Electrostatic Solvent Effect on the Formation of the Mixed-chelate Complex (Acetylacetonato)(diethyldithiocarbamato)copper(II)

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Spectrophotometric and e.s.r. analyses have been carried out on the mixed-chelate complex formation equilibrium $[Cu(acac)_2] + [Cu(S_2CNEt_2)_2] \rightleftharpoons 2[Cu(acac)(S_2CNEt_2)]$, where acac = acetylacetonate. The equilibrium constant in non-aqueous solution is found to decrease with increasing dielectric constant of the solvent. The results are analyzed in terms of an electrostatic model in which each complex molecule is assumed to be in a cavity surrounded by uniform solvent.

Mixed-chelate complexes are currently of particular interest because their structural and electronic properties are possibly distinct from those of bis(chelate) complexes and because they are regarded as models for metalloenzyme–substrate complexes. In a previous paper[1] we reported on an e.s.r. study of the mixed-chelate complex $[Cu(S_2CNEt_2)(S_2PEt_2)]$. In the present study we report spectrophotometric and e.s.r. analyses of equilibrium (1) in non-aqueous solutions, where acac = acetylacetonate. The equilibrium constant K is found to decrease with increasing dielectric constant, κ, of the solvent. The results are analyzed in terms of an electrostatic model.

$$[Cu(acac)_2] + [Cu(S_2CNEt_2)_2] \rightleftharpoons 2[Cu(acac)(S_2CNEt_2)] \quad (1)$$

$$K = [Cu(acac)(S_2CNEt_2)]^2/[Cu(acac)_2][Cu(S_2CNEt_2)_2] \quad (2)$$

Results

Calculations.—The equilibrium constant K defined as in equation (2) was calculated from spectrophotometric data. The absorbance d at wavelength λ/nm of a mixed solution of $[Cu(acac)_2]$ and $[Cu(S_2CNEt_2)_2]$ with initial concentrations (mol dm^{-3}) a and b respectively is related to K as in equation (3),

$$\frac{(a+b)(d-d_0)}{ab} = \frac{K-4}{K\varepsilon}\cdot\frac{(d-d_0)^2}{ab} + \varepsilon \quad (3)$$

where $d_0 = \varepsilon_A a + \varepsilon_B b$, $\varepsilon = 2\varepsilon_{AB} - \varepsilon_A - \varepsilon_B$, and ε_A, ε_B, and ε_{AB} are the molar absorption coefficients at λ/nm of $[Cu(acac)_2]$, $[Cu(S_2CNEt_2)_2]$, and $[Cu(acac)(S_2CNEt_2)]$, respectively. Using a and/or b as variables, K was calculated by the least-squares method. E.s.r. data gave K values in good agreement.

Dependence of K *on Solvent.*—Representative visible spectra observed for toluene solutions are shown in Figure 1, and the analysis of the data in Figure 2. The fit correspondence with equation (3) is excellent, and hence no reaction other than (1) is detected. The same conclusion was drawn from e.s.r. data. The values of the equilibrium constant K at 25 °C calculated from the data at 390 nm for various solvents are summarized in Table 1 together with the (relative) dielectric constant κ.[2] The increasing order of K appears to be opposite to that of κ.

Table 1. Equilibrium constants K for $[Cu(acac)(S_2CNEt_2)]$ in various solvents with dielectric constants κ

Solvent	κ [a]	K [b]
CCl_4	2.24	0.32
Benzene	2.28	0.45
Toluene	2.38	0.39
Chlorobenzene	5.62	0.30
CH_2Cl_2	9.08	0.17
o-Dichlorobenzene	9.93	0.21
Acetone	20.7	0.17
CH_3OH	32.6	0.045
CH_3CN	37.5	0.034

[a] Taken from ref. 2. [b] Calculated from absorbance data at 390 nm and 25 °C.

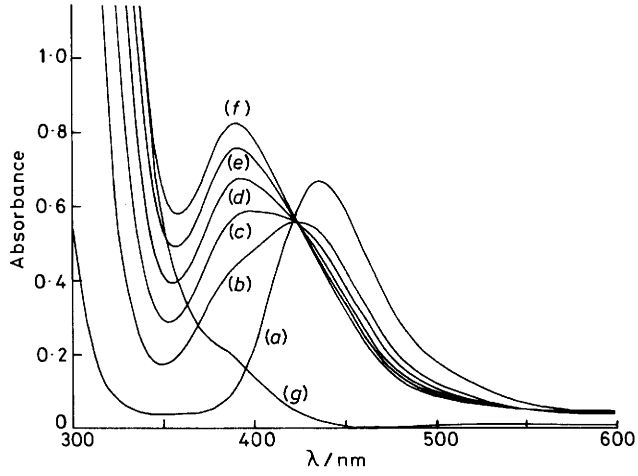

Figure 1. Visible spectra at 25 °C of toluene solutions. $[Cu(S_2CNEt_2)_2]_0 = 5.0 \times 10^{-5}$ mol dm^{-3}; $[Cu(acac)_2]_0/[Cu(S_2CNEt_2)_2]_0 = 0$ (*a*), 2 (*b*), 4 (*c*), 6 (*d*), 8 (*e*), or 10 (*f*). For (*g*) $[Cu(S_2CNEt_2)_2]_0 = 0$, $[Cu(acac)_2]_0 = 5.0 \times 10^{-4}$ mol dm^{-3}

To examine this correlation in more detail, the mixed-solvent system of dichloromethane–carbon tetrachloride was employed for spectrophotometric measurements. Figure 3 shows these data plotted as ln K *vs.* κ^{-1}, where κ is regarded as the sum of the products of the dielectric constant of each pure solvent and its molar fraction. It can be seen that ln K increases linearly with κ^{-1} (see below). A similar relationship was obtained also in the mixed solvent benzene–*o*-dichlorobenzene.

Dependence of K *on Temperature.*—Spectrophotometric measurements were carried out at temperatures between 0 and 40 or 60 °C for dichloromethane or carbon tetrachloride as a

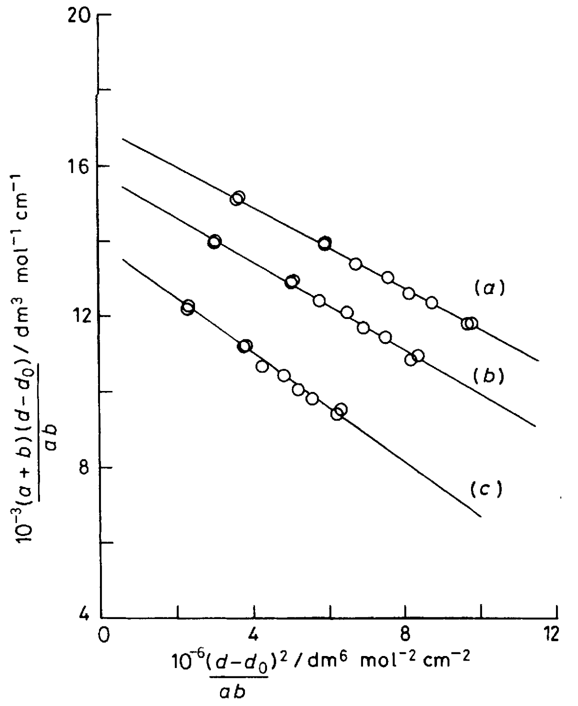

Figure 2. Method of analysis of absorbance data for the formation of $[Cu(acac)(S_2CNEt_2)]$ in toluene at 25 °C: λ = 390 (*a*), 380 (*b*), or 400 nm (*c*)

Table 2. Comparison of optical and e.s.r. parameters[a]

Complex	$\lambda_{max.}$/nm	$\varepsilon_{max.}$[b]	g_0	A_0/mT
$[Cu(acac)_2]$	380	0.04	2.12	7.6
$[Cu(S_2CNEt_2)_2]$	435	1.3	2.04	7.8
$[Cu(acac)(S_2CNEt_2)]$	390	1.0	2.08	7.6

[a] Obtained for toluene solutions at 25 °C. [b] In units of 10^4 dm^3 mol^{-1} cm^{-1}.

solvent. In each case, K was found to increase with increasing temperature: the change in the enthalpy ΔH of reaction (1) is positive.

E.S.R. Spectra.—Typical spectra of toluene solutions at room temperature are shown in Figure 4. The signals with asterisks are assigned to $[Cu(acac)(S_2CNEt_2)]$. E.s.r. parameters together with optical parameters are summarized in Table 2. The g value, hyperfine coupling constant, and wavelength of the absorption maximum obtained for $[Cu(acac)(S_2CNEt_2)]$ fall between the values for $[Cu(acac)_2]$ and $[Cu(S_2CNEt_2)_2]$. Thus, the mixed-chelate complex has essentially the mean of the bonding and electronic properties of the parent bis(chelate) complexes.

Discussion

Many factors are responsible[3] for the stability of mixed-ligand complexes: statistical effect, electrostatic factors, ligand interactions, nature of the solvent, *etc.* Among these, we shall confine ourselves to the electrostatic factors and the nature of the solvent to explain the linear relationship in Figure 3.

Change in Enthalpy of Electrostatic Origin.—As far as the purely ionic aspect of co-ordination is concerned, it is possible to calculate the electrostatic formation enthalpy of a mixed-ligand complex. In the work of Kida[4] it is assumed that a complex species consists of point charges representing a central metal ion M and its ligands A and B. He calculated (for linear, square-planar, tetrahedral, and octahedral configurations) the stabilization energy, ΔE, expressed as in equation (4) for the

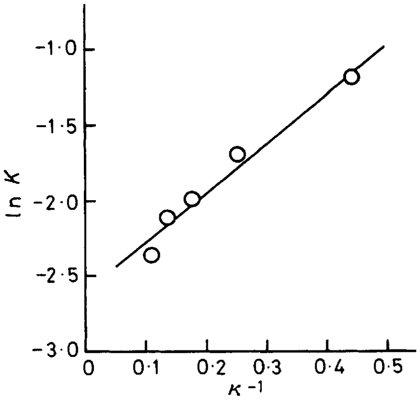

Figure 3. Dependence of the equilibrium constant K at 25 °C on the dielectric constant κ of the mixed solvent dichloromethane–carbon tetrachloride

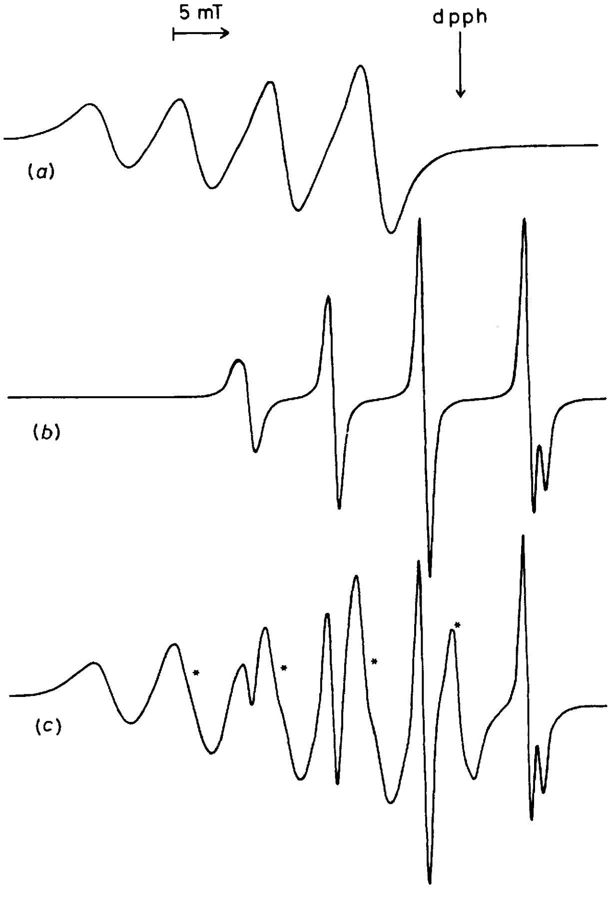

Figure 4. E.s.r. spectra of toluene solutions at 25 °C: (*a*) 1 × 10^{-4} mol dm^{-3} $[Cu(acac)_2]$, amplitude = 200; (*b*) 1 × 10^{-4} mol dm^{-3} $[Cu(S_2CNEt_2)_2]$, amplitude = 32; (*c*) $[Cu(acac)_2]_0$ = 0.83 × 10^{-4}, $[Cu(S_2CNEt_2)_2]_0$ = 0.17 × 10^{-4} mol dm^{-3}, amplitude = 250. The signals with asterisks are assigned to $[Cu(acac)(S_2CNEt_2)_2]$; dpph = diphenylpicrylhydrazyl

$$\Delta E = E_{\mathrm{MA_2B_2}} - \tfrac{1}{2}(E_{\mathrm{MA_4}} + E_{\mathrm{MB_4}}) = \frac{\sqrt{2}+1}{2r}(q_{\mathrm{A}} - q_{\mathrm{B}})^2 \qquad (4)$$

reaction $\mathrm{MA_4 + MB_4 \longrightarrow 2MA_2B_2}$ (square planar, *cis*), where q_{A} and q_{B} are the charges of A and B and r is the ligand–metal distance. It is tacitly assumed that each complex molecule lies in a vacuum, and ΔE is expressed in c.g.s. units per molecule of $\mathrm{MA_2B_2}$. In the following discussion, a similar system is employed. However, ΔE is replaced by ΔH_{e0}, the change in enthalpy of electrostatic origin for reaction (1) expressed in S.I. units. Then, we obtain equation (5) where N is Avogadro's number and ε_0 is the dielectric constant of a vacuum.

$$\Delta H_{\mathrm{e0}} = -\frac{(\sqrt{2}+1)N}{4\pi\varepsilon_0 r}(q_{\mathrm{A}} - q_{\mathrm{B}})^2 \qquad (5)$$

Consider a model in which each complex molecule $\mathrm{MA_4}$, $\mathrm{MB_4}$, or $\mathrm{MA_2B_2}$ lies in a cavity surrounded by uniform solvent with (relative) dielectric constant κ. In the present case, M corresponds to $\mathrm{Cu^{II}}$ and $\mathrm{A_2}$ and $\mathrm{B_2}$ to $\mathrm{acac^-}$ and $\mathrm{S_2CNEt_2^-}$ respectively. The local electric field in the cavity, E_{c}, is related to the macroscopic field in the solvent, E, as [5,6] in equation (6), where

$$E_{\mathrm{c}} = E + sP/\varepsilon_0 \qquad (6)$$

P is the polarization of the solvent and s is a constant which depends on the shape of the cavity and the direction of the field. For a thin slot cavity, for instance, $s = 0$ if E is in the longitudinal direction of the cavity, and $s = 1$ if E is in the transverse direction. The polarization P is proportional to E, *i.e.* as in equation (7). Substituting for P in equation (6) we obtain expression (8). The field E is reduced to $1/\kappa$ of the field in vacuum, E_0, and hence we can write equation (9). Since the

$$P = \varepsilon_0(\kappa - 1)E \qquad (7)$$

$$E_{\mathrm{c}} = E(1 - s + s\kappa) \qquad (8)$$

$$E_{\mathrm{c}} = E_0\left(\frac{1-s}{\kappa} + s\right) \qquad (9)$$

electrostatic energy is modified in the same manner as the electric field, the change in enthalpy of electrostatic origin ΔH_{e}, when each molecule lies in a cavity in a solvent, is related to ΔH_{e0} by equation (10).

$$\Delta H_{\mathrm{e}} = \Delta H_{\mathrm{e0}}\left(\frac{1-s}{\kappa} + s\right) \qquad (10)$$

Linear Relationship between ln K *and* κ^{-1}.—The total change in enthalpy ΔH of reaction (1) consists of ΔH_{e} and the remaining contribution ΔH_{c} [equation (11)]. The equilibrium constant K may be expressed in terms of ΔH and ΔS, the change in entropy, as in equation (12). Provided ΔH_{c} and ΔS are independent of the composition of the mixed solvent $\mathrm{CH_2Cl_2}$–$\mathrm{CCl_4}$, a plot of ln K against κ^{-1} should be linear. Since $\Delta H_{\mathrm{e0}} \leqslant 0$ from equation (5), and $0 \leqslant s \leqslant 1$,[6] the slope should be positive, as is the case in Figure 3.

$$\Delta H = \Delta H_{\mathrm{e}} + \Delta H_{\mathrm{c}} \qquad (11)$$

$$\begin{aligned}\ln K &= -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \\ &= -\frac{1}{RT}\left[\Delta H_{\mathrm{e0}}\left(\frac{1-s}{\kappa} + s\right) + \Delta H_{\mathrm{c}}\right] + \frac{\Delta S}{R} \qquad (12)\end{aligned}$$

For a planar complex, the cavity is approximated as a thin slot, and electrostatic forces act in nearly longitudinal directions: s is close to 0. If $s = 0$, ΔH_{e0} is determined to be -8.0 kJ mol^{-1} from the slope. In crystalline $[\mathrm{Cu(S_2CNEt_2)_2}]$ the Cu–S bond length is reported to be 2.3 Å.[7] Thus $|q_{\mathrm{A}} - q_{\mathrm{B}}| = 0.074e$ (e is the elementary electric charge) for $\Delta H_{\mathrm{e0}} = -8.0$ kJ mol^{-1} and $r = 2.3$ Å in equation (5).

Since ΔH is found to be positive from the dependence of K on temperature, and ΔH_{e} as well as ΔH_{e0} is negative, ΔH_{c} is required to be positive and have a greater absolute value than that of ΔH_{e}. It is reported [3,4] that in general no mixed-ligand complex can be formed when the reacting species (parent complexes) differ in geometrical configuration. In the present case, both the parent complexes have the same configuration. However, a four- and a six-membered ring in a mixed-chelate complex may not be favoured for stable σ and/or π bonds, leading to positive ΔH_{c}.

Our discussion is somewhat oversimplified: the exact nature of ΔH_{c} and ΔS remains to be elucidated. Nevertheless, the linear relationship between ln K and κ^{-1} in Figure 3 is explained successfully. The observed trend in Table 1 may be attributed in part to the electrostatic solvent effect although solvation and ligation effects may also play a significant rôle. The electrostatic solvent effect may possibly be associated with the substrate specificity of metalloenzymes, which is closely related to the formation of enzyme–metal ion–substrate complexes in biological fluids, as summarized by Sigel.[8]

Experimental

Materials.—The parent complexes $[\mathrm{Cu(acac)_2}]$[9] and $[\mathrm{Cu(S_2CNEt_2)_2}]$[10] were prepared and purified following published methods. The non-aqueous solvents were distilled over appropriate drying agents before use. The initial concentrations of $[\mathrm{Cu(S_2CNEt_2)_2}]$ in the sample solutions for spectrophotometric and e.s.r. measurements were (1—10) × 10^{-5} mol dm^{-3}, and those of $[\mathrm{Cu(acac)_2}]$ were from 2 to 10 times these.

Physical Measurements.—Visible spectra were recorded on a Hitachi 200-10 spectrophotometer with quartz 10-mm cells. Temperatures between 0 and 60 °C were controlled with a thermostatted cell holder (type 0510) to ±0.2 °C. E.s.r. spectra were obtained at room temperature on a JEOL FE 3AX spectrometer with 100-kHz field modulation.

References

1 M. Sato and T. Ohya, *Inorg. Chem.*, 1979, **18**, 2627.
2 'CRC Handbook of Chemistry and Physics,' 62nd edn., eds. R. C. Weast and M. J. Astle, CRC Press, Florida, 1982.
3 R. P. Martin, M. M. Petit-Ramel, and J. P. Scharff, in 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1973, vol. 2, p. 7.
4 S. Kida, *Bull. Chem. Soc. Jpn.*, 1961, **34**, 962.
5 R. P. Feynman, R. B. Leighton, and M. Sands, The Feynman Lectures on Physics, Addison-Wesley, Massachusetts, 1964, vol. 2, ch. 11.
6 C. Kittel, 'Introduction to Solid State Physics,' 4th edn., Wiley, New York, 1971, ch. 13.
7 P. D. W. Boyd, S. Mitra, C. L. Raston, G. L. Rowbottom, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 13.
8 H. Sigel, in 'Metal Ions in Biological Systems,' ed. H. Sigel, Marcel Dekker, New York, 1973, vol. 2, p. 63.
9 M. M. Jones, *J. Am. Chem. Soc.*, 1959, **81**, 3188.
10 L. Cambi and C. Coriselli, *Gazz. Chim. Ital.*, 1936, **66**, 779.

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