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OFFICE OF NAVAL RESEARCH

Contract N00014-84-G-0201

Task No. 0051-865

Technical Report #26

Solvatochromism of Dinuclear Complexes: An Alternative Explanation

By

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in

Inorganic Chemistry

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89 11 02 075

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY Unclassified			3 DISTRIBUTION/AVAILABILITY OF REPORT As it appears on the report		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Report #26			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
6a NAME OF PERFORMING ORGANIZATION A.B.P. Lever, York University Chemistry Department		6b OFFICE SYMBOL (if applicable)	7a NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c ADDRESS (City, State, and ZIP Code) 4700 Keele St., North York, Ontario M3J 1P3 Canada		7b ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217 U.S.A.			
8a NAME OF FUNDING/SPONSORING ORGANIZATION		8b OFFICE SYMBOL (if applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-G-0201		
8c ADDRESS (City, State, and ZIP Code)		10 SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO
11 TITLE (Include Security Classification) Solvatochromism of Dinuclear Complexes: An Alternative Explanation					
12 PERSONAL AUTHOR(S) E.S. Dodsworth* and A.B.P. Lever					
13a TYPE OF REPORT Technical		13b TIME COVERED FROM Aug. 89 TO Aug. 90		14 DATE OF REPORT (Year, Month, Day) October 20, 1989	
15 PAGE COUNT 22					
16 SUPPLEMENTARY NOTATION					
17 COSAT CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Solvatochromism, Dinuclear Complexes		
FIELD	GROUP	SUB-GROUP			
19 ABSTRACT (Continue on reverse if necessary and identify by block number) The very large solvatochromism of the metal to ligand charge transfer transitions in various, formally non-polar, ligand-bridged dinuclear metal carbonyl complexes is discussed. The similarity of this behaviour 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 which have attributed the solvatochromism to changes in dispersion forces. It is concluded that, in the simplest approximation, the molecules may be regarded as two 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.					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified/unlimited		
22a NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert K. Grasselli			22b TELEPHONE (Include Area Code)		22c OFFICE SYMBOL

Contribution from the Department of Chemistry
York University, North York, Ontario, Canada, M3J 1P3.

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 non-polar, ligand-bridged dinuclear metal carbonyl complexes is discussed. The similarity of this behaviour 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 which have attributed the solvatochromism to changes in dispersion forces. It is concluded that, in the simplest approximation, the molecules may be regarded as two 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.

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INDEXED	☐
FILED	☐
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FBI - NEW YORK	
RECEIVED	
MAR 1 1990	
FBI - NEW YORK	
A-1	

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 which 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 $M(CO)_4(\text{diimine})$ complexes where M is Cr, Mo or W.¹⁻²⁰ The solvatochromic transition involves metal to ligand charge transfer (MLCT) from the d^4 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 solvents compared to non-polar (referred to as negative solvatochromism).^{1,2}

The strong solvatochromism of the mononuclear $M(CO)_4(\text{diimine})$ complexes is normally attributed to 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 non-polar 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 pentacarbonyl-metal groups linked by a bridging N-donor (aromatic) ligand, such as 2,2'-bipyrimidine (bpm) or pyrazine (pyz).^{3,5,11-13,16,20,22-24} 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 comparable magnitude 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 who attribute the solvatochromism to differences in the polarizability of the molecule between the ground and excited states,^{11,12,23,24} 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 two polar halves, as has been (briefly) suggested by Stufkens²² and Haga.²⁴

Theory

The various contributions to the solvatochromism can be described 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 (neglecting the quadratic Stark effect term):²⁷

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

Δv 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 :

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

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

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 using Bayliss' expression³⁴ (use of McRae's expression requires knowledge of both ground and excited state transition energies which are difficult to evaluate); it is relatively small ($\sim 100 \text{ cm}^{-1}$) and varies very little between solvents. Thus it can be neglected for highly polar solutes, such as $\text{Mo(CO)}_4(\text{diimine})$, where the solvatochromism is large. The magnitudes of μ_g and μ_e can then, in principle, be obtained from a two-parameter fit to equation (1).

In the situation where both ground and excited state are non-polar, 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, the excited state is localized on one metal of the dinuclear complex, so that there is 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:

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

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' 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.²³

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.²⁴

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' 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 to 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_0 in the range of 8-10 Debye.³⁴ 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 which involves (3) and therefore should be zero when μ_0 is zero.

iv) Lees has shown, for $(CO)_5WpyzW(CO)_5$ in "select" solvents (aprotic, non-aromatic, non-chlorinated⁴⁰), that a good correlation ($R = 0.96$) is obtained between the MLCT energy and $(D_0 - 1)/(2D_0 + 1)$,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.

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_{op} function alone. The equation obtained (in cm^{-1}) is:

$$\nu_{max} = 15100(\pm 330) + 16300(\pm 6900)(D_{op}-1)/(2D_{op}+1) + \\ 5610(\pm 420)[(D_{op}-1)/(D_{op}+2) - (D_{op}-1)/(D_{op}+2)] \quad (5)$$

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 non-polar 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 behaviour is clearly

very different from that of the dinuclear complexes under discussion here.

Discussion

The evidence above clearly indicates that these formally non-polar 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 behaviour of the dinuclear species can be found in McRae's original paper²⁷ "if either the solvent or solute molecule is non-polar but contains highly polar groups whose moments cancel, it is not realistic to put the time-average of the field E^u equal to zero" (E^u is the field at the solute dipoles due to the permanent dipoles of the surrounding 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 two 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).

(1a)

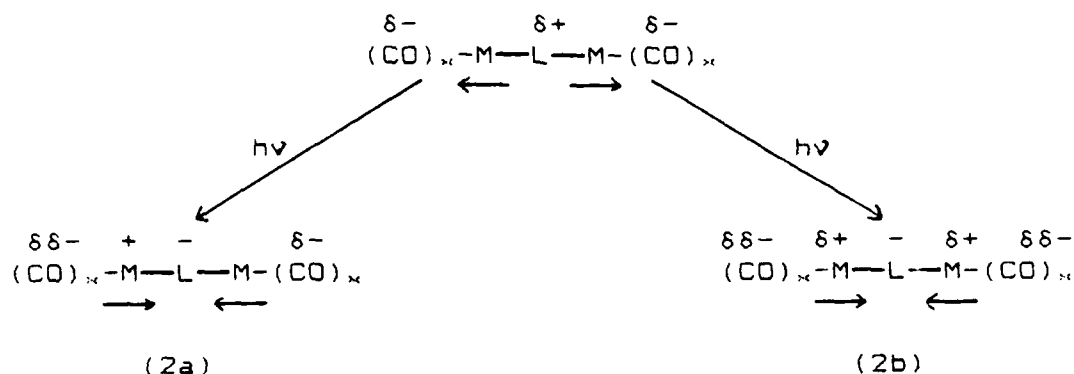
(1b)

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

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,^{12,29} 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 non-planar 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 dinuclears 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 $(\text{CO})_5\text{WpyzW}(\text{CO})_5$ the excited state is related to the ground state of the mixed-valence Creutz-Taube ion, $[(\text{NH}_3)_5\text{RupyzRu}(\text{NH}_3)_5]^{3+}$; the former can be written as $\text{W}(\text{d}^6)(\text{pyz}^-)\text{W}(\text{d}^5)$ and the latter $\text{Ru}(\text{d}^6)(\text{pyz})\text{Ru}(\text{d}^5)$. 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, $\mu(h)_0$, of both halves of the molecule. In the ground state the two halves have equal and opposite dipole moments which both interact with the solvent. In the excited state the two halves are different; the half from which the electron was excited will have a small dipole moment, $\mu(h^*)_0$, which may be in the opposite direction to that in the ground state. The dipole moment, $\mu(i)_0$, 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.

The delocalized case (2b) is easier to treat using 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:

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

where $\mu(h)_g$ and $\mu(h)'_g$ 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 $(\text{CO})_2\text{WpyzW}(\text{CO})_2$

The results of the fit to McRae's expression for $(\text{CO})_2\text{WpyzW}(\text{CO})_2$ (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_{00} 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.²⁵ 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 delocalised 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. This should cause an increase in outer sphere (i.e. solvent) reorganization energy, which is synonymous with an increase in solvatochromism. The average arrangement of solvent molecules will also differ from that in the mononuclear 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 (1). Tom Dieck has demonstrated the effect of decreasing the difference between μ_0 and μ_{π} , by increasing the amount of mixing of the metal and diimine ligand orbitals, in an extensive series of $\text{Mo(CO)}_4(\text{diimine})$ 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 $(\text{CO})_5\text{WpyzW(CO)}_5$ being much greater than that of its PBu_3 -substituted analogue (Table 1).

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.^{13,20,24,31,32}

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

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properly understood.

Acknowledgement

We are grateful to the Office of Naval Research (Washington) for support of this work.

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

Bridging Ligand ^a	Metal core	Slope, F, (R) ^b		Number of solvents ^c	Ref.
		Mononuclear	Dinuclear		
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
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

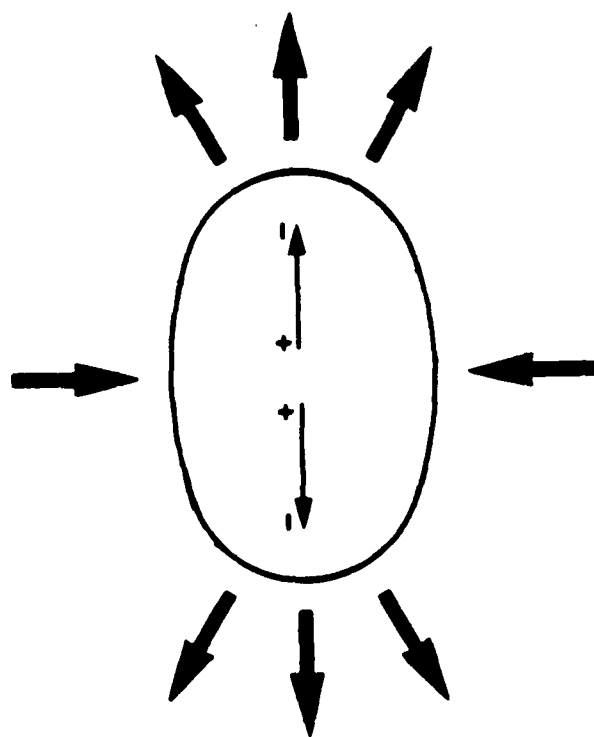
a) bpm = 2,2'-bipyrimidine; abpy = 2-(2'-pyridylazo)pyridine; bptz = 2,5-bis(2'-pyridyl)tetrazine; 2,3-bpp = 2,3-bis(2'-pyridyl)pyrazine; 2,5-bpp = 2,5-bis(2'-pyridyl)pyrazine; pyz = pyrazine; quin = quinoxaline; bod = 2,1,3-benzoxadiazole; bpy = 2,2'-bipyridine.

b) Slope (cm⁻¹) of plot of lowest MLCT band energy vs E*_{MLCT} parameter.⁴
Correlation coefficient, R, in parentheses.

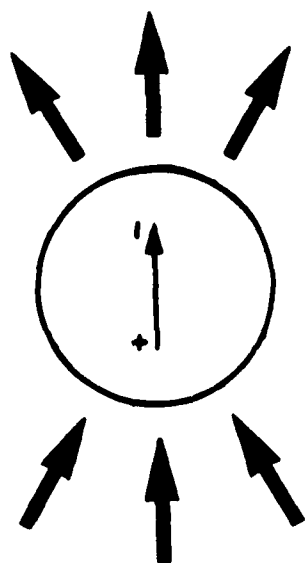
- c) Solvents used were DMF, acetone, THF, toluene and isooctane - see original literature. All are select solvents except for toluene.
 - d) Using other methods to evaluate the solvatochromism and more solvents, this band appears less solvatochromic than its mononuclear analogue.³⁹
 - e) A very large 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.³⁹
 - f) Data for 4 solvents used for dinuclear complex.
 - g) Difference between band energies in THF and toluene.
 - h) Corresponding slope for second MLCT transition.
 - i) Solvents as in Figure 1.
- tw = this work, calculated from data in ref. 11.

Figure Legend**Figure 1**

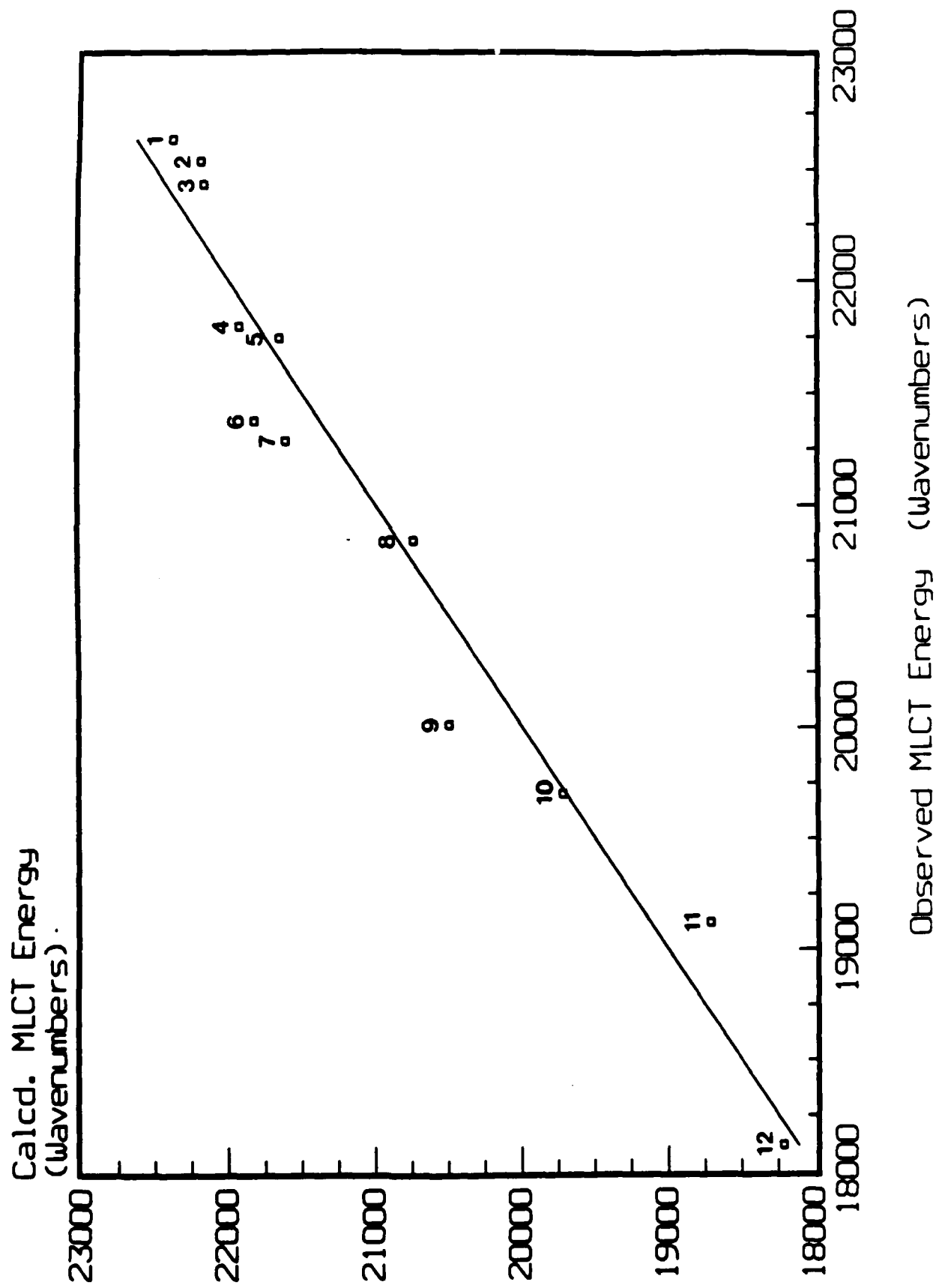
Plot of calculated vs observed MLCT energy for $(CO)_5WpyzW(CO)_5$. Values were calculated using equation 5. Data are taken from reference 11. 1 - dimethylsulphoxide; 2 - dimethylacetamide; 3 - dimethylformamide; 4 - acetonitrile; 5 - acetone; 6 - cyclohexanone; 7 - 3-pentanone; 8 - tetrahydrofuran; 9 - piperidine; 10 - diethyl ether; 11 - triethylamine; 12 - isooctane.



(1b)



(1a)



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