of the methyl group proximity to the heteroaromatic system of bpy, this proximity being due to the solvophobic interaction.[55]

Comparison of the data in Table VII with those in Table X shows that the ternary complexes in which ^{1}H NMR data suggest the presence of solvophobic interaction are those whose formation is enthalpically favored and entropically unfavored. However, it should be emphasized that, in these systems, no quantitative estimation of the extent of solvophobic interaction may be made by comparing the upfield shift values for two distinct reasons. First of all, the spectrum is always the weighted mean of the contributions due to the different labile species of the observed ligand. In particular, in order to obtain acceptable percentages of the ternary complex, it is necessary to increase the zinc(II) ion concentration and, consequently, in order to avoid the hydroxide precipitation, it is necessary to slightly lower the pH, thus favoring the monoanion formation. In such species, the methyl is shifted downfield, contributing to a decrease in the upfield shift due to the intramolecular solvophobic interaction.

Second, if we also neglect the speculation on the open-form–closed-form equilibrium,[51] the upfield shift is a complex function of the electronic and geometric factors occurring in the specific system.

Concluding Remarks

Both thermodynamic parameters and the ^{1}H NMR data show that in the ternary zinc(II) complexes a solvophobic interaction occurs between the diimine heteroaromatic system and an alkyl side chain of the mono- or disubstituted malonate, provided that the side chain is long enough (at least three carbon atoms), as we have already noted in the stereoselective protonation of linear dipeptides.[64]

Usually, the stability data of ternary complexes, through the use of $\Delta \log K$ (the constant for the equilibrium $MA + MB \rightleftharpoons MAB + M$), have been correlated with the upfield shifts observed for the hydrogen atoms involved in the interaction.[65] However, in the case of copper(II) complexes, owing to the broadness of the ^{1}H NMR peaks caused by the copper(II)-promoted paramagnetic nuclear relaxation, the occurrence of intramolecular interactions between side chains has been also inferred by comparing the $\Delta \log K$ values with those of the mixed complexes, in which the length of the side chain prevents an intramolecular interaction.[54-57] Also our ternary copper(II) complexes have $\Delta \log K$ values higher than that of the ternary malonate one, but the $\Delta H°$ and $\Delta S°$ values, diagnostic in the case of zinc(II) complexes, show no occurrence of noncovalent interaction. An accidental masking effect, due to a different copper(II)–solvent interaction in the ternary complexes, can be excluded on the basis of the EPR data. Furthermore, the EPR data are in agreement with the thermodynamic data, especially in the cases of copper(II) IProMAL, DProMAL, and DBuMAL complexes. Even in the slightly tetrahedrally distorted complexes of the substituted phenanthroline, the different length and size of the alkyl chains do not give rise to significant differences in the EPR parameters. Thus, in these systems for the occurrence of intramolecular solvophobic interaction, a typical tetrahedral coordination geometry must be reached.

Acknowledgment. We thank the Ministry of Education (Rome, Italy) and CRRNSM (Palermo, Italy) for partial support of this work.

Registry No. MeMAL, 516-05-2; ProMAL, 616-62-6; IProMAL, 601-79-6; BuMAL, 534-59-8; IBuMAL, 4361-06-2; DMeMAL, 595-46-0; DProMAL, 1636-27-7; DBuMAL, 2283-16-1.

---

(64) Calì, R.; Cucinotta, V.; Impellizzeri, G.; Maugeri, M. C.; Rizzarelli, E. *Int. J. Pept. Protein Res.* **1988**, *32*, 262.

(65) Chauduri, P.; Sigel, H. *J. Am. Chem. Soc.* **1977**, *99*, 3142.

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305, and Department of Inorganic Chemistry, The University of Sydney, Sydney, NSW 2006, Australia

Reactions of Hexachloroosmate(IV) with Hydrazine Hydrate: Syntheses and Properties of Pentaammine(dinitrogen)osmium(II) Chloride and Decaammine(μ-nitrido)diosmium(IV) Chloride

Peter A. Lay[*,†] and Henry Taube[*,‡]

Received January 23, 1989

Slow addition of powdered $(NH_4)_2[OsCl_6]$ to $NH_2NH_2{\cdot}H_2O$, followed by refluxing for 10 h, results in a mixture of $[Os(NH_3)_5(N_2)]Cl_2$ and *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$. Further reaction of the mixture with $NH_2NH_2{\cdot}H_2O$ results in ~90% yield of $[Os(NH_3)_5(N_2)]Cl_2$. When the reverse addition is performed (i.e. $NH_2NH_2{\cdot}H_2O$ is added to $(NH_4)_2[OsCl_6]$), the very exothermic reaction that follows produces the previously unknown nitrido-bridged complex $[(NH_3)_5OsNOs(NH_3)_5]Cl_5{\cdot}H_2O$ in ~90% yield. This compound is a convenient starting material for the preparation of a variety of *trans,trans*-$[X(NH_3)_4OsNOs(NH_3)_4X]^{n+}$ complexes in high yields. The electronic absorption spectrum of $[(NH_3)_5OsNOs(NH_3)_5]Cl_5{\cdot}H_2O$ has been assigned with the aid of a MO diagram and a comparison of its spectrum with those of other μ-N^{3-} complexes of Ru and Os.

Introduction

Allen and co-workers first described the reaction of $NH_2NH_2{\cdot}H_2O$ with $(NH_4)_2[OsCl_6]$ under conditions that result in moderate to good yields of $[Os(NH_3)_5(N_2)]Cl_2$.[1,2] Because the dinitrogen complex is the starting material for the synthesis of a variety of pentaammine[3-12] and tetraammine[13-17] complexes, the reaction has been improved on by various workers.[3-5] In the same spirit, we have examined the reaction in more detail and also describe the results of the reverse addition of $NH_2NH_2{\cdot}H_2O$

[†] The University of Sydney.

[‡] Stanford University.

(1) Allen, A. D.; Stevens, J. R. *J. Chem. Soc., Chem. Commun.* **1967**, 1147.

(2) Allen, A. D.; Stevens, J. R. *Can. J. Chem.* **1972**, *50*, 3093-3099.

(3) Elson, C. M.; Gulens, J.; Page, J. A. *Can. J. Chem.* **1971**, *49*, 207-210.

(4) Bottomley, F.; Tong, S.-B. *Inorg. Synth.* **1976**, *16*, 9-13.

(5) Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2208-2212.

(6) Sen, J. P.; Taube, H. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 125-135.

(7) Allen, A. D.; Stevens, J. R. *Can. J. Chem.* **1973**, *51*, 92-98.

(8) Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658-7659.

Table I. Electronic Absorption Spectra and Characteristic IR Stretching Modes for the Dinitrogen and μ-Nitrido Osmium Complexes

complex	λ_{max},[a] nm	IR,[b] cm^{-1}
$[Os(NH_3)_5(N_2)]Cl_2$[c]	208 (25.1×10^3)	$\nu_{N\equiv N}$ 2022 (vs)
cis-$[Os(NH_3)_4(N_2)_2]Cl_2$[d]	222 (20.0×10^3)	$\nu_{N\equiv N}$ 2097 (vs), 2168 (vs)
$[(NH_3)_5OsNOs(NH_3)_5]Cl_5 \cdot H_2O$	248 (48×10^3), 263 sh, 384 (335), 466 (430)	$\nu_{Os\equiv N\equiv Os}$ 1100 (vs, b)
trans,trans-$[\{Cl(NH_3)_4Os\}_2N]Cl_3$[e]	242 (49.0×10^3), 265 sh (13.0×10^3)	$\nu_{Os\equiv N\equiv Os}$ 1104 (vs, b)

[a] UV/vis spectra; ϵ_{max} in M^{-1} cm^{-1} in parentheses; sh = shoulder. [b] IR spectra in KBr disks; vs = very strong; b = broad. [c] Reference 4. [d] Reference 2. [e] Reference 19.

to $(NH_4)_2[OsCl_6]$, which provides a new entry into the nitrido-bridged Os(IV) complexes.[18-20]

Experimental Section

OsO_4 (Alfa) was converted to $(NH_4)_2[OsCl_6]$ or $K_2[OsCl_6]$ by standard procedures.[21] Hydrazine hydrate (Aldrich) was used without further purification. *Caution! Hydrazine hydrate is toxic, is a suspected carcinogen, and is potentially explosive. The reactions must be performed in a well-ventilated fume hood, preferably behind a safety screen, although to the author's knowledge, no explosions have occurred with these reactions.*

$[Os(NH_3)_5(N_2)]Cl_2$. Our preparative route is an adaptation of the method of Buhr and Taube.[5] Finely powdered $(NH_4)_2[OsCl_6]$ (10 g, 22.8 mmol) is added slowly, with rapid stirring, over ~15 min to $N_2H_4 \cdot H_2O$ (90 mL) contained in a 250-mL round-bottomed flask fitted with a reflux condenser. It is essential to add the compound slowly in a finely ground form. Lumps cause locally high concentrations of $[OsCl_6]^{2-}$, which results in the formation of the nitrido-bridged complex. This impurity is not converted to the desired product under the reaction conditions. The solution is refluxed for 10 h, during which time the color changes from brown to golden yellow (due to minor impurities of the nitrido complex), and a pale yellow precipitate forms. After the solution is allowed to cool to room temperature, the solid (6–7 g) is collected on a medium-porosity frit. A further amount of compound (1–1.5 g) is precipitated by adding anhydrous ethanol (~400 mL). The remainder may be precipitated by the addition of more ethanol, but the resulting solid is a mixture comprising, as shown by the IR spectra, $[Os(NH_3)_5(N_2)]Cl_2$, *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$, and $[(NH_3)_5OsNOs(NH_3)_5]Cl_5 \cdot H_2O$. The first two fractions are combined and refluxed with a second amount (90 mL) of $N_2H_4 \cdot H_2O$, as described before. The precipitate that is obtained after this reflux is checked by IR spectroscopy for the presence of *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$ ($\nu_{N\equiv N}$ 2097 and 2168 cm^{-1}, strong, in KBr disks) as an impurity. If it is absent, and the nitrido-bridged complex is also absent ($\nu_{Os\equiv N\equiv Os}$ 1100 cm^{-1}, strong and broad), further purification is not necessary. A third reflux may be required in order to remove all of the *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$ impurity. The yield is 6.8–8.1 g (80–95%). Anal. Calcd for $Cl_2H_{15}N_7Os$: Cl, 18.95; H, 4.04; N, 26.20. Found: Cl, 19.01; H, 4.20; N, 26.38.

When $K_2[OsCl_6]$ is used instead of $(NH_4)_2[OsCl_6]$ as a reactant, somewhat higher yields of *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$ appear to be present after the first reflux. However, this is removed in the second and third refluxes, as described above.

If *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$ is the desired product, the solid obtained after the first reflux is used directly in the synthesis of the bis(dinitrogen) complex from $[Os(NH_3)_5(N_2)]Cl_2$.[15]

$[(NH_3)_5OsNOs(NH_3)_5]Cl_5 \cdot H_2O$. Finely powdered $(NH_4)_2[OsCl_6]$ (10 g, 22.8 mmol) is placed in a 250-mL round-bottomed flask and is cooled in an ice bath. $N_2H_4 \cdot H_2O$ (90 mL) is added dropwise over 0.5–1 h. (*Caution! This is a very exothermic reaction. The hydrazine hydrate must be added very slowly at first, and the reaction should be performed in a well-ventilated fume hood.*) Once the addition is complete, the solution is stirred and refluxed as described in the previous section. After the solution is allowed to cool to room temperature and then to cool in an ice bath, the golden yellow precipitate is collected (3.7 g). A second (3.6 g) and a third crop (0.9 g) are obtained by the addition of ethanol (200 mL and 2 L, respectively) to the filtrate. The total yield is 8.2 g (95%). The purities of the three crops are checked by IR spectroscopy, which reveals similar characteristics for all three. Usually, a very small amount of $[Os(NH_3)_5(N_2)]Cl_2$ is observed as an impurity, with the initial crops containing slightly more of the dinitrogen complex (consistent with its lower solubility). Anal. Calcd ($Cl_5H_{32}N_{11}OOs_2$) Cl, H, N. IR, cm^{-1} (KBr): 3490 br, m; 3240 br, vs; 3160 br, vs; 1610 br, s; 1468 w; 1342 br, s; 1099 s; 939 w; 840 sh; 800 s; 580 w; 528 m; 470 br, m. Upon prolonged storage, the compound decomposes, as evidenced by a color change from golden yellow to dark brown.

Chromatographic Separation of μ-Nitrido and Dinitrogen Complexes. Precipitated fractions that contain mixtures of dinitrogen and μ-nitrido complexes obtained in the previous syntheses are separated and purified by the use of cation-exchange chromatography, as follows. A sample of the solid (0.5 g) is dissolved in 0.1 M CF_3CO_2H (30 mL) and sorbed onto a column of Dowex 50W-X2 (10 cm × 2 cm). The column is washed with water (100 mL), and the Os(II) complexes are eluted with 2 M CF_3CO_2H (500 mL) as a white band. The eluate is evaporated to dryness by using a rotary evaporator (40 °C). The μ-nitrido complex is eluted with 5 M HCl (200 mL) and isolated in a similar manner.

UV, visible, and near-IR spectra were recorded by using a Beckman Model 5270 spectrophotometer. IR spectra were recorded as KBr disks by using a Perkin-Elmer Model 621 infrared spectrometer. All microanalyses were performed by the Stanford University Microanalytical Service.

Results

The slow addition of $(NH_4)_2[OsCl_6]$ to a rapidly stirred solution of hydrazine monohydrate results in $[Os(NH_3)_5(N_2)]Cl_2$ and *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$ as the major products. If care is not taken to eliminate local high concentrations of $[OsCl_6]^{2-}$, then $[(NH_3)_5OsNOs(NH_3)_5]Cl_5 \cdot H_2O$ also becomes a significant byproduct. Refluxing the mixture of dinitrogen complexes with fresh hydrazine hydrate converts *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$ into the desired complex, $[Os(NH_3)_5(N_2)]Cl_2$. This operation also eliminates traces of the nitrido-bridged complex, since it is much more soluble in hydrazine hydrate than either of the dinitrogen complexes.

Data on the electronic transitions and characteristic IR absorptions of these complexes are summarized in Table I. Both dinitrogen complexes are almost colorless, and the slight yellow color is ascribable to the MLCT transitions tailing into the visible region. A yellow to brown coloration that is often attributed to the pentaammine–dinitrogen complex is due to an admixture with the nitrido-bridged complex.

When hydrazine hydrate is added to solid $(NH_4)_2[OsCl_6]$, an extremely exothermic reaction ensues, resulting in a yellow-brown solution. If the addition is performed slowly, in a dropwise fashion, $[(NH_3)_5OsNOs(NH_3)_5]Cl_5 \cdot H_2O$ is formed in ~90% yield. This compound has not been reported previously, but it was characterized by microanalysis, the very strong $Os{\equiv}N{\equiv}Os$ stretch at 1100 cm^{-1}, and the typical UV/vis absorption spectra of the nitrido-bridged complexes (they are dominated by a charge-transfer band at 248 nm).[19] The presence of a water of crystallization is established by the presence of the O–H stretch at 3490 cm^{-1} in the IR spectrum. No prominent electronic transitions are observed in the near-IR region of the electronic absorption spectrum. Only the weak O–H and N–H combination bands at 4587, 4789, 5000, and 5215 cm^{-1} are observed in this region. Similarly, the weak combination and overtone bands are observed in the near-IR spectrum of $[Os(NH_3)_5(N_2)]Cl_2$ at 4587, 4836, and 6361 cm^{-1}. The spectroscopic results are summarized in Table

---

(9) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Synth.* **1986**, *24*, 269–277.
(10) Richardson, D. E.; Sen, J. P.; Buhr, J. D.; Taube, H. *Inorg. Chem.* **1982**, *21*, 3136–3140.
(11) Magnuson, R. H.; Lay, P. A.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 2507–2509.
(12) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.*, in press.
(13) Scheidegger, W.; Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 3263–3264.
(14) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1972**, *94*, 7213–7214.
(15) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5129–5136.
(16) Buhr, J. D.; Winkler, J. R.; Taube, H. *Inorg. Chem.* **1980**, *19*, 2416–2425.
(17) Lay, P. A.; Magnuson, R. H.; Taube, H. To be submitted for publication.
(18) Dwyer, F. P.; Hogarth, J. W. *Proc. R. Soc. N. S. W.* **1950**, *84*, 117–122.
(19) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1970**, 1117–1125.
(20) Hall, J. P.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2410–2414 and references therein.
(21) Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1957**, *5*, 206–207.

Table II. Assignments of Electronic Absorption Spectra of μ-Nitrido Complexes

complex	assignments[a]			
	$\delta \rightarrow \pi^*$	$e_g \rightarrow \pi^*$	$e_g \rightarrow d_{z^2}$	$e_g \rightarrow d_{x^2-y^2}$
$[(NH_3)_5OsNOs(NH_3)_5]^{5+}$	*b*	40.3 (48.0)	38.0 sh	26.0 (0.34), 21.5 (0.43)
[{*trans*-$[Cl(NH_3)_4Os]\}_2N]^{3+}$	52.6 (7.0)	41.3 (49.0)	37.7 (13.0)	*c*, *d*
[{*trans*-$[H_2O(Cl)_4Os]\}_2N]^{3-}$	51.0 (20.0)	36.6 (34.6)	*c*	*c*, *d*
[{*trans*-$[H_2O(Cl)_4Ru]\}_2N]^{3-}$	48.5 (28.3)	34.0 (20.8)	*c*	*c*, *d*
[{*trans*-$[H_2O(Br)_4Ru]\}_2N]^{3-}$	44.4 (61.0)	32.1 (32.4)	*c*	*c*, *d*

[a] Energies in 10^3 cm^{-1}; extinction coefficients in 10^3 M^{-1} cm^{-1} in parentheses. [b] This transition is observed as a rising transition in the far-UV region. [c] Not reported. [d] Reference 19.

I and are compared with those for *trans*,*trans*-$[Cl(NH_3)_4OsNOs(NH_3)_4Cl]Cl_3$.[19]

The trans ammine ligands of the $[(NH_3)_5OsNOs(NH_3)_5]^{5+}$ ion are relatively labile, and the complex undergoes a variety of substitution reactions to give the known class of compounds *trans*,*trans*-$[X(NH_3)_4OsNOs(NH_3)_4X]^{n+}$ in essentially quantitative yields. This also serves to establish the nature of the initial product.

Discussion

The complete stoichiometry of the reactions that produce $[Os(NH_3)_5(N_2)]^{2+}$ has not been investigated and may be too complex to yield useful information without exhaustive study. The complication is that there is disproportionation of N_2H_4 (according to reaction 1), in addition to the consumption of N_2H_4 to reduce

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad (1)$$

$[OsCl_6]^{2-}$, and the consumption of N_2H_4 to produce the ingredients needed to convert the Os(II) intermediates to the final products ($[Os(NH_3)_5(N_2)]^{2+}$ and *cis*-$[Os(NH_3)_4(N_2)_2]^{2+}$). One of the interesting mechanistic questions is concerned with whether the Os–N bonds are established by hydrazine or by the products of the independent disproportionation of N_2H_4. Little that is useful can be said at this point on the basis of our limited information. As to the conversion of *cis*-$[Os(NH_3)_4(N_2)_2]^{2+}$ to $[Os(NH_3)_5(N_2)]^{2+}$: it is known from other work[14-17] that one N_2 is rather readily lost from *cis*-$[Os(NH_3)_4(N_2)_2]^{2+}$, which then opens up a coordination site to attack by NH_3 or N_2H_4.

There is some indication that the yield of the tetraammine complex compared to the pentaammine complex is greater when $K_2[OsCl_6]$ rather than $(NH_4)_2[OsCl_6]$ is used as the source of osmium. This suggests that the NH_4^+ counterion is used as a source of NH_3. Although the proton affinity of NH_3 ($pK_a(NH_4^+) = 9.24$) is larger than that of $N_2H_5^+$ ($pK_a = 7.93$) in water, the ammonium ion will be substantially deprotonated because hydrazine is in considerable excess. If the different results obtained for $K_2[OsCl_6]$ and $(NH_4)_2[OsCl_6]$ are due to the nature of the cation, this suggests that large amounts of free ammonia are not produced by N_2H_4 disproportionation during the initial reaction phase.

The complex $[(NH_3)_5OsNOs(NH_3)_5]^{5+}$ is a byproduct of the reactions under conditions designed to yield $[Os(NH_3)_5(N_2)]^{2+}$. It becomes the major product when the neat reagents are added in the reverse order. From a reaction run under such conditions, $[(NH_3)_5OsNOs(NH_3)_5]Cl_5{\cdot}H_2O$ can be recovered in ~90% yield. The change in stoichiometry may of course depend also on the difference in the reaction temperature. When $N_2H_4{\cdot}H_2O$ is added to $(NH_4)_2[OsCl_6]$, the reaction mixture becomes very hot during the mixing procedure.

The species $[(NH_3)_5OsNOs(NH_3)_5]^{5+}$ has not hitherto been described. In earlier work, entry into the *trans*,*trans*-$[X(NH_3)_4OsNOs(NH_3)_4X]^{n+}$ class of complexes was gained by the reaction of $[OsCl_6]^{2-}$ with $NH_3(aq)$ under forcing conditions. This resulted in moderate yields of *trans*,*trans*-$[Cl(NH_3)_4OsNOs(NH_3)_4Cl]Cl_3$.[18-20] The dichloro complex was also prepared in essentially quantitative yields by substitution of $K_3[Os_2N(Cl)_8(OH_2)_2]$ with aqueous ammonia at elevated temperatures.[19] The spectra of the decaammine and octaammine complexes are similar (Table II).

The trans position of the octaammine nitrido-bridged complexes is relatively labile compared to the cis position, and this enables a range of X^- ligands to be substituted selectively in the trans position.[19] The decaammine complex is similarly substituted in the trans position to give the octaammine series of complexes, and it thus provides a convenient and high-yielding route to this class of binuclear ions.

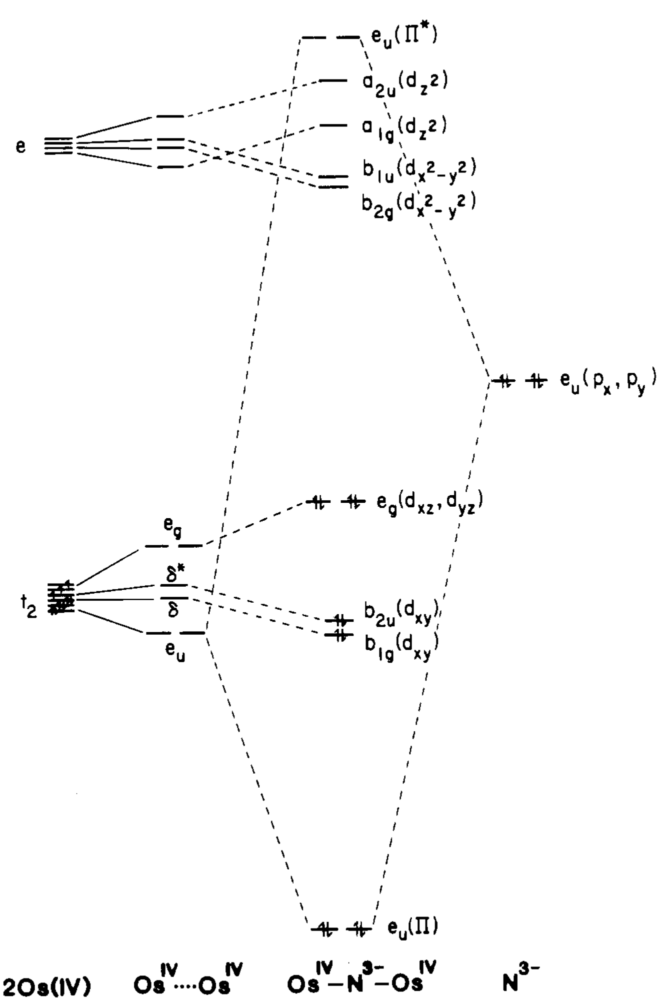

Figure 1. Qualitative molecular orbital description of bonding within the $Os^{IV}–N^{3-}–Os^{IV}$ moiety.

The conditions under which the nitrido-bridged complex forms give clues to ways to maximize the yields of the dinitrogen complexes. Clearly, localized high concentrations of $[OsCl_6]^{2-}$ need to be avoided in order to prevent condensation of the initial products to form the nitrido-bridged complexes. Thus, slow addition to a rapidly stirred solution and fine grinding of $(NH_4)_2[OsCl_6]$ serve to maximize the yields of the desired dinitrogen products.

The observation that the reactions of $[OsCl_6]^{2-}$ with $NH_2NH_2{\cdot}H_2O$ lead to the starting materials for three classes of Os complexes, viz. pentaammine, tetraammine, and μ-nitrido complexes, makes it a very useful reaction, even more so because it can be tuned so that the desired products are obtained in high yields.

Electronic Structures of the Nitrido-Bridged Complexes. The μ-nitrido osmium(IV) species have D_{4h} symmetry. They are strongly coupled electronically and are diamagnetic.[19] Generally, Os(IV) complexes are paramagnetic, and spin–orbit coupling within the t_2^4 electronic configuration gives rise to internal t_2^4 transitions in their near-IR spectra.[16,22] The absence of such transitions in the nitrido-bridged complexes is consistent with the diamagnetism, since the diamagnetic ground state will not be affected by spin–orbit coupling. Strong coupling between the osmium centers via the p_x and p_y orbitals of the N^{3-} ligand gives rise to strong Os≡N triple bonds. The molecular orbital description of the bonding (Figure 1) is similar to that initially put forward by Griffith (for other μ-nitrido complexes)[19] and Dunitz and Orgel (for μ-oxo complexes).[23] Interactions between the ligand p_x and p_y orbitals (e_u symmetry) with the e_u combinations of the d_{xz} and d_{yz} metal ion orbitals result in strongly bonding π (e_u) and strongly antibonding π^* (e_u) combinations of orbitals. The antibonding e_g (d_{xz}, d_{yz}) combinations of the d orbitals of the metal ions remain relatively unaffected, as they do not have the correct symmetry to interact with the p orbitals of the bridging nitrido ligand. In this qualitative picture, the e_g (d_{xz}, d_{yz}) set of orbitals is the HOMO level and is filled, which gives rise to the observed diamagnetism. The strong tetragonal distortion that is induced by the strong Os≡N≡Os bonds will result in a further raising of the energy of the antibonding e_g (d_{xz}, d_{yz}) combinations, while the b_{2g} ($d_{x^2-y^2}$) and b_{1u} ($d_{x^2-y^2}$) combinations are lowered in energy. The intensities of the low-energy transitions at 21 500 and 26 000 cm^{-1} suggest that they are d–d in nature, and they have been assigned as e_g (d_{xz}, d_{yz}) → $d_{x^2-y^2}$, d_{z^2} transitions. An intense metal to ligand charge-transfer e_g (d_{xz}, d_{yz}) → e_u (π^*) transition that is *z*-allowed is expected, and this has been assigned to the intense transition at 40 300 cm^{-1}. The nature of the shoulder at 38 000 cm^{-1} is less certain but may be a symmetry-allowed e_g (d_{xz}, d_{yz}) → d_{z^2} transition or a δ,δ^* (d_{xy}) → $d_{x^2-y^2}$, d_{z^2} transition. A further intense charge transfer is expected between the δ (b_{1g}) combination of the d_{xy} orbitals and the e_u (π^*) orbitals. It is anticipated that this transition will be lower in intensity than the e_g → e_u transition, but it is *x*,*y*-allowed. Indeed, an intense transition is observed at 52 600 cm^{-1} for *trans,trans*-$[(Cl)(NH_3)_4OsNOs(NH_3)_4(Cl)]^{3+}$, and the rising absorption in the far-UV spectrum of $[(NH_3)_5OsNOs(NH_3)_5]^{5+}$ indicates that a similar transition occurs here. The charge-transfer transitions of the ruthenium complexes[20] are at lower energies than those of their osmium analogues. Since interactions between the ruthenium orbitals and the ligand orbitals are expected to be weaker, the difference in the energy between the e_u (π^*) and e_g orbitals would be lower. This is consistent with the assignments that have been made here.

Table II contains the tentative assignments of the transitions observed in the osmium and ruthenium nitrido complexes. More detailed analyses will require polarized spectral data and semiquantitative calculations of the energies of the electronic states.

Acknowledgment. P.A.L. gratefully acknowledges the receipt of a CSIRO Postdoctoral Fellowship and, in part, support from the Australian Research Grants Scheme. We are also grateful for support from National Science Foundation Grant No. CHE79-08633 and National Institutes of Health Grant No. GM13638-17.

---

(22) Piepho, S. B.; Dickinson, J. R.; Spencer, J. A.; Schatz, P. N. *Mol. Phys.* **1972**, *24*, 609–630.

(23) Dunitz, J. D.; Orgel, L. E. *J. Chem. Soc.* **1953**, 2594–2596.

Contribution from the Institut für Anorganische und Analytische Chemie, Universität Freiburg,
D-7800 Freiburg, FRG, and Laboratoire de Cristallochimie, Université de Rennes, F-35042 Rennes, France

Intramolecular Conversion of an Azoalkane Ligand to Two Nitrene Ligands on a Triiron Cluster

Edward J. Wucherer,[†] Miklos Tasi,[†] Bernhard Hansert,[†] Anne K. Powell,[†] Maria-Theresa Garland,[‡]
Jean-Francois Halet,[‡] Jean-Yves Saillard,[‡] and Heinrich Vahrenkamp*[,†]

Received February 16, 1989

The azoalkanes R_2N_2 (**1**; R = Et, Pr) have been reacted with $Fe(CO)_3(c\text{-}C_8H_{14})_2$ or $Fe_3(CO)_{12}$ to yield the azoalkane complexes $Fe_2(CO)_6(\mu\text{-}\eta^2\text{-}R_2N_2)$ (**2**) and $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}R_2N_2)$ (**3**). Thermolysis of the clusters **3** in solution has resulted in N–N cleavage without loss of CO to form the nitrene-bridged clusters $Fe_3(CO)_9(\mu_3\text{-}NR)_2$ (**4**). From the reactions of azobenzene with the iron carbonyl starting materials only products resulting from N–N cleavage have been isolated. The crystal and molecular structures of $Fe_2(CO)_6(\mu\text{-}\eta^2\text{-}Et_2N_2)$ (**2a**), $Fe_3CO)_9(\mu_3\text{-}\eta^2\text{-}Et_2N_2)$ (**3a**), and $Fe_3(CO)_9(\mu_3\text{-}NEt)_2$ (**4a**) have been determined and refined to *R* values of 0.076, 0.046, and 0.058, respectively. (**2a**, monoclinic, $P2_1/c$, *a* = 7.541 (5) Å, *b* = 14.609 (5) Å, *c* = 14.205 (4) Å, β = 106.70 (4)°, *Z* = 4; **3a**, monoclinic, $P2_1/n$, *a* = 8.860 (3) Å, *b* = 12.900 (2) Å, *c* = 16.147 (2) Å, β = 92.68 (2)°, *Z* = 4; **4a**, orthorhombic, *Pbca*, *a* = 27.214 (8) Å, *b* = 12.391 (8) Å, *c* = 11.140 (6) Å, *Z* = 8). With use of a mixture of the N–Et and N–Pr compounds it was ascertained that the azoalkane–nitrene cleavage is intramolecular. It is inhibited under a CO atmosphere. Kinetic analysis has shown the reaction to be approximately first order with an activation energy of ca. 35 kcal/mol. The observations can be explained by CO elimination as the first step in the rearrangement. A molecular orbital analysis with EH calculations has led to two possible pathways. One is a simple rearrangement between seven-SEP nido-type square-based-pyramidal isomers and involves a reaction intermediate or transition state in which one nitrogen atom caps an Fe_3N distorted square. The other one, which is fully consistent with the kinetic experiments, involves two intermediates with a six-SEP closo-type trigonal-bipyramidal structure; the first, resulting from CO loss and an R_2N_2 slippage, has an Fe_2N pyramidal base, while the second, due to rearrangement and N–N cleavage, has an Fe_3 pyramidal base. The final reaction step, readdition of a CO ligand, involves the opening of one Fe–Fe bond.

Introduction

Our investigations on the activation of multiply bonded organic substrates in the ligand sphere of clusters have so far been focused on C–C- and C–N-bonded systems.[1] Obvious extensions offer themselves in the form of C–O- and N–N-bonded systems. Whereas the former of these (acyl, formyl, alkoxy, alkoxycarbene) are well established in organometallic cluster chemistry, the latter (azo compounds, hydrazides) have not been used in great detail as ligands or substrates in cluster-centered reactions. In our opinion they have potential for basic cluster reactions as well as for organic reactions in the ligand sphere, due to their electron-rich

---

[†] Universität Freiburg.

[‡] Université de Rennes.

(1) Vahrenkamp, H. In *Organometallics in Organic Synthesis*; Werner, H., Erker, G., Eds.; Springer-Verlag: Heidelberg, FRG, 1989; p 235.