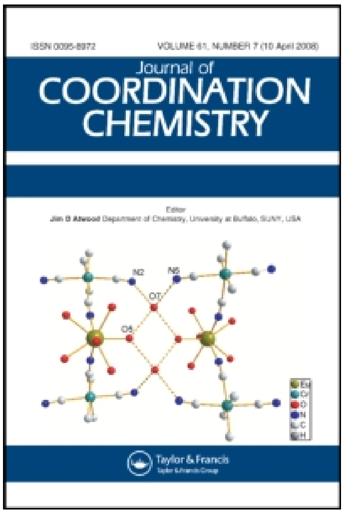

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# ESTIMATION OF THE ACCEPTOR NUMBERS OF CATIONS BY MEANS OF AN ACID-BASE INDICATOR*

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The shift of the visible charge-transfer absorption bands of $Fe(phen)_2(CN)_2$ in various solvents resulting from the interaction of solvent molecules or of cationic species with the free electron pair on the -CN group(s) has been investigated and the results have been used to establish Acceptor Numbers ($AN_{M,NM}$) for cations, $M^{n+}$, dissolved in solvents of low donicity. Nitromethane (NM) has been used as a reference solvent because it is both a very weak donor and a relatively weak acceptor solvent. (The solvent must exhibit *some* donor and acceptor properties in order to ensure solubility of the cationic species and the $Fe(phen)_2(CN)_2$ indicator.) Apparent Acceptor Numbers ($AN_{M,solv}$) for cations dissolved in various solvents other than nitromethane are also given and used to show that the acceptor properties of cations vary in a way directly related to the Donor Number of the solvent (*i.e.*, a decrease in the effective Acceptor Number of the cations is observed with increasing $DN_{Solv}$. This arises from competition between solvent and acceptor ion for the $Fe(phen)_2(CN)_2$ used as the Lewis-acid indicator). Results are compared with the spectroscopic shift of the analogous complex $Ru(phen)_2(CN)_2$. The relationship between the proposed AN scale for cations and other practical and theoretical measurements of the Lewis acidity of cations is discussed.

*Keywords:* Lewis acid-base indicators; $Fe(phen)_2(CN)_2$; non-aqueous solvents; solvated species

In a recent paper[1] we proposed a method of evaluating Donor Numbers of anions in aqueous and nonaqueous solutions. The approach was based on a comparison of the solvatochromic shifts of some mixed-ligand Cu(II) complexes in various solvents in both the presence and absence of anionic species; this has encouraged us to apply an analogous method in order to establish Acceptor

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[*] Dedicated to Prof. Dr. mult. Victor Gutmann on the occasion of his 75th birthday.

[†] Author for correspondence.

Numbers[2] of cations in solution. It is surprising that attempts to measure the Lewis acidity of cations are so rare, since cations play an important role as catalysts in many chemical reactions and it is clear that they act predominantly in terms of their electron pair acceptor properties.

There is a large number of solvatochromic dyes[3–7] which might be potential candidates for evaluating acidities of cations.[3] One attempt by Reichardt *et al.*[4] to measure these properties based on the 'halo-solvatochromism' of betaines should be mentioned here because the obtained $E_t$ parameters are closely related to the Acceptor Numbers used in the present paper. Unfortunately only a few cationic species were investigated, these showing strongly pronounced but non-linear concentration dependencies.

However, another solvatochromic compound, $Fe(phen)_2(CN)_2$, is known to be applicable to the evaluation of Lewis acidities of solvents in terms of Acceptor Numbers[2] (AN), and it therefore appeared to be a suitable candidate for a Lewis acidity indicator in order to establish Acceptor Numbers for cations in solution. Compared to the above mentioned betaines it might also have the advantage of being itself a stronger Lewis base and, more importantly, interacting more specifically with Lewis acid centres such as cationic species.

## EXPERIMENTAL

Chemicals were obtained from Aldrich, Alfa Inorganics, Ventron, Fluka, Loba Feinchemie, Merck, and Riedel de Haen. Solvents were purified using standard methods.[8] The water content of the solvents used (except the ketones) was shown to be below 190 mg/l by means of Karl-Fischer titrations. $Fe(phen)_2(CN)_2$ was prepared according to the method of Schilt[9] and dried *in vacuo* for several hours at 35°C.

Electronic spectra were obtained with a Cary 17D spectrophotometer (Varian Instruments) using 1 cm quartz cells at room temperature and with a Hitachi U-2000 spectrophotometer fitted with a cell having a path length of 3 cm and thermostated by a Haake F4 thermostat.

Stock solutions of $Fe(phen)_2(CN)_2$ were prepared in different solvents and further stock solutions of the perchlorate salts were prepared in the corresponding solvents. Stock solutions of the perchlorate salts and the $Fe(phen)_2(CN)_2$ complex in the same solvent were mixed in an appropriate way with a micropipette in order to obtain a four- to ten-fold concentration ratio of cation to $Fe(phen)_2(CN)_2$ complex the ratio of the concentration of cation to $Fe(phen)_2(CN)_2$ complex in a given solvent was constant for different cations. Higher concentrations of cations were sometimes required and these cases are noted in Table I and their significance discussed below.

TABLE I Absorption maxima ($\nu_{max,solv}$/ $10^3$ cm$^{-1}$) of Fe(phen)$_2$(CN)$_2$ dissolved in various solvents in the presence of metal cations added as perchlorate salts

| *Cation* | *NM* | *NE* | *THF* | *MeCN* | *PC* | *AC* | *HMPA* | *MeOH* | *EtOH* | *DMF* | *DMSO* | *acetic acid* | *formic acid* | *$H_2O$* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| — | 16.95 | 16.53 | 16.00 | 16.67 | 16.69 | 16.23 | 15.75 | 18.28 | 17.89 | 16.34 | 16.53 | 18.94 | 24.39 | 19.53 |
| $Bu_4N^+$ | | | 17.06 | | 16.69 | | 16.10 | | 17.83 | | 16.56 | 19.01 | | |
| $K^+$ | 16.95 | 16.53 | 17.39 | 16.67 | [d] | 16.23 | | [d] | 17.89 | 16.34 | 16.56 | 19.34 | | |
| $Na^+$ | 17.86 | 17.64 [c] | 17.64 | 17.42 [f] | [d] | 17.27 [f] | 16.75 | 18.28 | 17.89 | 16.34 | 16.56 | 19.23 | | |
| $Li^+$ | 18.62 [d] | 18.48 | 17.79 | 18.18 [f] | 17.95 [f] | 17.86 [f] | 16.18 | 18.28 | 17.80 | 16.34 | 16.56 | 19.19 | | 19.53 |
| $Ba^{2+}$ | 19.12 [d] | 18.87 [b] | 18.05 | 18.15 [f] | 16.69 | 16.29 | 16.67 | 18.28 | 17.89 | 16.34 | 16.56 | 18.98 | | |
| $Mg^{2+}$ | 19.42 | 19.42 [d] | 19.08 | 19.01 | 18.79 | 18.66 | 17.18 | 18.42 | 18.55 | 16.34 | 16.56 | 19.34 | | |
| $Ni^{2+}$ | 19.65 | 19.57 | 19.12 | 19.19 | 19.16 | 18.94 | 18.52 | 18.87 | 18.66 | 17.89 | | 19.61 | | 19.65 |
| $Mn^{2+}$ | 20.08 | 19.96 | 19.31 | 19.42 | 19.53 | 19.38 | 17.54 | 18.90 | 18.80 | 17889 | 16.56 | 19.88 | 23.42 | |
| $Ce^{3+}$ | 20.16 | 20.00 | [e] | 20.12 | 19.30 | 19.46 | 17.54 | 19.12 | 18.98 | 16.37 | 16.58 | 21.83 | 24.63 | 19.65 |
| $Co^{2+}$ | 20.41 [c] | 20.28 [c] | 19.42 | 20.53 [c] | 20.00 | 19.76 | 17.86 | 18.87 | 18.76 | 17.89 | 16.58 | 19.34 | | 19.61 |
| $Cr^{3+}$ | | 20.62 [b] | 20.41 [b] | 17.99 | [e] | [e] | 20.62 [c] | | 18.28 | 19.46 | 16.34 | 16.56 | | |
| $Cu^{2+}$ | 20.79 | 20.58 | 20.12 | [e] | 20.33 | 20.16 | 19.46 | 19.88 | 19.80 | 19.96 | 18.32 | 20.53 | 23.04 | 19.80 |
| $Zn^{2+}$ | 21.51 [c] | 21.10 | | 21.14 [c] | 21.01 | 20.92 [c] | | 19.92 [f] | 20.88 | 18.32 | 16.57 | | | |
| $Fe^{2+}$ | 20.62 [d] | 20.83 [b] | | 19.80 [c] | 20.20 [b] | 21.28 [b] | | 18.87 | 18.80 | 17.86 | 16.61 | | | |
| $Fe^{3+}$ | [a] | [e] | | [a] | [e] | [a] | | [a] | 20.66 [d] | [e] | 16.53 | | | |

[2] Fe(phen)$_2$(CN)$_2$ is, in the presence of this cation in the solvent, not stable and discoloured immediately after adding the cation. An evaluation is therefore not possible.

[3] The two absorption bands overlap to such an extent that they could not be separated; the absorption maximum has been estimated.

[4] Here $\nu_2$ becomes less intense than $\nu_1$ and appears as a shoulder.

[5] Values refer to freshly prepared solutions because a slow decomposition of the solution is observed within a day.

[6] The cation spectrum overlaps strongly with the indicator spectrum making an accurate evaluation of the required absorption maximum impossible.

[7] The concentration of the cation was increased until a maximum the shift was found.

$Ru(phen)_2(CN)_2$ was prepared by methods similar to those of Bignozzi *et al.*[10] and Sullivan *et al.*:[11] 29.8 mmol of $RuCl_3.3H_2O$, 60 mmol of 1,10-phenanthroline, 0.2 mol of LiCl and 50 cm$^3$ DMF were refluxed together for 8 hours. After cooling, the solution was poured into 37 cm$^3$ of acetone and kept for 2 days at −16°C. The resulting black crystals were filtered off and washed with small amounts of water and thereafter with diethylether. The product was dried *in vacuo* (Yield 60%). As an alternative procedure, 1 g of $Ru(phen)_2Cl_2$ was dissolved with 8.56 g of KCN (this reacted better than NaCN) in 40 cm$^3$ of water. After addition of 30 cm$^3$ of methanol, the solution was heated for 3 hours and evaporated to about half its volume. The resulting black crystals were filtered off and treated as above (Yield 89%).

## RESULTS AND DISCUSSION

### (i) Solvatochromism

The solvatochromism of $Fe(phen)_2(CN)_2$ arises from the coordination of Lewis acid molecules to the free electron pair(s) located at the N-atoms of the -CN group (see Figure 1). The complex itself is very stable and can be handled even in strongly acid solutions (although under these extreme conditions a slow hydrolysis does occur).[12] However, it is observed that the phenanthroline ligands become detached, or at least unstable, in some organic solvents (*e.g.* aqueous acetone and nitromethane[13] but the reason for this remains unclear. The spectra therefore had to be measured within a reasonable time after preparation of the solutions.

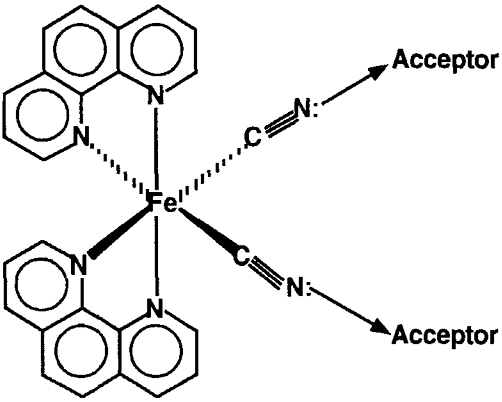

FIGURE 1 Coordination of $Fe(phen)_2(CN)_2$ with acceptors.

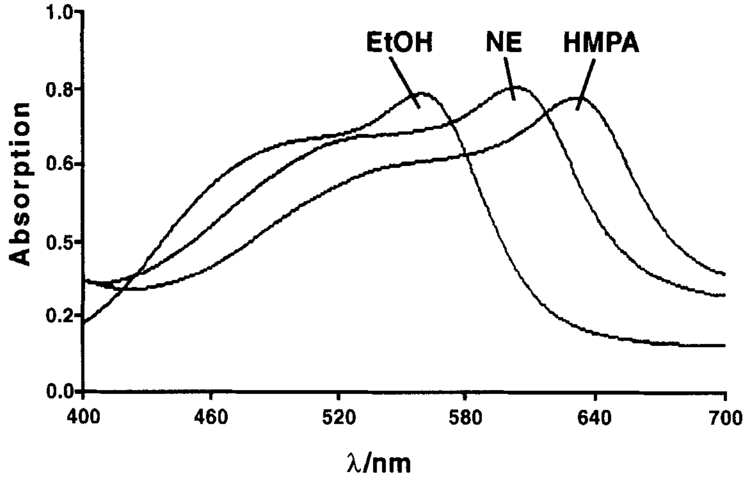

FIGURE 2 Typical spectra of $Fe(phen)_2(CN)_2$ with some of the solvents used.

The spectra (Figure 2) show essentially two broad bands ($\nu_1$ and $\nu_2$ 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 $\pi^*$ orbitals of the phenanthroline ligands. A comparison of the spectra obtained with the *tris*-phenantroline species and with hexacyanoferrates[14] lends support to this assignment as do the results of semi-quantitative *quasi*-relativistic INDO calculations.[15] The latter show a large number of closely-lying $\pi^*$ 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. However, the occurrence of essentially 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[16] as $t_2^+$, $t_2^-$).

Electron withdrawal due to interaction with a Lewis acid thus leads to changes in the σ bonding MO orbitals (including the $e_g$ levels of the iron) which in turn leads to a deformation of $Fe(phen)_2(CN)_2$ and the concomitant *p* orbitals (including the split $t_{2g}$ levels of the coordination centre), which then influences the energeties of the antibonding $\pi^*$ ligand orbitals.

The (originally more intense) $\nu_2$ band observed at lower transition energies is shifted towards higher energies and decreases its intensity relative to the second observed band with increase in Lewis acidity of the substrate. This leads, for strong Lewis acids, to spectra where the band observed at higher energies becomes the more intense. The $\nu_1$ band is less strongly influenced. It also shifts towards higher energies, and therefore the interval between the two bands

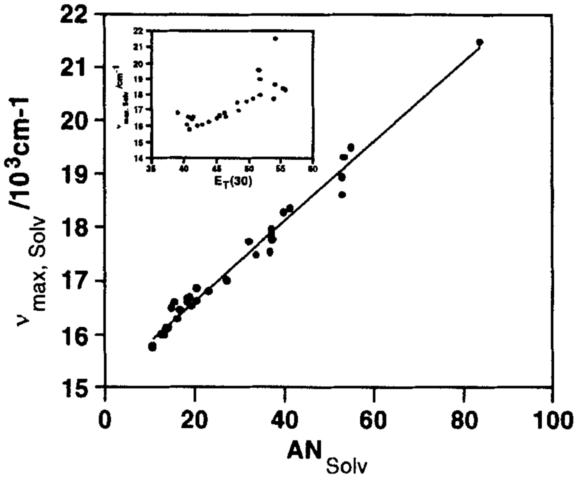

FIGURE 3 Linear relationship between the absorption maxima $\nu_2$ of Fe(phen)$_2$(CN)$_2$ *vs* the Acceptor Number (AN). A plot of these values *vs* E$_T$(30) is given in the insert.

becomes smaller. 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 band found at higher wavelength because its shifts are the greater (*i.e.*, more sensitive to change) and absorption maxima can be more readily identified.

A linear relationship[17] between the maximum absorption frequency, $\nu_2$, of Fe(phen)$_2$(CN)$_2$ and the Acceptor Number of the respective solvents has been established (see Figure 3) and a linear regression analysis of all values available to us yields (*1*) which can be expressed as (*2*).

$$\nu_{\mathrm{max,solv}} = (15.2 + 0.073\ \mathrm{AN}_{\mathrm{solv}})10^3\ (r = 0.991) \quad (1)$$

$$\mathrm{AN}_{\mathrm{solv}} = 13.09 \times 10^{-3}\ \nu_{\mathrm{max,solv}} - 197.45 \quad (2)$$

Concerning the evaluation of Lewis acidities based on the solvatochromic properties of an appropriate indicator, the associated donor-acceptor interactions differences between Reichardt's[3,4] E$_T$(30) scale (based on the solvatochromic shift of betaines) and Gutmann's AN scale (based on the shift of the $^{31}$P NMR chemical shift of Et$_3$PO in the respective solvent)[2] should be mentioned: Although these solvent parameters are considered to be linearly related, a detailed analysis[19] yields several groups of solvents, for example hydroxylic and non-hydroxylic solvents, aromatics, amines, *etc.* This becomes clear in a plot of the absorption maxima of $Fe(phen)_2(CN)_2$ *versus* $E_T$ parameters as shown in the insert of Figure 3. A similar effect is found for the solvatochromism of molybdenum and wolfram diimine carbonyl analogues, where, using $E_T$ parameters, the split between hydroxylic and non-hydroxylic solvents becomes quite obvious.[20,21] These findings have been discussed in detail[19] based on solvato- and thermochromic results concerning betaines and using isokinetic relationships as a tool for separating different interaction mechnisms.[22-24] The split into several groups of solvents arises from the induction of increased acceptor properties in acceptor molecules when interacting with the strong donor molecule $Et_3PO$.[19]

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. Figure 3 shows clearly that in a plot of $\nu_{max,solv}$ *vs* AN the separation (especially 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 [19] if preferred, but this is only really straight forward when 'well behaved solvents,[19] are used.

## (ii) Cationochromism

In the presence of cations the absorption maxima observed for different solvents change in a similar way to the changes observed for different solvents (see Figure 4). 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.

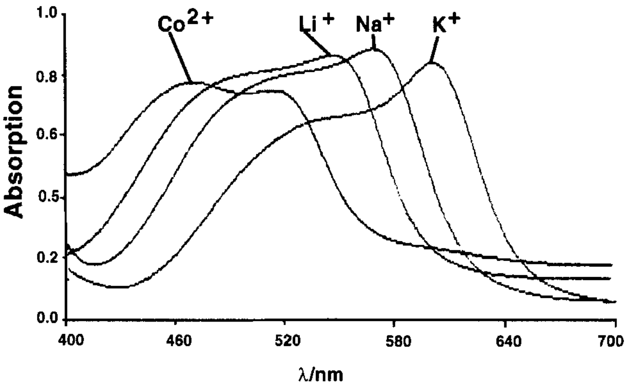

FIGURE 4 Typical spectra of $Fe(phen)_2(CN)_2$ in NM in the presence of $K^+$, $Na^+$, $Li^+$ and $Co^{2+}$ perchlorates.

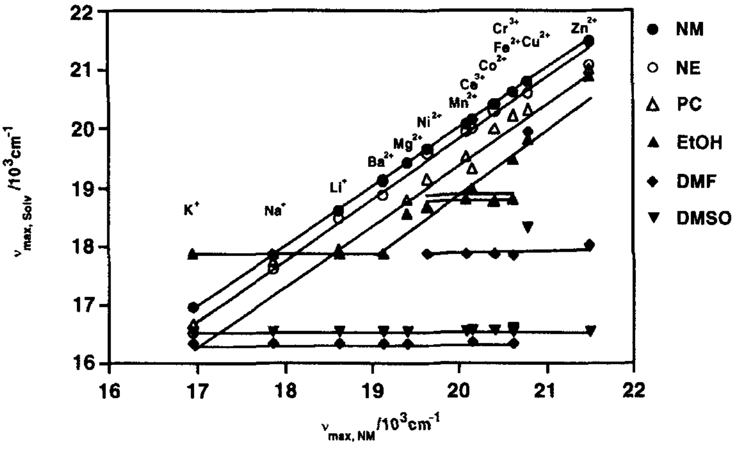

FIGURE 5 Absorption maxima ($\nu_{max,solv}$) in the spectra of $Fe(phen)_2(CN)_2$ dissolved in various solvents in the presence of metal cations *vs* the absorption maxima ($\nu_{max,NM}$) observed in NM solutions.

The observed spectroscopic changes due to the presence of cations depend also on the anion (due to their Lewis basicity described by their $DN_{X,solv}$ values[1] and on the concentration of the metal ion. In order to minimise any possible variation due 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). Table I summarises these data.

Figure 5 depicts the absorption maxima of $Fe(phen)_2(CN)_2$ measured in the presence of a cation in a given solvent *vs* the absorption maxima found under the same conditions using nitromethane (NM) as solvent. Some representative solvents have been chosen to illustrate the general behaviour. For the reference solvent it can be seen that nearly all cations yield a shift to higher wavenumbers with expected increasing Lewis acidity in line with shifts observed with different solvents in the absence of cations. In general, two distinct parts of each plot are found for a given solvent. 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 an extent that the indicator is not able to interact with the cation. In this case, however, solvated species might themselves shift the absorption of the indicator (see below).

TABLE III Apparent Acceptor Numbers of cations ($AN_{max,solv}$) in various solvents calculated using (5) with NM as reference solvent. 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).

| *Cation* | *NM* | *acetic acid* | *MeCN* | *PC* | *AC* | *$H_2O$* | *MeOH* | *THF* | *EtOH* | *DMF* | *DMSO* | *HMPT* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Na^+$ | 35.3 | *30.6* | 28.5 | 27.9 | 26.8 | 26.2 | 25.6 | 25.0 | *25.0* | 21.1 | [19.2] | [13.8] |
| $Li^+$ | 44.6 | *39.9* | 37.8 | 37.2 | 36.0 | 35.5 | 34.9 | 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 |
| $Ce^{2+}$ | 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 |
| $Zn^{2+}$ | 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 species [a] | | | | | | | | | 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] Estimated values for $Ni^{2+}$, $Mn^{2+}$, $Co^{2+}$ and $Zn^{2+}$, see text.

With 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 lower energies. The shifts in this cation dependent part are parallel to the shifts obtained with respect to the reference solvent.

In the case of some transition metal ions and solvents, an apparent 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, Table III).

### (iii) Concentration dependence

As expected, 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, when excess metal ion over $Fe(phen)_2(CN)_2$ is present, the shift of the absorption maxima reaches a limiting value (usually arrived at before a 5-fold excess) and it is these limiting values that are used for the analysis below. However, a strong dependence of the absorption maxima (reminiscent of 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 *vs* those in the other solvent (Figure 5). Here also much larger concentrations of cations were required to reach the limiting value.

### (iv) The influence of anions

The anion influence relates clearly to our former work[1] concerning the donor properties of anions in various solvents. There is always competition between the indicator, the solvent, and the cation acceptor properties toward the anion 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 therefore 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. However, spectroscopic data for $Fe(phen)_2(CN)_2$ in the presence of some metal species associated with other anions in different solvents are given in Table II and might be used with the equations given below to estimate their Lewis acidity.

TABLE II Absorption maxima ($\nu_{max,solv}/10^3$ cm$^{-1}$) 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* | *acetic acid* | *formic acid* | *$H_2O$* |
|---|---|---|---|---|---|---|---|---|---|
| | | 16.00 | 16.67 | 15.75 | 17.86 | 16.53 | 18.94 | 24.39 | 19.53 |
| $Ag^+$ | $NO_3^-$ | 19.80 | 19.69 | 18.62 | 21.01 | 18.73 | | | 19.57 |
| $NH_4^+$ | $NO_3^-$ | 16.00 | 17.33 | | 18.02 | 17.04 | | | |
| $Ca^{2+}$ | $NO_3^-$ | 19.38 | 19.05 | | 18.52 | 17.36 | 19.38 | | |
| $Sr^{2+}$ | $NO_3^-$ | | 17.30 | | | 17.21 | | | |
| $Pb^{2+}$ | $NO_3^-$ | 20.37 | 20.12 | 17.09 | 19.34 | 17.92 | 19.31 | | |
| $Cd^{2+}$ | $NO_3^-$ | 19.31 | 19.88 | 17.54 | 19.46 | 19.12 | 20.00 | | |
| $Fe^{3+}$ | $NO_3^-$ | | 29.15 | | 21.10 | | 21.51 | 25.97 | |
| $La^{3+}$ | $NO_3^-$ | 18.76 | 19.46 | | 19.27 | 17.18 | 19.34 | | 19.57 |
| $Ce^{4+}$ | $NO_3^-$ | 21.28 | 19.16 | | 19.61 | | 24.27 | | |
| $Pr^{3+}$ | $NO_3^-$ | 19.31 | 19.53 | | 19.05 | 16.89 | 19.23 | | 19.57 |
| $Cu^+$ | $Cl^-$ | | 21.19 | 17.70 | 19.61 | 18.38 | 20.00 | 20.37 | |
| $Fe^{2+}$ | $Cl^-$ | 21.79 | 21.88 | 18.45 | 19.23 | 18.69 | 19.57 | | 19.76 |
| $Hg^{2+}$ | $Cl^-$ | 19.34 | 19.69 | 18.73 | | 21.05 | | | |
| $Hg_3^{2+}$ | $Cl^-$ | 16.05 | 17.01 | | | | | | |
| $Sn^{2+}$ | $Cl^-$ | 20.75 | 21.51 | 18.21 | 21.51 | 18.80 | 22.47 | 24.51 | |
| $Al^{3+}$ | $Cl^-$ | | | 20.24 | 21.23 | | 22.17 | 27.55 | |
| $V^{3+}$ | $Cl^-$ | 20.92 | 19.88 | 17.24 | 21.93 | 18.66 | 24.04 | 24.10 | |
| $Ru^{3+}$ | $Cl^-$ | 24.39 | | | 24.39 | | 22.47 | | |
| $NbCl_5$ | | 23.47 | 24.04 | | 20.62 | 19.42 | 21.69 | 25.91 | 21.19 |
| $ZrOCl_2$ | | 22.32 | 20.53 | | 20.83 | 17.45 | 21.93 | | 19.69 |
| $VO(acac)_2$ | | 23.26 | | | 25.19 | | | | |
| $Sn(CH_3)_3Cl$ | | | | | | 18.52 | | 24.10 | |

## (v) The Problem of the Reference Solvent

In order to establish Donor Numbers for anions[1], 1,2-dichlorethane (DCE) was used as reference solvent because this solvent was both reference and *diluting* solvent in the original Donor Number approach for solvents[18] and its Donor Number was defined as zero. The results showed clearly, however, 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.

The choice of a reference solvent for the determination of Acceptor Numbers for cations is less straightforward; Acceptor Numbers of solvents are defined in terms of 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 $AN_{solv} = 0$. Unfortunately, *n*-hexane is a solvent in which ionic species are scarcely soluble and it could not therefore be used for these investigations. A reference solvent should fit the following (contradictory!) requirements: on the one hand both its Donor Number and its Acceptor Number should be as low as possible: on the other hand both donor and acceptor properties must be sufficient to allow solubilites 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 adopted nitromethane (NM) as diluting and reference solvent because not only are its acceptor properties ($AN_{Solv} = 20.5$) low (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 $Fe(phen)_2(CN)_2$. Because not all cations investigated are soluble enough in this solvent we had also to make use of corrected values obtained in tetrahydrofurane (THF) as explained below.

As far as possible, significant traces of water in both the solvent and the dissolved salt were avoided. However, addition of water in small amounts did not significantly change the results within the cation dependent region. In the case of some transition metal ions, where salts containing water of crystallisation are soluble in non-aqueous solvents, no significant differences to water free species were observed.

### (vi) Estimation of Acceptor Numbers for Cations

The results plotted in Figure 5 show that similar behaviour is found for cations as was previously observed[1] for anions. As described above there exists for every solvent a more or less pronounced cation independent part (*i.e.*, a region where only solvent properties are of importance) and a cation dependent part. The cation dependent part takes the form of parallel lines. To describe this shift and the corresponding intersection with the cation independent part we have to consider two concurrent reactions: (*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 application of (*3*) in which NM is used as reference solvent. On taking $AN_{NM} = 20.5$ and $DN_{NM} = 2.7$, the data fit expression (*4*) (with $r = 0.960$)

$$(\nu_{M,solv} - \nu_{M,NM}) = A(AN_{Solv} - AN_{NM}) + B(DN_{Solv} - DN_{NM}) \qquad (3)$$

$$\nu_{M,solv} = \nu_{M,NM} - 5.62(AN_{Solv} - 20.5) - 48.7(DN_{Solv} - 2.7) \qquad (4)$$

The intersection point of solvent and cation dependent parts (See Figure 5) for each solvent implies equal apparent Acceptor Numbers of the solvent and the respective cation at this position and that, therefore, (by combining (*2*) and (*4*) and rearranging), equation (*5*) applies.

$$AN_{M,Solv} = 0.0122\nu_{M,NM} - 0.595DN_{Solv} - 181 \qquad (5)$$

Equation (*5*) enables apparent Acceptor Numbers for cations dissolved in various solvents to be calculated and values for the solvents used in this investigation are listed in Table III. We estimate these values to be accurate to within ±2–5% (due to the relatively imprecise evaluation of the coefficients in (*5*)). Values that are smaller than the respective Acceptor Numbers of the solvents are given in italics because they might conceivably be of significance for kinetic investigations (where weak interactions may be of importance).

Due to solubility problems it is sometimes not possible to use NM as the reference solvent. Analogously to the above procedure, it is, however, possible to establish equations for use with other reference solvents. For the other reference solvent used in this study, *i.e.*, tetrahydrofuran (THF), since (*4*) is still valid, (*6*), is obtained.

$$AN_{M,Solv} = 0.0122\nu_{M,Ref} - 0.595DN_{Solv} - 172 \qquad (6)$$

The apparent Acceptor Numbers for some metal ions could be calculated using the results from both NM and from THF reference solvents and can therefore be compared (See Tables III, and IV). It can be seen that the values from THF are slightly smaller than those based on NM as reference solvent and this is due to the fact that the values of both $AN_{NM}$ and $AN_{THF}$ deviate slightly from the respective values expected from (*2*).

However, the agreement is sufficiently within experimental accuracy for it to be assumed that the Acceptor Numbers obtained are indeed independent of the

TABLE IV Apparent Acceptor Numbers of cations ($AN_{max,solv}$) in various solvents calculated using (6) and based on THF as reference solvent (numbers in square brackets refer to Acceptor Numbers of the order of magnitude of the solvent)

| *Cation* | *NM* | *acetic acid* | *MeCN* | *PC* | *AC* | *$H_2O$* | *MeOH* | *THF* | *EtOH* | *DMF* | *DMSO* | *HMPT* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Bu_4N^+$ | 34.5 | *29.9* | 27.7 | 27.1 | 26.0 | *25.4* | *24.8* | 24.2 | *24.2* | 20.3 | [18.4] | [13.0] |
| $K^+$ | 38.6 | *33.9* | 31.8 | 31.2 | 30.0 | *29.4* | *28.9* | 28.3 | *28.3* | 24.3 | 22.4 | 17.1 |
| $Na^+$ | 41.6 | *37.0* | 34.8 | 34.2 | 33.1 | *32.5* | *31.9* | 31.3 | *31.3* | 27.4 | 25.5 | 20.1 |
| $Li^+$ | 43.4 | *38.8* | 36.6 | 36.1 | 34.9 | *34.3* | *33.7* | 33.1 | *33.1* | 29.2 | 27.3 | 22.0 |
| $Ba^{2+}$ | 46.6 | *42.0* | 39.8 | 39.2 | 38.1 | *37.5* | *36.9* | 36.3 | [36.3] | 32.4 | 30.5 | 25.1 |
| $Mg^{2+}$ | 59.2 | [54.5] | 52.4 | 51.8 | 50.7 | *50.1* | 49.5 | 48.9 | 48.9 | 44.9 | 43.0 | 37.7 |
| $Ni^{2+}$ | 59.7 | 55.0 | 52.9 | 52.3 | 51.1 | *50.6* | 50.0 | 49.4 | 49.4 | 45.4 | 43.5 | 38.2 |
| $Mn^{2+}$ | 62.0 | 57.3 | 55.2 | 54.6 | 53.5 | [52.9] | 52.3 | 51.7 | 51.7 | 47.8 | 45.9 | 40.5 |
| $Co^{2+}$ | 63.3 | 58.7 | 56.5 | 55.9 | 54.8 | 54.2 | 53.6 | 53.0 | 53.0 | 49.1 | 47.2 | 41.8 |
| $Cu^{2+}$ | 71.9 | 67.2 | 65.1 | 64.5 | 63.3 | 62.8 | 62.2 | 61.6 | 61.6 | 57.6 | 55.7 | 50.4 |
| $Cr^{3+}$ | 75.4 | 70.8 | 68.6 | 68.0 | 66.9 | 66.3 | 65.7 | 65.1 | 65.1 | 61.2 | 59.3 | 53.9 |
| 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 |

reference solvent used (at least as far as NM and THF are concerned). In many cases, THF might be the preferred reference solvent because of its higher Donor Number, which allows for higher solubilities, and its lower Acceptor Number which makes it more sensitive to the presence of cations of lower Lewis acidities.

## COMPARISON WITH RELATED EXPERIMENTAL AND THEORETICAL DATA

### (i) The Spectra of the Ruthenium Complex

For the purposes of comparison, we prepared the analogous complex $Ru(phen)_2(CN)_2$. This complex shows similar absorption MLCT spectra, again associated with two main bands around 400–500nm, the lower wavelength transition appearing as a shoulder.[25]

The frequency of the absorption maxima measured in some 15 solvents was found to be linearly related to the AN of the solvent (See (*7*) and (*8*)) and Table V gives the absorption maxima of $Ru(phen)_2(CN)_2$ in a few solvents in the presence of cations (a ten-fold excess of the cations was required in order to obtain a maximum shift).Figure 6 shows a plot of the absorption maxima obtained with $Ru(phen)_2(CN)_2$ *vs* the those obtained using $Fe(phen)_2(CN)_2$ for a series of cations dissolved in acetonitrile, and the linearity observed (similar linear relationships are found for all of the investigated solvents exhibiting cation effects) illustrates clearly the validity of the method.

TABLE V Absorption maxima ($\nu/10^3$ $cm^{-1}$) of 0.025 molar $Ru(phen)_2(CN)_2$ solutions in various solvents in the presence of a 10-fold excess of metal ions

| *Cation* | *Anion* | *MeCN* | *AC* | *DMF* | *MeOH* |
|---|---|---|---|---|---|
| – | – | 20.53 | 19.88 | 19.96 | 22.22 |
| $Na^+$ | $ClO_3^-$ | 21.37 | 20.19 | 19.96 | 22.15 |
| $Li^+$ | $ClO_3^-$ | 22.03 | 21.51 | 20.00 | 22.27 |
| $Ba^{2+}$ | $ClO_3^-$ | | | 10.71 | 22.41 |
| $Mg^{2+}$ | $ClO_3^-$ | | 22.42 | 21.41 | 22.67 |
| $Ni^{2+}$ | $ClO_3^-$ | 23.04 | | 21.65 | 22.99 |
| $Mn^{2+}$ | $ClO_3^-$ | 23.47 | | | 23.29 |
| $Ce^{3+}$ | $ClO_3^-$ | 24.27 | | 22.09 | 23.54 |
| $Co^{2+}$ | $ClO_3^-$ | 24.10 | | | 23.32 |
| $Cu^{2+}$ | $ClO_3^-$ | 24.39 | | 23.75 | 24.22 |
| $Zn^{2+}$ | $ClO_3^-$ | 25.00 | | | 24.56 |

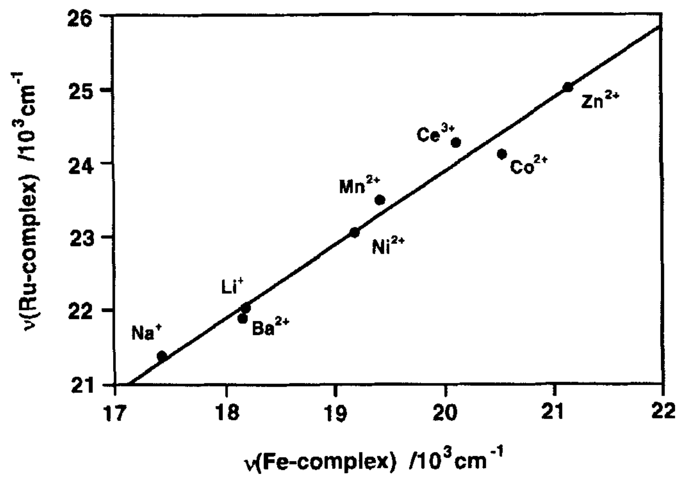

FIGURE 6 Absorption maxima in the spectra of $Ru(phen)_2(CN)_2$ *vs* those in the spectra of $Fe(phen)_2(CN)_2$ in the presence of different cations in acetonitrile. Regression line: $\nu_{Ru} = 0.991\nu_{Fe} + 4040$ (r = 0.991).

$$\nu_{max,solv} = (18.6 + 0.090\ AN_{solv})\ 10^3 + (r = 0.986) \qquad (7)$$

$$AN_{Solv} = 0.0111\,\nu_{max,solv} - 206 \qquad (8)$$

### (ii) Formation Constants of Metal Ion - EDTA-complexes

If they are valid, the apparent Acceptor Numbers for cations obtained by this spectroscopic method might be expected to correlate with complex formation constants of the cations in any solvent. Figure 7 shows the relation between Acceptor Numbers and log(stability constants) of various cations with ethylenddiamine-*N,N,N',N'*-tetra-acetic-acid, EDTA, in aqueous solution (values of logK are taken from the compilation by Sill én and Martell[26]). Despite the varied sources of the data, the linear correlation exhibited is highly satisfying.

### (ii) Gibbs Free Energies of Transfer of Metal ions from Water to Organic Solvents

Marcus[27–29] has reported a purely theoretical method of evaluating the Lewis acidities of cations. The method is based on the application of (*10*), simplified to (*11*), in which $\Delta_{tr}G°$ is the standard molar Gibbs free energy of transfer of a

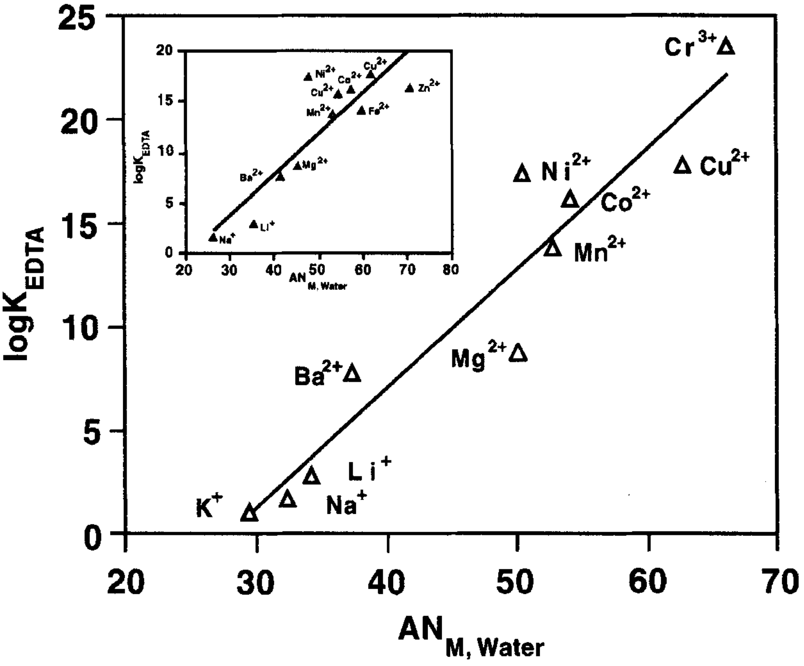

FIGURE 7 Logarithms of the equilibrium constants ($\log K_{EDTA}$) for complex formation between the metal ions and EDTA *vs* the apparent Acceptor Numbers ($AN_{M,Water}$) of these ions in aqueous solution using values using THF as reference solvent Table IV. The insert shows the respective values for AN using NM Table III as reference solvent.

given ion from water to a non-aqueous solvent (in kJ mol, z is the ionic charge, r the ionic radius (nm), $R_D$ the ionic molar refraction (cm$^3$ mol), $\sigma$ is the softness, $v = (4\pi/3)r^3$, $\Delta\alpha_s$ is the hydrogen bond activity, $\Delta\beta$ is the difference *of* the Kamlet-Taft electron-pair donicities (basicites) of the solvent and water and $\Delta\pi^*_s$ the difference of the polarity/polarizability of the solvent and water. This can be written as (*12*) where the $\alpha_+$ terms are '*pseudo*-solvatochromic' parameters of cations which measure their Lewis acidity.[28]

$$\Delta_{tr} G^0 = -(3{,}26\Delta\pi^*_s + 3.72\Delta\beta_s)z^2/r + 530\Delta\alpha_s v + 30.3\Delta\pi^*_s\sigma - 3.78\Delta\beta_s R_D \qquad (10)$$

$$= \text{other terms} - (3.72z^2 / r + 3.78\ R_D)\ \Delta\beta_s \qquad (11)$$

Linear regression then yields an expression (*13*) for the Acceptor Number for the reference solvent NM. Table VI gives some values calculated from this expression.[26]

TABLE VI $AN_{M,NM}^{Marcus}$ values calculated according to (*14*) compared with the experimental values

| *Cation* | $AN_{M^+,NM}^{Marcus}$ | $AN_{M^+,NM}$ (present work) |
|---|---|---|
| $Li^+$ | 38.9 | 45 |
| $Na^+$ | 35.7 | 36 |
| $K^+$ | 35.4 | 42 |
| $Ba^{2+}$ | 59.6 | 52 |
| $Co^{2+}$ | 70.1 | 68 |
| $Ni^{2+}$ | 73.2 | 58 |
| $Cu^{2+}$ | 70.6 | 73 |
| $Zn^{2+}$ | 69.6 | 82 |

Despite the quite different approaches employed the values show good agreement.

$$\Delta_{tr} G_i^{o} = \text{other terms} - 43.8\alpha_+ \Delta\beta \qquad (12)$$

$$AN_{M,NM}^{Marcus} = 27.7 + \alpha_+ \qquad (13)$$

## CONCLUSIONS

Despite some difficulties such as solubilities and the presence of solvent-separated interactions 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 thermodynamic data shows that it indeed reflects the acceptor properties with satisfying precision. We hope, therefore, that this Acceptor Number scale for cations will find wide-spread application, for example in studies of metal used as catalysts.

It is important to note that, as shown in Tables III and IV, the apparent Acceptor Numbers depend on both donor and acceptor properties of the solvent. This only to be expected because, as we have pointed out before, donor and acceptor properties cannot be completely described by independent parameters due to their mutual interactions.[19] It should be noted that such difficulties in the quantitative description of observed properties of solutions lead to interresting new developments in our understanding of liquid systems.[30]

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