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29. Pyrrole Ligands. III[1]). The Stability of Dipyrromethenato Complexes of Cu(II) and Ni(II) in Aqueous Solutions

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Dedicated to the memory of late Prof. *Gerold Schwarzenbach*

(9.X.78)

Summary

The protonation and complex formation of the new ligand 3,3′,5,5′-tetramethyldipyrromethene-4,4′-dicarboxylate in aqueous solutions was investigated by alkalimetric titrations and spectrophotometric measurements (25°, I = 1 (KNO_3)). The pK values for the N–H groups are 8.03 and 16.1 and logβ_2 of the complexes with Cu(II) and Ni(II) are 31.0 and 24.4, respectively. Comparison with other ligands shows that the dipyrromethenato group acts as a normal rigid aromatic dinitrogen ligand, despite the charge on one nitrogen atom.

Introduction. – Since 1923 [2] dipyrromethenes and their complexes with metal ions have been investigated in nonaqueous solvents or in the crystalline state by sophisticated methods [3-5]. Nevertheless only one qualitative investigation of the protonation and deprotonation of these biologically important ligands was made [6] and nothing is known about the stability of their complexes in aqueous solu-

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[1]) Part II see [1].

tions. 3,3′,5,5′-Tetramethyldipyrromethene-4,4′-dicarboxylic acid hydrochloride ($H_4DPM(Cl)$) was synthesized by condensations of 3,5-dimethylpyrrole-4-carboxylic acid with formic acid in conc. hydrochloric acid. Solutions of the different protonated forms of the ligand were reasonably stable over several hours, but the completely deprotonated ligand in conc. KOH-solution decomposed readily. Protonation and complex formation with Cu(II) and Ni(II) were investigated using alkalimetric titrations and spectrophotometric measurements.

Protonation of DPM. - The solubilities of $H_4DPM(Cl)$ and neutral H_3DPM are less than 10^{-4} M, hence the protonation of the carboxylate groups was investigated spectrophotometrically (at 460 to 480 nm). There was only a slight pH-dependence of the solution spectra and thus only estimates of the p*K*-values ($= -\log([H] \cdot [H_{p-1}DPM])/[H_pDPM]$) and of the spectral data could be obtained *(Table 1)*. These values (3.6 and 4.2) are of the same order of magnitude as those of aromatic carboxylic acids. For convenience we will define the 2 protonated nitrogen atoms in H_2DPM^- as being pyrrole-like and pyridinium-like. The p*K*-value of H_2DPM^- (*i.e.* of the 'pyridinium' group) was found from alkalimetric titrations of partially deprotonated H_2DPM^- with KOH using the computer program KONST [7]. The deprotonation of $HDPM^{2-}$ (*i.e.* of the 'pyrrolic' group) was examined spectrophotometrically at 440 and 483 nm in up to 11.6 M KOH. Because of the decomposition of DPM^{3-} the spectra were recorded within 2-3 min from the preparation of the mixtures. Only with 11.6 M KOH was there a significant correction (3%) on extrapolation to t = 0. Evaluation with the H_- scale established by *Yagil* [8] [9] resulted in a good fit of the experimental values with p*K* = 16.1 ± 0.1. This value is considered to be accurate within ±0.3 for 1 M KNO_3 solutions (0.1 M KOH has $H_- = 13.00$ and pH = 12.78 at I = 1 (KNO_3)).

H_4DPM^+:

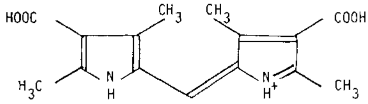

Table 1. p*K values, the method of their evaluation and the spectroscopic data for the different species $H_pDPM^{(p-3)+}$ (25°, I = 1 (KNO_3))*

p	p*K*	λ_{max} (nm)[a]	ε_{max}[b]	Method
4	3.6 ±0.3	463	1.12 10^5	Spectrophot.
3	4.2 ±0.3	≈470		Spectrophot.
2	8.03 ± 0.04	473	1.06 10^5	Alkalimetr.
1	16.1 ±0.3	483	0.98 10^5	Spectrophot. in conc. KOH-solution

[a] λ_{max} = Wave-length of the absorption maximum.
[b] ε_{max} = Molar absorbivity at λ_{max}.

Complex formation of DPM. - *1. Copper complexes.* Titrations of Cu^{2+} and H_4DPM^+ with KOH are not useful because of the formation of an insoluble complex, probably $Cu(H_2DPM)_2$, and the insolubilities of $H_4DPM(NO_3)$ and H_3DPM. With a 1:2 molar ratio of Cu^{2+} and H_4DPM^+ the precipitate only dissolves after the addition of 4 equiv. of KOH. Hence, use was made of competitive complex formation according to reaction (1) to investigate exchange equilibria with oxalate ion (Ox). Solutions of H_2DPM^- (0.002 M) in presence of $Cu(NO_3)_2$ (0.0008 M, 0.001 M and

$$Cu(Ox_2)^{2-} + 2\,H_2DPM^- \rightleftharpoons Cu(DPM)_2^{4-} + 2\,Ox^{2-} + 4\,H^+ \qquad (1)$$

0.002 M) and oxalate (0.02 M and 0.06 M) are titrated with strong base. From the data of the buffer region at pH 7 to 8 the equilibrium constant of (1) was evaluated with a modified version of the program KVARI [10] [11], including $[HOx^-]$ (p*K* of $HOx^- = 3.6$ [12]) and $[Ox^{2-}]$. The main species present was $Cu(DPM)_2^{4-}$ with a constant of $10^{21.49 \pm 0.01}$ according to equilibrium (1). Only one other complex, $Cu(HDPM)_2Ox^{4-}$, seems to be formed in small amounts: $[Cu(HDPM)_2Ox]/([CuOx_2][H]^2\cdot[$[illegible]$M]^2) = 10^{36.8 \pm 0.3}$. From the formation constants of $Cu(Ox)_2^{2-}$ ($\log K_1 = 4.01$ and $\log\beta_2 = 9.54$ [13]) $\log\beta_2$ for the formation of $Cu(DPM)_2^{4-}$ from the aquo ion was calculated *(Table 2)*. The constant for the formation of $Cu(HDPM)_2^{2-}$ from Cu^{2+} is probably of the same order of magnitude as *K' (Table 2)* for the formation of $Cu(HDPM)_2Ox^{4-}$ from CuOx, in analogy to the constants for the similar equilibria with ethylenediamine instead of $HDPM^{2-}$ [14] [15].

2. *Nickel complexes.* With Ni^{2+} using the same exchange reaction only $Ni(DPM)_2^{4-}$ was detected (see *Table 2;* $\log\beta_2$ for $Ni(Ox)_2^{2-} = 7.7$ estimated from [16]).

Table 2. *The formation and equilibrium constants*[a]) *for the complexes of DPM(= L) with* Cu^{2+} *and* Ni^{2+} *at 25° and I = 1 (KNO₃).*

Reaction[b])		Cu^{2+}	Ni^{2+}
$M(Ox)_2 + 2L \rightleftharpoons ML_2 + 2\,Ox$	$\log\beta_{2,Ox}$	21.49 (1)	16.69 (9)
$M + 2L \rightleftharpoons ML_2$	$\log\beta_2$	31.0 (3)	24.4 (3)
$M(Ox)_2 + 2\,HL \rightleftharpoons MOx(HL)_2 + Ox$	$\log K'_{Ox}$	4.6 (3)	-
$MOx + HL \rightleftharpoons MOx(HL)_2$	$\log K'$	8.6 (4)	-

[a]) In parentheses three times the standard deviation of the last digit. The large error of β_2 is due to that of the p*K* of $HDPM^{2-}$.

[b]) Charges are omitted for simplicity.

Discussion. - In the *Figure* the $\log\beta_2$ values of 4 different types of bidentate *N*-ligands are plotted against their $\log\kappa_2$ values ($= pK_1 + pK_2$): Bis-2-pyridylmethane (MONE [17]), 2-pyridylmethylamine (PA, [18]), ethylenediamine (EN, [15] [19]) and H_{-1}glycinamide ($H_{-1}GA$[2]), [20]). For both metal ions a correlation straight line was constructed with these points. The values for the Cu and Ni dipyrromethenato complexes are greater than expected by 6.5 and 8 logarithmic units, respectively. A similar result has been found for the complexes with phenanthroline (PHEN [21] [22]), suggesting that the results for DPM^{3-} can be attributed to the basicity, rigidity and aromaticity of the ligand. The Cu–N bonds in the corresponding complex with the diester of DPM are in fact of the normal length for Cu(II)–N bonds: 1.99 Å [23]. As the electronic spectra of the 1:2 complexes of DPM and of DPM diester [24] are essentially similar the same geometry is assumed (λ_{max}- and

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[2]) $\log\beta_2 = [Cu(H_{-1}GA)_2]/([Cu][H_{-1}GA]^2)$, p*K* of GA = 14.3 [9].

ε_{max}-values: 895 nm 240, 510 nm 84000, 472 nm 8400, 460 nm 6400, 260 nm 20000 and shoulders at 600 nm and 370 nm). The following values of the stability constants of the complexes CuN_4^{2+} are known: $N_4 = 2$ ethylenediamine ($\log\beta_2 = 19.7$) and $N_4 =$ 1,4,8,11-tetraazacyclotetradecane (cyclam $\log K_1 = 30$ [25]). The difference $30 - 19.7 = 10.3$ can be considered a measure of the gain in stability for further chelate ring formation and for the macrocyclic effect [26]. Using this value to estimate the stability of the Cu(II) complex with the cyclic ligand formed by 2 DPM molecules, *i.e.* porphyrin, one obtains $\log K_1 \simeq 41$. Because of the steric hindrance of the *a*-methyl groups in $Cu(DPM)_2^{4-}$, the obtained value can be considered as the lower limit. This is in agreement with the value for Cu(II)-tetra-meso-(*N*-methylpyridinium)-porphine ([27] $\log K = 43 \pm 5$, and pK of H_2L: 13 and 16). For a Ni(II)-porphyrin complex $\log K \geq 33$ is estimated, but no actual value was found for a comparison.

Thus, notwithstanding the presence of a negative charge on one of the nitrogens, dipyrromethene behaves as expected for a *N*-ligand. This is in good agreement with the results for monopyrrolic ligands, where also the pyrrolate group acts as normal *N*-ligand, forming strong complexes with Cu(II), Ni(II), Pd(II) and Ag(I) and none with Fe(III) [1] [9] [11].

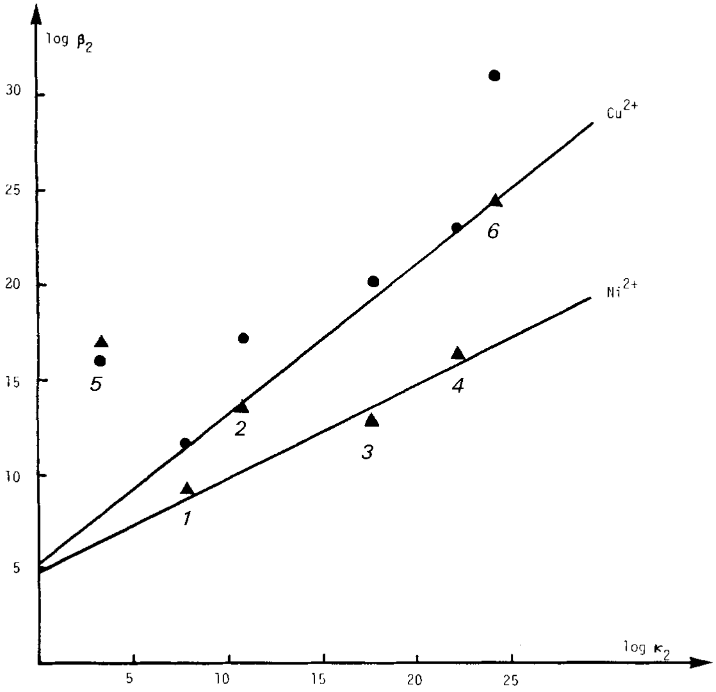

Figure. *The stability constants of the complexes of bidentate* N-*ligands with Cu(II)* ● *and Ni(II)* ▲ *as function of their overall protonation constants* κ_2. *1* MONE; *2* PA; *3* EN; *4* H_{-1}GA; *5* PHEN; *6* DPM

Experimental Part

The pH measurements, the calibration and the evaluation of the constants (25°, I = 1 (KNO_3)) are described in [9]. The electronic spectra were run on *Cary* 2 and Techtron spectrophotometers and the NMR. spectrum on a *Perkin Elmer* R 12 B (chemical shifts in ppm).

Synthesis of the ligand. - 3,5-Dimethylpyrrole-4-carboxylic acid [28] was prepared from 3,5-dimethylpyrrole-2,4-dicarboxylic acid diethyl ester by alkaline hydrolysis of the α-ester group followed by decarboxylation of the resulting acid in dry heat (*Bunsen* burner) and alkaline hydrolysis of the 4-ester group.

3,3',5,5'-Tetramethyl-dipyrromethene-4,4-dicarboxylic acid hydrochloride. To a stirred solution of 1.85 g (13 mmol) 3,5-dimethylpyrrole-4-carboxylic acid in 28 g conc. hydrochloric acid, 3.5 ml formic acid were added at RT., when a red precipitate formed. The mixture was stirred for 3 h, left over night and cooled in a refrigerator for 3 h. The precipitate was separated by filtration, washed with a little conc. HCl-solution and dried in high vacuum. The crude product (1.5 g) was mixed with ethanol and stirred for 3 h, followed by separation by filtration. After addition of water and 4.3 ml 1.0M KOH, the zwitterion obtained was separated from the mother liquor by centrifugation. This residue was dissolved in 50 ml of water with 7.0 ml 1.0M KOH and the product precipitated again with 10 ml 2.0M HCl with stirring. After 3 h the product was separated by filtration, washed with 0.1M HCl and dried in high vacuum. Yield: 1.3 g (4 mmol, 61%) $H_4DPM(Cl)$, m.p. 210° (dec.). - ^1H-NMR. (D_2O, K_2CO_3): 2,16 (*s*, 6 H, CH_3); 2,36 (*s*, 6 H, CH_3); 6,5-6,7 (*s*, 1 H, meso-H, position variable with different K_2CO_3 concentrations). - Mol. wt. (by titration): 335 ± 3.

$C_{15}H_{17}ClN_2O_4$	Calc.	C 55.47	H 5.28	Cl 10.92	N 8.63%
(324.77)	Found	„ 55.49	„ 5.36	„ 10.77	„ 8.58%

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