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Chromotropism of coordination compounds and its applications in solution

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Abstract

Chromotropic properties of coordination varying solvent, ionic species in solution, temperature, pressure, magnetic field or light irradiation are reviewed. Structural varieties and changeabilities of coordination compounds connected with these effects are discussed. Applications of solvatochromic Lewis-acid and Lewis-base indicators are presented in some detail.

Keywords: Solvatochromism; Donor number; Acceptor number; Thermochromism; Piezochromism; Photochromism; Magnetochromism; Valence tautomerism

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1. Introduction

One of the most beautiful and exciting aspects of chemistry, in particular of coordination chemistry, is the wide range of colours compounds may have. Even more unusual still are the changes in colour brought about by chemical reactions and alteration of the physical parameters of environments.

Many substances exhibit reversible variation of colour under differing physical or chemical conditions such as temperature, pressure, light and solvent. Such reversible colour changes are collectively termed 'chromotropism'. Chromotropic phenomena may overlap. For example, it is not unusual for the same substance to exhibit both solvato- and thermochromism. However, this is not a necessary condition.

These chromotropic phenomena are detailed below with examples.

2. Solvatochromism

When dissolving simple chemical species such as iodine or some metal salts in various solvents, the extent of colour change, dependent on the choice of solvent, is sometimes surprising. An excellent review concerning such properties has been written by Reichardt [1]. Although there is a multitude of such cases, solvatochromic Lewis-acid and Lewis-base indicators, such as $[Cu(acac)(tmen)]^+$, $[Ni(acac)(tmen)]^+$, $[Fe(phen)_2(CN)_2]$ and $[Cu(acac)(tmen)Cl]$ should be mentioned [2–5]. Their structures are shown in Fig. 1, and their behaviour will be considered in detail in separate sections.

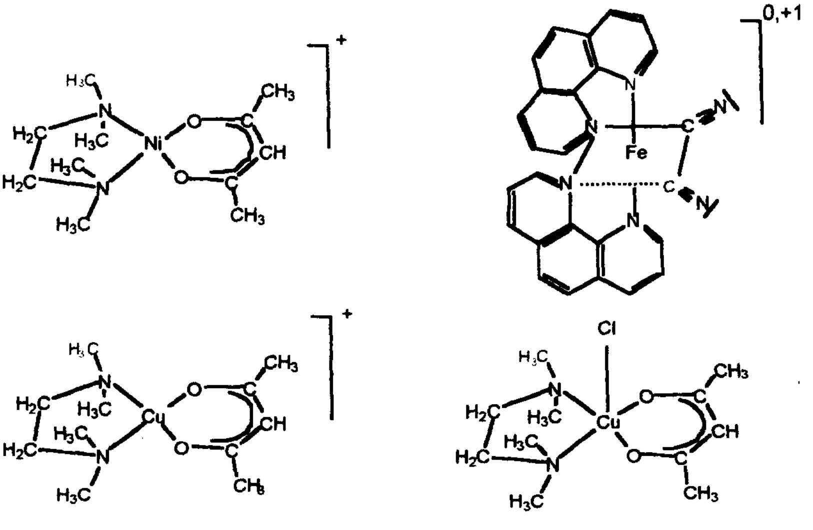
2.1. *Solvatochromism of mixed-ligand nickel(II) and copper(II) complexes*

2.1.1. *Synthesis and origin of the solvatochromism*

Mixed-ligand Ni(II) and Cu(II) complexes with β-diketonates (dike) and diamines (diam) show a pronounced solvatochromism and thermochromism.

$$[M(dike)(diam)]^+ + 2S \rightleftharpoons [M(dike)(diam)S_2]^+ \quad (M^+ : Cu^{2+}, Ni^{2+}) \qquad (1)$$

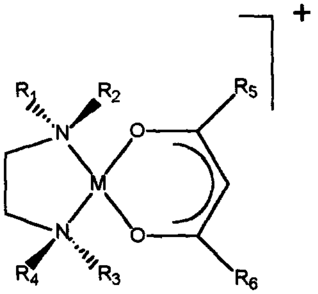
The synthesis of mixed-ligand complexes is not a trivial procedure because the formation of homogeneous ligand complexes must be suppressed. In the case of diamines [6], the alkylation of nitrogen atoms by bulky substituents prevents the stabilisation of bis- or tris-diamine complexes. If, on the other hand, another ligand is 'slim', (e.g. acetylacetonate (acac)), the corresponding complex will be stable when a mixed-ligand system is formed. In accordance with this rule the *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (tmen) ligand does not form bis-complexes with the transition metal ions of first-row transition metal elements such as Cu(II). However, the binuclear μ_2-dihydroxo-complex, $[(tmen)Cu(OH)_2Cu(tmen)]^{2+}$ is quite stable.



Indicators for Lewis Base Properties

Indicator for Lewis Acid Properties

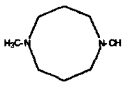
Fig. 1. Several solvatochromic complexes used as Lewis-acid–base indicators.

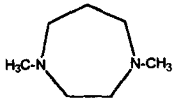


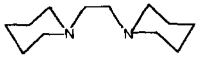
The diamin ligand carries R_1-R_4 which may be symmetric or asymmetric combinations of H, Me, Et.

Abbreviation	R_1	R_2	R_3	R_4
Tmen	Me	Me	Me	Me
Teen	Et	Et	Et	Et
Trimen	Me	Me	Me	H
trieen	Et	Et	Et	H
Sym-dmen	Me	H	Me	H
Unsym-dmen	Me	Me	H	H
Sym-deen	Et	H	Et	H
Unsym-deen	Et	Et	H	H

The diamine might also be cyclic, for example, 1,5-dimethyldiazacyclooctane (dmdaco), 1,4-dimethyldiazacycloheptane (dmdach) and dipiperidinoethane (dipe) respectively:







R_5-R_6 β-diketonate may again be symmetric or assymetric combinations of Me, ϕ, CF_3, tert-Bu, etc.:

Abbreviation	R_5	R_6
Acac	Me	Me
Bzac	Me	Ph
Dibm	Ph	Ph
Tfac	Me	CF_3
Hfac	CF_3	CF_3
Dipm	Tert-Bu	Tert-Bu

Fig. 2. Solvatochromic and thermochromic mixed-ligand [M(dike)(diam)]X complexes (M^{2+}: Ni^{2+}, Cu^{2+}; X^-: BPh_4^-, ClO_4^-, NO_3^-, halide, pseudohalide) [10] (with permission from Research Trends).

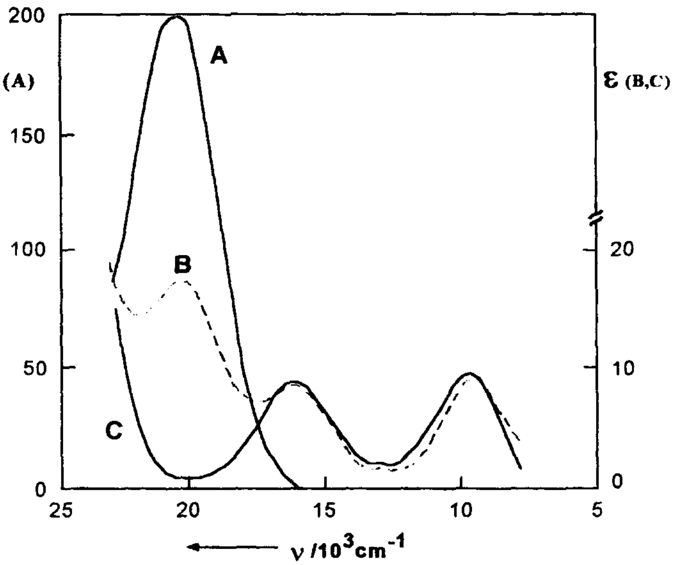


Fig. 3. UV–vis absorption spectra of [Ni(acac)(tmen)]Bϕ$_4$ in: (A) DCE; (b) acetone; and (C) DMF at 25°C [15] (with permission from Springer Verlag and authors).

Also, a number of mononuclear mixed-ligand complexes M(dike)(diam)X(Solv) can be prepared using an *N*-alkylated diamine (diam) and a β-diketone (coordinating in his first anionic form *dike*) as ligands (X represents the counter-anions such as BPh_4^-, ClO_4^-, NO_3^- and pseudohalides). A further bidentate ligand molecule ox^{2-} (oxalate) or pseudohalide might also act as coordinating anion thus forming dinuclear complexes. Solv represents a solvent molecule. Dinuclear complexes can also be formed using tetraketonates or tetramines as ligands. Fig. 2 shows a variety of complexes of the β-diketonates and diamines which have been studied in detail [2,5,7–9]. Two metal ions are of importance for such complexes, namely Ni(II) which is described in some detail in this section and Cu(II) given in Section 2.1.3. Both are solvatochromic indicators with different properties, due to their different electronic structures.

Complexes of Ni(II) and Cu(II) with tmen and diketonates are soluble in various organic solvents, which is a necessary condition to observe pronounced solvatochromism. The absorption spectra of [Ni(acac)(tmen)]BPh_4 (see Fig. 3) in solvents with different donor strength, 1,2-dichloroethane (DCE), acetone (AC) and *N*,*N*-dimethylformamide (DMF) are drastically different giving rise to the pronounced colour changes.

The colour changes associated with these spectral changes can be explained by the simplified ligand-field splitting of the d orbitals of the Ni(II) system given in Fig. 4. This also explains the change from diamagnetic to paramagnetic when going from a square-planar to an octahedral species.

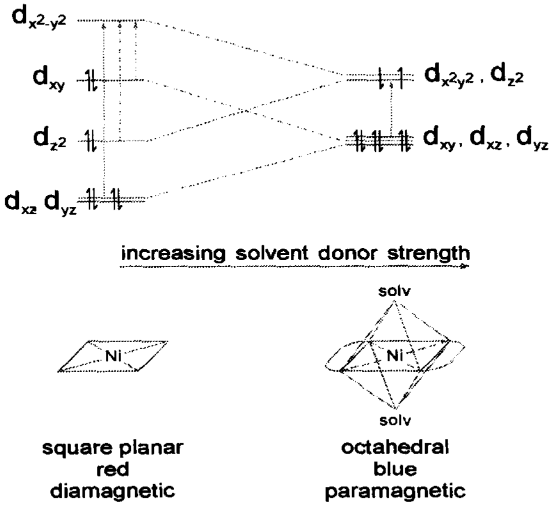


Fig. 4. Solvatochromism and thermochromism of [Ni(dike)(diam)]$^+$ complexes are due to a change from square-planar to octahedral coordination. In the case of the Ni(II) system (d^8) this leads, besides the spectral changes, to a change in the magnetic behaviour from diamagnetic to paramagnetic species [37,10] (with permission from Research Trends).

The change of colour is connected with the solvation of the complex associated with the transformation of a square-planar structure to an octahedral structure (Fig. 4). In the low-strength donor solvent, like dichloroethane, the non-solvated square-planar species dominate as the corresponding spectrum shows. On the other hand in strong donor solvents, like DMF and DMSO, this complex is almost completely solvated, i.e. only octahedral species are visible in the electronic spectrum. In solvents of intermediate donor strengths (like acetone and higher alcohols) both square-planar and octahedral species are present.

The solvation of solvatochromic Ni(II)-diamino-β-diketonate proceeds in two steps (see Fig. 5). First, a five-coordinated single solvated complex is formed. Its structure depends on the donor strength of the solvent molecule: the Ni-coordination centre is increasingly pulled out of the bis-chelate plane. At a certain critical solvent donor strength, this results in a trigonal-bi-pyramidal coordination geometry.

The second step of solvation (i.e. the formation of a six-coordinated bis-adduct) results either in a *trans*- (typical for weak donor molecules) or a *cis*-species (characteristic for strong donor systems) This complicates the application of this complex to be used as a tool for measuring Lewis-base strength, which can be overcome by using the respective Cu complex (see Section 2.1.3).

2.1.2. Structural variations of five-coordinated mixed-ligand nickel(II) complexes

N,N,N′,N″,N″-Pentamethyldiethylenetriamine (pmdt) acts as a tridentate ligand and with β-diketonate forms nickel(II) mixed complexes which are five-coordinated.

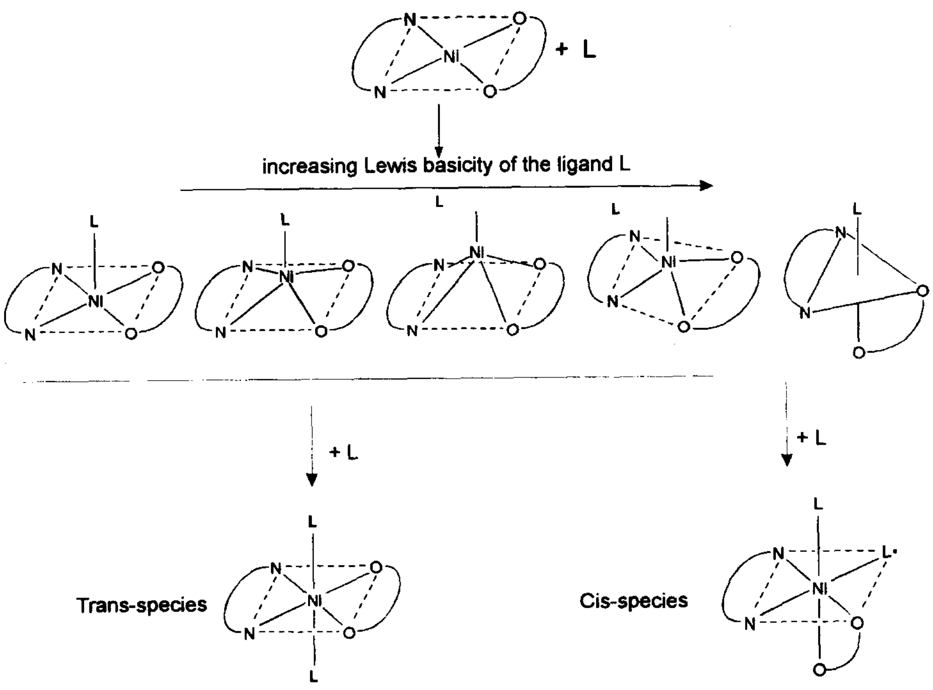


Fig. 5. The effects of donor strength (Lewis basicity) on the mode of entry of coordinated solvent molecules (L) [10] (with permission from Research Trends).

This leaves one coordination site free for interaction with a donor species like a solvent molecule. Spectra and thermodynamics of these complexes have been investigated in non-aqueous solutions [11,13].

The extinction coefficient of the absorption bands of Ni(acac)(pmdt)NO_3 for the five-coordinated species (especially the band at 620 nm) found in the weak donor solvent DCE are lower than those of the Ni(acac)(pmdt)BPh_4 complexes supporting the observation that the NO_3^- group is coordinated to the sterically hindered sixth coordination site of Ni(II). The extinction coefficients of the band at about 620 nm are almost unchanged in the presence of NO_3^- when increasing the solvents' donor strength from DCE to acetonitrile and acetone. This means that these solvents cannot replace the NO_3^- ion and is in agreement with the observation that the donor number (DN) of NO_3^- equals about 20 (see later).

The solutions in strong donor solvents like DMF and DMSO are blue and two absorption bands appear, namely near 1025 and 620 nm, indicating an octahedrally surrounded Ni-coordination centre [8]. These bands can be assigned to a $^3T_{2g} \leftarrow {}^3A_{2g}$ transition and to a $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition, respectively. The small absorption band observed for the octahedral complexes at about 800 nm may be assigned to a $^1E_g \leftarrow {}^3A_{2g}$ transition. The blue colour indicates that in solvents of high donor number a solvent molecule (L) combines with the five-coordinated chelate, and converts it into a six-coordinated chelate according to:

$$[\mathrm{Ni(dike)(pmdt)}]^+ + \mathrm{L} \rightleftharpoons [\mathrm{Ni(dike)(pmdt)(L)}]^+ \quad (2)$$

Further analysis of the UV–vis and the far-IR results indicated a structural change depending on the donor strength of the coordinating solvent molecule. Fig. 6 summarises this situation.

2.1.3. Solvatochromism of mixed-ligand copper(II) complexes

The solution behaviour of the (generally) highly soluble, analogous mixed-ligand Cu(tmen)(acac)X complexes in various solvents depends mainly on: (i) the more or less pronounced coordination of solvent molecules to the complex; and (ii) the more or less pronounced coordination of anions (X^-) to the complex [14]. Both forms of coordination lead to significant changes in the d–d transitions and to a strong change in the colour of the complexes in solution. The former effect is governed by the donor strength of the respective solvent molecules and, in fact, the observed solvatochromism can be used to visualise and to measure donor properties of solvents and even solvent mixtures.

Due to this, $[\mathrm{Cu(tmen)(acac)}]^+$ may be used as an excellent 'universal' Lewis-base indicator in solution. Anions may act similarly to Lewis bases or donor species and coordinate to the Cu complex. However, they are usually present in lower concentration than the solvent. An anion of strong donor ability, which might be expected to coordinate to the Cu complex, will nevertheless be dissociated and solvated by solvent molecules of sufficient acceptor strength.

This leads to three useful effects. Fig. 7 illustrates this situation. First, to the solvatochromism of the $[\mathrm{Cu(tmen)(acac)}]^+$. Second, to the possibility of using strong donor anions (e.g. halides), to visualise the acceptor properties of a solvent (this is based on an increasing dissociation of the anion due to its solvation by strong acceptor molecules of a solvent). Third, these effects can be combined to obtain a solvent-dependent donor number for anions.

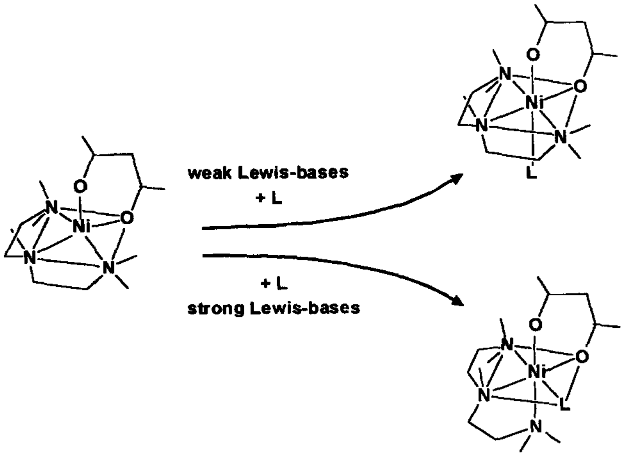


Fig. 6. Structural variation of the five-coordinated mixed-ligand Ni(II) complex [Ni(□-dike)(pmdt)]$^+$ interacting with donor molecules of different Lewis basicity [10] (β-dike).

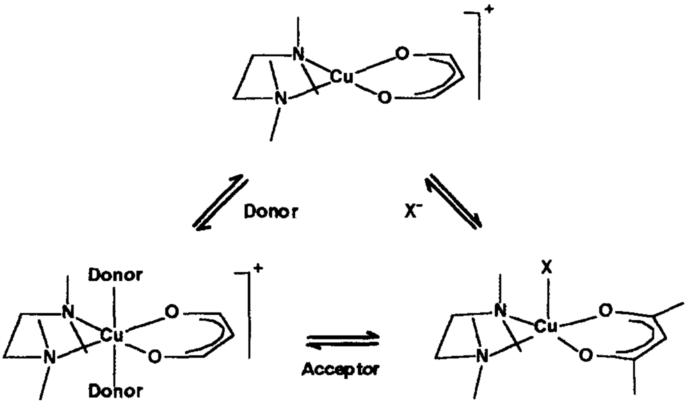


Fig. 7. Solvatochromic square-planar Cu(dike)(diam)$^+$ species are able to coordinate with donor species forming five and six-coordinated species. The former species are preferred when coordinations with anions happen, the latter occur with donor solvent molecules. The situation leads to the d-orbital splittings depicted in Fig. 10. It can be seen that the electron-transition spectra expected from both five- and six-coordinated cases are similar [10] (with permission from Research Trends).

The electronic transition scheme given in Fig. 4 can be applied to the case of Cu^{2+} noting that now a d^9 system has to be considered, which leads to paramagnetic species both for the square-planar and the octahedral case. Due to this the 'spin-barrier' present at the Ni^{2+} case vanishes and the strong Jahn–Teller ability of Cu^{2+} leads to a continuous colour change with variation of the Lewis-acid and Lewis-base interaction between the indicator and the respective ligand (see Fig. 8).

2.1.4. *The solvent-dependent behaviour of [Cu(acac)(tmen)]$^+$ halides*

In the presence of halides (Cl^-) or pseudohalides the dependence of the absorption maxima is reversed as can be seen in Fig. 9. This effect is increasingly pronounced with increasing donor number of the anion. Halogenic and pseudohalogenic complexes are practically non-electrolytes in DCE and acetone, meaning that the anions strongly coordinate to the Cu(II) coordination centre. In solvents with increasing acceptor strength, the anions become increasingly solvated leading finally to completely dissociated 1:1 electrolytes. This leads to a solvatochromism dependent on the acceptor strength of the solvent rather than on the donor strength, as was the case with the non-coordinating anions (BPh_4^- and ClO_4^-). These properties are most strongly pronounced with the Cl^- and the NCO^- complexes, which therefore can be used as indicators for the Lewis acidity of solvents.

2.2. *Structural variations of vanadylacetylacetonate*

Vanadyl(IV)-acetylacetonate ($VO(acac)_2$) is known to interact with various donor solvents, exhibiting solvatochromic behaviour (Fig. 10) [5,12,17]. The solvation reaction leads to a colour change from blue to green.

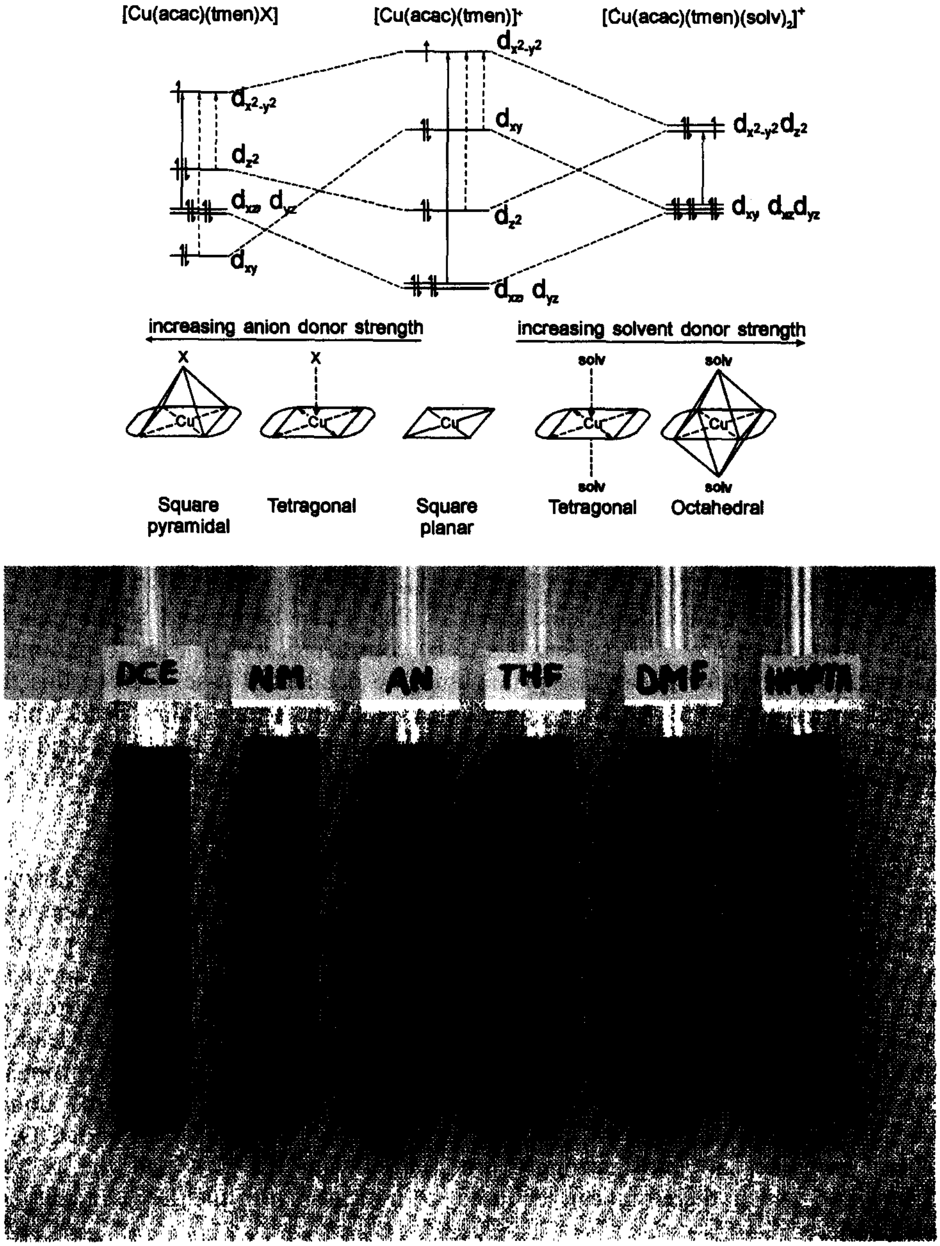


Fig. 8. Orbital schemes and associated d–d transitons of solvatochromic mixed-ligand [Cu(dike)(diam)]$^+$ complexes. In contrast to the previously described Ni analogues, the Cu species do not change their magnetic properties. No spin barrier has to be overcome and the strong Jahn–Teller effect exhibited by Cu(II) leads to a continuous colour change. Spectral changes expected for five- and six-fold coordination is similar [4] (reproduced by permission of the Royal Society of Chemistry).

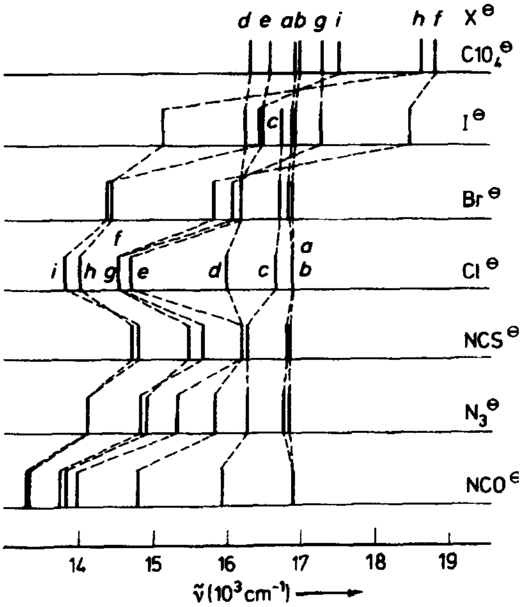
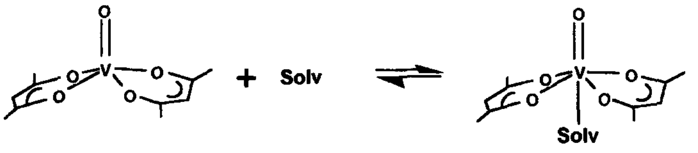


Fig. 9. Comparison of ν_{max} values of the chelates [Cu(tmen)(acac)]X (X = halide or pseudohalide ion). The data for the chelate perchlorate are also given for comparison. The symbols (a)–(i) correspond to: (a) H_2O; (b) CH_3OH; (c) C_2H_5OH; (d) DMSO; (e) DMF, (f) CH_3NO_2; (g) CH_3CN; (h) DCE; and (i) acetone. Conc.: ca. 5×10^{-3} M [5,15,16] (with permission from Springer Verlag and authors).



(I) blue

(II) green

Fig. 10. Solvatochromism of $VO(acac)_2$.

For the previous Ni(II) system, the equilibrium between the $VO(acac)_2$ and $VO(acac)_2 \cdot$ Solv becomes visible in the UV and the IR spectra. From the integral ratio of the most intense IR absorption bands arising from the $\nu_{VO_4}(A_1)$ stretching vibration of the free $VO(acac)_2$ and of the coordinated $VO(acac)_2 \cdot$ Solv species, formation constants can be calculated under the assumption that the absorption coefficient of this vibration is the same for both species. The values obtained confirm largely the values obtained by Gutmann and Mayer [18] and can be taken as a continuation of these values towards lower DN. Solutions were used where the donor solvent was diluted in CH_2Cl_2, whose DN should be close to zero, and in acetonitrile (An), whose donor number of 14.1 shows significant ability to coordinate in concurrence with other solvents to $VO(acac)_2$. For weak donor solvents ($DN < 13$) almost no frequency shift is observed. Intermediate donors ($14 < DN < 21$) show bands for uncoordinated $VO(acac)_2$ and coordinated $VO(acac)_2 \cdot Solv$. In strong donor solvents ($DN > 21$) only the band of the coordinated species is found.

The splitting of the bands (B_1) in the far-IR spectra of $VO(acac)_2$ in pyridine solution can be attributed to a *cis–trans* equilibrium in solution, as has been found in solid adducts of $VO(acac)_2$ with a series of substituted pyridines [19]. From the intensities of both peaks, we conclude that a ratio of about 2:1 for the concentrations of species (**III**) to (**IV**) is present in pyridine solutions (Fig. 11).

Through the analysis of the far-IR spectra bond angles at the coordination centre can be obtained [19–21]. From the C_{2v} symmetry of the $VO(acac)_2$ molecule, one can derive the following relationships:

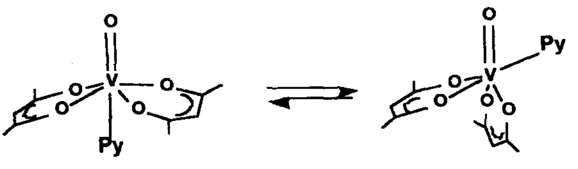
$$\frac{I_{B_2}}{I_{A_1}} = \left(\frac{\cos(\beta/2)\sin(\gamma/2)}{\cos(\beta/2)\cos(\gamma/2)}\right) = \tan^2\frac{\gamma}{2} \tag{3}$$

$$\alpha = 90 + \arcsin\left[\sin\left(90\frac{\beta}{2}\right)\sin\left(90\frac{\gamma}{2}\right)\right] \tag{4}$$

In this α is the O=V–O angle, γ the angle between the two planes including the vanadium atom and the pair of oxygen atoms belonging to an acetylacetonate molecule, and β the O–V–O bonding angle within an acac moiety, which is assumed to have invariably the same value as in the free solid $VO(acac)_2$, namely 88°. It can be expected [19] that the VO_4 moiety opens like an umbrella upon coordination of a donor molecule. For free $VO(acac)_2$ a value of 133.2° is found. This corresponds to an O=V–O angle of 106.8°, which is in good agreement with the value obtained by X-ray diffraction of 106° [22]. The results show that γ increases with increasing DN of the solvent, as expected. In the solid state the angles between the two acac planes are generally larger than in solution. The value of γ for the solid pyridine adduct is 153.5°, corresponding to an O=V–O angle of 99.5° and is in good agreement with the value obtained from X-ray diffraction ($\gamma = 159.5°$) [22].

2.3. Solvatochromism of mixed-ligand iron(II) and iron(III) complexes

The solvatochromism of $Fe(phen)_2(CN)_2$ and $[Fe(phen)_2(CN)_2]^+$ arises from the coordination of Lewis-acid molecules to the free electron pair(s) located at the



(III) **(IV)**

Fig. 11. Structural variability of $VO(acac)_2Py$.

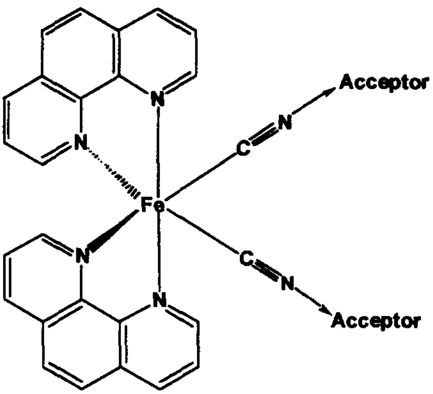


Fig. 12. Coordination of $Fe(phen)_2(CN)_2$ with acceptor molecules.

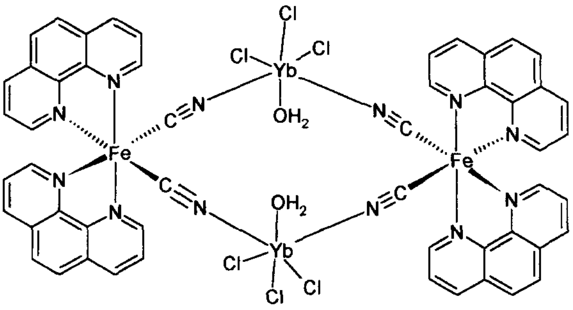


Fig. 13. Tetranuclear complex built of two $[YbCl_3(H_2O)]$ units combined with two units of $[Fe(phen)_2(CN)_2]$ [24].

N-atoms of the –CN groups (see Fig. 12) [2]. The complex itself is very stable and can be handled even in strong acid (and aqueous) solutions [23].

That coordination of $[Fe(phen)_2(CN)_2]$ as suggested in Fig. 12 occurs can be seen from the crystal structures of tetranuclear species given in Fig. 13. In this case two $[YbCl_3(H_2O)]$ units are combined with two units of $[Fe(phen)_2(CN)_2]$ via the expected interaction sites [24].

The electronic spectra (Fig. 14) show two broad bands (ν_1 and ν_2, referring to higher and lower transition energies, respectively).

Both are metal-to-ligand charge-transfer bands (MLCT), i.e. from the iron coordination centre to the π^* orbitals originating from the phenanthroline ligands (see Fig. 15). A comparison of the spectra obtained with the tris-phenanthroline species and with hexacyanoferrates lends support to this assignment, as do the results of semi-quantitative quasi-relativistic INDO calculations [25]. The latter show a large number of closely lying π^* orbitals available for such charge-transfer transitions and this explains the relatively broad nature of the bands, but at the same time, makes an exact assignment of any particular transition rather difficult.

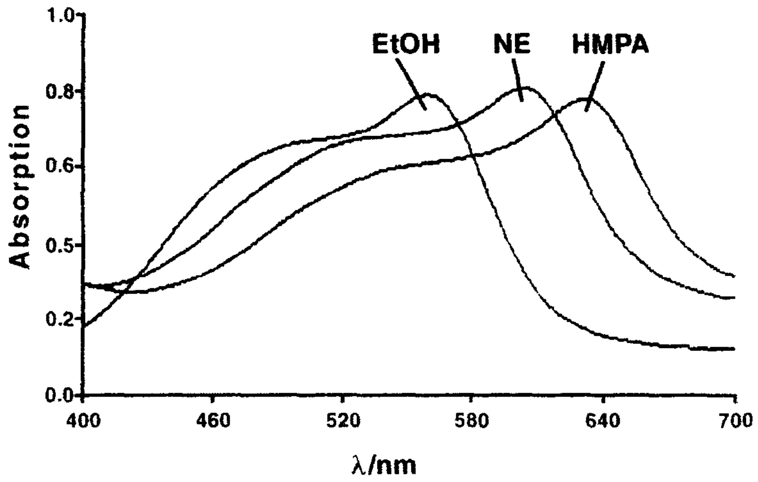


Fig. 14. Typical colours of Fe(phen)$_2$(CN)$_2$ dissolved in some solvents used with different acceptor properties for visible spectra see Fig. 19 [23] (with permission from Gordon and Breach Publishers).

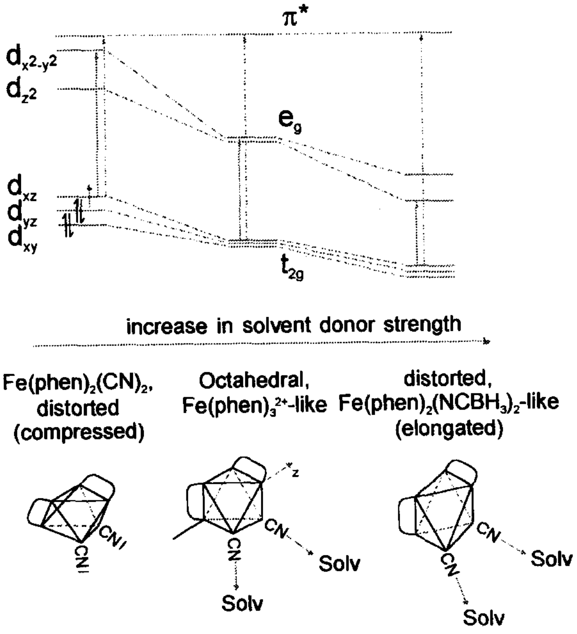


Fig. 15. Solvatochromism of Fe(phen)$_2$(CN)$_2$ and [Fe(phen)$_2$(CN)$_2$]$^+$ [52]. (used with permission from the Journal of Chemical Education, vol. 62, no. 6, 1985, pp. 459–462; ©copyright 1985, Division of Chemical Education, Inc.).

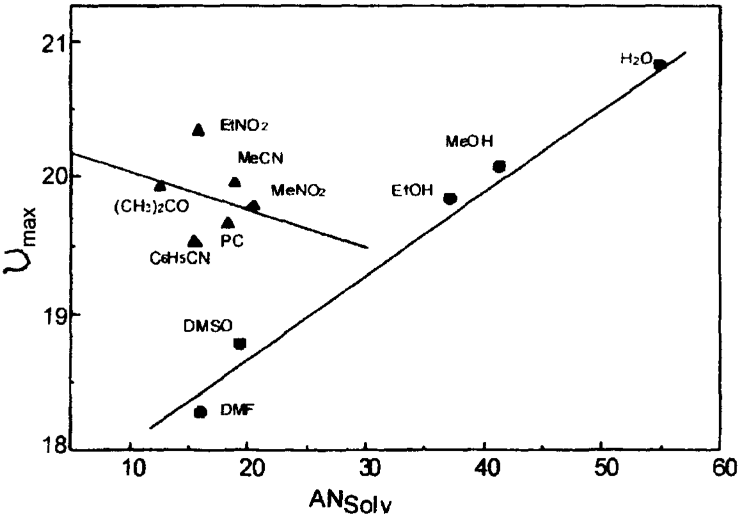


Fig. 16. Solvatochromism of $[Fe(III)(phen)_2(CN)_2]^+$ in a variety of solvents.

However, the occurrence of basically only two bands can be explained by the splitting of the t_{2g} levels into a lower-lying A_1 term and two higher-lying E terms (also described [26] as t_2^+ and t_2^-).

Electron withdrawal due to the interaction with a Lewis-acid thus leads to changes in: (i) the σ-bonding MOs (including the e_g levels of the iron), which in turn leads to a deformation of the $Fe(phen)_2(CN)_2$ itself; and (ii) the concomitant π orbitals (including the split t_{2g} levels of the coordination centre), which then influence the energetic location of the antibonding π* ligand orbitals (see Fig. 15) [23,52].

The (originally more intense) band (ν_2) observed at lower transition energies is shifted towards higher energies and decreases its intensity relative to the second observed band with increasing Lewis acidity of substrate. In fact, this leads, for strong Lewis acids, to spectra where the band observed at higher energies becomes the most intense. The band (ν_1), i.e. the band at lower wavelength, is less strongly influenced. It also shifts towards higher energies. These effects are found to be essentially the same for interactions with either solvents or cations showing significant acceptor properties. For these investigations we used the absorption bands found at higher wavelength because its shifts are more pronounced, i.e. are more sensitive to change, and the absorption maxima can be more readily identified.

By analogy to $Fe(II)phen_2CN_2$, the complex $[Fe(III)(phen)_2(CN)_2]^+$ also exhibits pronounced solvatochromism. Fig. 16 depicts the variation of the maximum respective charge-transfer absorption in various solvents.

It can be seen that most of the solvents (with the exception of DMF, DMSO, EtOH, MeOH) show reversed solvatochromism compared to the respective Fe(II)complex, i.e. the absorption frequencies decrease with increasing acceptor number (AN). Solvents with high dielectric constants like the mentioned exceptions and some others lead to the increasing wave numbers with increasing AN_{Solv} [51]. The extinction coefficients are smaller compared to the respective Fe(II) complex (in analogy to $[Fe(II)(phen)_3]^{2+}$ and $[Fe(III)(phen)_3]^{3+}$. Therefore, preferably the Fe(II) complex should be used as Lewis-basicity indicator. However, in some cases, when interactions with charged species or polar active surfaces are observed, the Fe(III) complex might be preferable (see Section 3.6).

3. Applications: use of solvatochromic dyes as indicators for acid–base properties

3.1. Estimation of donor numbers of solvents

The ν_{max} values of the d–d transition spectra of various solutions of $[Cu(acac)(tmen)]BPh_4$ have been measured for a large number of solvents [8,27] interacting with different solvent molecules reacting with the complex according to the reaction:

$$[Cu(tmen)(acac)]^+ + 2L \rightleftarrows [Cu(tmen)(acac)]L_2 \tag{5}$$

A linear correlation of the (energy related) ν_{max} values with the solvent donor numbers (DN_{Solv}) yields the following expressions:

$$\nu_{max} = 20 - 0.103DN_{Solv} \quad (r = 0.97) \tag{6}$$

or

$$DN_{Solv} = 194.18 - 9.709\nu_{max} \tag{7}$$

A collection of donor number (DN_{Solv}), acceptor numbers (AN_{Solv}) and their dielectric constants (ε) are given in Table 1. Both data based on the original definitions for DN and AN, and those obtained from measurements based on solvatochromic indicators are given when available. Some data are only accessible via solvatochromism.

It might be recalled here that the donor number of a solvent has been originally defined by Gutmann [3] according to the negative ΔH value of the coordination formation with $SbCl_5$ in DCE solution. The acceptor numbers which are given in Table 1 and which will be discussed later, are defined as the chemical shifts of the ^{31}P-NMR signal of triethylphosphineoxide dissolved in the respective Lewis acids, normalised to AN = 100 for $SbCl_5$, the original probe substance for donor number.

Obviously, it is necessary to measure the shift of the absorption maxima using weakly coordinating ClO_4^- or BPh_4^- as anions to avoid the effects of anion association.

3.2. Estimation of donor numbers of anionic species in non-aqueous solvents

Like solvents, anions are able to coordinate due to their donor properties. In addition to the interactions already known from solvents their negative charges

Table 1
Classification of solvents by donor number (DN_{Solv}), acceptor number (AN), dielectric constant (ε)[a]

Solvent	DN_{Solv}	DN_{λ}[b]	AN_{solv}	AN_{λ}[c,d]	ε[e]
Acetic acid (AcOH)		10.5	52.9	(25.7)	6.2
Acetic anhydride (Ac_2O)	10.5			16.2	20.7 (19°C)
Acetaldehyde (AcH)		18.9	13.4[f]		21.1 (21 °C)
Acetone (AC)	17.0	17.0	12.5	14.0	20.7
Acetonitrile (An)	14.1	13.2	18.9	18.9	36.0
Acetophenone (AP)		14.1		12.9	17.4
2-Aminoethanol			33.7	(26.4)	37.7
Aniline		33.3		16.7	6.9
Anisole		7.9		7.6	4.3
Benzaldehyde		13.6	12.8[f]		17.8 (20°C)
Benzene (Bz)	0	3.5	8.2	4.1	2.3
Benzonitrile (BN)	11.9	12.0	15.5	13.8	25.2
Benzyl cyanide	15.1			14.9	18.7 (27°C)
Bromobenzene (BrBz)		2.2		8.0	5.4
n-Butanol (BuOH)	220	24.0	36.8	(24.4)	17.5
t-Butanol (*t*-BuOH)	220		27.1	(16.2)	12.5
Butanone (mek)		14.3		12.9	17.9
Carbondisulfide (CS_2)	<5			1.6	2.6
Carbontetrachloride (CCl_4)	(0)	0	8.6	1.5	2.2
Chloroform ($CHCl_3$)	(0)	0	23.1	10.0	4.7
Chlorobenzene (ClBz)	(0)	2.2		8.0	5.6
Cyclohexane	(0)	0		0	2.0
Cyclohexanone	–	18.7		12.2	18.3 (20°C)
sec-butylamine	–	44.7			
di-(*sec*-butylamine)	–	45.6			
Isobutylamine	–	46.2			4.4
n-butylamine	–	45.9			4.71
t-butylamine	–	52.3			
Di-*n*-butyl ether (Bu_2O)	–	18.1		2.6	3.1
1,2-Dichloroethane (DCE)	(0)	1.5	16.7	13.6	10.1
Dichloromethane (CH_2Cl_2)	(0)	1.2	20.4	12.6	8.9
Diethylamine (Et_2NH)	≤ 50	28.6	9.4	5.2	3.7
Diethylformamide	30.9	30.9			
Diethylene glycol dimethyl ether (diglyme)			9.9	9.4	7.23
Diethyl ether (Et_2O)	19.2	18.1	3.9	4.2	4.2
Dimethoxyethane (glyme)	20	17.0	10.2	8.8	7.2
Dimethylacetamide (DMA)	27.8	28.6	13.6	15.0	37.8
3,3-Dimethylbutanone (bmk)		12.0		10.5	13.2
Dimethylformamide (DMF)	26.6	25.1	16.0	16.1	36.7
Dimethylsulfoxide (DMSO)	29.8	30.1	19.3	17.6	46.7
1,4-Dioxane (diox)	14.8	18.0	10.8	6.0	2.2
Dipropylamine		37.8			2.923
Epichlorohydrin (Epi)		12.0		12.0	22.6 (22 °C)
Ethanol (EtOH)	$\sim$20[h]	22.9	37.1	(26.6)	24.3
Ethyl acetate (EtOAc)	17.1	10.9	9.3	8.7	6.0
Ethylamine ($EtNH_2$)	55	52.2	(4.8)[f]		6.2
Ethylenediamine (en)	55		20.9		12.9
Ethyl propionate (EtOPr)		8 7[i]	6.7		5.6 (19°C)
Ethylensulfite	15.3	11.8			
n-Hexylamine	–	46.2			4.08
Formamide (FA)	24		39.8	(32.6)	109.5

Table 1 (*Continued*)

Solvent	DN_{Solv}	DN_{λ} [b]	AN_{solv}	AN_{λ} [c,d]	ε [e]
Formic acid (HCOOH)			83.6		57.9 (20°C)
Furan		4.3	3.3t		2.9
Hexamethylphosphoric triamide (HMPA)	38.8	38.1	10.6	12.3	29.6
Hexane	(0)	0		0	1.9
Methanesulphonic acid			126.3		
Methanol (MeOH)	~19 [h]	23.3	41.3	(31.2)	32.6
Methyl acetate (MeOAc)	16.5	10.3	10.7	11.2	6.7
2-(Methylamino)ethanol	–	38.3			
N-Methylformamide (NMF)	27		32.1	(29.4)	182.4
2-Methylpyridine	–	34.0			10.18
N-Methyl-2-pyrrolidinone (NMP)	27.3		13.3	14.0	33.0
Nitrobenzene (NB)	4.4	3.7	14.8	13.8	34.8
Nitroethane (NE)		5.0		15.8	28.5
Nitromethane (NM)	2.7	4.8	20.5	19.3	36.7
Octylamine	–	45.6			3.58
3-Pentanone (dek)		12.6		10.3	16.6
n-Pentylamine	–	45.9			4.27
Piperidine (Pip)	51	52.3		5.4	5.8 (22°C)
Phosphorous oxychloride	11.7		11.0 [f]		13.0
n-Propanol (PrOH)	>20		37.3	(25 0)	20.3
i-Propanol (*i*-PrOH)	>20		33.5	(22 3)	18.3
Propylene carbonate (PC)	15.1	12.9	18.3	19.7	65.0
Propionaldehyde	–	27.3			18.5
Propionitrile (PN)	16.1	13.4		16.0	27.2 (20°C)
n-Propylamine	–	45.9			5.08
Pyridine (Py)	33.1	28.2	14.2	11.5	12.3
Sulfolane (TMS)	14.8		19.2		43.3 (30°C)
Tetrahydrofuran (THF)	20.0	20.6	8.0	7.8	7.5
Tetramethylurea (TMU)	31			12.5	23.4
Toluene (To)		3.9		3.3	2.4
Tri-*n*-butyl phosphate (TBP)	23.7		9.9	10.7	7.9 (30°C)
Triethanolamine	–	24.4			
Triethylamine (Et_3N)	61 resp. 30.1	34.6	1.4	2.5	2.4
Trifluoroacetic acid	0 [j]		105.3		8.2
Trifluoroethanol [g]	0 [j]		53.5	(36 4)	26.7 (20°C)
Trifluoromethanesulfonic acid	0 [j]		129.1		
Trimethyl phosphate (TMP)	23.0		16.3	15.8	20.6 (20°C)
Water (H_2O)	18 [h]	17.0 (19.5)	54.8	(41.0)	78.4
Xylene (mixed isomers)		4.8		2.4	2.3

[a] DN_{λ} and AN_{λ} values are estimated values from spectral data of the solvatochromic indicators. Several values are only available due to the use of the solvatochromic indicators [10] (with permission from Research Trends).

[b] Calculated from $DN = -6.36 + 0.19(B^*)$ [22].

[c] Calculated from Reichardt's E_T values [28].

[d] Values in parentheses refer to highly structured solvents.

[e] Solvent dielectric constant at 25°C, except when indicated.

[f] Estimated from values of DN and ε according to $AN = -2.33 - 0.056DN + 12.73 \log \varepsilon$.

[g] Estimated from $\Delta G_{trans}(K+)$ [30].

[h] For highly structured solvents different bulk donicity is expected.

[i] Calculated from a linear relationship between $\Delta \upsilon_D$ [29] and DN.

[j] We expect values similar to CF_3CH_2OH, i.e. close to zero.

might be of importance, so that the chromotropic methods described above to estimate Lewis basicity of solvents have to be adapted, if they should be used to quantify anions properties.

A procedure, described in Ref. [23] based on the intersection of the lines representing anion-dependent and solvent-dependent colour changes leads to the definition of dependent donor numbers of anions according to:

$$DN_{x,\ Solv} = 129.6 - 0.548AN_{Solv} - 6.024\nu_{max,\ DCE} \qquad (8)$$

where $\nu_{max,DCE}$ is the absorption maxima of [Cu(tmen)(acac)]BPh$_4$ in presence of the anion. Table 2 gives donor numbers of anions in some solvents based on this equation.

In order to establish donor numbers for anions, DCE was used as a reference solvent, because this solvent was both reference and diluting solvent in the original donor number approach for solvents and its donor number was defined as equal to zero. The results, however, showed clearly (see Fig. 18) that the effective donor numbers of anions depend upon the Lewis acidities (acceptor properties) of the solvent, and that the choice of a reference solvent is extremely important.

Table 2 shows that the chosen solvent influences the observed Lewis basicity of the anion strongly: strong acceptor properties of the solvent lead to a strong solvation of the anion decreasing its donor properties towards other species. Strong donor properties of the solvent compete with those of the anion and often make their presence undetectable. Therefore Lewis basicities of anions are almost not observed in aqueous solvents, leading to the impression that only electrostatic interactions are of importance. Apparent donor numbers for anions that lie well below the donor number of the solvent itself (DN_{Solv}) are given in *italics* and imply that the anions exhibit no donor properties towards hard acceptors in this particular solvent.

On the other hand, for a given anion, for Cu(tmen)(acac)X (halides might be used advantageously) Eq. (8) may be rewritten in a form convenient for the estimation of acceptor numbers of a solvent using the following relationship with a strongly coordinating anion X:

$$\nu_{max,Solv} = \nu_{max,DCE} + 0.063DN_{Solv} + 0.091(AN_{Solv} - 16.7) \qquad (9)$$

In the case of $X^- = Cl^-$ this yields, for example:

$$AN_{Solv} = 137.14 - \nu_{max,\ Solv} - 1.055DN_{Solv} \qquad (10)$$

Numbers in bold refer to solution in DCE, i.e. they are donor numbers on same scale as Gutmann's donor numbers for solvents. Brackets indicate that this ion may exhibit donor properties in this solvent.

Fig. 17 show free energies of transfer of anions from water to various solvents, plotted versus the respective donor numbers of the anion in DCE (i.e. the reference solvent for the originally defined donor number) and the donor numbers associated with the solvent used, respectively.

By using solvent-dependent donor numbers the linear relationship between the free energies of transfer all fall together in one line (Fig. 17), showing the importance of taking the respective solvent properties into account.

Table 2
Donor numbers (DN_X) of anions and apparent donor numbers of anions dissolved in various solvents ($DN_{X,Solv}$), calculated from Eq. (9) [4] (reproduced by permission of the Royal Society of Chemistry)[a]

Anion	DCE	NM	An	Ac	H_2O	MeOH	EtOH	DMF	DMSO
$B\phi_4^-$	**0.00**	*−2.07*	*−1.20*	*2.31*	*−20.9*	*−13.6*	*−11.6*	*0.39*	*−1.42*
BF_4^-	**6.03**	[3.95]	*.83*	*8.33*	*−14.8*	*−7.56*	*−5.69*	*.42*	*.61*
ClO_4^-	**8.44**	*6.36*	*7.24*	*.7*	*−12.4*	*−5.15*	*−3.18*	*8.83*	*.02*
CO_3^{2-}	**13.3**	11.2	*.1*	*1 .6*	*−7.62*	*−0.33*	*.64*	*.6*	*1 .8*
$CF_3SO_3^-$	**16.9**	14.8	[15.7]	[19.2]	*−4.00*	*3.29*	*.26*	*.3*	*1 .5*
NO_3^-	**21.1**	19.0	19.9	23.4	*0.21*	*7.50*	*.47*	*.5*	*1 .7*
CN^-	**27.1**	25.0	25.9	29.4	*.24*	*13.5*	*1 .5*	[27.5]	*25.7*
I^-	**28.9**	26.8	27.7	31.2	*8.04*	*15.3*	*1 .3*	29.3	*27.5*
Ac^-	**29.5**	27.4	28.3	31.8	*8.65*	*15.9*	*1 .9*	29.9	[28.1]
SCN^-	**31.9**	29.9	30.7	34.2	*11.1*	*18.3*	[20.3]	32.3	30.5
Br^-	**33.7**	31.7	32.5	36.0	*12.9*	[20.2]	22.1	34.1	32.3
N_3^-	**34.3**	32.3	33.1	36.6	*13.5*	20.8	22.7	34.7	32.9
OH^-	**34.9**	32.9	33.7	37.2	*14.1*	21.4	23.3	35.3	33.5
Cl^-	**36.2**	34.1	34.9	38.5	*15.3*	22.6	24.5	36.5	34.7
NCO^-	**40.4**	38.3	39.2	42.7	[19.5]	26.8	28.8	40.8	38.9
DN_{Solv}	0.0	2.7	14.1	17.0	19.5	19.1	19.0	26.6	29.8
AN_{Solv}	16.7	20.5	18.9	12.5	54.8	41.5	37.9	16.0	19.3

[a] Numbers in bold refer to solution in DCE, i.e. they are donor numbers on same scale as Gutmann's Donor Numbers for solvents. Brackets indicate that this ion may exhibit donor properties in this solvent.

3.3. Estimation of the acceptor numbers of solvents

The method used above to evaluate the donor numbers of anions in aqueous and non-aqueous solutions was based on a comparison of the solvatochromic shifts of some mixed-ligand Cu(II) complexes in various solvents in the presence and absence of anionic species. This has encouraged us to apply an analogous method in order to establish acceptor numbers [3] of cations in solution [4]. It is surprising that attempts to measure the Lewis acidity of cations are so rare, since many cations play an important role as catalysts in many chemical reactions, and it is clear that they do this predominantly in terms of their ability to act as electron-pair acceptors.

There are quite a large number of solvatochromic dyes [1,2,5,23,29,31] exhibiting Lewis basicity which might be potential candidates for evaluating the acidities of cations. One attempt by Reichardt et al. to measure these properties based on the 'Halo-solvatochromism' of betaines should be mentioned here because the E_T parameters are closely related to the acceptor numbers developed here [32]. Unfortunately only a few cationic species were investigated, they showed strongly pronounced but non-linear concentration dependencies.

However, $Fe(phen)_2(CN)_2$ is known to be applicable to the evaluation of Lewis acidities of solvents in terms of AN [3], and it therefore appeared to be a suitable candidate for a Lewis acidity indicator when attempting to establish acceptor numbers for cations in solution [23]. Compared to the betaines mentioned above it might also have the advantage of being itself a stronger Lewis-base and, more

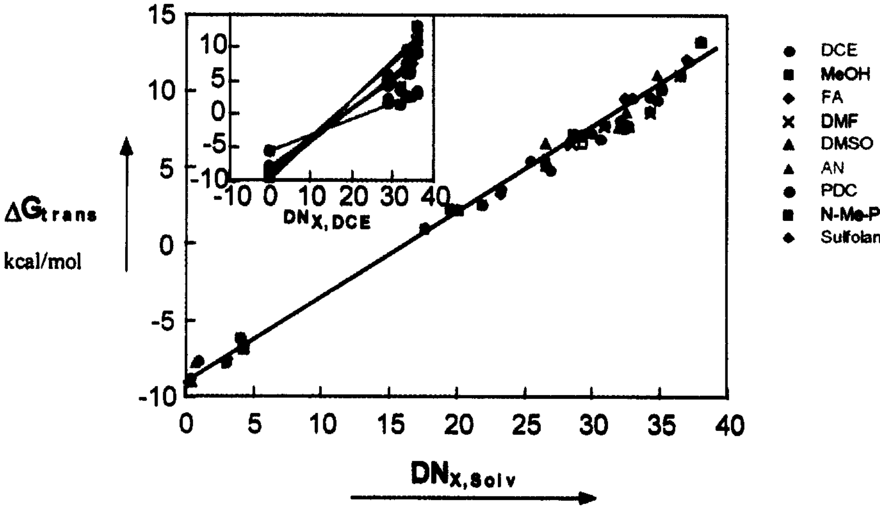


Fig. 17. Free energies of transfer (ΔG_{trans}) of various anions ($B\phi_4^-$, I^-, Br^-, SCN^-, Cl^-) from water to various solvents versus the donor number of the anion in 1,2-dichloroethane ($DN_{X,DCE}$), given in the insert, and versus the donor number of the anion in the respective solvent $DN_{X,Solv}$ [4] (reproduced by permisssion of The Royal Society of Chemistry).

important, interacting more specifically with Lewis-acid centres such as cationic species.

A linear relationship [23] between the maximum absorption frequency ν_2 of $Fe(phen)_2(CN)_2$ and the acceptor number of the respective solvents has been established (see Fig. 17), and a linear regression analysis of all values available yields:

$$\nu_{max,Solv} = (15.2 + 0.073AN_{Solv}) \times 10^3 \quad (r = 0.991) \tag{11}$$

$$AN_{Solv} = 13.09 \times 10^{-3}\nu_{max,Solv} - 197.45 \tag{12}$$

Concerning the evaluation of Lewis acidities based on the solvatochromic properties of an appropriate indicator, the associated donor–acceptor interaction differences between Reichardt's $E_T(30)$ scale [1,28] (based on the solvatochromic shift of betaines), and Gutmann's AN scale [3] (based on the shift of the ^{31}P-NMR chemical shift of Et_3PO in the respective solvent), should be mentioned. Although these solvent parameters are considered to be linearly related, a detailed analysis [32] yields five different groups of solvents each showing solute–solvent mechanism and being characterised by their functional groups: for example hydroxylic and non-hydroxylic solvents, aromatics, amines, etc. This becomes visible when plotting the absorption maxima of $Fe(phen)_2(CN)_2$ versus the E_T parameters as shown in the insert of Fig. 18. A similar effect is found for the solvatochromism of molybdenum and tungsten diimine–carbonyl analogues, where — using E_T parameters — the difference in the behaviour of hydroxylic and non-hydroxylic solvents becomes strongly visible [32]. These observations have been discussed in detail on the basis of solvato-and thermochromic results on betaines and using isokinetic relationships as a tool for separating different interaction mechanisms [9]. The splitting into several groups of solvents arises from the induction of increased acceptor properties in acceptor molecules when interacting with the strong donor molecule Et_3PO [32].

Because cationic species are expected to be relatively strong acceptors it can be assumed that the AN scale will reflect the Lewis acidity of these species better and therefore it has been used exclusively. Fig. 18 shows clearly that in a plot of $\nu_{max,Solv}$ versus AN the deviation from linearity needed for the following analysis is indeed negligible. The data are, of course, readily re-scaled to the E_T scale if preferred, but this is only really straightforward when 'well-behaved solvents' [32] are used.

3.4. Estimation of the acceptor number of cationic species in non-aqueous solvents

In the presence of cations $Fe(phen)_2(CN)_2$ exhibit similar colour changes as observed for different solvents (see Fig. 19).

The main characteristics of these changes are the same as those due to solvent differences, including the variation of relative extinction and distance between the two observed absorption maxima (see Fig. 20).

The observed spectral changes due to the presence of cations depend also on the anion (due to their Lewis basicity described by their $DN_{X,Solv}$ values [23]), and on the concentration of the metal ions. In order to minimise any possible variation due

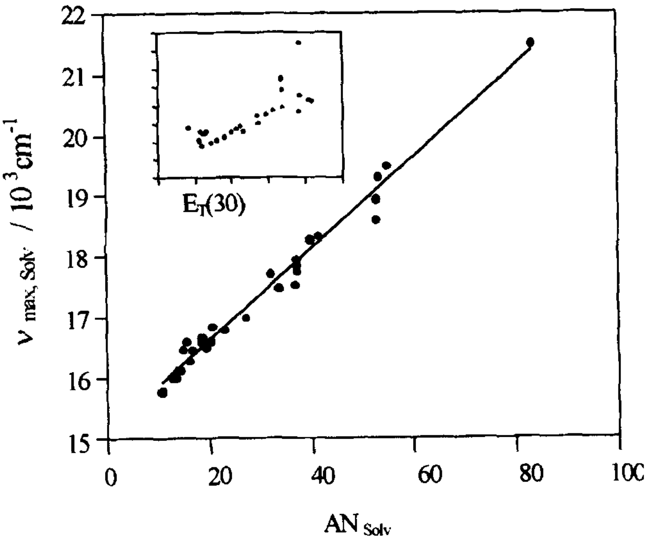


Fig. 18. Linear relationship between the absorption maxima (ν_2) of Fe(phen)$_2$(CN)$_2$ versus the acceptor number (AN). A plot of these values versus E_T is given in the insert [23] (with permission from Gordon and Breach Publishers).

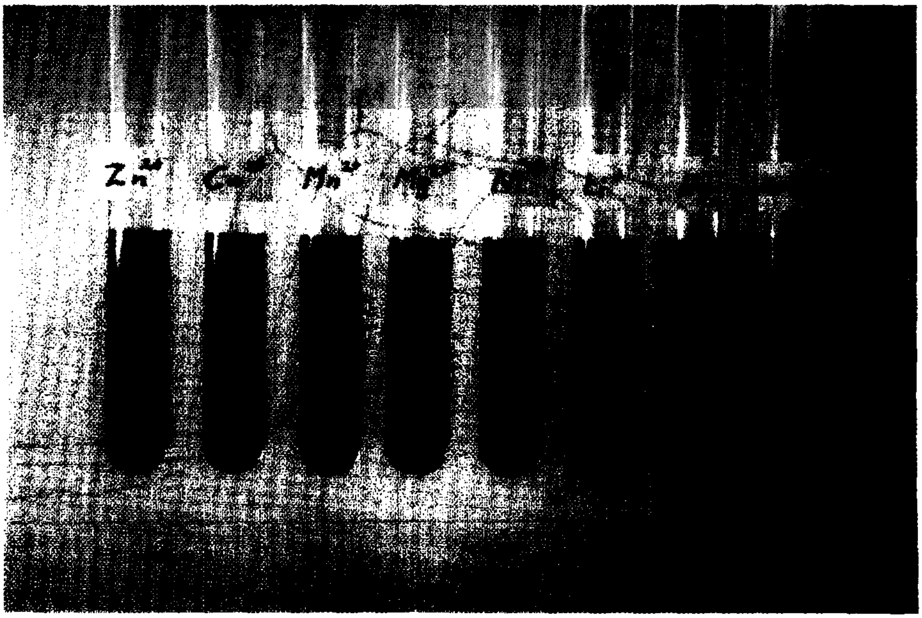


Fig. 19. Colours of [Fe(phen)$_2$(CN)$_2$] in nitromethane (NM) in the presence of various cations. The Lewis acidity of the cations decreases from left to right.

to the anion, metal cations were added in the form of their perchlorates. (Because in most cases the addition of water had minimal effects on the shift, some of these salts could be used as hydrates.)

The absorption maxima of $Fe(phen)_2(CN)_2$ measured in the presence of a cation in a given solvent, in general, show two distinct parts. These are:

(A) a *solvent-only dependent part* showing negligible influence of the dissolved cation and for which a more or less parallel line to the abscissa is found. In this case, the solvent is interacting with the indicator alone, because it is either a significantly stronger Lewis-acid than the cationic species, or the solvent is a Lewis-base strong enough to solvate the cations to the extent that the Lewis-base properties of the indicator are not able to interact with the anion. In this case, however, solvated species might themselves shift the absorption of the indicator.

With the increasing Lewis acidity of the cation, however, this interaction leads to changes resulting in a *cation-dependent part* (B), where cations with increasing acceptor properties shift the absorption maxima to higher energies. The shifts in this cation-dependent part are parallel to the shifts obtained with respect to the reference solvent.

3.4.1. Concentration dependence

As expected, the variation of the concentration of the cation within the former group has little or no effect on the shifts in absorption maxima originating from the interaction between $Fe(phen)_2(CN)_2$ and solvent.

For the *cation-dependent part*, when either direct or solvent separated interactions are involved, concentration again has little effect on the shifts. Thus, after an excess

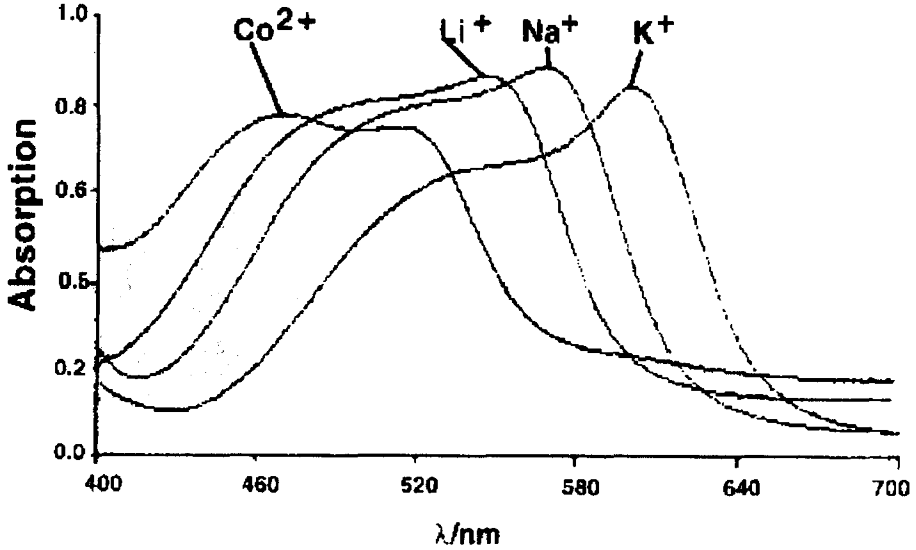


Fig. 20. Typical spectra of $Fe(phen)_2(CN)_2$ in NM in the presence of K^+, Na^+, Li^+ and in Co^{2+} perchlorates (right side) [23] (with permission from Gordon and Breach Publishers).

of the concentration of metal ion over that of the $Fe(phen)_2(CN)_2$ has been arrived the shift of the absorption maxima reaches a limiting value (usually arrived at before a fivefold excess), and it is these limiting values that are used for the analysis below. However, a strong dependence of the absorption maxima (derived by a titration curve) is found for cations lying near the point of intersection of *solvent* and *cation-dependent parts* exhibited in the plot of the absorption maxima in the reference solvent versus those in the other solvent. Here also, much larger concentrations of cations were required to reach the limiting value.

We should also consider two concurrent interactions: (i) acceptor properties of the solvent *and* of the cation are competing for the donor site located at the –CN groups; and (ii) donor properties of the solvent and donor properties of the –CN groups are both competing to coordinate with the cation. Both effects can be taken into account by the application of Eq. (13) in which nitromethane (NM) is used as a reference solvent:

$$(\nu_{\mathrm{M,Solv}} - \nu_{\mathrm{M,NM}}) = A(\mathrm{AN}_{\mathrm{Solv}} - \mathrm{AN}_{\mathrm{NM}}) + B(\mathrm{DN}_{\mathrm{Solv}} - \mathrm{DN}_{\mathrm{NM}}) \quad (13)$$

On taking $\mathrm{AN}_{\mathrm{NM}} = 20.5$ and $\mathrm{DN}_{\mathrm{NM}} = 2.7$, the data fit Eq. (13) (with $r = 0.960$)

$$\nu_{\mathrm{M,Solv}} = \nu_{\mathrm{M,NM}} - 5.62(\mathrm{AN}_{\mathrm{Solv}} - 20.5) - 48.7(\mathrm{DN}_{\mathrm{Solv}} - 2.7) \quad (14)$$

The intersection point of the solvent and cation-dependent parts (see Table 3) for each solvent implies apparently equal acceptor numbers of the solvent and the respective cation at this position and therefore the following equation applies:

$$\mathrm{AN}_{\mathrm{M,Solv}} = 0.0122\nu_{\mathrm{M,NM}} - 0.595\mathrm{DN}_{\mathrm{Solv}} - 181 \quad (15)$$

Eq. (15) enables acceptor numbers for cations dissolved in various solvents to be calculated and values for the solvents used in this investigation are listed in Table 3 We estimate these values to be accurate within some ±2–5% (due to the relatively imprecise evaluation of the coefficients in Eq. (15)). Values that are smaller than the respective acceptor numbers of the solvents are in *italics*, because they might be of conceivable significance for kinetic investigations (where even weak-coordinative interactions may be of importance).

As shown in Table 3 the apparent acceptor numbers depend on both the donor and acceptor properties of the solvent. But this has only to be expressed, because as we have pointed out before donor and acceptor properties cannot be completely described by independent parameters due to their mutual interactions [23]. Such difficulties in the quantitative description of the observed properties of solutions lead to interesting new developments in our understanding of liquid systems [33].

3.4.2. The problem of the reference solvent

The choice of a reference solvent for the determination of acceptor numbers for cations is less straightforward than for the determination of donor numbers for anions: the acceptor numbers of solvents are defined as the relative ^{31}P chemical shift of the 1:1 solvent adduct of Et_3PO in the *particular solvent*, with *n*-hexane as the reference solvent required to define $\mathrm{AN}_{\mathrm{Solv}} = 0$ [3]. But *n*-hexane is a solvent in which ionic species are scarcely soluble and it could not, therefore, be used for these

Table 3

Apparent acceptor numbers of cations ($AN_{M,Solv}$) in various solvents calculated using Eq. (15) with NM as reference solvent [a]

Cation	NM	Acetic acid	MeCN	PC	AC	H_2O	MeOH	THF	EtOH	DMF	DMSO	HMPT
Bu_4N^+ [b]	34.5	*29.9*	27.7	27.1	26.0	*25.4*	*2 .8*	24.2	*24.2*	20.3	[18.4]	[13.0]
NA^+	35.3	*30.6*	28.5	27.9	26.8	*26.2*	*2 .6*	25.0	*25.0*	21.1	[19.2]	[13.8]
K^+ [b]	38.6	*33.9*	31.8	31.2	30.0	*29.4*	*2 .9*	28.3	*28.3*	24.3	22.4	17.1
Li^+	44.6	*39.9*	37.8	37.2	36.0	*35.5*	*3 .9*	34.3	*34.3*	30.3	28.4	23.1
Ba^{2+}	50.7	*46.0*	43.9	43.3	42.1	*41.6*	[41.0]	40.4	40.4	36.4	34.5	29.2
Mg^{2+}	54.3	*49.7*	47.5	46.9	45.8	*45.2*	44.6	44.0	44.0	40.1	38.2	32.8
Ni^{2+}	57.1	[52.5]	50.3	49.7	48.6	*48.0*	47.4	46.8	46.8	42.9	41.0	35.6
Mn^{2+}	62.4	57.7	55.6	55.0	53.9	*53.3*	52.7	52.1	52.1	48.1	46.2	40.9
Ce^{3+} [b]	63.3	58.7	56.6	56.0	54.8	[54.2]	53.6	53.1	53.1	49.1	47.2	41.9
Co^{2+}	66.4	61.8	59.6	59.0	57.9	57.3	56.7	56.1	56.1	52.2	50.3	44.9
Fe^{2+}	69.0	64.3	62.2	61.6	60.4	59.9	59.3	58.7	58.7	54.7	52.8	47.5
Cu^{2+}	71.0	66.4	64.2	63.7	62.5	61.9	61.3	60.7	60.7	56.8	54.9	49.6
Cr^{3+} [b]	75.4	70.8	68.6	68.0	66.9	66.3	65.7	65.1	65.1	61.2	59.3	53.9
Fe^{3+}	79.0	74.4	72.3	71.7	70.6	70.0	69.4	68.8	68.8	64.9	63.1	57.7
Zn^{2+}	79.8	75.2	73.0	72.4	71.3	70.7	70.1	69.5	69.5	65.6	63.7	58.3
Solvated metal ions [c]								51	37	50		
DN	2.70	10.5	14.1	15.1	17.0	18.0	19.0	20.0	20.0	26.6	29.8	38.8
AN	20.5	52.9	18.9	18.3	12.5	54.8	41.5	8.0	37.9	16.0	19.3	10.6

[a] The solvents are sorted according to increasing donor number. Values of metal ions which do not shift the absorption spectrum of $Fe(phen)_2(CN)_2$ in the respective solvent are omitted (numbers in square brackets refer to acceptor numbers only marginally differing from those of the solvent itself.) [23] (with permission from Gordon and Breach Publishers).

[b] THF as reference solvent.

[c] Estimated values for solvated species of Ni^{2+}, Mn^{2+}, Co^{2+} and Zn^{2+}; see text.

investigations. A reference solvent should fit in with the following (contradictory!) requirements: on the one hand both its donor number and its acceptor number should be as low as possible, whereas on the other hand both donor and acceptor properties must be sufficient to allow solubilities high enough to approach a characteristic limiting shift of the absorption maxima of the $Fe(phen)_2(CN)_2$ adduct.

For the present approach we have, in fact, adopted nitromethane (NM) as diluting and reference solvent, because NM not only exhibits low acceptor properties ($AN_{Solv} = 20.5$; even lower than those of cations such as NBu_4^+ which are commonly considered as being very weak acceptor species), but it also has donor properties strong enough to provide reasonable solubility of perchlorate salts (these donor properties are, of course, much smaller than those of the indicator system). At the same time, the presence of even weak acceptor cations leads to a shift of the absorption maxima of the $Fe(phen)_2(CN)_2$. Because, however, not all the cations investigated were sufficiently soluble in this solvent, we also had to make use of the corrected values obtained in tetrahydrofuran (THF). In analogy to the above procedure, it is possible to establish equations for the use of other reference solvents. For the other reference solvent (*Ref*) for example THF or anything else, Eqs. (13)–(15) can easily be adapted using the donor and acceptor numbers of the respective solvent.

3.4.3. Interaction of solvated metal ions

In the case of some transition-metal ions and solvents an apparently constant displacement from the solvent-only dependent part (e.g. Ni^{2+}, Mn^{2+}, Co^{2+} and Zn^{2+} in DMF and DMSO; Mn^{2+}, Co^{2+} in EtOH) is observed. This can be explained by assuming that in these cases the *solvated* species are coordinated to the indicator by an outer sphere mechanism, i.e. the cations are separated from the indicator by a solvent molecule. In this case, the central metal ion of the solvate serves to modify the acceptor properties of the solvent in a manner dependent (practically) only on the charge on the cation yielding the observed 'independence' from the cation (in fact, we estimate that these species have an effective acceptor number of 37, 50 and 51 for DMF, DMSO and EtOH, respectively (see Table 3)). This shows that ionic species are able to change the acceptor properties of solvent molecules drastically.

3.4.4. Comparison with formation constants of metal ion–EDTA complexes

If they are valid, then the apparent acceptor numbers for cations obtained by this spectrographic method might be expected to correlate with the complex formation constants of the cations in any solvent. The relationship, for example, between the acceptor numbers and the log(stability constants) of various cations with ethylendiamine-*N*,*N*,*N*',*N*'-tetraacetic acid (EDTA) in aqueous systems shows a highly satisfying linear correlation [23].

3.4.5. Comparison with Gibbs free energies of transfer of metal ions from water to organic solvents

Marcus [34] has reported a purely theoretical method of evaluating the Lewis acidities of cations. The method is based on the application of:

$$\Delta_{tr}G^\circ = -(3.26\Delta\pi^*_S + 3.72\Delta\beta_S)z^2/r + 530\Delta\alpha_S\sigma - 3.78\Delta\beta_S R_D \tag{16}$$

$$= \text{other terms} - (3.72z^2/r + 3.78R_D)\Delta\beta_S \tag{17}$$

Eq. (16) is simplified to Eq. (17) in which $\Delta_{tr}G^\circ$ is the standard molar Gibbs free energy of transfer of a given ion from water to a non-aqueous solvent (in kJ mol^{-1}), z the ionic charge, r the ionic radius (nm), R_D the ionic molar refraction (cm^3 mol^{-1}), σ the softness, $y = (4\pi/3)r^3$, $\Delta\alpha_s$ is the hydrogen bond activity and $\Delta\beta$ is the difference of the Kamlet–Taft electron-pair donicities (basicities) of the solvent and water and $\Delta\pi^*_S$, the differences of the polarity/polarisability of the solvent and water. This can be written in the form of the following equation where the α_+ are the 'pseudosolvatochromic' parameters of cations giving their Lewis acidity [35]:

$$\Delta_{tr}G^\circ_i = \text{other terms} - 43.8\alpha + \Delta\beta \tag{18}$$

Linear regression then yields expression (19) for the acceptor number of the reference solvent NM. Despite the quite different approaches employed the values show good agreement [23]:

$$\mathrm{AN}^{\mathrm{Marcus}}_{\mathrm{M,NM}} = 27.7 + \alpha \tag{19}$$

3.4.6. The effect of the anion on the acceptor numbers of cations

The anion's influence relates clearly to the donor properties of anions in various solvents. There is always competition between the indicator's, the solvent's, and the cation's acceptor properties towards the anion (see Table 4) and therefore, in general, increasing the donor properties of the anion (and, of course, the solvent), decreases the apparent acceptor properties of a cation and hence, lowers the observed shift in the cation-dependent region. We relied, therefore, on the values obtained for perchlorates in order to establish unambiguous acceptor numbers for cations.

Despite some difficulties such as solubilities and the presence of solvent-separated interaction with the indicator species, this method of obtaining acceptor numbers for cationic species is extremely easy to apply, and it enables the acceptor properties of cations to be described on the same scale as the acceptor numbers for solvents. Furthermore, the comparison with theoretical and thermodynamical data shows that it indeed reflects the acceptor properties with satisfying precision. This acceptor number scale for cations might find widespread application, for example in studies of metal-ion containing substrates used as catalysts.

Table 4

Acceptor numbers of cations in the presence of anions based on absorption maxima of $Fe(phen)_2(CN)_2$ dissolved in various solvents in the presence of saturated solutions of metal species added as non-perchlorate salts

Cation	Anion	THF	PC	HMPA	EtOH	DMSO	Aceticacid	Formicacid	H_2O
Ag^+	NO_3^-	65.9	59.8	87.7	78.3	68.4			43.0
NH_4^+	NO_3^-	24.2	35.0		44.1	30.9			
Ca^{2+}	NO_3^-	61.3	53.1		49.9	38.0	48.0		
Sr^{2+}	NO_3^-		34.6			34.7			
Pb^{2+}	NO_3^-	72.1	64.4	70.2	59.2	50.4	46.4		
Cd^{2+}	NO_3^-	60.5	61.8	75.4	60.6	77.1	62.1		
Fe^{3+}	NO_3^-				79.3		96.4	76.6	
La^{3+}	NO_3^-	54.5	57.4		58.4	34.0	47.1		43.0
Ce^{4+}	NO_3^-	82.1	54.3		62.3		159.0		
Pr^{3+}	NO_3^-	60.5	58.2		55.9	27.6	44.6		43.0
Cu^+	Cl^-		75.7	77.2	62.3	60.7	62.1		
Fe^{2+}	Cl^-	87.7	82.9	85.8	58.0	67.6	52.3		66.1
Hg^{2+}	Cl^-	60.8	59.8	89.0					
Hg_2^{2+}	Cl^-	24.8	31.6						
Sn^{2+}	Cl^-	76.3	79.0	83.0	84.0	70.0	118.2		
Al^{3+}	Cl^-			106.2	80.8		111.3		
V^{3+}	Cl^-	78.2	61.8	71.9	88.8	66.9			
Ru^{3+}	Cl^-	116.2			116.9		118.2		
$NbCl_5$		106.1	105.7		73.8	83.8	100.5	75.2	
$ZrOCl_2$		93.5	68.7		76.2	40.0	105.9		57.6
$VO(acac)_2$		103.8			126.0				
$Sn(CH_3)_3Cl$						63.8		34.2	

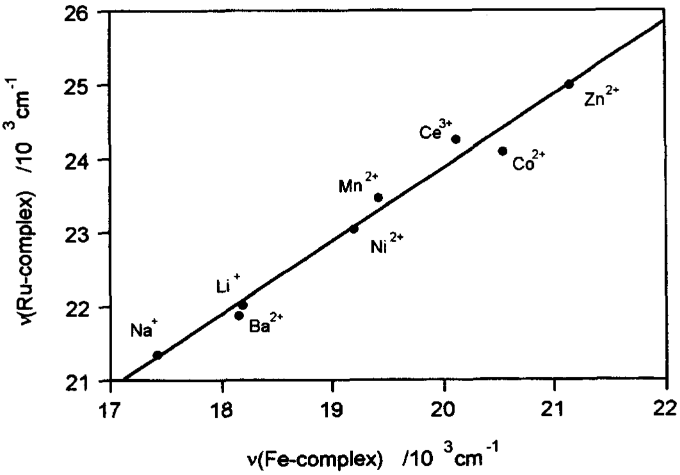


Fig. 21. Absorption maxima in the spectra of $Ru(phen)_2(CN)_2$ versus those in the spectra of $Fe(phen)_2(CN)_2$ in the presence of different cations in acetonitrile. $\nu_{Ru} = 0.991\nu_{Fe} + 4040$ ($r = 0.991$) [23] (with permission from Gordon and Breach Publishers).

3.5. Solvatochromism of ruthenium complexes

The analogous complex $Ru(phen)_2(CN)_2$ shows similar absorption MLCT spectra as its Fe(II) analogue, again associated with two main bands around 400–500 nm, the lower wavelength one appearing as a shoulder [23,24].

The frequency of the absorption maxima measured in some 15 solvents behave analogous to those of $Fe(phen)_2(CN)_2$ and were also found to be linearly related to the AN of the solvent (Eqs. (20a) and (20b)).

$$\nu_{\max,\ \text{Solv}} = (18.6 + 0.090\text{AN}_{\text{Solv}}) \times 10^3 \quad (r = 0.986) \qquad (20a)$$

$$\text{i.e. } \text{AN}_{\text{Solv}} = 0.011\nu_{\max,\ \text{Solv}} - 206 \qquad (20b)$$

A plot of the absorption maxima obtained with $Ru(phen)_2(CN)_2$ versus those obtained using $Fe(phen)_2(CN)_2$ for a series of cations dissolved in acetonitrile (see Fig. 21) illustrates the validity of the method. Similar linear relationships are found for all the investigated solvents exhibiting cation effects.

3.6. Estimation of the donor and acceptor properties of active surfaces

Many active surfaces, including surfaces of heterogenic catalysts exhibit important acidic and basic properties. In many cases they can be visualised using the acid–base indicators given above. For example UV–vis absorption spectra of these have been used to characterise surface properties of silicates [35] in various solvents and solvent mixtures like *N*,*N*-dimethylacetamide–lithium chloride (DMA–LiCl) and in cellulose–DMA–LiCl solutions [36].

Fig. 22 shows $[Fe(phen)_2(CN)_2]^+$ dissolved in pure acetonitrile with and without the presence of silica with an activated surface. The Fe(III) species of the indicator has been used, because of its stronger adsorption properties on the silica surface.

Fig. 23 gives an overview of possible investigations dealing with changes of surfaces in the presence of solvents, cations and anions. Solvents, ions and the indicators themselves are able to coordinate to the surface in a direct as well as in a separated mode.

The resulting solvatochromic shifts (ν_{max}) of the indicators reflect the corresponding properties of the surroundings, the dipolarity/polarisability (π^*), the Lewis acidity (α) and the Lewis basicity (β), respectively. This is expressed by linear solvation energy relationships (LSER) by Kamlet and Taft:

$$\nu_{max}(\text{indicator}) = \nu_{max,Ref} + s\pi^* + a\alpha + b\beta \tag{21}$$

Gutmanns donor and acceptor numbers (DN and AN), Kamlet–Taft α, β, and π^* and Reichardt's $E_T(30)$-polarity parameters are reported for cellulose, DMA–LiCl and cellulose–DMA–LiCl solutions for the first time. Cellulose, DMA–LiCl and the cellulose–DMA–LiCl solutions approach a similar polarity with an $E_T(30)$ parameter of about 52–53 kcal mol^{-1}. Knowledge of the individual parameters α, β, and π^* for cellulose and DMA–LiCl allows a detailed classification of specific

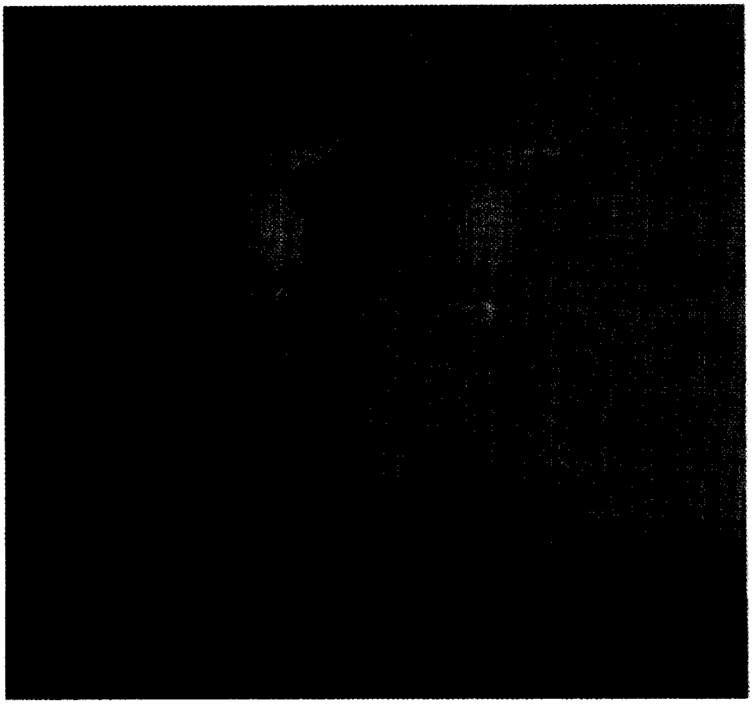


Fig. 22. $Fe(phen)_2(CN)_2^+$ dissolved in pure AN (left side) and in the presence of surface active silica (kindly supplied by S. Spange).

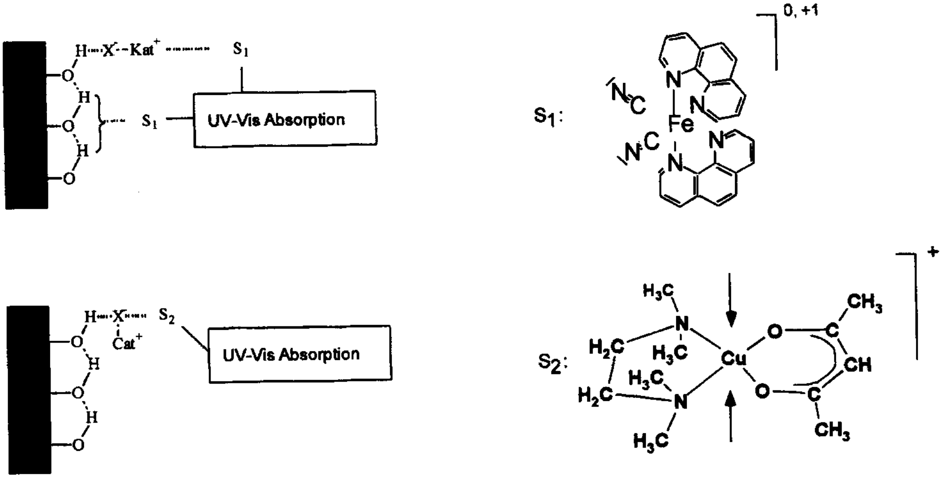


Fig. 23. Estimation of donor and acceptor properties of active surfaces and their interaction with cations and anions by means of solvatochromic indicators (kindly supplied by S. Spange).

and non-specific interactions being responsible for dissolving cellulose in DMA–LiCl. The specific interaction strength parameter (acid–base interactions, dipolar–dipolar interactions) between cellulose and DMA–LiCl are calculated by means of the individual Kamlet–Taft parameters α, β, and π^* of cellulose and DMA/LiCl via a multiparameter equation. The specific chloride–cellulose interaction plays a dominant role in the cellulose solvent DMA–LiCl as well as cooperative effects. Comparison of polarity parameters of DMA–LiCl with other solvent combinations than DMF–LiCl, DMA–NaCl or DMA–LiBr are discussed [35,36].

4. Thermochromism

The compound [Ni(acac)(tmen)]$^+$ exhibits strongly pronounced thermochromism. The acetone solution of this complex changes colour from red to green upon cooling. The origin of both the solvatochromic and thermochromic behaviour of this complex lies in the reversible exothermic reaction (1) given above (see Fig. 4) [2,5,37].

In case of the Ni^{2+} complexes the solvatochromism occurs depends on two specific species in contrary to the Cu^{2+} case, where the effect of the variable Jahn–Teller distortion is predominant. The former case therefore exhibits more or less pronounced thermochromism dependent on the chosen solvent.

Variation of temperature shifts the equilibrium of the solvation reaction (1) (see also Fig. 4) because of its exothermic character, so that solutions of intermediate donor strength solvents also exhibit thermochromism. For example [Ni(acac)(tmen)]$^+$ solutions in acetone and higher alcohols change their colour from green to red upon heating (see below Fig. 24).

The combination of solvatochromic and thermochromic properties of these compounds has been investigated from the point of view of their ability to act as Lewis-acid and Lewis-base indicators. The equilibrium constants of the nickel system have been measured for both diketonate and diamine ligands with varying substituents. The data on the temperature dependence of these equilibrium constants thereby allowed a detailed analysis for isokinetic and isoequilibrium relationships (IKR, IER) [38,39].

4.1. Thermochromism of spin-crossover compounds

Spectacular changes in the colour of coordination compounds upon cooling/heating are also observed in *spin-crossover* compounds [40,41]. In this case, however, the thermochromism is due to a completely different process: the change of spin state of the metal ion from low spin to high spin via thermal excitation of electrons. Typical representatives of this class of compounds are various complexes of Fe(II). Under certain conditions these complexes can also show piezochromism and photochromism (see Sections 5 and 6) originating from the transitions between low-spin and high-spin states induced by pressure and light. Fig. 25 shows the temperature variations in the absorption spectrum of a methanol solution of the spin-crossover complex $Fe(bzimpy)_2(ClO_4)_2$.

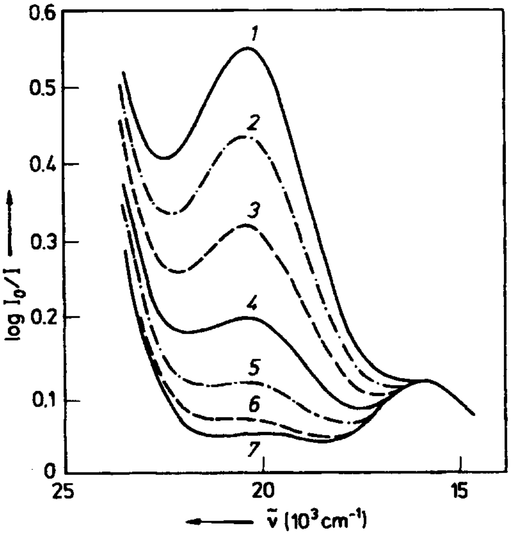


Fig. 24. Absorption spectra of $[Ni(dike)(diam)]ClO_4$ in *n*-PrOH (*n*-propanol) at various temperatures: (1) 73; (2) 67; (3) 59; (4) 47; (5) 36; (6) 25; (7) 11°C, Conc. — 1.63×10^{-3} [5,37] (with permission from Springer Verlag and authors).

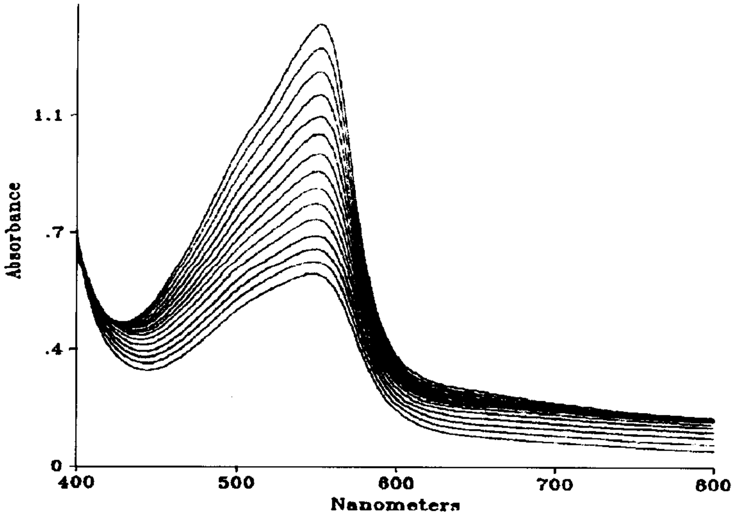


Fig. 25. Thermochromism of Fe(bzimpy)$_2$(ClO$_4$)$_2$ dissolved in methanol (from top to bottom: t = 50, 45, 40, 35, 30, 25, 20, 18, 14, 10, 5°C).

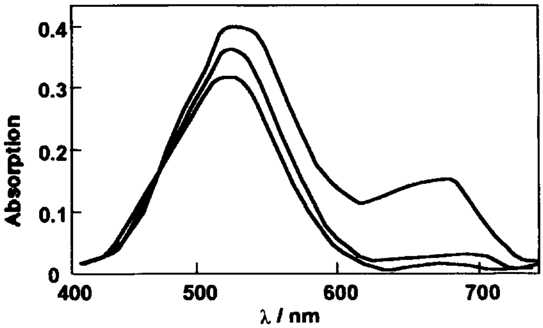


Fig. 26. Piezochromism of CoCl$_2$ in methanol at (from top to bottom) 1 × 10^3, 2 × 10^3, and 4 × 10^3 atm [5] (with permission from Springer Verlag and authors).

5. Piezochromism

The simple compound CoCl$_2$ presents an interesting combination of solvato-, thermo- and piezochromism. The solutions of CoCl$_2$ in acetone, and DMSO are dark blue, but they are pink in water and bluish violet in methanol, thus exhibiting solvatochromism.

The *piezochromism* of methanol solutions of CoCl$_2$ reveals itself in a pronounced dependence of their absorption spectra on pressure (see Fig. 26). The colour changes from blue to pink with increasing pressure.

Interestingly, the methanol solution of $CoCl_2$ becomes pink when cooled to about 0°C, while the ethanol solution needs cooling down to about −80°C before it exhibits a pink colour. However, the acetone solution of this compound does not show any visible changes of colour upon cooling. The thermochromism of solutions of $CoCl_2$ depends therefore on the actual solvent used (see Fig. 27) [42].

All three chromotropic phenomena observed in these solutions originate from the anion dissociation reaction:

$$\underset{\text{blue}}{[CoCl_2(S)_2]} + 4(S) \rightleftharpoons \underset{\text{pink}}{[CO(S)_6]^{2+}} + 2Cl^- \text{ (solvated)} \tag{22}$$

The reaction is exothermic and the associated ionisation (dissociation) process is favoured at low temperatures. Pressure shifts this equilibrium because the volume of solvent molecules in the solvation shells of the ions is smaller than the volume of free molecules. Thus, increasing the pressure shifts the equilibrium (22) to the right and turns the solution pink. In the case of acetone solutions, the acceptor property of the solvent is rather weak and instead of a solvation–dissociation reaction, an auto-ionisation reaction occurs [2]:

$$\underset{\text{blue}}{[CoCl_2(S)_2]} + 2(S) \rightleftharpoons \underset{\text{blue}}{[CoCl_3(S)]^-} + \underset{\text{pink}}{[CoCl(S)_5]^+} \tag{23}$$

One of the two resulting species (tetrahedral $[CoCl_3S]$) has a much higher extinction coefficient than the other ($\varepsilon_{tet} \cong 1000$ versus $\varepsilon_{oct} \cong 10$), therefore the blue coloration prevails and no colour change is observed.

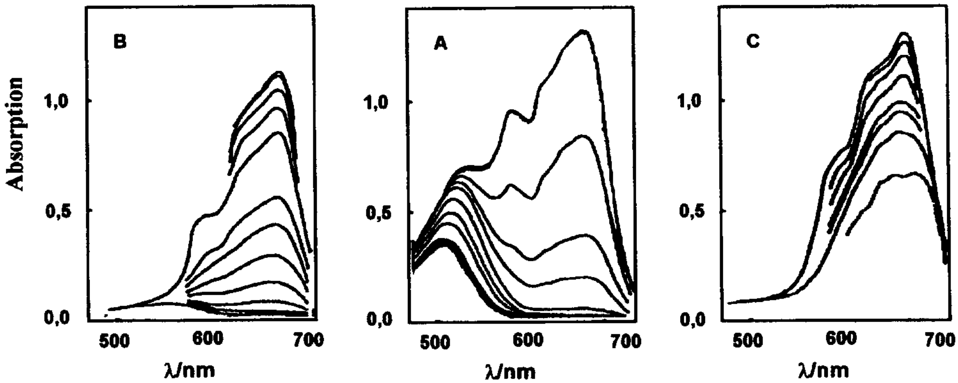


Fig. 27. Absorption spectra of $CoCl_2$ in (at various temperatures from top to bottom): (A) methanol (50, 42, 30, 20, 0, −20, −37, −70°C); (B) ethanol (62, 54, 45, 34, 23, 7, −10, −20, −30, −40, −55°C); and (C) *sec*-butanol (26, −20, −30, −40, −50, −54, −59, −78°C) [5] (with permission from Springer Verlag and authors).

6. Chromotropic phenomena involving photochromism, valence tautochromism and magnetochromism

6.1. Photochromism

Application of light can also lead to a reversible change in colour. Photochromism can be exemplified by Co(III) complexes with NO_2^-. This anion is ambidentate, i.e. it can be coordinated via the nitrogen atom as well as via the oxygen atom(s). The conversion from N-bonding to O-bonding in $[Co(NH_3)_5(NO_2)]$ is induced by light, yielding a change of colour. The process is reversed by heating [2]:

$$\underset{\text{orange}}{[\mathrm{Co(NH_3)_5(NO_2)}]} \underset{\text{temperature}}{\overset{h\nu}{\rightleftharpoons}} \underset{\text{red}}{[\mathrm{Co(NH_3)_5(ONO)}]} \tag{24}$$

Spin-crossover compounds exhibit photochromism under certain conditions. This effect is connected with the trapping of a metastable high-spin state at low temperatures by the excitation of the ground ($^1A_1$) state by a laser light of the wavelength 514 nm (green), to the higher lying singlet ($^1T_2$ or a $^1T_1$) states, with a subsequent relaxation into a paramagnetic $^3T_2$ or a $^5T_2$ state. At low temperatures (below 50 K, $kT < \Delta E_{HL}$), the relaxation to the ground state is very slow and the excited high-spin state is stable can, however, also be converted into the $^1A_1$ state by irradiation at another wavelength (red). These phenomena are described as light induced electron spin-state trapping (LIESST) in Fig. 28 [40–42].

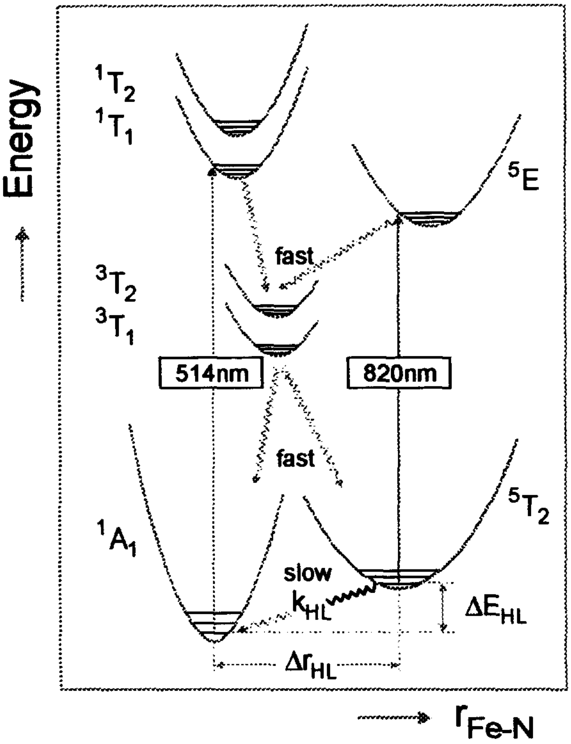
6.2. Magnetochromism

Several systems have been described above, which involve changes of their magnetic moments parallel to their colour changes. The solvatochromic and thermochromic mixed-ligand Ni complexes and spin-crossover complexes are examples. This raises the question, whether it is possible to induce visible colour changes due to variations of an applied magnetic field. A simple estimation shows that quite high fields are necessary to shift such equilibria. It can be estimated as an upper limit that 1 μ_B under an applied field of 1 T changes the associated equilibrium less than a temperature change of 1 K. Experiments have been performed by using a high-field pulse magnet and a fibre optical spectrometer by Varret and coworkers [44,45] confirming the order of magnitude of these effects. In other words, colour changes due to the change of the magnetic field are hardly visible with systems available today.

6.3. Valence tautochromism

Valence tautomerism involves an intramolecular reversible electron transfer between a reversibly oxidisable ligand and a reversibly reducible central metal ion.

In systems where thermodynamic and electronic effects are favourable, equilibria between valence tautomers, differing in charge distribution between ligand and



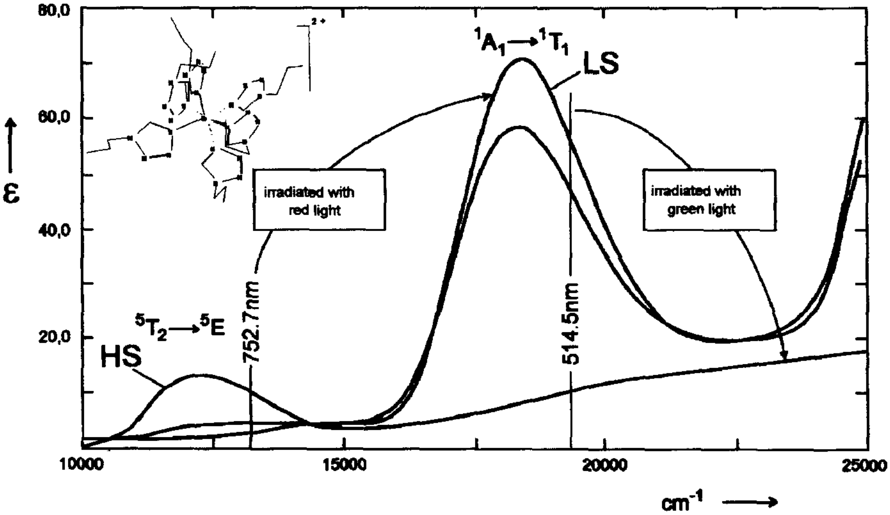


Fig. 28. LIESST effect of $Fe(ptz)_6(BF_4)_2$ at 10 K (ptz = 1-*n*-propyltetrazole). $Fe(ptz)_6(BF4)_2$ a spin-crossover compound exhibiting strongly pronounced, sharp thermally and optically excited spin transitions. The spin-crossover is visualised by a colour change from white (HS) to violet (LS) occurring around 130 K. Green light changes low-spin states to high-spin states. Red light reverses this process [41] (with permission from Springer Verlag and authors).

metal, may be observed in solution and in the solid state. In effect, these systems show thermally induced metal–ligand electron transfer properties under equilibrium conditions.

A unique feature of the quinone complexes is their ability to reversibly transfer electrons between ligand and metal under thermal conditions [46]. Many investigations of metal–quinone electron transfer in transition metal complexes (Mn and Co) have been carried in the last decade. Pierpont and co-workers [47] reported some observations on transition metal complexes containing semiquinonate (sq) and catecholate (cat) ligands chelated to Mn and Co. Equilibria between redox isomers (Eqs. (25a) and (25b)) has been observed by monitoring temperature-dependent changes in the electronic spectrum and magnetism [43,46].

$$\mathrm{Co^{III}(N\text{–}N)(sq)(cat)} \Leftrightarrow \mathrm{Co^{II}(N\text{–}N)(sq)_2} \tag{25a}$$

$$\mathrm{Mn^{II}(N\text{–}N)(sq)_2} \Leftrightarrow \mathrm{Mn^{III}(N\text{–}N)(sq)(cat)} \Leftrightarrow \mathrm{Mn^{IV}(N\text{–}N)(cat)_2} \tag{25b}$$

N–N is an ancillary chelating bidentate N-donor co-ligand bonded to the metal to give complex molecules as the *trans* isomers. The equilibria have been found to be extremely sensitive to the properties of this co-ligand [46].

Equilibria between valence tautomer occur in separate electron transfer and spin-transition steps converting from the low-spin centre metal at low temperatures to its high spin at high temperatures in a process that may be viewed as a charge-transfer induced spin transition.

Therefore, two fundamental conditions appear to be determinant for valence tautomeric equilibria. First, ligand-field effects must be such that metal–quinone electron transfer occurs with facility. Secondly, entropic changes are necessary for temperature-dependent shifts in component concentration [48].

Quinone complexes of copper do not present any electron-transfer equilibrium [47,49]. This is due, in part, to the different structural preferences of the metal and the large barrier to intramolecular electron transfer for planar Cu(II) and tetrahedral Cu(I).

Even quinone complexes of iron that are related to the Mn and Co complexes described above fail to undergo similar shifts in charge distribution [50].

There also exist polynuclear mixed-valence clusters that are tautochromic. We should note here $[\mathrm{Mn^{II}(3,5\text{-di-tert-butyl-1,2-benzoquinone})_2}]_4$ [47].

7. Conclusions

We hope to have given an insight into the interesting and strongly developing field of variations of colours due to changes in the molecular environment of chemical species. Beside attractive visible effects these properties might be applied to characterise and quantise molecular interactions, but also for technical problems like fast and safe storage of information and optical devices.

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