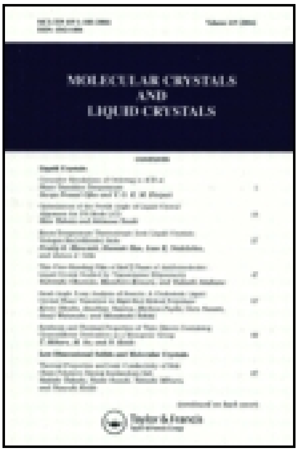

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THE DEPENDENCE OF LIGAND TO METAL CHARGE TRANSFER OSCILLATOR STRENGTH ON THE NATURE OF THE RUTHENIUM(III)–CYANAMIDE BOND: OUTERSPHERE PERTURBATIONS.

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Abstract The extent of electronic coupling between donor and acceptor wavefunctions can play a dominant role in determining the rate of electron transfer. This is particularly true for biological electron transfer systems in which the redox sites are far apart or linked by a bridging ligand. In this study, we have investigated the extent to which electronic coupling between Ru(III) and an anionic phenylcyanamide ligand as measured by the $b_1^* \leftarrow b_1$ LMCT oscillator strength is affected by the nature of the outer coordination sphere. The LMCT oscillator strength was found to decrease with increasing solvent donor number. We suggest that the trend in oscillator strength can largely be rationalized in terms of the magnitude of the π overlap between Ru(III) and cyanamide anion group. When the cyanamide anion group is incorporated into the bridging ligand of a Ru(III,II) mixed–valence complex, the oscillator strength of the resulting LMCT band will be a probe of the extent to which the acceptor wavefunction is coupled to the bridging ligand. By varying solvent donor properties, it will be possible to tune this interaction and observe this effect on the coupling between ruthenium ions as measured by the intervalence transition.

Keywords: Ligand to metal charge transfer, oscillator strength, solvent dependence, ruthenium (III)-cyanamide

INTRODUCTION

Evaluation of the importance of electronic coupling in determining the rate of thermal electron transfer or the probability of photo–induced charge transfer is an ongoing challenge to the experimentalist. For thermal adiabatic electron transfer, the interdependence of thermodynamic and kinetic parameters is well treated by Marcus theory.[1] However, when electron transfer is diabatic, electronic coupling becomes important and can no longer be ignored. The extent of electronic coupling between donor and acceptor wavefunctions is determined by their relative separation, orientation and energy. The last of these factors links electronic coupling to the thermodynamic and kinetic parameters associated with electron transfer. This interdependence should be accounted for in any theory of diabatic electron transfer.

Our approach to this problem has been to study the LMCT transitions arising out of the interaction of Ru(III) with the anionic cyanamide group for pentaammineru–

thenium(III) complexes of phenylcyanamide ligands.[2] Seventeen complexes were prepared in order to explore the dependence of the $b_1^* \leftarrow b_1$ LMCT oscillator strength on the nature of the Ru(III)–cyanamide bond. This was achieved by substituting electron withdrawing or donating substituents onto the phenyl ring of the phenylcyanamide anion ligand. The electronic properties of the cyanamide group could then be "tuned" in a predictable manner. The oscillator strength of the $b_1^* \leftarrow b_1$ band was shown to be dependent on the degree of overlap between cyanamide donor and ruthenium(III) acceptor wavefunctions. In addition, the solvent dependence of the $b_1^* \leftarrow b_1$ LMCT oscillator strength for $[(NH_3)_5Ru(2,3\text{–}Cl_2pcyd)]^{2+}$, where $2,3\text{–}Cl_2pcyd^-$ is (2,3–dichlorophenyl)cyanamide anion, was investigated.[3] A linear correlation was found in which oscillator strength decreases with increasing solvent donor number. It was suggested that the donor–acceptor interaction of the solvent with the ammine protons weakens the Ru(III)–cyanamide π bond and that this is reflected by a reduction in $b_1^* \leftarrow b_1$ LMCT oscillator strength.

In this study, we elaborate on the dependence of oscillator strength on the overlap between donor and acceptor and present novel data for the solvent dependence of the $b_1^* \leftarrow b_1$ LMCT oscillator strength for the complexes $[(NH_3)_5RuL][ClO_4]_2$, where L = 3,4,5– methoxy–, 4–chloro–, 2,6–dichloro–, and 2,3,5,6–tetrachloro– phenylcyanamide anion.

EXPERIMENTAL

The synthesis of the $[(NH_3)_5RuL][ClO_4]_2$ complexes used in this study has been described previously.[2,4] Accusolv grade dimethylsulfoxide, tetrahydrofuran, acetone and acetonitrile were purchased from Anachemia. Spectrograde dimethylformamide and nitromethane (99+ %) were purchased from Aldrich. All solvents were stored over 4A molecular sieves and used without further purification. UV–vis spectra were recorded using a Perkin–Elmer Lambda 4b spectrophotometer. At least two quantitative measurements, (weight and volume to four significant figures), were perfomed in each solvent.

RESULTS

The electronic absorption data of the solvent studies are compiled in Table I. The experimental oscillator strength of the $b_1^* \leftarrow b_1$ LMCT band was calculated with the expression,[5a]

$$f = 4.6 \times 10^{-9}\,\bar{\nu}_{1/2}\varepsilon_{max} \qquad (1)$$

where $\bar{\nu}_{1/2}$ is the band width in cm^{-1} at one–half band height and ε_{max} is the max–imum extinction coefficient in $M^{-1}cm^{-1}$.

TABLE I Electronic absorption data[a] for the $b_1^* \leftarrow b_1$ LMCT transition of $[(NH_3)_5Ru(L)][ClO_4]_2$, where L = a substituted phenylcyanamide anion ligand.

L		NM[b]	AN[c]	AC[d]	THF[e]	DMF[f]	DMSO[g]
3,4,5–MeO_3pcyd							
	f	0.167	0.162	0.151		0.131	0.122
	$\bar{\nu}$	10750	12330	12750		13770	14080
	$\bar{\nu}_{1/2}$	4690	4710	4740		4880	4840
4–Clpcyd							
	f	0.206	0.166	0.159		0.128	0.117
	$\bar{\nu}$	12830	13640	14030		14950	15310
	$\bar{\nu}_{1/2}$	5400	4660	4650		4510	4420
2,3–Cl_2pcyd							
	f	0.180	0.144	0.135	0.125	0.108	0.100
	$\bar{\nu}$	13710	14410	14850	14860	16110	16320
	$\bar{\nu}_{1/2}$	5450	4580	4480	4280	4280	4260
2,6–Cl_2pcyd							
	f	0.148	0.140	0.139	0.130	0.108	0.096
	$\bar{\nu}$	14350	15090	15480	15660	16500	16830
	$\bar{\nu}_{1/2}$	4950	4890	4661	4862	4510	4340
2,3,4,5–Cl_4pcyd							
	f	0.120	0.112	0.110	0.109	0.094	0.075
	$\bar{\nu}$	15100	15800	16300	16400	17300	17700
	$\bar{\nu}_{1/2}$	4949	4657	4450	4490	4400	4190

[a] all data in cm^{-1} except f (eq. 1) which is dimensionless [b] nitromethane [c] acetonitrile [d] acetone [e] tetrahydrofuran [f] dimethylformamide [g] dimethylsulfoxide

DISCUSSION

Theory

Oscillator strength is a dimensionless quantity which is used to express transition probability and can be calculated theoretically by using the expression,[5a]

$$f = 1.085 \times 10^{11}\, G\, \bar{\nu}\, M^2 \qquad (2)$$

where G refers to the degeneracy of the states concerned, $\bar{\nu}$ is the energy in cm^{-1} at ε_{max} and M is the charge transfer dipole moment. For a one electron system,

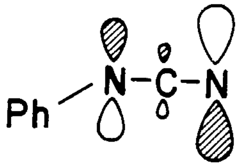
$$M = \int \psi_g\, er\, \psi_e\, d\tau \qquad (3)$$

where ψ_g and ψ_e are ground and excited state wavefunctions respectively and er is the transition moment dipole operator. The form of the transition moment depends on whether the coupling between donor and acceptor wavefunctions is a strong or weak coupling case. For these complexes, a weak coupling model is not appropriate,[3] since the overlap between π donor and acceptor wavefunctions, S_π, is expected to be significantly greater than zero. In this case, the transition dipole moment is dependent on the extent of overlap and has the form,[3,6]

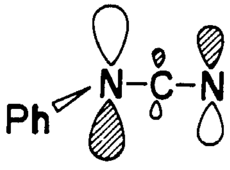
$$M \approx ekS_\pi R \qquad (4)$$

where k is an adjustable constant that depends on the orbital type[7] and R is the transition dipole length.

The anionic cyanamide group is a three atom, resonance stabilized π system, $\mathrm{Ph{-}\bar{N}{-}C{\equiv}N} \leftrightarrow \mathrm{Ph{-}N{=}C{=}N^-}$. A crystal structure[2] of $[(NH_3)_5Ru(2,3\text{-dichlorophenylcyanamide})][SO_4]$ shows the cyanamide group coordinated to Ru(III) by the cyano nitrogen and nearly coplanar with the phenyl ring. In this coordination mode, there are two pairs of non–bonding electrons of π symmetry that can delocalize into the cyanamide π system and the resulting orthogonal π_{nb1} and π_{nb2} molecular orbitals may appear as shown below where atomic orbital size approximates[8] the magnitude of the electron density coefficient. It is important to note that the electron density coefficient of the terminal cyano nitrogen depends to a large degree on the contribution of the $\mathrm{Ph{-}N{=}C{=}N^-}$ resonance structure to the molecular orbital. π_1 is more stable than π_2 because only π_1 has the correct symmetry to delocalize into the



π_{nb2}



π_{nb1}

phenyl ring as well as the nitrile group. These give rise to two ligand LMCT transitions in the visible region of the complex's electronic absorption spectrum. The lower energy LMCT band has been assigned to an allowed $b_1^* \leftarrow b_1$ ($d\pi^* \leftarrow \pi_{nb2}$) transition[4] and is completely separated from any other absorption, allowing accurate calculation of the band's oscillator strength using eq. 1.

For a given complex, the experimentally determined oscillator strength of the $b_1^* \leftarrow b_1$ band can be compared to the theoretically derived oscillator strength by first recognizing that the overlap of the π bond associated with the $b_1^* \leftarrow b_1$ LMCT transition is of the form:

$$S_\pi = \int \psi_{4d}\, C_n \psi_{2p}\, d\tau = C_n S \qquad (5)$$

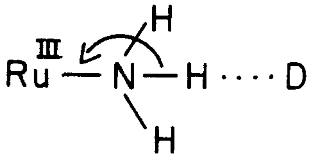
where S is the optimum overlap between a 4d and 2p orbital at a given Ru(III)–cyanamide bond length and C_n is the electron density coefficient of the terminal cyanamide nitrogen of the π_{2nb} MO described above. For the $b_1^* \leftarrow b_1$ LMCT transition, $G = 1$ and by solving for M with eq. 4 and 5, and substituting the result into eq. 2, its theoretical oscillator strength is approximated by

$$f \approx 1.085\ \mathrm{x}10^{11}\, \bar{\nu}\, k^2 C_n^{\,2} S^2 R^2 \qquad (6)$$

The oscillator strength of the $b_1^* \bullet b_1$ LMCT transition is therefore expected to increase in magnitude with increasing energy of the transition, π overlap and transition dipole length.

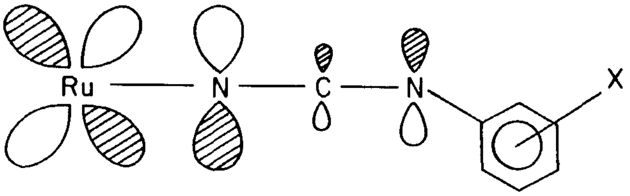
Outersphere Perturbation

The perturbation of solvent on charge transfer transition energy has been well studied.[5b] For pentaamineruthenium(III) complexes of π donor ligands,[9] linear correlations have been determined in which LMCT energy increases with increasing solvent donor number.[10] This was interpreted to result from the ground state stabilization of the complexes via a donor–acceptor interaction between the solvent and the ammine protons as shown below:



Direct evidence for the strengthening of the Ru(II)–ammine bond via the above mechanism has been obtained from preresonance Raman studies[11] of MLCT transitions in $[(NH_3)_4Ru(2,2'\text{–bipyridine})]^{2+}$. The strengthening of the Ru(III)–ammine bond via this mechanism should be even greater because of the greater acidity of the ammine protons.

The situation for the π overlap between the cyanamide π_{2nb} MO and the Ru(III) 4d orbital is illustrated below.



In strongly donating solvents, the ammine ligands of the complexes in this study will contribute more electron density to Ru(III), raising the energy of the dπ orbital and increasing $\bar{\nu}$ for the $b_1^* \leftarrow b_1$ transition (Table I). As a result, the ability of Ru(III) to polarize electron density to itself and stabilize the $Ph\text{–}N\text{=}C\text{=}N^-$ resonance structure will diminish. It follows that the contribution of the $Ph\text{–}\bar{N}\text{–}C{\equiv}N$ resonance structure to the π_{2nb} MO will become greater and result in a decrease in C_n and an increase in R. Therefore, both $\bar{\nu}$ and R are expected to increase with increasing donor number while ${}^{S}\pi$ is expected to decrease. Figure 1 illustrates the dependence of the $b_1^* \leftarrow b_1$ oscillator strength on solvent donor number for five pentaammineruthenium(III) complexes of phenylcyanamide anion ligands. It is clear from the trend in oscillator strength vs donor number that the degree of π overlap is the dominant factor of eq. 6 in determining the magnitude of the $b_1^* \leftarrow b_1$ oscillator strength for this series of similar complexes.

Two of the complexes, $[(NH_3)_5Ru(2,3\text{–}Cl_2pcyd)]^{2+}$ and $[(NH_3)_5Ru(4\text{–}Clpcyd)]^{2+}$

show a linear correlation between f and DN, with $f = -2.94 \times 10^{-3}$DN + 0.186, R = 0.998 and $f = -3.25 \times 10^{-3}$DN + 0.214, R = 0.999, respectively. The other complexes show evidence of curvature in low donor number solvents which we attribute to ion pairing effects.[12] The presence of counter anions in the outer coordination sphere would increase the effective donor number and decrease the oscillator strength. Where deviation from a linear relationship is not evident, the complexes show roughly the same oscillator strength dependence on donor number. This suggests that the nature of the phenylcyanamide ligand does not significantly perturb the interaction of the pentaammineruthenium(III) moiety with the solvent.

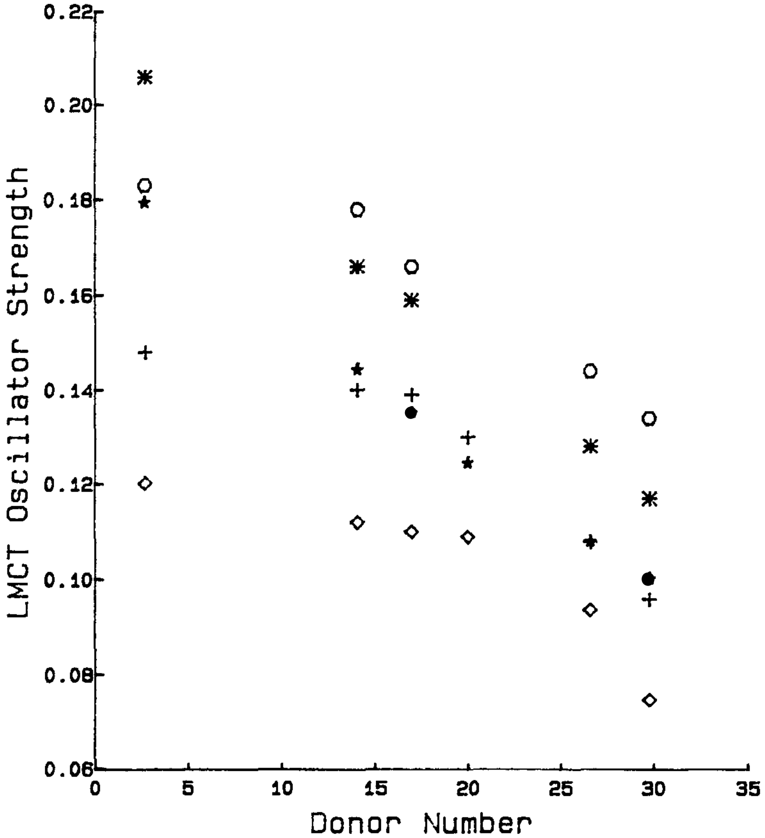


FIGURE 1 Effect of solvent donor number on the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT band for $[(NH_3)_5Ru(L)][ClO_4]_2$ complexes. L = 3,4,5–MeO_3pcyd (o), 4–Clpcyd (*), 2,3–Cl_2pcyd (⋆), 2,6–Cl_2pcyd (+), 2,3,5,6–Cl_4pcyd (◊).

Evidence for the weakening of the Ru(III)–cyanamide π bond with increasing solvent donor number is shown by the change in LMCT band widths with solvent (Table I). For charge transfer transitions between bonding and antibonding molecular orbitals, band width is predicted to decrease as the difference between ground and excited state internuclear separation for both inner and outer coordination spheres becomes smaller. Since the outer coordination sphere contribution to band width is expected to increase with increasing solvent donor number,[9] the overall decrease in band width with increasing solvent donor number (see Table I) for all the complexes except $[(NH_3)_5Ru(3,4,5\text{–}MeO_3pcyd)]^{2+}$ is probably due to the dominant decrease in π bonding and antibonding character between Ru(III) and cyanamide anion. For the complex, $[(NH_3)_5Ru(3,4,5\text{–}MeO_3pcyd)]^{2+}$, band width appears to slightly increase with solvent donor number. This may indicate that the inner-sphere internuclear separation does not change significantly with donor number in the complex, although the band width of the complex in nitromethane may be depressed because of ion pairing effects.[12]

FUTURE STUDIES

The above discussion of the effect of solvent donor number on the $b_1^* \leftarrow b_1$ LMCT oscillator strength has been qualitative. We intend to perform extended Huckel calculations on these systems in order to derive theoretical estimates of C_n and R as a function of solvent and the nature of the phenylcyanamide ligand. In addition, the solvent dependent redox couples of these complexes will be determined in order to correlate thermodynamic and electronic parameters.

Other researchers[13] have studied tetra– and penta–ammineruthenium(III,II) mixed–valence complexes with a pyrazine bridging ligand in various solvents. The perturbation of thermodyanamic and kinetic parameters and their effect on intervalence band energy were interpreted on the basis of the solvent donor–acceptor interactions already discussed. In a later paper,[14] the solvent dependence of electronic coupling in these complexes appeared to support (in part) a hole–transfer pathway between ruthenium ions. The mechanism of electronic coupling can be directly studied by incorporating the cyanamide anion group into the ligand bridging the two redox sites, since the oscillator strength of the resulting LMCT band will be a probe of the extent to which the acceptor wavefunction is coupled to the bridging ligand. By varying the solvent, it will be possible to "tune" this interaction and observe this effect on the coupling between ruthenium ions as measured by the oscillator strength of the intervalence transition.

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