulfonic acid to precipitate the salt.

Preparation of (μ-Dinitrogen)bis(pentaammineruthenium(II)) Tetrafluoroborate. We have found that the synthesis of the title compound by the method outlined by Harrison[10] using 0.1 M H_2SO_4 as the reaction medium leads to partial loss of the auxiliary ligand ammonia. We modified Harrison's procedure by using a reaction medium at a pH of 4–6. A suspension of finely ground $[Ru(NH_3)_5Cl]Cl_2$ was bubbled with purified argon over zinc amalgam for about 45 min to give a 0.05 M solution of ruthenium in 1×10^{-4} M CF_3SO_3H. Purified dinitrogen was bubbled through the solution in the dark for 10 h. The solution was then acidified to 1 M with concentrated HCl. A yellow solid precipitated on adding saturated $NaBF_4$; this was collected and washed with ethanol. The crude solid was dissolved in 1.5 M HCl (about 25 mL/100 mg) and reprecipitated by the slow addition of saturated $NaBF_4$ to a stirred solution. The solid (bright yellow) that formed was collected and washed with dilute HBF_4, ethanol, and ether. The solid was stored in a freezer to minimize the discoloration that is observed in storage at room temperature. The purity of the product was confirmed by its UV spectrum[4] ($\lambda_{max} = 262$ nm, $\epsilon = 4.7 \times 10^4$ M^{-1} cm^{-1}), the absence of a dinitrogen stretch in the infrared spectrum, and analysis for tetrafluoroborate (1.95 ± 0.10 BF_4 per Ru).

The binuclear product prepared as described has an oxidation wave at 0.73 V (vs. NHE), which is independent of pH over the range 1–7. In contrast to the product described by Harrison et al.,[4] our complex does not decompose significantly in 10 min at pH 10.4, and the half-life for decomposition in basic or acidic solution is greater than 10 h.

Preparation of Solids Containing $[(Ru(NH_3)_5)_2N_2]^{5+}$. On the basis of the observations (vide infra) that the half-life for aquation of $[(Ru(NH_3)_5)_2N_2]^{5+}$ in 1 M acid at 25 °C is about 25 s, there was reason to believe that the mixed-valence complex could be isolated

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[1] Formal metal oxidation states in dimers are represented by [II, II] etc. This notation in no way implies valence localization but provides a convenient way to express the overall oxidation state.

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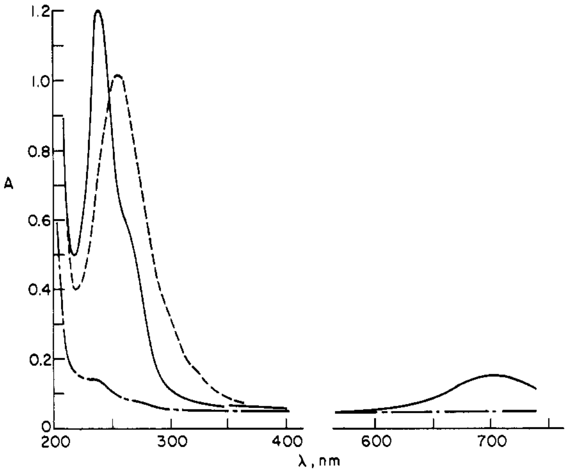

Figure 1. UV–vis spectrum of $[(Os(NH_3)_5)_2N_2]^{n+}$: solid line, $n = 5$; dotted line, $n = 4$; dot and dash, base line.

as a salt. The oxidation of the [II, II] to the [III, II] form takes place quantitatively and rapidly, using either excess Br_2 or stoichiometric Ce(IV) as oxidant, and at 0 °C the half-life for aquation is 3–4 min. A light green solid was obtained when solutions containing the [III, II] form were treated with BF_4^- or $IrCl_6^{3-}$. In no case was a solid obtained free of contamination in varying amounts by $Ru(NH_3)_5N_2^{2+}$, $[(Ru(NH_3)_5)_2N_2]^{4+}$, or a Ru^{III} species, but all solids showed a near-IR absorption at 9800 cm^{-1} characteristic of the [III, II] species.

Instrumentation and Techniques. Ultraviolet, visible, and near-IR spectra were recorded with a Beckman Model 5270 or Hewlett-Packard Model 5480 spectrophotometer equipped with a thermostated cell holder. A digital thermometer with a miniprobe was used to monitor the solution temperature directly during rate studies.

Infrared spectra (200–4000 cm^{-1}) were recorded with a Perkin-Elmer Model 621 instrument. Samples were prepared as KBr pellets or mulls (Nujol or hexachlorobutadiene). A Spex Model 1401 double monochromator equipped with an RCA Model FW130 photon-counting detector was used to obtain Raman and resonance Raman spectra. The excitation source was either an Ar^+ (4880, 5145 Å) or a Kr^+ (6764, 6471 Å) laser. Samples prepared in aqueous solution were sealed in a capillary tube.

The electrochemical apparatus and techniques are described elsewhere.[11] All potentials are reported vs. NHE.

All elemental analyses were performed by the Stanford University Microanalytical Laboratory. An indirect spectrophotometric method was used to analyze for tetrafluoroborate.[12]

Results

Spectral and Electrochemical Properties of Osmium Complexes. The absorption spectra of the [II, II] and the [III, II] species as measured for the UV–visible region are shown in Figure 1. A summary of the salient features for the bromide salt dissolved in 0.1 M HCl follows (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 4+ ion, 256 (3.3×10^4); 5+ ion, 238 (4.1×10^4), 260 (shoulder, 2.0×10^4), 700 (4.0×10^3).

The absorption spectrum in the near-IR region for the [III, II] species is shown in Figure 2 for a sample prepared in a KBr pellet. Band maxima and extinction coefficients as summarized in the following are based on measurements made with the *p*-toluenesulfonate salt in 0.12 M DCl/D_2O (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 1175 (7.2×10^2), 1740 (shoulder, $\sim 2.7 \times 10^3$), 1840 (3.9×10^3), 2090 (3.3×10^3). The band maxima are very much the same for a sample dissolved in dimethylformamide, except that the highest energy band shifts to 1195 nm. The [III, III] species is so unstable that we were unable to obtain its spectrum.

The *p*-toluenesulfonate salt of the [III, II] ion shows a sharp, very weak IR absorption at 2010 ± 5 cm^{-1}. Raman measurements on the [III, II] bromide salt (5145 and 6764-Å excitation) revealed three major peaks at 2015, 275, and 162 cm^{-1}. Raman spectra of aqueous solutions of the bromide salt show the same three peaks, but now shifted to 1990, 265, and 150 cm^{-1}, respectively. Deuteration shifts the 265-cm^{-1} band to 235 cm^{-1}, while the others are unchanged. Relative intensities among the bands change with excitation wavelength. At an excitation wavelength of 6764 Å, within the visible band centered at 700 nm, the three principal bands have roughly the same intensity while under nonresonant conditions (4880 or 5145 Å) the 1990-cm^{-1} band is more intense by a factor of 10. Also seen under resonance conditions is a broad, unresolved band system at 400–500 cm^{-1}. On the basis of the present results and earlier work,[13] the following assignments are made (idealized D_{4h} symmetry has been assumed): 1990 cm^{-1}, A_{1g} N_2 stretch; 400–500 cm^{-1}, Os–NH_3 stretching modes; 265 cm^{-1}, A_{1g} Os–NH_3 bend; 150 cm^{-1}, A_{1g} Os–N_2 stretch.

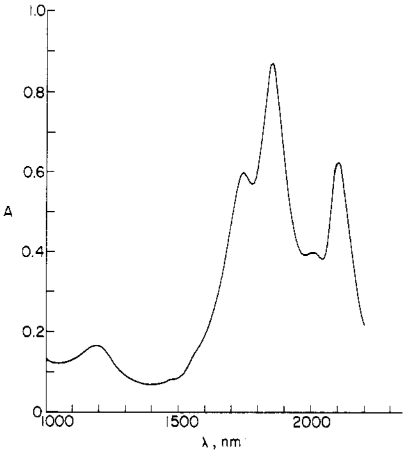

Figure 2. Near-IR spectrum of $[(Os(NH_3)_5)_2N_2]Br_5$ in a KBr pellet.

A strong Raman peak at 2010 ± 5 cm^{-1} was observed for the [II, II] ion in solution (0.10 M HCl).

Cyclic voltammetry in 0.1 M HCl showed a reversible wave at −0.16 V (NHE). A second wave is observed at 1.04 V in the anodic scan, but the corresponding reduction wave is absent (sweep rate 0.2 V s^{-1}).

Electrochemistry of Ruthenium Dinitrogen Complexes. The electrochemistry of $[Ru(NH_3)_5N_2]^{2+}$ was originally investigated by Elson et al.[6] In H_2SO_4–K_2SO_4 electrolyte ($\mu = 0.3$, pH 2.3) they saw no evidence of $[Ru(NH_3)_5N_2]^{3+}$ in cyclic voltammetry even when the sweep rate was 100 V s^{-1}. The loss of dinitrogen from Ru^{III} is expected to be fast owing to the low basicity of dinitrogen and the evidence that back-bonding for Ru^{III} tends to be small.

In the course of the present work, a reinvestigation of the dinitrogen complex in 1 M HCl and 1 M CF_3SO_3H showed that the Ru^{III}–N_2 complex could be detected easily in cyclic voltammetry at scan rates as low as 5 V s^{-1}. In the K_2SO_4–H_2SO_4 electrolyte used by Elson et al.,[6] the peaks are broadened at scan rates >2 V s^{-1} and detection of the Ru^{III}–N_2 complex is impossible. Broadening of peaks is usually a sign that electron transfer at the electrode is becoming slow compared to the scan time.[14] Application of the method of Nicholson and Shain[14] to the cyclic voltammetric data yields a rate constant $k = (7 \pm 2) \times 10$ s^{-1} at 25 °C (rough estimate—error limits give precision) for the aquation of $[Ru(NH_3)_5N_2]^{3+}$ in 1 M CF_3SO_3H. The rates are not significantly different in 1 M HCl.

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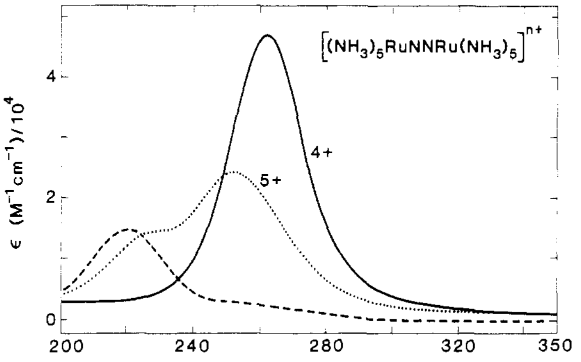

Figure 3. UV spectra of $[(Ru(NH_3)_5)_2N_2]^{n+}$ (n = 4, 5). The n = 5 spectrum was obtained 3 s after ceric oxidation of the n = 4 solution (1 M H_2SO_4, 25 °C). The dashed line represents the spectrum of the n = 5 solution after 10 min. See text for further details.

The electrochemistry of $[(Ru(NH_3)_5)_2)N_2]^{4+}$ was also studied by Elson et al.[6] The 4+ binuclear ion can be oxidized in one-electron steps to yield the [III, II] and [III, III] species:

$$Ru_2N_2^{6+} \xrightarrow[\sim 1.2\ V]{} Ru_2N_2^{5+} \xrightarrow[0.73\ V]{} Ru_2N_2^{4+}$$

The 5+ and 6+ species aquate according to

$$Ru_2N_2^{5+} \xrightarrow{k_1} RuN_2^{2+} + RuH_2O^{3+}$$

and

$$Ru_2N_2^{6+} \xrightarrow{k_2} RuN_2^{3+} + RuH_2O^{3+}$$

Elson et al.[6] studied only the 5+/4+ couple and obtained an estimate of 0.1 s^{-1} for k_1 at 25 °C in 0.28 M H_2SO_4, and for $E_{1/2}$ a value of 0.71 V. The latter agrees well with the $E_{1/2}$ value entered above, which we obtained with 1 M HCl as reaction medium. In the same electrolyte only the oxidation wave corresponding to 6+/5+ stage is observed even at scan rates as high as 50 V s^{-1}. A cathodic peak does appear at scan rates >5 V s^{-1}, which we assign to the reduction of $[Ru(NH_3)_5N_2]^{3+}$, a product of aquation of the 6+ species. The specific rate for aquation of $[Ru(NH_3)_5N_2]^{3+}$ being known (ca. 10^2 s^{-1}), the failure to observe the reduction of the 6+ ion puts a lower limit of 10^3 s^{-1} on the specific rate for aquation of this species (k_2). Because of the uncertainty in this rate, $E_{1/2}$ for the 6+ species cannot be fixed with certainty, so that the estimate of $K_c = 10^8$, which is based on the two values of $E_{1/2}$ entered above, must be regarded as being approximate.

Spectra of the Ruthenium Complexes. The UV spectrum of $[(Ru(NH_3)_5)_2N_2]^{4+}$ (Figure 3) agrees with that reported by Harrison et al.[4] To obtain the spectrum of the 5+ species, also shown in Figure 3, we oxidized the 4+ species with Ce(IV) in 1 M H_2SO_4 at 25 °C and measured the spectrum at 1-s intervals using the pulse spectrophotometer. The oxidation by Ce(IV) under our conditions is substantially complete in <1 s. This stage is followed by a slower one corresponding to aquation of the 5+ species. The half-life for aquation was found to be ~25 s ($k_1 = 3 \times 10^{-2}$ s^{-1}). The spectrum for the 5+ ion 3 s after mixing appears in Figure 3 (λ_{max} = 248, 226 nm; $\epsilon \times 10^{-4}$ = 2.5, 1.4 M^{-1} cm^{-1}). The final spectrum is found to be that expected for equimolar amounts of $[Ru(NH_3)_5N_2]^{2+}$ (λ_{max} = 221 nm; $\epsilon = (1.82 \pm 0.66) \times 10^4$)[15] and $[Ru(NH_3)_5H_2O]^{3+}$ (λ_{max} = 268 nm).[16] The final absorbance at 221 nm showed that 95% of the expected amount of $[Ru(NH_3)_5N_2]^{2+}$ was obtained.

To obtain the spectrum of the 5+ ion in the near-IR, we prepared a solution of the 4+ species in 1 M HCl and cooled it to 10 °C. The band region was scanned rapidly after the addition of 1 equiv of Ce(IV)/mol of 4+, and the absorption at the maximum was recorded. The change in absorption as a function of time was monitored so that the absorption could be extrapolated to the time of mixing. Rate studies in 1 M HCl at 25 °C gave a first-order decay for the near-IR band with $k_1 = (2.4 \pm 0.1) \times 10^{-2}$ s^{-1}. Spectra were measured for propylene carbonate or acetone as the solvent, where k_1 at 25 °C is ~1 × 10^{-3} s^{-1}. Spectra were also obtained from solids prepared as described earlier, suspended in Nujol or pelleted in KBr. It is to be noted that the impurities formed by decomposition do not absorb in the near-IR region.

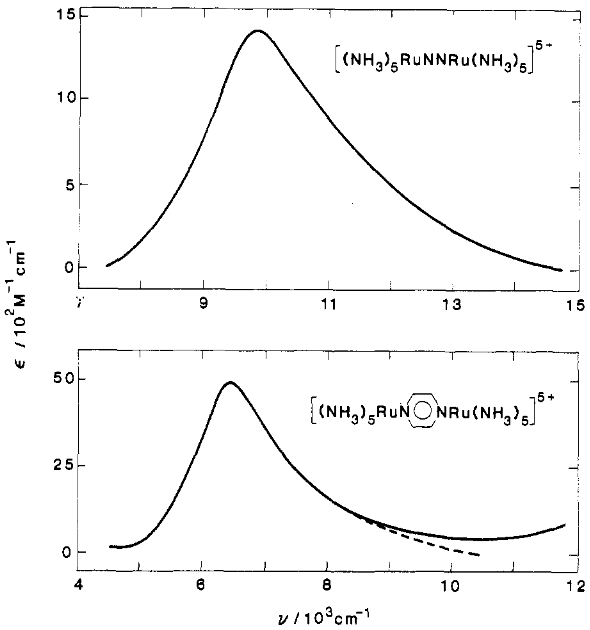

Figure 4. Near-IR spectrum of $[(Ru(NH_3)_5)_2N_2]^{5+}$ in 1 M HCl (10 °C). The near-IR band of $[(Ru(NH_3)_5)_2pyz]^{5+}$ is shown for comparison.

In all the solutions, including those in the organic solvents, the band maximum is at 9800 cm^{-1}. Extrapolation of the kinetic plots to t = 0 gave $\epsilon_{max} = (1.5 \pm 0.2) \times 10^3$ M^{-1} cm^{-1}. The width at half-height for the solution spectrum is 2630 cm^{-1} and is somewhat greater for the solid samples. The spectrum of the 5+ species in 1 M HCl is shown in Figure 4, along with the near-IR band of $[(Ru(NH_3)_5)_2pyz]^{5+}$.

The possibility was considered that the lability of the 5+ species is a consequence of the extremely rapid aquation of the 6+—that is, disproportionation of the 5+ to 4+ and labile 6+ species may occur rapidly enough, even though it is highly unfavorable energetically, to carry the 5+ aquation. However, this possibility was ruled out by the observation that the specific rate was invariant with the amount of excess 4+ species present in the solution. If the disproportionation were important, the observed rate constant would decrease with increasing concentrations of 4+ species, that is if the [III, II] species were maintained at equilibrium with the [II, II] and [III, III]; on the other hand, if the disproportionation were rate determining, the decay of the [III, II] would not be first order.

Discussion

Preparation and Properties of $[(Os(NH_3)_5)_2N_2]^{5+}$. The success of the particular preparative method used is mystifying, particularly when considered in the light of the fact that no $[Os(NH_3)_5N_2]^{2+}$ was detected in an experiment in which $[Os(NH_3)_5H_2O]^{3+}$ was kept over Zn amalgam with N_2 under pressure. Even with N_2 at 100 atm, so that the concentration of N_2 was at least as high as that of $[Os(NH_3)_5N_2]^{2+}$ in reaction mixtures that led to the successful preparation of the

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μ-dinitrogen complex, and with contact times as long as 48 h, no $[Os(NH_3)_5N_2]^{2+}$ was detected. The reduction potential for the $[Os(NH_3)_5OH_2]^{3+/2+}$ couple is –0.75 V,[17] making the concentration of $[Os(NH_3)_5OH_2]^{2+}$ in equilibrium with the zinc amalgam quite small. Owing to the rapid oxidation of $[Os(NH_3)_5OH_2]^{2+}$ by acid or even water,[17] the steady-state concentration of Os(II) is probably so low that simple substitution of $[Os(NH_3)_5N_2]^{2+}$ into $[Os(NH_3)_5OH_2]^{2+}$ cannot account for the success of the method. Direct substitution on Os(II) seems to be ruled out also by the observation already cited, namely, that the preparation of $[Os(NH_3)_5N_2]^{2+}$ following an analogous procedure failed. It is possible that the formation of the binuclear species capitalizes on the enormous stability of the mixed oxidation state and that an S_N2 process is involved. Moreover, the zinc may be acting not simply as a reducing agent but also as a catalyst.

The irreversibility of the oxidation of the [III, II] to the [III, III] ion on the time scale of cyclic voltammetry is probably not caused by slow electron transfer but rather by the rapid aquation of the [III, III] species. Thus 1.04 V as registered in the anodic scan is an upper limit on $E_{1/2}$ for the [III, III]/[III, II] couple but is probably not far removed from the true value of $E_{1/2}$. When 1.04 V is used as $E_{1/2}$ for the 6+/5+ stage, K_c, the quotient governing the comproportionation reaction is calculated as 10^{20}. This is probably an upper limit on K_c but is not much above the true value. At any rate, the decaammine, in common with a number of other μ-dinitrogen osmium ammines,[2,3] is very stable to disproportionation.

The peculiar stability of the [III, II] state is reflected also in the frequency of the N≡N stretching vibrational mode, which was registered as lower than that of the [II, II] stage (1990 and 2010 cm^{-1}, respectively; both in aqueous solution). There seems little doubt that the [III, II] molecule is valence delocalized. As a result, it is useless to try to identify any of the bands in the near-IR as an intervalence transition. If the general observations on the near-IR absorption described earlier,[2,3] which include the fact that the μ-dinitrogen [III, III] state also shows absorption in the near-IR region, are taken together with the fact that many Os^{III} complexes show absorption in this region, the bands are reasonably assignable to transitions between the levels that arise when the πd levels are split. Such transitions are not possible for d^6 Os^{II} but become possible in the d^5 case. In the case of the simple mononuclear complexes, the intensities are low—$\epsilon \sim 10^2$ M^{-1} cm^{-1} or less—and spin–orbit coupling is probably an important interaction leading to the splitting.[18,19] The intensities are very much greater for the mixed-valence species, $>10^3$ M^{-1} cm^{-1}, and the transitions likely have character deriving from what would be intervalence transitions in the valence-localized limit. Other observations suggest that there is substantial back-bonding in the interaction of N_2 with Os^{III}.[20]

Electronic Spectra of Ruthenium Complexes. The band at 262 nm in the 4+ spectrum is assigned as metal-to-bridging ligand charge transfer (MBLCT) and is analogous to the 221-nm band in $[Ru(NH_3)_5N_2]^{2+}$.[21] A careful study of the 4+ spectrum reveals a weak shoulder at about 400 nm with $\epsilon \simeq 50$ M^{-1} cm^{-1}, which is probably associated with d–d transitions on Ru^{II}.[22,23] The UV band of the 5+ ion is shifted to higher energy than that of the 4+ and is split into at least two broad bands (maxima at ~40 and ~44 × 10^3 cm^{-1}). The presence of two UV bands in the mixed-valence state parallels the observations made for $[(Os(NH_3)_5)_2N_2]^{5+}$. Comparison of the near-IR band for the μ-dinitrogen species with that of the analogous μ-pyrazine complex reveals similar shape and width (Figure 4). The 9800-cm^{-1} band is much narrower than predicted by the Hush theory[24] for localized mixed-valence systems (2630 cm^{-1} vs. 4750 cm^{-1} predicted for the localized case). The source of the asymmetry is most likely the same for both near-IR bands in Figure 4. In the original analysis of the μ-pyrazine complex by Piepho, Krauz, and Schatz,[25] a single-mode model was used to fit the band shape. As recently discussed by Wong and Schatz,[26] this approach gives physical parameters that seem to be unrealistic for ruthenium ammines (in particular, the theoretically derived bond length difference for $Ru^{II}–NH_3$ and $Ru^{III}–NH_3$ is about a factor of 2 too large). Hush[27] subsequently suggested that delocalized systems will show asymmetric bands due to contributions of a symmetrical vibrational mode to the transition intensity.

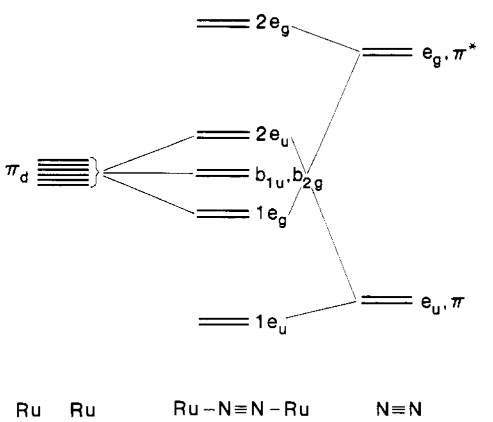

Figure 5. Molecular orbital diagram for $L_5M–N_2–ML_5$ complexes, assuming D_{4h} symmetry. The πd orbitals correspond to the t_{2g} in O_h symmetry.

The narrowness of the near-IR band and the absence of a N_2 stretch in the IR spectrum suggest that $[(Ru(NH_3)_5)_2N_2]^{5+}$ is valence delocalized. At the least, it is quite similar to $[(Ru(NH_3)_5)_2pyz]^{5+}$, which is believed to have strong metal–metal interactions.[27]

Molecular Orbital Description. A molecular orbital approach can be used to describe the electronic structure of valence-delocalized mixed-valence complexes. An approximate ordering[5] of one-electron levels for the μ-dinitrogen complexes is shown in Figure 5. In the [II, II] state, the valence configuration is $(1e_u)^4(1e_g)^4(b_{1u})^2(b_{2g})^2(2e_u)^4$ and the strong UV band is assigned as $2e_g \leftarrow 2e_u$ (the higher energy transition $2e_g \leftarrow b_{1u}$ is also allowed but not observed). Because the πd levels for Os^{II} are considerably higher in energy than for Ru^{II}, the MBLCT is expected to occur at lower energies for Os^{II}, but the bands are actually quite close in energy for the two cases.

Upon removal of an electron from $2e_u$ to form the mixed-valence state, the $2e_u \leftarrow 1e_g$ transition becomes possible, and the 9800-cm^{-1} band in $[(Ru(NH_3)_5)_2N_2]^{5+}$ is assigned to this process. In the case of $[(Os(NH_3)_5)_2N_2]^{5+}$, interpretation is complicated by the multiplicity of bands in the near-IR spectrum, not noticeably less than for the less symmetrical species,[2,3] and a detailed assignment of the spectrum must await further work on monomeric osmium(III) ammine compounds.[28] The UV bands in both complexes shift to higher

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energy compared to [II, II] and split into at least two components. In D_{4h} symmetry, the $e_u^2e_g^1$ excited state of the mixed-valence ion will split into four states, and transitions between the E_u ground state and each of these are allowed. It is not surprising therefore that the UV absorption for the mixed-valence species shows more structure than for the [II, II] species where only one transition ($A_{2u} \leftarrow A_{1g}$) is allowed. The shift of the MBLCT bands to higher energy is indicative of valence delocalization. In analogous weakly interacting, valence-localized systems (e.g., $[(Ru(NH_3)_5)_2(pyrimidine)]^{5+}$),[29] usually no shift or a small shift to lower energy is observed when the [II, II] species is oxidized to the [III, II]. In the case of a valence-trapped system, when the [II, II] species is oxidized to [III, II], the charge is lost from a single center. The energy the πd donor orbital is little affected while that of the ligand π^* orbital is lowered because of the increase in charge at the oxidized metal center, and thus the energy of the MBLCT is lowered. In the case of delocalized complexes, the electron is removed from an orbital that is shared by both metal centers. Therefore, the oxidation to the mixed-valence state results in a more strongly bound πd level because there is an increase in charge at both metal sites. As a result the MBLCT is shifted to higher energy.

It is of interest to compare the properties of the three mixed-valence molecules $[(Ru(NH_3)_5)_2L]^{5+}$ where L = N_2, NCCN[30] and pyrazine.[7,8] The energy and width of the near-IR transition decrease with increasing bridging-ligand size. The energy shifts are related to the splitting between $1e_g$ and $2e_u$ (Figure 5), which in turn depends on the interaction of the metals via the bridging ligands.[29,31] Qualitatively, the near-IR bands are similar in their degree of asymmetry.

In regard to the much debated question of the electronic structure and dynamics of the Creutz ion,[7,8] little can be said to clarify the description on the basis of the present work. It is to be noted, however, that the MBLCT band shifts to somewhat lower energy upon oxidation of $[(Ru(NH_3)_5)_2pyz]^{4+}$ to the mixed-valence ion.[8] This is in contrast to the shift to higher energy in the present μ-dinitrogen cases, which feature stronger metal–metal interaction. This observation is consistent with the view held by some[32,33] that the metal–metal interaction in the Creutz ion places it somewhere between the localized and completely delocalized regimes.

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Registry No. $[(Os(NH_3)_5)_2N_2]Br_5$, 81987-34-0; $[(Ru(NH_3)_5)_2N_2](BF_4)_4$, 26846-18-4; $[(Os(NH_3)_5)_2N_2]^{4+}$, 81815-34-1; $[(Ru(NH_3)_5)_2N_2]^{5+}$, 64826-69-3; $[(Ru(NH_3)_5)_2N_2]^{6+}$, 81815-33-0; $[Ru(NH_3)_5N_2]^{3+}$, 81815-32-9; $[(Os(NH_3)_5)_2N_2](p\text{-tos})_5$, 82113-28-8; $[(NH_3)_5OsN_2]Cl_2$, 20611-50-1; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1.

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Synthesis and Characterization of Mononuclear and Binuclear Ruthenium Complexes of 1,3-Bis(2-pyridylimino)isoindolines

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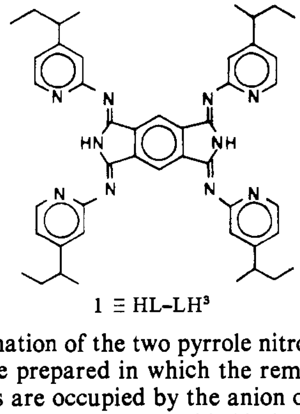
Ruthenium complexes were prepared containing the ligand 4′-MeLH, resulting from the condensation of 1,2-dicyanobenzene and 2-amino-4-methylpyridine. The ligand functions as a tridentate chelate in its anionic or neutral form. Ruthenium complexes were prepared with metal to ligand ratios of 1:1 and 1:2. The 1:1 complex of Ru(III) also contains three chlorides as ligands, Ru(4′-MeLH)Cl_3, while in the 1:2 complex, Ru$(4'\text{-MeL})_2$, the two deprotonated tridentate ligands provide a pseudooctahedral environment about the metal ion. Binuclear complexes were prepared in which the metals are bridged by the ligand made from the reaction of 1,2,4,5-tetracyanobenzene and 2-amino-4-*sec*-butylpyridine. The binucleating ligand binds two metal ions, providing three coordination sites for each, with the remaining coordination sites occupied by 4′-MeL^-. Binuclear Ru(II), Ru(III), and mixed-metal complexes were prepared. Spectral and electrochemical properties of these molecules were investigated.

Introduction

Binuclear transition-metal complexes, in which the two metals are bridged by the ligand **1**, 1,3,5,7-tetrakis(2-(4-*sec*-butylpyridyl)imino)benzodipyrrole, have been prepared and characterized.[2] The ligand **1**, HL–LH, binds two metal ions, functioning as a tridentate chelate for each metal. In the metal complexes the bridging ligand is normally present as a dianion due to deprotonation of the two pyrrole nitrogens. Binuclear complexes were prepared in which the remaining metal coordination sites are occupied by the anion of the isoindoline ligand **2**, 1,3-bis(2-(4-methylpyridyl)imino)isoindoline, re-



1 ≡ HL–LH[3]

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(3) The binucleating ligand with *sec*-butyl groups on the pyridine rings, **1**, is denoted as HL–LH. Mononucleating ligands, **2**, are denoted as RLH where substituents on the pyridine ring precede the abbreviation, e.g., 4′-MeLH. The organic molecule RLH (**2**) may function as a tridentate chelate in its neutral form or in its anionic form upon deprotonation of the pyrrole nitrogen.

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