that the reduced species are Mo^{III}_3 in 1 and 4 M HCl.[25] During the addition of Fe^{3+} ion to Mo^{III}_3 in 4 M HCl, a characteristic spectrum appears and this is ascribed to that of the intermediate $Mo^{IV}Mo^{III}_2$, while no characteristic spectrum appears in the same procedure in 1 M HCl. It seems that the oxidation state Mo^{IV}-Mo^{III}_2, is unstable in lower acidic concentration to give Mo^{IV}_3 and Mo^{III}_3 through a disproportionation reaction as in the case of the $Mo^{IV}Mo^{III}_2$ aqua ion having μ_3-O.[1e] An interesting phenomenon appears; that is, the spectrum of Mo^{III}_3 in 1 M HCl corresponds to that of $Mo^{IV}Mo^{III}_2$ as the HCl concentration increases to 8 M (Figure 4c). This indicates that Mo^{III}_3 in 8 M HCl reduces H^+, as shown in the reaction

$$Mo^{III}_3 + H^+ \rightarrow Mo^{IV}Mo^{III}_2 + \tfrac{1}{2}H_2$$

Determination of the amount of hydrogen gas ($H_2/Mo_3 = 0.48$) by use of a gas chromatograph supports the reaction.

Cyclic voltammograms of $Mo_3O_3S(aq)^{4+}$ (Figure 5) in some acid concentrations show that the midpoint potential shifts in the positive direction with increasing HCl concentration and that the second reduction peak develops at 8 M HCl. It seems that two- and one-electron processes appear.

Cyclic voltammograms of $[Mo_3O_3S(ida)_3]^{2-}$ (**2D**) and $[Mo_3O_3S(cys)_3]^{2-}$ (**2F**) are shown in parts a and b of Figure 6, respectively. The former shows three quasi-reversible waves, which can be attributed to three one-electron waves as was found in the case of $[Mo_3S_4(ida)_3]^{2-}$.[5b] The cysteinato complex **2F** shows only one quasi-reversible wave in the region down to −1.65 V, three waves appearing to be collapsed. Attempts to obtain reasonable samples of the reduced species of **2B**–**2F** have yet not succeeded.

Acknowledgment. We are grateful to Professor S. Ooi and Dr. K. Matsumoto of Osaka City University for the X-ray data collection (**2B**) and helpful discussions. Our thanks are due to Takashi Iwasaki for help with the preparation of the Mo(IV) cysteinato complex. Support of this research by a Grant-in-Aid for Scientific Research (No. 62470043) from the Ministry of Education, Science and Culture is also gratefully acknowledged.

Supplementary Material Available: Anisotropic thermal parameters (Tables III and V) and interatomic distances and angles for **2B** and **2F** (Tables VIIIS and IXS) (6 pages); tables of F_o and F_c values (26 pages). Ordering information is given on any current masthead page.

---

(25) Mo^{III}_3 in 1 and 4 M HCl is also air-oxidized to give the Mo^{IV}_3 aqua ion.

Notes

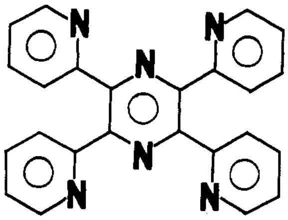
Contribution from the Department of Chemistry,
University of Colorado at Colorado Springs,
Colorado Springs, Colorado 80933-7150

Triammineruthenium(II) Complexes Bound with the Novel Bridging Ligand 2,3,5,6-Tetrakis(2-pyridyl)pyrazine (tppz)

Ronald Ruminski,* Jaqueline Kiplinger, Timothy Cockroft, and Charles Chase

Received February 26, 1988

There has been recent interest in the preparation and study of polymetallic complexes bound through novel bridging ligands.[1] Previous investigations of bimetallic Ru(II) polyazine complexes for photocatalyzed intramolecular energy-transfer processes have focused on nitrogen aromatic heterocyclic bridging ligands such as pyrazine,[2,3] 2,3-bis(2-pyridyl)quinoxaline (dpq),[4] 2,2′-bipyrimidine (bpym),[5-8] 2,3-bis(2-pyridyl)pyrazine (dpp),[9,10] and biimidazole (bim).[11] To efficiently function as photon-capture, energy-transfer complexes, in addition to the prerequisites of being highly absorbing and photostable, the bridging ligand must also be efficient at communicating electronic density between the metal centers. The Creutz–Taube dimer[2,3] $(NH_3)_5Ru(pz)Ru(NH_3)_5^{4+}$ has served as a model complex in comparative bridging ligand communicative studies.[12] The elegance of the complex is derived in part from the photo- and electrochemical stability and from the facts that (1) each ruthenium(II) center is surrounded by NH_3 ligands that undergo only σ interactions with the metal center and are therefore uncompetitive with Ru(II) d_π–pz p_{π^*} interactions, (2) the monodentate NH_3 ligands circumvent steric difficulties of the peripheral ligands such as in $(bpy)_2$ complexes, and (3) the planar nitrogen heterocyclic pyrazine bridging ligand coordinated to the ruthenium at the pyrazine 1,4-positions provides effective π delocalization through the pyrazine bridging ligand. Similar bidentate ligands such as bpym and dpp have been utilized in the preparation of tetraammineruthenium(II) complexes.[8,10] The bpym ligand utilizes nitrogen coordination at the 1,3-positions on both pyrimidine rings to simultaneously chelate the two Ru(II) centers, while dpp incorporates the pyrazine nitrogen 1,4-coordination and 1′,1″-coordination of the remote pyridine rings. As evaluated from electrochemical and absorption spectral results of the tetraamineruthenium(II) complexes, the bpym ligand offers significantly less metal–metal communication than through analogous pyrazine-bridged dimer, while dpp appears to be competitive with the pyrazine-bridged pentaammineruthenium(II) complex, probably as a result of the direct pyrazine linkage of the two ruthenium centers.



tppz

Figure 1. 2,3,5,6-Tetrakis(2-pyridyl)pyrazine (tppz).

We have used the novel tridentate nitrogen aromatic heterocyclic ligand 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) (Figure 1) to prepare mono- and bimetallic triammineruthenium(II) complexes bound to/through tppz. The bis-tridentate coordination through tppz in the bimetallic complex affords direct metal-bridging ligand–metal communication through the central pyrazine group, as well as through the remote pyridine rings. The ammine spectator ligands on the triammineruthenium(II) moiety provide a richer metal d_π electronic environment without competitive π

---

(1) Novel Main Group Element Ligands Symposium, 3rd Chemical Congress of North America, Toronto, Ontario, Canada, June 5–10, 1988.
(2) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988.
(3) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.
(4) Rillema, D. P.; Taghdiri, D. G.; Jones, D. S.; Keller, C. D.; Worl, L. A.; Meyer, T. J.; Levy, H. A. *Inorg. Chem.* **1987**, *26*, 578.
(5) Petersen, J. D.; Murphy, W. R., Jr.; Sahai, R.; Brewer, K.; Ruminski, R. R. *Coord. Chem. Rev.* **1985**, *64*, 261.
(6) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.
(7) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370.
(8) Ruminski, R. R.; Petersen, J. D. *Inorg. Chem.* **1982**, *21*, 3706.
(9) Braunstein, C. H.; Baker, A. D.; Strekas, T. C.; Gafney, H. D. *Inorg. Chem.* **1984**, *23*, 857.
(10) Ruminski, R. R.; Cockroft, T.; Shoup, M. *Inorg. Chem.* **1988**, *27*, 4026.
(11) Sahai, R.; Murphy, W. R., Jr.; Petersen, J. D. *Inorg. Chim. Acta* **1986**, *114*, 137.
(12) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94.

0020-1669/89/1328-0370$01.50/0

interaction of other ligands such as bpy or trpy, which allows for uncomplicated metal–metal communication assessments.

The preparation of the bimetallic complex opens a new class of potential metallopolymers and simultaneously dispels earlier speculations[13] on the ability of the bis-tridentate tppz ligand to coordinate two metal centers on the same tppz ligand, on the basis of the steric repulsions of the coplanar pyridine rings.

Experimental Section

Materials. Analytical reagent grade compounds were used for preparations described in this work. Argon was deoxygenated by passing it first through a chromous solution and then through a drying tube before use. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

Synthesis. The tppz ligand was prepared without difficulty according to literature procedures.[13] The syntheses of $[(NH_3)_3Ru(tppz)](ClO_4)_2$ and $[((NH_3)_3Ru)_2tppz](ClO_4)_4$ required the reaction of the previously reported air-stable $[(NH_3)_5(H_2O)Ru](TFMS)_3$ ($TFMS^-$ = trifluoromethanesulfonate) complex with tppz.[14]

$[((NH_3)_3Ru)_2tppz](ClO_4)_4$. A 0.175-g (0.27-mmol) sample of $[(NH_3)_5(H_2O)Ru](TFMS)_3$ and 0.036 g (0.093 mmol) of tppz were dissolved in 25 mL of anhydrous ethanol containing Zn(Hg) amalgam. The yellow mixture was heated at reflux and constantly stirred while being deaerated with a continuous stream of argon passing over the solution for 5 h. The blue-violet solution that formed was cooled to room temperature, and 50 mL of petroleum ether was added. The crude product was collected by vacuum filtration and dissolved through the filter in a minimum of acetone, and the mixture was eluted down a 15 cm (length) × 2 cm (diameter) alumina column with a 2-g $NaClO_4$/400-mL acetone solution. The blue fraction that separated from the red monometallic fraction was collected in a beaker and evaporated to dryness at room temperature. The product was dislodged from the beaker by washing with anhydrous ethanol to remove excess $NaClO_4$ and separated as a solid by centrifugation. After several washings with ethanol, the product was washed with petroleum ether and vacuum-dried. The dried product should be handled with gloves and behind a shield. The product should *not* be scraped out of the test tube to enhance the yield. Yield: 0.028 g (0.026 mmol), 28%. Anal. Calcd for $C_{24}H_{34}N_{12}Cl_4O_{16}Ru_2$: C, 26.43; H, 3.15; N 15.41. Found: C, 26.48; H, 3.17; N, 15.37.

$[(NH_3)_3Ru(tppz)](ClO_4)_2$. A 0.11-g (0.17-mmol) sample of $[(NH_3)_5(H_2O)Ru](TFMS)_3$ and 0.32 g (0.83 mmol) of tppz were dissolved in 25 mL of anhydrous ethanol containing Zn(Hg) amalgam. The yellow mixture was heated at reflux and constantly stirred while being deaerated with a continuous stream of argon passing over the solution for 5 h. The red solution that formed was cooled to room temperature, and 50 mL of petroleum ether was added. The crude product was dissolved through the filter in a minimum of acetone, and the mixture was eluted down an alumina column as previously described. The red monometallic fraction was collected in a beaker and evaporated to dryness at room temperature. The product was dislodged from the beaker by washing with anhydrous ethanol to remove excess $NaClO_4$ (although the product is slightly soluble) and was separated as a solid by centrifugation. After several washings with ethanol, the product was washed with petroleum ether and vacuum-dried. The dried products should be handled with gloves and behind a shield. The product should *not* be scraped out of the test tube to enhance the yield. Yield: 0.072 g (0.094 mmol), 54%. Anal. Calcd for $C_{24}H_{25}N_9Cl_2O_8Ru\cdot{}^3/_2H_2O$: C, 37.60; H, 3.69; N, 16.45. Found: C, 37.74; H, 3.67; N, 16.47.

Caution! Although no difficulty was encountered in the preparation of these complexes, perchlorate complexes in the presence of organic ligands are known to be explosive and should be handled with care only in small quantities (less than 10 mg) behind a shield. Under no circumstances were the entitled complexes evaporated to dryness by heating or scraped from the sides of dry containers. After purification, the mono- and bimetallic complexes should be recrystallized with PF_6^-.

Instrumentation. Electronic absorption spectra were recorded on a Beckman Model 5240 spectrophotometer with matching quartz cells.

Table I. Electronic Absorption Data and Quantum Yields for Ruthenium(II) Complexes

complex ion	λ_{max}, nm	ϵ, M^{-1} cm^{-1} × 10^3	assgnt	$10^4\Phi$	ref
$(NH_3)_3Ru(tppz)^{2+}$	550 sh[a]	3.1	MLCT	<1	*b*
	492	6.4	MLCT	<1	
	380	4.5	MLCT	<1	
	330	34	$\pi \rightarrow \pi^*$		
$((NH_3)_3)Ru)_2(tppz)^{4+}$	582	19	MLCT	<1	*b*
	430	6.7	MLCT	<1	
	380 sh	...	MLCT		
	350	35	$\pi \rightarrow \pi^*$		
$(NH_3)_4Ru(dpp)^{2+}$	545	45	MLCT	<1	10
	454	4.8	MLCT	1	
	368	5.0	MLCT	3	
	307	17	$\pi \rightarrow \pi^*$		
$((NH_3)_4)Ru)_2(dpp)^{4+}$	558	19	MLCT	<1	10
	368	9.8	MLCT	3	
	318	25	$\pi \rightarrow \pi^*$		
$(NH_3)_4Ru(bpym)^{2+}$	567	2.0	MLCT	<1	8
	402	8.4	MLCT		
$((NH_3)_4Ru)_2(bpym)^{4+}$	697	4.0	MLCT	<1	8
	424	18	MLCT		
$(NH_3)_5Ru(pz)^{2+}$	472		MLCT		3
$((NH_3)_5Ru)_2(pz)^{4+}$	547		MLCT		3

[a] Shoulder. [b] This work.

Cyclic voltammograms were recorded on a Bio Analytic Systems CV-1B cyclic voltammograph with a Hewlett Packard 7044A X-Y recorder. The glassy-carbon working electrode (3.0-mm diameter) was polished prior to each scan. A Ag/AgCl (3 M KCl, nominally −0.044 V vs SCE) reference electrode was used. All potentials are reported vs SCE and are uncorrected for junction potentials. The potentials reported for oxidation couples, $E_{1/2}$, are estimates obtained by averaging anodic and cathodic peak potentials, unless otherwise noted. Cyclic voltammograms were recorded in DMF with 0.1 M tetrabutylammonium perchlorate as the electrolyte and in H_2O with 0.1 M KCl as the electrolyte. The complexes are insoluble in CH_3CN, which would have provided a more ideal solvent window.

Samples were irradiated with a continuous-beam photolysis apparatus; procedures and calibrations were as previously described.[10] The desired wavelength of irradiation was isolated by using Hg-line (Hg source) or band filters (xenon source).

The [2+,2+] bimetallic complex was dissolved in 2 M H_2SO_4, the mixture was titrated with a primary standard Ce(IV)/2 M H_2SO_4 solution, and the absorption spectrum was recorded from 1300 to 400 nm. A Sn(II) solution and solid Zn/Hg were used separately in attempted rereductions of the oxidized [2+,3+] and [3+,3+] samples.

Results and Discussion

The synthesis of Ru(II) with the tridentate ligand tppz parallels the synthetic procedures for preparations of Ru(II) complexes with bidentate nitrogen aromatic heterocyclic ligands[6-9] and with the tridentate ligand 2,2′:6′,2″-terpyridine.[15-19] Coordination of $Ru(NH_3)_5(H_2O)^{2+}$ with tppz most likely proceeds stepwise, initially forming the mono- and bicoordinated intermediates before formation of the tridentate Ru(II) complexes. After chromatography and washing, identification of the products as exclusively $[(NH_3)_3Ru(tppz)](ClO_4)_2$ and $[(NH_3)_3Ru(tppz)Ru(NH_3)_3](ClO_4)_4$ was based on absolute percent C, H, and N, as well as the C/N ratio. The purity of each complex was further verified by the clarity of cyclic voltammograms.

The aqueous UV–vis electronic absorption spectra (Figure 2) maxima and extinction coefficients for $(NH_3)_3Ru(tppz)^{2+}$, $(NH_3)_3Ru(tppz)Ru(NH_3)_3{}^{4+}$, and similar Ru(II) amine complexes are summarized in Table I. The spectrum of the $(NH_3)_3Ru(tppz)^{2+}$ ion shows intense transitions at 380 nm (ϵ = 4500 M^{-1} cm^{-1}) and at 492 nm (ϵ = 6400 M^{-1} cm^{-1}) with a low-energy shoulder at 550 nm (ϵ = 3100 M^{-1} cm^{-1}). On the basis of the similarity in energy and molar absorptivity with previously reported complexes such as $(trpy)Ru(L)_3{}^{2+}$ and $(trpy)Ru(bpy)(NH_3)^{2+}$,[15,18] these are most likely Ru $d_\pi \rightarrow$ tppz p_{π^*} MLCT transitions. The highest absorption at 330 nm is assigned as a tppz intraligand $\pi \rightarrow \pi^*$ transition. An aqueous solution of $(NH_3)_3Ru(tppz)Ru$-

---

(13) Goodwin, H. A.; Lyons, F. *J. Am. Chem. Soc.* **1959**, *81*, 6415.

(14) Diamond, S. E.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5921.

(15) Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.

(16) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 5577.

(17) Murphy, W. R., Jr.; Takeuchi, K.; Barley, M. H.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1041.

(18) Adcock, P. A.; Keene, F. R.; Smythe, R. S.; Snow, M. R. *Inorg. Chem.* **1984**, *23*, 2336.

(19) Calvert, J. M.; Peebles, D. L.; Nowak, R. J. *Inorg. Chem.* **1985**, *24*, 3111.

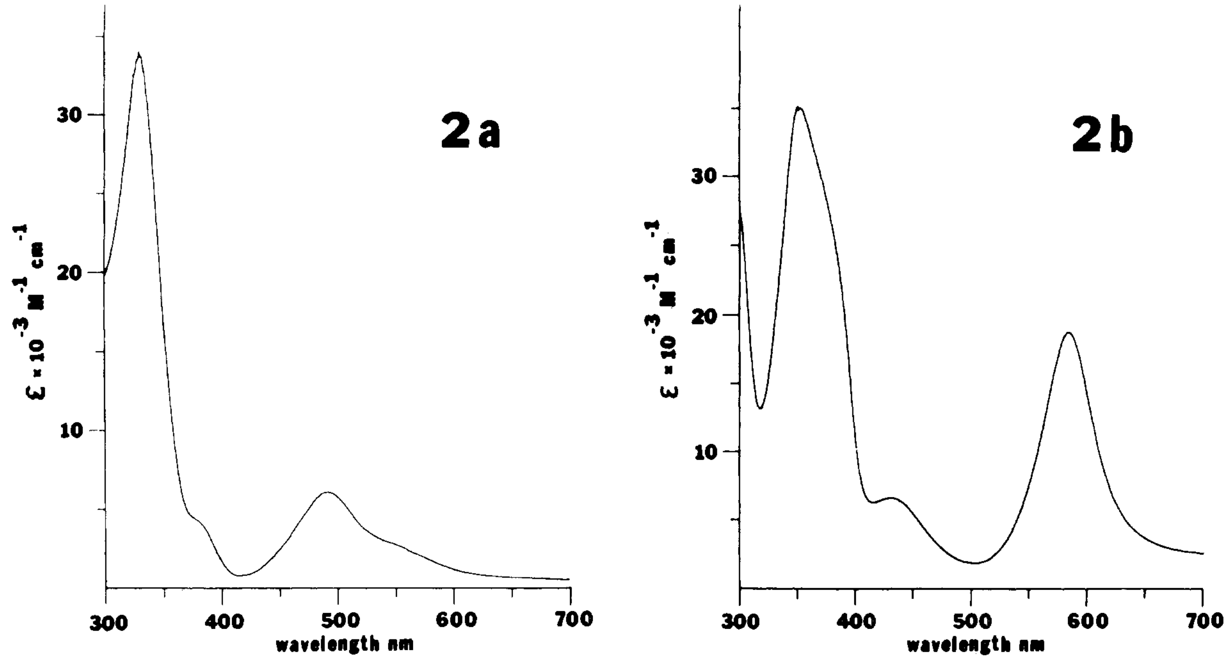


Figure 2. Electronic absorption spectra of (a) $(NH_3)_3Ru(tppz)^{2+}$ and (b) $((NH_3)_3Ru)_2(tppz)^{4+}$ in aqueous solutions.

Table II. Electrochemical Data for Mono- and Bimetallic Ruthenium Complex Ions

complex	solvent	$E_{1/2}$, V	$\Delta E_{1/2}$, mV[a]	$E_{1/2}(2)$, V	$\Delta E_{1/2}$, mV[a]	$\Delta E_{1/2}(2-1)$, mV	ref
$(NH_3)_3Ru(tppz)^{2+}$	H_2O	0.84[b]	80				*c*
	DMF	0.97[b]	95				
$((NH_3)_3Ru)_2(tppz)^{4+}$	H_2O	0.69[b]	85				*c*
	DMF	0.81[b]	85	1.31		500	
$(NH_3)_4Ru(dpp)^{2+}$	H_2O	0.86[d]	62				10
	CH_3CN	1.01[d]	65				
$((NH_3)_4Ru)_2dpp^{4+}$	H_2O	0.77[d]	65	1.13	110	360	10
	CH_3CN	0.90[d]	65	1.29	85	390	
$(bpy)_2Ru(dpp)^{2+}$	CH_3CN	1.58[d]	88				9
$((bpy)_2Ru)_2(dpp)^{4+}$	CH_3CN	1.57[d]	95	1.76	95	190	9
$(NH_3)_4Ru(bpym)^{2+}$	H_2O	0.75[d]					8
$((NH_3)_4Ru)_2(bpym)^{4+}$	H_2O	0.83[d]		1.02		190	8
$(NH_3)_5Ru(pz)^{2+}$	H_2O	0.49[d]					3
$((NH_3)_5Ru)_2(pz)^{4+}$	H_2O	0.37[d]		0.76		390	3

[a] Peak to peak separations of anodic and cathodic waves. [b] Aqueous solutions: 22 °C, 0.10 M KCl; scan rate 100 mV/s. DMF solutions: 22 °C, 0.10 M tetrabutylammonium perchlorate; scan rate 100 mV/s. All solutions were deaerated. $^{e}{}_{1/2}$ values were recorded vs a Ag/AgCl electrode (nominally −0.044 V vs SCE) and are reported vs SCE. [c] This work. [d] Potentials vs NHE.

$(NH_3)_3{}^{4+}$ exhibits a transition at 582 nm ($\epsilon = 18\,800$ M^{-1} cm^{-1}). The low-energy shift of the MLCT transition for bimetallic vs monometallic complexes has previously been attributed[2,3,8,9] to a combination of the lowering of the bridging ligand π^* LUMO and the formation of the metal d_π–bridging ligand p_{π^*}–metal d_π nonbonding HOMO, and therefore, this transition is assigned as a MLCT transition. The absorption at 430 nm ($\epsilon = 6700$ M^{-1} cm^{-1}) for the $(NH_3)_3Ru(tppz)Ru(NH_3)_3{}^{4+}$ ion is also assigned as a MLCT transition. The shoulder at 380 nm is most likely another MLCT transition on the side of the intense $p_\pi \rightarrow p_{\pi^*}$ transition at 350 nm.

Extended irradiation of aqueous solutions of $(NH_3)_3Ru(tppz)^{2+}$ at 546, 490, and 366 nm and of $(NH_3)_3Ru(tppz)Ru(NH_3)_3{}^{4+}$ at 578 and 436 nm results in no tppz loss ($\Phi_{max} < 0.0001$) and demonstrates the suitability of these complexes in photon-capture applications without tppz bridge cleavage. Photostability has previously been demonstrated for similar low-spin d^6 Ru(II), Cr(0), Mo(0), and W(0) complexes when the MLCT state lies at lower energy than the ligand field state.[20–22]

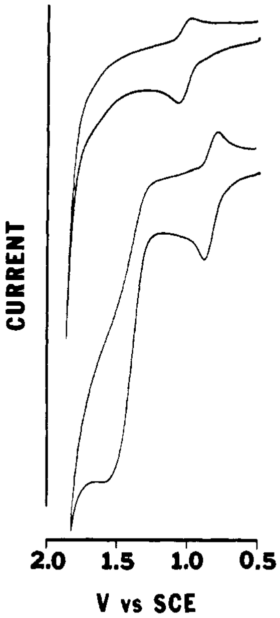


Figure 3. Cyclic voltammograms of $(NH_3)_3Ru(tppz)^{2+}$ (top) and $(NH_3)_3Ru(tppz)Ru(NH_3)_3{}^{4+}$ (bottom) recorded in deaerated DMF/0.10 M TBAP at 100 mV/s.

---

(20) Ford, P. C. In *Inorganic and Organometallic Photochemistry*; Wrighton, M. S., Ed.; Advances in Chemistry Series 168; American Chemical Society: Washington, DC, 1978; Chapter 5.

(21) Adamson, A. W.; Fleischaver, P. D., Eds.; *Concepts of Inorganic Photochemistry*; Wiley-Interscience: New York, 1975.

(22) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213.

The cyclic voltammograms of the $(NH_3)_3Ru(tppz)^{2+}$ and $(NH_3)_3Ru(tppz)Ru(NH_3)_3{}^{4+}$ complexes are shown in Figure 3, and the results are summarized in Table II. $E_{1/2}$ for the oxidation/reduction couple of $(NH_3)_3Ru(tppz)^{2+}$ is +0.97 V (vs SCE, DMF/0.10 M TBAP, 100 mV/s; $E_{1/2}$ is the average of the anodic and cathodic waves). Although the anodic/cathodic wave separation of 75 mV is larger than the theoretical value of 59 mV, on the basis of the reproducibility of several scans and the equivalence of wave height, the electrochemical couple is judged to be reversible. The $(NH_3)_3Ru(tppz)Ru(NH_3)_3{}^{4+}$ complex shows two waves at $E_{1/2}(1) = +0.81$ V and $E_{1/2}(2) = +1.31$ V. The difference in $E_{1/2}(1)$ and $E_{1/2}(2)$ couples for bimetallic complexes has previously been interpreted as a measure of metal–metal communication through a bridging ligand.[2,3,8,12,23,24] The unusually large $\Delta E_{1/2}(2-1)$ value of 0.50 V for $(NH_3)_3Ru(tppz)Ru(NH_3)_3{}^{4+}$ indicates that substantially greater metal–metal interaction occurs through tppz as compared with similar ruthenium amine-bridged complexes ($\Delta E_{1/2}(2-1) = 390$ mV − 50 mV).[2,3,8,10,17] The $E_{1/2}(1)$ value for $(NH_3)_3Ru(tppz)Ru(NH_3)_3{}^{4+}$ is 0.16 V less positive than the $E_{1/2}$ value (+0.97 V) for $(NH_3)_3Ru(tppz)^{2+}$ and also demonstrates the communicative effectiveness of tppz by the addition of σ-donating NH_3 groups, via the coordination of the remote $(NH_3)_3Ru$ center.

The $E_{1/2}(2-1)$ values of the bimetallic complex allow for the calculation of K_{com} according to the formula $\exp(\Delta E_{1/2}(2-1)/25.69)$, where $\Delta E_{1/2}$ is in millivolts and $T = 25$ °C; the comproportionation equilibrium is described by[24-26]

$$((NH_3)_3Ru)_2(tppz)^{4+} + ((NH_3)_3Ru)_2(tppz)^{6+} \rightarrow 2((NH_3)_3Ru)_2(tppz)^{5+}$$

The $K_{com} = 2.8 \times 10^8$ value is larger than the calculated value for the analogous tetraammineruthenium bpym- and dpp-bridged complexes.

Despite the high comproportionation constant, titration of the $((NH_3)_3Ru)_2(tppz)^{4+}$ [2+,2+] species with Ce(IV) produced a decrease and a broadening of the characteristic absorption at 585 nm without appearance of an intervalence band in the 700–1300-nm region. Throughout Ce(IV) addition, isobestic points at 720, 625, and 540 nm were observed as the 585-nm MLCT absorption decreased without a wavelength shift until the [3+,3+] equivalence point was reached. Attempted rereduction of the [2+,3+] and [3+,3+] samples with Sn(II) or by addition of Zn/Hg failed to regenerate the initial [2+,2+] spectrum, suggesting the 5+ and 6+ species decompose on the time scale of the experiment. Addition of excess Ce(IV) caused loss of the isobestic point, probably as a result of NH_3 oxidation to form NO, as has been reported for Ce(IV) oxidations of (trpy)Ru(bpy)-$NH_3{}^{2+}$.[17]

Conclusion

The transition energies, molar absorptivities, and visible-region photostability make this type of complex ideal in energy capture, storage, and conversion processes. Electrochemical results demonstrate the effective communication between the Ru(II) centers through the tppz bridging ligand. The impact of this new class of tppz-bridged complexes such as $(NH_3)_3Ru(tppz)Ru(NH_3)_3{}^{4+}$ is extensive, ranging from optical electron-transfer studies to potential intramolecular energy-transfer reactions.

Acknowledgment. We acknowledge the generous financial support of this work through a Bristol-Meyers Co. grant of the Research Corp.

Registry No. $[((NH_3)_3Ru)_2tppz](ClO_4)_4$, 117828-26-9; $[(NH_3)_3Ru(tppz)](ClO_4)_2$, 117828-28-1; $[(NH_3)_5(H_2O)Ru](TFMS)_3$, 53195-18-9; $((NH_3)_3Ru)_2(tppz)^{6+}$, 117828-29-2; $((NH_3)_3Ru)_2(tppz)^{5+}$, 117860-18-1; $Ru(NH_3)_3(tppz)^+$, 117828-30-5.

---

(23) Powers, M. J.; Meyers, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.
(24) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.
(25) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 381.
(26) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

Contribution from the Institute for Inorganic
Chemistry, University of Witten/Herdecke,
Stockumer Strasse 10, 5810 Witten, FRG

Volume Profiles for Solvolysis Reactions of Sterically Hindered Diethylenetriamine Complexes of Palladium(II) in Aqueous Solution

J. J. Pienaar,[1] M. Kotowski, and R. van Eldik*

Received May 18, 1988

The intimate nature of solvolysis reactions of diethylenetriamine (dien) and substituted dien complexes of palladium(II) has interested us for quite some time[2-5] due to the general importance of this process in the substitution behavior of square-planar complexes. We and others have adopted high-pressure kinetic techniques to gain insight into the volume changes involved in such processes.[6] Our recent study[4] emphasized the importance of the nature of the leaving group in determining the volume of activation for the solvolysis process. It was reported that ΔV^* is significantly more negative for anionic leaving groups during the solvolysis of $Pd(R_5dien)X^{(2-n)+}$ (R_5dien = methyl- and ethyl-substituted diethylenetriamine). In fact, the correct analysis of such data calls for the construction of a volume profile on which basis the transition state of the process can be located with respect to the partial molar volumes of the reactant and product species.[7,8] Such analyses were not possible in our previous investigations due to a lack of either the required partial molar volume data or the overall reaction volume of the process.

We have now completed a series of measurements in which volumes of activation were determined for solvolysis (k_1) and reverse anation (k_{-1}) reactions of some substituted dien complexes according to the overall process in (1), where R = CH_3 and C_2H_5.

$$Pd(R_5dien)X^{(2-n)+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pd(R_5dien)H_2O^{2+} + X^{n-} \quad (1)$$

These data enable us to construct volume profiles for a series of such reactions and to make quantitative correlations between the partial molar volumes of ground- and transition-state species.

Experimental Section

Complexes of the type $Pd(R_5dien)X^{(2-n)+}$, where R = Me or Et and $X^{n-} = H_2O$, Cl^-, Br^-, I^-, $N_3{}^-$, or $C_2O_4{}^{2-}$, were prepared and characterized in the same way as previously reported for these or closely related complexes.[3,4,9-11] UV–vis absorption spectra were recorded on Shimadzu UV250 and Perkin-Elmer Lambda 5 spectrophotometers. All measurements were performed at 25 °C and 0.1 mol dm^{-3} ionic strength ($NaClO_4$ medium). Kinetic experiments at ambient pressure were performed with a Durrum D110 stopped-flow instrument equipped with a data acquisition system,[12] whereas those at elevated pressure (up to 100 MPa) were performed with a high-pressure stopped-flow unit.[13] All reactions were studied under pseudo-first-order conditions, and the corresponding semilogarithmic plots were linear for at least 3 half-lives of the reaction. The reported rate constants are the mean values of at least six kinetic runs. UV–vis spectra at elevated pressure (up to 150 MPa) were re-

---

(1) On leave from the Research Unit for Chemical Kinetics, Potchefstroom University for CHE, Potchefstroom 2520, Republic of South Africa.
(2) Breet, E. L. J.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 1865.
(3) Kotowski, M.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 3310.
(4) Kotowski, M.; van Eldik, R. *Inorg. Chem.* **1986**, *25*, 3896.
(5) Kotowski, M.; Begum, S.; Leipoldt, J. G.; van Eldik, R. *Inorg. Chem.*, in press.
(6) Kotowski, M.; van Eldik, R. In *Inorganic High Pressure Chemistry: Kinetics and Mechanisms*; van Eldik, R., Ed.; Elsevier: Amsterdam, 1986; Chapter 4.
(7) van Eldik, R. *Comments Inorg. Chem.* **1986**, *5*, 135.
(8) Ducommun, Y.; Merbach, A. E.; Hellquist, B.; Elding, L. I. *Inorg. Chem.* **1987**, *26*, 1759.
(9) Basolo, F.; Gray, H. B.; Pearson, R. G. *J. Am. Chem. Soc.* **1960**, *82*, 4200.
(10) Breet, E. L. J.; van Eldik, R.; Kelm, H. *Polyhedron* **1983**, *2*, 1181.
(11) Breet, E. L. J.; van Eldik, R.; Kelm, H. *Inorg. Chim. Acta* **1984**, *85*, 151.
(12) Kraft, J.; Wieland, S.; Kraft, U.; van Eldik, R. *GIT Fachz. Lab.* **1987**, *31*, 560.
(13) van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* **1981**, *50*, 131.