Monatshefte für Chemie 127, 927–933 (1996)

Monatshefte für Chemie
Chemical Monthly

Reactivity of Pyrrole Pigments, XIX [1]. On the Structure of Cu(II) and Zn(II) Chelates of Dipyrrins in Solution

A. Jaumà, J.-A. Farrera, and **J. M. Ribó***

Departament de Química Orgànica, Universitat de Barcelona, E-08028 Barcelona, Spain

Summary. The Cu(II) and Zn(II) chelates of 1,2,3,7,9-pentamethyldipyrrin and 1,2,3,7,9-pentamethyl-8-sulfodipyrrin are studied. When metal acetates are used for the formation of the metal complexes, dipyrrinate metal acetates could be detected as precursors of the *bis*-dipyrrinates.

Keywords. Coordination compounds; Electrospray mass spectrometry; Dipyrrins.

Reaktivität von Pyrrolpigmenten, 19. Mitt. [1]. Über die Struktur von Cu(II)- und Zn(II)-Chelaten von Dipyrrinen in Lösung

Zusammenfassung. Die Cu(II)- und Zn(II)-Chelate von 1,2,3,7,9-Pentamethyldipyrrin und 1,2,3,7,9-Pentadimethyl-8-sulfodipyrrin wurden untersucht. Bei Einsatz von Metalldiacetaten für die Komplexbildung wurden Dipyrrinmetallacetate als Vorläufer der *bis*-Dipyrrinate nachgewiesen.

Introduction

The divalent transition metal complexes of dipyrrins, formerly called pyrromethenes [2], have been extensively studied [3]. In the solid state, these complexes show the constitutional formula of dipyrrins deprotonated at both nitrogen atoms and thus chelating the divalent metal cation. The stereochemistry of the chelates is determined by the type of the coordinated metal cation, but the ideal geometry is usually distorted because of the strong steric hindrance exerted by the substituents in positions 1 and 9 [3j].

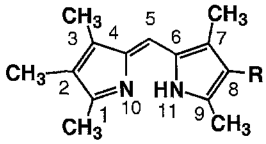
Linear pyrrole compounds have been proposed by *Plieninger* [4] as reagents for the extraction of transition metal cations. *Falk* has studied the behaviour of bile pigments as carriers for the cation transport through liquid membranes [5] and shown that dipyrrins are less efficient and selective than tripyrrinones. Dipyrrins are objects of chemical interest because they are models of well known metal complexing ligands, *i.e.* half-porphyrins and the linear tetrapyrrole pigments with biological significance (urobilins and biliverdins).

The solid state structure of the metal chelates of dipyrrins is well known, but little is known about their chemistry in solution; most of the reported solution refer data to the correlation of UV/Vis absorption spectra with solid state structure. Thus, we present a study of the Cu(II) and Zn(II) chelates of dipyrrins **1** and **2** in solution.

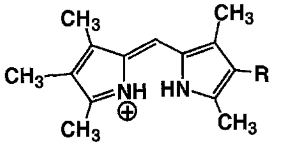
Results and Discussion

The zwitterionic sulfodipyrrin **2a** obtained from **1a** by sulfonation with concentrated sulfuric acid. It is only slightly soluble in water at acidic or neutral *pH* values. The sulfonate sodium salt **2** can be isolated from its alkaline water solution. The UV/Vis absorption spectra of **1** and **2** compared to those of **1a** and **2a** show the well known bathochromic and hypsochromic effects originating from protonation [6].

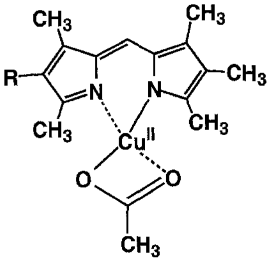
The complexes **3**–**6** are obtained as solids from a solution of the dipyrrin in CH_3OH or CH_3OH/CH_2Cl_2 by treatment with a CH_3OH solution of the *M*(II) salt (acetate or chloride); in some cases, small amounts of NH_4OH were added (see Experimental). The formation of the complex can be monitored by the colour change from the yellow free base dipyrrin to the red metal complex. The sulfonated metal chelates **5** and **6** were isolated as solids in the form of their NH_4^+/Cu^{2+} sulfonate salts ($2\,NH_4^+$ and $1\,M^{2+}$).

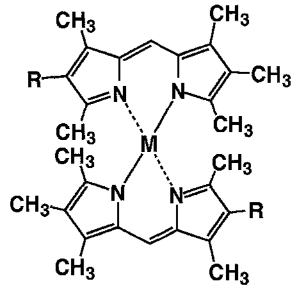


1; R = H
2; R = SO_3Na



1a ; R = H
2a ; R = $SO_3^{\ominus}$





	R	M
3	H	Cu^{II}
4	H	Zn^{II}
5	$SO_3Cu_{1/2}$	Cu^{II}
6	$SO_3Zn_{1/2}$	Zn^{II}

	R
7	H
8	$SO_3Cu_{1/2}$

The spectrophotometric titration of **1** with $CuCl_2$ in $EtOH/NH_4OH$ shows an isosbestic point and the expected spectrum of the Cu(II) *bis*-dipyrrinate (Fig. 1) [3, 6]. However, the spectrophotometric titration of **1** with Cu(II) acetate results in the absence of an isosbestic point and, at a high Cu(II) ratio with respect to **1**, in a bathochromic shifted single absorption band; only at low Cu(II) ratios the two absorption bands of the Cu(II) dipyrrinate can be detected (Fig. 1). Furthermore, this titration does not show a clear stoichiometry. The *Job* plots [8] (see Experimental) of **1** with $Cu(AcO)_2$ result in stoichiometric ratios between 2:1 and 1:1 and, at high Cu(II) molar fractions, in a single-band absorption spectrum. At high dipyrrin molar fractions, the spectrum shows the expected two bands. The spectra with a single absorption band around 500 nm could be due to a 1:1 complex or to a 2:1 complex with a 90° angle between the two dipyrrin planes [6]. Single-band absorption spectra are characteristic of the tetrahedral 2:1 Zn(II) complexes (90° dihedral angle between the two dipyrrin planes), whereas the two-band absorption is related to the 2:1 Cu(II) complexes which show an angle of about 70° between the two dipyrrin planes [3j]. In consequence, the single-band absorption spectrum could be interpreted assuming the formation of a 1:1 complex dominating at low dipyrrin:

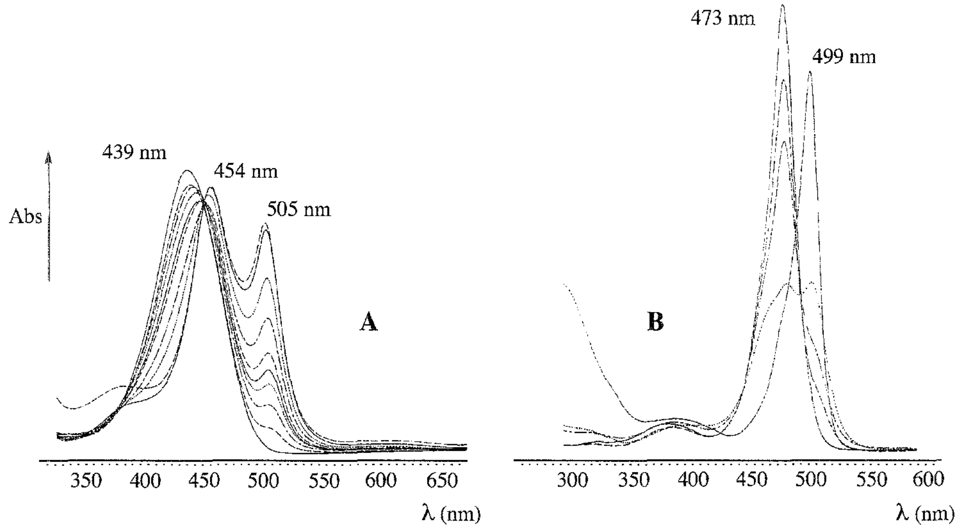


Fig. 1. Spectrophotometric titration of a solution of **1** (2.5×10^{-1} mol·l^{-1}); **A** with $CuCl_2$ in $EtOH/NH_4OH$; **B** with $Cu(AcO)_2 \cdot H_2O$ in EtOH

Cu(II) ratios. In this sense, a dipyrrino cryptand compound has recently been described in the literature [7] which, being sterically unable to yield the 2:1 complex, shows a single-band spectrum in the presence of Cu(II) similar to that reported here.

In the case of the Zn(II) dipyrrinates, the spectrophotometric titration of **1** results in the formation of an isosbestic point and in an approximate stoichiometry ratio of 1:1. The *Job* plot shows a maximum absorption for a stoichiometry ratio between 1:1 and 2:1. Assuming that a 1:1 Zn(II) dipyrrinate would show a UV/Vis absorption spectrum very similar to that of the 2:1 Zn(II) dipyrrinate (two orthogonal chromophores), these results point to the existence of a 1:1 complex preceding the 2:1 complex formation.

Similar results are obtained for the sulfonated dipyrrin **2**, $Cu(AcO)_2$ spectrophotometric titrations do not show an isosbestic point and give a single-band absorption spectrum; spectrophotometric stoichiometry ratios for $Cu(AcO)_2$ and $Zn(AcO)_2$ are near to 1:1, and *Job* plots show stoichiometry ratios between 1:1 and 2:1 . The spectrophotometric titration of **2** with Zn(II) acetate shows only a quasi-isosbestic point spectrum. This can be explained by the presence of the sulfonato Zn^{2+} salts which results in different oligomeric-polymeric associations in the solution. In fact, upon crystallization of **5** and **6**, correct elemental analyses could only be obtained by isolation of mixed NH_4^+ and M^{2+} sulfonato salts.

The formation of the 1:1 dipyrrinate with an additional acetate anion coordinating the divalent cation was confirmed by the isolation and characterization of the corresponding Cu(II) complex (**7**). **7** is an amorphous solid whose solutions show a single main absorption band in the visible region. Osmometric measurements in methanol solution result, after extrapolation to zero concentration, in a molecular weight of 335 (corresponding to 1 dipyrrin, 1 acetate, and 1 Cu). The osmometry values of **7** show association behaviour (*e.g.* $K = 440$ at $2.7 \cdot 10^{-2}$ mol·l^{-1}). The magnetic susceptibility of the solid amounts to 1.42 μ_B at room temperature. This

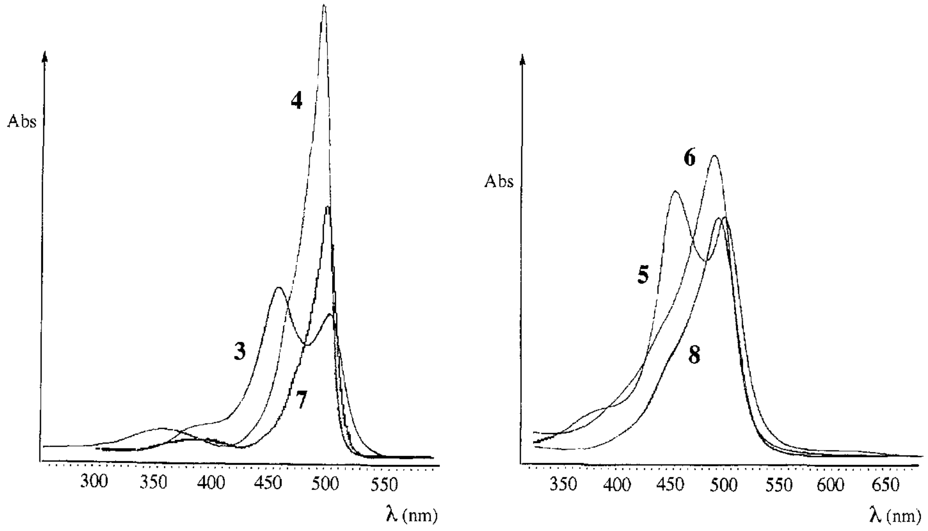


Fig. 2. UV/Vis absorption spectra of **3**–**8** in ethanol (for ε values, see Experimental); the spectra of **5** and **6** correspond to the ammonium sulfonate salts

value implies an antiferromagnetic coupling between two d^9 Cu atoms. This, in turn, implies a short distance between the Cu atoms (≈ 2.65 Å) as is the case with Cu(II) acetate, being a dimer in the solid state and an oligomer-polymer in solution [9]. The EPR spectrum of **7** in methanol at 77 K shows a single quasi-symmetric band with $g = 2.11$ and $\Delta H_{pp} = 196$ G. This EPR spectrum differs significantly from those of the 2:1 Cu-dipyrrin chelates [3g] which show the characteristic anisotropic EPR spectra of d^9 Cu species with the unpaired electron residing in the $d_{x^2-y^2}$ orbital. Probably, the dipyrrin ligand replaces part of the acetate ligands of Cu(II) acetate oligomers.

The mass spectroscopic analysis of methanolic solutions of the metal chelates (electrospray technique) was successful for **3**–**6** but not for **7** which – by positive ion analysis – only results in the detection of the protonated dipyrrin. **3** and **4** were easily detected as the protonated complexes. For **5** and **6**, the negative ion analysis results in the detection of the bisdipyrrinato Cu(II) species, *i.e.* in the differentation of ionic and chelated Cu (see Experimental).

These results show that the formation of the 2:1 complexes is preceded by the formation of a 1:1 complex, according to

$$D\mathrm{H} + MX \rightleftharpoons \mathrm{H}X + DMX \quad \text{and} \quad DMX + D\mathrm{H} \rightleftharpoons DMX + \mathrm{H}X$$

Basic media shift the equilibrium towards the 2:1 complex. In this sense, the differences observed in the formation of the chelates from chloride and acetate salts can be attributed to the different *pH* values necessary for their solubilization. The *bis*-dipyrrinate complexes of *M*(II) chloride salts can be obtained only after the addition of NH_4OH. However, the 1:1 complex also contains one of the anions of the initial salt. Probably, the coordination ability of the acetate anion allows the isolation of the Cu(II) 1:1 complex. The comparison of the Zn complex formation using acetate or chloride salts shows that the complex formation from acetates occurs at lower *pH* values than that from chlorides (the 1:1 Zn complex shows a similar absorption spectra as the 2:1 complex).

Experimental

Melting points were determined on a Kofler-Reichert micro hot-stage apparatus. UV/Vis spectra: Perkin-Elmer Lambda 5; FT-IR spectra: Nicolet 510; MS (FAB): Hewlett-Packard 5988A, Capillartron Frasor Cs gun (10 kV); MS (electrospray): VG-Quattro Fisons (80 °C, 3.5 kV, focus 45–125 V); NMR: Varian Gemini (200 MHz) or Varian Unity (300 MHz); EPR: Bruker EST 300E, band; magnetic susceptibility measurements: pendulum susceptometer (Manics DMS8 at 15 kG). Elemental analyses (C, H, N, S, Cl) were in accordance with the calculated values.

The *Job* plots [8] were generated recording the absorbance at λ_{max} of the complex for a set of several mixtures of the two coordinating species at different molar fractions but at the same total concentration ($2 \cdot 10^{-5}$ mol·l^{-1} total concentration; ethanol 96° Bé solutions of the dipyrrin and the *M*(II) salt). Before the measurements, the solutions were saturated with NaCl. The small amount of water in the ethanol, and – in the case of the metal acetates – the water of crystallization allows the dissolution of small amounts of NaCl which increases the ionic strength of the media and compensates the changes in ionic strength due to the different salt contents in the series of solutions. Without the addition of NaCl, the results were not reliable. Elemental analyses (C, H, N, S) were in accordance with the calculated values.

1,2,3,7,9-Pentamethyldipyrrin hydrochloride (**1a**, $C_{14}H_{19}ClN_2$)

1a was obtained according to Refs. [3a, 10] from 3,4,5-trimethylpyrrole-2-carbaldehyde [11b] and 2,4-dimethylpyrrole [12] in 86% yield (Ref. [3a]: 84%). M.p.: 240 °C (dec; Ref. [3a]: 244 °C dec); TLC (SiO_2, CH_2Cl_2:CH_3OH = 15:1): $R_f = 0.3$; MS(+)-ES (CH_3OH:H_2O = 1:1): *m/z* = 215 (M); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 477 (96500), 358 (5500) nm; UV/Vis (EtOH): λ_{max} (ε) = 473 (81100), 357 (4600) nm: FT-IR (KBR): 1613, 1528, 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 13.72 (broad s, NH), 13.55 (broad s, NH), 7.03 (s, HC=, C5), 6.12 (s, HC=, C10), 2.62, 2.62, 2.34, 2.25, 1.98 (5 s, 5 × CH_3) ppm.

1,2,3,7,9-Pentamethyldipyrrin-8-sulfonate (**2a**, $C_{14}H_{18}N_2O_3S$)

477 mg **1a** were dissolved in 130 ml H_2SO_4 (66° Bé) and stirred at room temperature for 40 h. The reaction mixture was added to 600 ml ice water (< 20 °C), adjusted to basic *pH* with $NaHCO_3$, and acidified to *pH* = 2 with dilute sulfuric acid. Most of the Na_2SO_4 was precipitated by the addition of CH_3OH and separated by filtration. The filtrate was evaporated *in vacuo*, and the residue was dissolved in EtOH anh., filtered, and again evaporated *in vacuo*. The residue was washed and centrifuged 4 times with water at *pH* = 2. 520 mg of **2a** were obtained (93% yield). M.p.: 250 °C (dec.); TLC (SiO_2, CH_2Cl_2:CH_3OH:AcOH = 75:25:1): $R_f = 0.45$; MS(−)-ES (CH_3OH:H_2O = 1:1): *m/z* = 293 (M-1); UV/Vis (CH_3OH): λ_{max} (ε) = 477 (71400), 361 (4800) nm; FT-IR (KBr): 1617, 1524, 1441, 1254, 1200, 1025, 945 cm^{-1}; ^{1}H NMR (CD_3OD, 200 MHz): δ = 7.54 (s, HC=, C5), 2.65, 2.57, 2.54, 2.36, 2.07 (5 s, 5 × CH_3) ppm.

Sodium 1,2,3,7,9-pentamethyldipyrrin-8-sulfonate (**2**, $C_{14}H_{17}N_2NaO_3S$)

0.04 mmol of a NaOH solution (0.25 mol·l^{-1}) were added to a suspension of 11.9 mg (0.04 mmol) of **2a** in 0.2 ml water. The solution was filtered through a nylon filter of 0.22 μm pore diameter and lyophilized (12.1 mg, 95% yield). TLC (SiO_2, CH_2Cl_2:CH_3OH:AcOH = 75:25:1): $R_f = 0.45$; MS(−)-ES (CH_3OH:H_2O = 1:1): (*m/z*) = 293 (M-Na); UV/Vis (EtOH): λ_{max} = 427, 223 nm; FT-IR (KBr): 1621, 1210, 1191, 1040, 1028 cm^{-1}; ^{1}H NMR (CD_3OD, 200 MHz): δ = 6.78 (s, HC=, C5), 2.53, 2.40, 2.28, 2.11, 1.94 (5 s, 5 × CH_3) ppm.

bis-(1,2,3,7,9-Pentamethyldipyrrinyl-η^2,$N^{10,11}$)Cu(II) (**3**, $C_{28}H_{34}CuN_4$)

3 was obtained according to Refs. [3a, 3d]. To 300 mg (1.2 mmol) **1a** dissolved in warm $CH_3OH:CH_2Cl_2 = 1:1$ solution, 300 mg (1.5 mmol) Cu(II) acetate dissolved in 1 ml 30% NH_4OH were added. After 5 min at reflux, the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2, filtered through a nylon filter of 0.22 µm pore diameter and again evaporated. Recrystallization from EtOH affords 137 mg of **3** (65% yield). M.p.: 220 °C (dec; Ref. [3a]: 220 °C dec.); TLC (SiO_2, $CH_2Cl_2:CH_3OH = 15:1$): $R_f = 0.3$; thermogravimetry: combustion: 600 °C, calc. residue as CuO: 16.2%, exp. residue: 16.2%; MS(+)-ES ($CH_3CN:H_2O = 1:1$): $(m/z) = 490$–488 (M + H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 506 (39900), 458 (49900), 370 (10600) nm; UV/Vis (CH_3OH): λ_{max} (ε) = 505 (41200), 454 (48100), 370 (10800) nm; FT-IR (KBr): 1605, 1519, 1233, 1218, 1104, 938 cm^{-1}; EPR (77 K, $CH_2Cl_2:CH_3OH = 1:1$): $g_{\parallel} = 2.28$, $g_{\perp} = 2.08$; EPR (298 K, solid): $g_{\perp} = 2.12$, $\Delta H_{pp} = 139$ G.

bis-(1,2,3,7,9-Pentamethyldipyrrinyl-η^2,$N^{10,11}$)Zn(II) (**4**, $C_{28}H_{38}N_4Zn$)

4 was obtained according to Refs. [3a, 3d]. To 210 mg (0.84 mmol) **1a** dissolved in 35 ml warm CH_3OH, 141 mg (0.64 mmol) Zn(II) acetate dissolved in 0.5 ml 30% NH_4OH was added. After 5 min at reflux, the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2, filtered through a nylon filter of 0.45 µm pore diameter, and again evaporated. Recrystallization from EtOH affords 99 mg of **4** (67% yield). M.p.: 265–270 °C (dec; Ref. [3a]: 277 °C dec); TLC (SiO_2, $CH_2Cl_2:CH_3OH = 15:1$): $R_f = 0.3$; MS(+)-ES ($CH_3CN:H_2O = 1:1$): $(m/z) = 494$–492–290 (M + H); MS(+)-FAB (Xe, NBA): $(m/z) = 494$–492–490 (M + 1); thermogravimetry: combustion: 600 °C, calc. residue as ZnO: 16.5%, exp. residue: 16.5%; UV/Vis (CH_3OH): λ_{max} (ε) = 492 (131900), 360 (9100) nm; FT-IR (KBr): 1598, 1522, 1227, 1108, 938 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 6.98$ (s, HC=, C5), 5.95 (s, HC=), 2.31, 2.20, 1.94, 1.90, 1.89 (5 s, 5 × CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 158.9$, 156.3, 140.8, 138.6, 136.5, 124.2, 121.5 (CH), 116.2 (CH), 16.8 (CH_3), 15.2 (CH_3), 12.2 (CH_3), 10.6 (CH_3), 10.1 (CH_3) ppm.

bis-(2-Ammoniumsulfonate-1,3,7,8,9-pentamethyldipyrrinyl-η^2,$N^{10,11}$)Cu(II) (**5**, $C_{56}H_{76}Cu_3N_{10}O_{14}S_4$)

To 31 mg (0.105 mmol) **2a** dissolved in 15 ml CH_3OH, 10.3 mg (0.052 mmol) Cu(II) acetate dissolved in 0.5 ml 30% NH_4OH were added at reflux. After 5 min at reflux, the solvent was evaporated *in vacuo*. To the residue (dissolved in a small amount of warm CH_3OH) acetone was added in order to precipitate **5**. The precipitate was washed with acetone and afforded 8.8 mg of **5** (26% yield). M.p.: 250 °C (dec); TLC (SiO_2, $CH_2Cl_2:CH_3OH:AcOH = 75:25:1$): $R_f = 0.45$; MS(−)-ES ($CH_3OH:H_2O = 1:1$): $(m/z) = 650$–648 (2 × **2a** − 3H + Cu), 324.5–323.5 (2 × **2a**-4H + Cu); UV/Vis (EtOH): λ_{max} (ε) = 499 (58600), 453 (70300), 360 (4400) nm; FT-IR (KBr): 1609, 1237, 1225, 1165, 1017 cm^{-1}; EPR: (77 K, $CH_2Cl_2:CH_3OH = 1:1$): $g_{\parallel} = 2.28$, $g_{\perp} = 2.08$; EPR (298 K, solid): $g_{\perp} = 2.12$, $\Delta H_{pp} = 170$ G.

bis-(2-Ammoniumsulfonate-1,3,7,8,9-pentamethyldipyrrinyl-η^2,$N^{10,11}$)Zn(II) (**6**, $C_{56}H_{76}N_{10}O_{14}S_4Zn_3$)

To 26 mg (0.088 mmol) **2a** dissolved in 15 ml warm CH_3OH 9 mg (0.041 mmol) Zn(II) acetate dissolved in 0.5 ml 30% NH_4OH were added. After 5 min at reflux, the solvent was evaporated *in vacuo*. To the residue (dissolved in a small amount of warm CH_3OH) acetone was added in order to precipitate **6**. The precipitate was washed with acetone and purified by column chromatography (Florisil). Dissolution in hexane and precipitation with CH_3OH/Acetone afforded 11.7 of **6** (44% yield). M.p.: 250 °C (dec); TLC (SiO_2, $CH_2Cl_2:CH_3OH:AcOH = 75:25:1$): $R_f = 0.45$; MS(−)-ES ($CH_3CN:H_2O = 1:1$): $(m/z) = 653$–651–649 (2 × **2a** + Zn − 3H); UV/Vis (EtOH): λ_{max} (ε) = 491 (75900), 363 (4500) nm; FT-IR (KBr): 1603, 1241, 1167, 1017, 945 cm^{-1}; ^{1}H NMR (CD_3OD, 200 MHz): $\delta = 7.18$ (s, HC=, C5), 2.51, 2.23, 2.15, 1.91 and 1.89 (5 s, 5 × CH_3) ppm.

1,2,3,7,9-Pentamethyldipyrrinyl-η^2,$N^{10,11}$-Cu(II) acetate (**5**, $C_{16}H_{20}CuN_2O_2$)

272 mg (1.37 mmol) Cu(II) acetate dissolved in 50 ml CH_3OH were added to a solution of 69 mg (0.275 mmol) **1a** in 10 ml $CH_3OH:CH_2Cl_2 = 1:1$. The solvent was evaporated *in vacuo* and the residue was dissolved in CH_2Cl_2 and filtered through a nylon filter of 0.22 μm pore diameter (excess of Cu(II) acetate is retained). The filtrate is evaporated. Its UV/Vis spectrum shows complete complexation. MS(+)-ES ($CH_3OH:H_2O = 1:1$): only the molecular peak corresponding to the protonated dipyrrine ligand is observed; osmometry (CH_3OH) apparent M.W. for 1.57×10^{-2} mol·l^{-1}, 2.72×10^{-2} mol·l^{-1}, and 3.68×10^{-2} mol·l^{-1} solutions: 420, 440, and 465; by extrapolation to zero concentration: M.W. = 335 ($C_{14}H_{17}N_2 \cdot C_2H_3O_2 \cdot Cu$; calc. M.W.: 335.9); UV/Vis (EtOH): $\lambda_{max}(\varepsilon) = 492$ (70600), 360 (5200) nm; FT-IR (KBr): 1609, 1441, 1385, 1252, 1233 cm^{-1}; EPR (298 K, solid): $g_\perp = 2.11$, $\Delta H_{pp} = 196$ G; magnetic susceptibility: 1.42 μ_B at 291 K.

Acknowledgements

This work is part of the project DGCYT (PB93-1257). A *Fundació Catalana de la Recerca* grant to *A. J.* is gratefully acknowledged.

References

[1] Part XVIII: Crusats J, Farrera J-A, Ribó JM (1996) Monatsh Chem **127**: 85

[2] IUPAC, "Nomenclature of Tetrapyrroles" (1987) Pure Appl Chem **59**: 779

[3] a) Fischer H, Wallach B (1926) Liebigs Ann Chem **450**: 117; Fischer H, Orth H (1937) Die Chemie eds Pyrrols, Band II. S 10; Akademische Verlagsgesellschaft, Leipzig, b) Fergusson JE, Ramsay CA (1965) J Chem Soc **1965**: 5222; c) Fergusson JE, West BO (1966) J Chem Soc **1966**: 1565; d) Murakami Y, Sakata K (1968) Inorg Chim Acta **2**: 273; e) Elder M, Penfold BR (1969) J Chem Soc A **1969**: 2556; Cotton FA, DeBoer BG, Pipal JR (1970) Inorg Chem **9**: 783; f) March FC, Couch DA, Emerson K, Fergusson JE, Robinson WT (1971) J Chem Soc A **1971**: 440; g) Murakami Y, Matsuda Y, Sakata K (1971) Inorg Chem **10**: 1728; h) Murakami Y, Matsuda Y, Sakata K (1971) Inorg Chem **10**: 1734; i) Dwyer PN, Buchler JW, Scheidt WR (1974) J Amer Chem Soc **96**: 2789; j) Falk H (1989) The Chemistry of Linear Oligopyrroles and Bile Pigments. Springer, Wien New York

[4] Plieninger H, Stumpf K (1970) Chem Ber **103**: 2562; b) Munder S, Pfaff E, Plieninger H, Sander W (1980) Liebigs Ann Chem **1980**: 2031

[5] Eichinger D, Falk H (1987) Monatsh Chem **118**: 91

[6] Falk H, Hofer O (1975) Monatsh Chem **106**: 97

[7] Seel C, Nieger M, Vögtle F (1992) Chem Ber **125**: 447

[8] Rossoti FJC, Rossoti H (1961) The Determination of Stability Constants. McGraw-Hill, New York, p 46

[9] Brian J, Fletcher JR (1987) In: Wilkinson G (ed) Comprehensive Coordination Chemistry, vol 5. Pergamon Press, London, p 634

[10] Marks GS, Dougall DK, Bullock E, MacDonald SF (1960) J Amer Chem Soc **82**: 3183

[11] a) Fischer H, Wallach B (1926) Liebigs Ann Chem **450**: 115; Fischer H, Orth H (1937) Die Chemie des Pyrrols, Band I. Akademische Verlagsgesellschaft, Leipzig, p 154; b) Paine III JB, Kirshner WB, Moskowitz DW, Dolphin D (1976) J Org Chem **41**: 3857

[12] Fischer H, Wallach B (1926) Liebigs Ann Chem **447**: 41: Fischer H, Orth H (1937) Die Chemie des Pyrrols, Band I. Akademische Verlagsgesellschaft, Leipzig, p 42

Received December 29, 1995. Accepted February 7, 1996