

Qualitatively and quantitatively different solvatochromism of the MLCT and MMCT absorption bands of centrosymmetric acceptor-bridged diiron(II,II) and diiron(III,II) cyanide complexes

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Abstract

The energies of the metal-to-ligand charge transfer (MLCT) and metal-to-metal charge transfer (MMCT) absorption bands of a number of heterocycle-bridged diiron(II,II) homovalent and diiron(III,II) mixed-valent complexes correlate linearly with Gutmann's acceptor number (AN). The compounds are $(\text{NEt}_4)_6[(\text{NC})_5\text{Fe}(\mu\text{-tz})\text{Fe}(\text{CN})_5]$ and $(\text{NEt}_4)_5[(\text{NC})_5\text{Fe}(\mu\text{-tz})\text{Fe}(\text{CN})_5]$, tz = 1,2,4,5-tetrazine; $(\text{NEt}_4)_4[(\text{NC})_4\text{Fe}(\mu\text{-bptz})\text{Fe}(\text{CN})_4]$ and $(\text{NEt}_4)_3[(\text{NC})_4\text{Fe}(\mu\text{-bptz})\text{Fe}(\text{CN})_4]$, bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine; $(\text{NEt}_4)_4[(\text{NC})_4\text{Fe}(\mu\text{-bmtz})\text{Fe}(\text{CN})_4]$, bmtz = 3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine; $(\text{NEt}_4)_4[(\text{NC})_4\text{Fe}(\mu\text{-bpym})\text{Fe}(\text{CN})_4]$, bpym = 2,2'-bipyrimidine. Mononuclear analogues of the tz and bpym ligands were also studied. Various degrees of negative and positive solvatochromism are observed for centrosymmetric dinuclear systems. Unusual observations include the large negative solvatochromism of MLCT bands in Fe(II)Fe(II) species lacking a permanent dipole moment, the positive solvatochromism of MLCT/LMCT bands and the small negative solvatochromism of MMCT bands in the valence-averaged $\text{Fe}^{2.5}\text{Fe}^{2.5}$ systems. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Charge transfer; Cyano complexes; Iron compounds; Mixed valence; Solvatochromism

1. Introduction

The metal-to-ligand charge transfer (MLCT) absorption spectra of cyanoiron(II) complexes with unsaturated N-heterocyclic ligands L have long attracted attention because of their typically strong solvent dependence ('solvatochromism') [1,2]. Compounds of pyridine, bipyridine and phenanthroline ligands [2–6] were studied in detail, and the energies of the absorption maxima of these negatively charged systems $[(\text{NC})_n\text{Fe}(\text{L})]^{(n-2)-}$ were generally found to correlate well with the acceptor number (AN) solvent parameter of Gutmann et al. [7].

Recent advances [8–10] in the synthesis and characterization of symmetrically dinuclear homovalent (Fe(II)Fe(II)) or mixed-valent compounds (Fe(II)Fe(III)

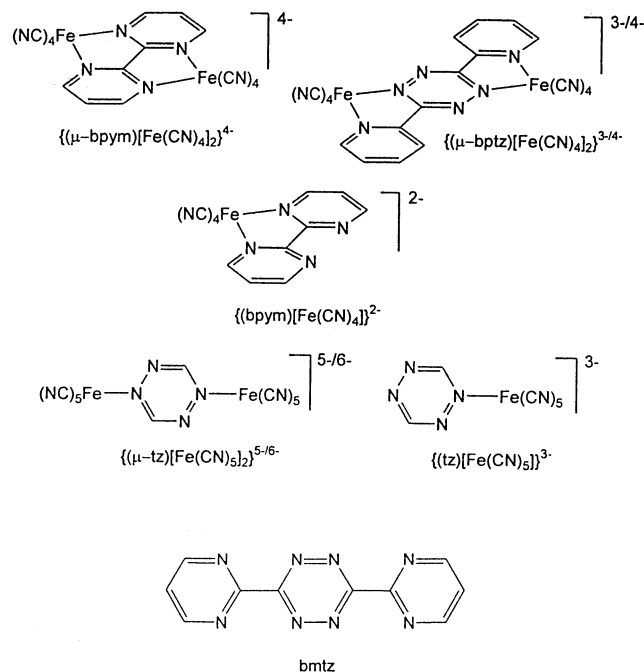
or $\text{Fe}^{2.5}\text{Fe}^{2.5}$) with bridging polyazine heterocycles have now allowed us to extend these studies to hitherto less common situations. Whereas the centrosymmetric diiron(II) compounds exhibit long-wavelength MLCT transitions, the mixed-valent species have an additional band in the near infrared, formally attributed to a metal-to-metal or inter-valence charge transfer (MMCT or IVCT) [11,12]. In the case of delocalized valencies ($\text{Fe}^{2.5}\text{Fe}^{2.5}$, centrosymmetric 'class III' situation [11]) this transition is described as a $\pi \rightarrow \pi^*$ process between delocalized MOs. In fact, the absence of strong solvatochromism has often been cited as evidence for a 'Class III' mixed-valence behavior [11]. The frequently strong solvatochromism of centrosymmetric homovalent species with their lack of a permanent dipole moment has previously attracted some attention [13–15] either polarizability [13,14] or local dipole effects [15] were invoked to account for this effect.

In this work we describe the solvatochromic behavior of the diiron(II) species $(\text{NEt}_4)_6[(\text{NC})_5\text{Fe}(\mu\text{-tz})\text{Fe}(\text{CN})_5]$

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[8], $(\text{NEt}_4)_4[(\text{NC})_4\text{Fe}(\mu\text{-bptz})\text{Fe}(\text{CN})_4]$ [9], $(\text{NEt}_4)_4[(\text{NC})_4\text{Fe}(\mu\text{-bmtz})\text{Fe}(\text{CN})_4]$ [10] and $(\text{NEt}_4)_4[(\text{NC})_4\text{Fe}(\mu\text{-bpym})\text{Fe}(\text{CN})_4]$ [9], and of the stable mixed-valent systems $(\text{NEt}_4)_5[(\text{NC})_5\text{Fe}(\mu\text{-tz})\text{Fe}(\text{CN})_5]$ [8] and $(\text{NEt}_4)_3[(\text{NC})_4\text{Fe}(\mu\text{-bptz})\text{Fe}(\text{CN})_4]$ [9]; tz = 1,2,4,5-tetrazine, bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, bmtz = 3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine and bpym = 2,2'-bipyrimidine. The mononuclear complexes $(\text{NEt}_4)_3[(\text{tz})\text{Fe}(\text{CN})_5]$ [8] and $(\text{NEt}_4)_2[(\text{bpym})\text{Fe}(\text{CN})_4]$ [9] were also investigated for comparison purposes.



2. Experimental

The cyanoiron complexes containing tz [8], bptz [9], bmtz [10] and bpym [9] were described previously. Absorption spectra were measured using an Omega 10 spectrophotometer of Bruins Instruments (Puchheim, Germany). For band deconvolution we employed the program GRAMS/32 (Version 4.02).

3. Results and discussion

3.1. Iron(II) compounds

The syntheses and basic charge transfer absorption features of the complexes studied here have been described [8–10]. The mononuclear Fe(II) complexes and the dinuclear Fe(II)Fe(II) systems are distinguished by intense ($\epsilon > 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ [8–10]) long-wavelength MLCT bands involving allowed transitions from metal

d_π orbitals to the π^* orbitals of the bridging acceptor ligands. Table 1 summarizes the results for the mono- and dinuclear pentacyanoiron(II) complexes of 1, 2, 4, 5-tetrazine, a weak, ligand-centered $n \rightarrow \pi^*$ transition in the visible region has also been included.

The MLCT absorption maxima for both complexes in different solvents correlate with Gutmann's AN [1b,7], (see Table 6), revealing 'negative' solvatochromism [1c] (i.e. increasing absorption energy with increasing solvent 'polarity', positive gradient B in equation $\tilde{\nu} = A + B \cdot \text{AN}$). The $n \rightarrow \pi^*$ values for the dinuclear compound show better correlation with Reichardt's E_T parameter [1c] than with AN (Table 1): $\nu_{n \rightarrow \pi^*} = 11\,752 + 163.0 \cdot E_T$ ($R^2 = 0.988$).

The bptz-bridged diiron(II) complex $(\text{NEt}_4)_4[(\text{NC})_4\text{Fe}(\mu\text{-bptz})\text{Fe}(\text{CN})_4]$ exhibits distinctly structured MLCT bands in all solvents used; the band profiles could be fitted using five Gaussian components MLCT(n) (Figs. 1 and 2 and Table 2), of which the very broad component MLCT(2) was invoked only for graphical fitting reasons.

The observation of several, at least four clear, intense bands with Gaussian shape in the visible region of this complex can be attributed to the presence of two close-lying π^* MOs of bptz (a_u and b_{1u}) at low energies and another MO (b_g) not very far away [16]. Tentatively we assign MLCT(1) as a band from a transition to b_g whereas the close-lying MLCT(3)–MLCT(5) bands are attributed to transitions involving the a_u and b_{1u} π^* MOs. In the low-spin d^6 configuration each iron(II) center contains three energetically different occupied d orbitals, d_{xy} (a_2), d_{yz} (b_2) and $d_{x^2-y^2}$ (a_1) [17] from which MLCT transitions to π^* levels can take place. Fig. 3 illustrates the four possible linear correlations of the MLCT(n) bands (except MLCT(2)) with AN. From these excellent correlations we conclude that the sequence of transitions does not change in different solvents.

The related complex $(\text{NEt}_4)_4[(\text{NC})_4\text{Fe}(\mu\text{-bmtz})\text{Fe}(\text{CN})_4]$ with the still better π accepting bridge bmtz [10,18] exhibits only two discernible bands, both of which change linearly with AN (Tables 3 and 6). They are assigned to transitions to the a_u and b_{1u} orbitals [18].

In the visible region, the mononuclear and dinuclear tetracyanoiron(II) complexes of 2,2'-bipyrimidine [9,19] exhibit two and three MLCT bands, respectively (Table 4), which involve different π^* MOs (b_{2u} , a_u , b_{3g} [13,16b,20]) as target orbitals.

All MLCT bands of the dinuclear Fe(II)Fe(II) complexes exhibit negative solvatochromism albeit to different extent (see Table 6). The same holds for the mononuclear complexes $(\text{NEt}_4)_3[(\text{tz})\text{Fe}(\text{CN})_5]$ (Table 1) with $A = 14196 \text{ cm}^{-1}$ and gradient $B = 4.8 \text{ cm}^{-1}$ ($R^2 = 0.958$, $n = 4$) and $(\text{NEt}_4)_2[(\text{bpym})\text{Fe}(\text{CN})_4]$ (Table 4) with $A = 18171 \text{ cm}^{-1}$ and gradient $B = 113.1 \text{ cm}^{-1}$

Table 1
Absorption maxima $\tilde{\nu}^a$ of $\{(tz)[Fe(II)(CN)_5]\}^{3-}$ and $\{(\mu-tz)[Fe(II)(CN)_5]_2\}^{6-}$ in different solvents

Solvent	AN ^b	E_T ^b	$\{(\mu-tz)[Fe(II)(CN)_5]_2\}^{6-}$		$\{(tz)[Fe(II)(CN)_5]\}^{3-}$
			$\tilde{\nu}_{MLCT}$	$\tilde{\nu}_{n \rightarrow \pi^*}$	$\tilde{\nu}_{MLCT}$
CH ₃ CN	18.9	45.6	9790	19 230	14 490
CH ₂ Cl ₂	20.4	40.7	9860	^c	14 160
<i>i</i> -C ₃ H ₇ OH	33.8	49.2	10 220	19 760	n.d.
C ₂ H ₅ OH	37.9	51.9	10 650	20 280	n.d.
CH ₃ OH	41.3	55.4	10 880	20 580	14 180
H ₂ O	54.8	63.1	11 790	22 120	14 600

^a In cm⁻¹.

^b From refs. [1b,7].

^c Too low intensity due to low solubility.

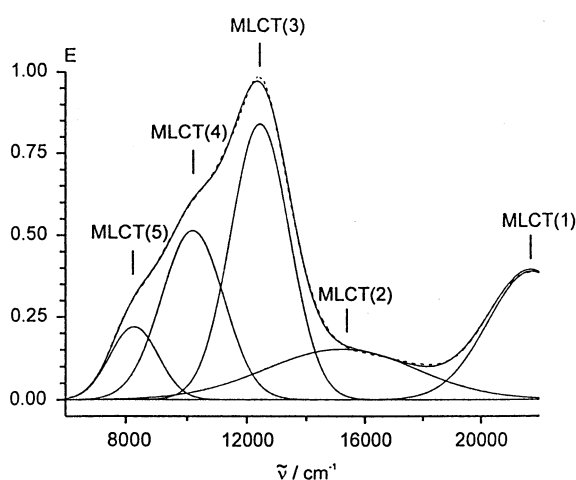


Fig. 1. Long-wavelength section of the absorption spectrum of $(NEt_4)_4[(NC)_4Fe(\mu-bptz)Fe(CN)_4]$ in DMF: band deconvolution.

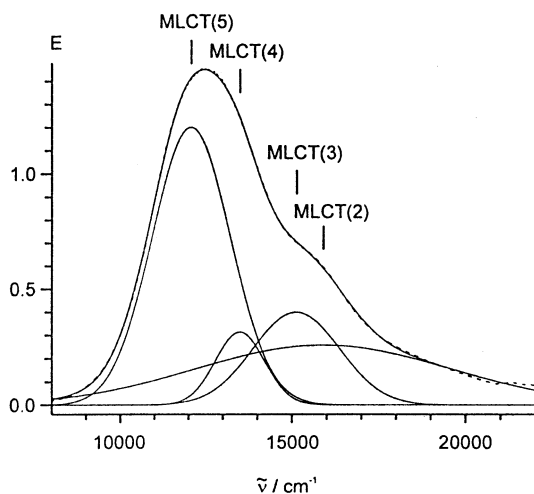


Fig. 2. Long-wavelength section of the absorption spectrum of $(NEt_4)_4[(NC)_4Fe(\mu-bptz)Fe(CN)_4]$ in H₂O: band deconvolution.

($R^2 = 0.958$, $n = 6$) for MLCT(1) and $A = 11186 \text{ cm}^{-1}$ and gradient $B = 127.3 \text{ cm}^{-1}$ ($R^2 = 0.926$, $n = 6$) for MLCT(2).

Table 2
Absorption maxima $\tilde{\nu}_{MLCT}^a$ of $\{(\mu-bptz)[Fe(II)(CN)_4]_2\}^{4-}$ in different solvents

Solvent	AN ^b	$\tilde{\nu}_{MLCT}$			
		$\tilde{\nu}_{MLCT(1)}^c$	$\tilde{\nu}_{MLCT(3)}^d$	$\tilde{\nu}_{MLCT(4)}^d$	$\tilde{\nu}_{MLCT(5)}^d$
DMF	16.0	21 740	12 430	10 180	8 260
CH ₃ CN	18.9	22 370	12 520	10 430	8 700
DMSO	19.3	21 830	12 480	10 290	8 290
CH ₃ NO ₂	20.5	22 620	12 650	10 610	9 010
<i>i</i> -C ₃ H ₇ OH	33.8	23 700	13 350	11 460	9 790
C ₂ H ₅ OH	37.9	24 750	13 690	11 970	10 780
CH ₃ OH	41.3	25 000	13 840	12 190	11 020
H ₂ O	54.8	27 780	15 120	13 490	12 080

^a In cm⁻¹.

^b From refs. [1b,7].

^c Directly measured.

^d Determined via band deconvolution.

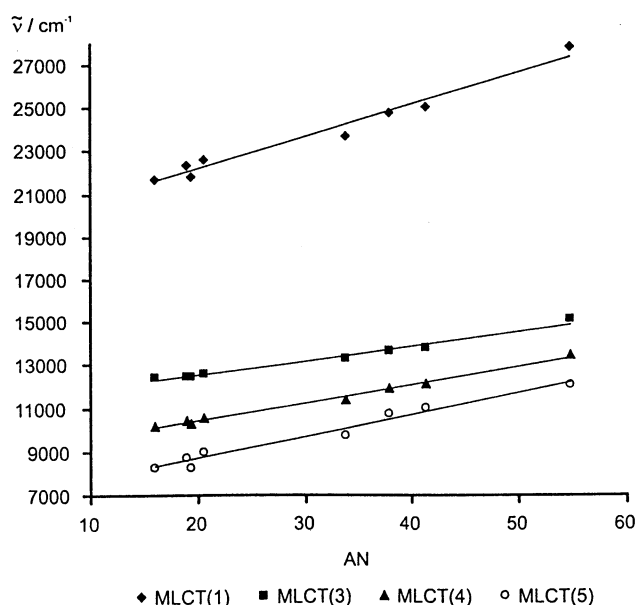


Fig. 3. Linear correlations of absorption maxima $\tilde{\nu}$ vs. AN for MLCT(n) bands of $(NEt_4)_4[(NC)_4Fe(\mu-bptz)Fe(CN)_4]$.

The variation in the gradients can be discussed within the concepts put forward previously [21]: For the intense

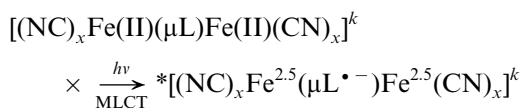
Table 3
Absorption maxima $\tilde{\nu}_{\text{MLCT}}$ ^a of $\{(\mu\text{-bmtz})[\text{Fe}(\text{II})(\text{CN})_4]_2\}^{4-}$ in different solvents

Solvent	AN ^b	$\tilde{\nu}_{\text{MLCT}(1)}$	$\tilde{\nu}_{\text{MLCT}(2)}$
DMF	16.0	19460	11700
CH ₃ CN	18.9	20380	12150
DMSO	19.3	20280	11740
C ₂ H ₅ OH	37.9	22120	12420
CH ₃ OH	41.3	23150	12690
H ₂ O	54.8	24630	12440

^a In cm^{-1} .

^b From refs. [1b,7].

long-wavelength transitions of bis(tetracyanoiron(II)) species the gradient or solvent sensitivity parameter B decreases on going from the complex with the moderate π acceptor bpym ($B \approx 100 \text{ cm}^{-1}$, average) via the bptz compound ($B \approx 80 \text{ cm}^{-1}$, av.) to the complex with the best π acceptor bmtz ($B = 20$). This trend reflects diminishing polarity differences between ground and excited states through increasing metal/ligand orbital mixing [21].



The bis(pentacyanoiron(II)) complex of tz has an intermediate value B of 54.3 cm^{-1} . In accordance with the above argument most MLCT absorptions at higher energies (with less orbital mixing) exhibit a more pronounced negative solvatochromism (Table 6).

Remarkably, the two pairs of mono- and dinuclear complexes exhibit very different behavior: whereas the long-wavelength absorptions of mononuclear $(\text{NEt}_4)_2[(\text{bpym})\text{Fe}(\text{CN})_4]$ are slightly more solvatochromic ($B \approx 120 \text{ cm}^{-1}$, av.) than those of the dinuclear form ($B \approx 100 \text{ cm}^{-1}$, av.), the mononuclear $(\text{NEt}_4)_3\text{-(tz)Fe}(\text{CN})_5]$ exhibits virtually no solvatochromism ($B = 4.8 \text{ cm}^{-1}$), in contrast to the dimer. The counter-intuitive higher solvent sensitivity of centrosymmetric dinuclear species (without permanent dipole moment)

Table 4
Absorption maxima $\tilde{\nu}_{\text{MLCT}}$ ^a of $\{(\mu\text{-bpym})[\text{Fe}(\text{II})(\text{CN})_4]_2\}^{4-}$ and $\{(\text{bpym})[\text{Fe}(\text{II})(\text{CN})_4]\}^{2-}$ in different solvents

Solvent	AN ^b	$\{(\mu\text{-bpym})[\text{Fe}(\text{II})(\text{CN})_4]_2\}^{4-}$			$\{(\text{bpym})[\text{Fe}(\text{II})(\text{CN})_4]\}^{2-}$	
		$\tilde{\nu}_{\text{MLCT}(1)}$	$\tilde{\nu}_{\text{MLCT}(2)}$	$\tilde{\nu}_{\text{MLCT}(3)}$	$\tilde{\nu}_{\text{MLCT}(1)}$	$\tilde{\nu}_{\text{MLCT}(2)}$
CH ₃ CN	18.9	19340	12850	11360	20240	13530
CH ₂ Cl ₂	20.4	19720	13190	11710	20920	14430
<i>i</i> -C ₃ H ₇ OH	33.8	20410	13790	12330	21600	14930
C ₂ H ₅ OH	37.9	21320	14580	13250	22320	15770
CH ₃ OH	41.3	21370	14730	13350	22680	16130
H ₂ O	54.8	23360	16530	15500	24690	18690

^a In cm^{-1} .

^b From refs. [1b,7].

relative to asymmetrical mononuclear analogues has been discussed in terms of dominant polarizability contributions [13,14] or local dipolar effects [15]. At least for the tz complexes we suggest that polarizability differences have a major effect.

3.2. Diiron(2.5) compounds

Solvatochromism for mixed-valent dinuclear complexes could be studied in the case of the persistent compounds $(\text{NEt}_4)_5[(\text{NC})_5\text{Fe}(\mu\text{-tz})\text{Fe}(\text{CN})_5]$ and $(\text{NEt}_4)_3[(\text{NC})_3\text{Fe}(\mu\text{-bptz})\text{Fe}(\text{CN})_4]$. Both the (shifted) MLCT/LMCT bands and the new MMCT bands, alternatively formulated as IVCT bands, display solvatochromism with linear correlation to AN (Figs. 4 and 5, Tables 5 and 6).

Both results are remarkable: the MLCT/LMCT bands exhibit distinct positive solvatochromism (Fig. 4 and

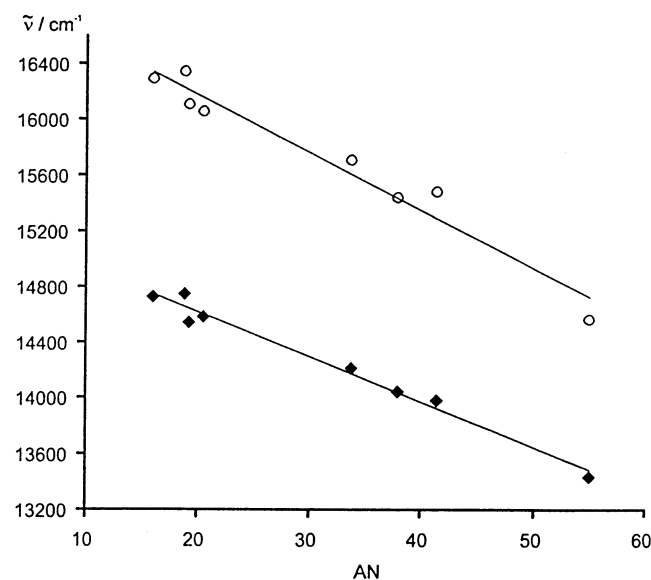


Fig. 4. Linear correlations of absorption maxima $\tilde{\nu}$ vs. AN for MLCT bands of $(\text{NEt}_4)_3[(\text{NC})_4\text{Fe}(\mu\text{-bptz})\text{Fe}(\text{CN})_4]$ (○) and $(\text{NEt}_4)_5[(\text{NC})_5\text{Fe}(\mu\text{-tz})\text{Fe}(\text{CN})_5]$ (◆).

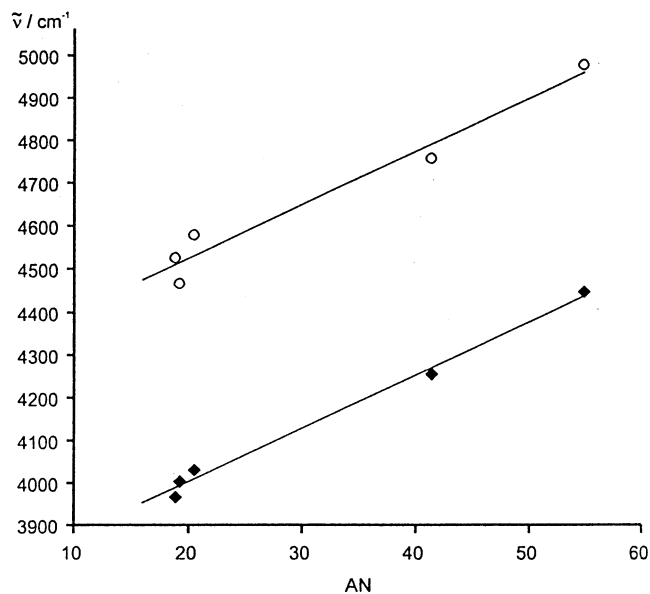


Fig. 5. Linear correlations of absorption maxima $\tilde{\nu}$ vs. AN for MMCT bands of $(\text{NEt}_4)_3[(\text{NC})_4\text{Fe}(\mu\text{-bptz})\text{Fe}(\text{CN})_4]^{3-}$ (○) and $(\text{NEt}_4)_5[(\text{NC})_5\text{Fe}(\mu\text{-tz})\text{Fe}(\text{CN})_5]^{5-}$ (◆).

Table 6) whereas the MMCT bands show a small degree of negative solvatochromic effect (Fig. 5 and Table 6).

To start with the latter, it has often been asserted [11] that completely delocalized (valence-averaged, ‘Class III’ [22]) mixed-valent complexes should exhibit no solvatochromism of their MMCT bands due to the absence of asymmetry (and thus polarity). However, the tetrazine-bridged cyanoiron complexes discussed here have high negative charges and several available Lewis-basic sites for solvent interaction (free tetrazine N atoms, CN co-ligands) so that the complete absence of any solvent effect cannot be expected. The small gradient B of only about 12 cm^{-1} (Table 6) agrees

Table 5

Absorption maxima $\tilde{\nu}^a$ of $\{(\mu\text{-bptz})[\text{Fe}^{2.5}(\text{CN})_4]_2\}^{3-}$ and $\{(\mu\text{-tz})[\text{Fe}^{2.5}(\text{CN})_5]_2\}^{5-}$ in different solvents

Solvent	AN ^b	$\{(\mu\text{-bptz})[\text{Fe}^{2.5}(\text{CN})_4]_2\}^{3-}$		$\{(\mu\text{-tz})[\text{Fe}^{2.5}(\text{CN})_5]_2\}^{5-}$	
		$\tilde{\nu}_{\text{MLCT/LMCT}}$	$\tilde{\nu}_{\text{MMCT}}$	$\tilde{\nu}_{\text{MLCT/LMCT}}$	$\tilde{\nu}_{\text{MMCT}}$
DMF	16.0	16 290	^c	14 730	^c
CH ₃ CN	18.9	16 340	4530	14 750	3970
d ₆ -DMSO	19.3	16 100	4460	14 540	4000
CD ₃ NO ₂	20.5	16 050	4580	14 580	4030
<i>i</i> -C ₃ H ₇ OH	33.8	15 700	^c	14 210	^c
C ₂ H ₅ OH	37.9	15 430	^c	14 050	^c
CD ₃ OD	41.3	15 480	4760	13 990	4250
D ₂ O	54.8	14 560	4980	13 440	4440

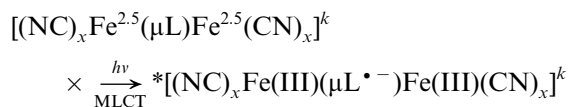
^a In cm^{-1} .

^b From refs. [1b,7] (for non-deuterated solvents).

^c Not available due to strong solvent absorption.

with the notion that these complexes have no asymmetry and hence dipole moment to produce large solvatochromism.

The MLCT excited states of the mixed-valent species



appear to be more polar than the delocalized [8,9] ground states thus resulting in positive solvatochromism. This result (Fig. 4) may also indicate a mixing of states. It is to be noted that $[(\text{NC})_4\text{Fe}(\text{III})(\mu\text{-bptz})\text{Fe}(\text{III})(\text{CN})_4]^{2-}$, also displays an intense visible band ($\epsilon_{\text{max}} = 8260 \text{ M}^{-1} \text{ cm}^{-1}$ [9]) at a wavelength ($\lambda_{\text{max}} = 656 \text{ nm}$, in MeCN [9]) which is close to that of $[(\text{NC})_4\text{Fe}^{2.5}(\mu\text{-bptz})\text{Fe}^{2.5}(\text{CN})_4]^{3-}$ ($\lambda_{\text{max}} = 610 \text{ nm}$, $\epsilon_{\text{max}} = 10 530 \text{ M}^{-1} \text{ cm}^{-1}$ in MeCN [9]) Similar observa-

Table 6

Linear correlation parameters^a for charge-transfer absorption maxima in complexes $[(\text{NC})_x\text{Fe}(\mu\text{-L})\text{Fe}(\text{CN})_x]^k$

L	Band	x	k	A	B	n	R^2
<i>Fe(II)Fe(II) systems</i>							
Tz	MLCT	5	6-	8659	54.3	6	0.954
Bptz	MLCT(1)	4	4-	19 289	146.3	8	0.969
Bptz	MLCT(3)	4	4-	11 220	67.3	8	0.980
Bptz	MLCT(4)	4	4-	8778	84.1	8	0.993
Bptz	MLCT(5)	4	4-	6680	101.0	8	0.971
Bmtz	MLCT(1)	4	4-	17 334	131.0	6	0.96
Bmtz	MLCT(2)	4	4-	11 537	20.0	6	0.71
Bpym	MLCT(1)	4	4-	17 295	105.1	6	0.958
Bpym	MLCT(2)	4	4-	10 964	96.0	6	0.956
Bpym	MLCT(3)	4	4-	9201	107.7	6	0.944
<i>Fe^{2.5}Fe^{2.5} systems</i>							
Tz	MLCT/LMCT	5	5-	15 261	-32.3	8	0.980
Tz	MMCT	5	5-	3754	12.4	5	0.993
Bptz	MLCT/LMCT	4	3-	17 009	-41.7	8	0.954
Bptz	MMCT	4	3-	4275	12.4	5	0.961

^a From equation $\tilde{\nu}_{\text{CT}} = A + B \cdot \text{AN}$ (AN: acceptor numbers; A and B in cm^{-1}). Number of data n , correlation parameter R .

tions were made for the tz complex [8]. These absorptions may include ligand field (LF) bands, with contributions from $\text{CN}^- \rightarrow \text{Fe(III)}$ LMCT (ligand-to-metal-charge transfer) transitions, as reflected in the high ϵ values such as noted previously for visible bands for the pyridine and pyrazine complexes of pentacyanoferate(III) [23]. Characteristically, a series of pentacyanoiron(III) complexes with ligands such as aminopyridines, pyrazoles or imidazoles have visible bands arising from $\text{L} \rightarrow \text{Fe(III)}$ LMCT transitions that also show positive solvatochromism due to increased dipole moment in the Fe(II) containing excited state [24,25]. We would then expect that a mixture of $\text{CN} \rightarrow \text{Fe(III)}$ LMCT and $\text{Fe(II)} \rightarrow \text{L}$ ($\text{L} = \text{tz}, \text{bptz}$) MLCT transitions in the $\text{Fe}^{2.5}\text{Fe}^{2.5}$ species will induce a solvatochromism qualitatively different from that observed for pure MLCT bands in the Fe(II)Fe(II) complexes.

Summarizing, we have shown that mono- and dinuclear cyanoiron(II) and bis(cyanoiron(2.5)) compounds with polyazine heterocyclic acceptor ligands exhibit a remarkably variable solvatochromism, both regarding the sign and the magnitude of the effect. Since some related compounds have been used as photosensitizers on semiconductor surfaces [26], the specific influence of the environment on such chromophores is of significance. In agreement with previous observations, we have found rather large negative solvatochromism of MLCT bands in dinuclear species lacking a permanent dipole moment. In addition, the positive solvatochromism of MLCT/LMCT bands and the small negative solvatochromism of MMCT bands in the valence-averaged [8,9] $\text{Fe}^{2.5}\text{Fe}^{2.5}$ systems are also remarkable.

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