Intramolecular Charge-transfer Spectra of Compounds *cis*-$M(LL)_2(L')_2$ and $M(LL)(L')_4$ in Single and Mixed Solvents

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The solvent variation of the wavenumbers of maximum absorption for intramolecular charge-transfer spectra of a variety of complexes *cis*-$Fe(LL)_2(CN)_2$ and $M(LL)(CO)_4$ (M = Mo or W: LL = bidentate nitrogen ligand) in several series of mixed solvents is described.

IT has been known for many years that the wavelengths of maximum absorption for intramolecular charge-transfer bands of some mixed bidentate (LL) and monodentate (L′) transition-metal complexes of the type *cis*-$M(LL)_2(L')_2$, for example *cis*-$Fe(bipy)_2(CN)_2$, are markedly solvent-sensitive.[1] The phenomenon has been described for several complexes of this type, *e.g.* *cis*-$Fe(phen)_2(CN)_2$ and several substituted derivatives,[2] related anionic and cationic species $[Fe(bipy)(CN)_4]^{2-}$ and *cis*-$[Fe(phen)_2(CN)_2]^+$,[3] and the organometallic analogues $Mo(bipy)(CO)_4$ [4] and Mo(diazabutadienes)-$(CO)_4$.[5,6] In these investigations measurements have generally been restricted to solutions in single solvents; previous reports of solvent effects on charge-transfer spectra of this type of compound in mixed solvents have included those of dimethylformamide–benzene solutions of $Mo(diazabutadiene)(CO)_4$ and Mo(oxa-azabutadiene)-$(CO)_4$,[6] and t-butyl alcohol–water solutions of $Fe(bipy)_2$-$(CN)_2$.[2] The main object of the present paper is the extension of this work to solutions in a variety of mixed solvents and in aqueous solutions of tetra-alkylammonium salts. Solutes concerned include the $Mo(LL)(CO)_4$ series [LL = 1,10-phenanthroline(phen) or 2,2′-bipyridine(bipy)], the tungsten analogue $W(bipy)(CO)_4$, and the iron(II) complexes $Fe(LL)_2(CN)_2$ [LL = bipy,phen, 4,7-dimethyl-1,10-phenanthroline and 3,4-dimethyl-(2-pyridylmethylene)aniline (SB)]. The choice of solute in a particular set of solvent mixtures was often dictated by solubility considerations.

RESULTS AND DISCUSSION

Experimental results are listed in Supplementary Publication No. SUP 20441 (7 pp., 1 microfiche).*

In illustrating what may be regarded as ' normal ' behaviour for these compounds in mixed solvents it is advisable to avoid solvent mixtures containing water as one component. Figure 1 shows the variation of wavenumbers of maximum absorption for the lowest-energy charge-transfer bands for two compounds in solvent mixtures consisting of one solvent of good solvating properties and one of poor solvating properties, specifically $Fe(bipy)_2(CN)_2$ in methanol–chloroform and Mo-$(bipy)(CO)_4$ in ethanol–benzene. The curved dependence of $\bar{\nu}_{max.}$ on solvent mole-fraction composition is consistent with considerable selectivity of solvation of the solute by the more strongly solvating component. The Figure also shows results for $W(bipy)(CO)_4$ in mixtures of methanol and the similar, though somewhat less well solvating, solvent n-butyl alcohol. Here the dependence of $\bar{\nu}_{max.}$ on solvent composition (mole fraction) is practically linear.

The dependence of $\bar{\nu}_{max.}$ on solvent composition for mixed aqueous solvents is slightly different; the system $Fe(LL)_2(CN)_2$ (LL = 4,7-dimethyl-1,10-phenanthroline) in aqueous acetone (Figure 2) is typical. The $\bar{\nu}_{max.}$ against mole-fraction curve shows a point of inflection. In organic-rich solvents this curve is similar to that for mixed organic-solvent systems, but in water-rich solvent

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[1] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, 1956, **10**, 329.

[2] J. Burgess, *Spectrochim. Acta*, 1970, **26***A*, 1369.

[3] J. Burgess, *Spectrochim. Acta*, 1970, **26***A*, 1957.

[4] J. Burgess, *J. Organometallic Chem.*, 1969, **19**, 218.

[5] H. Bock and H. tom Dieck, *Angew. Chem. Internat. Edn.*, 1966, **5**, 520; *Chem. Ber.*, 1967, **100**, 228.

[6] H. tom Dieck and I. W. Renk, *Angew. Chem. Internat. Edn.*, 1970, **9**, 793.

mixtures there is an unexpectedly rapid shift of $\bar{\nu}_{max.}$ to lower wavenumbers as the mole fraction of the organic co-solvent increases from zero. It is interesting that the size of this effect is very similar for a variety of co-solvents (Figure 3). The inflected curves of Figures 2 and 3 are typical of, but not unique to, mixed aqueous solvents, for the variation of $\bar{\nu}_{max.}$ with solvent composition for Mo(phen)(CO)$_4$ in dimethyl sulphoxide–chloroform mixtures also shows a similar inflection. The special structural properties of water-rich mixed aqueous solvents must play an important role in determining the shapes of the curves of Figures 2 and 3, but they cannot therefore be the sole factor involved.

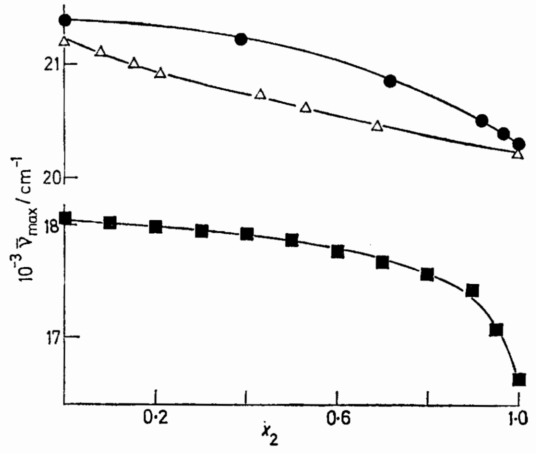

FIGURE 1 Dependence of wavenumbers of maximum absorption $\bar{\nu}_{max.}$ on mole fraction of solvent x_2 for the lowest-energy charge-transfer bands in binary solvent mixtures. (●), Mo(bipy)(CO)$_4$ In ethanol-benzene; (△), W(bipy)(CO)$_4$ in methanol-n-butyl alcohol; (■), Fe(bipy)(CN)$_2$ in methanol–chloroform. For each plot x_2 represents the mole fraction of the last-named of the pair of solvents

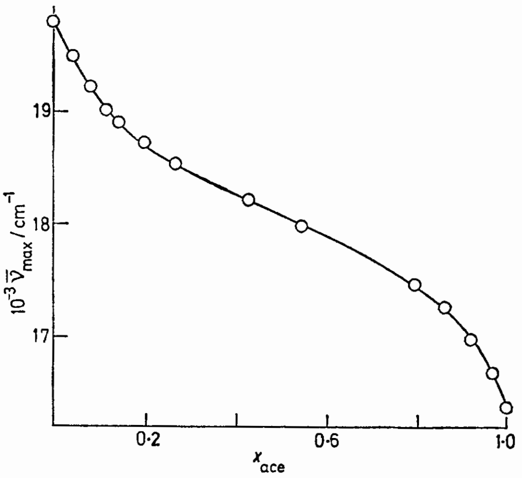

FIGURE 2 Dependence of wavenumbers of maximum absorption $\bar{\nu}_{max.}$ on mole fraction of acetone x_{ace} for the lowest-energy charge-transfer band of Fe(LL)$_2$(CN)$_2$ (LL = 4,7-dimethyl-1,10-phenanthroline) in aqueous acetone

Solvent parameters[7] such as the kinetically based *Y* scale of Grunwald and Winstein and spectroscopically based scales of Reichardt (E_T) and Kosower (*Z*) are widely applied to pure solvents, sometimes used for mixed solvents, and very rarely quoted in respect of solutions of salts. Recently *Z* values have been determined for solutions of tetrabutylammonium perchlorate in a range of organic solvents;[8] we have therefore studied the variation of $\bar{\nu}_{max.}$ with solution composition for two of our transition-metal compounds, Fe(bipy)$_2$(CN)$_2$ and Mo(phen)(CO)$_4$, in methylene chloride solutions of tetra-n-butylammonium iodide, to see if the behaviour parallels that reported for Kosower's organic alkylpyridinium iodides. Our results (Table 5 of Supplementary Publication) show that the variation of $\bar{\nu}_{max.}$ with salt concentration is similar for the organic and inorganic substrates in that in both cases a maximum shift is attained by about 0·2—0·3M concentration of the salt. In aqueous solution there is a small shift in $\bar{\nu}_{max.}$ on adding tetra-n-butylammonium iodide. This shift is in the opposite direction to that observed in methylene chloride solutions, but in the same direction as that observed in aqueous alcohol solvent mixtures.

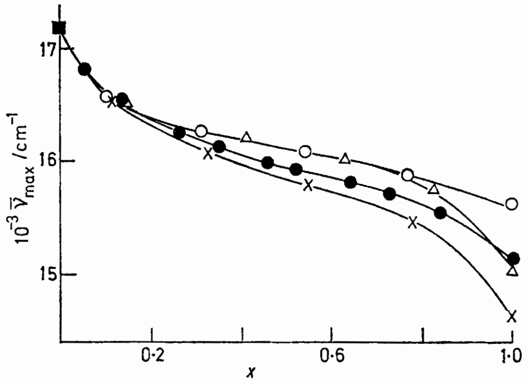

FIGURE 3 Dependence of wavenumbers of maximum absorption ($\bar{\nu}_{max.}$ on mole fraction of the organic component (x) for the lowest-energy charge-transfer band of Fe(SB)$_2$(CN)$_2$ [SB = 3,4-dimethyl-(2-pyridylmethylene)aniline] in aqueous isopropyl alcohol (○), acetonitrile (△), dioxan (●), and acetone (×) mixtures

E_T Values are available for some series of mixed solvents. In Figure 4 $\nu_{max.}$ values for Fe(phen)$_2$(CN)$_2$ are plotted against solvent E_T values for ethanol–, isopropyl-alcohol–, and acetone–water mixtures. In each case the correlation line is curved, with the direction of the deviation from linearity suggesting that Fe(phen)$_2$(CN)$_2$ may have a greater preference for water in its solvation shell than the organic betaine upon whose spectra the E_T scale is based.

The observations reported in this paper reflect the effects of the solvent mixtures on the charge-transfer spectra of the complexes. These solvation effects presumably reflect changes in the primary solvation shell of the complexes, which in turn will be affected by the extent and nature of interactions between the solvents.

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[7] These and other solvent parameters have been reviewed by C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

[8] M. Mohammad and E. M. Kosower, *J. Phys. Chem.*, 1970, **74**, 1153.

There have been many experimental approaches to the investigation of solvation of solutes in mixed solvents.

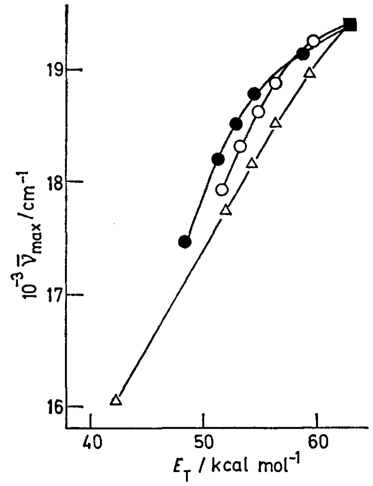

FIGURE 4 Correlation of wavenumbers of maximum absorption $\tilde{\nu}_{max.}$ with solvent E_T values for the lowest-energy charge-transfer band of $Fe(phen)_2(CN)_2$ for mixed aqueous ethanol (○), isopropyl alcohol (●), and acetone (△) solvents

Both n.m.r.[9] and visible–ultraviolet [10] spectroscopy have proved particularly useful; in the particular case of the $[Cr(NCS)_6]^{3-}$ anion in aqueous acetonitrile, these two techniques have led to the same conclusions concerning the composition of the primary solvation shell.[11] The variation of visible absorption spectra with solvent composition for solutions of Lifschitz salts [bis(stilbenediamine)nickel(II) salts] in mixed solvents has proved useful as a probe of solvent structure.[12] The solvent shifts of the charge-transfer bands of *cis*-$M(LL)_2(L')_2$ and of $M(LL)(L')_4$ reported in our present paper may yield information on the composition of the primary solvation shell around these species and/or structural features of mixed solvents, but insufficient information is available at present to disentangle these two different but related effects.

EXPERIMENTAL

The compounds $M(LL)_2(L')_2$ and $M(LL)(L')_4$ used were from batches prepared and characterised previously.[2-4] Visible–ultraviolet spectra were run on a Unicam SP 800A recording spectrophotometer whose wavelength calibration was periodically checked against standard holmium and didymium glass filters.

We thank the Royal Society for the award of a grant for the purchase of the SP 800A spectrophotometer.

[1/1829 *Received, 7th October,* 1971]

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[9] See, for example, L. S. Frankel, C. H. Langford, and T. R. Stengle, *J. Phys. Chem.*, 1970, **74**, 1376 for a detailed discussion of the compounds $Co(acac)_3$ and $Cr(acac)_3$, V. S. Sastri and C. H. Langford, *ibid.*, p. 3945 for $Cr(oxalate)_3^{3-}$, and J. Burgess and M. C. R. Symons, *Quart. Rev.*, 1968, **22**, 276 for references to several illustrative examples.

[10] For example, J. Midwinter and P. Suppan, *Spectrochim. Acta*, 1969, **25***A*, 953.

[11] S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, 1969, **91**, 2236.

[12] R. D. Gillard and H. M. Sutton, *J. Chem. Soc.* (*A*), 1970, 1309, 2172, 2175.