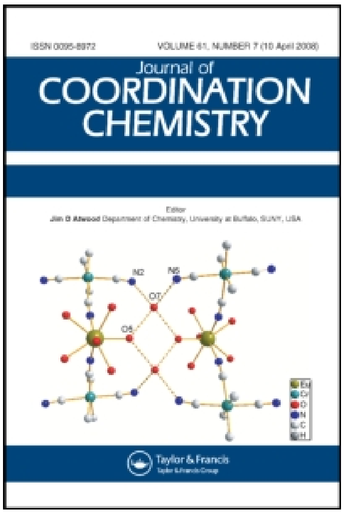

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SPECTROSCOPIC, THERMODYNAMIC AND QUANTUM MECHANICAL STUDIES ON SOLVATOCHROMIC MIXED LIGAND COPPER(II)-CHELATES

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Coordination of donor solvent molecules to square planar $Cu(acac)(tmen)^+$ ($acac^-$ = acetylacetonate, tmen = tetramethylethylenediamine) leads to a continuous shift of the d-d absorption band which is used to estimate donor numbers for a series of amines. Spectrophotometric methods are used to evaluate formation constants, enthalpies and entropies of formation for the consecutive coordination of one or two solvent molecules to the square planar $Cu(acac)(tmen)^+$ complex. The results are compared with those of the corresponding Ni(II) chelate showing larger formation constants than the copper(II) system. Quantum mechanical calculations were carried out within the CNDO/2 framework and related to experimental data. With increasing charge on the Cu atom, formation constants and ESR $g_{\parallel}$ values are increased.

KEY WORDS: Copper(II) chelates, donor numbers, chromotropic complexes, enthalpy and entropy of formation, CNDO/2 calculations.

INTRODUCTION

Detailed spectroscopic, thermodynamic and electrochemical studies of solvato- and thermochromic $[Ni(\beta\text{-dik})(diam)]B\phi_4$ ($\beta\text{-dik}^-$ = β-diketonates, diam = diamines) complexes have been reported previously.[1-3] In the present paper these investigations are extended to $[Cu(acac)(tmen)]B\phi_4$ in nonaqueous solvents. The nickel complexes are present in solution as two distinct species: a red square planar and a blue octahedral complex. In contrast to those, the copper(II) complexes show a continuous shift of d-d absorption maxima in the visible region associated with a distortion of the coordination sphere around the copper coordination centre. This shift is related to the solvent's donor numbers (DN),[4-11] which stimulated us to evaluate unknown

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DN of amines. Formation constants and thermodynamic parameters of complex formation for $[Cu(acac)(tmen)S_n]B\phi_4$ (where S = donor solvent molecule, n = 1 or 2) in non-aqueous solution were investigated and related with the obtained DN values. The obtained results can be compared with results originating from the respective Ni(II) chelate.[1] Quantum mechanical calculations were performed to yield insight into charge redistribution due to the coordination of solvent molecules.

EXPERIMENTAL AND THEORETICAL METHODS

Chemicals were obtained from Merck and Rathburn Chemicals. Solvents were purified using standard methods.[12,13] The amines were refluxed over calcium hydride and freshly distilled before use. The water contents of the solvents were found to be below 30 mg/l by means of Karl-Fischer titration (except the ketones).

Preparation of [Cu(acac)(tmen)]Bϕ₄

Some 10 g of twice recrystallized $Cu(acac)(tmen)NO_3.H_2O$[14] were dissolved in a small amount of 1,2-dichloroethane (DCE) and a suspension of 12 g of $NaB\phi_4$ in 50 cm^3 DCE was added with vigorous stirring. The solution was kept at 60°C for 1 hour. The resulting pale red violet precipitate was filtered off, washed with DCE, and dried *in vacuo* for several hours at 35°C. Elemental analysis: found: C, 70.25; H, 7.30; N, 63%; calculated for $CuC_{35}H_{43}BN_2O_2$: C, 70.29; H, 7.25; N, 4.68%.

Electronic spectra were recorded on a Hitachi U-2000 spectrophotometer equipped with a cell compartment (optical pathlength of 1 cm) thermostated to 25.00 ± 0.02°C. The concentration dependence of the absorption maxima in DCE was found to be insignificant, a fact which indicates that there is no decomposition of the copper(II) chelate by solvent attack.[9] The spectrum of 5 cm^3 of a 3×10^{-3} M stock solution of $[Cu(acac)(tmen)]B\phi_4$ in DCE was mixed with 2 cm^3 of the donor solvent; in the case of formamide and pyridine 0.5 cm^3 of a 0.1 M stock solution in DCE was used. The mixture was diluted to 10 cm^3 with DCE. These procedures were performed in a glove box under a dry nitrogen atmosphere. To study the effect of a mixed solvent system on the spectra and hence to evaluate the DN of this system 5 cm^3 of a stock solution of $[Cu(acac)(tmen)]B\phi_4$ (3×10^{-3} M) in DCE plus 1 cm^3 of the appropriate mixture of DMF and PDC (absolute) was diluted to 10 cm^3 with DCE.

Equilibrium constants and thermodynamic parameters were determined[1] using a 3×10^{-3} M stock solution of the Cu-chelate in DCE which was titrated with 0.1 M solutions of amines or the respective donor-solvent dissolved in DCE. Up to ten spectra were recorded and stored in a multichannel memory unit. The obtained titration curves were fitted by means of a combined Marquardt-Newton method[15] to calculate the equilibrium constants (logK) for the reaction with the donor solvent (S) as follows.

$$[Cu(acac)(tmen)]^+ + S \overset{K}{\rightleftarrows} [Cu(acac)(tmen)S]^+ \qquad (1)$$

$$[Cu(acac)(tmen)S]^+ + S \overset{K}{\rightleftarrows} [Cu(acac)(tmen)S_2]^+ \qquad (2)$$

Quantum chemical calculations were performed within the usual CNDO/2-MO-SCF framework extended to include transition metals.[16] Input parameters have been already described.[17] Molecular geometries for the $[Cu(acac)(tmen)]^+$ chelate were taken from X-ray diffraction data of the corresponding Ni(II) chelates adapted to fit Cu(II) bond distances.[18] Atomic charges were defined by (3),

$$Q = n - \Sigma P_{\lambda\sigma} \tag{3}$$

where the summation runs over all occupied atomic orbitals of the atom, n being the number of valence electrons in the atom. The $P_\lambda{}^\sigma$ values are elements of the density matrix according to the relation (4),

$$P_\lambda{}^\sigma = \Sigma 2 C_{i\lambda} C_{i\sigma} \tag{4}$$

where $C_{i\lambda}$ and $C_{i\sigma}$ are the coefficients of the atomic orbitals λ and σ.

Table 1 Absorption maxima (λ_{max}/nm) and molar extinction coefficients (ε) of the visible d-d band of $Cu(acac)(tmen)B\phi_4$ in various solvents. Donor numbers of the solvents are calculated according to $DN_\lambda = (\lambda - 505{,}71)/3.451$

Solvent	DN	Cu-λ_{max}/nm	ε	DN_λ
1,2-dichloroethane	0.00	500.5	131.0	−1.510
1,4-dioxane	10.8	529.0		6.749
ethylene sulfite	15.3	546.5	100.0	11.82
propylenedicarbonate	15.1	550.5	122.5	12.98
acetone	17.0	564.5	133.25	17.03
ethanol	18.5	585.0	112.5	22.98
methanol	19.1	586.0	125.8	23.26
tetrahydrofuran	20.0	577.0		20.66
propionaldehyde		600	100	27.32
dimethylsulfoxide	29.8	609.5	128.33	30.07
hexamethylphosphotriamide	38.8	637.7	129.17	38.25
acetonitrile	14.1	571.0	129.17	18.92
formamide	24.0	588.5	128.3	24.0
tri-ethanolamine		590		24.4
N,*N*-dimethylformamide	26.6	602.0	128.9	27.9
pyridine	33.1	603		28.2
N,*N*-dimethylacetamide	27.8	604.5	125.0	28.6
N,*N*-diethylformamide	30.9	612.5		30.9
2-methylpyridine	39[a]	623		34..0
triethylamine	61,30,1[a]	625		34.6
dipropylamine	40[a]	636	100.8	37.8
2-(methylamino)ethanol		638	71.7	38.3
di-*sec*-butylamine		660	100	44.7
octylamine		663		45.6
sec-butylamine		663	100	45.6
n-propylamine	38[a]	664	109.2	45.9
n-butylamine	42[a]	664	107.5	45.9
n-pentylamine		664	112.5	45.9
iso-butylamine		665		46.2
n-hexylamine	57	665	109.2	46.2
t-butylamine	57.5[a]	671	150.0	47.9
piperidine	52	686	141.7	52.3

[a] Source from reference.[21]

RESULTS AND DISCUSSION

Visible spectra of $[Cu(acac)(tmen)]^+$ were measured in different donor solvents diluted with DCE (see Table 1). A linear regression analysis of λ_{max} *versus* the donor number yields (5).

$$DN_\lambda = (\lambda_{max} - 526{,}2)/2.98 \qquad (r = 0.964) \qquad (6)$$

Found λ_{max} values differ somewhat from values obtained in *bulk* donor solvents[8-10] which yield a linear relationship (6).

$$DN_\lambda = (\lambda_{max} - 526{,}2)/2.98 \qquad (r = 0.964) \qquad (6)$$

Differences in DN originating from (5) and (6) are larger for solvents with small donor numbers, apparently due to weak coordination of DCE in solution. Stronger coordinating donor solvent molecules (S) yield almost completely $[Cu(acac)(tmen)(S)_2]^+$ so that differences in the coordination of the copper complex in the respective bulk solvents are hardly noticeable. In the case of weakly donating solvents the weak DCE coordination is more pronounced and differences between dilute solutions and bulk solutions are increased. In general, equation (5) gives DN_λ values in better agreement with the original DN values than equation (6). Equation (5) and the absorption maxima of $[Cu(acac)(tmen)]B\phi_4$ in various solvents (mainly amines) are used to evaluate donor numbers (Table 2). Reported values for some of the amines evaluated according to spectra of $VO(acac)_2$[19] in solution, NMR chemical shifts of $\delta^{23}Na$[20] or weighted average values calculated from other data[21] differ in part. Estimation of the donor number of ethylenediamine failed due to template reaction yielding a Schiff base. This has been found also with other systems, such as $VO(acac)_2$.[22]

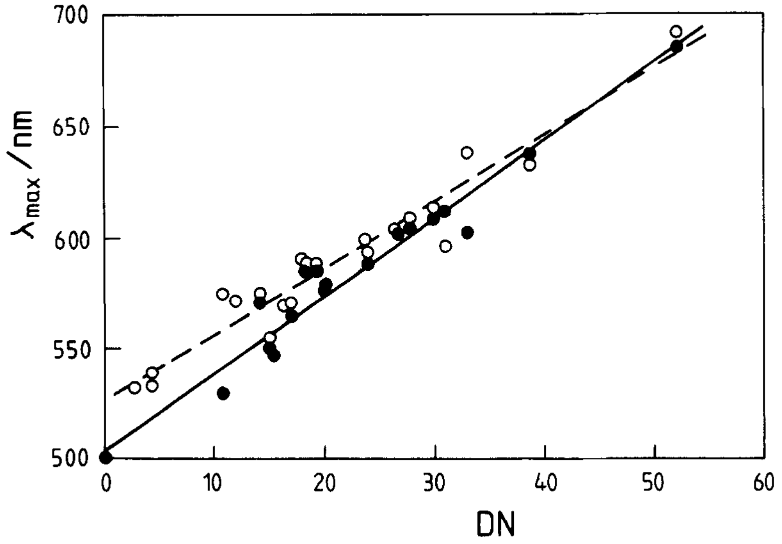

Figure 1 Absorption maxima (λ_{max}/nm) of $[Cu(acac)(tmen)]B\phi_4$ with different solvent species in diluted DCE solution (—●—, present work) and in the pure solvents taken from Persson[10] and Soukup[9] (- -○- -).

Table 2 Equilibrium constants at 298 K (in mol L^{-1}), enthalpies (in kJ/mol) and entropies (in J/mol K) of the stepwise coordination of solvent molecules on [M(acac)(tmen)]$B\phi_4$ (where M(II) = Cu(II) or Ni(II)) for the equilibria (1) and (2), respectively, in DCE solution

		[Cu(acac)(tmen)]$B\phi_4$			[Ni(acac)(tmen)]$B\phi_4$[a]		
		K_1	K_2	K_2/K_1	K_1	K_2	K_2/K_1
An	K	0.745	0.86	1.18	0.138	16.22	117
	ΔH	−4.81	−4.80		−28.44	−25.27	
	ΔS	−13.48	−16.98		−113.9	−65.13	
Ac	K	0.317	0.624	1.969	0.024	6.50	271
	ΔH	−4.08	−12.82		−44.37	−53.59	
	ΔS	−22.76	−46.08		−181.70	−166.40	
n-BuOH	K	0.315	0.699	2.219	0.087	11.22	129
	ΔH	−7.93	−16.31		−36.46	−33.25	
	ΔS	−35.53	−56.68		−144.6	−93.35	
Fa	K	4.25	26.37	6.21	16.17	351.7	21.8
	ΔH	−7.00	−8.71		−35.60	−16.64	
	ΔS	34.21	54.51		−97.89	−7.85	
DMF	K	9.10	217.20	23.90	21.98	415.90	18.92
	ΔH	−8.05	−11.23		−40.32	−14.35	
	ΔS	−8.54	−6.67		−112.5	−0.91	
DMSO	K	19.10	540.60	28.3	38.67	733.30	18.96
	ΔH	−6.56	−8.819		−23.75	−26.58	
	ΔS	2.38	21.85		−49.78	−34.91	
Py	K	5.22	33.00	6.32	13.21	140.0	10.60
	ΔH	30.70	12.48		−42.71	−28.38	
	ΔS	115.77	69.61		−123.7	−55.33	
PDC	K	0.146	0.609	4.17			
HMPA	K	222	4745.5	21.38			
n-$PrNH_2$	K	15.50	190.85	12.31			
n-$BuNH_2$	K	13.69	164.95	12.05			
n-$PenNH_2$	K	14.44	155.16	10.75			
n-$HexNH_2$	K	14.92	144.6	9.69			
di-$PrNH_2$	K	0.442	2.216	5.01			
sec-$BuNH_2$	K	1.50	11.70	7.80			
tert-$BuNH_2$	K	0.907	4.77	5.26			

[a] Taken from reference[1]; *n*-$PrNH_2$ = *n*-propylamine, *n*-$BuNH_2$ = *n*-butylamine, *n*-$PenNH_2$ = *n*-pentylamine, *n*-$HexNH_2$ = *n*-hexylamine.

The present results show the DN for these amines increase in the order *tert*-amine < *sec*-amine ≤ primary amine. For primary amines, the DN increase in the series *t*-$BuNH_2$ > *sec*-$BuNH_2$ ≈ *n*-$BuNH_2$. The same trend was found by Abe *et al.*,[23] for the corresponding alcohols with the exception of *t*-BuOH.

Figure 2 depicts estimated donor numbers for mixtures of PDC and DMF, both diluted in DCE. The non-linear behaviour is due to preferential solvation or coordination in the presence of even small concentration of DMF, which is a stronger donor than PDC. The figure clarifies the fact that solvent mixtures cannot be treated in a simple manner (for example using linear interpolation of solvent parameters).[24] After a steep increase up to a molar ratio of $\chi_{DMF} \geq 0.3$, the donor number

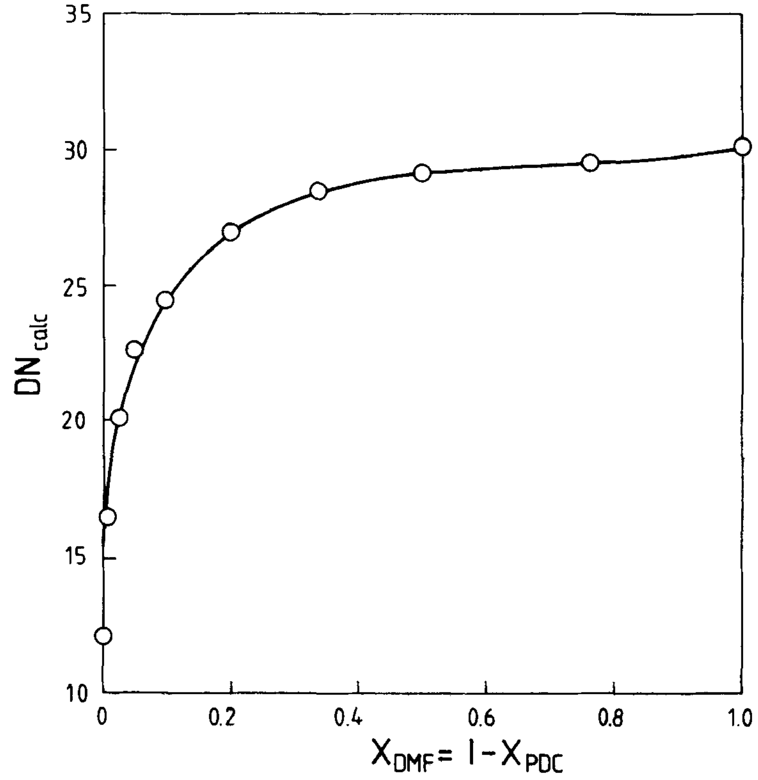

Figure 2 Dependence of DN_{λ} on the molar ratio of DMF (X_{DMF}) in a mixture of PDC and DMF both diluted in DCE ($X_{DMF} = 1 - X_{PDC}$).

passes through a flat part until a small further increase at $\chi_{DMF} > 0.7$ occurs. Dimethylpropyleneurea-water mixtures show similar results.[25] In view of this, solvatochromic Lewis-acid-base indicators might be useful for estimation of actual solvent parameters of solvent mixtures.

An example of the spectra obtained in the course of the titration procedure of [Cu(acac)(tmen)]$B\phi_4$ with n-$PrNH_2$ in DCE at 25°C is depicted in Figure 3. The absorption at the maximum decreases on addition of donor-solvents. This can be used to evaluate the respective equilibrium constants. An isosbestic point near 620 nm holds for all coordinating solvents investigated, and is assigned to the equilibrium between square planar and five-coordinated species. The isosbestic point near 650 nm refers to the equilibrium between five-coordinated and octahedral species. This, as well as the least-square evaluation of the titration curves, shows that the coordination of donor solvent molecules proceeds *via* a two-step process involving a five-coordinated species as mentioned in the previous section.

K_2 is found to be somewhat larger than K_1, this being associated with a strong *trans* influence for the second coordination. Both equilibrium constants show linear dependence upon the donor number (see Figure 4). This linear dependence has not been observed for the analogous Ni(II) chelates[1] and reflects the much stronger

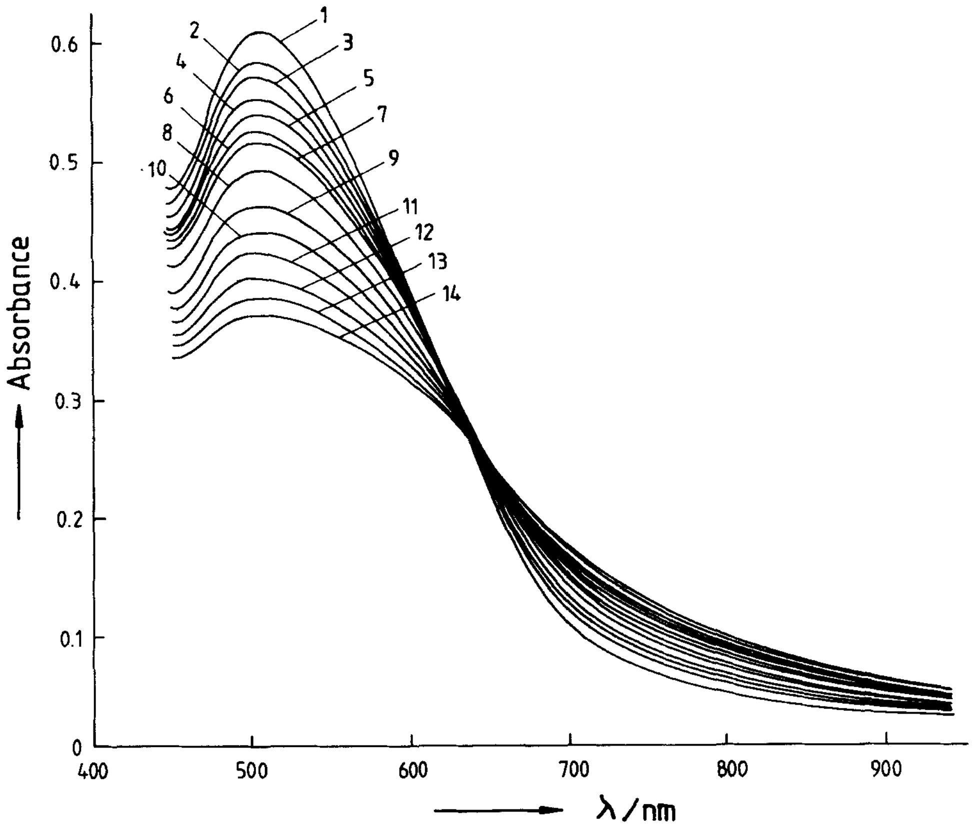

Figure 3 Spectra of a 1.5×10^{-3} M [Cu(acac)(tmen)]$B\phi_4$ solution in DCE with increasing concentrations of n-$PrNH_2$ at 25°C in DCE; (n-$PrNH_2$ concentrations in mmole dm^{-3}: 1 = 0.0, 2 = 0.35, 3 = 0.69, 4 = 1.03, 5 = 1.35, 6 = 1.67, 7 = 1.97, 8 = 2.56, 9 = 3.13, 10 = 3.66, 11 = 4.17, 12 = 4.65, 13 = 5.11 and 14 = 5.56.

sensitivity of the Cu(II) chelate to the donor strength of solvents. From Table 2 it is evident that in general the values for K_1 and K_2 are larger for the Ni(II) complex than for the corresponding Cu(II) chelate (except for K_1 for weakly coordinating solvents like An, Ac and n-BuOH). This means that the ability of a solvent to coordinate with Ni(II) is stronger than with the Cu(II) chelate. However, the ability of Cu(II) complex to form five-coordinated species with weakly coordinating solvents is greater than for the Ni(II) chelates.

The formation constants (logβ) for amines decrease in the order n-$PrNH_2 >$ n-$BuNH_2 \geqslant$ n-$PenNH_2 \geqslant$ n-$HexNH_2 \gg$ *sec*-$BuNH_2 >$ *tert*-$BuNH_2 >$ *di*-$PrNH_2$. Formation constants appear to be not affected by electron withdrawing or donating groups. Steric effects may be the reason for the unexpected insensitivity towards substituent variation which has also been found for similar systems.[26,27]

Formation of the octahedral species is exothermic,[1,26,28] except for Py. The endothermicity of Py may be attributed to ligand exchange for $[Cu(acac)(tmen)]^+$ where tmen[14] is replaced. From Table 2 it can be seen that this is also the case for

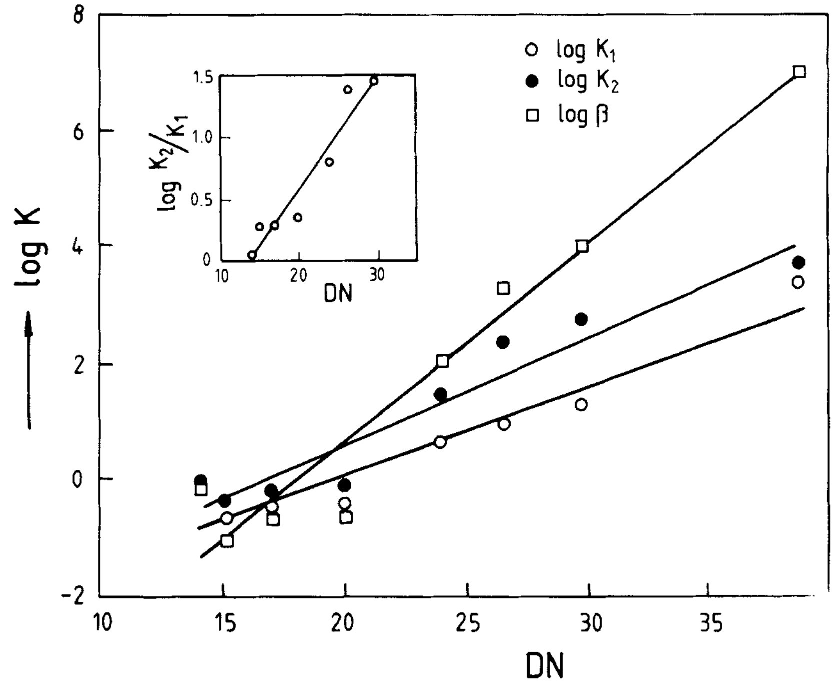

Figure 4 Relation to logK_1, logK_2 and logβ *versus* DN for [Cu(acac)(tmen)]$^+$ with various coordinating solvents in DCE; the insert shows the relation of logK_2/K_1 *versus* DN.

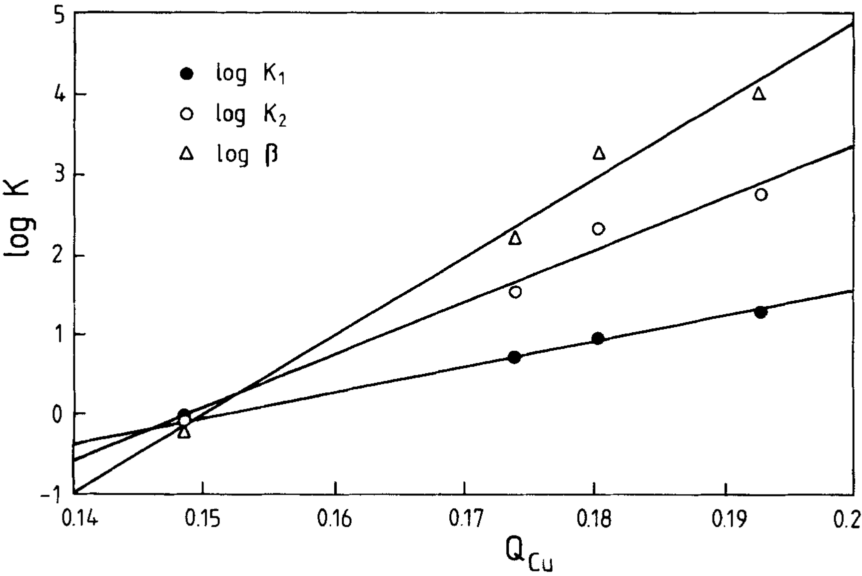

Figure 5 Relation between the charge on the copper atom (Q_{Cu}/atomic units) *versus* logK_1, logK_2 and logβ for [Cu(acac)(tmen)]$^+$ with various coordinating solvents.

the formation of the five-coordinated species. ΔH values associated with K_1 are in general similar to those of K_2, but the entropic contributions differ strongly. Values of both ΔH and ΔS are much smaller than the corresponding values found for $[Ni(acac)(tmen)]^+$. In general, negative ΔS values are found. Exceptions are for Fa, Py and DMSO with the Cu complex and with $[Ni(tfac)(tmen)]^+$ and $[Ni(dbm)(tmen)]^+$ complexes.[1] The negative entropic contributions disfavour the coordination of solvent ligands and are more or less overcompensated by the enthalpic contribution. By coordination of donor solvents, the Cu-O and Cu-N bonds to β-diketones and diamines are weakened according to predictions of the bond length variation rules.[4] This leads to increasing labilities of the β-diketonate and diamine ligands by which the loss in entropy due to coordination of the solvent donors is compensated. In case of the mentioned exceptions, this effect yields positive entropic contributions.

The ratio K_2/K_1 expresses the relative stability of the six-coordinated species to the five-coordinated one. For the Cu species this ratio is found to increase linearly with DN (see the insert in Figure 4). To the contrary, it decreases for the Ni complexes with increasing DN showing a more complicated, non-linear relationship. This underlines the differences between the Cu(II) and the Ni(II) complexes. Although both are able to form five- and six-coordinated species, the former exhibit a strong Jahn-Teller effect. This allows for the continuous shift of d-d absorption maxima of the Cu complexes and (relatively) stabilizes asymmetric five-coordinated species especially for weak donating solvents. The Ni complexes, on the other hand, show a spin state change on coordination and display *cis-trans* isomerism[29] from four to six-fold coordination. This yields discrete species where the equilibrium constants change with DN rather than the absorption maxima.

Equilibrium constants ($\log K_1$ and $\log K_2$ as well as $\log\beta$) of $[Cu(acac)(tmen)]^+$ coordinating with various solvent molecules increase with more negative reduction potentials obtained by cyclic voltammetry on the hanging drop mercury electrode (E_{pc}/Hg/[V]),[30] reflecting the stability of the formed octahedral complex.

Experimental results can be compared with others from a semi-empirical quantum mechanical description on the basis of CNDO/2 calculations (see Table 3). As

Table 3 Atomic charges (Q/atomic units) and energy levels from a CDNO/2 calculation for $[Cu(acac)(tmen)]^+$ surrounded by two solvent molecules

	An	Ac	DMF	DMSO	Py	H_2O	MeOH
Q_{Cu}	0.149	0.186	0.180	0.193	0.174	0.178	0.191
ΣQ_n[a]	−0.255	−0.129	−0.414	−0.379	−0.274		
HOMO orbital	66	74	80	76	80	58	64
Homo energy level/eV	−4.15	−2.79	−4.46	−4.62	−4.57	−4.53	−4.77
LUMO orbital	67	75	81	77	81	59	65
Lumo energy level	6.63	6.45	5.88	5.81	5.18	6.86	6.70
Total energy	−15.70	−16.73	−19.19	−15.42	−14.25	−12.24	−15.53
Number of orbitals	122	136	146	146	150	104	116
Number of electrons	131	147	159	151	159	115	127

[a] Sum over the charges of the next neighbor atms of Cu.

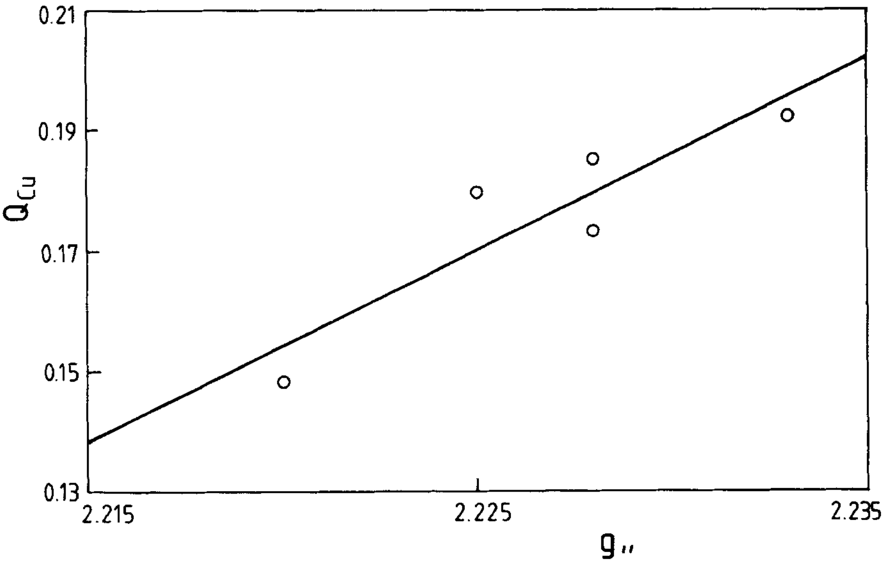

Figure 6 Relation between the charge on the copper atom (Q_{Cu}) and $g_{\parallel}$ values.[30]

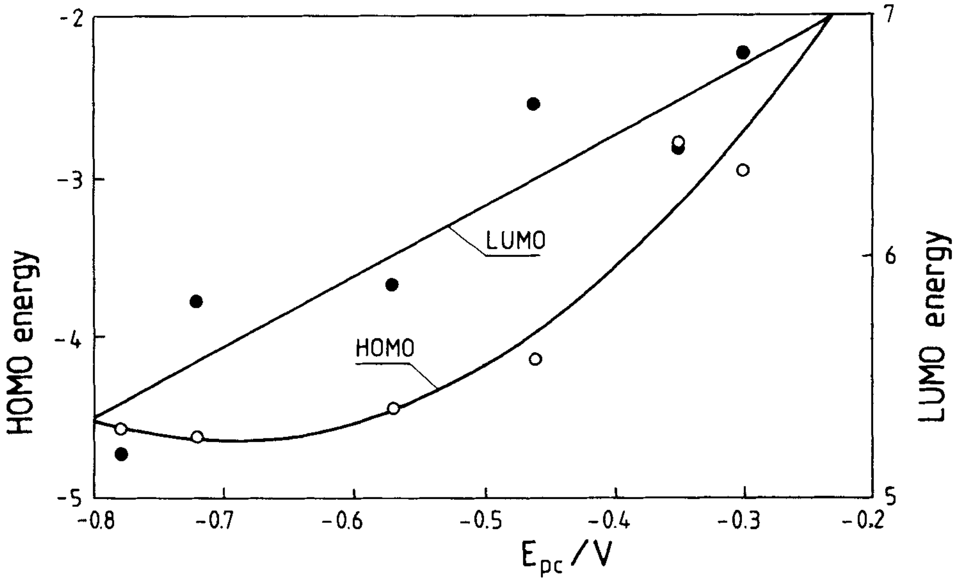

Figure 7 Relation between reduction potentials (E_{pc}/Hg)[29] and LUMO and HOMO energy levels.

mentioned previously, solvent molecules are assumed to attack the axial sites of the Cu(II) chelate.[30] The charges at the central copper atom (Q_{Cu}) of the solvated species are plotted *versus* the measured equilibrium constants in Figure 5. It can be seen that larger equilibrium constants (related to increasing donor ability of the solvents) are associated with increasing Q_{Cu} values ($r = 0.991$, excluding acetone). The deviation of Ac can be attributed to steric hindrance on complex formation, yielding low equilibrium contants).

The charge at the Cu atom ($Q_{Cu\text{-}atom}$) for the solvated species increases as a result of increasing strength of the axial coordination of $[Cu(acac)(tmen)]^+$ chelate with the donor solvents. This leads mainly to higher energy of the $d_{x^2-y^2}$ level which is reflected in an increase of ESR $g_{\|}$ values.[31] This trend is even stronger when correlating $Q_{Cu\text{-}atom}$ with the ESR results (Figure 6).

The calculated LUMO (mainly consisting of the copper D_{xz}-orbital) and HOMO energy levels are decreased with increasing donor ability of the coordinated solvent. *Quasi*-reversible cathodic potentials (E_{pc}/Hg/[V])[29] become more negative with decreasing LUMO and HOMO energies being both involved in the redox process due to the uneven number of electrons in the system (Figure 7).

Acknowledgements

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