minimizes the constraints. As the two metals become of more similar size, the system that minimizes the Madelung energy becomes preferable. In Figure 1, we show that the former arrangement is the $AgCrP_2S_6$ structure while the latter is the $AgInP_2S_6$ type. Thus, we see the larger Sc(III) cation leads to one structure, while the smaller V(III) and Cr(III) lead to the other.[15] Calculating the constraint energy difference between the two superstructures is a difficult task and has not yet been done. Consequently, it cannot be stated which out of the steric and band effects is the predominant one in determining the structure type in this series when the metals are of different oxidation state. They seem to be concomitant, and both explain the observed structures of the compounds synthesized so far.

Registry No. $AgScP_2S_6$, 113087-64-2; $CdFeP_2S_6$, 113087-65-3; Sc, 7440-20-2; Cd, 7440-43-9; Fe, 7439-89-6; P, 7723-14-0; S, 7704-34-9; $Cd_{0.2}Fe_{0.8}PS_3$, 113087-66-4; $Cd_{0.4}Fe_{0.6}PS_3$, 113087-69-7; $Cd_{0.6}Fe_{0.4}PS_3$, 113087-67-5; $Cd_{0.8}Fe_{0.2}PS_3$, 113087-68-6; $FePS_3$, 20642-11-9; $CdPS_3$, 28099-03-8; $AgVP_2S_6$, 105355-00-8; $AgCrP_2S_6$, 86745-59-7; $AgInP_2S_6$, 98319-31-4; Ag, 7440-22-4.

Supplementary Material Available: For the two structures, listings of anisotropic thermal parameters (1 page); listings of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

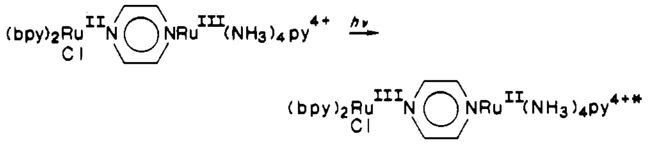
Contribution from the Department of Chemistry,
University of San Francisco, San Francisco, California 94117

Evidence for a Specific Solvent–Solute Interaction as a Major Contributor to the Excited-State Distortion of the Emitting Charge-Transfer State in the Complex $(bpy)_2Ru^{II}(CN)_2$

Ella Y. Fung, Arthur C. M. Chua, and Jeff C. Curtis*

Received April 8, 1987

A recent paper from this laboratory presented evidence showing that specific solvent–solute interactions of a Lewis acid–base nature in the second coordination sphere of a ruthenium ammine complex could give rise to a significant contribution to the Franck–Condon barrier to optical electron transfer in a mixed-valence dimer such as the one shown here:[1]



The origin of the effect in this molecule arises from the differential Lewis acidity of the ammine protons between the ground- and excited-state electronic distributions and the subsequent rearrangement of the hydrogen bonds in the secondary coordination sphere about the ammine moiety upon electron transfer.

We wish to report here a related observation concerning the $(bpy)_2Ru^{II}(CN)_2$ molecule. In this case the solute acts as a Lewis base and the solvent as a Lewis acid. The strength of this interaction depends on the electronic state of the solute. The ruthenium complex in its lowest lying metal-to-ligand-charge-transfer (MLCT) state has an electron largely transferred from the Ru(II) center out to one of the bpy rings.[2] The drop in electron density at the cyano nitrogens compared to the ground state is profound; for example, the K_a of the protonated complex has been shown to increase by nearly 6 orders of magnitude in the excited state relative to the ground state.[2b] This dramatic contrast in chemical nature between ground and excited states gives rise to a rather subtle manifestation if we investigate the charge-transfer absorption and emission spectra of the neutral molecule in a range of solvents with varying Lewis acidity. In this case we find that the Stokes shift exhibits a strong dependence on the strength of the specific solvent–solute interaction.

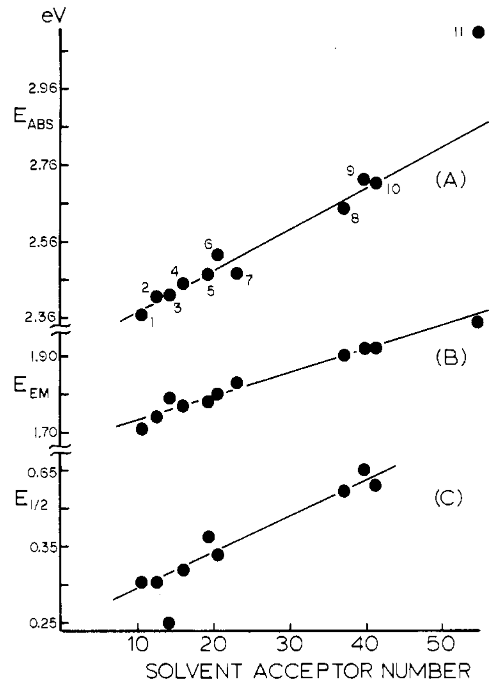


Figure 1. Dependences of (A) absorption band maximum, (B) emission band maximum, and (C) $Ru^{II/III}$ potential (fc/fc$^+$ reference) on solvent acceptor number.

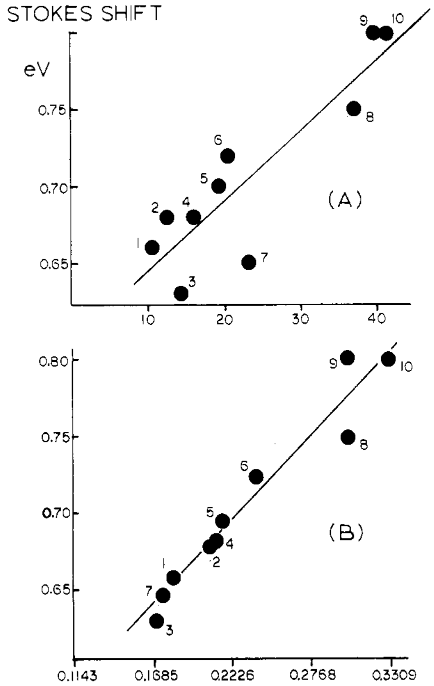


Figure 2. Dependence of Stokes shift on (A) solvent acceptor number and (B) composite function $X = 0.0038(\text{acceptor number}) + 0.316(1/n^2 - 1/Ds)$.

Results and Discussion

Table I lists the different solvents used along with their Gutmann acceptor numbers (a convenient measure of Lewis acidity),[3]

---

[1] De La Rosa, R.; Chang, P. S.; Salaymeh, F.; Curtis, J. C. *Inorg. Chem.* **1985**, *24*, 4229.

[2] (a) Demas, J. N.; Turner, T. F.; Crosby, G. A. *Inorg. Chem.* **1969**, *8*, 674. (b) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1976**, *98*, 7880. (c) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1979**, *101*, 6571. (d) Demas, J. N.; Peterson, S. H.; Harris, E. W. *J. Phys. Chem.* **1977**, *81*, 1039.

0020-1669/88/1327-1294$01.50/0

Table I. Solvent Parameters, Electrochemical Potential Data, and Spectroscopic Data for $Ru(bpy)_2(CN)_2$

no.	solvent	acceptor no.[a]	$E_{1/2}(Ru^{II/III})$[b] vs fc/fc$^+$, eV	E_{abs}(MLCT), eV	E_{em}(MLCT),[d] eV	$E_{abs} - E_{em}$, eV (Stokes shift)	$\Delta\nu_{1/2}$(abs),[e] eV	$\Delta\nu_{1/2}$(em),[f] eV
1	hexamethylphosphoramide	10.6	0.351 ± 0.006	2.368 ± 0.003	1.71 ± 0.01	0.66 ± 0.01	0.224	0.25
2	acetone	12.5	0.357	2.418	1.74	0.68	0.230	0.29
3	pyridine	14.2	0.249	2.419	1.79	0.63	0.210	0.32
4	dimethylformamide	16.0	0.390	2.452	1.77	0.68	0.260	0.33
5	dimethyl sulfoxide	19.3	0.472	2.472	1.78	0.70	0.249	0.32
6	nitromethane	20.5	0.429	2.524	1.80	0.72	0.266	0.33
7	chloroform	23.1	*c*	2.477	1.83	0.65	0.228	0.32
8	ethanol	37.1	0.597	2.649	1.90	0.75	0.319	0.33
9	formamide	39.8	0.652	2.722	1.92	0.80	0.336	0.35
10	methanol	41.3	0.612	2.716	1.92	0.80	0.344	0.32
11	water	54.8	*c*	3.113	1.99	1.12	0.414	0.38

[a] From ref 2. [b] 0.1 M tetraethylammonium hexafluorophosphate supporting electrolyte. [c] Complex insolubility prevented accurate determination. [d] Emission spectra corrected for instrument response by using the standard dye 4-(dimethylamino)-4′-nitrostilbene and published absolute spectrum. See: White, C. E.; Arganer, R. J. *Fluorescence Analysis, A Practical Approach*; Dekker: New York, 1970. [e] Full width at half-height obtained by doubling the low-energy side of the band. [f] Full width at half-height obtained by using complete band.

Table II. Regression Parameters for Fits of Various Experimental Observables vs Solvent Acceptor Number[a]

observable	slope, eV/AN	intercept, eV	correln coeff
E_{abs}	0.011 ± 0.002	2.27	0.985
E_{em}	0.006 ± 0.002	1.07	0.978
$E_{abs} - E_{em}$	0.005 ± 0.003	0.60	0.884
$\Delta\nu_{1/2}$(abs)[b]	0.004 ± 0.002	0.17	0.938
$\Delta\nu_{1/2}$(em)	0.0015 ± 0.002	0.28	0.614
$E_{1/2}(Ru^{II/III})$	0.940 ± 0.005	0.25	0.983

[a] Excluding data for H_2O. [b] Due to a shoulder on the high-energy side of the absorption band, the width at half-height was obtained by doubling of the low-energy side.

the $E_{1/2}(Ru^{II/III})$ values, MLCT absorption energies, charge-transfer emission energies, and the Stokes shift values obtained. Figure 1 shows how the absorption and emission energies as well as the $Ru^{II/III}$ potentials vary with solvent acceptor number. The regression parameters are listed in Table II. Figure 2 shows the dependence of the Stokes shift value $E_{abs} - E_{em}$ on solvent acceptor number and also on the dual-parameter solvent function a(acceptor number) + $b(1/n^2 - 1/Ds)$ where $a = 0.00378$, $b = 0.325$, n is the solvent's refractive index, and Ds is the static dielectric constant.

The strong solvent dependence of the emission maximum of this complex has been noted by others[2d,4] and in fact previously correlated with solvent acceptor number.[5,6] Additionally, Burgess has identified the donor–acceptor interaction in the second coordination sphere as the source of the solvatochromism in the iron analogue.[7] The observation we wish to add with the data collected and presented in this work is that the strong acceptor number dependence of the Stokes shift points to the specific solvent–solute interaction in the second coordination sphere as the major solvent-dependent component of the excited-state distortion of the complex. The same effect is apparently operative in the $(bpy)Ru^{II}(CN)_4^{2-}$ ion investigated recently by Bignozzi et al., where it was noted that the solvent dependence of the absorption band maximum is greater than that of the emission.[8]

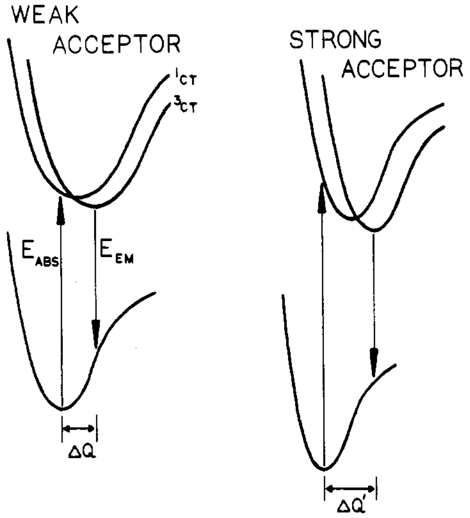


Figure 3. Schematic diagram representing the effect of increasing solvent acceptor number on the potential energy surfaces governing absorption and emission.

Figure 3 is a schematic representation of the potential energy surfaces relevant to the absorption and emission processes. In analogy with the tris(bipyridine) complex, we assume that the initially populated CT state, largely singlet in character, decays rapidly to a manifold of largely triplet, emitting CT states. The stronger Lewis base strength of the cyano nitrogens in the ground state relative to the initial excited state causes the energy gap between the two to increase upon going from a weak to a strong acceptor solvent.

The same shifting of potential surfaces would cause an equivalent increase in the energy gap defining the emission maximum in the absence of solvent-dependent relaxation effects. The observed solvent dependence of the emission energy, however, is only about 60% that of the absorption, and the resulting fact that the Stokes shift depends so clearly on acceptor number tells us that the strength of the second coordination sphere donor–acceptor interaction is critical in defining the overall amount of nuclear reorganization attending relaxation to the emitting state.

In a related observation we find that the absorption bandwidth correlates very well with acceptor number. This is consistent with an acceptor number dependent contribution to the Franck–Condon energy of the transition. For the emission bandwidth, however, only a weak general trend with acceptor number is observed. This may simply reflect the lesser precision of the emission data.

Water falls considerably above the line defined by the rest of the points in Figure 1A, and it would also fall well above the lines in Figure 2 if the abscissas were extended. This may be related to a similar effect that was noted recently by Hupp and Meyer[10] in connection with intervalence transfer in mixed-valence molecules and that was ascribed to the high-frequency librations of water. Alternatively, it may arise from some other unique aspect of water such as its ability to exhibit long-range structure.[11]

---

(3) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum: New York, 1978.
(4) Bignozzi, C. A.; Scandola, F. *Inorg. Chem.* **1984**, *23*, 1540.
(5) Nagle, J. K., unpublished results.
(6) (a) Winkler, J. R.; Sutin, N. *Inorg. Chem.* **1987**, *26*, 220. (b) Belser, P.; Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Gazz. Chim. Ital.* **1985**, *115*, 723.
(7) Burgess, J. *Spectrochim. Acta, Part A* **1970**, *26A*, 1369.
(8) Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi Scandola, M. A.; Scandola, F. *J. Am. Chem. Soc.* **1986**, *108*, 7872.
(9) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967.
(10) Hupp, J. T.; Meyer, T. J. *J. Phys. Chem.* **1987**, *91*, 1001.

One might expect that since the excited state involves a substantial change in the dipole moment of the molecule, some aspect of the dielectric properties of the solvent should be important in defining the Stokes shift. We find evidence of this if we perform dual-parameter fitting procedures on the Stokes shift data. The correlation coefficient improves from the value of 0.884 found for pure acceptor number (excluding water) to 0.973 if the solvent dielectric continuum[12] parameter $(1/n^2 - 1/Ds)$ is used in a dual-parameter fit along with acceptor number. The improvement in the fit is illustrated in Figure 2B. An improvement of nearly equal magnitude is obtained if the dipole-solvation solvent parameter $(1 - Ds)/(2Ds + 1)$ due to Onsager is used.[13]

Experimental Section

$Ru(bpy)_2(CN)_2$ was synthesized according to the method outlined by Demas and co-workers. MLCT band maxima and extinction coefficients were found to be in good agreement. All solvents were reagent grade or better and were stored over activated 3-Å molecular sieves for at least 8 h prior to use.

The electrochemical data were collected on an IBM 225 EC instrument by differential-pulse polarography vs an SCE. Absorption measurements were made on a Perkin-Elmer 330 spectrophotometer, and emission measurements were made on a Hitachi 650 recording fluorimeter thermostated to 23 ± 1 °C. Emission spectra were corrected for instrument response by using the standard dye 4-(dimethylamino)-4'-nitrostilbene.

Acknowledgment. Thanks are gratefully expressed to the Research Corp. for its generous support of this work.

Registry No. $(bpy)_2Ru^{II}(CN)_2$, 58356-63-1; $(bpy)_2Ru^{III}(CN)_2^+$, 58356-64-2.

---

(11) Conway, B. E. *Ionic Hydration in Chemistry and Biophysics*; Elsevier: Amsterdam, 1981.

(12) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. (b) Hush, N. S. *Trans. Faraday Soc.* **1965**, *43*, 557.

(13) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486. For a recent discussion of this work in relation to polypyridyl complexes, see ref 14.

(14) Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098.

Contribution from Rocketdyne, a Division of Rockwell
International, Canoga Park, California 91303

Convenient Synthesis of Xenon Oxide Tetrafluoride

Karl O. Christe* and William W. Wilson

Received December 1, 1987

Xenon oxide tetrafluoride, $XeOF_4$, is generally prepared by partial hydrolysis of XeF_6 using either dynamic or static methods. In the static methods XeF_6 is reacted with either H_2O or SiO_2.[1] These reactions, particularly on a larger scale, are very hazardous and, unless great care is exercised, can result in violent explosions due to the localized formation of highly explosive XeO_3. This hazard of the static methods can be diminished somewhat by the dynamic method of bleeding air saturated with water vapor into a circulating loop filled with XeF_6 vapor and monitoring the XeF_6 consumption by infrared spectroscopy.[2] The main drawback of this dynamic method is the requirement for complex hardware. A third method, involving the reaction of XeF_6 with SeO_2F_2,[3] avoids the explosion hazard and appears scalable, but the SeO_2F_2[3] starting material is a highly toxic gas and is not readily available.[4]

Therefore, a safer and more convenient synthesis, using readily available reagents and lending itself to an easy scaleup, was highly desirable.

Experimental Section

Materials and Apparatus. $NaNO_3$ (J. T. Baker, 99.5%) was dried in a vacuum oven at 120 °C prior to its use. Xenon hexafluoride was prepared from Xe and F_2 and purified by complexing with NaF and subsequent vacuum pyrolysis of the adduct.[5,6] Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon-FEP U-traps, 316 stainless steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge.[7] Chlorine trifluoride was used for the passivation of the vacuum line, reactors, and any connections between them. Nonvolatile materials were handled in the dry N_2 atmosphere of a glovebox. Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer using a 5-cm path length Teflon cell with AgCl windows for gases and AgCl disks, pressed in an Econo press (Barnes Engineering Co.), for solids.

Preparation of $XeOF_4$. In a typical experiment, finely powdered $NaNO_3$ (3.09 mmol) was loaded inside the glovebox into a prepassivated 10-mL stainless steel cylinder equipped with a stainless steel valve. The cylinder was connected to the vacuum line, and XeF_6 (3.41 mmol) was added at −196 °C. The cylinder was allowed to warm to room temperature and was then placed into a 70 °C oven for 10 h. It was reconnected to the vacuum line and cooled to −196 °C, and the volatile products were separated on warmup of the cylinder to ambient temperature by fractional condensation through two U-traps kept at −78 and −196 °C, respectively. The −78 °C trap contained pure $XeOF_4$ (2.54 mmol, 82% yield based on the limiting reagent $NaNO_3$), which was identified by its vapor pressure,[2] infrared spectrum as a gas,[8] and Raman spectrum as a liquid.[8] The −196 °C trap contained FNO_2 (3.01 mmol). The white solid residue in the cylinder (338 mg; weight calculated for 3.01 mmol of NaF + 0.08 mmol of $NaNO_3$ + 0.63 mmol of XeF_6 + 0.24 mmol of XeO_2F_2 = 333 mg) was spectroscopically identified as NaF and contained larger amounts of $NaXeF_7$ and Na_2XeF_8[9] and smaller amounts of XeO_2F_2[10] and $NaNO_3$.

Results and Discussion

The reaction of $NaNO_3$ with a slight excess of XeF_6 provides a convenient, one-step synthesis of $XeOF_4$ according to

$$NaNO_3 + XeF_6 \rightarrow NaF + XeOF_4 + FNO_2 \qquad (1)$$

The use of an excess of $NaNO_3$ should be avoided to suppress the secondary reaction

$$NaNO_3 + XeOF_4 \rightarrow NaF + XeO_2F_2 + FNO_2 \qquad (2)$$

The extent of (2) was less than 10% when a 10% excess of XeF_6 was used in (1). The reaction conditions for (1) were chosen in such a manner that the NaF byproduct complexes the excess XeF_6 by forming the $NaXeF_7$ and Na_2XeF_8 salts,[9,11] thus allowing easy product separation. The $NaXeF_7$ and Na_2XeF_8 salts, NaF, and XeO_2F_2 are all nonvolatile at ambient temperature, and the only volatile products, $XeOF_4$ and FNO_2, can be readily separated by fractional condensation through two traps kept at −78 and −196 °C, respectively. The yield of $XeOF_4$ is about 80% based on the limiting reagent $NaNO_3$. The excess of XeF_6, complexed with NaF, could easily be recovered by vacuum pyrolysis, if desired.

Compared to the previously used methods,[1-3] the above synthesis offers the following advantages: (i) elimination of the explosion hazard associated with the hydrolysis of XeF_6, (ii) scalability, (iii)

---

(1) Chernick, C. L.; Claassen, H. H.; Malm, J. G.; Plurien, P. L. In *Noble-Gas Compounds*; Hyman, H. H., Ed.; University of Chicago Press: Chicago, IL, and London, 1963; p 287.

(2) Smith, D. F. *Science* (*Washington, D.C.*) **1963**, *140*, 899.

(3) Seppelt, K.; Rupp, H. H. *Z. Anorg. Allg. Chem.* **1974**, *409*, 331.

(4) Seppelt, K. *Inorg. Synth.* **1980**, *20*, 36.

(5) Chernick, C. L.; Malm, J. G. *Inorg. Synth.* **1966**, *8*, 258.

(6) Sheft, I.; Spittler, T. M.; Martin, F. H. *Science* (*Washington, D.C.*) **1964**, *45*, 701.

(7) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

(8) Begun, G. M.; Fletcher, W. H.; Smith, D. F. *J. Chem. Phys.* **1963**, *42*, 2236.

(9) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1982**, *21*, 4113.

(10) Claassen, H. H.; Gasner, E. L.; Kim, H. *J. Chem. Phys.* **1968**, *49*, 253.

(11) Moody, G. J.; Selig, H. *Inorg. Nucl. Chem. Lett.* **1966**, *2*, 319. Peacock, R. D.; Selig, H.; Sheft, I. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2561. Holloway, J. H.; Selig, H.; El-gad, U. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3624.

0020-1669/88/1327-1296$01.50/0