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Solvent Control of Orbital Mixing and Electronic Coupling in Ligand-Bridged Mixed-Valence Complexes: Evidence for an Intervalence Hole-Transfer Pathway

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Abstract: Solvent-induced electronic effects exist for intervalence charge-transfer reactions involving complexes of the type (2,2′-bipyridine)$_2$ClRu^{II}(pyrazine)Ru^{III}(NH$_3$)$_4$L^{4+}, where L = NH$_3$ or various pyrazyl, pyridyl, or polypyridyl ligands. Specifically the following are found: (1) Mixing between appropriate donor and acceptor metal orbitals can be influenced substantially by the nature of the solvent. (2) The metal–metal interaction energy, $\bar{H}_{13}$, is also affected. (3) From the solvent effects, intervalence transfer appears to follow (in part) a hole-transfer pathway.

Recently, Chang, Fung, and Curtis described the results of a study of optical intervalence transfer (eq 1) as a function of solvent in a series of $(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4L^{4+}$ complexes (bpy = 2,2′-bipyridine; pyz = pyrazine; L = NH$_3$ or various pyrazyl, pyridyl, or polypyridyl ligands).[1] Their goal was to understand

$$(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4L^{4+} \xrightarrow{h\nu} (bpy)_2ClRu^{III}(pyz)Ru^{II}(NH_3)_4L^{4+*} \quad (1)$$

the way in which specific solvent–ligand interactions can help to define the Franck–Condon barrier to charge transfer. We have recently discovered that the detailed experimental information collected by them can also be used to understand another interesting issue: the way in which the solvent modulates the electronic part of the intervalence charge-transfer problem. We describe here three main findings: (1) Mixing between appropriate donor and acceptor metal orbitals involved in intramolecular charge transfer can be influenced substantially by the nature of the external solvent. (2) The metal–metal interaction energy, $\bar{H}_{13}$, is also affected by solvent.[2] (3) From the solvent effects, intervalence transfer in reactions like eq 1 appears to follow (in part) a hole-transfer pathway.

Results and Discussion

Solvent Effects. From first-order perturbation theory[3-5] the extent of mixing, c_{13}^2, between nonbonding valence orbitals located on bridge-separated metal sites can be written as a function of the energy (E_{op}), intensity (ϵ_{max}), and width at half-height ($\Delta\bar{\nu}_{1/2}$) of the metal-to-metal (or "intervalence") charge-transfer absorption band, together with the dipole length or site-to-site distance (R_{MM}):

$$c_{13}^2 = (4.24 \times 10^{-4})\epsilon_{max}\Delta\bar{\nu}_{1/2}/E_{op}R_{MM}^2 \quad (2)$$

Based on existing data[1] for $(bpy)_2RuCl(pyz)Ru(NH_3)_4(pyridine)^{4+}$ and $(bpy)_2RuCl(pyz)Ru(NH_3)_5^{4+}$ and using R_{MM} = 6.9 Å, Figure 1 illustrates how c_{13}^2 depends on solvent and on the thermodynamics of the reaction.[6,7] The main observation is that as the energy difference, ΔE,[7] between the two trapping sites decreases (as estimated electrochemically[1]), mixing between the metal sites increases. The effect is substantial (ca. fourfold for the solvents considered here) and is qualitatively consistent with the simplest ideas from perturbation theory. Evidently, the primary role of the solvent in modulating orbital mixing is simply to adjust the zero-order separation energy.

Table I. Ligand and Solvent Dependence of $\bar{H}_{13}^2$ for Complexes of the Type $(bpy)_2ClRu^{II}(pyz)Ru(NH_3)_4L^{4+}$

L	$\bar{H}_{13}^2(CH_3CN)/\bar{H}_{13}^2(DMF)$[a]
NH$_3$	1.7
4-methylpyridine	2.0
3,5-dimethylpyridine	1.4
pyridine	2.1
2,2′-bipyridine (–NH$_3$)	1.4
3-chloropyridine	1.7
isonicotinamide	1.7
2,6-dimethylpyrazine	1.9

[a] Calculated from eq 2 and 3 using data from ref 1.

A more interesting question is whether the fundamental interaction energy, $\bar{H}_{13}$, is affected. From Fermi's golden rule, $\bar{H}_{13}^2$ determines (along with the Franck–Condon factors) the rate of charge transfer for nonadiabatic thermal pathways.[8,9] Thus, $\bar{H}_{13}$ is a key quantity for kinetics studies. From perturbation theory, it is given approximately by

$$\bar{H}_{13} = -c_{13}E_{op} \quad (3)$$

Using the available literature data[1] for $(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4(pyridine)^{4+}$, Figure 2 illustrates how $\bar{H}_{13}$ depends on the solvent-modulated separation energy.[6] The salient finding is that the interaction energy increases with decreasing separation energy. Again, the role of the solvent appears to be simply to manipulate the energy gap between the donor and acceptor (however, see next section).

Table I shows that the effect is a more general one. For a series of complexes where L is varied,[1] $\bar{H}_{13}^2$ in acetonitrile as solvent exceeds by almost twofold $\bar{H}_{13}^2$ in dimethylformamide.

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[1] Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.

[2] The notation $\bar{H}_{13}$ is used in anticipation of a role for the bridging ligand (site 2).

[3] Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.

[4] For an excellent example of applications in metal–complex chemistry, see: Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

[5] See also: Hale, P. D.; Ratner, M. A. *Int. J. Quant. Chem.: Quant. Chem. Symp.* **1984**, *18*, 195.

[6] The available evidence for pyrazine-bridged systems suggests that c_{13}^2 and $\bar{H}_{13}$ are underestimated when obtained from first-order perturbation theory in this way. Nevertheless, reasonably accurate trends in parameters should be obtainable. Compare, for example: de la Rosa, R.; Chang, P. J.; Salaymeh, F.; Curtis, J. C. *Inorg. Chem.* **1985**, *24*, 4231; Mayoh, B.; Day, P. *Inorg. Chem.* **1974**, *13*, 2273.

[7] As a crude, but very useful approximation, we have equated the experimentally measured difference in potential for stepwise reduction of the two Ru^{III} centers with both the free-energy change accompanying thermally induced intramolecular charge transfer and the spectroscopic zero-order separation energy.

[8] See, for example: Brunschwig, B. S.; Sutin, N. *Comments Inorg. Chem.* **1987**, *6*, 209.

[9] Examples of inherently nonadiabatic systems might include pyrimidine-bridged analogues of the present systems; for pyrazine-bridged species, thermal electron transfer is undoubtedly adiabatic, so $\bar{H}_{13}^2$ will have no direct impact upon the rate constant. (A secondary effect might exist, however, due to modulation of the lower adiabatic potential energy surface in the vicinity of the cusp; i.e., "barrier rounding" might occur.)

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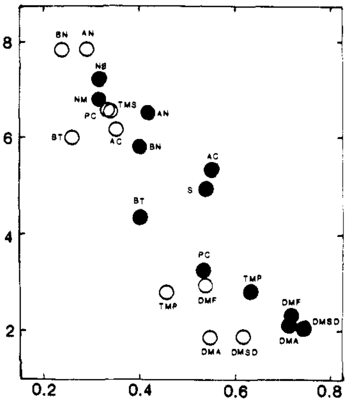

Figure 1. Dependence of $c_{13}{}^2$ on separation energy for (○) $(bpy)_2ClRu(pyz)Ru(NH_3)_4(pyridine)^{4+}$ and (●) $(bpy)_2ClRu(pyz)Ru(NH_3)_5{}^{4+}$. Key to solvents: NM = nitromethane, NB = nitrobenzene, BN = benzonitrile, AN = acetonitrile, S = sulfolane, PC = propylene carbonate, BT = butyronitrile, AC = acetone, TMP = trimethyl phosphate, DMF = dimethylformamide, DMA = dimethylacetamide, DMSO = dimethyl sulfoxide.

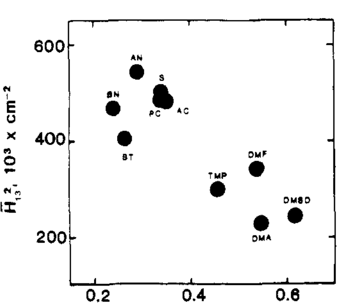

Figure 2. Dependence of $\bar{H}_{13}{}^2$ on donor–acceptor separation energy for $(bpy)_2ClRu(pyz)Ru(NH_3)_4(pyridine)^{4+}$. Key to solvents as in Figure 1.

Charge-Transfer Pathways. The question that remains is, what is the origin of the dependence of $\bar{H}_{13}{}^2$ on the nature of the solvent and on the magnitude of the separation energy? The answer is doubly interesting because it ultimately provides a detailed picture of the charge propagation pathway.

For pyrazine-bridged d^5–d^6 species, intervalence transfer is almost certainly a bridge-mediate process and the orbital basis for charge propagation is likely to be in superexchange interactions.[4,5] Analysis of the superexchange problem suggests two primary charge-transfer pathways: electron transfer through (in a virtual sense) low-lying, empty bridge orbitals, or hole transfer through relatively high-lying, filled orbitals. According to Marcus[10] (see also, McConnell[11]), the overall interaction energy will depend in either case on the donor (acceptor)/bridge separation energy (E_{12}; E_{23}) the donor/bridge or bridge/acceptor interaction energy ($\bar{H}_{12}$ or $\bar{H}_{23}$), and the intrabridge interaction energy (β) for n degenerate bridge states:

$$\bar{H}_{13} = (-2\bar{H}_{12}\bar{H}_{23}/E_{12})(-\beta/E_{12})^{n-1} \quad (4a)$$

$$\bar{H}_{13} = (-2\bar{H}_{12}\bar{H}_{23}/E_{23})(-\beta/E_{23})^{n-1} \quad (4b)$$

In eq 4, site 1 denotes the electron donor, site 2 the bridge, and site 3 the electron acceptor. For symmetrical donor–acceptor systems, $\bar{H}_{12} = \bar{H}_{23}$, $E_{12} = E_{23}$, and eq 4a and 4b are equivalent. The only real subtlety is that one must be careful to specify whether site 2 is filled (σ, π, etc.) or empty (σ^*, π^*, etc.).

For unsymmetrical systems the problem is more complicated because the various energies are no longer equivalent. According to Marcus and Sutin, the relevant E_{ij} is then the one that corresponds to vertical excitation from the initial state to whichever virtual state best facilitates charge transfer.[10,12] For hole transfer the choice is E_{23}; for electron transfer it is $E^*{}_{12}$, where the asterisk denotes transfer to an empty (antibonding) bridge orbital. Equations 5 and 6 further illustrate the possibilities:

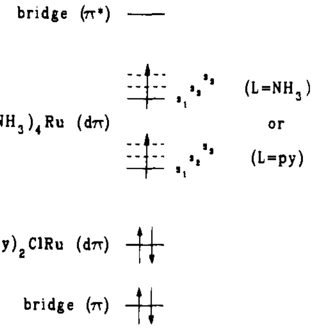

Figure 3. Molecular orbital diagrams for $(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4(pyridine)^{4+}$ and $(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_5{}^{4+}$ in three solvents.

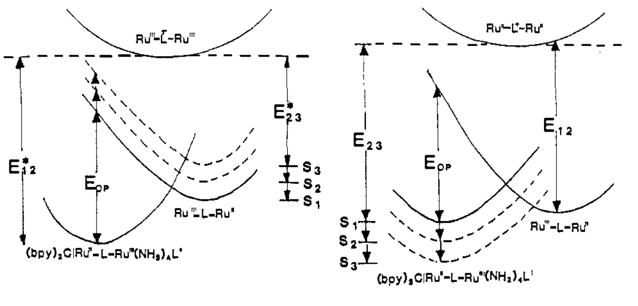

Figure 4. Solvent-dependent energy relationships among virtual states and initial and final mixed-valence states: left, electron-transfer virtual state; right, hole-transfer virtual state.

$$(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4L^{4+} \xrightarrow{E^*{}_{12}\ (=E^{MLCT})} (bpy)_2ClRu^{III}(pyz^{\bullet-})Ru^{III}(NH_3)_4L^{4+} \quad (5)$$

$$(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4L^{4+} \xrightarrow{E_{23}\ (=E^{LMCT})} (bpy)_2ClRu^{II}(pyz^{+})Ru^{II}(NH_3)_4L^{4+} \quad (6)$$

Presumably, $\bar{H}_{12}$, $\bar{H}_{23}$, and $E^*{}_{12}$ are reasonably constant for any given mixed-valence ion of the type shown in eq 5 and 6.[13,14] On the other hand, in these same systems E_{23} is known to be strongly dependent on the nature of the solvent.[15-17] (E_{23} increases with increasing Lewis basicity). Furthermore, E_{23} should scale approximately with ΔE as the solvent is varied.[15,16]

The molecular orbital diagram in Figure 3 summarizes qualitatively the relative donor–bridge–acceptor energetics. In the diagram, six different acceptor energy levels are sketched, corresponding to three different solvent environments and two different ancillary ligands. The consequences in terms of spectroscopic transitions are shown in Figure 4. *This figure presents the crux of the analysis.* In the left panel, as the solvent varies, E_{op} also varies (as required by the available experimental data). Importantly, however, the vertical distance ($E^*{}_{12}$) between the initial state ($(bpy)_2ClRu^{II}(pyz)Ru^{III}(NH_3)_4L^{4+}$) and the virtual state with the odd electron on the bridging ligand does *not* vary.[17] Consequently, for this reaction pathway (*electron* transfer via π^* virtual states) $\bar{H}_{13}$ should be unperturbed by the solvent (see eq 4a). This is contrary to the experimental data given in Figure

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[10] Marcus, R. A. *Chem. Phys. Lett.* **1987**, *133*, 471; **1988**, *146*, 13.

[11] McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508.

[12] Marcus, R.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

[13] Evidence is available from both electrochemical[1] and spectral[15] studies.

[14] We have confirmed from model studies that $\bar{H}_{23}$, at least, is solvent independent. (Roberts, J., Hupp, J. T., unpublished data.)

[15] Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224.

[16] Ennix, K. S.; McMahon, R. T.; Curtis, J. C. *Inorg. Chem.* **1987**, *26*, 2660.

[17] One could argue that for very short bridges, sufficient coupling might exist such that E_{12} could vary detectably with E_{23}. Note, however, that the superexchange theory in its simplest form requires *zero-order* separation energies; to zeroth order, E_{12} is independent of E_{23}.

Table II. Anticipated Influence of Increasing Solvent Basicity upon $\bar{H}_{13}^2$ in Complexes of the Type $(bpy)_2ClRu(bridge)Ru(NH_3)_4L^{4+}$

	solvent-tunable acceptor[a]		solvent-tunable donor[b]	
	optical	thermal	optical	thermal
$\bar{H}_{13}^2$(HT)	↓	↓	no effect	↓
$\bar{H}_{13}^2$(ET)	no effect	↑	↑	↑
$\bar{H}_{13}^2$(total)	↓	variable	↑	variable

[a] Ground-state configuration: $(bpy)_2ClRu^{II}(bridge)Ru^{III}(NH_3)_4L^{4+}$.
[b] Ground-state configuration: $(bpy)_2ClRu^{III}(bridge)Ru^{II}(NH_3)_4L^{4+}$.

2. On the other hand, in the right panel, where the virtual state features a hole on the bridging ligand, the initial-state/virtual-state separation energy (E_{23}) should be strongly dependent upon solvent. Consequently, from eq 4b the component of $\bar{H}_{13}^2$ associated with hole transfer (π pathway) should decrease with increasing E_{23} or ΔE. Reference to Figure 2 confirms the prediction.

The preceding analysis seems to implicate the HOMO of the bridge in the charge propagation process. This is, at first glance, somewhat surprising since E^{MLCT} (E^*_{12}) almost certainly lies below E^{LMCT} (E_{23}) for these complexes. All else being equal, eq 4 then predicts that *electron* transfer will be the dominant redox pathway. Further reflection shows, however, that these seemingly disparate observations are mutually consistent. Recall that eq 4 promises a solvent dependence in $\bar{H}_{13}$ for the hole-transfer pathway (only). In principle, a parallel solvent-independent contribution could exist (ET pathway). The observable total interaction energy would then be

$$\bar{H}_{13}(\text{total}) = \bar{H}_{13}(\text{eq 4a; ET}) + \bar{H}_{13}(\text{eq 4b, HT}) \qquad (7)$$

In theory, the contributions could be separated by constructing a plot of $\bar{H}_{13}$(total) versus E_{23}^{-n} and extrapolating to infinite separation energy (see eq 4). Unfortunately, values for neither E_{23} nor n are known with sufficient accuracy.[18] Nevertheless, it seems reasonable to suppose that hole transfer is the minority pathway. The ability to identify this pathway apparently stems from the "solvent selection rules" unique to these types of complexes (i.e., from eq 4, $\bar{H}_{13}$(HT) is solvent dependent while $\bar{H}_{13}$(ET) is solvent independent). It is interesting to note that the "selection rules" should be reversed when the ground-state donor, rather than acceptor, is the solvent-tunable site; for example[19]

$$(bpy)_2ClRu^{III}(NC_5H_4C{\equiv}N)Ru^{II}(NH_3)_4(py)^{4+} \xrightarrow{h\nu} (bpy)_2ClRu^{II}(NC_5H_4C{\equiv}N)Ru^{III}(NH_3)_4(py)^{4+*} \qquad (8)$$

Thus, for the reaction in eq 8, $\bar{H}_{13}$(ET) should vary with solvent, but $\bar{H}_{13}$(HT) should not.

Thermal "Selection Rules", Rate Effects, and Trans Ligand Effects. One further point is worth noting: the selection rules for thermal charge transfer should differ appreciably from those for the optical reactions. The basis for the difference is in the necessity, in the thermal case, to evaluate E_{ij} (E^*_{ij}) at the charge-transfer transition-state geometry (rather than at the geometry of the fully relaxed initial state).[10,12] The distinction is illustrated in Figure 4. From the figure, $\bar{H}_{13}^2$(HT)(thermal) for reaction 1 should display a weaker dependence on solvent basicity than does $\bar{H}_{13}^2$(HT)(optical). (Both should decrease with increasing basicity.) On the other hand, $\bar{H}_{13}^2$(ET)(thermal) should show a weak *increase* with increasing basicity.[20] Perhaps surprisingly, for reaction 8 or for the reverse of reaction 1, these same thermal rules should apply[20,21] (even though the optical rules are reversed). The reason for the concurrence is that the forward and reverse reactions must proceed through the same transition state; as noted above, it is the transition state that is relevant in determining $E_{ij}(E^*_{ij})$(thermal) and therefore, $\bar{H}_{13}^2$(thermal).[10,12]

Table II summarizes the various solvent-based selection rules. From the table, it seems clear that the thermal selection rules will be much less helpful then the optical rules in identifying specific redox pathways. Furthermore, for the complexes considered here, at least, it is difficult to predict (in any particular case) just how the thermal charge-transfer kinetics might be influenced by solvent effects upon $\bar{H}_{13}^2$.[22] Perhaps the most that can be said is that such effects ought certainly to exist, but that it would be ill-advised to attempt to describe them based solely upon optical investigations.

With the selection rules in place, it is appropriate to mention a final set of experimental observations.[1] In the $(bpy)_2ClRu(pyz)Ru(NH_3)_4L^{4+}$ series where L is varied (but the solvent is constant), $\bar{H}_{13}^2$ increases as ΔE increases. This is precisely opposite to the trend observed when the solvent is varied and L is held constant (cf. Figure 4; Table I). The explanation for this behavior is not obvious; it is predicted by none of the optical selection rules. One possibility, however, is that with changes in L, the value of $\bar{H}_{23}$ ($\bar{H}^*_{23}$) may also change systematically. (In the solvent study, we have taken $\bar{H}_{23}$ to be constant.[13]) Another is that the onset of significant L-induced valence delocalization might lead to more complex oscillator strength behavior than can be satisfactorily explained by localized-valence models.[21] A complete explanation may need to await additional studies with less strongly interacting metal centers.

Concluding Remarks

Although electron transfer is usually assumed to be the charge propagation mechanism in redox chemistry, there do exist other reports that implicate hole-transfer pathways.[4,23-27] For example, the ferric/ferrous self-exchange appears to be dominated by hole-transfer type interactions.[26,27] In light of the particularly direct evidence provided by the intervalence experiments, it will be interesting to see just how general such pathways eventually turn out to be.

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(18) For example, from Richardson and Taube's work (Figure 4 of ref 4) an n value of either 3 or 6 would seem appropriate. On the other hand, if β is larger than E_{ij} (E^*_{ij}) (almost certainly the case for these complexes), the value of n is irrelevant and the $(\beta/E_{ij})^{n-1}$ term should be omitted from eq 4.

(19) Roberts, J.; Blackbourn, R. L.; Curtis, J. C.; Hupp, J. T., unpublished data (redox isomerization studies).

(20) The thermal "selection rule" arguments are based simply upon the way in which the values for E_{ij} (E^*_{ij}) (transition state → virtual state) are anticipated to vary with systematic variations in solvent basicity (Figure 4).

(21) These complexes clearly fall within the realm of class II mixed-valence behavior. The extent of localization, however, is known to be considerably less than implied by eq 3.[6a]

(22) It is tempting, nevertheless, to try. From Figure 4, E^*_{12}(thermal) and E_{23}(thermal) for reaction 1 should be affected more or less equally (but oppositely) by changes in solvent basicity. It follows (eq 4) that $\bar{H}_{13}^2$(ET)(thermal) and $\bar{H}_{13}^2$(HT)(thermal) should likewise be influenced in opposite ways. If it is accepted that ET is the majority pathway, then changes in $\bar{H}_{13}$(ET)(thermal) will dominate in $\bar{H}_{13}$(total) (eq 7). This leads to the interesting and peculiar conclusion that $\bar{H}_{13}^2$(thermal) will increase with increasing solvent basicity even as $\bar{H}_{13}^2$(optical) decreases for the same reaction. The limitation to this analysis is that it presupposes that the shapes of the virtual-state potential-energy surfaces and their relative positions along the reaction coordinate are essentially as sketched in Figure 4. If these suppositions are not appropriate (for example, a virtual state might more correctly be positioned directly above either the initial state or final state, rather than midway between), then the analysis would need to be altered and the conclusions might ultimately change.

(23) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746.

(24) Guarr, T.; McGuire, M. E.; McLendon, G. *J. Am. Chem. Soc.* **1985**, *107*, 5104.

(25) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584.

(26) Newton, M. D. *J. Phys. Chem.* **1988**, *92*, 3502.

(27) Newton, M. D. Proceedings of the 22nd Jerusalem Conference on Quantum Chemistry, May 1989, to be published.