

Solvent Effects and Correlation with Reichardt's E_T Values on Charge Transfer Spectra of Bis(2,2'-bipyridyl)biscyanoiron(II)

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Abstract. The solvatochromic behaviour of biscyano-bis(2,2'-bipyridyl) iron(II) in a variety of solvents is described. The frequencies are correlated with Reichardt's solvent parameter E_T . Various trends are indicated, solvatochromic shifts of the title complex in various aqueous mixtures of DMF and 2-butoxy ethanol are also reported.

Keywords. Solvatochromism; Reichardt's E_T values; Bis(2,2'-bipyridyl)biscyanoiron(II); 2-*n*-Butoxy ethanol; Solvents; Dimethylformamide.

Lösungsmittelleffekte der Charge-Transfer-Spektren von Bis(2,2'-bipyridyl)biscyano-eisen(II) und Korrelation mit den E_T -Werten nach Reichardt

Zusammenfassung. Es wird das solvatochrome Verhalten von Bis(2,2'-bipyridyl)biscyano-eisen(II) in einer Reihe von Lösungsmitteln beschrieben. Die Frequenzen der Absorption werden nach der E_T -Lösungsmittelskala von Reichardt korreliert. Dabei zeigen sich verschiedene Gesetzmäßigkeiten. Es wurden auch die solvatochromen Verschiebungen in Mischungen von DMF und 2-Butoxyethanol untersucht.

Introduction

Solvatochromism, or the solvent dependance of the frequency of an electronic transition of a molecule can be used as a probe for the solvent environment [1]. This property is dependant on specific solvent – solute interactions. The effect of the hydrophilic or hydrophobic character of the periphery of complexes on their solvation characteristic will then be highlighted. The monitoring of solvation of inorganic complexes in binary aqueous solvent mixtures is important in kinetic and thermodynamic considerations [2]. The solvent shifts of solvatochromic compounds should be of value in assessing preferential solvation in binary aqueous solvent mixtures [1].

Recently there has been considerable interest in the study of solvatochromism and solvation of ternary iron-diimine cyanide complexes [3–5]. To study this effect,

solvent effects on charge-transfer spectra of bis(2,2'-bipyridyl) biscyanoiron(II) are reported.

Solvatochromism is concerned with both solvent donor properties and solvent acceptor properties. The present paper is exclusively concerned with solvent acceptor properties. *DMF* and 2 butoxyethanol are important solvents and much used in chemistry. Therefore it seemed of interest to study the solvation behaviour of the title complex in various aqueous mixtures.

Experimental Part

The title complex was prepared by published methods [6]. Solvents were of Analar grade and dried by standard procedures. Spectra were run using a Unicam SP 800 A recording spectrophotometer.

Results and Discussion

Besides the E_T -values, wavelengths of maximum absorption are reported in Table 1 for the main metal to ligand charge transfer band of biscyano-bis(2,2'-bipyridyl) iron(II) in a variety of solvents. The above complex exhibits intense charge-transfer (MLCT) bands in the visible spectrum, which can be assigned to charge transfer from iron to the Schiff base ligand ($t_{2g} \rightarrow \pi^*$).

To categorize the acceptor properties of a solvent, an empirical parameter is used, either Gutmann's acceptor number [7] or Reichardt's E_T parameters. The E_T parameters are themselves derived from the $\pi-\pi^*$ transition in a betaine dye [8].

The plot of maximum absorption frequencies against solvent E_T values for the solvent listed in Table 1 was linear (Fig. 1). In general, graphs of maximum absorption frequencies against solvent E_T values for inorganic complexes of this type exhibit two lines, one for hydroxylic solvents and another for non hydroxylic solvents [9]. This reflects the importance of hydrogen bonding on the charge-transfer energies of the systems studied. Table 1 shows that increasing the length of the n -alkyl chain going from methanol to octanol will result in a steadily diminishing wave number. This is to be expected because paralleling the increasing size of the non polar hydrocarbon portion of these alcohols, we observe a corresponding decrease of their solubility in water.

Table 1. Solvent effects and E_T values for the charge-transfer spectra of bis(2,2'-bipyridyl)biscyanoiron(II)

Solvent	λ (nm)	ν_{\max} (cm^{-1})	E_T (kcal/mol)
Water	521	19194	63.1
Acetonitrile	600	16667	45.8
Dimethylformamide	616	16234	43.8
Methanol	555	18018	55.5
Ethanol	568	17606	51.9
1-Hexanol	581	17212	48.8
1-Octanol	580	17241	48.3
2-Ethoxyethanol	577	17331	—
2-n-Butoxyethanol	578	17301	50.2

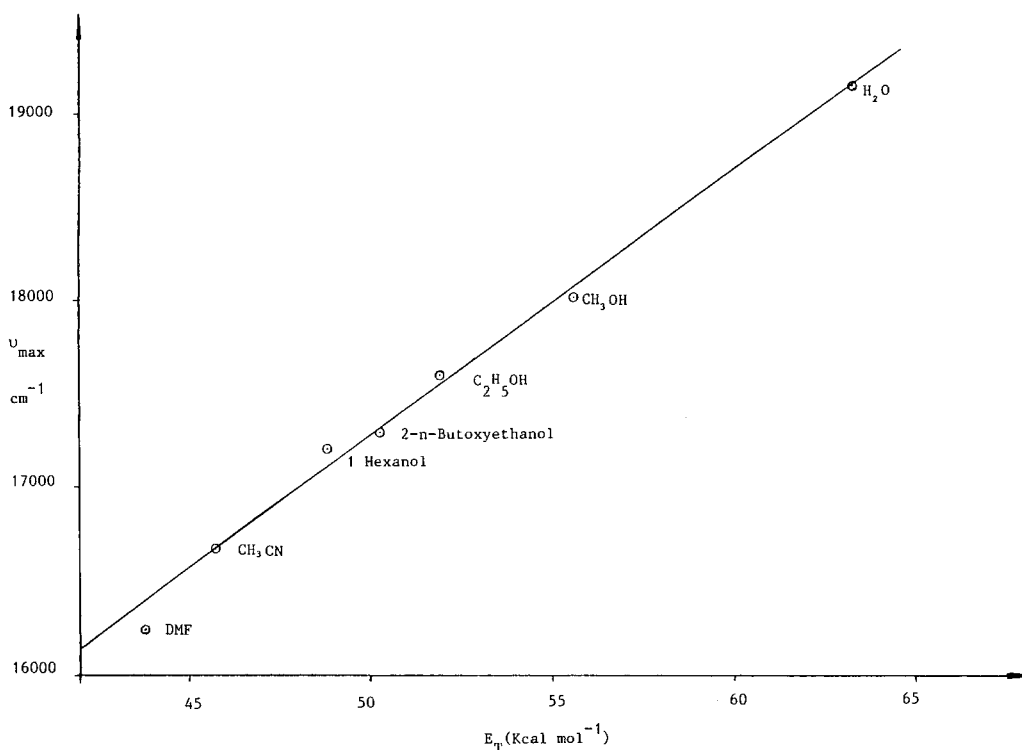


Fig. 1. Relation between $\nu(\text{MLCT})$ values for $\text{Fe}(\text{bipy})_2(\text{CN})_2$ and solvent E_T values ν_{max} (E_T compound)

Therefore, on going from methanol to octanol we are changing to a less polar solvent. This will decrease the solvation of the cyanide ligand and thus consequently decrease the $\text{Fe} \leftrightarrow \text{CN}\pi$ back bonding raising the ground state energy and thus resulting in decreased wavenumbers. Table 1 shows also the modest effects of alkoxy substitution on going from ethanol to 2-ethoxy and 2-butoxy ethanol.

Ternary low-spin iron(II) complexes of $\text{Fe}(\text{CN})_2$ (diimine)₂ were discovered several decades ago [10]. Their use in titration of aromatic amines [11] and in solvatochromic [12] work has long been established. *DMF* and 2-butoxyethanol are quite important solvents and much used in various areas of chemistry. Therefore in this study the solvatochromism of $\text{Fe}(\text{bipy})_2(\text{CN})_2$ in various aqueous mixtures of *DMF* and 2-butoxyethanol has been established. Table 2 lists wavelengths and wavenumbers of maximum absorption for the lowest energy metal to ligand charge transfer band of $\text{Fe}(\text{bipy})_2(\text{CN})_2$ in various aqueous mixtures. As can be seen from Table 2 the solvatochromic shift goes to lower energies as the proportion of the organic solvent increases. This is due to the decreased solvation of the cyanide ligands which would decrease the $\text{Fe} \rightarrow \text{CN}\pi$ back bonding. Therefore, as hydrogen-bonded water is replaced by the organic solvent, the frequencies shift to lower energies. This demonstrates that the cyanide ligand is a specific site of solvation. Replacement of cyanide ligands by bipyridyl as in $[\text{Fe}(\text{bipy})_3]^{2+}$ results in removal of solvatochromism, whereas addition of cyanide ligands as in $[\text{Fe}(\text{bipy})(\text{CN})_4]^{2-}$ increases the sensitivity to solvent variation and thus increased marked solvatochromism will be produced [3].

Table 2. Wavenumbers and Wavelengths of maximum absorption (ν_{\max}) for the lowest energy-transfer band of Fe(*bipy*)₂(CN)₂ in various 2-butoxyethanol and DMF water mixtures

Vol [% 2-butoxyethanol]	λ (nm)	ν_{\max} (cm ⁻¹)	Vol [% DMF]	λ (nm)	ν_{\max} (cm ⁻¹)
0	521	19194	10	530	18868
10	530	18868	20	536	18657
20	535	18692	30	543	18416
30	538	18587	41	550	18182
41	539	18553	50	557	17953
50	543	18416	59	561	17825
59	547	18282	70	572	17483
80	555	18018	80	582	17182
90	560	17857	90	596	16779
100	578	17301	100	616	16234

These solvatochromic shifts should be highly valuable in spectroscopic studies such as vibrational [13] and NMR [14]. Solvation changes on transfer from one medium to another can generally be put on a quantitative basis in terms of appropriate thermodynamic transfer parameters [15].

It is to be noted that Burgess has recently studied the solvatochromism of Fe(*phen*)₂(CN)₂ in a variety of hydroxylic solvents [5]. Correlation with E_T was made and a linear plot was obtained.

However, our title complex is also important in solvation studies. Using it as a standard, relative solvatochromic effects can be estimated by plotting ν_{\max} (MLCT) against the respective ν_{\max} (MLCT) values for [Fe(*bipy*)₂(CN)₂]. Thus solvent sensitivity values, relative to 1.0 for [Fe(*bipy*)₂(CN)₂] are established.

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