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Piezochromic and Thermochromic Behaviour of Ternary Diimine–Cyanide–Iron(II) and –Iron(III) Complexes

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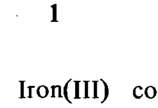
Abstract

Solvent, pressure, and temperature effects on charge-transfer spectra of several iron(II)– and iron(III)–diimine–cyanide complexes are described. The effects for MLCT and LMCT bands are in opposite direction; the solvatochromic, piezochromic, and thermochromic behaviour of the iron(II) complexes parallels that of molybdenum(0)–carbonyl–diimine complexes.

Introduction

It has been known for many years that ternary diimine–cyanide and diimine–carbonyl complexes of t_{2g}^6 transition metal ions exhibit intense charge transfer bands whose maxima are strongly affected by the nature of the solvent [1, 2]. Such solvatochromic behaviour has been described for a large number of iron(II) complexes, such as $Fe(LL)_2(CN)_2$, with LL = bipy or phen [3, 4] or one of a range of diimines of the type shown as **1** [3, 5], and $Fe(LL)(CN)_4^{2-}$ with LL = bipy [3]. Similar behaviour is shown by carbonyl derivatives of the Group VI metals $M(CO)_4(LL)$, with LL = bipy or phen [5–8], and $Mo(CO)_4(LL)$ with LL = **2** with a variety of groups R,R′ [2, 9–11] or btz (**3**) [12]. In all these complexes the charge-transfer band is of MLCT character, and ν_{max} increases as the polar character of the solvent increases.



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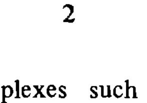

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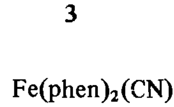

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Iron(III) complexes such as $Fe(phen)_2(CN)_2^+$ also show marked solvatochromism, but the solvent effect now acts in the opposite direction [3]. This opposite solvatochromic effect corresponds to charge-transfer from ligand to metal (LMCT) in these metal(III) complexes.

It has recently been shown that maxima of charge-transfer bands for $Mo(CO)_4(LL)$, with LL = bipy, phen, or dab (**2**; R = Me, R′ = Ph) are affected to a small but significant degree by application of high pressures (up to 2 kbar), or by change in temperature (10 to 70 °C). The pressure and temperature effects on ν_{max} parallel those of solvent variation, with all three medium effects correlated with solvent polarity trends [11]. We have been investigating these pressure, temperature, and medium effects further [13], with particular interest in ascertaining whether the change in direction of charge-transfer, from MLCT in Mo(0) and Fe(II) to LMCT in Fe(III) complexes, reverses the direction of the piezochromic and thermochromic effects in the same way that this change reverses the direction of the solvatochromic effect. In order to be sure that the observed effects could be assigned to change in charge-transfer direction and not simply to change in metal, we investigated the piezochromic and thermochromic behaviour of a selection of iron(II) complexes of the $Fe(LL)_2(CN)_2$ and $Fe(LL)(CN)_4^{2-}$ type. In this paper we report the expected similarities between the iron(II) and molybdenum(0) complexes, and the predicted differences between LMCT iron(III) and MLCT iron(II) and molybdenum(0) complexes.

Experimental

The iron(II) complexes $Fe(bipy)_2(CN)_2$, $Fe(phen)_2(CN)_2$, $Fe(bipy)(CN)_4^{2-}$, and $Fe(phen)(CN)_4^{2-}$ were prepared by Schilt's method [14]; the tetracyano complexes were isolated as their potassium salts. The iron(III) complex $Fe(bipy)_2(CN)_2^+$ was prepared from its iron(II) analogue and isolated as its nitrate, while $Fe(bipy)(CN)_4^-$ was isolated as the so-called acid $H[Fe(bipy)(CN)_4]$

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TABLE I. Piezochromic, Thermochromic, and Solvatochromic Effects

Complex	Solvent	ν_{max} (cm^{-1})	$\partial\nu/\partial p$[a] (cm^{-1}) ($kbar^{-1}$)	$\partial\nu/\delta T$[b] (cm^{-1}) ($kbar^{-1}$)	Solvent sensitivity with reference to	
					$Fe(bipy)_2(CN)_2$[c]	$Mo(CO)_4(bipy)$[d]
Iron(II)						
$Fe(phen)_2(CN)_2$	methanol[e]	18250	+90 ± 40	−30 ± 10	0.89	0.6
$Fe(bipy)_2(CN)_2$	water	19270	+55 ± 20	−20 ± 10	1	0.7
$Fe(phen)(CN)_4^{2-}$	water	21690	+95 ± 55	−80 ± 40	1.55	1.1
$Fe(bipy)(CN)_4^{2-}$	water	20830	+110 ± 25	−85 ± 30	1.49	1.1
Iron(III)						
$Fe(bipy)_2(CN)_2^+$	water	19270	−170 ± 125	+30 ± 45	−0.50	−0.35
$Fe(bipy)(CN)_4^-$	water	19840	−60 ± 50	0	−1.0	−0.7

[a] At 298.2 K. [b] At 1 bar. [c] Slope of ν_{max} (iron complex) *vs.* ν_{max} ($Fe(bipy)_2(CN)_2$). [d] Slope of ν_{max} (iron complex) *vs.* ν_{max} ($Mo(CO)_4(bipy)$), *cf.* text. [e] Compound too sparingly soluble in water.

[14]. All complexes were characterized by the positions and intensities of their charge-transfer bands in at least two solvents. The pressure and temperature dependences of the charge-transfer spectra were monitored using the apparatus and methods developed earlier for the $Mo(CO)_4(LL)$ series of compounds [11].

Results

The iron(II)–diimine–cyanide complexes were stable for at least several weeks in solution, in water or in alcohols, but the iron(III) complexes were much less stable. It proved impossible to obtain satisfactorily reproducible results for $Fe(phen)_2(CN)_2^+$ or for $Fe(phen)(CN)_4^-$, though interesting qualitative indications of pressure effects on solvolysis rates were obtained*. Even for the bipy analogues our results are less precise than those for iron(II) or molybdenum(0) complexes of this type.

Pressure and temperature effects on charge-transfer bands of the iron(II) and iron(III) complexes are reported in Table I. This gives values of $\partial\nu/\partial p$ and $\partial\nu/\partial T$ determined over the ranges 20 to 1500 bar and 15 to 55 °C; the uncertainties quoted are 2σ values. Table I also includes solvent sensitivities, expressed as slopes of plots of ν_{max} for the complex in question against ν_{max} for $Fe(bipy)_2(CN)_2$ and for $Mo(CO)_4(bipy)$. The former solvent sensitivities were obtained by direct correlation using all available points for each compound, but the latter solvent sensitivities had to be estimated by an indirect route. Plots of ν_{max} for $Fe(diimine)_2(CN)_2$ against solvent E_T values [15] give two lines, for protic and for aprotic solvents [3]. The same is true for ν_{max} for $Mo(CO)_4(diimine)$ compounds [7]. However the relation between the two lines is markedly different for the two series of compounds, and it is therefore not surprising that plots of ν_{max} for a compound $Fe(diimine)_2(CN)_2$ against ν_{max} for its $Mo(CO)_4(diimine)$ analogue give separate lines, of different slopes, for protic and for aprotic solvents. In the particular case of diimine = bipy there is an additional problem in that $Fe(bipy)_2(CN)_2$ is extremely sparingly soluble in aprotic solvents of low E_T values. We have therefore had to convert solvent sensitivities with respect to $Fe(bipy)_2(CN)_2$ into solvent sensitivities with respect to $Mo(CO)_4(bipy)$ by multiplying by the slope of ν_{max} ($Fe(bipy)_2(CN)_2$) *versus* ν_{max} ($Mo(CO)_4(bipy)$) in primary alcohols.

The estimation of solvent sensitivies for some of the iron complexes included in Table I required the measurement of wavelengths (wavenumber) of maximum absorption for certain solutions. These new data are reported in Table II.

Discussion

The most significant result is that the signs of $\partial\nu/\partial p$ and of $\partial\nu/\partial T$ for the iron(III) complex $Fe(bipy)_2(CN)_2^+$ are opposite to those for iron(II) and molybdenum(0) complexes of this type (Table I and ref. 11). The results for $Fe(bipy)(CN)_4^-$ are less definitive, since although $\partial\nu/\partial p$ is negative, as for $Fe(bipy)_2(CN)_2^+$, $\partial\nu/\partial T$ is zero within the rather large experimental uncertainty. However it does seem that pressure, temperature, and solvent effects on LMCT spectra of these iron(III) complexes are indeed opposite to those on MLCT spectra of analogous iron(II) and molybdenum(0) complexes. The general correlation of pressure and

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*It is tempting to speculate that the favouring of solvolytic decomposition by pressure indicates an associative mechanism for solvolysis at these iron(III) complexes.

TABLE II. Solvatochromism of Iron–Diimine–Cyanide Complexes (ν_{max} (cm^{-1}) at 298.2 K, atmospheric pressure)

Solvent	E_T	$Fe(phen)(CN)_4^{2-}$	$Fe(bipy)(CN)_4^-$	$Fe(bipy)_2(CN)_2^+$
Water	63.1	18940	23920	18400
MeOH	55.5	19230	24040	19230
EtOH	51.9	19420		19300
n-PrOH	50.7	19490		
i-PrOH	48.6		25510	19420
MeCN	46.0		25640	
$MeNO_2$	43.3		26880	19840

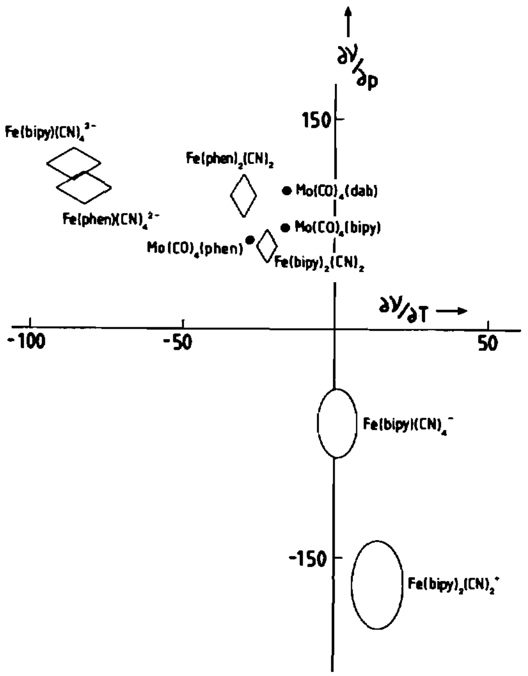

Fig. 1. Correlation between piezochromic and thermochromic behaviour for iron(II)–diimine–cyanide and molybdenum(0)–diimine–carbonyl complexes (in water, methanol, or n-butanol).

temperature effects with solvent polarity developed earlier for molybdenum(0) complexes seems to apply equally well to these iron(II) and iron(III), MLCT and LMCT, species.

Figure 1 shows the correlation between $\partial\nu/\partial p$ and $\partial\nu/\partial T$ for iron(II), iron(III), and molybdenum(0) complexes. In this plot we have had perforce to mix data from three different, though essentially similar, solvents, *viz.* water, methanol, and n-butanol. Figure 2 shows $\partial\nu/\partial p$ plotted against $\partial\nu/\partial T$ for $Mo(CO)_4$-(LL) complexes in a variety of solvents, to show that solvent effects will not have a major effect on $\partial\nu/\partial p$ *versus* $\partial\nu/\partial T$ relations. Indeed Fig. 3 shows that $\partial\nu/\partial p$ values correlate with solvent sensitivities. We have included the trend for molybdenum(0)–Schiff base–carbonyl complexes [13] here to emphasize this correlation; as for Fig. 1 the $\partial\nu/\partial p$ values are of necessity for water, methanol, or n-butanol.

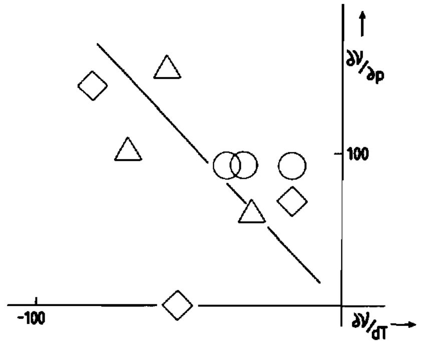

Fig. 2. Correlation between piezochromic and thermochromic behaviour for molybdenum(0)–diimine–carbonyl complexes in a range of solvents (diimine ligands: ◇ bipy; △ phen; ○ dab).

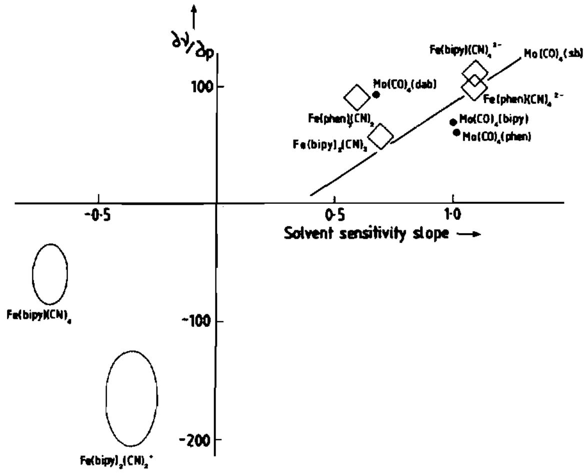

Fig. 3. Correlation between piezochromism and solvatochromism for iron(II)– and iron(III)–diimine–cyanide and molybdenum(0)–diimine–carbonyl complexes. The line labelled $Mo(CO)_4(sb)$ represents the trend established for a variety of complexes with sb = a pyridine Schiff base or diazabutadiene ligand (from ref. 13).

It may be this non-constancy of solvent which makes the general trend line appear not to pass through the origin.

Comparisons between the iron(II) and molybdenum(0) series of complexes may be affected by the fact that not only the metal but also the non-diimine ligands are different; solvation characteristics of cyanide and carbonyl ligands are likely to differ markedly. In principle it might be possible to provide a link via studies on iron(0) complexes $Fe(CO)_3$-(diimine). In practice such complexes are either negligibly solvatochromic [16, 17] or exhibit solvatochromic behaviour whose discussion is complicated by steric [16] or orbital energy level ranking [18]. Interestingly, very similar comments apply to other d^8-diimine series of complexes, of nickel(II) and of platinum(II) [19].

We hope to obtain further information to supplement our very limited data on the relation between solvatochromism and piezochromism for LMCT bands. There are data available on piezochromism of a range of iron(III)–β-diketonate complexes, but unfortunately their absorption bands in the visible region are not simply LMCT in character [20].

An overall general picture of the relation between pressure, temperature, and solvent effects on metal–diimine charge-transfer bands is now beginning to emerge. Relatively large uncertainties in $\partial \nu/\partial p$ and in $\partial \nu/\partial T$, and certain restrictions imposed by very low solubilities, prevent us at the moment from establishing whether there are deviations resulting from specific physical or chemical interactions in the cases of certain solvents or types of complexes. Apparatus development and the study of further complexes of this general type should in time lead to a more sharply defined picture of correlations and deviations, thereby giving precise insights into solvation in this area.

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