Donor Numbers of Anions in Solution: the Use of Solvatochromic Lewis Acid–Base Indicators†

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The shift of the visible d–d absorption bands of $[Cu(acac)(tmen)]^+$ (acac = acetylacetonate, tmen = *N,N,N′,N′*-tetramethylethylenediamine) in various solvents resulting from the co-ordination of solvent molecules and anionic species X has been investigated. The results have been used to establish donor numbers ($DN_{X,dce}$) of anions dissolved in 1,2-dichloroethane (dce) on the same scale as that already established for solvents. Apparent donor numbers for anions dissolved in various solvents other than dce ($DN_{X,solv}$) are also given and used to show that the donor properties of anions are directly related to the acceptor number (AN_{solv}) of the solvent. This arises from competition between solvent and acceptor ion for the anion leading to a steady decrease in the effective donor number of the anion as AN_{solv} increases, culminating in an effective donor number of zero for all anions in the strong acceptor solvent water (ion pairing is at a minimum in water). The values of the anion donor numbers are related to some experimental results such as spectral, equilibrium, kinetic and thermodynamic data for selected systems. This method of establishing donor numbers for anions is shown to be reliable and easy to apply.

Donor numbers of solvents[1] are regularly in use as a means of discussing solvent–solute interactions, but the role of anions as electron pair donors is less clear-cut. For example, anions such as perchlorate and tetraphenylborate are often used as counter ions as they are assumed to have low basicity and thus not to interfere significantly with the donor and acceptor properties of the solvent,[1–10] despite occasional difficulty in handling or preparation. Thus it would be of considerable advantage to be able to predict the role of other anions in solution for which purpose a donor number scale would be appropriate. A first attempt to estimate the donor numbers (DN) of anions, suggested by Gutmann and Mayer,[8,9] was based on measured free energies (*i.e.* equilibrium constants) of the reaction $[VO(acac)_2(MeCN)] + D \rightleftharpoons [VO(acac)_2D] + MeCN$, where D was either an anion or a solvent of comparable donor strength and acac = acetylactonate. These investigations yielded a qualitative sequence of the donor strength of anions together with approximate values for some of them.[8,9] The following sequence (1) of increasing donor properties was found.

$$I^- < Br^- < Cl^- < SCN^- < F^- \approx CN^- < N_3^- \quad (1)$$

It was estimated that the donor properties of Cl^- were similar to those of *N,N*-dimethylformamide ($DN_{solv} = 26.6$; for clarity we use the index solv for solvent donor numbers) and that the donor strength of the F^- ion corresponds to that of hexamethylphosphoramide ($DN_{solv} = 38.8$). Later, however, it was argued[9,10] that the co-ordination ability of these ions is much larger than these approximate values would suggest and that the sequence itself might also have to be changed (for example $SCN^- < Cl^- \approx N_3^-$).[10] Furthermore, there are several reasons to question the applicability of the solvatochromic $VO(acac)_2$ system which appeared to us to be of importance after repetition of some of the underlying experiments (see below).

Solvatochromic compounds have, however, been used successfully in the past for estimating donor–acceptor properties of solvents[11–15] and it seemed feasible to us that such systems could be employed in the estimation of donor numbers for anions. This encouraged us to reinvestigate the problem in detail, hoping to obtain a quantitative measure of the donor properties of anions in solution whilst taking the properties of the respective solvents into account.

Experimental

Chemicals.—These were obtained from Merck and Rathburn Chemicals. Solvents were purified using standard methods.[16,17] The water content of the solvents was found by means of Karl–Fischer titration to be below 30 mg dm^{-3} (except for acetone). Abbreviations for the solvents are: 1,2-dichloroethane (dce), *N,N*-dimethylformamide (dmf), dimethyl sulfoxide (dmso), *N*-methylpyrrolidone (mpyr), propanediol-1,2-carbonate (pdc).

Tetrabutylammonium hydroxide (40% solution in water) was extracted by diethyl ether several times, then the organic layer was evaporated and the product was dried under reduced pressure. The respective tetrabutylammonium salts were prepared according to ref. 8. For the anions $MeCO_2^-$ and CO_3^{2-} ammonium salts are used.

Bis(acetylacetonate)oxovanadium(IV) $[VO(acac)_2]$ was prepared according to refs. 8 and 18 and recrystallized from dichloromethane, yielding blue-green crystals.

For the preparation of $[Cu(acac)(tmen)]BPh_4$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine) (the bulky tetraphenylborate ion is used since its donor number can safely be assumed to be zero) twice recrystallized $[Cu(acac)(tmen)]NO_3 \cdot H_2O$ (10 g) (prepared according to ref. 19) was dissolved in a small amount of dce and then added, with vigorous stirring, to a suspension of $NaBPh_4$ (12 g) in dce (50 cm^3). The mixture was kept at 60 °C for 1 h. The pale red-violet precipitate obtained was filtered off, washed with dce, and dried *in vacuo* for several hours at 35 °C (Found: C, 70.25; H, 7.30; N, 4.65. Calc. for $CuC_{35}H_{43}BN_2O_2$: C, 70.30; H, 7.25; N, 4.70%).

Measurements.—Electronic spectra were recorded with a Hitachi U-2000 spectrophotometer equipped with a thermo-

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† *Non-SI unit employed:* cal ≈ 4.184 J.

electric cell holder. The temperature was kept at 25 ± 0.02 °C. A 3×10^{-3} mol dm^{-3} stock solution of [Cu(acac)(tmen)]BPh$_4$ or [VO(acac)$_2$] in dce (5 cm^3) was mixed with tetrabutylammonium salts (0.5 cm^3, 0.1 mol dm^{-3} stock solutions in dce). The mixture was made up to 10 cm^3 with dce. These procedures were performed in a glove box under a dry nitrogen atmosphere.

For the determination of the equilibrium constants a 3×10^{-3} mol dm^{-3} stock solution of [Cu(acac)(tmen)]BPh$_4$ in dce was titrated with 0.01 mol dm^{-3} solutions of tetrabutylammonium salts NBu$_4$X (X = Cl, Br, I, SCN, CN or N$_3$) dissolved in dce. Up to ten spectra were recorded and stored in a multichannel memory unit. The spectral titration curves so obtained were fitted by means of a combined Marquardt–Newton method[20] to evaluate equilibrium constants (log K) and molar absorptions (ε_{CuX}) for the reaction of the copper(II) complex with anions X$^-$ [equilibrium (2)].

$$[Cu(acac)(tmen)]^+ + X^- \rightleftharpoons [Cu(acac)(tmen)X] \quad (2)$$

Results and Discussion

Estimation of Donor Numbers of Anions in Solution.—Donor numbers of anions have been estimated previously[8,9] by correlating equilibrium constants of the reaction (3) with

$$[VO(acac)_2(solv)] + D \rightleftharpoons [VO(acac)_2D] + solv \quad (3)$$

solvent donor numbers and comparing this relationship with anion complexation. As mentioned above, there are several important reasons to question the application of the VO(acac)$_2$–solvent system to the problem of establishing donor numbers for anions.[13]

First, to make it possible to measure equilibrium constants of reaction (3), solvents exhibiting relatively strong acceptor properties have to be used in order to get the respective species into solution (*i.e.* acetonitrile and dichloromethane have been used). However, acceptor properties of the solvent result in solvent interactions with anions which can affect the determined values and might even affect the sequence of anions quite strongly. The solvatochromism of the VO(acac)$_2$ system yields for some solvents and especially for the anions a shift of the bands as well as changes of the molar absorptions.[13] Both lead to difficulties in evaluating equilibrium constants as the Lambert–Beer law fails under these conditions. Secondly, estimation is only possible for a restricted number of solvents and anions (N$_3^-$, NCS$^-$ and Cl$^-$) because of the magnitude of the equilibrium constants resulting in concentration and solubility difficulties.[8] Thirdly, the measured equilibrium constants refer to ΔG values whilst the donor number is based on ΔH measurements in dilute solutions using an inert solvent. It is not to be expected that entropic contributions of the co-ordination of solvents to [VO(acac)$_2$] would yield the same value as for the co-ordination of anions. Successful correlation of the donor number with ΔG values of a series of similar reactions demands an underlying isokinetic effect compensating entropic contributions.[21,22] Co-ordinating (uncharged) solvents and co-ordinating (charged) anions do not yield a common isokinetic relationship because the entropic contributions due to the desolvation of anions that occurs when they are co-ordinated are much too large. This would suggest that the application of spectroscopic experiments may be preferable as absorption frequencies are related to ΔE which should not be influenced by entropic changes.

Finally, however, the solvatochromism of [VO(acac)$_2$] cannot be used as a measure of donor properties because not only the band positions but also the differences of the observed transitions [*i.e.* $^2B_2 \longrightarrow {}^2E(I)$ and $^2B_2 \longrightarrow {}^1B_1$] are not linearly related to the donor number of the respective solvents,[13] despite the fact that this has been claimed previously.[23,24] Indeed a plot of ν_{max} versus DN$_{solv}$ yields a stepped curve (Fig. 1) reflecting the transition of five-co-ordinated [VO(acac)$_2$] to the octahedral species [VO(acac)$_2$D] (both forms being present for donor numbers between 10 and 20) thus showing similar behaviour to the Ni(tmen)(acac)$^+$ system.[25–28]

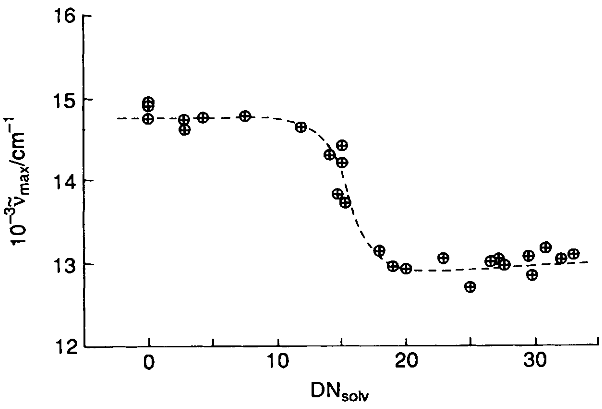

Fig. 1 Absorption maxima $\tilde{\nu}_{max}$ of the $^2B_2 \longrightarrow {}^2E(I)$ transition of [VO(acac)$_2$] in various solvents versus the donor number of the solvent

Unlike the above mentioned VO(acac)$_2$ system and the Ni(tmen)(acac)$^+$ system, the Cu(tmen)(acac)$^+$ system exhibits a pronounced Jahn–Teller effect so that the solvatochromism yields a continuous shift of the band maxima with the donor properties of non-aqueous solutions.[13–15]

Solutions of [Cu(β-diketonate)(diamine)]BPh$_4$ in various solvents exhibit solvatochromic behaviour with respect to the donor properties of the solvents,[25–28] and we found that the same behaviour could be observed with anions. In fact the d-orbital splitting of Cu^{2+} due to five- and six-fold co-ordination is changed similarly by increasing co-ordination ability of a ligand leading to a square-pyramidal structure for the former and an octahedral structure for the latter case[29–31] (Fig. 2). Due to Jahn–Teller distortion these geometrical transitions lead to spectral changes that are quite smooth, *i.e.* a continuous shift of absorption maxima with changing donor properties is observed.

It is, however, very difficult to distinguish the electronic spectra of the five- and the six-co-ordinated forms. The spectra are comparable to those of the analogous co-ordinated nickel(II) complexes which are also found to be almost indistinguishable.[26–28] Elemental analyses of the solid complexes indicated the formulation [Cu(acac)(tmen)X] for co-ordinated anions and [Cu(acac)(tmen)(solv)$_2$]X for co-ordinated solvents.[32–34] Spectral titration of [Cu(acac)(tmen)]$^+$ with a solution of NBu$_4$X in dce and analyses of the results using the molar ratio method[35] and Job's method[36] show that in solution five-co-ordinated species are also formed by the co-ordination of only one anion. The same methods show that when solvent molecules are co-ordinated, octahedral species are formed, including two donor solvent molecules. It is therefore clear that the already recognized relationship between the donor number of solvents and the position of the absorption maxima cannot be applied directly to anions in solution.

Table 1 gives the frequencies of the absorption maxima of the visible d–d absorption bands of [Cu(acac)(tmen)X] complexes in various donor solvents and Fig. 3 shows these observed absorption maxima plotted *versus* the absorption maxima in dce. The shift of the absorption maxima with anion variation for the solid complexes varies linearly (as expected) with respect to the corresponding shifts in the inert solvent dce (Fig. 3).

The behaviour of the salts in solution in the various solvents, however, is complex and requires explanation. The interaction of anions with [Cu(acac)(tmen)]$^+$ depends upon both the donor and the acceptor properties of the solvent. This arises because,

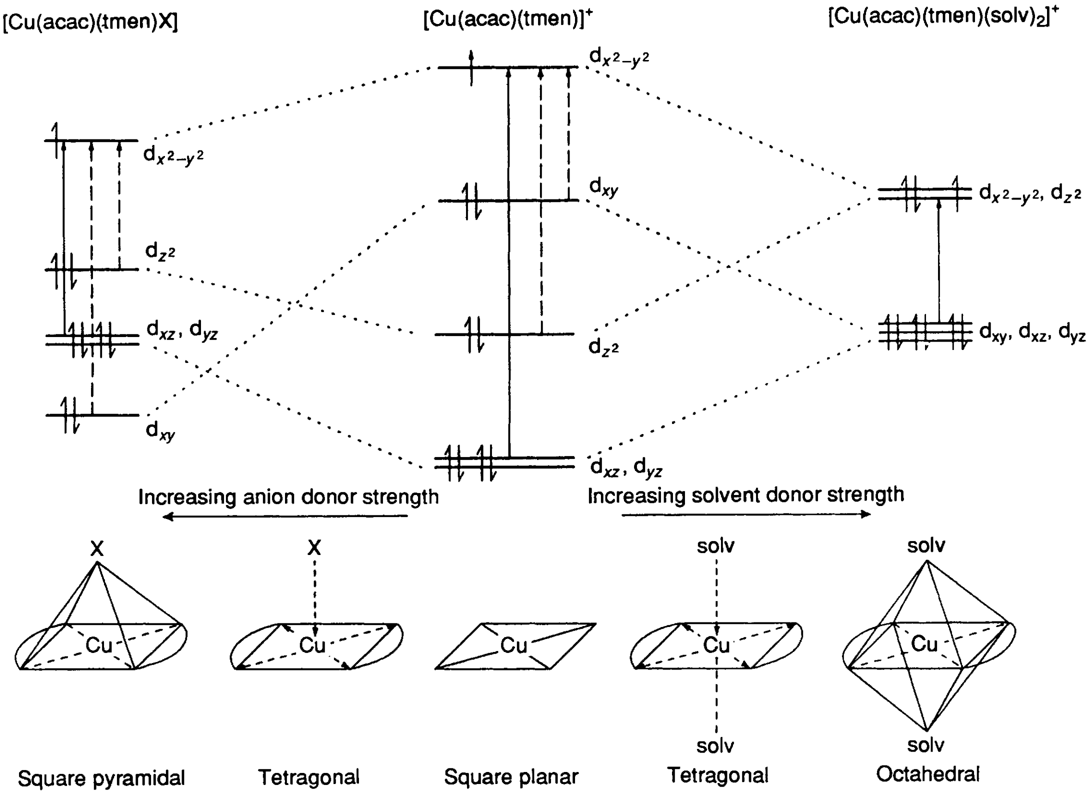

Fig. 2 Scheme of the d-orbital splitting in five-co-ordinated [Cu(acac)(tmen)X], square-planar $[Cu(acac)(tmen)]^+$, and six-co-ordinated $[Cu(acac)(tmen)(solv)_2]^+$. The separation of the energy levels has been exaggerated for clarity

Table 1 Absorption maxima $\tilde{\nu}_{max}$(solv) for [Cu(acac)(tmen)X] in different solvents and in the presence of various anions (absorption coefficients are in the range 110–160 $dm^3\ mol^{-1}\ cm^{-1}$)

	$10^{-3}\ \tilde{\nu}_{max}$(solv)/$cm^{-1}$									
Anion	Solid	dce	$MeNO_2$	MeCN	Me_2CO	H_2O	MeOH	EtOH	dmf	dmso
BPh_4^-	20.0	20.0	23.5	17.5	17.7		17.1	17.1	16.6	16.5
BF_4^-	18.9	19.0					17.0			
ClO_4^-	18.6	18.6	19.0	17.3	17.5		16.9	17.1	16.6	16.5
CO_3^{2-}	17.5	17.8								
$CF_3SO_3^-$	17.2	17.2								
NO_3^-	16.5	16.5			16.5		16.9	16.9		
CN^-		15.5								
I^-	15.2	15.2	19.0	17.1	16.9	16.9	16.8	16.5	16.3	
$MeCO_2^-$		15.1	18.9							
SCN^-	14.8	14.7	18.8	15.7	14.8	16.9	16.8	16.3	16.2	16.2
Br^-	14.5	14.4	18.8	15.6	14.4	16.9	16.8	16.7	16.2	16.2
N_3^-	14.4	14.3	18.7	15.0	14.1	16.9	16.8	16.3	15.3	16.1
OH^-		14.2	18.7							
Cl^-	14.1	14.0	18.6	14.5	13.8	16.9	16.9	16.7	14.7	15.7
NCO^-	13.4	13.3	18.4	13.7	13.3	16.9	16.9	15.9	14.0	14.8

on the one hand, when the donor strength of the solvent is higher than that of the anion the solvent preferably co-ordinates to the copper complex, but on the other hand a solvent exhibiting strong acceptor properties will compete for co-ordination of the anion (preferentially solvating the anion).

Thus when $[Cu(acac)(tmen)]^+$ is dissolved in a series of solvents the $\tilde{\nu}_{max}$ values remain constant until an anion with a larger donor strength is reached. As long as this situation is not reached the (constant) $\tilde{\nu}_{max}$ values refer to the spectra of solvated $[Cu(acac)(tmen)]^+$ and *thus reflect the donor number of the solvent*. For example, in the case of strong acceptor solvents such as MeOH (acceptor number AN = 41.5) or water (AN = 54.8) even strongly donating anions do not alter this value because in this case the solvent preferentially solvates the anion.

Increasing the donor properties of the anion leads to a point where the anions co-ordinate significantly to $[Cu(acac)(tmen)]^+$ so that further increase in the donor strength of the anion will lead to decreasing (now anion-governed) shifts of $\tilde{\nu}_{max}$, parallel to the shift observed for dce solutions (see Fig. 3). This discontinuity occurs in the case of dmf, for example, with I^- and in the case of dmso with Br^-.

The ascending parts of the curves (*i.e.* to the left of the discontinuity) therefore depend on both the donor and acceptor numbers of the respective solvent, and, since dce has been taken as the standard solvent, relationship (4) holds, in which the

$$10^{-3}\ \tilde{\nu}_{max}(solv) = 10^{-3}\ \tilde{\nu}_{max}(dce) + a(DN_{solv} - DN_{dce}) + b(AN_{solv} - AN_{dce}) \quad (4)$$

donor and acceptor numbers for dce are known (0 and 16.7 respectively).

A multiple regression analysis of the data yielded values of $a = 0.063 \pm 0.003$ and $b = 0.091 \pm 0.022$ ($r = 0.968$) leading to equation (5).

$$10^{-3}\,\tilde{\nu}_{max}(solv) = 10^{-3}\,\tilde{\nu}_{max}(dce) + 0.063\,DN_{solv} + 0.091\,(AN_{solv} - 16.7) \quad (5)$$

The $\tilde{\nu}_{max}$ values have been measured for a large number of solvents interacting with $[Cu(acac)(tmen)]BPh_4$.[14] We have linearly correlated the (energy related) $\tilde{\nu}_{max}$ values with the solvent donor numbers (DN_{solv}) and arrived at expression (6).

$$10^{-3}\,\tilde{\nu}_{max} = 20 - 0.103\,DN_{solv} \qquad (r = 0.97) \quad (6)$$

Setting equations (5) and (6) equal gives the condition for the intersection of the curve governed by the solvent properties with the curve depending on the anion. At this intersection point the donor properties of the solvent and those of the anion (dissolved in this solvent) are equal and thus the donor number obtained by equation (7) can be defined, as indicated, as the apparent donor number of the anion dissolved in that particular solvent ($DN_{X,solv}$).

$$DN_{X,solv} = 129.6 - 0.548\,AN_{solv} - 0.006\,02\,\tilde{\nu}_{max}(dce) \quad (7)$$

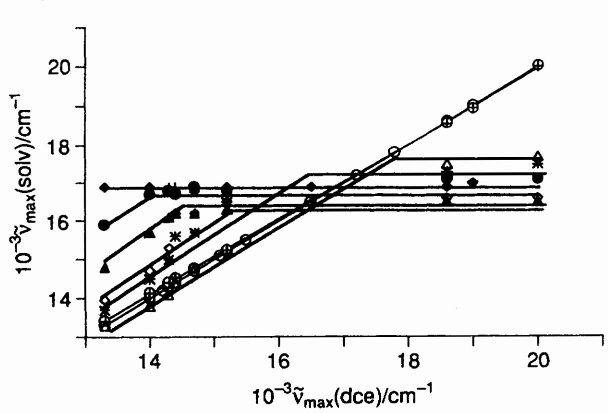

Fig. 3 Absorption maxima of [Cu(acac)(tmen)X] in various solvents, $\tilde{\nu}_{max}$(solv), solv = dce (○), MeCN (✱), Me_2CO (△), H_2O (+), MeOH (◆), EtOH (●), dmf (◇), dmso (▲), $MeNO_2$ (+) and in the solid state (⊕) *versus* the absorption maxima found in dce $\tilde{\nu}_{max}$(dce)

When the solvent is dce the number obtained is the donor number, $DN_{X,dce}$ of the anion X^- on the *same scale as Gutmann's donor numbers of solvents*.[1] Table 2 gives some of these donor numbers for a series of anions and solvents calculated by use of equation (7). Obviously values for other solvents and anions can readily be obtained by this method. Virtual gas phase donor number of anions can be obtained using $AN_{solv} = 0$ or by adding 9.15 to the $DN_{X,dce}$ values. The table shows that whenever solution properties are considered both acceptor and donor properties of solvent (and solute) have to be taken into account even when only one of them seems to be of importance to an investigated reaction. $DN_{X,solv}$ values which are considerably smaller than the donor number of the solvent are given in italics because they exhibit no donor properties toward hard acceptors in this particular solvent. However, they might still contain information, for example when investigating reaction kinetics where even low concentrations of co-ordinated species can be important and they show that the order still persists.

The $DN_{X,MeCN}$ values obtained in this way differ markedly from those estimated by Gutmann and Mayer,[8,9] especially the values for the halide ions which are much larger than those given by these authors [based on $VO(acac)_2$–anion association constants in MeCN], and possible reasons for this have been discussed above.

It is perhaps surprising that the CN^- ion does not exhibit a higher DN_X value. However, the co-ordination ability of CN^- is strongest towards soft cations where strong back-donation is involved. The DN scale refers generally to hard–hard interactions and the copper(II) co-ordination centre of the complex employed in these studies is unlikely to be involved in strong p_π–d_π interactions.

Application of the Parameters to Equilibrium Constants.—As a first step for testing the significance of the obtained donor numbers, equilibrium constants of the reaction (2) have been measured by spectrophotometric titration in dce.[13,15,26,27] The logarithms of the formation constants (Table 3) are found to be linearly related with $DN_{X,dce}$ yielding ($\log K = -2.02 + 0.443\,DN_{X,dce}$; $r = 0.993$) suggesting that the entropy contribution to ΔG for this system is low or linear [*i.e.* following an

Table 2 Donor numbers (DN_X) of anions and apparent donor numbers of anions dissolved in various solvents ($DN_{X,solv}$), calculated from equation (7)*

		Apparent donor numbers ($DN_{X,solv}$)							
Anion	DN_X dce	$MeNO_2$	MeCN	Me_2CO	H_2O	MeOH	EtOH	dmf	dmso
BPh_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]	*4.83*	*8.33*	*−14.8*	*−7.56*	*−5.69*	*6.42*	*4.61*
ClO_4^-	**8.44**	6.36	*7.24*	*10.7*	*−12.4*	*−5.15*	*−3.18*	*8.83*	*7.02*
CO_3^{2-}	**13.3**	11.2	*12.1*	*15.6*	*−7.62*	*−0.33*	*1.64*	*13.6*	*11.8*
$CF_3SO_3^-$	**16.9**	14.8	[15.7]	[19.2]	*−4.00*	*3.29*	*5.26*	*17.3*	*15.5*
NO_3^-	**21.1**	19.0	19.9	23.4	*0.21*	*7.50*	*9.47*	*21.5*	*19.7*
CN^-	**27.1**	25.0	25.9	29.4	*6.24*	*13.5*	*15.5*	[27.5]	*25.7*
I^-	**28.9**	26.8	27.7	31.2	*8.04*	*15.3*	*17.3*	29.3	*27.5*
$MeCO_2^-$	**29.5**	27.4	28.3	31.8	*8.65*	*15.9*	*17.9*	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

* Numbers in bold refer to solution in dce, *i.e.* they are donor numbers on the same scale as Gutmann's donor numbers for solvents. Brackets indicate that the ion may exhibit donor properties in this solvent. 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 anion exhibits no donor properties toward hard acceptors in this particular solvent.

Table 3 Equilibrium constants log K for the reaction $[Cu(acac)(tmen)]^+ + X^- \rightleftharpoons [Cu(acac)(tmen)X]$ and molar conductivity data in various solvents

	log K^a	Λ_M/Ω^{-1} cm^2 mol$^{-1\,b}$		
Anion	dce	dce	$MeNO_2$	dmso
ClO_4^-		24.8 (100)		
NO_3^-		6.6 (33)		
CN^-	3.20	6.6 (33)		
I^-	3.32	6.6 (33)	83.6 (98)	35.4 (100)
NCS^-	3.42	1.2 (6)	56.6 (65)	39.8 (100)
Br^-	3.49	1.1 (5)	70.5 (83)	36.1 (100)
N_3^-	3.55	1.0 (3)	27.0 (32)	32.0 (92)
Cl^-	3.60	0.6 (3)	43.7 (51)	21.7 (26)
NCO^-		0.5 (3)	21.7 (26)	14.8 (42)

[a] From spectrophotometric titration. [b] From conductivity data[10,32–34] (1 mmol dm^{-3} solution); estimated percentage of degree of dissociation given in parentheses.

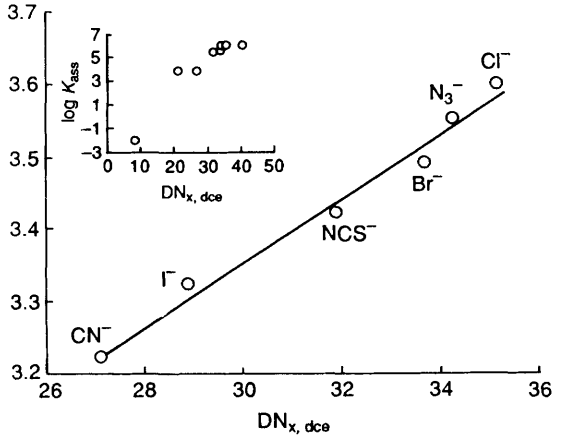

Fig. 4 Logarithms of the equilibrium constants for the reaction $[Cu(acac)(tmen)]^+ + X^- \rightleftharpoons [Cu(acac)(tmen)X]$ in dce *versus* anion donor number. [Logarithms of the estimated association constants K_{ass} calculated from conductivity data are given *versus* $DN_{X,dce}$ as an insert]

isoparametric relationship[37,38] (Fig. 4)]. For comparison molar conductivity data,[10,32–34] which can be used to estimate degrees of ion-pair dissociation are given for various solvents. They are in agreement with the spectrophotometric results obtained for dce. The data show that in solvents of higher donor number (for example dmso) complete dissociation is found for anions with donor numbers smaller than that of the respective solvent. For anions with stronger donor properties than the solvent the conductivity data correlate linearly with the $DN_{X,solv}$ values ($r > 0.95$).

Kinetic Data.—The obtained $DN_{X,solv}$ values can also be related to kinetic data. As an example we use the rate constants for reaction (8) (terpy: 2,2′:6′,2″-terpyridine) which has been

$$Ni^{2+} + X^- + terpy \longrightarrow [NiX(terpy)]^+ \qquad (8)$$

observed in acetonitrile solution.[39] It has been proposed that a fast pre-equilibrium [equation (9)] of the formation of NiX^+, $Ni^{2+} + X^- \rightleftharpoons NiX^+$, is followed by addition of terpy, equation (10).

$$NiX^+ + terpy \longrightarrow [NiX(terpy)]^+ \qquad (10)$$

It has been suggested[39] that the rate constant of reaction (8) is mainly governed by the pre-equilibrium (9) and that the reaction step (10) appears to be only weakly influenced by X^-. The effect of the donor numbers of the anion on reaction (8) is shown in Fig. 5; the overall rate constants for the reaction (8) are plotted versus $DN_{X,MeCN}$ yielding the linear relationship log $K = -0.43 + 0.191\ DN_{X,MeCN}$ ($r = 0.998$).

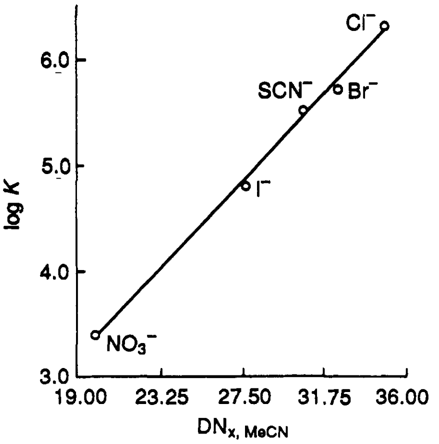

Fig. 5 Logarithms of the rate constants observed in acetonitrile solution for the reaction $Ni^{2+} + X^- + terpy \longrightarrow [NiX(terpy)]^+$ versus $DN_{X,MeCN}$ of the anion

Free Energy of Transfer.—Free energies of transfer (ΔG_{trans}) of anions from one solvent to another solvent can be considered as a characteristic parameter for solvation of ions. Such values are available for a transfer from water to various solvents[40] and are plotted in Fig. 6 versus $DN_{X,solv}$ and in an insert *versus* $DN_{X,dce}$. Non-co-ordinating anions show negative $\delta\Delta G_{trans}$ values within a given solvent, *i.e.* anions such as BF_4^- and BPh_4^- are better solvated in non-aqueous solvents than in water (BPh_4^- values fit the given regression line but are omitted in Fig. 6 for clarity of the plot).

The ΔG_{trans} values for a given solvent increase linearly with the $DN_{X,dce}$ values ($r > 0.98$). The obtained straight lines show a common point of intersection, *i.e.* isoparametric behaviour, meaning that slopes and intercepts are linearly dependent.[37,38] According to this an anion with a $DN_{X,solv}$ of about 14 (for example CO_3^{2-}) should show a minimal variation in $\delta\Delta G_{trans}$ between water and one of the investigated solvents. The occurrence of an isoparametric relationship includes the existence of a generalized linear free-energy relationship (l.f.e.r.)[37,38] which is found in a linear dependence of both the slopes and the intercept *versus* the solvent AN_{solv}. It is this parameter which is responsible for the solvation of anions and which yields $DN_{X,solv}$ according to equation (7). Using therefore the newly defined solvent-specific $DN_{X,solv}$ values combines the points from various solvents to a single smooth curve [$\Delta G_{trans} = 0.35 + \exp(0.092\ DN_{X,solv})$, $r = 0.98$]. The non-linearity of this curve (the slope of the curve increases towards increasing DN values) reflects increasing solvent–solvent interactions due to interactions of the acceptor and the donor properties of the solvent which are increasingly disturbed by the donor properties of anions.

Conclusion

The result that the apparent donor numbers of anions depend upon both the donor and the acceptor properties of the solvent (Table 2) strongly suggests that, in general (*i.e.* not only for anions but also for the solvents themselves), donor and acceptor properties cannot be described by independent parameters. Thus donor- and acceptor-number scales are only viable when the contrary attribute can safely be disregarded or can be taken as a constant value. A good example where both solvent attributes must be considered is the correlation of the degree of ionization of a given solute with the properties of a series of solvents. Gutmann[41] correlated the degree of ionization with the donor number by disregarding the solvation of the anion when assuming the initiation step to be as represented by

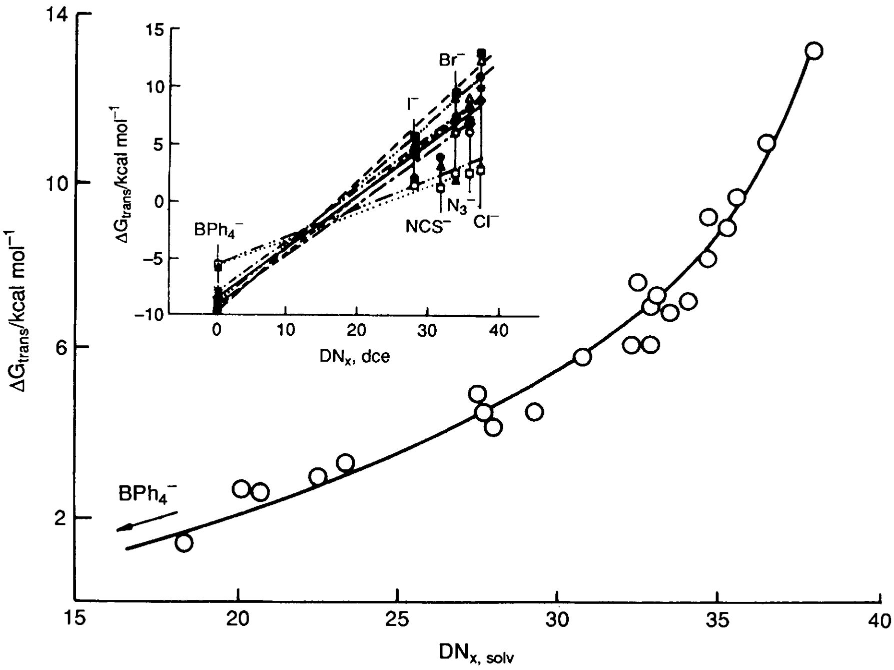

Fig. 6 Free energies of transfer (ΔG_{trans}) of anions from water to various solvents *versus* the donor number of the anion in the respective solvent [the insert shows ΔG_{trans} versus the donor number of the anion in dce: tetramethylene sulfone (□), dmf (✱), MeOH (○), dmso (△), MeCN (+), H_2NCHO (○), pdc (◆) and mpyr (□)]

equation (11). This can only be valid if either the anion has weak donor properties or the solvent is a weak acceptor.

$$D\colon + A{-}B \rightleftharpoons [D{-}A]^+[B]^-_{\text{ion pair}} \qquad (11)$$

Difficulties must also be expected to arise when assigning a donor number to any solvent (or ion) that has strong acceptor properties (*e.g.* water, where self association is largely due to this effect and has a marked role to play). In this respect it is of course of importance to remember that dce was taken as the standard solvent in this work and that its acceptor properties may not be ignored (AN = 16.7). It should be noted that a solvent with an extremely low acceptor number would be impractical for the measurement of donor numbers because of solubility problems—in itself emphasizing the interdependence of these parameters. Thus donor or acceptor numbers of solvents should only be used as a single parameter as a means for correlating data or as a predictive tool when the contrary attribute may safely be ignored or taken as constant.[42] This of course only slightly detracts from the immense value of these two solvent parameters.

Acknowledgements

Thanks are due to the Fonds zur Forschung der wissenschaftlichen Forschung in Österreich for financial support (Project 8795), and to the Ministry of Education of Egypt for the support *via* their channel-program allowing A. T. to stay in Vienna while performing this work.

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Received 27*th May* 1993; *Paper* 3/03029F