Solvatochromism and Solvation of Water-soluble Molybdenum(0)–Tetracarbonyl–Diimine Complexes

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(Received October 7, 1987)

Abstract

Solvatochromic behaviour is described for the water-soluble molybdenum(0)–carbonyl–diimine complexes $[Mo(CO)_4(LL)]^{n-}$, where LL = fz (ferrozine; 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p'*-disulphonate) and $n = 2$ or LL = sb (Schiff base from 2-acetyl pyridine plus β-alanine) and $n = 0$, in water and in a range of non-aqueous solvents, and in water–isopropanol solvent mixtures. The possibility of using solvatochromic compounds of this type to probe selective solvation in solvent mixtures is assessed, with particular reference to water–isopropanol and acetone–chloroform mixtures, and to microemulsions.

Introduction

Since the first reports of the marked solvatochromism of $Mo(CO)_4(bipy)$, bipy = 2,2'-bipyridyl (1) and related complexes [1], there have been numerous investigations of the dependence of this solvatochromism behaviour on the nature of the metal M and the diimine ligand LL in a series of complexes $M(CO)_4(LL)$ [2]. The metals M are chromium, molybdenum, and tungsten, while the ligands LL have included a number of 2,2'-bipyridyl and 1,10-phenanthroline derivatives, pyridylalkyl-imines (2), and diazabutadienes (3). As the great majority of these complexes are extremely sparingly soluble in water, descriptions of their solvatochromic behaviour are perforce restricted to non-aqueous media. This situation contrasts with that for, e.g. $Fe(bipy)_2(CN)_2$, whose solubility in water, though low, is sufficient for its solvatochromic behaviour to have been established in water and binary aqueous solvent media [3, 4]. The presence of strongly hydrophilic substituents on diimine ligands greatly enhances water solubility of their complexes and indeed themselves. The sulphonato-substituted ligand

3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p'*-disulphonate (trivial name 'ferrozine', abbreviations ppsa or fz, formula 4) gives the complex $[Mo(CO)_4(fz)]^{2-}$, which is sufficiently water-soluble for high pressure kinetic studies of its reaction with cyanide to have proved possible in aqueous solution [5]. In this paper we describe the solvatochromic behaviour of this complex in aqueous, mixed aqueous, and non-aqueous media. We also report the preparation, characterisation, and solvatochromism in a similar range of solvent media of a complex $Mo(CO)_4(LL)$ in which LL is a Schiff base of type 2 derived from 2-acetyl pyridine and β-alanine (5, abbreviation sb). This species is closely related to other ternary complexes with amino acid based Schiff base ligands reported recently, e.g. those derived from pyridine 2-aldehyde and histamine or β-alanine (in ternary copper(II)–azide species) and from 2,6-diacetyl-pyridine and histidine (iron(II) derivatives) [6]. We also examine the possible role of solvatochromism as a probe for solvation of complexes of this type in mixed solvents.
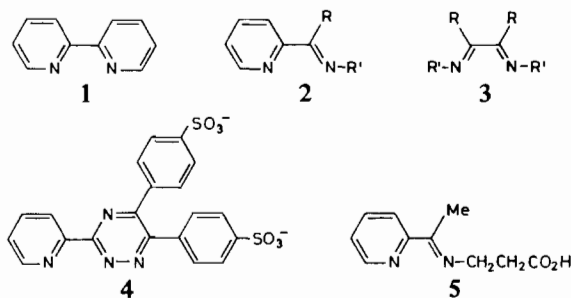
Experimental

The ferrozine complex was prepared as previously [5] and isolated as its sodium salt $Na_2[Mo(CO)_4(fz)] \cdot nH_2O$. The hygroscopic nature of this material prevented assignment of a value for n. The Schiff base complex was generated by refluxing *cis*-$Mo(CO)_4(piperidine)_2$ [7] with stoichiometric quantities of 2-acetyl pyridine and β-alanine in isopropanol for a few minutes. It was isolated in the acid form as an oily hygroscopic solid. This material

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was used for the preparation of the solutions used for spectrophotometry; its nature was confirmed through precipitation and characterisation (CHN analysis) of its potassium salt.

Spectra were run on a Unicam SP8-100 or Hewlett-Packard HP8451A spectrophotometer, in 1 cm cells in the respective cell compartments, in all cases thermostatted at 298 K.

Results and Discussion

It is usual to compare the solvatochromism of inorganic complexes with that of Reichardt's betaine, the substrate for the E_T scale of solvent polarity [8]. Table I lists wavenumbers of maximum absorption for the lowest energy metal to ligand charge-transfer (MLCT) band* of the two complexes in a selection of solvents, ordered according to their E_T values. Figure 1 shows a plot of ν_{max}(MLCT) against E_T for the ferrozine complex. As for $Mo(CO)_4$(bipy), the parent complex of this type, solvents can be grouped into two types—hydroxylic (water, alcohols) and the rest. For the former group, there is a good ν/E_T correlation. The points for the latter, non-hydroxylic, group of solvents form a small cluster. Unfortunately the properties which confer water solubility almost inevitably confer insolubility in certain types of organic solvents, and it is not

TABLE I. Frequencies of Maximum Absorption for the Lowest Energy MLCT Band for $(Mo(CO)_4(fz)^{2-}$ and $Mo(CO)_4(sb)$

Solvent	E_T	ν_{max}	
		$Mo(CO)_4(fz)^{2-}$	$Mo(CO)_4(sb)$
Water	63.1	19230	22220
Methanol	55.5	18450	20960
Ethanol	51.9	17950	20450
n-Butanol	50.2	17910	20120
i-Propanol	48.6	17750	20280
Nitromethane	46.3	19160	22120
Acetonitrile	46.0	19340	21740
DMSO	45.0	19860	22080
DMF	43.8	19610	21930
Acetone	42.2	19120	21280
Dichloromethane	41.1	17640	20590
Chloroform	39.1	17330	20080
Ethyl acetate	38.1		
Diethyl ether	34.6		
Toluene	33.9	insoluble	insoluble
Carbon tetrachloride	32.5		
n-Hexane	30.9		

*The next higher energy absorption band, at about 380–390 nm, shows very little solvatochromism, and is probably $\pi \to \pi^*$ rather than MLCT in nature.
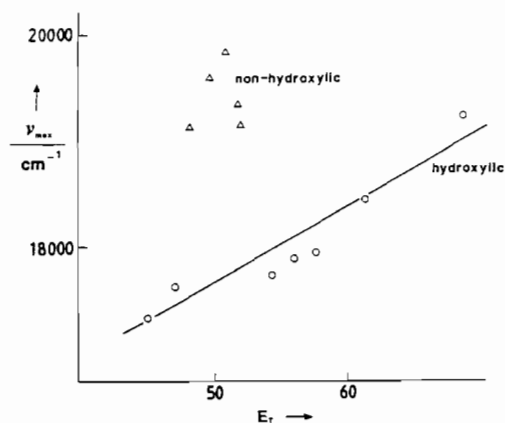

Fig. 1. Plot of ν_{max}(MLCT) for $Mo(CO)_4(fz)^{2-}$ against solvent E_T values.

possible to obtain ν_{max} for these water-soluble molybdenum–carbonyl–diimine complexes in solvents with low E_T values. A ν_{max}(MLCT) versus E_T plot for the Schiff base complex would look entirely analogous to Fig. 1.

The solvatochromic behaviour of these two complexes can conveniently be compared with that of $Mo(CO)_4$(bipy) by plotting $\nu_{max}\{Mo(CO)_4(LL)\}$ against $\nu_{max}\{Mo(CO)_4$(bipy)$\}$. It has recently been shown [9] that the slopes of such plots are in the range 0.4 to 0.8 for LL = a diazabutadiene ligand (3), 0.88 to 1.06 for pyridyl Schiff base of type 2, and 1.0 or above for bipyridyl and phenanthroline derivatives. Figure 2 shows the correlation of ν_{max}-$\{Mo(CO)_4(fz)]^{2-}\}$ with $\nu_{max}\{Mo(CO)_4$(bipy)$\}$; the slope of this plot ('solvent sensitivity') is 1.06 ± 0.09, which falls within the range for bipyridyl-type ligands. For the $Mo(CO)_4$ complex with Schiff base (5), the solvent sensitivity is 0.98 ± 0.05, within the range for derivatives containing diimines of type 2.
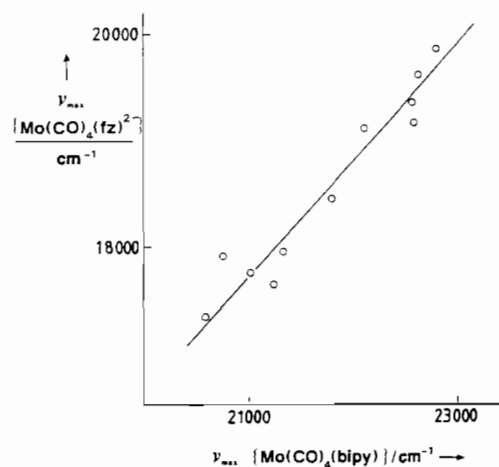

Fig. 2. Correlation of ν_{max}(MLCT) for $Mo(CO)_4(fz)^{2-}$ and $Mo(CO)_4$(bipy).

The variation of ν_{max} with composition in binary solvent systems should provide an indicator of preferential solvation. The more curved such a plot, the more strongly preferential is the solvation. This could be a useful approach for charged complexes (though its application would be severely limited by the very small number of complexes that display marked solvatochromism), since the use of transfer chemical potentials as a probe for selective solvation of ions is complicated by the need for extrathermodynamic single ion assumptions [10]. Solvatochromism is a 'single ion' parameter, like NMR or ESR, for example, but unlike thermodynamic parameters, ionic conductances, and other such properties which can only be measured in pairs, *i.e.* for whole salts. The variation in ν_{max}(MLCT) for $[Mo(CO)_4(fz)]^{2-}$ in isopropanol–water mixtures is reported in Table II, and depicted in Fig. 3. Figure

TABLE II. Frequencies of Maximum Absorption for the Lowest Energy MLCT Bands of $Mo(CO)_4(fz)^{2-}$ in Water–Isopropanol Mixtures

Isopropanol		0	20	40	60	80	90	100
	vol.%	0	20	40	60	80	90	100
	mole fraction		0.056	0.136	0.262	0.486	0.681	1
ν_{max}(MLCT) (cm^{-1})		19230	18520	18350	18210	18000	17910	17750

(a)

(b)
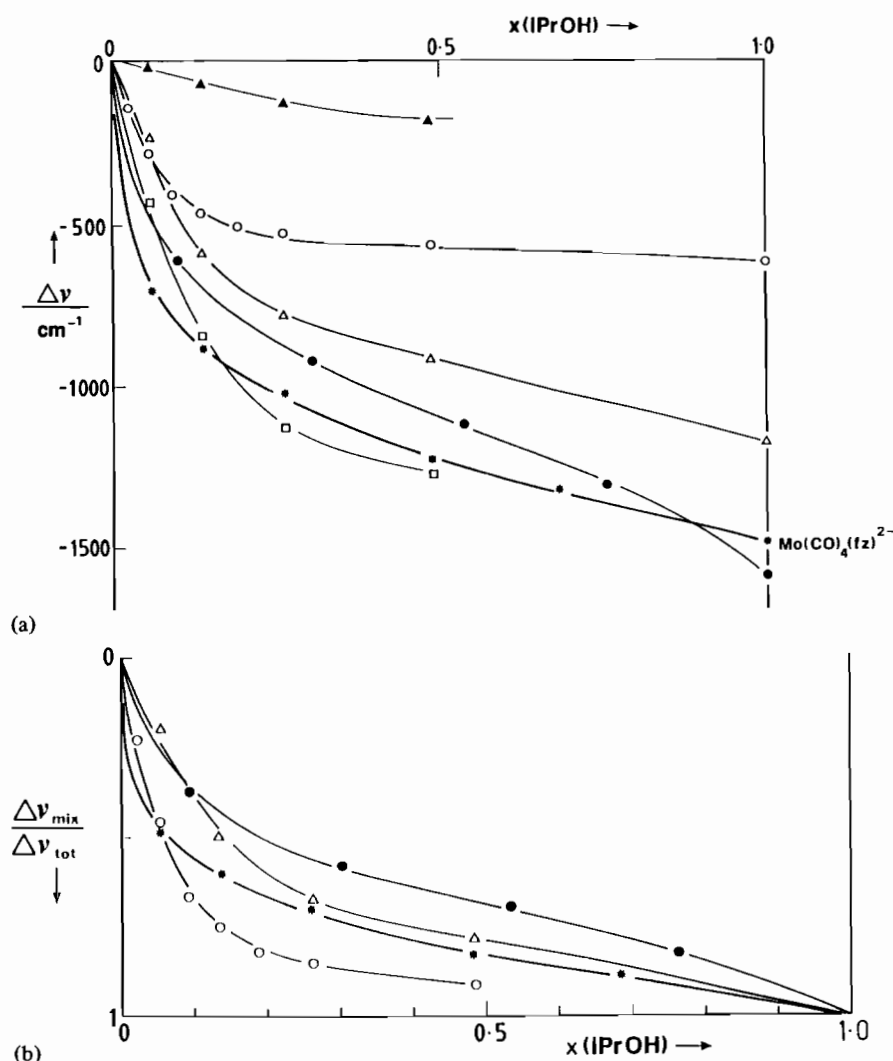
Fig. 3. (a) Dependence of solvatochromic shift on mole fraction of isopropanol for: ▲, *trans*-$[Co(cyclam)(NCS)_2]^+$; ○, $[Fe(CN)_5$-$(NMepz)]^{2-}$; △, $[Fe(hxsb)(CN)_3]^-$; ●, $[Fe(bsb)_2(CN)_2]$; *, $[Mo(CO)_4(fz)]^{2-}$; □, $[Fe(CN)_5(4CNpy)]^{3-}$; all shifts relative to aqueous solution. (b) Data from (a) normalised as described in the text.

3 also includes ν_{max} trends for other ternary inorganic complexes, including $Fe(LL)_2(CN)_2$ where LL = the Schiff base ligand (**6**, bsb) [4], [Fe(LLL)-(CN)$_3$]$^-$ where LLL is the potentially hexadentate ligand (**7**, hxsb) behaving as terdentate [11], the pentacyanoferrates(II) [Fe(CN)$_5$L]$^{n-}$ with L = 4-cyanopyridine [11] or *N*-methylpyrazinium (**8**) [12], and the *trans*-[Co(cyclam)(NCS)$_2$]$^+$ cation [11].

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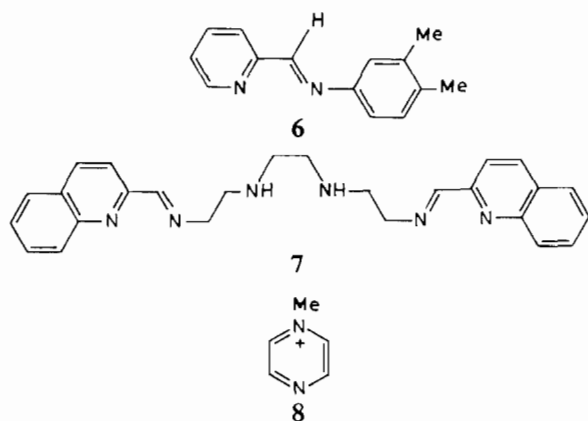
In all cases the direction of curvature indicates preferential solvation by the isopropanol. As the periphery of each compound is predominantly hydrophobic, this is not unreasonable. It is easier to assess preferential solvation in plots of the type shown as Fig. 3b, where the y scale has been normalised $(\Delta\nu_{mix}/\Delta\nu_{tot} = (\nu_{water} - \nu_{mixture})/(\nu_{water} - \nu_{iPrOH}))$, than Fig. 3a, where frequency shifts have been plotted directly. Of course the Fig. 3b type of plot can only be used if data are available for both of the pure solvents as well as solvent mixtures. Differences between the plots in Fig. 3b are hardly dramatic, presumably because a certain balance between hydrophobicity and hydrophilicity is required in order to have sufficient solubility both in water and in isopropanol. However the relative degrees of curvature suggest that the preferences of the various ternary complexes for isopropanol become less marked in the order
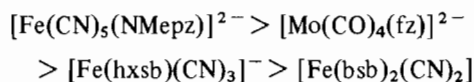
$$[Fe(CN)_5(NMepz)]^{2-} > [Mo(CO)_4(fz)]^{2-}$$
$$> [Fe(hxsb)(CN)_3]^- > [Fe(bsb)_2(CN)_2]$$

Fig. 4. Plot of $\nu_{max}\{[Mo(CO)_4(fz)]^{2-}\}$ vs. $\nu_{max}\{Mo(CO)_4$-(bipy)$\}$ in acetone–chloroform mixtures.

which is not quite the order expected. The fact that the curves intersect in some cases suggests that the selective solvation situation is not entirely straightforward.

The preferential solvation just discussed in isopropanol–water solvent mixtures can be contrasted with almost statistical solvation in acetone–chloroform mixtures (Table III). Table III suggests only slightly curved plots for ν_{max}(MLCT) *versus* mole fraction composition, both for the [Mo(CO)$_4$(fz)]$^{2-}$ anion and for Mo(CO)$_4$(bipy). Perhaps a very slight preference for the acetone could be discerned. A plot of $\nu_{max}\{[Mo(CO)_4(fz)]^{2-}\}$ *versus* $\nu_{max}\{Mo-(CO)_4(bipy)\}$ for this series of solvent mixtures is linear (Fig. 4), suggesting no significant difference in solvation characteristics for these two complexes in this system.

We recently tried to probe the environment of Mo(CO)$_4$(LL) complexes in oil/water microemulsions through solvatochromism [13]. This approach was gravely hampered by the lack of ν_{max} values for these complexes in aqueous solution. We have therefore measured ν_{max} for the [Mo(CO)$_4$(fz)]$^{2-}$ anion in the microemulsions previously studied (Table IV). Comparison with data in Table I shows immediately that ν_{max} values in the microemulsions are very different from ν_{max} in water. Indeed in microemulsion I, ν_{max} is approximately the same as in isopropanol. The molybdenum compound is probably in the non-aqueous regions, strongly

TABLE III. Frequencies of Maximum Absorption for the Lowest Energy MLCT Bands for $Mo(CO)_4(fz)^{2-}$ and $Mo(CO)_4(bipy)$ in Acetone–Chloroform Mixtures

				30	60	80	90	100
Chloroform	vol.%		0	30	60	80	90	100
	mole fraction			0.281	0.578	0.785	0.892	1
ν_{max} (cm^{-1})	$Mo(CO)_4(fz)^{2-}$		19120	18800	18200	17860	17640	17330
	$Mo(CO)_4(bipy)$		22080	21760	21320	21100	20770	20580

TABLE IV. Frequencies of Maximum Absorption for the Lowest Energy MLCT Band of $Mo(CO)_4(fz)^{2-}$ in Microemulsions of Stated Composition

Microemulsion		I		II	
Composition (wt%)		isopropanol n-hexane water	42.1 53.7 4.2	n-butanol toluene water SDS[a]	26.1 4.3 56.5 13.1
ν_{max} (cm^{-1})	$Mo(CO)_4(fz)^{2-}$	17990		17730	
	$Mo(CO)_4(phen)^b$	21190		21150	

[a]SDS = sodium dodecylsulphate.   [b]From ref. 13.

preferentially solvated by the isopropanol (it is insoluble in hexane). In microemulsion II ν_{max} is again very similar to ν_{max} in isopropanol or n-butanol, so again presumably the immediate environment of the molybdenum compound is predominantly n-butanol.

Acknowledgements

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