18. On the Complex Formation of Tris-(dipivalomethanato)-europium with Pyridine

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Summary. The complexation of the shift reagent tris-(dipivalomethanato)-europium with pyridine in deuteriochloroform has been studied by means of ^{1}H-NMR. Shift parameters $S = 28.0$, 9.9, and 9.2 ppm respectively for pyridine protons 2, 3 and 4 are obtained. The results indicate that the shift reagent complexes a single pyridine molecule with an association constant $K_1 > 100$ mole^{-1}l.

Several paramagnetic compounds of rare earth elements form reversible co-ordination complexes with organic molecules bearing lone electron pairs. Characteristic of such complexes are large shifts in the resonance positions of the ligand protons close to the co-ordination site. These paramagnetic compounds, hence described as 'shift reagents', are widely used for obtaining simplified ^{1}H-NMR. spectra of complex organic molecules [1] [2]. To date the shifted ^{1}H-NMR. spectra have been interpreted mainly in terms of an empirical shift parameter 'S'. In this paper the relation between 'S' and the mechanism of complex formation shall be discussed for the particular case of the reaction of pyridine (py) with tris-(dipivalomethanato)-europium [eu(dpm)$_3$].

A crystalline eu(dpm)$_3$(py)$_2$ complex has been obtained from the above reaction [1] and it may be assumed that two pyridine molecules at most can be hence accommodated in the inner coordination sphere of eu(dpm)$_3$. Since the complex formation of a compound M with two or more ligands L is stepwise, we therefore limit the discussion to the following two-step mechanism:

$$M + 2L \underset{}{\overset{K_1}{\rightleftarrows}} ML + L \overset{K_2}{\rightleftarrows} ML_2,$$

where K_1 and K_2 denote the stepwise stability constants.

The shifted ^{1}H-NMR. spectrum corresponds to a time-averaged spectrum of the bonded and the non-bonded ligands. Based on the above mechanism the shift $\Delta\delta$ of the resonance position of a specific ligand proton (*i.e.* the difference in the chemical shifts between the complexed and the uncomplexed substrate) can be calculated from

$$\Delta\delta = (\Delta\delta_{ML}/c_L^0)\ (c_{ML} + 2c_{ML_2}) \tag{1}$$

where c_L^0 is the total concentration of the ligand L, c_{ML} and c_{ML_2} denote the equilibrium concentration of the species ML and ML$_2$, and $\Delta\delta_{ML}$ is the maximum shift characteristic of those ligands which are incorporated in the inner coordination sphere. It is assumed that the ligand L experiences the same shift, $\Delta\delta_{ML}$, in an ML as in an ML$_2$ complex.

Eq. (1) is unsuitable for a direct analysis of the experimental data since the equilibrium concentrations c_{ML} and c_{ML_2} are unknown. However, if $K_1 \gg 1$ and $c_L^0 \gg c_M^0$

(c_M^o = total concentration of the shift reagent) practically all shift reagent is complexed with ligand molecules, *i.e.*,

$$c_M^o \approx c_{ML} + c_{ML_2} \quad \text{for } K_1 \gg 1;\ c_L^o \gg c_M^o. \tag{2}$$

Furthermore, since

$$c_{ML},\ c_{ML_2} \ll c_L \approx c_L^o,$$

where c_L is the equilibrium concentration of the ligand L, relationship (3) holds for the second step of the complex formation.

$$c_{ML_2}/c_{ML} \approx K_2 c_L^o \quad \text{for } K_1 \gg 1;\ c_L^o \gg c_M^o. \tag{3}$$

Combination of relationship (1), (2) and (3) gives

$$\varDelta\delta \approx (S/c_L^o)\, c_M^o \quad \text{for } K_1 \gg 1;\ c_L^o \gg c_M^o, \tag{4}$$

where the shift parameter S is given by

$$S = \varDelta\delta_{ML}\,(1 + 2K_2 c_L^o)/(1 + K_2 c_L^o). \tag{5}$$

Under the conditions stated above a linear dependence of $\varDelta\delta$ on the total concentration of the shift reagent is to be expected. Such a relationship has been found experimentally for a large number of organic ligands and was the initial reason for the introduction of the shift parameter 'S'. The above prediction is also confirmed by the complex formation of eu(dpm)$_3$ with pyridine in deuteriochloroform (see Fig. 1). From the gradient of the straight line the shift parameters can be evaluated as S = 28.0, 9.9 and 9.2 ppm, respectively for protons 2, 3, and 4 (see Fig. 1). It is however clearly advantageous to determine $\varDelta\delta_{ML}$ rather than S, since the former is a characteristic constant independent of the mechanism and stability constants of the complex forma-

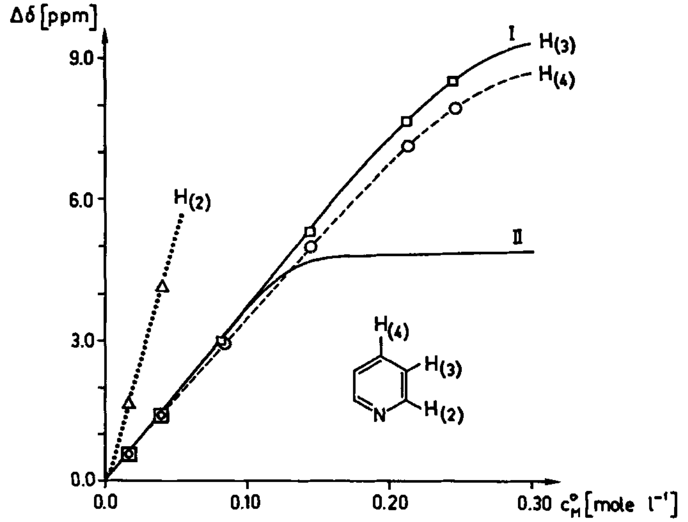

Fig. 1. *Variation in the paramagnetic shift $\varDelta\delta$ for the different protons of pyridine with increasing concentration of eu(dpm)$_3$* (c_L^o = 0.2605 mole l^{-1})

Solid lines I and II are the theoretical curves for H$_{(3)}$. □, ○ and △ are the experimental points for H$_{(3)}$, H$_{(4)}$, and H$_{(2)}$, respectively tion. Although, $\Delta\delta_{\mathrm{ML}}$ cannot be measured directly owing to the limited solubility of eu(dpm)$_3$ in deuteriochloroform the following approximation can be made. If in the reaction scheme described above the binding of the second ligand is negligible (*i.e.*, $K_2 = 0$) then $\Delta\delta_{\mathrm{ML}} = S$. Similarly if $K_2 \gg K_1$ then $\Delta\delta_{\mathrm{ML}} = S/2$. Thus for the H$_{(3)}$-proton of the pyridine $\Delta\delta_{\mathrm{ML}}$ must fall in the range $4.95 \leq \Delta\delta_{\mathrm{ML}} \leq 9.9$ ppm. In Fig. 1 we have included for these two extreme situations computer-calculated saturation curves. Curve II, which is based on a two-step association, with $K_1 = K_2 = 300$, levels off at too low values of $\Delta\delta$ whereas curve I with $K_1 = 300$ and $K_2 = 0$ is a good approximation of the experimental situation. Therefore, we may conclude that the association of eu(dpm)$_3$ and pyridine in deuteriochloroform involves only one molecule of pyridine and has $\Delta\delta_{\mathrm{ML}} \approx 28.0$, 9.9 and 9.2 ppm respectively for pyridine protons 2, 3, and 4.

Attempts were made to determine the equilibrium constant K_1 by measuring the pyridine-eu(dpm)$_3$ association at different dilutions, *i.e.*, for a fixed ratio of pyridine and shift reagent increasing amounts of solvent were added. Fig. 2 shows an example of such a dilution experiment with $c_{\mathrm{M}}^{\circ}/c_{\mathrm{L}}^{\circ} = 0.148$. The solid line representing the curve calculated for a one-step mechanism from eq. (6), with $K_1 = 97$ and $\Delta\delta_{\mathrm{ML}} =$ 28.9 ppm,

$$\Delta\delta = (\Delta\delta_{\mathrm{ML}}/2c_{\mathrm{L}}^{\circ})\,\{c_{\mathrm{L}}^{\circ} + c_{\mathrm{M}}^{\circ} + K_1^{-1} - [(c_{\mathrm{L}}^{\circ} + c_{\mathrm{M}}^{\circ} + K_1^{-1})^2 - 4c_{\mathrm{L}}^{\circ}c_{\mathrm{M}}^{\circ}]^{1/2}\} \qquad (6)$$

fits best the experimental data. The dilution experiment is extremely sensitive to the presence of water, traces of which lead to smaller K_1 and larger $\Delta\delta_{\mathrm{ML}}$ values. Although the deuteriochloroform was carefully dried and all dilution experiments were performed in a dry-box, consecutive measurements with the same solvent resulted in steadily decreasing values of K_1. Therefore, the value 97 can only be regarded as a lower limit for K_1.

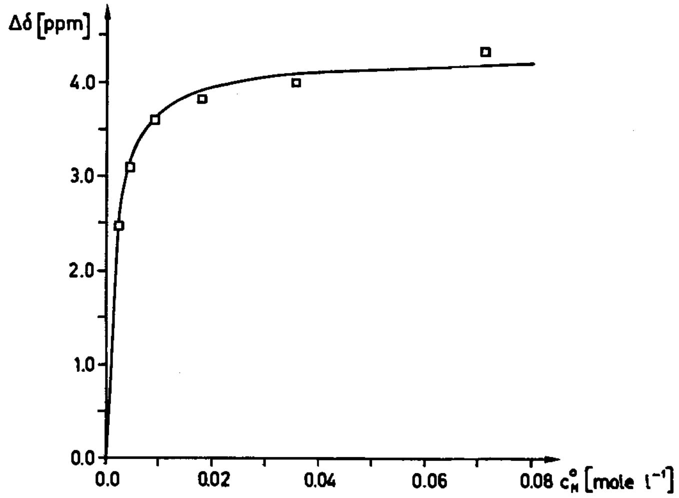

Fig. 2. *Dilution experiment* ($c_{\mathrm{L}}^{\circ}/c_{\mathrm{M}}^{\circ} = 0.148$), *see text*

Experimental. – All spectra were recorded at ~27°C on a *Varian* HA-100 NMR spectrometer. Deuteriochloroform (*Merck*, Uvasol, 99.8% deuterated) was dried for 24 h over molecular sieves and then distilled. $Eu(dpm)_3$ (*Alfa Inorganic*) and pyridine (*puriss. p.a., Fluka*) were used without further purification.

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19. Anil-Synthese

4. Mitteilung[1])

Über die Basen-katalysierte Umsetzung von 4-Methyl-azobenzol-Derivaten mit Anilen aromatischer Aldehyde

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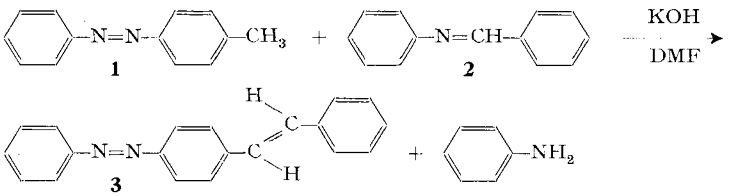
Zusammenfassung. 4-Methyl-azobenzol-Derivate ohne elektronenanziehende Substituenten und ohne Gruppen, die mit Basen Salze bilden, werden mit Anilen aromatischer Aldehyde in Dimethylformamid in Gegenwart von Kaliumhydroxid oder Kalium-*t*-butylat zu Styryl-Derivaten umgesetzt («Anil-Synthese»). Bei Anwesenheit von elektronenanziehenden Gruppen dagegen werden die 4-Methyl-azobenzol-Derivate zu symmetrischen Dibenzyl- bzw. Stilben-Derivaten oxydiert. Mit 4-Benzyl-azobenzol-Derivaten gelingt die Anil-Synthese nur bei gleichzeitiger Anwesenheit von Elektronen-Donatoren in 4'-Stellung des Azobenzols.

Problemstellung. – 4-Styrylazobenzol-Derivate sind bislang nur vereinzelt bekannt geworden. Es war deshalb der Anreiz gegeben, solche Verbindungen mit Hilfe der Anil-Synthese [2] darzustellen, zumal die als Ausgangsprodukte benötigten 4-Methylazobenzol-Derivate in einfacher Weise zugänglich sind.

Nach dem Prinzip der Anil-Synthese sollte 4-Methylazobenzol (**1**) mit Benzalanilin (**2**) in Dimethylformamid (DMF) in Gegenwart von Kaliumhydroxid zum 4-*trans*-Styryl-azobenzol (**3**) umgesetzt werden können:



Die Voraussetzungen zum Gelingen dieser Synthese sind in zweifacher Weise gegeben. Einerseits verlangt nach *Becker* [3] die Umsetzung von Methylgruppen an aromatischen Systemen mit aromatischen Aldehydanilen unter basischen Bedin-

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[1]) 3. Mitteilung siehe [1].

[2]) Teil der Inaugural-Dissertation No. 677 von *B. Weickhardt*, Universität Freiburg, Schweiz.