Inorg. Chem. **1990**, *29*, 499-503

ergy-transfer mechanism seems inappropriate.

Electrochemistry. In the potential window examined, all the complexes exhibit an almost reversible oxidation wave and three almost reversible reduction waves. The potential values are reported in Table II, where the corresponding values previously found for Ru(bpy)$_3^{2+}$ and **1**[Ru]$^{2+}$ are also shown. Comparison of the current intensities of the voltammograms of the three complexes (mono-, di-, and trinuclear) with the 2+/3+ oxidation wave of Ru(5,5′-Me$_2$-2,2′-bpy)$_3^{2+}$ (+1.16 V) as internal standard indicated monoelectronic, dielectronic, and trielectronic waves, respectively. Since the oxidation potential is the same for the three mixed-ligand complexes, the interaction between the Ru centers must be very small. The difference between the formal potentials for the first and last pair of oxidation states in a molecule with n identical noninteracting redox centers follows simple statistics and is given by $(2RT/F)\ln n$.[38] Thus, differences of 0.035 and 0.056 V would be expected between the first and second oxidation waves of **1**[Ru(bpy)$_2$]$_2^{4+}$ and the first and third oxidation waves of **1**-[Ru(bpy)$_2$]$_3^{6+}$. Such differences, however, are too small to be resolved in ordinary cyclic voltammograms. The reduction potentials are also very similar for the three mixed-ligand complexes. Since **1**[Ru]$^{2+}$ reduces at potentials less negative than those of Ru(bpy)$_3^{2+}$ (Table II), the first reduction wave of the mixed-ligand complexes can be attributed to the reduction of the bpy-type coordinated arm(s) of the tripod ligand. The second and third reduction waves concern, of course, the bpy ligands of the Ru(bpy)$_2^{2+}$ unit(s). The expected linear correlations[2,39] between spectroscopic and electrochemical quantities are verified.

Conclusions

No spectroscopic, photophysical, or electrochemical evidence has been found of an interaction between the metal-containing units in the binuclear and trinuclear complex. However, for the mononuclear complex **1**[Ru(bpy)$_2$]$^{2+}$ there is clear evidence of electronic energy transfer with high efficiency from the noncoordinated arms of **1** to the metal-containing units. Presumably, such an interaction requires a perturbation energy so small (e.g., of the order of 10–100 cm^{-1}) that it cannot be detected in the spectroscopic and electrochemical measurements. It should also be noted, however, that the geometrical conformation of the bridging ligand **1** can be quite different in **1**[Ru(bpy)$_2$]$^{2+}$ and **1**[Ru(bpy)$_2$]$_3^{6+}$. In the monomer, the noncoordinated arms of **1** are likely to approach the ligands coordinated to the Ru center, giving a molecular structure quite different from that drawn in this paper to represent **1**[Ru(bpy)$_2$]$^{2+}$. In the trimer, all the three arms of the tripod ligand **1** are coordinated to a Ru^{2+} center and thus will tend to stay away from each other, as shown by our schematic representation of this complex.

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Solvatochromism of Dinuclear Complexes: An Alternative Explanation

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The very large solvatochromism of the metal to ligand charge-transfer transitions in various, formally nonpolar, ligand-bridged dinuclear metal carbonyl complexes is discussed. The similarity of this behavior to that of related mononuclear species and the good correlations obtained with the "polar" part of McRae's equation are used to demonstrate that dipole–dipole interactions are the main cause of the solvatochromism. This contradicts previous explanations that have attributed the solvatochromism to changes in dispersion forces. It is concluded that, in the simplest approximation, the molecules may be regarded as having polar halves, each of which interacts with the solvent. Detailed interpretation in terms of McRae's equation is not possible without knowing whether the metal to ligand charge-transfer excited state is localized on one metal center or delocalized over both. The data available do not allow us to distinguish between these possibilities.

Introduction

Solvatochromism refers to changes in electronic absorption spectra with solvent. Although most, if not all, complexes are solvatochromic to some extent, the term is usually applied to species that show shifts in energy of at least a few hundred wavenumbers with variation in solvent. Many of the reports of solvatochromism in the inorganic literature involve M(CO)$_4$(diimine) complexes, where M is Cr, Mo, or W.[1-20] The solvatochromic transition involves metal to ligand charge transfer (MLCT) from the d^6 Cr, Mo, or W core to the lowest energy π^* orbital of the diimine. These intense absorptions, which normally occur in the visible region, are, in most cases, blue shifted in polar

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Table I. Comparative Data for Solvatochromism of Mononuclear and Dinuclear Complexes

bridging ligand[a]	metal core	slope, F (R)[b] mononuclear	slope, F (R)[b] dinuclear	no. of solvents[c]	ref
bpm	$Mo(CO)_4$	3340 (0.984)	4410 (0.993)[d,e]	4	10, 12
abpy	$Mo(CO)_4$	550 (0.983)	1460 (0.964)	5 (4)[f]	12
bptz	$Mo(CO)_4$		1870 (0.982)	4	12
bptz	$Mo(CO)_4$	1164	777	2[g]	13
2,3-bpp	$Cr(CO)_4$	2845 (1.000)	2818 (0.999)	4	20
2,3-bpp	$Mo(CO)_4$	3063 (0.996)	3257 (0.999)	4	20
2,3-bpp	$W(CO)_4$	2886 (0.996)	3028 (0.997)	4	20
2,5-bpp	$Mo(CO)_4$		3110 (0.999)	4	12
2,5-bpp	$Mo(CO)_4$		3770 (0.997)[h]	4	12
pyz	$W(CO)_5$		4310 (0.987)	12[i]	11, tw[j]
pyz	$W(CO)_4(PBu_3)$		2390 (0.999)	3	24
quin	$W(CO)_5$	3410 (0.987)	3980 (0.995)	5	24
bod	$W(CO)_5$	2790 (0.997)	4040 (0.993)	5	24
bpy	$Mo(CO)_4$	3520 (0.997)		4	10

[a] bpm = 2,2′-bipyrimidine; abpy = 2-(2′-pyridylazo)pyridine; bptz = 2,5-bis(2′-pyridyl)tetrazine; 2,3-bpp = 2,3-bis(2′-pyridyl)pyrazine; 2,5-bpp = 2,5-bis(2′-pyridyl)pyrazine; pyz = pyrazine; quin = quinoxaline; bod = 2,1,3-benzoxadiazole; bpy = 2,2′-bipyridine. [b] Slope (cm^{-1}) of plot of lowest MLCT band energy vs E^*_{MLCT} parameter.[4] Correlation coefficient, R, in parentheses. [c] Solvents used were DMF, acetone, THF, toluene, and isooctane—see original literature. All are select solvents except for toluene. [d] With use of other methods to evaluate the solvatochromism and more solvents, this band appears less solvatochromic than in the mononuclear analogue.[35] [e] A very large value was reported for the solvatochromism of the second MLCT band. This is not included because (i) the band overlaps badly with a ligand field band and (ii) the value of F is heavily biased by an MLCT energy for toluene, which we find to be at least 1500 cm^{-1} too low.[35] [f] Data for four solvents used for the dinuclear complex. [g] Difference between band energies in THF and toluene. [h] Corresponding slope for the second MLCT transition. [i] Solvents as in Figure 1. [j] tw = this work; calculated for data in ref 11.

solvents compared to nonpolar solvents (referred to as negative solvatochromism).[1,2]

The strong solvatochromism of the mononuclear $M(CO)_4$(diimine) complexes is normally attributed to the fact that the transition moment of the main (z-polarized) component of the MLCT transition lies antiparallel to the ground-state dipole moment of these highly polar molecules.[2] The dipole moment in the excited state is thus much reduced compared to the ground state or may even reverse its direction.[7,21] The ground state is strongly solvated in polar solvents, and the Franck–Condon excited state will be correspondingly destabilized relative to that in nonpolar solvents. In the latter the interactions in both the ground and excited states are weaker and the transition lies at lower energy.

Recently, several groups have reported solvatochromism of related dinuclear species, tetra- or pentacarbonylmetal groups linked by a bridging N-donor (aromatic) ligand, such as 2,2′-bipyrimidine (bpm) or pyrazine (pyz).[3,5,11-13,16,20,22-26] All except one of the dinuclear complexes have no net ground-state dipole moment and therefore, according to the simple interpretation above, should not be significantly solvatochromic. However, the solvatochromism is invariably of magnitude comparable to that of the corresponding mononuclear species, and in some cases it appears to be greater. This has been discussed in some detail by both Lees and Kaim and their co-workers. The former do not clearly identify the source of the solvatochromism,[11,26] while the latter group attribute it to differences in the polarizability of the molecule between the ground and excited states,[12,25] i.e. to changes in dispersion forces.

We show here that this interpretation is incompatible with the experimental evidence and the theory of solvatochromic shifts and suggest that the dinuclear complexes are better regarded as polar halves, as has been (briefly) suggested by Stufkens[22] and Haga.[24]

Theory

The various contributions to the solvatochromism can be described by using a dielectric continuum model, such as is used in generating McRae's equation.[27] This model has some weaknesses in that it does not allow for ordering of the solvent around the solute and it assumes the solute to be a point dipole in a spherical cavity. Recently, there have been a number of discussions of these problems and attempts have been made to allow for some solvent–solute interaction. However, the more complex functions that have been suggested do not, in general, give significantly better fits to experimental data.[28-33] McRae's equation can be written as (neglecting the quadratic Stark effect term)[27]

$$\Delta\nu = \mathbf{A}(D_{op} - 1)/(2D_{op} + 1) + \mathbf{B}(D_{op} - 1)/(2D_{op} + 1) + \mathbf{C}[(D_s - 1)/(D_s + 2) - (D_{op} - 1)/(D_{op} + 2)] \quad (1)$$

$\Delta\nu$ 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 (square of refractive index), and D_s is the static dielectric constant of the solvent. **A** involves a sum over all the electronic transitions of the molecule, including those of the excited state, and the first term represents the contributions to the solvent shift due to dispersion forces. **B** and **C** involve the ground- and excited-state dipole moments of the solute, μ_g and μ_e (these are vectors), and the effective cavity radius of the solute, a:

$$\mathbf{B} = (\mu_g^2 - \mu_e^2)/a^3 \quad (2)$$

$$\mathbf{C} = 2\mu_g(\mu_g - \mu_e)/a^3 \quad (3)$$

The term including **B** reflects the interaction between the solute dipole and the solvent-induced dipoles, and the third term of McRae's equation is the contribution from solvent–solute dipole–dipole forces.

The dispersion term can be calculated with Bayliss's expression[34] (use of McRae's expression requires knowledge of both ground- and excited-state transition energies, which are difficult to evaluate); it is relatively small (~100 cm^{-1}) and varies very little between solvents. Thus, it can be neglected for highly polar solutes, such as $Mo(CO)_4$(diimine), where the solvatochromism is large.

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The magnitudes of μ_g and μ_e can then, in principle, be obtained from a two-parameter fit to eq 1.

In the situation where both ground and excited states are nonpolar, i.e. μ_g and μ_e are zero, *only* the dispersion term will contribute to the solvent shift, which will then be relatively small and vary with the function of D_{op} in the first term of eq 1. If, however, μ_g is zero but the excited state has a net dipole moment, both the first (**A**) and second (**B**) terms will contribute, but not the third (**C**). Both of these terms (**A** and **B**) will have a negative sign, indicating a red shift from the gas phase. The magnitude of the red shift increases with increasing D_{op}.

Results

Measurements of solvatochromism for a number of pairs of mono- and dinuclear complexes are given in Table I. Other data, such as for $Mo(CO)_4bpy$, are given for comparison. The slope of a plot of the form

$$\nu_{max} = FE^*_{MLCT} + \text{constant} \qquad (4)$$

is used as a measure of the solvatochromism. ν_{max} is the wavenumber of maximum absorption for the MLCT transition and E^*_{MLCT} is Lees's solvent parameter based on the solvatochromism of $W(CO)_4bpy$ (bpy = 2,2′-bipyridine).[4] Note that the solvatochromism of mono- and dinuclear analogues tends to be of similar magnitude and that in all but two cases it is slightly larger for the dinuclear species. However, these apparent increases may be due to the particular parameter being used here; other measures of the extent of solvatochromism show the bipyrimidine-bridged dinuclear complex to be somewhat less solvatochromic than its mononuclear counterpart.[35]

For detailed examination and discussion the results reported by Lees and co-workers for $(CO)_5WpyzW(CO)_5$ will be used, since data for a large number of solvents are available.[11,23] Unfortunately, comparison with the solvatochromism of the mononuclear analogue, $W(CO)_5pyz$, is not possible due to overlap of the MLCT absorption with a ligand field band in the spectrum of this species.[26]

The following evidence is relevant to our understanding of the solvatochromism of these species.

(i) The solvatochromism of mono- and dinuclear species is similar; it appears that good correlations are obtained for all of this general type of complex with Lees's E^*_{MLCT} parameter,[10,12,20,25] indicating that any explanation of the solvatochromism must be applicable to both mono- and dinuclear species alike. In addition, the solvatochromism of the 2,3-bpp dinuclear species is almost identical with that of the 2,5-bpp species (Table I), despite the fact that the former has a net ground-state dipole moment and the latter does not.

(ii) Dipole moment measurements on some of the mononuclear complexes show them to be highly polar, with μ_g in the range 8–10 D.[36] Thus, dipole–dipole interactions are expected to play a major role in their solvatochromism. This idea is supported by the blue shift in the MLCT transition when the temperature is lowered.[9,37,38] (dipole–dipole interactions increase with decreasing temperature, whereas dispersion and dipole–induced dipole forces are temperature-independent).

(iii) The data for various (mononuclear) $M(CO)_4$(diimine) species correlate well with McRae's equation.[21,35,39] The dominant effect here is the dipole–dipole interaction term that involves (3) and therefore should be zero when μ_g is zero.

(iv) Lees has shown, for $(CO)_5WpyzW(CO)_5$ in "select" solvents (aprotic, nonaromatic, nonchlorinated[40]), that a good correlation ($R = 0.96$) is obtained between the MLCT energy and $(D_s - 1)/(2D_s + 1)$,[11] which is very closely related to the function that largely determines the variation in the dipole–dipole term of McRae's equation. No correlation was found with functions containing only D_{op}. A good correlation with the solvent dipole moment was also found,[11] again suggesting that dipole–dipole interactions are of prime importance.

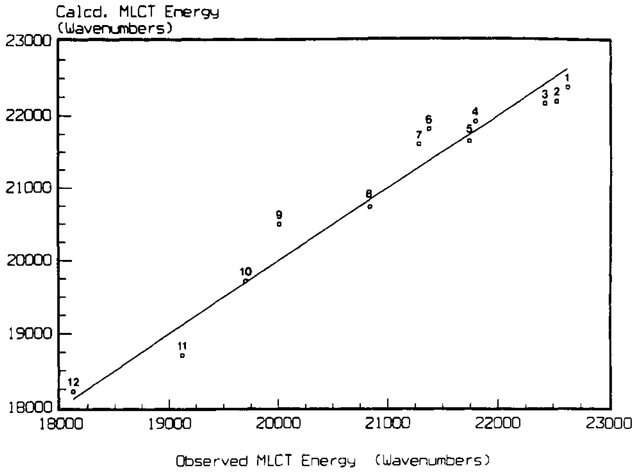

Figure 1. Plot of calculated vs observed MLCT energy for $(CO)_5W(pyz)W(CO)_5$. Values were calculated by using eq 5. Data are taken from ref 11. Solvent key: 1, dimethyl sulfoxide; 2, dimethylacetamide; 3, dimethylformamide; 4, acetonitrile; 5, acetone; 6, cyclohexanone; 7, 3-pentanone; 8, tetrahydrofuran; 9, piperidine; 10, diethyl ether; 11, triethylamine; 12, isooctane.

(v) We have fitted the data for $(CO)_5WpyzW(CO)_5$ to McRae's equation using a two-parameter fit. The correlation obtained ($R = 0.98$, 12 points, select solvents) is slightly better than that found by Lees for the D_s function alone. The equation obtained (in cm^{-1}) is

$$\nu_{max} = 15\,100\ (\pm 330) + (16\,300\ (\pm 6900))(D_{op} - 1)/(2D_{op} + 1) + (5610\ (\pm 420))[(D_s - 1)/(D_s + 2) - (D_{op} - 1)/(D_{op} + 2)] \quad (5)$$

The interpretation of this correlation is discussed below, and a plot of observed versus calculated results is shown in Figure 1. If the Stark effect term, which depends on the difference in polarizabilities of the ground and excited states, is included, the correlation is not improved and the error in this term is larger than the number itself. Thus, there is no statistical reason for including it. Inclusion of alcohols or aromatic or chlorinated solvents lowers the correlation coefficient significantly.

(vi) The use of McRae's equation for a nonpolar complex, $[Ru(bpy)_3]^{2+}$, has been demonstrated by both Kober et al.[41] and Milder.[42] Good correlations ($R = 0.94$) are obtained with only the $(D_{op} - 1)/(2D_{op} + 1)$ function, and the solvatochromism observed is small, only about 300 cm^{-1}. There is disagreement between the two groups about whether this represents dispersion forces or both dispersion and dipole–induced dipole forces, the latter resulting from the presence of a dipole in the excited state. Whichever of these is correct, the behavior is clearly very different from that of the dinuclear complexes under discussion here.

Discussion

The evidence above clearly indicates that these formally nonpolar dinuclear complexes behave as polar species with respect to their solvatochromism. Explanations in terms of polarizability (dispersion forces) alone are untenable.

The explanation of the apparently anomalous behavior of the dinuclear species can be found in McRae's original paper:[27] "if either the solvent or solute molecule is nonpolar but contains highly polar groups whose moments cancel, it is not realistic to put the time-average of the field $\mathbf{E}^u$ equal to zero" ($\mathbf{E}^u$ is the field at the solute dipoles due to the permanent dipoles of the surrounding

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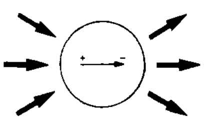
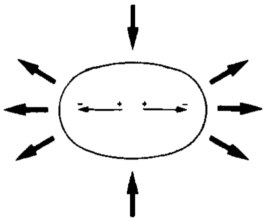
solvent molecules). Thus, the question is not whether there is a net dipole moment in the ground state but whether the solvent is oriented around the ground-state solute molecule. Given the size of the solute, which is considerably larger than a typical solvent molecule, the polar halves of these dinuclear complexes could be considered to interact separately to order the solvent. The extent of this ordering is, from the solvatochromism, comparable to that in the mononuclear complexes. Possible arrangements of solvent around mononuclear and dinuclear species are shown schematically in **1a** and **1b**. To fit the continuum model literally, the dinuclear species should be regarded as two point dipoles in the solute cavity, and the short-range ordering of the solvent implied above is not specifically allowed for. However, since the fit obtained is good, it appears that the model is still useful, at least qualitatively. Further, the absence of strong donor–acceptor interactions has been demonstrated by Connor and co-workers, who report that there are no anomalous changes in the electronic spectra of this type of complex upon addition of strong donors or acceptors such as Et_3N or BF_3.[6]



1a

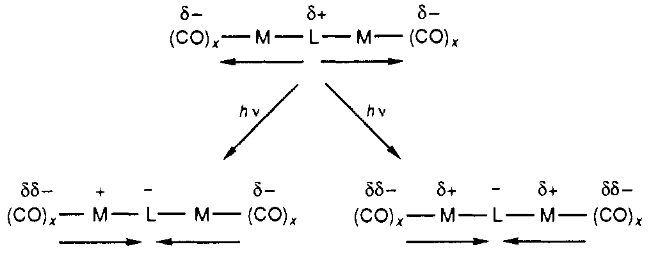


1b

It is also necessary to consider the nature of the excited state in these dinuclear species, in order to make comparisons of their solvatochromism with that of mononuclear complexes. The excited state may be localized on one metal center or, as assumed by Kaim,[12,25] delocalized over both. It is likely that the same situation does not pertain in all of the dinuclear species listed in Table I. For example, the 2,3-bpp ligand is nonplanar as a result of steric interactions between the two pyridyl H3 atoms.[43] Consequently, its symmetry is lowered, there is little interaction between the metal centers, and delocalization is unlikely. For this bridging ligand the solvatochromism of the three dinuclear complexes appears to be the same as that of the corresponding mononuclear species, within experimental error. It seems reasonable to regard each half as essentially independent as far as the solvent–solute interactions are concerned. For the complex $(CO)_5WpyzW(CO)_5$ the excited state is related to the ground state of the mixed-valence Creutz–Taube ion, $[(NH_3)_5RupyzRu(NH_3)_5]^{5+}$; the former can be written as $W(d^6)(pyz^-)W(d^5)$, and the latter, as $Ru(d^6)(pyz)Ru(d^5)$. It has been generally concluded that the Creutz–Taube ion is delocalized, mixed-valence class III,[44-46] and it is therefore possible that the excited state of the pyz-bridged W complex is similarly delocalized.

Use of McRae's Equation for Dinuclear Species. If the excited state is localized on one metal (**2a**), the simplest way to describe the solvatochromism is to assume that the second metal center is equivalent to a substituent on the bridging ligand and causes only a small perturbation. The solvatochromism of each half of the molecule is then treated essentially independently. This may be reasonable for bridging ligands such as 2,3-bpp but seems rather unrealistic for situations in which the two metal centers are close together and linked by a planar bridging ligand (e.g. abpy). It is difficult to interpret a correlation with McRae's equation here because the effective cavity radius is unknown.

More realistically, we may consider the molecule as a whole, including the changes in the solvent effects upon excitation on the local (net) dipole moments, $\mu(h)_g$, of both halves of the molecule. In the ground state the halves have equal and opposite dipole moments that both interact with the solvent. In the excited state the halves are different; the half from which the electron was excited will have a small dipole moment, $\mu(h^*)_e$, which may be in the direction opposite to that in the ground state. The dipole moment, $\mu(h)_e$, of the "substituent" (unexcited) end of the molecule will also change because of the additional formal negative charge on the bridging ligand. This will affect the M–N bond, and the negative charge may be distributed over this metal and the carbonyl ligands to a small extent. Conceivably, the direction of the dipole moment in the unexcited half of the molecule will also reverse. Thus, the solvent–solute interactions over the entire molecule may be affected in a complex manner even though the excitation is localized on one metal.



2a **2b**

The delocalized case (**2b**) is easier to treat with McRae's equation—we can consider half of the molecule interacting with the solvent and use a hypothetical cavity radius (a') corresponding to half the long axis length of the molecule. The relevant dipole moments are then those of each half of the complex, $\mu(h)_g$, from one set of carbonyls in the plane to the center of the bridging ligand. The change in dipole moment of each half of the molecule upon excitation is then expected to be significantly smaller than that in the mononuclear case because there is effectively excitation of only half an electron from each metal to the bridging ligand. However, the whole expression for the solvent shift should be multiplied by two because the relevant solvent–solute interactions are occurring twice for each electronic transition, once for each end of the molecule. Thus, neglecting the dispersion force term, we can write

$$\Delta\nu = [2(\mu(h)_g^2 - \mu(h)'^2_e)/a'^3](D_{op} - 1)/(2D_{op} + 1) + 2[2\mu(h)_g(\mu(h)_g - \mu(h)'_e)/a'^3][(D_s - 1)/(D_s + 2) - (D_{op} - 1)/(D_{op} + 2)] \quad (6)$$

where $\mu(h)_g$ and $\mu(h)'_e$ are the effective ground- and excited-state dipole moments of each half of the molecule. This should only be regarded as an approximation because of the neglect of the fact that one end of the hypothetical cavity, at the bridging ligand, is obviously not in a "dielectric continuum" of solvent.

Results for $(CO)_5W(pyz)W(CO)_5$. The results of the fit to McRae's expression for $(CO)_5WpyzW(CO)_5$ (Figure 1, eq 5) can be considered in the light of the above modification. Unfortunately, the value for **A** + **B** is unrealistic; if **B** > **C**, calculation of $\mu(h)_g$ and $\mu(h)'_e$ yields imaginary numbers (**A** is expected to be negative—see above). The fit is very insensitive to this term of McRae's equation because the variation in D_{op} is so small for the select solvent set and this term is very sensitive to the particular set of solvents chosen. However, similar large values for **A** + **B** are obtained for bpm-bridged species, for the lower of the two charge-transfer bands only.[35] It is unlikely that **A** would be large and positive,[27] so the reason for this observation remains unclear.

Cause of the Changes in Solvatochromism. Differences between the solvatochromism of mono- and dinuclear species may be due to changes in solvation or in bonding or a combination of both. It is possible that a delocalized excited state may show subtle differences in solvatochromism compared to the mononuclear species. Changes in solvation occur in the sense that the dinuclear complex interacts with a larger number of solvent molecules than the mononuclear complex. This should cause an increase in outer-sphere (i.e. solvent) reorganization energy, which is syno-

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nymous with an increase in solvatochromism. The average arrangement of solvent molecules will also differ from that in the mononuclear complex, as shown in (1).

Changes in bonding will alter the effective ground- and excited-state dipole moments, which will affect the strength of the solvent-solute interactions, i.e. the second and third terms of McRae's equation (eq 1). tom Dieck has demonstrated the effect of decreasing the difference between μ_g and μ_e, by increasing the amount of mixing of the metal and diimine ligand orbitals, in an extensive series of Mo(CO)$_4$(diimine) complexes (and phosphine-substituted analogues).[47-50] Increasing the mixing, by making the ligand a stronger π acceptor or by substituting phosphines for two of the carbonyls, gives the electronic transition less charge-transfer character and thus decreases the solvatochromism. This effect can be seen in the dinuclear complexes, the solvatochromism of (CO)$_5$WpyzW(CO)$_5$ being much greater than that of its PBu$_3$-substituted analogue (Table I).

The lowering of the π^* level when the second metal is coordinated may increase the metal-ligand orbital mixing and decrease the solvatochromism. However, both σ and π effects should be considered in this context. Unfortunately, there is little conclusive evidence to indicate what changes in bonding are occurring; changes in (C-O) force constants are small and variable, and metal oxidation potentials are irreversible.[13,20,26,51,52]

Conclusion

The available experimental evidence supports the view that the solvatochromism of centrosymmetric dinuclear metal carbonyl complexes is caused mainly by dipole-dipole interactions. However, the reasons for differences in the solvatochromism of the mono- and dinuclear species remain unclear. Clearly, more detailed studies, employing larger numbers of solvents and related series of bridging ligands, are necessary before the subtleties of the solvatochromism of these species can be properly understood.

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Binuclear Bis(μ-oxo)dimanganese(III,IV) and -(IV,IV) Complexes with *N,N'*-Bis(2-pyridylmethyl)-1,2-ethanediamine

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The magnetic susceptibility, EPR and visible spectra, and electrochemical properties of the mixed-valence complex [(bispicen)MnO$_2$Mn(bispicen)](ClO$_4$)$_3$ [bispicen = *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine, C$_{14}$H$_{18}$N$_4$] are reported. The complex has a doublet ground state with $J = -140 \pm 1$ cm^{-1}; the EPR spectrum shows a 16-line pattern. The complex exhibits quasi-reversible waves at 191 and 798 mV (vs Ag/AgCl), corresponding to the III/III $\leftrightarrow$ III/IV and III/IV $\leftrightarrow$ IV/IV couples, respectively. The IV/IV complex [(bispicen)MnO$_2$Mn(bispicen)](ClO$_4$)$_4$·2CH$_3$CN has been synthesized, and its crystal structure has been determined. The complex crystallizes in the monoclinic space group *C*2/*c* with four centrosymmetric binuclear complexes in a cell of dimensions $a = 12.070$ (3) Å, $b = 15.871$ (3) Å, $c = 22.016$ (5) Å, and $\beta = 97.46$ (2)°. The structure has been refined to a final value of $R = 0.040$ based on 3078 independent intensities gathered at −100 °C. The Mn-Mn separation is 2.672 (1) Å, and the Mn-O-Mn bridging angle is 95.0 (2)°. The magnetic properties of the dimer are consistent with a singlet ground state, and $J = -125.6 \pm 0.2$ cm^{-1}. The electronic spectrum is in some ways similar to that of the III/IV complex, but there is no intervalence charge-transfer band.

Introduction

There is continuing interest in the bis(μ-oxo)dimanganese complexes, both because of the similarity of some of their physical properties to those of the water-oxidizing enzyme in photosystem II[2] and because of their inherent potential to act as redox catalysts. Gref et al.[3] have shown that the mixed-valent 2,2'-bipyridine complex $[(bpy)_2MnO_2Mn(bpy)_2]^{3+}$ and its 1,10-phenanthroline (phen) analogue serve as electrocatalytic oxidants for alcohols and ethers, and Ramaraj et al.[4] have reported that the bpy complex oxidizes water in the presence of a chemical oxidant. As a result of this work, and some preliminary results of our own,[5,6] we have undertaken a comprehensive synthetic program designed to produce bis(μ-oxo)dimanganese species whose electrochemical properties may permit their use as redox catalysts.

In order to stabilize the manganese(III) species that are formed during the presumed catalytic cycles, we have focused our attention on complexes formed with tetradentate ligands. We have provided brief preliminary accounts of the synthesis of the mixed-valent manganese(III,IV) species formed from the ligands *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen)[5] and tris(2-pyridylmethyl)amine (tmpa),[6] and Suzuki et al. have subsequently described the oxidized manganese(IV,IV) form of the latter complex.[7] Other workers have structurally characterized the mixed-valent forms of the bpy[8] and phen[9] complexes and more recently the tris(2-aminoethyl)amine (tren),[10] 1,4,7,10-tetraaza-

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