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Pyrazine-Bridged Complexes. Synthesis of and Spectroscopic Studies on Binuclear Pyrazine Complexes of Osmium, Ruthenium, and Rhodium Ammines

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The compound $[(NH_3)_5Os(pz)Os(NH_3)_5]Cl_6$ is obtained (~40% yield) by the reaction of pyrazine (pz) with a small excess of $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ in dry acetone for 8 days and, more conveniently, by the reaction of $[Os(NH_3)_5(pz)]^{2+}$ with $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ in acetone. The best method of preparation of the binuclear ion involves the in situ generation of $[Os(NH_3)_5(pz)]^{2+}$ by reducing a mixture of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ and pz (2:1 molar mixture) in a weakly coordinating solvent. The comproportionation constant, 1.0×10^{13} (0.1 M HCl, 22 °C), obtained from electrochemical measurements ($E°(6+/5+)$ = 0.32 V and $E°(5+/4+)$ = -0.44 V vs NHE) is 7 orders of magnitude greater than that observed for the ruthenium analogue. The mixed-valence ion is thought to be delocalized, since the transitions arising from the effects of spin–orbit coupling on the ground electronic state, which are observed for all mononuclear and binuclear Os(III) complexes (1500-2100 nm), are absent. Instead, intense electronic transitions (ϵ ~(3–4) $\times$ 10^3 M^{-1} cm^{-1}) are present in the normal-IR region (3000-3400 cm^{-1}), which have been assigned the spin–orbit transitions of the delocalized complex. The very low intensity of the symmetric pyrazine mode in the IR spectrum (1600 cm^{-1}) is also consistent with a symmetric delocalized description. The synthesis and properties of the binuclear complexes $[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{n+}$ (n = 4, 5, 6), $[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{m+}$ (m = 3, 4, 5), $[(NH_3)_5Os(pz)Rh(NH_3)_5]^{m+}$ (m = 6, 5), and $[(NH_3)_5Rh(pz)Rh(NH_3)_5]^{6+}$ are also described, in addition to improved syntheses of the binuclear Ru_2 and RuRh complexes. The mixed-valence ion $[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{4+}$ has spectral properties similar to those of $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$ and is believed to possess an electronic structure close to the delocalized description. By contrast, $[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$ has properties typical of a valence-localized species. The $[(NH_3)_5Rh(pz)Rh(NH_3)_5]^{5+}$ ion is very unstable and rapidly decomposes to form $[Rh(NH_3)_5(pz)]^{3+}$ and an uncharacterized product. The species $[(NH_3)_5Os(pz)Rh(NH_3)_5]^{5+}$ also is unstable and appears to undergo a slow intramolecular reduction of Rh(III) by Os(II).

Introduction

Since the initial preparation of the Creutz–Taube species (I),[1,2] the electronic descriptions of the 5+ mixed-valence ion have been the center of much controversy.[3–6] In analogous Ru and Os

$$[(NH_3)_5RuN\bigcirc NRu(NH_3)_5]^{n+} \qquad n = 4,5,6$$

I
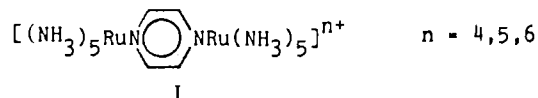
complexes, the electrostatic charge types are identical, and the Franck–Condon barriers to optical electron transfer in a valence-trapped approximation (class II) are expected to be dominated by solvent effects and thus to be comparable. Apart from the contributions of spin–orbit coupling, the differences in properties are ascribable to the differences in the extent of electron delocalization. The moderately intense transitions brought about by the effects of spin–orbit coupling on the ground electronic state of the Os(III) complexes occur in the near-IR region of the spectrum.[7–9] Since these are absent for Os(II), they can be very useful diagnostic tools for determining whether or not a valence-delocalized description is appropriate for mixed-valence osmium ions.[10] To gain an improved understanding of the much studied ruthenium complexes,[1–6] and because of their inherently interesting physical properties, we undertook the study of μ-pyrazine binuclear osmium ammine complexes.

Apart from the μ-dinitrogen ammine complexes,[11–16] no osmium complexes analogous to the ruthenium binuclear species had been investigated, chiefly because of the lack of suitable synthetic methods. Recently, we reported the preparation of the useful synthetic intermediate $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$,[8] from which a large variety of mononuclear[8,17] and binuclear[15,18–20] species (including the binuclear pyrazine-bridged ions)[18] have been prepared. In this paper the syntheses and properties of the binuclear pyrazine complexes are described and discussed.

Experimental Section

UV, visible, and near-IR spectra were recorded on a Beckman Model 5270 spectrophotometer. Spectra of air-sensitive complexes were obtained by reducing the complexes (Zn(Hg) or $[Ru(NH_3)_6]^{2+}$) in a Zwickel flask[21,22] under an argon atmosphere, followed by transferral (under argon) to a Beckman spectrophotometer cell. Alternatively,

milder and more selective reductions were performed with the use of an electrochemical Zwickel flask[23] and a Hg pool or a Pt basket as a working electrode. IR and near-IR spectra were recorded with the use of KBr or CsI disks and either Perkin-Elmer Model 621 or Nicolet 7199 FT infrared spectrophotometers. Electrochemical experiments were performed by using a three-electrode system and a PAR 173 potentiostat. The potentiostat was used in conjunction with a PAR 179 universal programmer for cyclic voltammetric measurements and a PAR 179 digital coulometer for controlled-potential electrolysis. A BAS 100 electrochemical analyzer was used for some experiments. All argon used was deoxygenated and dried by using Cr^{2+} and H_2SO_4 bubblers, respectively. The electrochemical experiments were performed with the use of a glassy-carbon working electrode and a SCE or a Ag/AgCl/saturated KCl reference electrode, with 0.1 M HCl as the supporting electrolyte. Experiments on the binuclear rhodium complex were performed at a

(1) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988-3989.
(2) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086-1094.
(3) Day, P. *Int. Rev. Phys. Chem.* **1981**, *1*, 149-193.
(4) Hush, N. S. *Mixed Valence Compounds*; Brown, D. B., Ed.; Reidel: Dordrecht, Holland, 1980; p 151.
(5) Wong, K. Y.; Schatz, P. N. *Prog. Inorg. Chem.* **1983**, *28*, 369-449.
(6) Creutz, C. *Prog. Inorg. Chem.* **1981**, *30*, 1-73.
(7) Sen, J.; Taube, H. *Acta Chem. Scand., Ser. A.* **1979**, *A33*, 125-135.
(8) Lay, P. A.; Magnuson, R. H.; Sen, J. P.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658-7659.
(9) Dubicki, L.; Ferguson, J.; Krausz, E. R.; Lay, P. A.; Maeder, M.; Taube, H. *J. Phys. Chem.* **1984**, *88*, 3940-3941.
(10) Dubicki, L.; Ferguson, J.; Krausz, E. R.; Lay, P. A.; Maeder, M.; Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1985**, *107*, 2167-2171. Also, manuscripts in preparation.
(11) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5129-5136.
(12) Lazarus, M. S.; Sham, T. K. *J. Am. Chem. Soc.* **1979**, *101*, 7622-7623.
(13) Richardson, D. E.; Sen, J. P.; Buhr, J. D.; Taube, H. *Inorg. Chem.* **1982**, *21*, 3135-3140.
(14) Bomben, K. D.; Jolly, W. L.; Magnuson, R. H.; Richardson, D. E., to be submitted for publication.
(15) Lay, P. A.; Magnuson, R. H.; Taube, H., to be submitted for publication.
(16) Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2208-2212.
(17) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Chem.*, in press.
(18) Magnuson, R. H.; Lay, P. A.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 2507-2509.
(19) Lay, P. A.; Taube, H., to be submitted for publication.
(20) Lay, P. A.; Magnuson, R. H.; Taube, H., submitted for publication.
(21) First described by: Zwickel, A. M. Ph.D. Thesis, University of Chicago, 1959. Also, appearing in more accessible form in ref 22.
(22) Kuehn, C.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689-702.
(23) Lay, P. A., submitted for publication in *J. Chem. Educ.*

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PAR 303 static mercury-drop electrode in 0.1 M NaCl. The solvents sulfolane and triethyl phosphate were distilled under reduced pressure prior to their use. Acetone (AR grade) was dried over 4-Å molecular sieves for at least 24 h.

$(NH_4)_2OsCl_6$ was prepared from OsO_4 (Alfa) by the literature procedure[24] and converted to $[Os(NH_3)_5N_2]Cl_2$ in ~90% yield by an improvement[25,26] of the published procedures.[27-29] This complex was oxidized in anhydrous trifluoromethanesulfonic acid by Br_2 to give an essentially quantitative yield of $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$.[8,17,25] $[Ru(NH_3)_5Cl]Cl_2$ was prepared from $[Ru(NH_3)_6]Cl_3$[30,31] (Matthey Bishop). $[Ru(NH_3)_5Cl]Cl_2$ and $[Rh(NH_3)_5Cl]Cl_2$ (Alfa) were converted to their triflato complexes by following the published procedures.[32-33] *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$ was prepared by Magnuson's variation[34] of the original method[35] and was converted to *cis*-$[Os(NH_3)_4(N_2)(pz)]Cl_2$.[34] The BPh_4^- salt was prepared by metathesis with $NaBPh_4$. *cis*-$[Os(NH_3)_4(Cl)(pz)]Cl_2$ was obtained by air oxidation of *cis*-$[Os(NH_3)_4(N_2)(pz)]Cl_2$ in aqueous HCl.[34] $[Os(NH_3)_5(pz)](CF_3SO_3)_3$,[8] $[Ru(NH_3)_5(pz)](CF_3SO_3)_3$, and $[Rh(NH_3)_5(pz)](CF_3SO_3)_3$ were obtained by recently reported methods.[17]

Separations of binuclear and mononuclear complexes were performed with SP-Sephadex C-25 (H⁺ form) cation-exchange resin. The mononuclear complexes were eluted with 0.3 M HCl, while the binuclear species were eluted with 1 M HCl. Rotary evaporation of the HCl eluates (20–40 °C) resulted in the precipitation of crystalline samples of the binuclear complexes as their chloride salts. The columns were quickly rinsed with water after elution of the complexes with acid in order to minimize acid-catalyzed decomposition of the resin.

$[(NH_3)_5Os(pz)Os(NH_3)_5]Cl_6 \cdot H_2O$. Method 1. $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (1.00 g, 1.38 mmol) and pz (43.0 mg, 0.54 mmol) were dissolved in dry acetone (3–4 mL) contained in a 15-mL test tube. A micro magnetic stirrer was placed in the tube, which was then sealed. The mixture was allowed to react for 8 days at room temperature with constant stirring. During this time, the solution turned black. The test tube was opened, and the contents were diluted with 0.2 M HCl (100 mL). After the complexes were sorbed onto a column of SP-Sephadex C-25, the mononuclear and binuclear complexes were separated as described. Two binuclear complexes were eluted; a purple, minor fraction trailed the dark brown band of the desired complex. The pyrazine-bridged complex was isolated in 40% yield (based on pz, the limiting reagent) as the chloride salt. Anal. $(C_4H_{36}N_{12}Cl_6OOs_2)$ C, H, N. The compound may be recrystallized from aqueous solutions of 4-toluenesulfonic acid (TosH) to give quantitative yields of the tosylate salt $[(NH_3)_5Os(pz)Os(NH_3)_5](Tos)_6 \cdot H_2O$. Anal. $(C_{46}H_{78}N_{12}O_{19}S_6Os_2)$ C, H, N.

The purple binuclear species is under investigation and is believed to be a nitrido-bridged species. Microanalytical data showed one pz group per osmium, and C, H, N, and Cl analysis fitted the following formula. Anal. $(C_8H_{39}N_{12}O_5Cl_6Os_2)$ C, H, N, Cl.

The N-deuterated complex was prepared by deuterium exchange of the ammine hydrogens. $[(NH_3)_5Os(pz)Os(NH_3)_5]Cl_6$ (30 mg) was dissolved in 3–4 mL of D_2O with stirring. A solution of 0.01 M Li_2CO_3 (1 mL) in D_2O was added, and the mixture was stirred for 40 s. It was acidified by the addition of 15 drops of 12 M DCl in D_2O with stirring. After it was cooled on ice for 15 min, the resultant dark brown precipitate (17.6 mg) was collected by filtration, washed with ethanol and ether, and air-dried. If the mixture is allowed to stand for too long under the basic

conditions, considerable hydrolysis occurs, yielding the mononuclear pyrazine complex.

$[(NH_3)_5Os(pz)Os(NH_3)_5]Cl_6 \cdot H_2O$. Method 2. $[Os(NH_3)_5(pz)](CF_3SO_3)_3$ (0.1 g) and $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.1 g, 0.14 mmol) were dissolved in dry distilled sulfolane (1 mL, 30 °C) contained in a 5-mL test tube. The tube was sealed with a serum cap and was heated at 80 °C for 1 day while the solution was being stirred rapidly. Separation of the complexes, performed as before, yielded 23 mg (21%) of the desired product, with no detectable amount of the purple impurity. The purity of the product was established by the comparison of its spectral and electrochemical properties with the sample reported in the previous preparation. The use of triethyl phosphate as a solvent resulted in similar yields of the binuclear pyrazine-bridged complex, but considerable quantities of $[Os(NH_3)_5(Etpz)]^{4+}$ (Etpz = 1-ethylpyrazinium) were also formed. The $[Os(NH_3)_5(Etpz)]^{4+}$ byproduct was identified from the similarity of its spectral properties and its elution behavior[8,17] with those of $[Os(NH_3)_5(Mepz)]^{4+}$.

$[(NH_3)_5Os(pz)Os(NH_3)_5]Cl_6 \cdot H_2O$. Method 3. $[Os(NH_3)_5(pz)](CF_3SO_3)_3$ (0.1 g) in AR acetone (5 mL dried over 4-Å molecular sieves) was reduced under Ar either by Zn(Hg) in a Zwickel flask or by a Pt electrode (and 0.1 M $Me_4NCF_3SO_3$ as the supporting electrolyte) in an electrochemical Zwickel flask.[23] After reduction for 0.5 h, the solution was transferred into a degassed solution of $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.1 g, 0.1 mmol) in acetone (2 mL), and the solution was heated at 50 °C for 4 h under Ar. After dilution to 200 mL with 0.05 M HCl, the solution was oxygenated for 1 h and then chromatographed as before. The yield was somewhat variable (40–80%), the variability presumably caused by base-catalyzed reactions in the presence of water.

$[(NH_3)_5Os(pz)Os(NH_3)_5]Cl_6 \cdot H_2O$. Method 4. $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.20 g, 0.28 mmol) and pz (10 mg, 0.13 mmol) were dissolved in acetone solutions (AR, 10 mL) containing 0.1 M $Me_4NCF_3SO_3$ or 0.1 M $NaCF_3SO_3$. The solution was placed in an electrolysis cell containing a Pt-mesh basket as a working electrode. The reference and auxiliary electrodes were separated from the working electrode by the use of a salt bridge containing the acetone/electrolyte solution. After the solution was degassed for 15 min, controlled-potential electrolysis was performed at −0.50 V vs SCE. At this potential, $[Os(NH_3)_5(pz)]^{3+}$ is reduced to $[Os(NH_3)_5(pz)]^{2+}$ and the solution darkened rapidly due to the formation of the 2+ ion and $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$. The solution was maintained at this potential for 1–2 h and was then diluted with 0.05 M HCl (200 mL). A stream of air or oxygen was passed through the solution for 1 h. The complexes were sorbed onto a column of SP-Sephadex C-25 and chromatographed as before. The yield was 95–100 mg (85–90% based on pz).

$[(NH_3)_5Os(pz)Os(NH_3)_5](Tos)_5 \cdot 4H_2O$. Method 1. Into a sample of $[(NH_3)_5Os(pz)Os(NH_3)_5]Cl_6 \cdot H_2O$ dissolved in deaerated 0.01 M HTFMS was injected a solution of $[Ru(NH_3)_6]^{2+}$ (20% molar excess, obtained by the Zn(Hg) reduction of $[Ru(NH_3)_6]^{3+}$, under argon). A deaerated solution of TosH (2 M) was added until precipitation of the highly colored binuclear ion was essentially complete. The solid was collected under an inert atmosphere. Anal. $(C_{39}H_{77}N_{12}O_{19}S_5Os_2)$ C, H, N.

$[(ND_3)_5Os(pz)Os(ND_3)_5](Tos)_5 \cdot 4D_2O$ was prepared in a similar fashion from $[(ND_3)_5Os(pz)Os(ND_3)_5]Cl_6 \cdot D_2O$, except that D_2O was used as the solvent and the precipitation was achieved by the addition of solid TosH·H_2O. The solid is only slightly air-sensitive, so that filtration is possible in air when this is done rapidly. The solid was washed with deaerated ethanol and diethyl ether and immediately transferred to a vacuum storage tube, which was pumped down. The extent of deuteriation was estimated to be ≥80% from the intensity of the 1310-cm⁻¹ IR band, which is due to the δ_s(N–H) mode of the NH_3 ligands.

$[(NH_3)_5Os(pz)Os(NH_3)_5](Tos)_5 \cdot 4H_2O$. Method 2. This follows a strategy similar to that outlined above, except the 6+ ion in 0.1 M CF_3CO_2H was reduced in an electrochemical Zwickel flask, and the reduced solution was transferred to a 2 M solution of deaerated TosH.

$[(NH_3)_5Os(pz)Os(NH_3)_5]Br_5$. $[(NH_3)_5Os(pz)Os(NH_3)_5](Tos)_6 \cdot H_2O$ (0.05 g) in acetone (10 mL) was reduced to the 5+ ion in an electrochemical Zwickel flask under Ar. The solution was transferred into a degassed solution of Et_4NBr (1 g) in acetone (5 mL). The required complex precipitated immediately and was collected and washed with degassed acetone.

$[(NH_3)_5Os(pz)Os(NH_3)_5]^{4+}$ was generated by Zn(Hg) reduction in a Zwickel flask and transferred directly into a spectrophotometric cell for spectral measurements.

***cis*-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]Cl_5 \cdot H_2O$.** $[(NH_3)_5Os(OSO_2CF_3)](CF_3SO_3)_2$ (0.202 g, 0.28 mmol) and *cis*-$[(NH_3)_4(N_2)Os(pz)](BPh_4)_2$ (0.136 g, 0.135 mmol) were mixed in 1–1.5 mL of dry acetone and allowed to react for 1.5 h at room temperature. Absolute ethanol (8 mL) and 6 M HCl (ca. 1 mL) were added with stirring. The resultant black precipitate was dissolved in 0.2 M HCl (100 mL), and the solution

(24) Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1957**, *5*, 206–207.
(25) Lay, P. A.; Magnuson, R. H.; Taube, H. *Inorg. Synth.* **1986**, *24*, 269–279.
(26) Lay, P. A.; Taube, H., to be submitted for publication.
(27) Allen, A. D.; Stevens, J. R. *Can. J. Chem.* **1972**, *50*, 3093–3099.
(28) Bottomley, F.; Tong, S. B. *Inorg. Synth.* **1976**, *16*, 9–13.
(29) Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2208–2212.
(30) Vogt, L. H.; Katz, J. L.; Wiberley, S. E. *Inorg. Chem.* **1965**, *4*, 1157–1163.
(31) Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. *Inorg. Synth.* **1986**, *24*, 257–263.
(32) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 846–847; **1984**, *23*, 2940–2947.
(33) Dixon, N. E.; Sargeson, A. M. *Inorg. Synth.* **1986**, *24*, 253–256.
(34) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* **1972**, *94*, 7213–7214.
(35) Scheidegger, W.; Armor, J. N.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 3263–3264.
(36) Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161–6164.
(37) Ridd, M. T.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 5733–5740.
(38) Rudd, DeF.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1543–1544.
(39) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1970**, 1117–1125.
(40) Hall, J. P.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2410–2414 and references therein.

was chromatographed on the Sephadex resin. An impurity was detected spectrally in the first half of the very dark band containing the ion of interest. The second half of this band was rotary-evaporated to dryness, and the resultant solid was washed with ethanol and diethyl ether. The yield was 34.6 mg (33%). Anal. ($C_4H_{33}N_{13}OCl_5Os_2$) C, H, N, Cl.

Further chromatography of the first fraction above, on a BioRad AG Dowex 50W-X2 column with strong HCl solutions as eluant, gave a clear separation of the impurity. The yield of the pyrazine-bridged (dinitrogen)nonaamminediosmium complex ion in this fraction was estimated at about 37%, spectrophotometrically, giving an overall yield of ca. 70%. The binuclear complex was not isolated, but rather this 5 M HCl fraction was used directly in the synthesis of the $[(NH_3)_4(Cl)Os-(pz)Os(NH_3)_5]^{5+}$ ion. Presumably, the other binuclear species contained N_2 as the bridging ligand.

***cis*-[(NH₃)₄(N₂)Os(pz)Os(NH₃)₅](Tos)₅·H₂O.** The chloride salt was converted to the tosylate as reported for the decaammine analogue.

***cis*-[(NH₃)₄(N₂)Os(pz)Os(NH₃)₅]I₄·H₂O.** The 5+ tosylate complex was reduced under Ar in an electrochemical Zwickel flask and was isolated as the iodide salt by addition of (*n*-Bu)₄NI.

***cis*-[(NH₃)₄(Cl)Os(pz)Os(NH₃)₅]Cl₅.** The 5 M HCl ion-exchange fraction (170 mL) described above, which contained approximately 0.05 mmol of the *cis*-[(NH₃)₄(N₂)Os(pz)Os(NH₃)₅]⁵⁺ ion, was heated at 90 °C for 5 h under a stream of dioxygen. After cooling and dilution with water, the complex ion of interest was chromatographed and isolated as before (39.8 mg, 95%). Anal. ($C_4H_{31}N_{11}Cl_6Os_2$) C, H, N.

***cis*-[(NH₃)₄(Cl)Os(pz)Os(NH₃)₅]⁴⁺** for spectrophotometric measurements was generated from the corresponding 5+ ion by reduction with [Ru(NH₃)₆]²⁺.

***cis*-[(NH₃)₄(Cl)Os(pz)Os(NH₃)₅]I₄** was prepared from a solution of the tosylate salt of the 5+ ion in acetone by reduction in an electrochemical Zwickel flask, followed by the addition of (*n*-Bu)₄NI.

***cis*-[(NH₃)₄(Cl)Os(pz)Os(NH₃)₅]³⁺** for spectrophotometric measurements was generated by Zn(Hg) reduction of the 4+ ion.

[(NH₃)₅Os(pz)Rh(NH₃)₅]Cl₆·H₂O was prepared in high yield by method 2 from [Os(NH₃)₅(pz)](CF₃SO₃)₃ and [Rh(NH₃)₅(OSO₂CF₃)](CF₃SO₃)₂ or from [Os(NH₃)₅(pz)]²⁺ and [Rh(NH₃)₅(OSO₂CF₃)]²⁺, as described in method 3. Anal. ($H_{36}C_4N_{12}OCl_6RhOS$) C, H, N. The reaction using method 2 is somewhat faster, but more side products are produced.

[(NH₃)₅Os(pz)Rh(NH₃)₅]⁵⁺ for spectrophotometric measurements was generated by Zn(Hg) reduction.

[(NH₃)₅Rh(pz)Rh(NH₃)₅]Cl₆·H₂O was prepared by the reaction of [(NH₃)₅Rh(OSO₂CF₃)](CF₃SO₃)₂ (400 mg, 0.63 mmol) with pyrazine (17 mg, 0.21 mmol) in sulfolane (0.5 mL) at 95–100 °C for 3 h. It was isolated by the chromatographic procedures described earlier as a white microcrystalline solid (68 mg, 48% based on pz). Anal. ($C_4H_{36}N_{12}$-Cl_6ORh_2) C, H, N.

[(NH₃)₅Ru(pz)Ru(NH₃)₅]I₄. [Ru(NH₃)₅(OSO₂CF₃)](CF₃SO₃)₂ (0.20 g, 0.31 mmol) was dissolved in degassed (30 min, Ar) acetone (AR, 10 mL) contained in a Zwickel flask. A lump of freshly prepared Zn(Hg) was added, and the reduction was allowed to proceed for 30 min. Solid pyrazine (0.012 g, 0.15 mmol) was added, and the solution immediately became deep purple. After ∼30 min, the solution was transferred to a degassed solution of (Bu₄N)I (1.0 g in acetone 10 mL). The iodide precipitate was collected under an argon atmosphere, washed twice with deaerated acetone (2 × 5 mL), and dried under an inert atmosphere. The yield was quantitative (based on pyrazine). Anal. ($C_4H_{34}N_{12}I_4Ru_2$) C, H, N.

[(NH₃)₅Ru(pz)Ru(NH₃)₅]I₅. This was prepared in essentially the same manner as the 4+ complex except that air was bubbled through the solution for 30 min prior to precipitation with (Bu₄N)I. The yield was 0.16 g (95%). Anal. ($C_4H_{34}N_{12}I_5Ru_2$) C, H, N.

[(NH₃)₅Ru(pz)Ru(NH₃)₅]Cl₆·H₂O was prepared by standard techniques,[1,2,41] after removal of I⁻ from the 5+ ion by anion-exchange chromatography.

Microanalyses were performed by Stanford University, University of California, Berkeley, or ANU Microanalytical Services. Standard C, H, N analyses using an automatic analyzer gave low values for N for most of the osmium complexes. Often, it was necessary to use the Kirsten–Dumas method in order to obtain satisfactory nitrogen analyses for these complexes.[36]
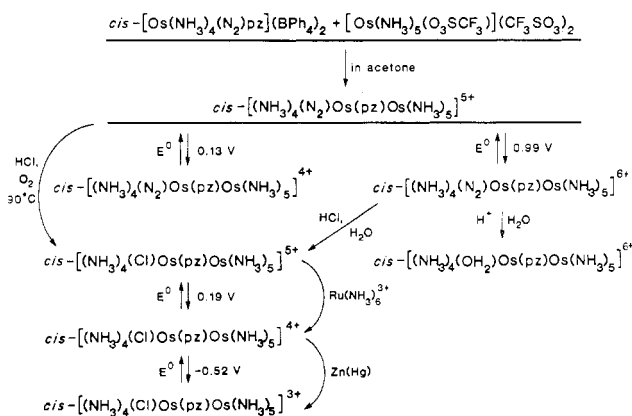
Results

Syntheses and Electrochemistry. The routes for the syntheses of the decaammine- and nonaamminediosmium pyrazine-bridged species are summarized in Schemes I and II, respectively. The

(41) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223–8227.
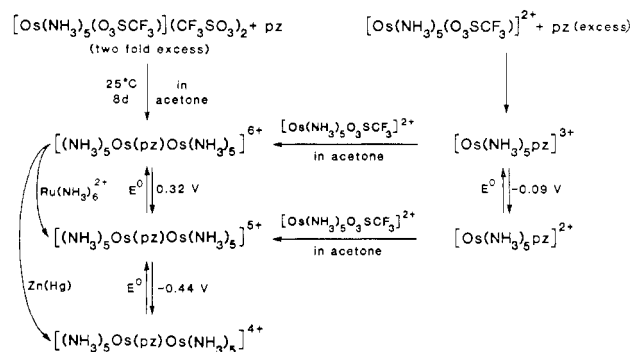
Scheme I

Scheme II

diruthenium, dirhodium, and mixed-metal complexes were synthesized by similar methods. Where possible, the synthetic methods exploiting the nucleophilic properties and lower charges of the [Os(NH₃)₅(pz)]²⁺ ⁷ or [Ru(NH₃)₅(pz)]²⁺ ions is preferable, since such reactions are more rapid and efficient than those using the alternatives. Most of the binuclear complexes are synthesized in moderate to high yields by the reactions of such species with [M(NH₃)₅(solv)]³⁺ ions (solv = solvent; obtained by dissolution of the corresponding [M(NH₃)₅(OSO₂CF₃)]²⁺ complexes in the appropriate weakly coordinating solvent) under Ar in nonaqueous solvents. The use of [M(NH₃)₅(pz)]³⁺ intermediates, which are less nucleophilic and more highly charged than the corresponding 2+ species, required longer reaction times and led to lower yields of the dimeric complexes. Moreover, in the cases of Ru and Os, there are complications due to competitive disproportionation reactions, which are circumvented by the use of the M(II) oxidation states. The combined use of the nucleophilic properties of [Ru(NH₃)₅(pz)]²⁺ with the lability of the [Ru(NH₃)₅(OSO₂CF₃)]⁺ or [Ru(NH₃)₅(solv)]²⁺ ion leads to >90% yields in relatively short reaction times.

The one-electron reduction products of the M(III)–M′(III) species were conveniently obtained by reductions in an electrochemical Zwickel flask, in nonaqueous solvents, followed by precipitation as the I⁻ or Br⁻ salts. They were also obtained by [Ru(NH₃)₆]²⁺ reductions. Isolation of the M(II)–M′(II) species required rigorous exclusion of O₂. However, spectral measurements were conveniently made by direct transfer of solutions from the electrochemical Zwickel flask to a spectrophotometer cell. Alternatively, Zn(Hg) reductions were performed in a Zwickel flask.

The reduction potentials of the binuclear mixed-valence ions are collected in Table I, along with the comproportionation constants (K_{com}) derived from them. The binuclear complexes containing only osmium and ruthenium generally exhibit two reversible couples ($\Delta E_p \sim 60$ mV in cyclic voltammetry). An exception is *cis*-[(NH₃)₄(N₂)Os(pz)Os(NH₃)₅]⁵⁺, the oxidation of which by cyclic voltammetry in 0.10 M CF₃SO₃H proved to be irreversible at low scan rates (<100 mV s⁻¹) due to the rapid loss of dinitrogen from the 6+ ion to give *cis*-[(NH₃)₄(OH₂)-

Table I. Formal Redox Potentials[a] and Comproportionation Results for Pyrazine-Bridged Complexes

complex	$E_f(6+/5+)$	$E_f(5+/4+)$	K_{com}	ref
$[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{n+}$	+0.772	+0.376	6.6×10^6	this work
	+0.74	+0.35	4×10^6	2, 6[b]
$[(NH_3)_5Os(pz)Os(NH_3)_5]^{n+}$	+0.324	-0.438	1.0×10^{13}	this work
cis-$[(NH_3)_4(OH_2)Os(pz)Os(NH_3)_5]^{n+}$	+0.303			this work[c]
cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{n+}$	+0.187[d]	-0.552[e]	1.4×10^{12}	this work
cis-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{n+}$	+1.047[f]	+0.007	6×10^{17}	this work
$[(NH_3)_5Os(pz)Rh(NH_3)_5]^{n+}$	+0.257			18
$[(NH_3)_5Ru(pz)Rh(NH_3)_5]^{n+}$	+0.709			1, 2[b]
$[(NH_3)_5Rh(pz)Rh(NH_3)_5]^{n+}$	-0.423[g]	-0.555[g]		this work
cis-$[(NH_3)_4(Cl)Os(pz)Ru(NH_3)_5]^{n+}$	+0.67[d]	-0.26[e]	8×10^{15}	h

[a] 0.1 M HCl; 22 ± 2 °C; in V vs NHE. [b] 25 °C. [c] 0.1 M CF_3SO_3H. [d] 5+/4+ couple. [e] 4+/3+ couple. [f] Irreversible at slow scan rates (<100 mV s^{-1}). [g] Irreversible at all scan rates up to 50 V s^{-1}[; 0.1 M NaCl; Hg electrode. Peaks obtained by differential-pulse polarography; scan direction negative; scan rate 4 mV s^{-1}; pulse amplitude 50 mV; pulse width 60 ms; drop time 1 s. The first reduction is due to the reduction of the 6+ ion, while the second is due to the reduction of $[Rh(NH_3)_5(pz)]^{2+}$. [h] Magnuson, R. H. Ph.D. Thesis, Stanford University, 1974; p 192.

Table II. Electronic Spectral Data for Binuclear Pyrazine Complexes

	λ_{max}, nm ($10^{-3} \epsilon_{max}$, M^{-1} cm^{-1})	
complex	$\pi-\pi^*$	$d\pi \rightarrow \pi^*$
$[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{4+}$	254 (2.7)	547 (30)[a]
$[(NH_3)_5Os(pz)Os(NH_3)_5]^{4+}$	247 (7.2)	~275 (2.3), ~420 sh (2.9), 555 (29), 777 (11)[b]
$[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$	252 (5.6)	270 sh, 565 (21), 770 (~1), 1570 (5.0)[a]
$[(NH_3)_5Ru(pz)Rh(NH_3)_5]^{5+}$	263 (6.5)	528 (18)[a]
$[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$	265 (4.0)	~325 sh (1.6), 492 (25), 607 (2.0), 890 (2.7)[c]
$[(NH_3)_5Os(pz)Rh(NH_3)_5]^{5+}$	261 (5.0)	464 (15) 920 (1.3)[d,e]
$[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{6+}$	245 (4.4)	288 (5.6), 352 (6.1)[a]
$[(NH_3)_5Ru(pz)Rh(NH_3)_5]^{6+}$	268	275, 310, 350[a]
$[(NH_3)_5Os(pz)Os(NH_3)_5]^{6+}$	257 (5.5)	~300 sh (2.1), ~400 sh (8.3), 416 (8.5), ~490 sh (2.9), ~570 sh (0.85)[c]
$[(NH_3)_5Os(pz)Rh(NH_3)_5]^{6+}$	246 (5.3)	360 (5.3)8 ~475 sh (0.80)[d]
cis-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$	260 (5.0)	340 (1.5), 455 (10), 558 (6.8), 878 (0.57)[c]
cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{3+}$	249 (6.1)	275 sh (2.2)[f] ~420 sh (3.0), ~490 sh[f] 552 (23), 778 (8.8)[b]
cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{5+}$	258 (5.6)	~315 sh (3.0), 492 (25), 604 (1.2), 886 (2.2)[c]
cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{5+}$	258 (4.9)	299 (2.9), 423 (8.5), ~495 sh (3.6), ~570 sh (1.1), ~700 sh (0.26)[c]
cis-$[(NH_3)_4(Cl)Os(pz)Ru(NH_3)_5]^{3+}$		400 sh, 536 (~30), 793 (~2.3)[g]
cis-$[(NH_3)_4(Cl)Os(pz)Ru(NH_3)_5]^{4+}$		352 (~3.0), 525 (~20)[g]
cis-$[(NH_3)_4(Cl)Os(pz)Ru(NH_3)_5]^{5+}$	259 (~5.0)	370 (~2.5), 400 (~2.6), 510 (~1.2)[g]

[a] References 1 and 2. [b] HOAc/NaOAc buffer, $\mu = 0.01$ M; pH 4.65. [c] 0.01 M HCl. [d] 0.1 M HCl. [e] Some uncertainty in the values of ϵ_{max} due to a decomposition of the 5+ ion. [f] Possibly attributable to a small amount of unreduced 4+ ion. [g] Magnuson, R. H. Ph.D. Thesis, Stanford University, 1974; p 3.

$Os(pz)Os(NH_3)_5]^{6+}$ or a mixture of cis-$[(NH_3)_4(OH_2)Os(pz)$-$Os(NH_3)_5]^{6+}$ and cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{5+}$ in 0.1 M HCl. At higher scan rates, or by the use of differential pulse voltammetry, the reversible oxidation of cis-$[Os(NH_3)_4(N_2)Os$-$(pz)Os(NH_3)_5]^{5+}$ is observed. When differential pulse voltammograms (DPV's) are performed by scanning in a negative direction, the reduction peak due to cis-$[(NH_3)_4(N_2)Os(pz)Os$-$(NH_3)_5]^{6+}$ is much smaller than that due to the reduction of the 5+ ion. However, when the DPV's are scanned in a positive direction, the peak currents for the 6+/5+ and 5+/4+ couples are the same, within experimental error, and the currents are equal to those observed in the 6+/5+ and 5+/4+ couples of $[(NH_3)_5Os(pz)Os(NH_3)_5]^{n+}$, under identical conditions. Thus, the DPV data were used to obtain the formal redox potentials and the comproportionation constant for the cis-$[Os(NH_3)_4(N_2)Os$-$(pz)Os(NH_3)_5]^{n+}$ ions. The electrochemistries of the $[(NH_3)_5Os(pz)Os(NH_3)_5]^{6+}$, cis-$[(NH_3)_4(OH_2)Os(pz)Oz$-$(NH_3)_5]^{6+}$, and cis-$[(NH_3)_4ClOs(pz)Os(NH_3)_5]^{5+}$ were similar except that the latter couples are slightly positive and negative (respectively) to those of the symmetric species for the aqua- and chloro-substituted species. $[(NH_3)_5Ru(pz)Rh(NH_3)_5]^{6+}$ and $[(NH_3)_5Os(pz)Rh(NH_3)_5]^{6+}$ both exhibited a reversible one-electron reduction to the 5+ ion and a further irreversible reduction of the rhodium center. On a longer time scale, the 5+ Os–Rh species proved to be unstable, generating $[(NH_3)_5Os(pz)]^{3+}$ over a period of 0.5 h, while the Ru–Rh species decomposed less rapidly. The binuclear rhodium complex exhibited two one-electron irreversible reductions, which moved to more negative potentials as the scan rate was increased in the cyclic voltammograms. No signs of reversibility are observed even at scan rates up to 50 V s^{-1}. These reductions occurred between -0.5 and 1.0 V vs the

Ag/AgCl/saturated KCl reference electrode and are separated by ~1.5 V. These results will be discussed in more detail elsewhere.

Electronic and IR Spectra. Data on the electronic spectra of the binuclear pyrazine complexes are contained in Table II, and the internal t_2 transitions peculiar to Os(III) (and the delocalized osmium binuclear mixed-valence species) are collected in Table III. Analogous osmium and ruthenium complexes have very similar spectral characteristics, except that the corresponding transitions for osmium are moved to higher energies. The binuclear Os(III) and heterobinuclear Os(III) complexes exhibit the typical transitions due to spin–orbit coupling observed for mononuclear Os(III) complexes in the region 1500–2200 nm,[7-9] except that the former spectra are more complex and the bands are more intense (Table III). The mixed-valence decaamminediosmium ion does not exhibit the same type of transitions, but instead, weak transitions in the region 1300–2000 nm and intense electronic transitions ($\epsilon \sim 10^3$ M^{-1} cm^{-1}) in the normal-IR region (3000–3500 nm) are observed. The assignment of the IR bands as electronic in origin is confirmed by the deuteriation of the ammine ligands, whereby new transitions are observed at 2300–2450 cm^{-1} due to N–D stretches, but the more intense electronic transitions remain largely unaltered in the region 3000–3500 nm. Similar transitions are noted for the mixed-valence ion cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{4+}$, but not for cis-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$. The latter mixed-valence ion exhibited typical Os(III) transitions in the near-IR spectral region and its electronic spectrum is similar to that expected for a combination of cis-$[Os^{II}(NH_3)_4(Mepz)(N_2)]^{3+\;34}$ and $[Os^{III}$-$(NH_3)_5(Mepz)]^{4+\;8}$ (Mepz = 1-methylpyrazinium). Similarly, the mixed-valence ion $[(NH_3)_5Os(pz)Rh(NH_3)_5]^{5+}$ has absorption

Table III. Near-IR and IR Electronic Transitions of the Binuclear Osmium Pyrazine Complexes

complex	λ_{max} $(\epsilon_{max})^a$
$[(NH_3)_5Os(pz)Os(NH_3)_5]^{6+}$	~1580 sh (98), 1674 (220), 1788 (630), ~1860 (370), 1880 (390), ~1915 sh (300), ~1965 sh (160), 2100 (1410), 2150 sh (1.05 × 10³)^b
$[(NH_3)_5Os(pz)Rh(NH_3)_5]^{6+}$	1680 (130)8 1725 (160), 1760 (310), 1875 (130), 1925 (98), 2103 (560)^c
cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{5+}$	~1572 (240), ~1616 sh (300), 1670 (370), ~1696 sh (340), 1780 (470), 1860 (300), 1906 (280), ~1970 sh (120), 2095 (1.22 × 10³), 2202 (470)^b
$[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$	1185 (130), 1470 (150), 1593 (190), ~1720 sh (150), ~2035 (50), 2940 (~3 × 10³), 3330 (~4 × 10³)^b
$[(NH_3)_5Os(pz)Rh(NH_3)_5]^{5+}$	1670 (200)^{c,d}
cis-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$	~1260 sh (27), ~1460 sh (31), 1578 (55), 1776 (190), 1866 (340), 1934 (280), 2118 (2.4 × 10³)^b
cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{4+}$	~1180 sh (160), 1460 (190), 1540 (180), 1778 (340), ~1900 sh (80), 2036 (113), 2640 sh (~3 × 10³), 2860 (~4 × 10³)^b

^{a} λ_{max} in nm; ϵ_{max} in M^{-1} cm^{-1} in parentheses. ^{b} 0.01 M DCl/D$_2$O in the near-IR region; IR region in KBr diskcs (ϵ_{max} values in KBr estimated by comparisons to absorptions in the near-IR region in the same disk). ^{c} 0.1 M DCl/D$_2$O. ^{d} Some uncertainty in the extinction coefficient due to the reactivity of the 5+ ion.

characteristics expected of an Os(II)–Rh(III) species. In particular, no near-IR transitions are observed, with the exception of a weak band at 1670 nm. In the IR spectrum of *cis*-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$, there is a strong absorption for the symmetric-stretching pyrazine ring mode (1600 cm^{-1}). The same transition for the *cis*-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{4+}$ ion is weak, and it is extremely weak for the decaamminediosmium mixed-valence ion and for all of the symmetric binuclear 6+ ions. The *cis*-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$ ion also has a very strong $\nu(N_2)$ transition at 2075 cm^{-1}, such a frequency being typical of Os(II) complexes.[34]

Discussion

Syntheses. The use of the relatively labile $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$, $[Ru(NH_3)_5(OSO_2CF_3)]^{2+}$, and $[Rh(NH_3)_5(OSO_2CF_3)]^{2+}$ ions[8,31-33] has greatly facilitated the synthesis of the binuclear complexes, and several synthetic routes have been outlined. The symmetric binuclear M(III)–M(III) species can be prepared by the reaction of the appropriate triflato complex and pyrazine (2:1 molar ratio) in weakly coordinating solvents. While this method is suitable for the syntheses of the dirhodium species, it suffers from several drawbacks for the diruthenium(III) and diosmium(III) analogues, the chief problem being the base-promoted disproportionation of the M(III) species. Such disproportionation of Ru(III) and Os(III) amine complexes to M(II) and M(IV) species is being increasingly recognized.[16,17,36-38] In this instance, the reaction is promoted because pyrazine acts as a base, weak though it is. Ion-exchange chromatography of the reaction solution for the osmium complex showed as a major byproduct a purple complex that moved at about the same rate as the μ-pyrazine decaammine complex. The chromatographic behavior and microanalytical data (Experimental Section) suggest a binuclear structure with two pyrazine ligands, eight ammine ligands, and one chloro or aquo ligand. Structure II, featuring a μ-nitrido group, seems to us to be the most likely of the alternative structures on the basis of this evidence and other experience with the chemistry of similar osmium species. Its exact

II
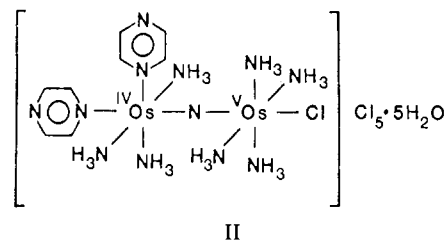
nature is still under investigation.

Chromatography showed that trinuclear and higher oligomers are also formed, and these have spectral characteristics similar to those of trinuclear Os(IV) nitrido complexes.[39,40] The problems of base-catalyzed disproportionation are exacerbated for the reactions with ruthenium(III), as compared to those of osmium(III), where the desired complex $[(NH_3)_5Os(pz)Os(NH_3)_5]^{6+}$ was obtainable in ~40% yield. An improved method involves the reaction of $[M(NH_3)_5(pz)]^{3+}$ with $[M'(NH_3)_5(OSO_2CF_3)]^{2+}$ in a poorly coordinating solvent. Such reactions served for the syntheses of both homo- and heterobinuclear ions and did not suffer from the side reactions mentioned above. Good to high yields of the desired products were obtained, although long reaction times at elevated temperatures were required, and all reactants and solvents must be as dry as possible. The slowness of these reactions is ascribable to two causes. First, electrostatic repulsions slow down the bimolecular substitution reactions. Second, as evidenced by the pK_a values of the protonated species (<0),[8,17] the $[M(NH_3)_5(pz)]^{3+}$ ions are weak nucleophiles and, therefore, may not be strong competitors in comparison to solvent molecules in either a nucleophilic or a dissociative displacement mechanism. These ideas are borne out by the observation that the $[M(NH_3)_5(pz)]^{2+}$ complexes lead to more rapid reactions and improved yields. However, for $[(NH_3)_5Os(pz)Rh(NH_3)_5]^{5+}$, there is interference by intramolecular electron transfer leading to reductive decomposition of the Rh(III) ion. The μ-pyrazine Rh–Os species is best synthesized from $[Os(NH_3)_5(pz)]^{3+}$ and $[Rh(NH_3)_5(OSO_2CF_3)]^{2+}$. The alternative reaction of $[Rh(NH_3)_5(pz)]^{3+}$ with $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ is not as appropriate because $[Os(NH_3)_5(solv)]^{3+}$ complexes are much more inert than are $[Rh(NH_3)_3(solv)]^{3+}$ intermediates.[8,32]

The diosmium and diruthenium complexes are most conveniently produced in situ by using a 2:1 molar ratio of $[M(NH_3)_5(OSO_2CF_3)]^{2+}$ and pyrazine under argon and performing the reductions of the ions electrolytically. $[M(NH_3)_5(pz)]^{2+}$ is much more nucleophilic and has a lower charge than the M(III) analogue. Both properties are advantageous in forming binuclear ions. However, the very fact that the M(II) pyrazine ions are so nucleophilic promotes an undesirable side reaction, the base-catalyzed disproportionation of the Os(III) and Ru(III) coreactants. For Ru, the use of the M(II) species $[M(NH_3)_5(OSO_2CF_3)]^+$ and $[M(NH_3)_5(solv)]^{2+}$ as the reactants circumvents this problem. In general, the M(II) complexes also have the advantages of being much more labile and having lower charges (reducing Coulombic repulsion) than their M(III) analogues. In the case of osmium, the $[Os(NH_3)_5(acetone)]^{2+}$ complex is not labile,[41] and other solvents are preferable for generating labile $[Os(NH_3)_5(solv)]^{2+}$ reactants.[42] In method 4 as it was applied, the working potential is somewhat oxidizing relative to the formal potential of the $[(NH_3)_5Os(\eta^1\text{-acetone})]^{3+}/[(NH_3)_5Os(\eta^2\text{-acetone})]^{2+}$ couple. This couple is not established with facility at an electrode surface, but should any of the reduced η^2 species be formed, it would be oxidized rapidly by $[Os(NH_3)_5(pz)]^{3+}$ and would not affect the yield of the desired product.

In summary, the use of reduced solutions of the $[M(NH_3)_5(OSO_2CF_3)]^{2+}$ ions have the following advantages over other methods for the syntheses of homobinuclear complexes of Ru and Os:

(i) The salts of the complexes are readily soluble in a variety of organic solvents.

(42) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 1883–1885.

(ii) The labile M(II) ions facilitate substitution reactions.

(iii) The mononuclear M(II) complexes initially formed are much stronger nucleophiles than their M(III) analogues and often stronger than the free ligand.

(iv) Base-catalyzed disproportionation reactions of M(III) complexes leading to undesirable side products are eliminated.

(v) Coulombic work terms involved in forming binuclear complexes are greatly reduced, thus facilitating the reactions.

(vi) The need rigorously to remove water from all solvents and reactants is eliminated, as the $[M(NH_3)_5(OH_2)]^{2+}$ ions are also labile.

These principles are general to the syntheses of binuclear complexes of a variety of bridging ligands, and the results of further investigations will be reported in papers to follow.

The syntheses of the binuclear nonaamminediosmium species also depend on the nucleophilic properties of osmium(II) pyrazine complexes. Clearly, the reaction between cis-$[Os(NH_3)_4$-$(pz)(N_2)]^{2+}$ and $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ could have resulted in either a dinitrogen or a pyrazine bridging ligand, but the major product from such a reaction is the pyrazine-bridged complex. This was established by oxidizing the product in HCl, whereupon the terminal dinitrogen ligand was substituted by Cl⁻. The preferential capture of the terminal pyrazine nitrogen as compared to the terminal dinitrogen donor is no doubt a reflection of a combination of the stronger nucleophilic properties and the greater distance from the Os(II) charge center of the former donor. It is likely that the minor binuclear impurity observed was due to the formation of the dinitrogen-bridged isomer. The oxidation of the binuclear 5+ ion in aqueous HCl labilizes the dinitrogen ligand in a fashion similar to that observed for mononuclear ions.[13,34]

Physical Measurements. The binuclear ruthenium mixed-valence ion has been subjected to a large variety of spectroscopic measurements to learn whether or not the complex is a delocalized system.[3-6] The conclusions as to the electronic nature of the species as drawn from these various spectroscopic techniques were often contradictory, and these ambiguities have been resolved only very recently;[43-48] all spectroscopic techniques now point to the ion being delocalized (class III) or being on the borderline of the delocalized/localized descriptions. The decision as to whether the osmium complexes are delocalized is somewhat easier because the spin–orbit transitions for Os(III) can often be diagnostic.[10,18] The absence of these Os(III) electronic transitions[7-9,18] for the mixed-valence decaamminediosmium ion is very strong evidence for a delocalized structure. Molecules in which an Os(III) center is unambiguously present (e.g., $[(NH_3)_5Os(pz)M(NH_3)_5]^{6+}$ (M = Rh, Os)) all exhibit these near-IR transitions. In addition, the cis-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$ mixed-valence ion also exhibits these near-IR transitions. It also shows electronic spectral properties typical of an Os(II) center coordinated to a dinitrogen and pyrazinium ion and typical of a pentaammine(pyrazinium)osmium(III) center.[8,34] Finally, a strong dinitrogen stretching frequency at 2075 cm⁻¹ in the IR spectrum is typical of Os(II),[34] and a strong IR pyrazine ring stretching mode at 1600 cm⁻¹ is indicative of an unsymmetric (localized) electronic structure about the pyrazine bridge.[49] By contrast, the decaammine mixed-valence ion does not have the spectral features expected for discrete Os(II) and Os(III) centers, and the pyrazine ring stretching mode is very weak in the IR spectrum. All these features indicate that $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$ is electronically delocalized and

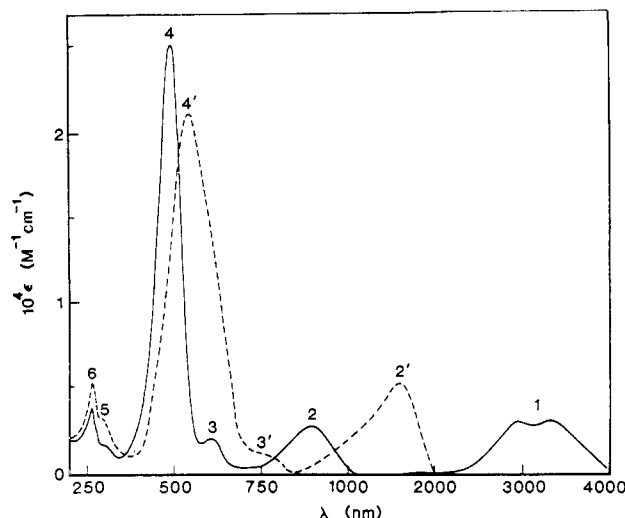**Figure 1.** Ultraviolet, visible (0.1 M HCl), near-infrared (0.1 M DCl), and infrared (KBr) absorption spectra of the electronic transitions of $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$ (—) and $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ (- - -). The numbers refer to analogous transitions in ruthenium and osmium complexes. The value of ϵ_{max} for transition 1 is approximate because the absorption intensity has been measured in a KBr disk.

cis-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$ is localized. The intense ($\epsilon \sim 10^3$–10^4 M⁻¹ cm⁻¹) electronic transitions in the IR region of the spectrum (3000–3500 cm⁻¹) are a unique feature of the delocalized mixed-valence ion and can be considered as being due to the transition between spin–orbit states that are split by the coupling of the Os(II.5) centers in the symmetric description. The weaker features observed in the region of 1500–2000 nm are also spin–orbit transitions, which contain the same vibronic structure built upon the origins of these internal t_2^5 transitions as is observed for all mononuclear and binuclear Os(III) and Ru(III) complexes.[50] The cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{4+}$ ion has an electronic spectrum remarkably similar to the decaammine mixed-valence ion, including the IR electronic transitions. Clearly, the electronic structure of the ion is dominated by the Os–pz–Os moiety, and substitution of an ammine ligand for a chloro ligand does little to perturb this structure. This is also evidenced in the IR spectra, where the pyrazine ring mode is stronger than for the symmetric complexes but is still very weak in comparison to the same mode for cis-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$. Therefore, the chloro-substituted complex is also best described as having an electronic structure close to that of the delocalized description.

The similarities in the spectral features of $[(NH_3)_5Os(pz)$-$Os(NH_3)_5]^{5+}$ and cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{4+}$ highlight the problems associated with classifying mixed-valence ions into the class II or class III descriptions. Obviously, the two osmium centers cannot be equivalent in the cis-$[(NH_3)_4(Cl)Os(pz)Os$-$(NH_3)_5]^{4+}$ ion. It is expected that the cis-$[(NH_3)_4(Cl)Os(pz)]$ moiety will have more Os(III) character than the $[Os(NH_3)_5(pz)]$ moiety in the mixed-valence ion. The similarities in the spectral properties illustrate the continuous nature of the variation in the properties of mixed-valence ions in going from the class II to the class III description and may be part of the reason for the difficulties that have arisen in classifying the $[(NH_3)_5Ru(pz)Ru$-$(NH_3)_5]^{5+}$ ion.

It is interesting to compare the electronic spectra of the decaamminediosmium and -diruthenium mixed-valence ions (Figure 1). The two spectra are remarkably similar, save that all the transitions are at higher energy for the osmium complex. Only the putative spin–orbit transitions (transition 1) of the ruthenium complex are not observed, since they are both weak and broad and are obscured by vibrational modes in the region (1000–1600 cm⁻¹). However, recent MCD results have shown the expected transitions in the IR spectra for I.[48] Since the osmium complex

(43) Fuerholz, U.; Burgi, H.-B.; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M. I.; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121–123.

(44) Stebler, A.; Ammeter, J. H.; Fuerholz, U.; Ludi, A. *Inorg. Chem.* **1984**, *23*, 2764–2767.

(45) Krausz, E. R.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 939–943.

(46) Fuerholz, U.; Joss, S.; Burgi, H. B.; Ludi, A. *Inorg. Chem.* **1985**, *24*, 943–948.

(47) Dubicki, L.; Ferguson, J.; Krausz, E. R. *J. Am. Chem. Soc.* **1985**, *107*, 179–184.

(48) Krausz, E. R.; Mau, A. W. H. *Inorg. Chem.* **1986**, *25*, 1484–1488.

(49) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064–1073.

(50) Ferguson, J.; Krausz, E. R.; Lay, P. A.; Maeder, M.; Taube, H., to be submitted for publication.

is believed to be delocalized, band 2 cannot be an intervalence transition, as both osmiums are equivalent. It follows that the corresponding transition in the ruthenium ion, 2′, is also not an intervalence transition in the class (III) description. It is likely that this transition is a charge-transfer transition from a bonding combination of the d_{xz} orbitals to a weakly antibonding combination.[51] It is not present in the 4+ ion because the metal t_2 orbitals are full, and it is probably at energies too low to observe in the 6+ ion, where splitting of the energies of the t_2 orbitals due to metal–ligand interaction will be much less. This is supported by a recent single-crystal polarized absorption spectrum that shows the transition to be y-polarized ($b_{3u} \rightarrow b_{2g}$) in $[(NH_3)_5Ru(pz)$-$Ru(NH_3)_5]Cl_5$.[45] However, the nature of the near-IR transitions in the 5+ ions may be slightly different, since the b_{2g} combination of the d_{xz} orbitals may be lower in energy than the nonbonding combinations of the d_{yz} and $d_{x^2-y^2}$ orbitals. This would arise because the osmium orbitals are higher in energy than their ruthenium counterparts, which means the interaction between the $d_{xz}(b_{2g})$ and the ligand $\pi^*(b_{2g})$ orbital may be stronger than the interaction between the $d_{xz}(b_{2g})$ and $\pi(b_{2g})$ orbitals for osmium, but the converse is true for ruthenium. Detailed analyses of the spectra, which will be reported later, suggest that these expectations are correct.

In the same way that the similarities between the spectral features of $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$ and cis-$[(NH_3)_4(Cl)$-$Os(pz)Os(NH_3)_5]^{4+}$ show only that the latter ion is close to the borderline between the class II and class III, the similarities between the complexes $[M(NH_3)_5(pz)M(NH_3)_5]^{5+}$ (M = Os, Ru) cannot be taken as proof of a class III description for $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$. However, what is clear is that $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$ either is a class II ion or is very close to the II–III border. Similar conclusions have been reached from the detailed analysis from other laboratories.[43-48] Another point that is often overlooked is that all of the charge-transfer transitions in class II ions have some intervalence character, not just the lowest energy transition normally assigned to the intervalence transition. This arises because the ground and excited states have different degrees of mixing between the ligand orbitals with the nominally M(II) and M(III) centers of the two distinct metal centers. Therefore, the charge density at one metal center must change relative to that of the other during the electronic transitions. Again, this illustrates the difficulty in assigning electronic classifications to mixed-valence ions, because the charge-transfer transitions of cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{4+}$ must be intervalence transitions (involving a change in relative charge distribution at the metal centers). By contrast, in $[(NH_3)_5Os$-$(pz)Os(NH_3)_5]^{5+}$ they are not intervalence transitions, because the charge density on the two osmiums will be identical in both the ground state and excited states (although the osmiums will have different charge densities in the different electronic states). As expected, the biggest discernible differences in the electronic spectral properties of $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$ and cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{4+}$ lie in the low-energy transitions brought about by spin–orbit coupling. Clearly, the energy of these transitions for cis-$[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{4+}$ are intermediate between those of the delocalized $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$ ion and the typical trapped-valence ion $[(NH_3)_4(N_2)Os(pz)Os$-$(NH_3)_5]^{5+}$.

The comproportionation constants obtained for the decaamminediosmium complexes with a variety of bridging ligands are approximately the squares of those obtained for the ruthenium analogues.[1-20] When the equilibrium constants are converted to energies, the relationship shows that the interaction leading to stabilization of the osmium mixed-valence species is twice that for the ruthenium analogues. Although it is fortuitous that the factor is 2, there may be significance to the fact that the factor is approximately the same for different compositions. The important part is that communication between the metal centers with pyrazine as a bridging group is far greater for osmium than for ruthenium.

The enhanced back-bonding tendency of Os(II) as compared to that of Os(III) is undoubtedly the major factor contributing to the relatively high stability of the mixed-valence osmium species, but for a complete analysis additional factors need to be taken into account. Thus, while whatever role back-bonding may play in the chemistry of $(NH_3)_5Ru^{III}$ has thus far escaped detection, it appears to be significant in the chemistry of the osmium analogues. For instance, the Os–N(pz) bond is the shortest metal–ligand bond in the binuclear Os(III) complex $[(NH_3)_5Os(pz)$-$Os(NH_3)_5]Cl_6 \cdot 2H_2O$,[52] whereas it is the longest bond, within experimental error, in the isostructural binuclear ruthenium complex.[43,46] Further, nucleophilic attack at nitriles coordinated to Os(III) is very slow in comparison to that for Ru(III).[17] The binuclear Os(III) complex is diamagnetic at low temperatures,[9] indicating a splitting of the energy of the nonbonding t_2 orbitals, and this moderate exchange coupling may be a result of the back-bonding interaction, but it may be indicative of weak direct metal–metal interactions. If this be the case, direct metal–metal interactions would be expected to be progressively stronger in the 5+ and 4+ ions since the lower charged Os(II) ion is expected to have a greater extension of its d orbitals than would Os(III). Of course, the larger spin–orbit coupling constant for Os(III), in comparison to Ru(III), would tend to stabilize the ground state of Os(III) complexes to a greater extent. This factor would also affect comproportionation constants; for both Ru and Os they are also solvent and temperature dependent, although not strongly so.[53]

The comproportionation data in Table I show an interesting feature. In a valence-trapped system (e.g., $[(NH_3)_4(N_2)Os$-$(pz)Os(NH_3)_5]^{n+}$) when the electron delocalization in the mixed-valence state contributes little to the stability, if the two centers are made more dissimilar, K_c will always increase, for obvious reasons. But, in the case of $[(NH_3)_4(Cl)Os(pz)Os(NH_3)_5]^{n+}$, which is a strongly delocalized system, K_c is less than that observed for $[(NH_3)_5Os(pz)Os(NH_3)_5]^{n+}$.

Detailed discussions of structural,[44] electronic, vibrational, MCD, and ESR measurements on the binuclear complexes bridged by pyrazine and other bridging ligands have been or will be published elsewhere.[9,10,14,15,19,20,50,53,54]

Since the observations reported here were made, the great tendency of $(NH_3)_5Os^{II}$ to engage in binding by the η^2-mode has been discovered.[41,42,55] In reviewing our observations in the light of these newer findings, we have no reason to believe that the η^2-bonding played a role in the particular chemistry we have described.

(51) Creutz, C.; Chou, M. H. *Inorg. Chem.* **1987**, *26*, 2995-3000.

(52) Bino, A.; Lay, P. A.; Taube, H.; Wishart, J. F. *Inorg. Chem.* **1985**, *24*, 3969-3971.

(53) Lay, P. A.; Powell, D. W.; Taube, H., to be submitted for publication.

(54) Lay, P. A.; Magnuson, R. H.; Taube, H.; Ferguson, J.; Krausz, E. R. *J. Am. Chem. Soc.* **1985**, *107*, 2551-2552.

(55) Cordone, R.; Taube, H. *J. Am. Chem. Soc.* **1987**, *109*, 8101-8102.

(Cl)Os(pz)Ru(NH₃)₅]⁵⁺, 114595-33-4; *cis*-[(NH₃)₄(Cl)Os(pz)Ru-(NH₃)₅]⁴⁺, 114595-34-5; *cis*-[(NH₃)₄(Cl)Os(pz)Ru(NH₃)₅]³⁺, 114595-35-6; [(NH₃)₅Ru(pz)Ru(NH₃)₅]Cl₆, 94750-87-5; [(NH₃)₅Ru(pz)Ru-(NH₃)₅]I₅, 104626-97-3; [(NH₃)₅Ru(pz)Ru(NH₃)₅]I₄, 114595-28-7; [Os(NH₃)₅(OSO₂CF₃)](CF₃SO₃)₂, 83781-30-0; [Os(NH₃)₅(pz)]-

(CF₃SO₃)₃, 83781-35-5; [Os(NH₃)₅(Etpz)]⁴⁺, 114595-30-1; [Ru-(NH₃)₆]³⁺, 18943-33-4; *cis*-[(NH₃)₄(N₂)Os(pz)](BPh₄)₂, 85282-29-7; [Rh(NH₃)₅(OSO₂CF₃)](CF₃SO₃)₂, 84254-57-9; [Ru(NH₃)₅(OSO₂C-F₃)](CF₃SO₃)₂, 84278-98-8; [Rh(NH₃)₅(pz)]²⁺, 114595-32-3; D₂, 7782-39-0.

Notes

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A Novel Series of 1:1, 2:1, and 3:1 Heterobimetallic Adducts from the Reaction of Copper(I) Halides with Tris(dithiocarbamato)cobalt(III) Complexes†

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The tendency for neutral dithiocarbamate complexes, M-(S₂CNR₂)ₙ, to act as chelating ligands via the sulfur atoms to form heterometallic adducts is relatively unexplored, and only a small number of such compounds have been well characterized.¹⁻³ We have obtained very small crystals of the 1:1 adducts of CuBr with Co(S₂CN(CH₂)₄)₃² and of CuI with Co(S₂CN-*n*-Pr₂)₃ and Co-(S₂CN-*i*-Pr₂)₃³ by slow interdiffusion of the appropriate copper and cobalt compounds. Structural studies on these compounds have shown that two Co(S₂CNR₂)₃ molecules chelate to a Cu₂X₂ dimer to form molecules of the type
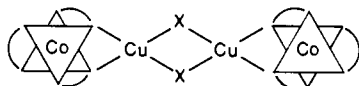
in which the Co(S₂CNR₂)₃ molecules may be of similar or opposed chirality.

In these compounds, only one of the three possible interligand S···S chelating sites is employed. We have now isolated the compounds [CuBr]₂[Co(S₂CNEt₂)₃]·2CH₃CN (**1**) and [CuI]₃-[Co(S₂CN(CH₂)₄)₃] (**2**), in which respectively two and three of the possible sites are utilized to give adducts of 2:1 and 3:1 stoichiometry. We have also found that for several cobalt(III) dithiocarbamate complexes, no adduct formation takes place at all.

Experimental Section

Synthesis. Small dark brown crystals of **1** are formed slowly after a period of days by allowing a dilute solution of Co(S₂CNEt₂)₃ in CH₃CN to stand over solid CuBr under an argon atmosphere. During this period the solution changes color from green to deep brown. The crystals are relatively stable to air, slowly losing solvent to give amorphous powders. Small dark brown/black crystalline needles of **2** could be prepared by the slow interdiffusion of dilute solutions of CuI in CH₃CN and Co-(S₂CN(CH₂)₄)₃ in CH₂Cl₂ in a variety of stoichiometric ratios. Attempts to form an adduct of Co(S₂CN(CH₄)₂)₃ with CuCl, or adducts of Co-(S₂CNH₂)₃, Co(S₂CNMePh)₃, Co(S₂CNPh₂)₃, Co(S₂CNBz₂)₃ or Co-(S₂COEt)₃ with either CuBr or CuI were unsuccessful. In each case no reaction was observed to take place, either by color changes in the reaction mixture or by the precipitation of crystalline material other than the parent compounds. With Co(S₂CNMe₂)₃ and CuI very small, fragile crystals were obtained and these were isomorphous with **2**. [space group *I*4̄3*d*, *a* = 23.31 (1) Å; a structure determination carried out on data to

Table I. Crystal Data for Compounds **1** and **2**

	1	**2**
stoichiometry	[Co(dtc)₃]·2CuBr·2MeCN	[Co(dtc)₃]·3CuI
ligand substituent	C₂H₅	(CH₂)₄
formula	C₁₉H₃₆Br₂CoCu₂N₅S₆	C₁₅H₂₄CoCu₃I₃N₃S₆
M_r	872.7	1069.1
cryst syst	monoclinic	cubic
space group	*C*2/*c*; No. 15	*I*4̄3*d*; No. 220
a, Å	18.91 (2)	23.637 (10)
b, Å	14.583 (4)	
c, Å	13.705 (8)	
β, deg	118.82 (6)	
V, Å³	3312 (2)	13 207 (10)
D_{calcd}, g cm⁻³	1.75	2.15
D_{measd}, g cm⁻³	...	2.16 (1)
Z	4	16
F(000)	1744	8064
μ_{Mo}, cm⁻¹	48	57
specimen dimens, mm	0.15 × 0.07 × 0.07	0.30 × 0.20 × 0.15
A*: min, max	...	1.72, 1.91
$2\theta_{max}$, deg	45	60
N	2154	1716
N_o	1101	905
n_v	160	95
R	0.049	0.051
R_w	0.040	0.054

$2\theta_{max} = 40°$ (341 "observed" reflections, *R* = 0.087) establishing its essential similarity.]

Structure Analysis. Unique data sets were measured at 295 K to the specified $2\theta_{max}$ limits by using Syntex P2₁ and ENRAF-Nonius CAD-4 four-circle diffractometers (monochromatic Mo Kα radiation sources, λ = 0.7106₉ Å) operating in conventional $2\theta/\theta$ scan mode. *N* independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement, minimizing $\sum w\Delta F^2$. Difference map artifacts in **1** were successfully modeled as acetonitrile solvent with assignment of C and N derived from the behavior of geometric, thermal, and statistical parameters. Remaining difference map residues were assigned as hydrogen atoms in the latter stages of refinement. Data for **2** were corrected for absorption (analytical correction). Anisotropic thermal parameters were refined for the non-hydrogen atoms (in the preferred enantiomeric setting for **2**). *x*, *y*, *z*, and U_{iso} for hydrogen were constrained to estimated values. Residuals on |*F*| at convergence were *R* and R_w; statistical weights used were derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0001\sigma^4(I_{diff})$. Each structure refined smoothly in the chosen space group with no anomalies with respect to features such as thermal envelopes or disorder. Neutral-atom complex scattering factors were employed;⁴ computation used the XTAL programme system⁵ implemented by S. R. Hall on a Perkin-Elmer 3241 computer. Crystal and refinement data are given in Table I. Non-hydrogen atom coordinates for **1** and **2** are listed in Tables II and III and relevant geometric parameters are given in Table IV.

(1) (a) Cras, J. A.; Willemse, J. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1226. (b) McCleverty, J. A.; McLuckie, S.; Morrison, N. J.; Bailey, N. A.; Walker, N. W. *J. Chem. Soc., Dalton Trans.* **1977**, 359.
(2) Engelhardt, L. M.; Healy, P. C.; Papasergio, R. I.; White, A. H. *Inorg. Chem.* **1985**, *24*, 382.
(3) Engelhardt, L. M.; Healy, P. C.; Skelton, B. W.; White, A. H. *Aust. J. Chem.*, in press.
(4) Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.
(5) Hall, S. R.; Stewart, J. M. "XTAL USERS' Manual: Version 2.2", Universities of Western Australia and Maryland, 1987.