Bis(1,10-phenanthroline)dicyanoiron(II): an Almost Universal Inorganic Solvent Polarity Indicator

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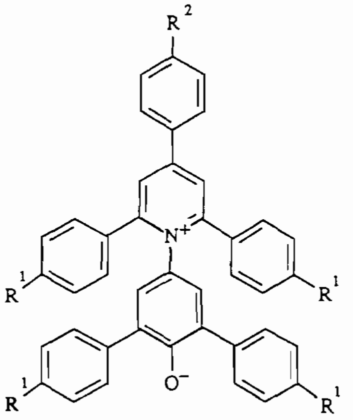
Abstract

Wavelengths of maximum absorption are reported for the main metal to ligand charge transfer band of biscyano-bis(1,10-phenanthroline)iron(II) in a variety of hydroxylic solvents, including alcohols, diols and alkoxyethanols. Correlations with solvent acceptor numbers and E_T values are examined, and the versatility of the title complex as a probe of solvent polarity discussed.

Introduction

Ternary low-spin iron(II) complexes of the $Fe(CN)_2(diimine)_2$ type were discovered some 55 years ago [1]. Their use as indicators in redox titrations [2] and in titrations of aromatic amines [3] was described many years ago, as was the markedly solvatochromic behaviour of $Fe(CN)_2(bipy)_2$** [4]. Over the past two decades the solvatochromism of this type of complex in various non-aqueous [5–8] and mixed [9] solvents has been reported. The solvatochromism of $Fe(CN)_2(phen)_2$** in a range of hydroxylic solvents has recently been examined and the observations are reported here. In the process of carrying out this investigation it has become clear that the solubility characteristics of this particular ternary iron–cyanide–diimine complex are almost ideal for its use as a universal solvent polarity indicator. Therefore, its characteristics are compared with those of the widely used $E_T(30)$ scale of Reichardt [8, 10, 11], based on the strongly solvatochromic behaviour of the charge-transfer band of betaine (1).



	R^1	R^2
1	H	H
2	H	CO_2^-
3	^{t}Bu	^{t}Bu

Experimental

$Fe(CN)_2(phen)_2$ was prepared by Schilt's method [12]. Appropriate modifications were used in the preparation of analogous Schiff base complexes from $[Fe(sb)_3]^{2+}$ cations, themselves generated from iron(II), 2-acetyl pyridine and t-butylamine or 4-t-butylaniline. Solvents were the best available grade, dried by standard procedures. Visible absorption spectra were run on a Shimadzu UV-160 spectrophotometer.

Results and Discussion

Wavelengths of maximum absorption for the lowest energy metal to ligand charge transfer band of $Fe(CN)_2(phen)_2$ are reported in Table 1. Various trends with solvent nature are indicated in Fig. 1. This shows the effects of lengthening the n-alkyl chain of primary alcohols, of chain branching, of going to cyclic alcohols and of replacement of CH_3 groups by CF_3. Increasing the length of the n-alkyl chain has a steadily diminishing effect until 1-octanol is reached. Thereafter there is a barely significant (a saturated solution in 1-dodecanol is about 10^{-5} mol dm^{-3} so there is a significant uncertainty in the maximum absorption wavelength for such a low intensity peak (absorbance = 0.07)) decrease in maximum absorption wavelength on increasing the length of the carbon chain to ten and twelve atoms. Branching (n-PrOH to i-PrOH; n-BuOH to t-BuOH) and cyclisation have small but significant effects. The substitution of CF_3 for CH_3, however, has a large effect, with the replacement of both methyl

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**bipy = 2,2'-bipyridyl; phen = 1,10-phenanthroline.

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TABLE 1. Wavelengths and wavenumbers of maximum absorption for the main metal to ligand charge-transfer band of $Fe(CN)_2(phen)_2$

Solvent	λ (nm)	ν_{max} (cm^{-1})	Source	E_T (kcal mol^{-1})
1,1,1,3,3,3-Hexafluoro-2-propanol	499	20040	a	
Water	516	19380	b	63.1
2,2,2-Trifluoroethanol	518	19310	a	59.5
1,2-Ethanediol (glycol)	541	18480	b	56.3
Methanol	545	18350	b	55.5
Ethanol	557	17950	b	51.9
1,2-Pentanediol	557	17950	a	54.1
Diethyleneglycol	558	17920	c	53.8
Benzyl alcohol	560	17860	b	46.7
1-Propanol	566	17670	a	50.7
Triethyleneglycol	568	17610	c	53.5
1-Decanol	(568)[d]	(17610)	a	
2-Methoxyethanol	569	17570	a	52.3
1-Dodecanol	(570)[d]	(17540)	a	
1-Butanol	570	17540	b	50.2
2-Ethoxyethanol	571	17510	a	
1-Hexanol	572	17480	a	48.8
1-Octanol	572	17480	a	48.3
Cyclopentanol	572	17480	a	46.9
2-n-Butoxyethanol	574	17420	a	50.2
Cyclohexanol	581	17210	a	47.7
t-Butyl alcohol	586	17060	b	43.6
Acetonitrile	596	16780	b	45.8
2,4-Pentanedione (acacH)	601	16640	a	49.2
Dimethyl sulphoxide	602	16600	c	45.0
1,2-Dichloroethane	608	16450	c	41.9
Dimethylformamide	614	16290	b	43.8
Acetone	625	16000	b	42.2

[a] This work. [b] Ref. 5. [c] Ref. 6. [d] Due to very low solubility there is a doubt of perhaps ±2 nm in these values.

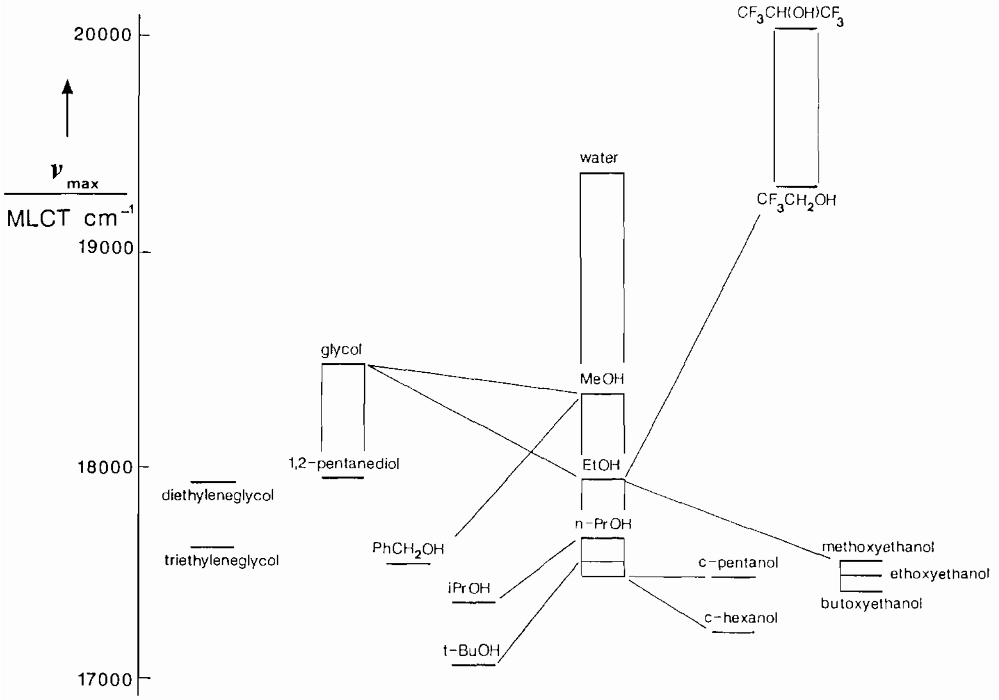


Fig. 1. Relations between ν(MLCT) values for $Fe(CN)_2(phen)_2$ in various solvents.

groups in i-PrOH by CF_3 resulting in ν_{max}(MLCT) shifting to a value considerably higher than that in water. Figure 1 and Table 1 also illustrate and document the modest effects of alkoxy substitution, and relate the properties of diols to mono-ols.

Soukup and Schmid have reported [13], and subsequently Gutmann has depicted [14], a correlation between wavelengths of maximum absorption for $Fe(CN)_2(phen)_2$ and solvent acceptor numbers. This correlation was based on results for twelve solvents. The dependence of wavenumbers (i.e. energies) of maximum absorption on solvent acceptor numbers is shown in Fig. 2 for a somewhat larger group of solvents [5, 14]. It will be seen that while there is indeed an overall qualitative correlation, in detail there are separate correlation lines for the alcohols (plus formamide) and for non-hydroxylic solvents. Points for water and for carboxylic acids fall on neither of these lines. These small complications do not detract from the general picture of correlation of charge-transfer fequencies with acceptor numbers here, but it should be added that an analogous graph for $Mo(CO)_4(bipy)$ shows a considerable more scattered distribution of wavenumbers of maximum absorption [15] in relation to acceptor numbers. This is hardly surprising, as a plot of $\nu_{max}[Mo(CO)_4(bipy)]$ against $\nu_{max}[Fe(CN)_2(bipy)_2]$ consists of two well separated lines, for hydroxylic and non-hydroxylic media.

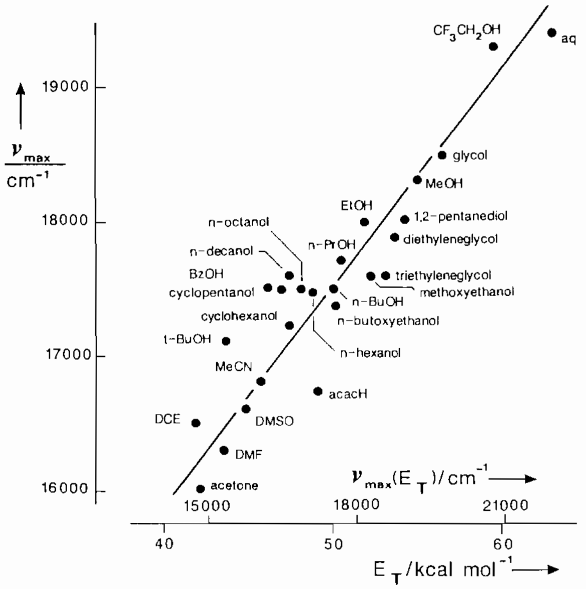


Fig. 3. Relation between ν(MLCT) values for $Fe(CN)_2$-$(phen)_2$ and solvent E_T values (ν_{max}(E_T compound)).

Figure 3 shows a correlation between ν_{max}(MLCT) for $Fe(CN)_2(phen)_2$ and ν_{max} for betaine (1), i.e., with solvent E_T values, for the solvents included in Table 1 and Fig. 1 and for the few non-hydroxylic solvents for which ν_{max}(MLCT) values are available [5] for $Fe(CN)_2(phen)_2$. The correlation is moderately good, although clearly there are small but significant differences in the way that solute–solvent interactions affect ν_{max} values for these two rather

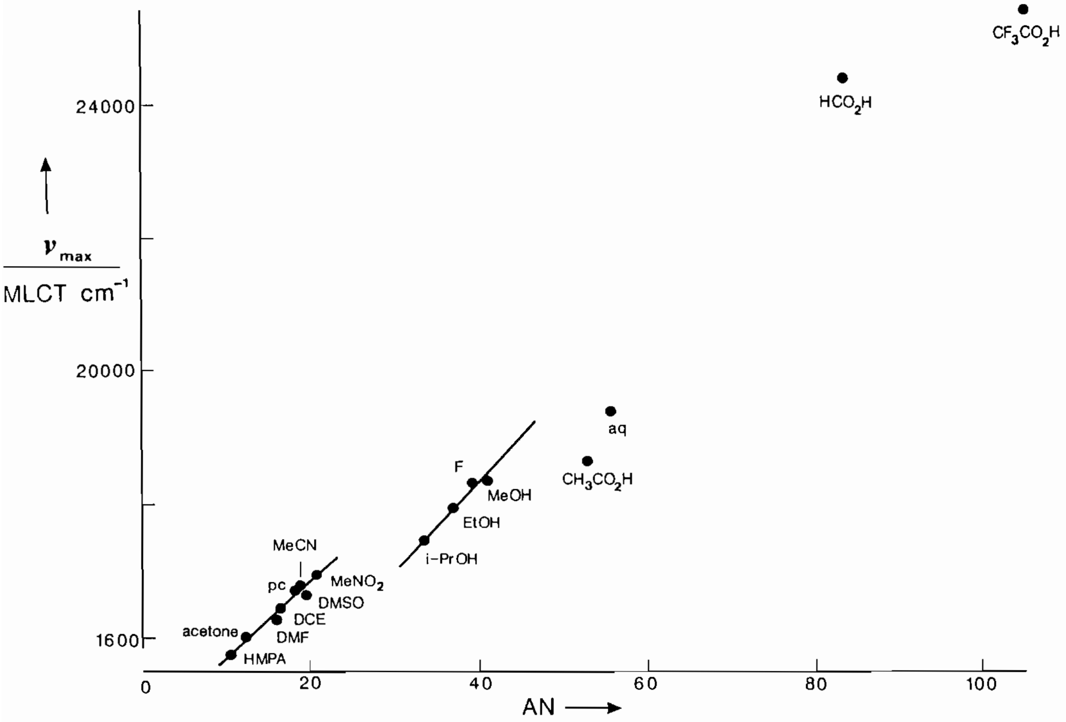
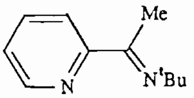


Fig. 2. Relation between ν(MLCT) values for $Fe(CN)_2(phen)_2$ and solvent acceptor numbers.

different solutes. Overall the slope of Fig. 2 is about 0.5, in other words the solvent sensitivity of $Fe(CN)_2(phen)_2$ is about half that of Reichardt's $E_T(30)$ betaine (**1**). There are several other ternary inorganic complexes with significantly greater solvent sensitivies than $Fe(CN)_2(phen)_2$, but all of them have more restricted solubility ranges (and, incidentally, are still less solvatochromic than Reichardt's compound). Thus, for example, $Mo(CO)_4$(diimine) complexes are more solvatochromic than their $Fe(CN)_2(diimine)_2$ analogues [6, 7, 15], but are generally effectively insoluble in water. The presence of a sulphonate group or of an amino acid moiety in this type of molybdenum compound confers water-solubility [16], but renders these derivatives insoluble in many solvents of low E_T values. Anionic complexes of the $[Fe(CN)_4(diimine)]^{2-}$ type show greater solvent sensitivity than their $Fe(CN)_2(diimine)_2$ analogues [7]. Alkali metal salts of such anions are freely soluble in water, sparingly or insoluble in organic solvents, though tetralkylammonium salts are soluble in a number of organic solvents [17].

Like Reichardt's $E_T(30)$ compound **1**, $Fe(CN)_2(phen)_2$ causes problems in aqueous media by reasons of its low solubility. Modification of **1** by the introduction of a carboxylate substituent gives a compound ($E_T'(6) = 2$) with very similar solvent sensitivity but considerably increased solubility in aqueous media [18]. In the case of our ternary complexes, a slight change in ligand to $Fe(CN)_2(bipy)_2$ results in appreciably higher solubility in aqueous media. This bipy compound is thus to be preferred for studies of binary aqueous solvent mixtures [9, 19]. However, $Fe(CN)_2(bipy)_2$ is considerably less soluble in, for example, the higher alcohols than $Fe(CN)_2(phen)_2$. On balance the latter is to be preferred as a solvent polarity indicator, despite the (somewhat half-hearted) claims made previously [20] on behalf of $Fe(CN)_2(bipy)_2$.

At the other extreme of solvent behaviour from water and other hydroxylic media, $Fe(CN)_2(phen)_2$ is as reluctant to dissolve in, e.g. paraffins as is Reichardt's $E_T(30)$ compound. Reichardt's E_T scale has been extended to include such solvents as paraffins by using a t-butyl derivative (**3**) as a secondary standard [11]. In like vein, we have examined two more lipophilic analogues of $Fe(CN)_2(phen)_2$, complexes $Fe(CN)_2(LL)_2$ with LL = **4** or **5**. Here the incorporation of t-butyl groups does not, unfortunately, increase solubilities in paraffins enough for wavelengths of maximum absorption to be measurable.



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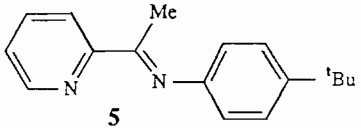

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It thus seems that $Fe(CN)_2(phen)_2$ is the most versatile and most widely usable inorganic solvatochromic indicator. Its limited solubility in water means that its bipy analogue is more convenient for examining highly aqueous media, but the phen compound could still be used, preferably in cells with path lengths longer than the usual 10 mm. In addition, $Fe(CN)_2(phen)_2$ shows the expected and necessary long-term stability in solution. In the majority of solvents there is no detectable decomposition over a period of days (at room temperature); there is a report of 'incipient dissociation' in about one day for solutions in aqueous acetone or aqueous acetonitrile [21].

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