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SOLVATOCHROMISM OF NON-POLAR COMPLEXES

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SUMMARY

The solvatochromism of various, formally non-polar, complexes is analysed using the McRae equation. The solvatochromism of the dinuclear species, $[M(CO)_4]_2bpm$ (M = Mo, W; bpm = 2,2′-bipyrimidine) is found to result from the individual dipoles of each half of the molecule interacting with the solvent. This is contrary to previously published explanations. The solvatochromism of non-polar $Ru(DTBSq)_3$ (DTBSq = 3,5-di-t-butylsemiquinone) is also found, unexpectedly, to correlate with the polar terms of McRae′s equation. Possible reasons for this are discussed.

INTRODUCTION

Solvatochromism provides a probe of both ground and excited state electronic structures and solvent-solute interactions. It is particularly important because it is one of very few probes of the Franck-Condon excited state. Solvatochromism is observed in many different complexes, but it is most pronounced for molecules which have a large net dipole moment, particularly those in which the transition moment is parallel or anti-parallel thereto.[1] The solvent molecules are then strongly oriented around the ground state dipole (Fig. 1a).

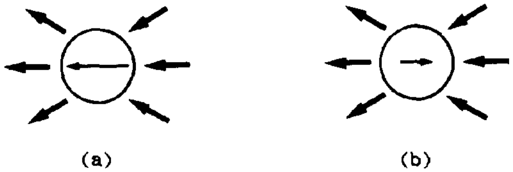

Fig. 1. Simple diagram showing solvation of a polar molecule in the ground (a) and Franck-Condon excited (b) states. The dipole moment changes direction upon excitation.

If the dipole moment decreases in the excited state, or changes its direction, the excited state will be destabilised in polar solvents relative to non-polar (Fig. 1b). This is the usual case for charge transfer transitions. If the excited state has a larger dipole moment in the same direction as that in the ground state the transition will red-shift in polar solvents.

Non-polar complexes are usually much less solvatochromic than polar ones.

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Their solvatochromism is normally due to differences in polarisability of the ground and excited state molecules, or to the presence of a dipole in the excited state.[2]

We discuss here some examples of non-polar complexes which are unusually solvatochromic; firstly the dinuclear carbonyl complexes, $[M(CO)_4]_2bpm$ (M = Mo, W; bpm = 2,2′-bipyrimidine), which will be compared with their mononuclear analogues, and secondly $Ru(DTBSq)_3$ (DTBSq = 3,5-di-t-butylsemiquinone). $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) is also discussed briefly for comparison.

The solvatochromism of a number of dinuclear carbonyls has been reported previously.[3-14] The origin of their solvatochromism has not been clearly identified and has been attributed by some authors to differences in polarisability between the ground and excited states.[8,13] We have recently shown that this latter explanation is incompatible with the experimental data for $[W(CO)_5]_2$pyrazine and with theory.[15]

EXPERIMENTAL

$W(CO)_4bpm$ (Wbpm) and $[W(CO)_4]_2bpm$ (WbpmW) were prepared by Petersen′s method,[4] and the Mo analogues (Mobpm and MobpmMo) by a similar method using toluene instead of xylene as the solvent. Mononuclear complexes were recrystallised from toluene (Mo) or tetrahydrofuran (W) and dinuclear complexes from acetone. Elemental analyses were satisfactory and molar absorption coefficients were in agreement with literature data (where available).[4,8] These complexes were stored in a freezer and spectra were run immediately after making up the solutions to avoid decomposition. $Ru(DTBSq)_3$ was prepared by reaction of $Ru_2(OAc)_4Cl$ with 3,5-di-t-butylcatechol.[16]

Spectra were obtained using a Perkin Elmer-Hitachi Model 340 spectrophotometer (carbonyls) or a Guided Wave Inc. Optical Waveguide Spectrum Analyzer Model 100 (Ru complex).

Solvents, generally of spectroscopic or analytical grade, were dried using activated molecular sieves before use. Acetonitrile, cyclohexanone, dimethylsulphoxide, piperidine and tetrahydrofuran were dried (by literature methods)[17] and distilled before use.

THEORY

In the absence of H-bonding, McRae′s equation (1)[18] can be used to determine the origin of solvatochromism in different systems. This equation is based on the reaction field model. The molecules are treated as point dipoles within spherical cavities in the solvent.

$$\begin{aligned}\Delta\nu = {} & A(D_{op}-1)/(2D_{op}+1) + B(D_{op}-1)/(2D_{op}+1) \\ & + C[(D_s-1)/(D_s+2) - (D_{op}-1)/(D_{op}+2)] \qquad (1)\end{aligned}$$

The quadratic Stark effect term is neglected here. $\Delta\nu$ is the difference between the energy of the optical transition in the solvent and in the gas phase, **A**, B and C are constants characteristic of the solute, D_{op} is the optical dielectric constant (refractive index squared) and D_s is the static dielectric constant.

The first term describes the contribution to the solvatochromism due to changes in dispersion forces. This term is normally small and negative and contributes for all molecules.[2] **A** involves sums of all electronic transitions in the molecule in the ground and excited states. The second term represents the interaction between solute dipoles and solvent induced dipoles and is non-zero if either the ground or excited state has a dipole moment. The third term is the dipole-dipole interaction term, and is non-zero only if there is a dipole moment in the ground state.

$$B = (\mu_g^2 - \mu_e^2)/a^3 \qquad (2)$$

$$C = 2\mu_g(\mu_g - \mu_e)/a^3 \qquad (3)$$

a is the effective cavity radius of the solute and μ_g and μ_e (vectors) are the ground and excited state dipole moments of the solute molecule.

The dispersion force term is difficult to calculate using McRae's expression because electronic transitions of the excited state are not normally known. An alternative expression, given by Bayliss,[19] results in values of less than 100 cm^{-1} for the first term, e.g. 80 cm^{-1} for $Mo(CO)_4bpm$ in hexane (assuming a = 5.2 Å, f = 0.1).

RESULTS AND DISCUSSION

1. Tris(bipyridine)ruthenium(II)

The solvatochromism of $[Ru(bpy)_3]^{2+}$ has been discussed by both Meyer and co-workers[20] and Milder.[21] The behaviour is as expected for a complex with no ground state dipole moment, i.e. there is a good correlation with D_{op} (R = 0.94), which is not improved by including a term containing D_s. The shift observed in the metal to ligand charge transfer (MLCT) band is approximately 300 cm^{-1}, though the range of solvents for this complex is limited by its positive charge. Two conflicting interpretations of the data have been given. Meyer et al. have concluded that the shift is too large to be accounted for by dispersion forces alone, therefore the excited state is polar due to the excited electron being localised on one ligand.[20] Milder, on the other hand, has shown that the solvatochromism is less than that of one of the bpy internal $\pi \longrightarrow \pi^*$ transitions in the complex and in the bpy free ligand. Since neither of these transitions should give a polar excited state only dispersion forces (first term of McRae's equation) can be responsible for the solvatochromism.[21]

Assuming that the solvent effect on the $\pi \longrightarrow \pi^*$ transition in $[Ru(bpy)_3]^{2+}$ is due to dispersion forces, the expected solvent effect, **A**, for the MLCT band due to dispersion forces can be calculated. This is based on the ratios of the oscillator strengths (a maximum value of 0.25 was used for the MLCT transition) and frequencies of the two transitions, using Bayliss' expression.[19] The value calculated for **A** is the same, within experimental error, as that observed by Meyer, suggesting that Milder's conclusion[21] is correct.

2. Bipyrimidine complexes

The complexes $[M(CO)_4]_2$bpm have D_{2h} symmetry and are formally non-polar, being composed of two polar $M(CO)_4$(diimine) groups with their dipole moments opposed (negative ends lie along the z axis between the trans CO groups). The polar mononuclear analogues, $M(CO)_4$bpm, are discussed here for comparison. Spectra of the Mo mono- and dinuclear complexes are shown in Fig. 2.

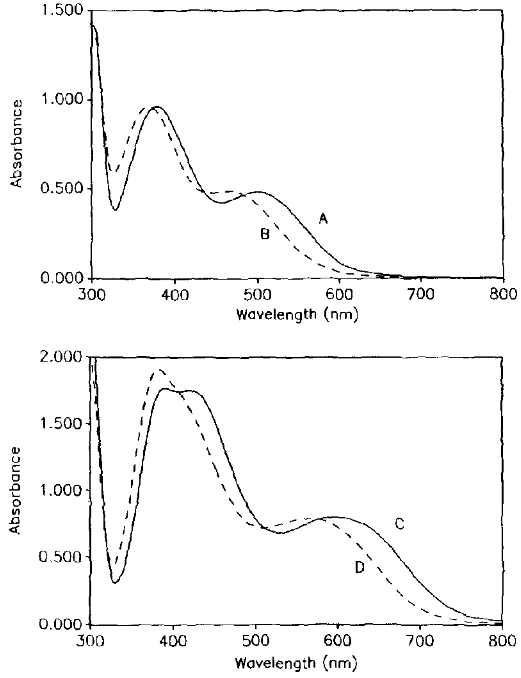


Fig. 2. Top: 1.5×10^{-4} M $Mo(CO)_4$bpm in butyl acetate —— (A) and acetonitrile --- (B). Bottom: 1.5×10^{-4} M $[Mo(CO)_4]_2$bpm in butyl acetate —— (C) and acetonitrile --- (D).

Two intense MLCT bands are observed in the visible-near UV region of the electronic spectrum.[3,4,6] Both bands comprise more than one MLCT transition and the higher energy band is superimposed on a ligand field (LF) transition. In the C_{2v} mononuclear species the lower energy band (MLCT 1) is mainly a z-polarised M⟶bpm transition ($b_2 \longrightarrow b_2^*$), with a weaker x-polarised transition at slightly higher energy (Fig. 3).[22] The higher energy band (MLCT 2) consists of a z-polarised ($a_2 \longrightarrow a_2^*$) and an x-polarised ($b_2 \longrightarrow a_2^*$) MLCT transition;[22] the latter is expected to be more intense due to better overlap.

The assignments in the dinuclear species depend on whether there is a strong interaction between the two metal centres. If there is no interaction, the two metals can be treated independently in their local C_{2v} symmetry and the assignments are as above for the mononuclear systems. If, however, there is an interaction, the symmetry, D_{2h}, of the whole molecule must be considered, metal orbitals of both odd and even parity result, and centrosymmetric selection rules apply. Again, two transitions to each of the bpm LUMO and SLUMO (second lowest unoccupied molecular orbital) are allowed. If there is significant interaction between the two halves of the molecule the two components of each band will be more widely separated than in the mononuclear species (Fig. 3).

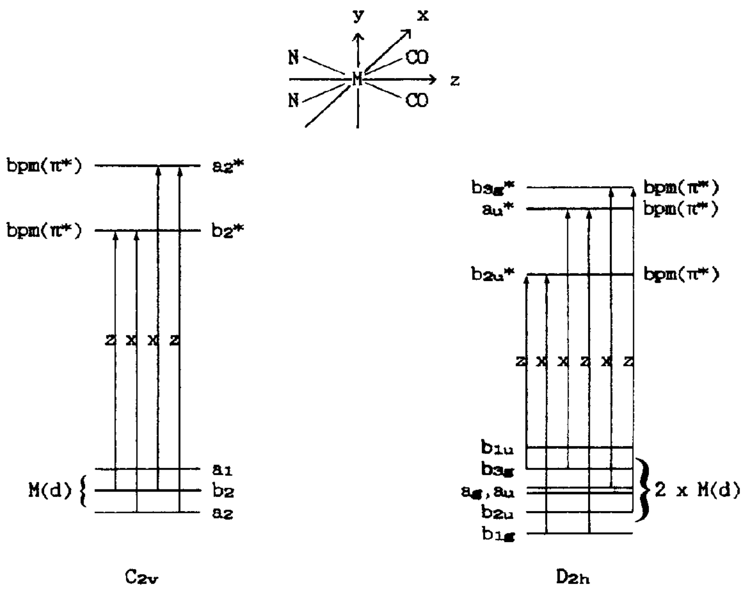


Fig. 3. Qualitative MO diagram to show allowed (symmetry and overlap) transitions in mononuclear (C_{2v}) and dinuclear (D_{2h}) complexes, assuming some M-M interaction in the dinuclear species. The a_g and a_u orbitals are not degenerate. Not to scale.

Deconvolution of representative spectra of mono- and dinuclear species shows the expected two transitions under each band, but there does not seem to be a significant increase in the separation of the two components of each band in the dinuclear species.

TABLE 1

Spectroscopic data for molybdenum and tungsten bipyrimidine complexes[a]

Mononuclear complexes	$Mo(CO)_4bpm$		$W(CO)_4bpm$	
Solvent	MLCT 1	MLCT 2	MLCT 1	MLCT 2
1. Dimethylsulphoxide	21950sh	27150	21000sh	27150
2. Propylene carbonate	21700	27100	21000sh	27050
3. Acetonitrile	21600	27100	21000sh	27050
4. Dimethylacetamide	21550	27100	21000	26900
5. Acetone	21250	26900	20600	26750
6. Butanone	20850	26750	20250	26600
7. Cyclohexanone	20700	26600	20100	26600
8. Ethyl acetate	20450	26600	19750	26450
9. Tetrahydrofuran	20400	26500	19750	26500
10. 3-Heptanone	20300	26500	19550	26250
11. n-Butyl acetate	20200	26500	19400	26300
12. Piperidine	19750	26250	19000	26200
13. Diethyl ether	19400	26200	18800	24050sh,26200
14. n-Butyl ether	18800	24050sh,26050	18000	24400sh,25850
15. Cyclohexane	16950,18200	23450sh,25450	16350,17650sh	23900,25400sh
16. Hexane	16850,18300	22950sh,25650		

Dinuclear complexes	$[Mo(CO)_4]_2bpm$		$[W(CO)_4]_2bpm$	
Solvent	MLCT 1	MLCT 2	MLCT 1	MLCT 2
1. Dimethylsulphoxide	18750	26300	17400	24050sh,26050
2. Propylene carbonate	18400	26250[b]	16900	24050,25900
3. Acetonitrile	17800	26200[b]	16400	23700,25800sh
4. Dimethylacetamide	18800	26100	17300	24000,25900
5. Acetone	17900	25950[b]	16400	23600,25750sh
6. Butanone	17700	25900[b]	16300	23300,25500sh
7. Cyclohexanone	17600	25750[b]	16300	23250,25550sh
8. Ethyl acetate	17050	23800sh,26450	15750	23100,25400sh
9. Tetrahydrofuran	16850	24050sh,25900	15450	23050,25900sh
10. 3-Heptanone	17350	23900sh,25750	15900	24150,25400sh
11. n-Butyl acetate	16800	23900,25700	15550	23000,25500sh
14. n-Butyl ether	15450	22300,25650		
15. Cyclohexane	15400	22400,25400	15350	22100,25400sh

a) Data in cm^{-1}. b) Shoulder to low energy side. sh = shoulder.
Solubility of these complexes decreases in the order Mobpm > Wbpm > MobpmMo> WbpmW. Blank spaces above indicate insufficient solubility.

There is also a third LUMO (TLUMO) of b_{3g} symmetry which is accidentally degenerate with the SLUMO in the absence of interactions with the metal.[8,23] Transitions to this orbital are forbidden if there is no metal-metal interaction, but allowed from a_u and b_{2u} if there is a M-M interaction. These transitions are expected to the high energy side of MLCT 2, the stronger the M-M interaction the greater the difference between MLCT 2 and transitions to the TLUMO. No extra transitions are observed in the near UV region, and the sum of the oscillator strengths of MLCT 1 and MLCT 2 in MobpmMo is exactly double the sum of the oscillator strengths of MLCT 1 and MLCT 2 in Mobpm (the sum was used because of the overlap of the two bands and the consequent uncertainty in deconvolution). These observations suggest (but do not prove) that there is little interaction between the two metal centres.

Data for all four complexes in 12-16 solvents (depending on solubility) are given in Table 1. Aprotic, non-chlorinated, non-aromatic solvents were used; i.e. "select solvents" as defined by Kamlet et al.[24] Where the two components of the bands are resolved average values are taken (note that the deconvolution indicates that the solvatochromism of the two components of MLCT 1 is similar) except in the case of $[W(CO)_4]_2$bpm MLCT 2. In this latter case the bands are resolved in all solvents and the higher energy band appears as a shoulder which varies very little with solvent, probably due to the influence of the ligand field transition underneath.

The solvatochromism of both MLCT bands of the mono- and dinuclear Mo and W complexes has been fitted to McRae's equation using a dual parameter fit. Correlations with the D_{op} term alone, which are expected for non-polar species, give $R < 0.5$. The results of the two-parameter fits are given in Table 2; reasonable correlations are obtained in all eight cases, though there is considerable scatter for the W dinuclear complex. Representative plots of calculated versus observed transition energies are shown in Fig. 4.

TABLE 2

Fits to McRae's equation[a]

Complex	Band	const.[b]	A+B[c]	C[c]	R[d]	N[e]
$Mo(CO)_4$bpm	MLCT 1	16950	4300(±6500)	5490(±365)	0.973	16
	MLCT 2	24700	-15(±6400)	3620(±357)	0.943	16
$W(CO)_4$bpm	MLCT 1	16750	2200(±6100)	5420(±368)	0.971	15
	MLCT 2	23300	7500(±6000)	3280(±380)	0.928	15
$[Mo(CO)_4]_2$bpm	MLCT 1	11250	19500(±7100)	4610(±409)	0.964	13
	MLCT 2	22100	7200(±6400)	3720(±370)	0.954	13
$[W(CO)_4]_2$bpm	MLCT 1	10550	22000(±8100)	2670(±525)	0.882	12
	MLCT 2	20550	7900(±6600)	2550(±430)	0.894	12

a) Data in cm^{-1}. b) Calculated gas phase transition energy. c) Figures in parentheses are standard errors. d) Correlation coefficient. e) Number of solvents.

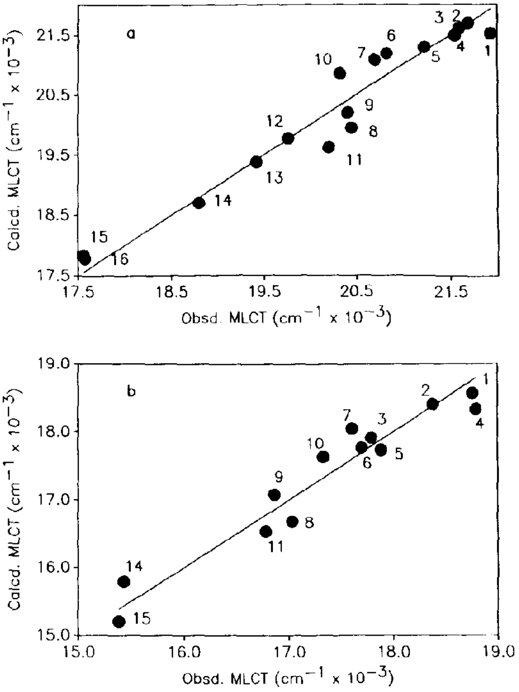


Fig. 4. Calculated versus observed transition energies for MLCT 1: (a) $Mo(CO)_4bpm$, (b) $[Mo(CO)_4]_2bpm$. Energies are calculated from equation 1 using parameters in Table 2. Solvents are numbered as in Table 1.

The variation in the $(A+B)(D_{op}-1)/(2D_{op}+1)$ term with solvent is so small that the errors are very large (changing the selection of solvents can cause large changes) and the fits are not significantly improved by including it, except for MLCT 1 in the dinuclear species. It is included in the data presented here because it has physical significance and including or neglecting it makes little difference to the value of **C** or the constant. By contrast, **C** and the constant term (gas phase transition energy) are well defined and change very little if the selection of solvents is varied, e.g. using only the first 12 solvents for the mononuclear species.

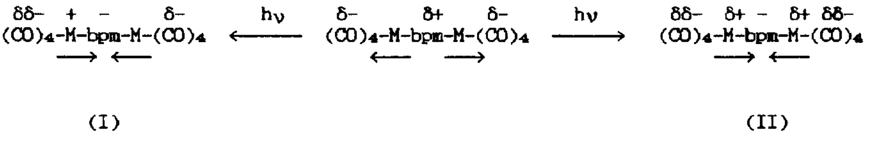
For comparison the solvent sensitivity of a particular band is most easily measured by the magnitude of **C** or by subtracting the band energy in a non-polar solvent (cyclohexane) from that in the most polar (DMSO). Using either measure the solvatochromism decreases in the order Mobpm = Wbpm > MobpmMo > WbpmW for MLCT 1. The solvatochromism of MLCT 1 is greater than that of MLCT 2 for a given complex. This result contradicts that of Kaim et al. who reported a very large solvent sensitivity for MobpmMo MLCT 2.[8] This seems to be largely due to the very low energy they obtained for MLCT 2 in toluene which differs from our own measurements by at least 1500 cm^{-1}.

The large values of (**A+B**) for MLCT 1 in the dinuclear species are consistent with the results obtained for $[W(CO)_5]_2$pyrazine[15] and appear from the statistics to be significant. However, the reason for these results is unclear. These large numbers preclude calculation of effective values of μ_g and μ_e because imaginary numbers are obtained if **B** > **C**.

The most important observation is that the solvatochromism of the mono- and dinuclear species is very similar, although the dinuclear complexes have no net ground state dipole moment. The mononuclear species are known to be highly polar; dipole moments of ~8-10 Debye have been measured for related complexes such as $Mo(CO)_4$bpy.[22] The correlation with D_s indicates that there must be some ground state (dipole-dipole) interaction, and the lack of correlation with D_{op} rules out an explanation based on dispersion or dipole-induced dipole forces. Even if (**A+B**) is very large it is still the variation in the dipole-dipole term, involving D_s, that dominates the solvatochromism. It can therefore be concluded that the dinuclear complexes should be regarded as polar entities as far as solvent-solute interactions are concerned.

McRae pointed out in his original paper that it was not realistic to assume that the electric field, created by the ordering of the solvent molecules around a polar solute, would be zero if the solute (or solvent) contained highly polar groups whose moments cancelled. Thus the two polar halves of the dinuclear complex must be considered to interact at least semi-independently with the solvent. The extent of the ordering of solvent around each half of the dinuclear complex seems, from the solvatochromism, to be comparable to that in the mononuclear species.

Interpretation of the fits to McRae's equation for the dinuclear complexes is not straightforward and depends on whether the excited states are localised on one metal (I) or delocalised over both (II), as assumed by Kaim et al.[8,23]



(I) (II)

If there is no M-M interaction in the ground state the Franck-Condon excited state is almost certainly localised on one metal. At present there is insufficient evidence to decide between these two possibilities. The consequences of the localisation/delocalisation problem for solvatochromism are discussed in more detail elsewhere.[15]

The solvent-sensitivity of the dinuclear species appears to be slightly less than that of the mononuclear analogues, contrary to the findings of Kaim.[8,13] However, when the the errors are taken into account the differences can become very small. The exception to this is $[W(CO)_4]_2bpm$ MLCT 1 which is both the least soluble complex and the one with the most scattered correlation. Thus the differences are not worthy of further discussion until more data are available.

3. Tris(semiquinone)ruthenium

Comparison of the solvatochromism of this species with that of the structurally similar $[Ru(bpy)_3]^{2+}$ is revealing. The "semiquinone" complex is ambiguous as far as oxidation state is concerned. It contains three non-innocent ligands (they may exist as catecholate, semiquinone or quinone) and a metal which may reasonably be in any oxidation state from II to VI. Since the crystal structure shows all three ligands to be equivalent and nearer to semiquinones than catecholates,[25] it is simplest to regard it as $Ru^{III}(DTBSq)_3$. However, all the electrons are paired so there is no hole in the "t_{2g}" set to allow typical ligand to metal (t_{2g}^5) charge transfer transitions to occur. A molecular orbital description must therefore be used (Fig. 5).[26]

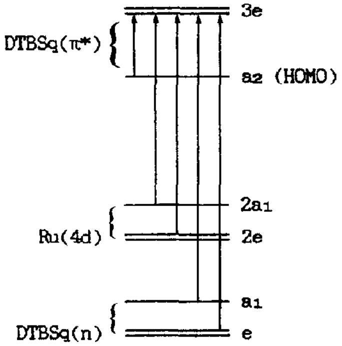


Fig. 5. Qualitative MO diagram to show expected transitions in $Ru(DTBSq)_3$. Orbitals are labelled according to D_3 symmetry. Not to scale.

Transitions are expected between three sets of molecular orbitals, deriving mainly from $Ru(t_{2g})$, DTBSq oxygen lone pairs (n) and DTBSq(π*). A rather complex spectrum results (Fig. 6). Most importantly the complex is quite strongly solvatochromic in spite of the fact that the ground state is apparently non-polar. The electronic spectrum in the solid state is not very different (except for some relative intensities) from that in polar solvents. As shown in Fig. 6 the shape of the band envelope in the visible region changes with solvent polarity. Deconvolution of spectra in several solvents (although rather uncertain) shows that this is probably due to the solvatochromism of the strongest visible region band, at around 600 nm.[18] This band is more solvatochromic than those either side of it and the amount of overlap with these bands varies, changing the overall shape of the spectrum. There is no evidence for the appearance of new bands in any solvent and irreversible decomposition of the complex can be ruled out as an explanation.

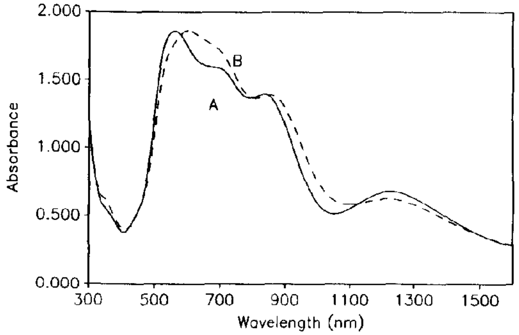


Fig. 6. Electronic spectra of 1.5×10^{-4} M Ru(DTBSq)$_3$ in hexane —— (A) and acetonitrile --- (B).

The 600 nm transition is tentatively assigned to "n-->π*", with both of these levels having significant Ru character. Evidence for this comes from comparison with the spectrum of Ru(bpy)(DTBSq)$_2$ (isoelectronic with Ru(DTBSq)$_3$) where a transition having similar energy and intensity is found.[27]

The visible region peak maximum is used here as it corresponds reasonably well with the energy of the strongest and most solvatochromic transition. A red shift of about 1000 cm^{-1} is found on going from non-polar to polar solvents. This is opposite to the normal behaviour of most solvatochromic complexes.[1] Surprisingly, there is a good correlation with functions of D_s and none at all with functions of D_{op} alone. A good correlation (R = 0.986, 10 solvents) is obtained with McRae's equation for the select solvents (excluding acetonitrile), both (A+B) and C being negative (equation 4).

$$\nu = 20100 - 12000(\pm2200)(D_{op}-1)/(2D_{op}+1) - 1550(\pm110)[(D_s-1)/(D_s+2) - (D_{op}-1)/(D_{op}+2)] \qquad (4)$$

Inclusion of alcohols or aromatics in the correlation does not significantly affect the results. It is interesting that the chlorinated aliphatic solvents appear to lie on a separate line with dichloroethane giving a larger red shift than the most polar solvent used (DMSO). A plot of the calculated versus the observed results is shown below (Fig. 7). Note that in this case both the (**A+B**) and **C** terms of equation 1 contribute significantly to the solvatochromism.

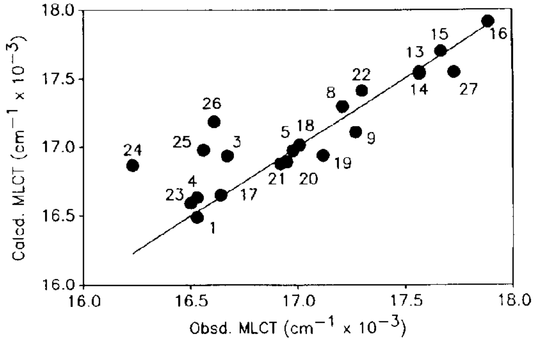


Fig. 7. Calculated versus observed λ_{max} for $Ru(DTBSq)_3$. Energies are calculated from equation 4. Solvents are numbered as in Table 1, with 17 = dimethylformamide, 18 = methanol, 19 = ethanol, 20 = 1-propanol, 21 = 1-butanol, 22 = toluene, 23 = 1,2-dichlorobenzene, 24 = 1,2-dichloroethane, 25 = dichloromethane, 26 = trichloromethane, 27 = tetrachloromethane.

The negative values of (**A+B**) and **C** are as expected for a complex with a polar ground state and a more polar excited state, with both dipole moments in the same direction. The correlation with D_s indicates some ground state interaction, other than random, of polar solvents with the complex. Since the ground state of the molecule is non-polar, and does not contain polar groups, this behaviour is unexpected and fundamentally different from that of $[Ru(bpy)_3]^{2+}$.

The red shift in polar (and chlorinated alkane) solvents indicates either destabilisation of the ground state or stabilisation of the excited state. Similar solvatochromism is not observed in the spectra of the analogous Rh(III) complex.[28] The most obvious difference between the Ru and Rh species is the extent of delocalisation in the bonding. Since there are many possible electronic structures for the Ru complex, and the system is probably highly delocalised, the electronic distribution may be sensitive to small variations in the environment, such as changes in solvent. A solvent-induced change in electronic structure of a related complex has been reported previously.[28] In particular the amount of mixing of the orbitals of e symmetry, and thus their energies, may be affected. In the extreme case a localised, polar electronic structure in which the ligands are no longer equivalent may result, e.g.

$Ru^{II}(DTBSq)_2(DTBQ)$ or $Ru^{IV}(DTBCat)(DTBSq)_2$ (Q = quinone, Cat = catechol), although IR spectra in various solvents show no shifts in the most intense band (ν(C-O)) as would be expected if the ligands became inequivalent.

The solvent effect may arise from a specific solvent-solute interaction in the ground state, involving either the oxygen lone pairs or semiquinone π system. For such a case in which the nature of the ground state varies with D_s McRae's equation no longer applies. A more complex correlation might be expected and the good fit above (4) may be fortuitous, though it does provide some useful information. Further studies are now in progress on this system.

CONCLUDING COMMENTS

It is evident that considerable solvatochromism may be exhibited by species which are formally non-polar and that more than one cause may be responsible for this. McRae's equation may be used with care in such cases to provide some insight into the solvent effects. More detailed interpretation of correlations with McRae's equation requires more complementary information on the nature of the excited states involved. As our understanding of this phenomenon improves we can expect to use it more reliably to answer questions such as those associated with localised and delocalised bonding in the ground and various excited states.

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