

$\text{Os}(\text{CO})_3$ turnstile reorientation can only occur by virtue of cooperative effects in the crystal lattice.

The observations described in this paper, coupled with those of previous studies,^{3–15} suggest some generalizations concerning the comparison of dynamic processes in solution and in the solid state. It might be imagined that placing a molecule in a crystal lattice may influence the fluxional processes of an isolated molecule in several distinct ways, and the evidence presented in this work allows for the discussion of these various possibilities. First, some low-energy processes are observed in solids, which are not detected in solution NMR, because they are always "fast" on the NMR time scale in solution. For example for **1** we observed an unexpected dynamic interchange process, involving the benzene and ethene ligands, between at least two different molecular conformers in the solid-state structure. Such processes may well be more common than expected from examination of solution NMR spectra, in which they are always rapid on the NMR time scale, and crystallographic data, in which they may show up as disorder, but perhaps not always of sufficient amplitude to be detected.

The activation barriers to some dynamic processes, the benzene and ethene ligand reorientations in **1** are examples, appear to be very similar in solution and in the solid state. This may be interpreted as meaning that such processes are controlled primarily by electronic factors involved in the rearrangement of valence electrons, compared to which steric effects, both *intra*- and *intermolecular*, are insignificant. However, sterically demanding processes such as the trigonal-twist process of the $\text{Os}(\text{C}_2\text{H}_4)(\text{CO})_2$ group in **1** may be prevented from occurring by the molecular packing characteristics. In such cases we may imagine that *intermolecular* steric effects, due to the specific packing arrangement, that act directly on the group or groups involved in the potential dynamic process are the cause of the increased barrier

to motion in the crystalline state. For other processes, for which the relative facility of motion in a solution environment is principally determined by *intramolecular* steric effects, the *intermolecular* packing effects of the crystalline state may be regarded as influencing the situation in two ways. In the first place, as discussed above, there are direct *intermolecular* steric effects acting on the potentially motional groups. The additional factor of *intermolecular* steric effects leads to such processes having larger activation barriers in the crystalline state than in solution. Second, the *intermolecular* steric effects on other groups of a molecule may modify the *intramolecular* steric forces acting within the molecule and ultimately influence the activation barrier to a fluxional process. There are two ways in which this might be conceived. First, the *intermolecular* steric effects could cause molecular conformational differences in the crystalline state compared to the situation in solution and so directly modify the *intramolecular* steric forces. Second, the facility of dynamic processes within a molecule is likely to be enhanced by relatively large amplitude vibrations of surrounding groups, which allow relaxation of the structure around the mobile functionality as the dynamic process occurs. Specific *intermolecular* interactions in the crystalline state may reduce the ability of the surrounding groups to relax around the mobile group and so increase the activation barrier to the dynamic process. This is illustrated by the reversal in the solid state relative to solution of the order of facility of the turnstile reorientations of the $\text{Os}(\text{CO})_3$ functionalities of **1**, control of these processes in the solid state is likely to be due to *intermolecular* steric effects acting both directly and also indirectly by influencing *intramolecular* effects.

Registry No. $\text{Os}_3(\text{CO})_8(\eta^2\text{-CH}_2\text{CH}_2)(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-C}_6\text{H}_6)$, 118772-73-9; Os, 7440-04-2.

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Solvent-Induced and Polyether-Ligand-Induced Redox Isomerization within an Asymmetrically Coordinated Mixed-Valence Ion:

trans-(py)(NH₃)₄Ru(4-NCpy)Ru(2,2'-bpy)₂Cl⁴⁺

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Received February 27, 1990

Advantage is taken of oxidation-state-dependent ligand (ammine)/solvent interactions to shift redox potentials and effect redox isomerization in the title complex. In poorly basic solvents, the stable isomeric form is *trans*-(py)(NH₃)₄Ru^{II}(NCpy)Ru^{III}(bpy)₂Cl⁴⁺ (py is pyridine; NCpy is 4-cyanopyridine; bpy is 2,2'-bipyridine). In contrast, in stronger Lewis bases or in a mixture of strong and weak bases (dimethyl sulfoxide + nitromethane), the preferred isomer is *trans*-(py)(NH₃)₄Ru^{III}(NCpy)Ru^{II}(bpy)Cl⁴⁺. Evidence for redox isomerization was obtained, in part, from plots of formal potentials versus solvent Lewis basicity. Confirmatory evidence was obtained from a combination of electrochemical reaction entropy and resonance Raman spectroscopic experiments. UV–vis–near-IR absorption experiments, however, were not found to be useful in demonstrating isomerization. In a related series of experiments, redox isomerization was also demonstrated based on ammine binding by either a low molecular weight poly(ethylene glycol) species or by a macrocyclic ligand, dibenzo-36-crown-12. Much smaller molar amounts of either the polymer (substoichiometric) or crown (approximately stoichiometric) are required, in comparison to basic solvent (severalfold excess), in order to induce isomerization in nitromethane as the initial solvent. The possible general utility of the redox isomerization concept in time-resolved intramolecular charge-transfer studies and in optical studies of competitive hole- and electron-transfer pathways is mentioned.

Introduction

A few years ago we reported on the first example of solvent-induced redox isomerization in a mixed-valence system.^{1,2} The system of interest was the symmetrically bridged, heteronuclear bimetallic complex, (bpy)₂ClOs(pyrazine)Ru(NH₃)₅⁴⁺ (bpy is

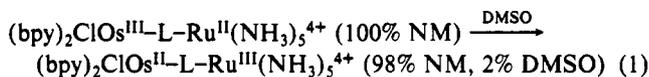
2,2'-bipyridine). The basis for isomerization was in the overall energetic proximity of the Os(III/II) and Ru(III/II) formal potentials (E_f) and in the marked solvent tunability of the latter. For this system the oxidation state distribution was found to be

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(1) Hupp, J. T.; Neyhart, G. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 5349.
(2) Related reports: (a) Neyhart, G. A.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 4808. (b) Olabe, J. A.; Haim, A. *Inorg. Chem.* **1989**, *28*, 3277.

Os^{III}-L-Ru^{II} in weakly basic solvents (such as nitromethane (NM)) and Os^{II}-L-Ru^{III} in strong Lewis bases (such as dimethyl sulfoxide (DMSO)). At that time our interests were focused on the possible role of the solvent in modulating electronic localization and on simply carrying out a proof-of-concept demonstration of isomerization.

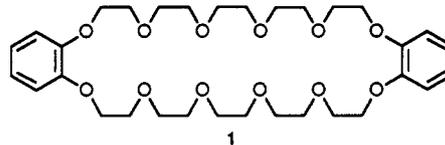
Recently our interests have returned to the redox isomerization phenomenon. The motivation for further investigation was 2-fold. First, the possibility exists in mixed solvents for *time-resolved* redox isomerization measurements (i.e. intramolecular electron-transfer rate measurements) based on selective solvation effects³ and rapid mixing methods.⁴ For example



With current mixing technologies,⁴ such an experiment would probably be feasible if the half-life for isomerization were on the order of a few microseconds or greater. The second point concerns the orbital pathways employed by bridged systems in transferring electrons intramolecularly.⁵ We have recently suggested that in asymmetric, solvent-tunable mixed-valence systems, filled-orbital (hole transfer) and empty-orbital (electron transfer) bridging pathways (superexchange pathways) are amenable to separate investigation, based on systematic optical intervalence studies involving one or the other ground electronic configuration.⁶ The details have been presented elsewhere.⁶ Basically, however, our earlier discussion focused on the consequences of solvent tuning of the energy gap between an initial state—(bpy)₂ClRu^{II}-L-Ru^{III}(NH₃)₄L⁴⁺—and either of two possible virtual states: (bpy)₂ClRu^{II}-L⁺-Ru^{III}(NH₃)₄L⁴⁺ (hole-transfer pathway) or (bpy)₂ClRu^{III}-L-Ru^{III}(NH₃)₄L⁴⁺ (electron-transfer pathway). (Note that the initial-state/virtual-state energy gap appears as a leading term in most quantitative expressions for superexchange coupling between covalently linked donor and acceptor sites.⁵) As described in more detail in the earlier report,⁶ we were able to investigate only the hole-transfer pathway (i.e. virtual reduction of the ammine ruthenium site) since only this pathway displayed a solvent dependence for the initial-state/virtual-state energy gap. It was noted, however, that the complementary electron-transfer pathway, in principle, could be investigated if the alternative mixed-valence form ((bpy)₂ClRu^{III}-L-Ru^{II}(NH₃)₄L⁴⁺) were available.^{6,7} Ideally, one would like to evaluate both pathways within a single system. This would be possible, of course, if one could induce redox isomerization.⁸

In this report, we wish to describe the redox isomerization of a homonuclear, mixed-valence metal complex: *trans*-(py)-(NH₃)₄Ru(NCpy)Ru(bpy)₂Cl⁴⁺ (NCpy is 4-cyanopyridine; py is pyridine). Induction of isomerization within the homonuclear complex required some additional synthetic manipulation on account of the inherent dissimilarities of Ru(III) reduction potentials in ammine versus polypyridyl environments.^{3a-c,9} The

key modification (apart from metal replacement) was the replacement of the symmetric bridge by the coordinatively asymmetric cyanopyridine ligand. As in the heteronuclear system,¹ we find that redox isomerization can be induced in *trans*-(py)-(NH₃)₄Ru(NCpy)Ru(bpy)₂Cl⁴⁺ by specific ligand-solvent interactions. Perhaps more importantly, it can also be induced by secondary coordination—more specifically by outer-sphere complexation of the tetraammine ruthenium site by low molecular weight poly(ethylene glycol) (H-(O-CH₂CH₂)_n-OH) or by a polyether macrocycle, dibenzo-36-crown-12 (**1**).¹⁰ We note



further that the polyether-induced isomerization requires only stoichiometric or substoichiometric amounts of the outer-sphere complexing agent.

In our earlier report,¹ proof of redox isomerization was fairly easy to obtain because of the unique visible and near-infrared absorption characteristics of (bpy)₂ClOs^{II} and (bpy)₂ClOs^{III}, respectively. In the present system, the two possible redox trapping sites are much less distinctive as chromophores. Consequently, we have had to devise alternative means for assessing ground-state valence distributions.

Experimental Section

Materials. [(bpy)₂RuCl(pyCN)](PF₆) was prepared by heating 0.5 g of (bpy)₂RuCl₂·2H₂O¹¹ and a 3-fold molar excess of NCpy at reflux for 1 h in a 70:30 ethanol-water mixture. Following addition of NH₄PF₆ and partial removal of ethanol, a solid was precipitated. Excess NCpy was removed by dissolving the solid in acetone and reprecipitating it from diethyl ether. Further purification was achieved by chromatography on alumina using 30:70 CH₃CN-toluene and 29:69:2 CH₃CN-toluene-CH₃OH as eluents. Anal. Calcd: C, 44.8; H, 2.9; N, 11.6. Found: C, 42.80; H, 2.87; N, 11.74.

[*trans*-(py)Ru(NH₃)₄(NCpy)RuCl(bpy)₂](PF₆)₃ was prepared and purified in the same manner as previously described⁹ ("method B") for the pyrazine-bridged analogue. Anal. Calcd: C, 30.8; H, 3.9; N, 10.4. Found: C, 31.3; H, 3.1; N, 10.4. To establish the mode of pyCN ligation, IR spectra of [(bpy)₂ClRu(pyCN)](PF₆) and the binuclear complex were compared. The noncoordinated nitrile functionality is expected to display a C≡N stretch at ~2240 cm⁻¹; binding to Ru(NH₃)_n should lower the stretching frequency to roughly 2180 cm⁻¹.¹² We found that, for the mononuclear ruthenium species above, ν_{C≡N} is 2235 cm⁻¹; for the binuclear complex, ν_{C≡N} is 2197 cm⁻¹. We further found upon oxidation of the monomer that ν_{C≡N} shifts only slightly (2237 cm⁻¹). Finally, a simple UV-vis absorption experiment with the precursor complex (bpy)₂ClRu(pyCN)⁺, in the presence and absence of acid (concentrated HCl in acetonitrile) revealed that the NCpy ligand could not be protonated. (Note that the pyridyl pK_a should lie near 2 while the nitrile pK_a should lie near -10.)¹³ Taken together, these results clearly imply that the NCpy bridge is coordinated to (py)(NH₃)₄Ru via the nitrile substituent. Electrochemical data, cited below, also support the assignment.

Tetraethylammonium hexafluorophosphate (TEAH) was prepared as described previously.^{3a} Solvents were purchased from Aldrich or from Mallinckrodt. Most were passed through alumina prior to use. Poly(ethylene glycol) (8000 Da) was purchased from Aldrich and was dried at room temperature under vacuum for several hours, prior to use. Dibenzo-36-crown-12 was prepared and purified according to the method of Colquhoun et al.¹⁴

Measurements. E_r values were determined by cyclic or differential-pulse voltammetry (DPV)¹⁵ with either a PAR 174A or IBM EC 225

- (3) (a) Curtis, J. C.; Blackburn, R. L.; Ennix, K. S.; Hu, S.; Roberts, J. A.; Hupp, J. T. *Inorg. Chem.* **1989**, *28*, 3791. (b) Blackburn, R. L.; Hupp, J. T. *Inorg. Chem.* **1989**, *28*, 3786. (c) Ennix, K. S.; McMahon, P. T.; Curtis, J. C. *Inorg. Chem.* **1987**, *26*, 2660. (d) Hupp, J. T.; Weydert, J. *Inorg. Chem.* **1987**, *26*, 2657. (e) Mayer, V.; Kotocova, A.; Gutmann, V.; Gerger, W. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *100*, 875.
- (4) Nemeth, M. T.; Fogelman, K. D.; Ridley, T. Y.; Margernum, D. W. *Anal. Chem.* **1987**, *59*, 283.
- (5) See, for example: Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40. (b) Marcus, R. A. *Chem. Phys. Lett.* **1987**, *133*, 471; **1988**, *146*, 13.
- (6) Hupp, J. T. *J. Am. Chem. Soc.* **1990**, *112*, 1563.
- (7) Note that the gap between (bpy)₂ClRu^{III}-L-Ru^{II}(NH₃)₄L⁴⁺ (ground state) and (bpy)₂ClRu^{III}-L-Ru^{III}(NH₃)₄L⁴⁺ (virtual oxidation of the tetraammine ruthenium site) is expected to be significantly solvent dependent but that the corresponding gap between (bpy)₂ClRu^{III}-L-Ru^{II}(NH₃)₄L⁴⁺ and (bpy)₂ClRu^{II}-L⁺-Ru^{III}(NH₃)₄L⁴⁺ (hole-transfer pathway) is not. See ref 6 for further discussion.
- (8) There are at least two additional requirements: (1) sufficient intervalence oscillator strength must exist in both ground-state electronic configurations, and (2) the intervalence absorption must not be obscured by other electronic transitions.

- (9) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.
- (10) Dibenzo-36-crown-12 is 6,7,9,10,12,13,15,16,18,19,26,27,29,30,32,33,35,36,38,39-eicosahydrodibenzo[*b,r*][1,4,7,10,13,16,19,22,25,28,31,34]dodecaoxacyclohexatriacontin.
- (11) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
- (12) Katz, N. E.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1988**, *27*, 1687.
- (13) See, for example: Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*; McGraw Hill: New York, 1970; pp 306-307.
- (14) Colquhoun, H. M.; Goodings, E. P.; Maud, J. M.; Stoddart, J. F.; Wolstenholme, J. B.; Williams, D. J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 607.

Table I. Formal Potentials for (py)(NH₃)₄Ru(NCpy)Ru(bpy)₂Cl^{5+/4+/3+}

solvent (DN)	$E_f(5+/4+)$, ^a mV	$E_f(4+/3+)$, ^a mV	$E_f(5+/4+)$, ^b mV	$E_f(4+/3+)$, ^b mV
DMSO (29.8)	937	575	442	80
dimethylacetamide (27.8)	908	585	412	89
acetone (17)	867	738	434	305
propylene carbonate (15.1)	836	714	496	374
acetonitrile (14.1)	845 ^c	730 ^c	480 ^c	365 ^c
benzonitrile (11.9)	822 ^c	690 ^c	444 ^c	312 ^c
nitrobenzene (4.4)	858	755	540	437
nitromethane (2.7)	887	741	604	458
50 mol% NM + 50 mol % DMSO	900	573	617	290
NM + dibenzo-36-crown-12 ^d	830	645	567	382
NM + poly(ethylene glycol) ^e	875 ^f	730 ^f	601	456

^a Referenced to SSCE. ^b Referenced to ferrocene. ^c E_f values obtained by using digital simulation of experimental cyclic voltammograms. ^d ~2 mM complex, 20 mM dibenzo-36-crown-12, 20 mM tetraethylammonium hexafluorophosphate. ^e 2 mM complex, 1 mM polyethylene glycol, 100 mM tetraethylammonium hexafluorophosphate. ^f Referenced to SCE.

potentiostat. Typically, 0.1 M solutions of supporting electrolyte (TEAH) were used. For experiments in nitromethane, the solutions additionally contained freshly activated molecular sieves (water scavengers) and measurements were made under dry nitrogen. The working electrode in all experiments was a Pt wire; a gold wire was used as the counter electrode. Potentials were measured against a saturated (NaCl) calomel electrode (SSCE). Variable-temperature experiments were carried out by employing a three compartment, nonisothermal cell.¹⁶

Electronic spectra were obtained under electrochemical control by using an OLIS Cary-14 spectrophotometer and the PAR potentiostat. The sample cell consisted of an SSCE reference electrode, a Pt counter electrode, and a gold mini-grid working electrode, which was placed between two microscope slides separated by Teflon tape. Solutions here were typically 1 mM in sample and 0.1 M in electrolyte.

IR spectra (KBr pellets) were obtained at 2-cm⁻¹ resolution by using a Mattson FTIR spectrometer. Resonance Raman spectra were obtained as previously described.^{17a} The excitation wavelength was 496 nm, and the incident power was typically 25 mW. The chromophore concentration was approximately 0.5 mM.

Results and Discussion

Solvent Effects. Metal-based formal potentials (SSCE reference) are listed in Table I as a function of solvent composition. To account for solvent-dependent liquid-junction effects and to

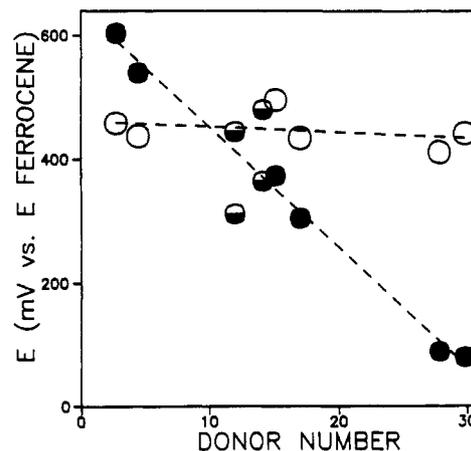


Figure 1. *trans*-(py)(NH₃)₄Ru(NCpy)Ru(bpy)₂Cl^{5+/4+/3+} redox potentials (ferrocene reference scale) versus solvent donor number (see text and Table I): filled circles, reduction of (py)(NH₃)₄Ru^{III}-; open circles, reduction of -Ru^{III}(bpy)₂Cl; half-filled circles, redox site assignments uncertain.

(15) In comparison to cyclic voltammetry, differential-pulse voltammetry (DPV) provides superior resolution of closely spaced redox waves and superior discrimination against solvent background current. A word of caution is appropriate, however, regarding quantitative studies by DPV. For binuclear complexes like the title compound, we have routinely observed smaller peaks for the metal-ammine versus metal-bpy redox couple, implying significant contamination with a monomeric component of the latter, even when alternative measures of complex purity indicate that significant contamination is absent. The disparate effects generally disappear, however, when the working electrode is heated in a flame just prior to use. Also observed following the flame treatment are shifts in the metal-ammine peak potential (generally to less positive potentials, if the potential is pulsed in the positive voltage direction). While the latter effects are usually small (a few tens of millivolts) they can lead to very large relative errors in variable temperature (reaction entropy) measurements. In retrospect, both effects (shift in potential; decrease in peak height) are obvious manifestations of slow interfacial electron-transfer kinetics (see, for example: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; p 196). (The slow kinetics are also manifest as a broadening of DPV peaks.) (For cyclic voltammetry, the errors in E_f tend to be much less since kinetic effects shift the anodic and cathodic current peaks in opposing (compensating) directions.) For DPV, we find that a useful diagnostic for the occurrence of deleterious kinetic effects is to compare peak potentials obtained from pulses in the positive direction (least positive initial potential) with those from pulses in the negative direction (most positive initial potential) (i.e. *not* a simple reversal of DPV scan direction). If kinetic effects are present, the peak potentials will differ. The kinetic effects can usually be eliminated, however, by using freshly cleaned (flame-treated) electrodes for each measurement.

(16) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.

(17) In both tetraammine- and pentaammineruthenium(II) species, photodecomposition appears to occur from a labile d-d state, which is accessed by intersystem crossing from a short-lived metal-to-ligand charge-transfer state. See: (a) Doorn, S. K.; Hupp, J. T. *J. Am. Chem. Soc.* **1989**, *111*, 4704. (b) Winkler, J. R.; Netzel, T. L.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1987**, *109*, 2381. (c) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213.

facilitate intercomparisons, the potentials have also been tabulated versus ferrocene/ferrocene (Fc⁺/Fc).^{18,19} (We have assumed that $E_f(\text{Fc}^+/\text{Fc})$ is independent of solvent.¹⁸) The tabulation suggests that one of the two reduction potentials changes substantially with solvent, while the other is more or less constant. Such a result is not unexpected: it is well-known that potentials for both mononuclear^{3b,4,20-22} and binuclear^{3a,c,6,9} metal ammine complexes shift strongly (in the negative direction) with increasing solvent Lewis basicity. The effect has been interpreted in terms of specific electron-pair donor (solvent)/acceptor (ammine ligand) interactions; the electrochemical effect evidently exists because the ammine ligands are better acceptors when bound to Ru(III) than Ru(II). Consistent with this interpretation, the E_f values in Table I correlate reasonably well with Gutmann's solvent "donor number" (DN), an empirical scale of Lewis basicity.²³ The same point is shown graphically in Figure 1. From the plot, it appears that the solvent-dependent and solvent-independent potentials "cross" in the vicinity of DN 12-14, implying redox isomerization. The extent of crossing, however, is sufficiently small (at least on the low DN end) that Figure 1 alone cannot be accepted as definitive proof of isomerization.

Further evidence for isomerization was initially sought from electronic absorption spectra. From Figure 1, the dimer should

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(19) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(20) Sahami, S.; Weaver, M. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *122*, 171.

(21) Hupp, J. T.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 1601.

(22) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 3639.

(23) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

Table II. Reaction Entropies for trans-(py)(NH₃)₄Ru(4-NCpy)Ru(bpy)₂Cl^{5+/4+/3+}

solvent	$\Delta S^{\circ}_{re}(5+/4+)$, eu	$\Delta S^{\circ}_{re}(4+/3+)$, eu
propylene carbonate	12 ± 2	39 ± 2
nitrobenzene	38	15
nitromethane	27	13
50 mol % NM + 50 mol % DMSO	8	36
nitromethane + dibenzo-36-crown-12	10 ± 4	33 ± 4

exist as trans-(py)₂(NH₃)₄Ru^{II}(NCpy)Ru^{III}(bpy)₂Cl⁴⁺ in nitromethane (DN = 2.7) and as trans-(py)(NH₃)₄Ru^{III}(NCpy)Ru^{II}(bpy)₂Cl⁴⁺ in propylene carbonate (PC) (DN = 15). In NM, absorption peaks appear at 435 and 461 nm. In PC they are at 417, 452, and 487 nm. Unfortunately the two spectra are neither sufficiently different nor sufficiently similar to support or refute the isomerization hypothesis.

In an attempt to clarify the nature of the electronic transitions and thereby establish the valence distributions, a series of Raman experiments was attempted. The reasoning was that resonance enhancement of Raman scattering would permit the dominant chromophore in each solvent to be identified. (Note that only the metal(II) sites are expected to be chromophoric in the visible region²⁴ and that only the chromophoric sites will display resonant scattering effects.) Experiments in PC with the mixed-valence complex, the fully reduced complex, the monomeric species (bpy)₂ClRu(pyCN)⁺, and free cyanopyridine (normal Raman) clearly indicated²⁴ that the oxidation state distribution is trans-(py)(NH₃)₄Ru^{III}(NCpy)Ru^{II}Cl(bpy)₂⁴⁺ and that the scattering chromophore in PC is the (NCpy)Ru^{II}Cl(bpy)₂ fragment.²⁵ In NM as solvent, the Raman experiments failed completely, due to rapid photodecomposition of both the 3+ and 4+ forms of the dimer; obviously, no direct information about the valence distribution was obtained. In view, however, of (1) the known photolability of ruthenium(II) ammine complexes¹⁷ (especially in weakly basic solvents), (2) the nonchromophoric character of the ruthenium(III) ammine,²⁴ and (3) the photostability of the (bpy)₂ClRu^{II}(pyCN) moiety, a reasonable *indirect* inference is that the mixed-valence form in NM is trans-(py)(NH₃)₄Ru^{II}(NCpy)Ru^{III}(bpy)Cl⁴⁺.

A confirmation of the oxidation state distribution in NM was ultimately obtained from thermodynamic half-reaction entropy (ΔS°_{re}) measurements. Yee et al. have shown that values for ΔS°_{re} (= $S^{\circ}_{red} - S^{\circ}_{ox}$) can be obtained approximately (± 2 eu) from variable-temperature E_f measurements by employing a nonisothermal cell configuration,¹⁶ where $\Delta S^{\circ}_{re} \approx F(dE_f/dT)_{ni}$. Further studies²² have shown that reaction entropies for transition-metal redox couples follow (at least qualitatively) the molecular charge and inverse size trends expected from Bornian solvation. It has also been shown that the individual redox centers in ligand-bridged species behave entropically as isolated redox sites.^{2a,26} We reasoned therefore, that ΔS°_{re} would be relatively large for the compact (py)(NH₃)₄Ru^{-3+/2+} couple and relatively small for the larger diameter -Ru(bpy)₂Cl^{2+/+} couple, in

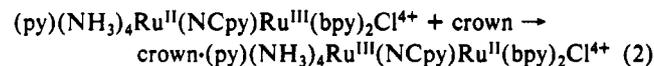
Table III. Formal Potentials for Mononuclear Ruthenium Redox Couples

redox couple	medium	E_f^a , mV
(bpy) ₂ ClRu(pyCN) ^{2+/+}	nitromethane	766
(bpy) ₂ ClRu(pyCN) ^{2+/+}	nitromethane + 20 mM crown	761
(bpy) ₂ ClRu(pyCN) ^{2+/+}	nitromethane + 1 mM (0.5 equiv) poly(ethylene glycol)	760
Ru(NH ₃) ₅ (py) ^{3+/2+}	nitromethane	504
Ru(NH ₃) ₅ (py) ^{3+/2+}	nitromethane + 20 mM crown	178
Ru(NH ₃) ₅ (py) ^{3+/2+}	nitromethane + 0.44 mM (0.22 equiv) poly(ethylene glycol)	347

^a Referenced to SSCE.

trans-(py)(NH₃)₄Ru(4-NCpy)Ru(bpy)₂Cl^{5+/4+/3+}. Table II confirms the prediction: the entropy change in PC as solvent is 12 eu for the first reduction (metal bpy site) and 39 eu for the second (metal ammine site), consistent with (py)(NH₃)₄Ru^{III}(NCpy)Ru^{II}(bpy)₂Cl⁴⁺ as the mixed-valence form. In both NM and nitrobenzene, however, the sequence is reversed. The first reduction involves a large entropy change and the second reduction a small one. It follows that in these solvents the mixed-valence form is (py)(NH₃)₄Ru^{II}(NCpy)Ru^{III}(bpy)₂Cl⁴⁺. An additional entropy experiment (see Table II) in an NM/DMSO mixture shows that conversion to (py)(NH₃)₄Ru^{III}(NCpy)Ru^{II}(bpy)₂Cl⁴⁺ can be induced by selective solvation (cf. eq 1).²⁷ (See also Table I.)

Polyether Ligand Studies. In view of the known ability of crown ethers to bind both cobalt and platinum ammine compounds (ammine hydrogen/ether oxygen interactions)²⁸ and in view of the appreciable Lewis basicity of diethyl ether,²³ we reasoned that it might be possible to use macrocyclic ethers and/or polymeric ethers as stoichiometric or substoichiometric redox isomerization reagents. To demonstrate the feasibility of this, we first examined the mononuclear fragments, (bpy)₂ClRu(pyCN)⁺ and Ru(NH₃)₅(py)²⁺ (Table III). We found (a) no shift in E_f and no evidence for binding of dibenzo-36-crown-12 to (bpy)₂ClRu(pyCN)⁺ (10-fold molar excess of crown) but (b) a very substantial shift in E_f (-326 mV) and compelling spectral evidence (red shift of visible region (MLCT) absorbance) for crown binding to the ammine complex. Variable-concentration experiments showed the binding to be approximately stoichiometric. Studies of the binuclear complex gave an initially surprising result: very small, almost negligible shifts in DPV peaks (± 20 mV) following crown addition. In contrast, visible-region absorption experiments (fully reduced complex) *did* indicate binding. A closer examination of the monomer data provided an explanation: with substoichiometric amounts of crown, cyclic voltammetry (CV) peaks for the Ru(NH₃)₅py²⁺-crown supracomplex were observed to appear at the expense of peaks for free Ru(NH₃)₅py²⁺ (i.e. two sets of peaks, separated by 330 mV, were observed simultaneously). This type of behavior would be expected if crown exchange between free and bound Ru(NH₃)₅py²⁺ were slow on the time scale of the CV experiment. The hypothesis for the binuclear complex then, is that in pure nitromethane as solvent, DPV peaks near 900 and 750 mV correspond, respectively, to reduction of (py)(NH₃)₄Ru^{III}- and (bpy)₂ClRu^{III}-. With added crown, nominally the same peaks correspond instead to (bpy)₂ClRu^{III}- and (py)(NH₃)₄Ru^{III}- reduction (see eq 2). Validation of the hypothesis proved possible



again with ΔS°_{re} measurements (Table II). A large reaction entropy (characteristic of the (py)(NH₃)₄Ru^{3+/2+}-fragment) was observed for the first peak in pure NM and for the second peak (lower potential) in NM + crown. Conversely, a small ΔS°_{re} value

(24) See, for example: Ford, P. C.; Rudd, D. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187.

(25) Resonance-enhanced Raman bands (cm⁻¹) and preliminary assignments are as follows. (py)(NH₃)₄Ru(4-NCpy)Ru(bpy)₂Cl⁴⁺ (PC solvent): 2200 ($\nu(C \equiv N)$), 1605 ($\nu(C=C)$ ring), 1563 ($\nu(C=C)$ ring), 1490 ($\nu(C=N)$ bpy ring), 1321 ($\nu(C=N)$ ring), 1275 ($\nu(C-C)$ ring), 1204 ($\nu(C-C)$ pyridine to nitrile), 1021 (ring breathing); 665 ($\delta(CCC)$ ring), 540 ($\nu(CN-Ru)$), 375 ($\nu(Ru-N(bpy))$), and 314 and 296 ($\nu(Ru-Cl)$) and $\nu(Ru-N)$ pyridyl end of cyanopyridine bridge). (bpy)₂ClRu(pyCN)⁺ (PC solvent): 2200, 1605, 1652, 1488, 1322, 1275, 1204, 1024, 669, 540, 375, and 298 (assignments as above; the two spectra are nearly identical). 4-cyanopyridine (normal Raman): 2248, 1600, 1195, and 994 (ring breathing); 672, 565, and 457 (remaining assignments as above). For (py)(NH₃)₄Ru(Ncpy)Ru(bpy)₂Cl³⁺ (PC as solvent; both sides chromophoric) we observe partial photodecomposition, with scattering (based on the above) only from the (bpy)₂ClRu(NCpy) fragment.

(26) Some minor manifestations of cooperative mixed-valence entropic behavior have been reported, however, with certain mixed-solvent compositions.^{2a}

(27) The bridge is no doubt too short (and the rate of isomerization too fast), however, to make this observation useful directly in the proposed time-resolved electron-transfer experiment illustrated in eq 1.

(28) Colquhoun, H. M.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 487 and references therein.

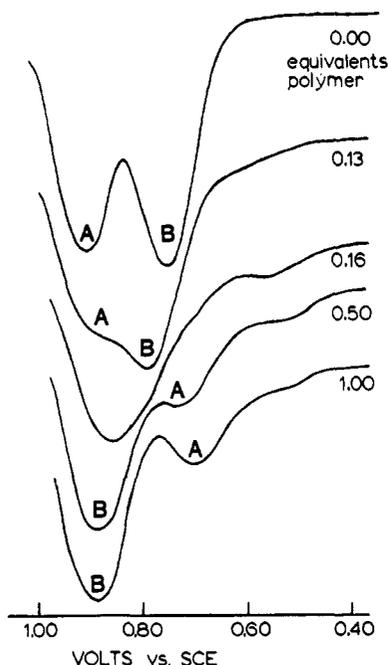


Figure 2. Representative differential-pulse voltammograms for 2 mM *trans*-(py)(NH₃)₄Ru(NCpy)Ru(bpy)₂Cl^{5+/4+/3+} in nitromethane (0.1 M TEAH) with added poly(ethylene glycol) (equivalents are indicated on the figure). Peak A is the *trans*-(py)(NH₃)₄Ru^{II/III}- couple. Peak B is the (bpy)₂ClRu^{II/III}- couple.

(characteristic of the (bpy)₂ClRu^{2+/+}- fragment) was observed for the second reduction peak in pure NM and for the first peak in NM + crown.

Studies with poly(ethylene glycol) yielded a somewhat different behavior. DPV peaks were still observed to (a) shift negatively for Ru(NH₃)₅py^{3+/2+} and (b) remain unchanged for (bpy)₂ClRu(NCpy)^{2+/+}. However, for the mononuclear ammine complex, a progressive (rather than stepwise) shift in *E*_f with increasing polymer concentration was found. Furthermore, somewhat less than 1 equiv of polymer was required in order to reach a limiting electrochemical response. As suggested by Figure

2, these same effects are manifest in the binuclear complex as a progressive shift (and eventual crossing) of differential pulse voltammetry peaks with increasing concentration of poly(ethylene glycol)—limiting behavior again appearing at concentrations well below 1 equiv. The “crossing” effect, together with the Ru(NH₃)₅py^{3+/2+} and (bpy)₂ClRu(pyCN)^{2+/+} results, provides clear evidence for binding-induced redox isomerization in the binuclear complex (cf. eq 2). The gradual nature of the shifts in *E*_f strongly suggests, however, that bound and free ammine-containing complexes (mononuclear as well as binuclear) are able to exchange rapidly between the polymer and solution environments. The observation that less than 1 equiv of poly(ethylene glycol) is needed to achieve apparently complete binding is broadly consistent with the idea that each polymer strand may bind multiple complexes. Note that each strand comprises, on average, roughly 200 repeating units.

Finally, the overall energetic basis for redox isomerization in the various solvation and ligation environments merits discussion. The redox energetics for (py)(NH₃)₄Ru(NCpy)Ru(bpy)₂Cl⁴⁺ can perhaps best be understood by comparison to (NH₃)₅Ru(pyrazine)Os(bpy)₂Cl⁴⁺.¹ Replacement of osmium by ruthenium causes a 0.4 V increase in redox potential at the polypyridyl end. This is approximately offset at the ammine end by replacement of NH₃ by pyridine ($\Delta E \approx 0.15$ V)⁹ and pyrazine by the nitrile-bound cyanopyridine ($\Delta E \approx 0.13$ V).²⁹

Acknowledgment. We thank Dr. Dong Yoon for supplying a sample of dibenzo-36-crown-12. J.C.C. acknowledges support from a PPG Industries Foundation Grant of the Research Corp. J.T.H. acknowledges support from the Department of Energy, Office of Energy Research, Division of Chemical Sciences (Grant No. DEFG02-87ER 13808). The modified CARY 14 spectrophotometer was obtained with funds from an NSF equipment grant (Grant No. CHE-87722985) and from a Presidential Young Investigator Award. The Raman facilities are part of the Materials Research Center at Northwestern (Grant NSF-DMR-8821571).

(29) The estimate here is fairly crude: studies of linkage isomers¹² suggest that replacement of a symmetrical bridge by the asymmetric 4-cyanopyridine ligand will lead, in a net sense, to a ΔE contribution of ~ 0.13 V.

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Photoisomerization and Other Reactions of Dimethylplatinum(IV) Complexes with Iminodiacetate and (Methylimino)diacetate

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Received February 7, 1991

The ligands L²⁻, RN(CH₂CO₂)₂ (R = CH₃, H), react with a solution of [Pt(CH₃)₂(OH)₂·1.5H₂O]_n in alkali to give initially Pt(CH₃)₂(OH)₂(L-N,O)²⁻ in which the ligand coordinates bidentate trans to the methyl groups. Ring closure to form Pt(CH₃)₂(OH)(L-N,O,O)⁻ is very slow under alkaline conditions, but is much faster in acid solution, to give Pt(CH₃)₂(H₂O)(L-N,O,O)⁻ (N trans to methyl). *fac*-Pt(CH₃)₂Br(H₂O)₃⁺ with LH⁻ gives Pt(CH₃)₂Br(L-N,O,O)⁻ (N trans to methyl). Irradiation with a mercury lamp causes facile isomerization to the isomer with N trans to bromide. This reaction occurs without dissociation of L²⁻. A side reaction at high pH produces Pt(CH₃)₂(OH)(L-N,O,O)⁻ (N trans to hydroxide). The colorless aqua complexes Pt(CH₃)₂(H₂O)(L) are photoisomerized much less efficiently than the pale yellow bromo complexes. Thermal isomerizations are very much slower.

Introduction

There has recently been considerable interest in the complexes of platinum with the versatile ligand iminodiacetate and its *N*-alkyl derivatives.¹⁻⁴ In square-planar platinum(II) complexes, these

ligands are either bidentate, coordinating through nitrogen and one carboxylate oxygen,¹⁻⁴ or meridionally tridentate.¹ In octahedral complexes (e.g., with cobalt(III)),⁵ facial tridentate coordination is typical. This coordination mode has been observed

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