Lewis acidity parameter for binary solvent mixtures and adduct formation studies using the solvatochromic dicyanobis(1,10-phenanthroline)iron(II) complex†

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The values of the Lewis acidity parameter (acceptor number) for acceptor compounds (AN_v) and twenty binary solvent mixtures (AN_m) were estimated using the solvatochromic dicyanobis(1,10-phenanthroline)iron(II) complex. The acceptor number values for the acceptor compounds (AN_v) are linearly correlated with the Taft constant (σ_{Taft}) and the formation constant values. On the other side, AN_m values for binary solvent mixtures over the whole composition range of the mixture are correlated with the other solvent parameters and equilibrium data. These correlations suggest the importance of the present AN_m values to correlate the reaction rates, and may be used as an aid in the interpretation of equilibrium studies in solvent mixtures. Equilibrium constants, for the stepwise interaction of one or two acceptor ligand molecules with $Fe(phen)_2(CN)_2$ in DMF solution at 25 °C to form adducts, $Fe(phen)_2(CN)_2(A)_n$, have been evaluated using a spectrophotometric technique. The equilibrium constants obtained were correlated with the values of the dissociation constant (pK_a), acceptor number, and σ_{Taft} of the acceptor ligands.

In the preceding communications detailed spectroscopic, thermodynamic, electrochemical studies, and quantum mechanical calculations on the solvato- and thermochromism of $[M(\beta\text{-dik})(diam)]^+$ complexes [M = Ni(II) or Cu(II), β-dik = β-diketonates, diam = diamines] have been reported.[1–8] Color changes for these complexes are brought about by a direct attachment of solvent molecules to the metallic center, which modifies the geometry and ligand field strength of the complex and affects its d-d transition bands.[9–12] The donor strength of the solvent was the dominant factor in these solvatochromic changes. In contrast, color changes of $Fe(L)_2(CN)_2$ complexes [L = diimine, *viz.* 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy)] are brought about by the attachment of solvent molecules onto the ligand(s), which affects the energy of metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) bands.[13–16] In this case, the acceptor properties of the solvent determine the direction and magnitude of the color change, according to the nature of the CT band and that of the solvent-ligand interaction.

In one of our previous studies, an estimation of the acceptor numbers of cations in aqueous and non-aqueous solutions using $Fe(phen)_2(CN)_2$ as a Lewis acid-base indicator was performed.[17] It seems important to extend these investigations to estimate the (unknown) acceptor numbers for some acids. Since many chemical reactions are carried out in solvent mixtures it is prudent to investigate the possible extension of Lewis acidity scales, such as the acceptor number values for binary solvent mixtures (AN_m). Such mixtures are very useful for studying solvent effects upon reactions, since the properties of various mixed solvents can be adjusted continuously by changing the composition of the mixture.

In the last decade, in parallel with the development of supramolecular chemistry, polynuclear cyano-bridged complexes have been incorporated in supramolecular structures for the design of photochemical molecular devices,[18] especially for the collection of electronic energy or charge and intramolecular electron transfer between remote redox centers.[19] Since $M(phen)_2(CN)_2$ has two cyano groups as potential bridging sites, both 1 : 1 and 1 : 2 adducts can be expected as the result of second-sphere donor-acceptor (SSDA) interactions with metal-containing moieties.[19] In order to give a quantitative insight into the dynamic electronic redistribution produced from the interaction of the acceptor ligand (A) with the iron(II) complex, equilibrium studies for the adduct formation of $Fe(phen)_2(CN)_2A_n$ were carried out in DMF solution.

Thus, the purpose of the current work was (*i*) to estimate the Lewis acidity for some acceptor compounds and binary solvent mixtures and (*ii*) to investigate the equilibrium constants of adduct formation, $Fe(phen)_2(CN)_2A_n$.

Experimental

Chemicals

The chemical reagents were from Merck and Aldrich and have been used without further purification. The solvents were purified using standard methods.[20] The indicator complex, $Fe(phen)_2(CN)_2$, was synthesized and characterized as low-spin octahedral as described in our previous work,[21] Scheme 1.

Measurements

A freshly prepared stock solution of 1.5×10^{-4} M $Fe(phen)_2(CN)_2$ in *N*,*N*-dimethylformamide (DMF) was employed to examine the electronic spectra and equilibrium constants at 25 ± 0.02 °C using a Jasco V-550 spectrophotometer equipped with a thermoelectric cell holder. For each acceptor compound or solvent mixture the spectrum was measured three times at

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† Electronic supplementary information (ESI) available: table of calculated AN_m values. See: http://www.rsc.org/suppdata/nj/b1/b110650n/

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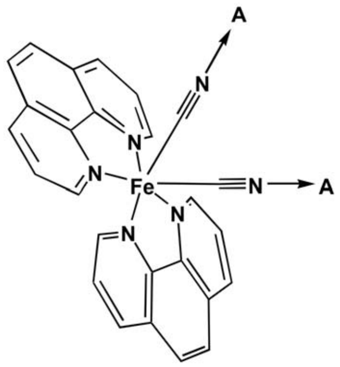

Scheme 1 Mode of the acceptor molecule (A) interactions with the indicator complex, $Fe(phen)_2(CN)_2$; the geometry was optimized by the Alchemy 2000 program.

three different concentrations of the indicator iron(II) complex in the range $0.5–1.5 \times 10^{-4}$ M. To obtain the equilibrium constant values the solution of the acceptor ligand compound in DMF was added to the complex solution in the course of the titration procedure. Up to ten spectra were recorded and stored in the multichannel memory. The spectral titration so obtained was fitted by means of the combined Marquardt–Newton method[22] to evaluate the equilibrium constant values for the reaction of iron(II) complex with the acceptor ligand (A) according to the following equilibria:

$$[Fe(phen)_2(CN)_2] + A \overset{K_1}{\rightleftharpoons} [Fe(phen)_2(CN)_2A] \qquad (1)$$

and

$$[Fe(phen)_2(CN)_2A] + A \overset{K_2}{\rightleftharpoons} [Fe(phen)_2(CN)_2A_2] \qquad (2)$$

Two replicates were obtained for each spectrum from identical and independently prepared test solutions.

Results and discussion

Spectroscopic studies

Frequencies of the absorption maximum (ν_{max}) for the lowest energy MLCT of the indicator complex, $Fe(phen)_2(CN)_2$, measured in different acceptor solvents and carboxylic acids diluted/dissolved with DMF solvent are reported in Table 1. DMF solvent was selected as a medium for the spectroscopic measurements because it has a relatively weak acceptor number (AN = 16).[23]

Table 1 Absorption maxima of 1.0×10^{-5} M of $Fe(phen)_2(CN)_2$ complex in twelve solutions of the acceptor compounds (10-fold excess) in DMF solvents and apparent acceptor numbers according to eqn. (3)

No.	Ligand	$\nu_{max}/10^3$ cm^{-1a}	$AN_v{}^b$	AN^c
1	H_2O	19.27	56.0	54.8
2	EtOH	17.85	36.3	37.9
3	$CHCl_3$	16.85	22.4	25.1
4	HCOOH	21.30	84.4	83.6
5	MeCOOH	18.86	50.3	52.90
6	$Cl_2CHCOOH$	22.15	96.0	–
7	CF_3COOH	22.95	107.1	105.3
8	EtCOOH	18.94	51.4	–
9	$CNCH_2COOH$	19.08	53.3	–
10	$SHCH_2COOH$	19.18	54.7	–
11	$PhCH_2COOH$	18.87	50.4	–
12	Ph_2CH_2COOH	17.95	37.6	–

[a] Measured in DMF solvent. [b] Calculated using eqn. (3). [c] Gutmann's AN taken from ref. 23.

Treatment of the results, $\nu_{max}/10^3$ cm^{-1}, for the indicator complex in various pure solvents *versus* the acceptor number (AN) by a linear regression analysis produces eqn. (3), with a standard deviation $S = 2.21$, $r = 0.99$ and statistical $F = 439.6$ for 6 data points.

$$AN_\nu = (13.93 \pm 0.65)\nu_{max} - (212.21 \pm 11.11) \qquad (3)$$

We justify the shift of MLCT band to higher frequencies, as the acceptor properties increase, because the acceptor molecules are strongly oriented in the neighborhood of the cyanide groups by donor-acceptor interactions as indicated in Scheme 1.[24,25] This interpretation is confirmed by the reported X-ray crystal data for $[(Fe(CN)_2(phen)_2)_2Yb_2]^{6+}$ and $Fe(CN)_2(phen)_2 \cdot 3H_2O$ adducts, where the Fe–C bond lengths were 1.86 and 1.917 Å, respectively.[26,27] These data refer to the dependence of Fe–C bond length on the Lewis acidity of the acceptor molecule, which reinforce the π-backbonding with the metal ion.[24] Since the Lewis acidity of Yb^{3+} is higher than that of H_2O,[17,23] so the Fe–C bond length is shorter in the former case than the latter one as expected from the extended donor acceptor concept.[28]

In fact, the continuous shift of the lowest energy metal-to-ligand charge transfer band (ν_{max}) of the indicator complex with changing acceptor properties could be used, by applying eqn. (3), to estimate the Lewis acidity parameter (AN_v) for some of the acceptor compounds and binary solvent mixtures. Table 1 shows the calculated AN_v values for acceptor compounds. The acceptor numbers (AN_m) for several aqueous and non-aqueous binary solvent mixtures over the whole composition range of the mixture are listed in Table S1 of the ESI.

Applications of the acceptor number parameter

The Lewis acidity values (AN_v) calculated for the acceptor compounds given in Table 1 are in quite good agreement with the original acceptor numbers (AN).[23,29] AN_v values for acceptor compounds (carboxylic acids) are found to be directly proportional to their acidic strength as measured by the pK_a values: $AN_v = -(12.3 \pm 0.75)\, pK_a + (108 \pm 2.75)$, $r = 0.99$ and $F = 266.2$ for 6 data points. Furthermore, AN_v values are found to be linearly correlated with the Taft constant (σ_{Taft}) of the acetic acid derivatives: $AN_v = -(37.30 \pm 2.84)\ \sigma_{Taft} + (51.20 \pm 2.32)$, $r = 0.98$, $F = 172.0$ for 6 data points. The negative slopes of the pK_a and Taft plots mean that with increasing acidity and/or electron-withdrawing properties of the substituents on the acceptor compound the AN_v value is increased.

The correlation data of the calculated Lewis acidity values (AN_m) with the available corresponding polarity parameter (E_T)[30–33] of various binary solvent mixtures, $AN_m = aE_T + b$, are summarized in Table 2. The differences in slope (a) and intercept (b) values of the AN_m *vs.* E_T plots might be attributed to the solvent-solute and solvent-solvent interactions. Since $Fe(phen)_2(CN)_2$ and betaine were used as probes to calculate the AN_m and E_T parameters,[33] respectively, the b values are different because the basicity of betaine is less than that of the iron(II) complex.[34] This finding is in consistent with that obtained by Linert *et al.*[34] However, solvent-solvent interactions strongly affect the obtained a and b values when using a mixed solvent. Furthermore, the linear dependence of both a and b values upon donor (DN) and acceptor strengths of the co-solvent supports the effect of solvent-solvent interactions on the slope and intercept of the AN_m *vs.* E_T plots according to the equation: $y = c_1\,DN + c_2\,AN + m_0$, the resulting data are summarized in Table 3. These data indicate increase of a and decrease of b as the acceptor strength of the co-solvent increases for both water and acetone systems. On the other

Table 2 Correlation data of the acceptor number for eight solvent mixtures (AN_m) *vs.* their corresponding E_T parameter, according to the following equation: $AN_m = aE_T + b$

No.	Mixture A–B	Intercept (*b*)	Slope (*a*)	r^a	F^b	n^c
1	H_2O–Me_2CO	−91.24 ± 2.21	2.48 ± 0.04	0.999	3313.8	9
2	H_2O–MeOH	−56.25 ± 2.67	1.83 ± 0.05	0.998	1542.4	9
3	H_2O–EtOH	−31.26 ± 3.40	1.38 ± 0.06	0.993	521.0	9
4	H_2O–Diox	−30.10 ± 2.66	1.39 ± 0.05	0.991	658.2	9
5	H_2O–DMSO	−81.70 ± 8.30	2.27 ± 0.16	0.986	207.9	5
6	H_2O–DMF	−1.06 ± 0.06	0.95 ± 0.02	0.999	3446.3	9
7	Me_2CO–EtOH	−105.40 ± 8.55	2.68 ± 0.17	0.988	247.7	8
8	Me_2CO–DMSO	−35.20 ± 3.56	1.18 ± 0.08	0.986	216.4	8
9	Me_2CO–$CHCl_3$	56.92 ± 3.48	−0.86 ± 0.08	0.986	108.1	5
10	MeOH–MeCN	−122.0 ± 8.91	2.94 ± 0.16	0.982	319	8
11	MeOH–$CHCl_3$	−16.6 ± 1.9	1.06 ± 0.04	0.99	692.8	9

[a] Correlation coefficient. [b] Statistical parameter. [c] Number of data points.

Table 3 Multiparameteric correlations of the slopes (*a*) and intercepts (*b*) of the AN_m *vs.* E_T plots (taken from Table 2) with donor and acceptor numbers of the co-solvent, $y = c_1\,DN + c_2\,AN + m_0$

System		c_1	c_2	m_0	r^a	F^a	n^a
Water	*a*	−0.17 ± 0.02	0.59 ± 0.01	4.68 ± 0.30	0.99	46.8	4
	b	10.2 ± 1.3	−3.63 ± 0.06	−218 ± 2.4	0.98	31.0	4
Acetone	*a*	0.084 ± 0.0005	0.064 ± 0.0005	−2.50 ± 0.21	0.99	208.0	4
	b	−3.87 ± 0.32	−2.83 ± 0.30	−130 ± 1.4	0.99	98.6	4

[a] See Table 2.

hand, as the donor strength of the co-solvent increases *a* decreases and *b* increases for the water system and *vice versa* for the acetone system. This confirms the converse relationship of the internally consistent scales, AN and DN, of the co-solvent.

Furthermore, AN_m values are found to be linearly correlated with the theoretical local mole fraction (X_L) values, which are calculated by applying the quasi-lattice-quasi-chemical theory of preferential solvation,[35,36] yielding: $AN_m = (0.034 \pm 0.001)\ X_L - (0.84 \pm 0.02)$, $r = 0.99$, for water–DMF solvent mixtures.

The obtained AN_m values are also related to the possible kinetic data in mixed solvents,[37–39] such as the solvolysis of $(CH_3)_3CCl$, α-phenylethyl chloride and neophenylethyl bromide $(CH_3)_3CBr$ in ethanol–water,[37] that of $(CH_3)_3CBr$ in acetone–water,[37,38] and that of *cis*-bromo(benzimidazole)-bis(en)Co(III) in methanol–water solvent mixtures, as shown in Fig. 1.[39] The linearity of the log *k vs.* AN_m plots confirms the importance of the present AN_m values to correlate the reaction rates, and may be used as an aid in the interpretation of equilibrium data in solvent mixtures.

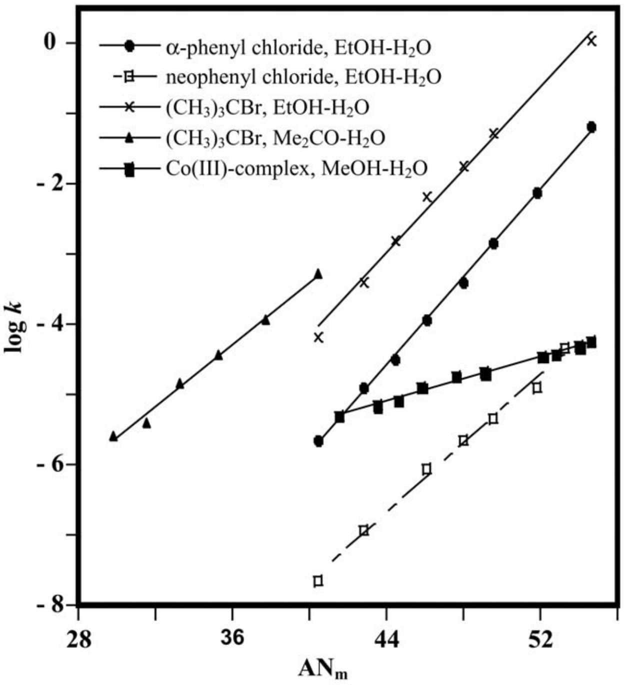

Fig. 1 Correlation of the rate constant values of the solvolysis of some organic halide compounds and Co(III) complexes in different binary solvent mixtures as a function of the AN_m parameter.

Equilibrium studies

The spectra obtained in the course of the titration of the indicator complex, $Fe(phen)_2(CN)_2$ with twelve acceptor ligands (A) in DMF solution at 25 °C shows a well-defined set of isosbestic points near 700, 475 and 455 nm. Consequently, three equilibrium species can be suggested, $Fe(phen)_2(CN)_2$, $Fe(phen)_2(CN)_2(A)$ and $Fe(phen)_2(CN)_2(A)_2$, respectively. The equilibrium between $Fe(phen)_2(CN)_2$ and $Fe(phen)_2(CN)_2(A)$ species might be related to the spectral series that show isosbestic points near 700 and 475 nm when the molar ratio of titrant (A) to the metal complex is less than unity. A distinctly new spectral set appears when the same ratio is greater than one and a new widespread isosbestic point is observed near 455 nm, referring to an equilibrium between $Fe(phen)_2(CN)_2(A)$ and $Fe(phen)_2(CN)_2(A)_2$ species. In the immediate neighborhood of a molar ratio of one, all three species are present in relatively significant amounts since the isosbestic character of the spectral series is not clear. This interpretation is supported by the evidence reported for the existence of stable protonated species of the $Fe(phen)_2(CN)_2$ complex and the exhibited dibasic character in strong mineral acids and in the presence of lanthanide ions.[26,40] The position of the interaction has been suggested to be at the nitrogen of the cyanide ligand.[14,17,21,34]

Table 4 Equilibrium constant values (in dm^3 mol^{-1}) of the adduct formation of Fe(phen)$_2$(CN)$_2$ complex with twelve acceptor ligands in DMF solution at 25 °C. The number of data points used for the calculations is greater than ten

No.	Ligand	K_1	K_2	S^{2a}	$K_1 * K_2$	K_2/K_1
1	H_2O	0.0068	0.60	3.0×10^{-5}	4.1×10^{-3}	88.4
2	EtOH	0.025	0.014	2.2×10^{-5}	3.5×10^{-5}	0.56
3	$CHCl_3$	0.0083	0.0025	3.8×10^{-5}	2.1×10^{-5}	0.30
4	HCOOH	0.67	2.43	5.3×10^{-5}	1.6	3.6
5	MeCOOH	0.053	0.60	1.9×10^{-5}	0.032	11
6	$Cl_2CHCOOH$	3.62	3.17	2.2×10^{-5}	11.5	0.88
7	CF_3COOH	2.89	64.5	1.3×10^{-5}	186	22.3
8	EtCOOH	0.25	0.0088	2.4×10^{-5}	2.2×10^{-3}	0.035
9	$CNCH_2COOH$	1.42	0.53	3.8×10^{-5}	0.75	0.37
10	$SHCH_2COOH$	0.89	0.0029	6.1×10^{-5}	2.6×10^{-3}	0.0033
11	$PhCH_2COOH$	0.011	10.27	3.1×10^{-5}	0.11	930
12	Ph_2CH_2COOH	0.022	7.30	2.3×10^{-5}	0.16	330

[a] Square of the standard deviation.

The absorbance value found at the maximum of the lowest energy MLCT absorption band of the iron(II) complex decreases on addition of acceptor ligands (A) and this has been used to evaluate the equilibrium constant values for adduct formation. The least-square analysis of up to ten data points suggests that the interaction of the acceptor ligand with the iron(II) complex proceeds *via* two steps as described in the previous section. The resulting equilibrium constant values (K_1 and K_2) for the present complex with several acceptor ligands are given in Table 4. The logarithms of the overall formation constant values are linearly correlated with pK_a and σ_{Taft} constant values of the acceptor ligands yielding: $\log K_1K_2 = -(0.89 \pm 0.11)\text{p}K_a + (2.33 \pm 0.38)$, $r = 0.97$, $F = 63.5$ and $\log K_1K_2 = (2.72 \pm 0.35)\sigma_{\text{Taft}} - (1.73 \pm 0.27)$, $r = 0.97$ and $F = 57.6$ for 7 data points in both cases, respectively. The negative and positive slopes obtained from the pK_a and Taft plots refer to increasing equilibrium constant values with increase of the ligand acidity and electron-withdrawing properties of the substituents at the acceptor ligand vicinity.

Fig. 2 shows the significance of the obtained acceptor numbers for the acceptor compounds (AN$_v$), where the logarithm of the obtained overall equilibrium constant value is found to be linearly correlated with AN$_v$, yielding $\log K_1K_2 = (0.073 \pm 0.03)\ \text{AN}_v - (6.33 \pm 0.19)$, $r = 0.99$ and $F = 616.2$ for 8 data points. The data points of cyanoacetic, propionic, naphthylacetic (Ph_2CH_2COOH) and phenylacetic ($PhCH_2COOH$) acid acceptor ligands are excluded from the regression linearity. The deviation of the adduct equilibrium constants of these ligands could be due to the preferential solvation of the reactants or the transition state.[21,41,42]

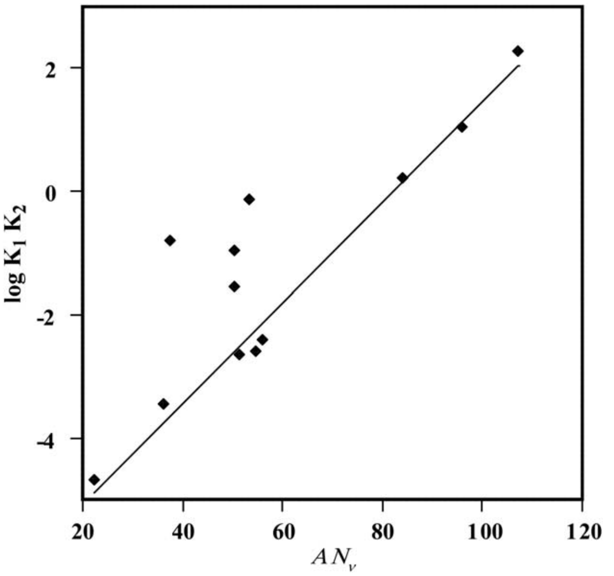

Fig. 2 Correlation of log K_1K_2 of the adduct formation between the Fe(phen)$_2$(CN)$_2$ complex and various acceptor ligands in DMF solution, *vs.* AN$_v$.

The data in Table 4 shows the following: (*i*) K values for acidic ligands are much higher than those of the neutral ligands, suggesting relatively weak basicity of the iron(II) complex, (*ii*) K_2 is much higher than K_1 for naphthylacetic, phenylacetic, triflouroacetic acids and water acceptor ligands, that is Fe(phen)$_2$(CN)$_2$(A)$_2$ is much more stable than the Fe(phen)$_2$(CN)$_2$(A) species. This trend might be attributed to strong intermolecular hydrogen bond formation for the molecules of the acceptor ligand in the cases of triflouroacetic acid and water ligands forming a cluster.[41,42] Moreover, the interaction between the first acceptor ligand molecule and cyanide of the iron(II) complex enhances the break-up of the hydrogen-bond network of the ligand molecules, giving a higher chance for the second ligand molecule to interact with the iron(II) complex. Furthermore, since the two cyano groups in the iron(II) complex are cis to each other (Scheme 1), the incoming second ligand molecule might stabilize the first one through its ability to form intermolecular hydrogen bonds.[19] However, the stabilization, in the presence of naphthylacetic and phenylacetic acid acceptor ligands, might be attributed to the extension of conjugation over the whole system *via* the interaction of the indicator complex with the second ligand molecule, as a result of second-sphere donor-acceptor (SSDA) interactions.[19]

The current results improve the worth of the correlations of the AN$_m$ parameter *versus* other parameters and rate constant data in the field of solution chemistry, along with the linearity of the equilibrium constant ($\log K_1K_2$) data with pK_a, σ_{Taft} and AN$_v$ values.

References

1 A. Taha, V. Gutmann and W. Linert, *Monatsh. Chem.*, 1991, **122**, 32.
2 W. Linert, V. Gutmann, A. Taha and S. El-Maraghy, *Rev. Roum. Chim.*, 1991, **36**, 4.
3 W. Linert, A. Taha and R. F. Jameson, *J. Coord. Chem.*, 1992, **25**, 29.
4 W. Linert and A. Taha, *J. Coord. Chem.*, 1993, **29**, 265.
5 A. Taha, W. Linert and Y. Fukuda, *J. Coord. Chem.*, 1993, **30**, 53.
6 W. Linert, R. F. Jameson and A. Taha, *J. Chem. Soc., Dalton Trans.*, 1993, 3181.
7 A. Taha, *Monatsh. Chem.*, 1994, **125**, 1189.
8 W. Linert and A. Taha, *J. Chem. Soc., Dalton Trans.*, 1994, 1091.
9 W. Linert, A. Taha and Y. Fukuda, *J. Coord. Chem.*, 1994, **33**, 235.

10 W. Linert and Y. Fukuda, *Coord. Chem. Rev.*, 2001, **218**, 113.
11 A. Taha, *Synth. React. Inorg. Met.-Org. Chem.*, 2001, **31**, 227.
12 A. Taha, *New J. Chem.*, 2001, **25**, 853.
13 J. Burgess, *Spectrochim. Acta, Part A*, 1970, **26**, 1369; J. Burgess, *Spectrochim. Acta, Part A*, 1970, **26**, 1957.
14 A. Al-Alousy and J. Burgess, *Inorg. Chim. Acta*, 1990, **169**, 167.
15 V. Gutmann, G . Resch and W. Linert, *Coord. Chem. Rev.*, 1982, **43**, 133.
16 R. W. Soukup and R. Schmid, *J. Chem. Educ.*, 1985, **62**, 459.
17 W. Linert, R. F. Jaeson, G. Bauer and A. Taha, *J. Coord. Chem.*, 1997, **42**, 211.
18 J. M. Lehn, *Angew. Chem., Int. Edn Engl.*, 1990, **29**, 1304.
19 R. Argazzi and C. A. Biggnozzi, *Coord. Chem. Rev.*, 1993, **125**, 283.
20 G. Porter and V. Hanten, *J. Inorg. Nucl. Chem.*, 1979, **18**, 2053.
21 A. Taha, A. A. T. Ramadan, M. A. El-Behairy, A. I. Ismail and M. M. Mahmoud, *New J. Chem.*, 2001, **25**, 1306.
22 D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 1963, **11**, 431.
23 U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235.
24 H. E. Toma and M. S. Takasugi, *J. Soln. Chem.*, 1983, **12**, 547.
25 N. K. Humer and L. E. Otgel, *Nature*, 1961, **190**, 439.
26 K. Harada, J. Yuzurihara, Y. Ishii, N. Sato, H. Kambayashi and Y. Fukuda, *Chem. Lett.*, 1995, 887.
27 Z. Zhan, Q. Meng, X. You, G. Wang and P. Zheng, *Polyhedron*, 1996, **15**, 2655.
28 V. Gutmann and G. Resch, *Monatsh. Chem.*, 1988, **119**, 1251.
29 U. Mayer, H. Hoffmann and R. Kellner, *Monatsh. Chem.*, 1988, **119**, 1223.
30 J. G. Dawber, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 287.
31 C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1988.
32 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.
33 E. Casassas, G. Fonrodona and A. de Juan, *J. Soln. Chem.*, 1992, **21**, 147.
34 W. Linert, F. Reginald and R. F. Jameson, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1415.
35 Y. Marcus, *J. Chem. Soc., Faraday Trans.*, 1989, **85**, 381.
36 T. M. Krygowski, P. K. Wrona and U. Zielkowska, *Tetrahedron*, 1985, **41**, 4519.
37 A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 1957, **79**, 1597; A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 1957, **79**, 1602; A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 1957, **79**, 1608.
38 E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 1948, **70**, 846.
39 A. C. Dash and N. Dash, *J. Chem. Soc., Faraday Trans.*, 1987, **83**, 2505.
40 A. A. Schilt, *J. Am. Chem. Soc.*, 1960, **82**, 3000.
41 E. Bosch, C. Rafols and M. Roses, *Anal. Chim. Acta*, 1995, **302**, 109.
42 (*a*) C. Rafols, M. Roses and E. Bosch, *J. Chem. Soc., Perkin Trans. 2*, 1997, 243; (*b*) C. Rafols, M. Roses and E. Bosch, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1341.