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Reactivity of Pyrrole Pigments, XX [1]. On the Structure of Cu(II) and Zn(II) Tripyrrin-1-one Chelates in Solution

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Summary. The Cu(II) and Zn(II) chelates of 12,14-dimethyl-2,3,7,8-tetraethyl-15*H*-tripyrrin-1-one, 12,13-dimethyl-2,3,7,8-tetraethyl-15*H*-tripyrrin-1-one, and their sulfonate derivatives are studied. The chelates show the expected structure of an NH dideprotonated ligand chelating the metal ion. However, in the case of the Zn chelate of 12,14-dimethyl-2,3,7,8-tetraethyl-15*H*-tripyrrin-1-one the ligand is only monodeprotonated, and the lactam ring is tautomerized to a hydroximino function.

Keywords. Coordination compounds; Bile pigments; d-π Orbital interaction.

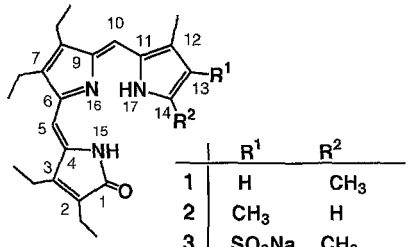
Reaktivität von Pyrrolpigmenten, 20. Mitt. [1]. Über die Struktur von Cu(II)- und Zn(II)-Chelaten von Tripyrrin-1-onen in Lösung

Zusammenfassung. Die Cu(II)- und Zn(II)-Chelate von 12,14-Dimethyl-2,3,7,8-tetraethyl-15*H*-tripyrrin-1-on, 12,13-Dimethyl-2,3,7,8-tetraethyl-15*H*-tripyrrin-1-on und ihrer Sulfonate wurden untersucht. Erwartungsgemäß findet man einen NH-dideprotonotierten Liganden im Chelat; im Zn-Complex von 12,14-Dimethyl-2,3,7,8-tetraethyl-15*H*-tripyrrin-1-on ist der Ligand nur einfach deprotoniert, und das Lactam ist zur Hydroximinogruppe tautomerisiert.

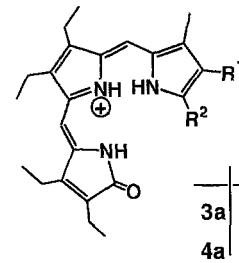
Introduction

The chelates of tripyrrin-1-ones [2] with transition metal cations have been less intensively studied than those of other linear pyrrole pigments (*e.g.* biliverdins or dipyrrins). In the case of the Zn(II) complexes of bile pigments, their absorption and luminiscence spectra have been used in the bile pigment chemistry years ago to differentiate between compounds with three or four conjugated rings [3]. The complexes of tripyrrin-1-ones with transition metal cations occur as intermediate products originating from the oxidative degradation of metal complexes of biliverdins [4, 5].

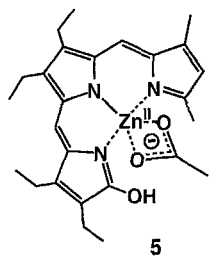
Bile pigments, especially tripyrrin-1-ones, have been proposed and studied by *Plieninger* [3] as reagents for the extraction of transition metal cations. Falk has studied tripyrrinones as cation transport carriers through bulk liquid membranes [6]. Tripyrrin-1-ones are very efficient carriers, better than other bile pigments, and they show a high selectivity for some divalent transition metal cations (especially for Cu(II) and Zn(II)). The solubility of some tripyrrn-1-ones, *e.g.* those substituted



	R^1	R^2
1	H	CH_3
2	CH_3	H
3	SO_3Na	CH_3
4	CH_3	SO_3Na



	R^1	R^2
3a	SO_3^-	CH_3
4a	CH_3	SO_3^-



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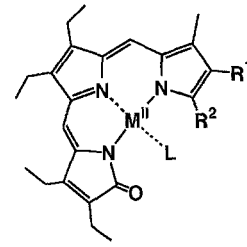


L = CH_3COOH, CH_3OH or H_2O

	R^1	R^2	M^{II}
6	H	CH_3	Cu
7	CH_3	H	Zn
8	CH_3	H	Cu
9	$SO_3Zn_{1/2}$	CH_3	Zn
10	$SO_3Cu_{1/2}$	CH_3	Cu
11	CH_3	$SO_3Zn_{1/2}$	Zn
11a	CH_3	SO_3Na	Zn
12	CH_3	$SO_3Cu_{1/2}$	Cu
12a	CH_3	SO_3Na	Cu

by sulfonate groups, and the ability to anchor bile pigments to a polymeric matrix [7] make tripyrrin-1-ones promising candidates as carriers for some transition metal cations in supported liquid membranes [8].

This paper concerns the investigation of Cu(II) and Zn(II) complexes of the tripyrrinones **1** and **2** and their sulfonate derivatives **3** and **4** in the solution.

Results and Discussion

The tripyrrin-1-ones **1**, **2**, **3a**, and **4a** were obtained by condensation of 2,3,7, 8-tetraethyldipyrrin-1(10*H*)-one with the corresponding pyrrole-2-carbaldehydes. The sulfopyrrole carbaldehydes were obtained from the corresponding formylpyrroles by sulfonation with concentrated sulfuric acid. The sulfotripyrrinones were isolated as zwitterions (**3a**, **4a**) and transformed into their free bases (**3**, **4**) by treatment of an organic solution of the zwitterion with aqueous hydrogen carbonate. The zwitterions and the free base forms can be identified by their UV/Vis absorption spectra.

The zwitterions are soluble in $CHCl_3$. **4a** is water insoluble, **3a** has very low solubility in water. However, these two sulfotripyrrin-1-ones can be solubilized as the free bases by formation of their sodium salts. The equilibration of the sulfonated tripyrrinones **3**, **4**, **3a**, and **4a** in a two phase system ($CHCl_3/H_2O$) shows that there are only zwitterionic forms in the organic phase and only free base forms in the aqueous phase (Table 1).

Spectrometric titration the system of **3a**/**3** in water yields pK_a of 5.7, an expected value for tripyrrin-1-ones [6e, 9]. The titration of **4a**/**4** in water in not possible because of the insolubility of **4a**. However, comparison of the titrations of **3** and **4** in

Table 1. Liquid–liquid partition of sulfotripyrrin-1-ones in the system $CHCl_3$:H_2O (water saturated with CO_2), $6 \cdot 10^{-4}$ mmol sulfotripyrrinone per 10 ml solvent (in parentheses: solubilized form)

	$CHCl_3$	H_2O
3	29% (3a)	71% (3)
3a	87% (3a)	13% (3)
4	≈99% (3a)	≈1% (3)
4a	100% (3a)	–

the system KOH/CH_3OH shows a ΔpK_a of about 0.5 units (**3a** less acidic than **4a**). In this system and at high *pH* values ($[OH^-] \approx 0.1\ mol \cdot l^{-1}$), a significant difference between **3** and **4** can be detected: **3** shows an incipient absorption around 625 nm, which is absent for **4**. This absorption originates from the NH deprotonated tripyrrinonate anion [10]. The results show that an exchange of the sulfo and methyl substituents between positions 13 and 14 causes a change in the acidity of the protonated tripyrrinone and also on the NH acidity of the free base (which gives the tripyrrinonate anion).

The tripyrrinonates of Cu(II) and Zn(II) (**6**–**10**) were isolated by extraction of the metal cation from an aqueous acetate solution with a CH_2Cl_2 solution of the tripyrrinone. Evaporation of the organic phase afforded the complex. Only few of the chelates could be purified by crystallization or by chromatographic methods without partial decomplexation. In this sense, the Cu(II) chelates show higher stability with respect to dissociation than the Zn(II) chelates, and the sulfotripyrrinone complexes are significantly more stable than their unsubstituted counterparts. However, in the case of the Cu(II) complexes, the presence of ionic Cu^{2+} in solution results in an oxidative degradation of the tripyrrinone. This can be attributed to the well known catalytic effect of the Cu(II)–Cu(I) system on the oxidation by O_2.

The preparation described above leads to the metal ion sulfonates of the tripyrrinonate-*M*(II) complexes (**9**–**12**). The metal ion of the sulfonate can easily be replaced by extraction with a NaCl solution: **11a** and **12a** were isolated from **11** and **12**.

The Zn(II) tripyrrinonate **5** could not be obtained by means of the extraction procedure described above; **1** shows only a slow and partial complexation towards **5**. This accounts for the lower stability of the tripyrrinone chelates when position 14 is occupied by substituents with electron donor effects, *i.e.* when the tripyrrin-1-one is less NH acidic. However, mixing of stoichiometric amounts of **1** and Zn(AcO) in CH_3OH under addition of small amounts of NH_4OH yields quantitatively the chelate **5**. Figure 1 shows the UV/Vis absorption spectra of **5**–**12**.

The spectrophotometric titration of **1**–**4**, **3a**, and **4a** with Zn(II) or Cu(II) acetate in ethanol results in the formation of isosbestic points and an approximate 1:1 stoichiometry (see Fig. 2 for examples). Furthermore, the *Job* plots also show a 1:1

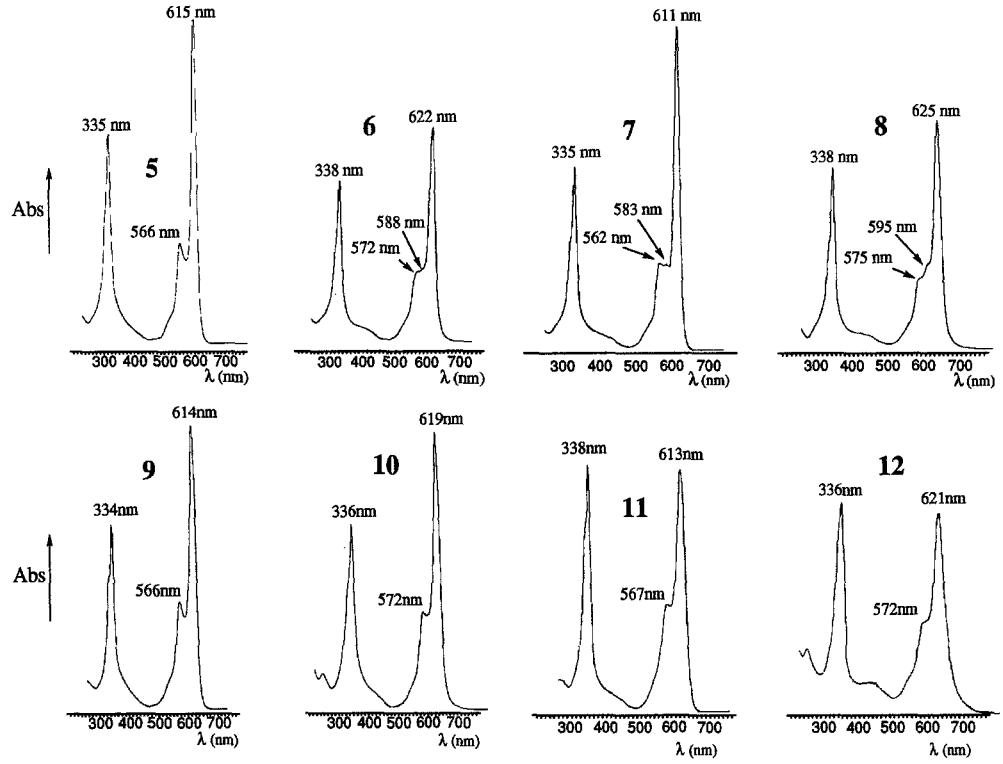


Fig. 1. UV/Vis absorption spectra of the tripyrrinonates of Zn(II) (**5**, **7**, **9**, **11**) and Cu(II) (**6**, **8**, **10**, **12**) in ethanol; for ε values, see Experimental

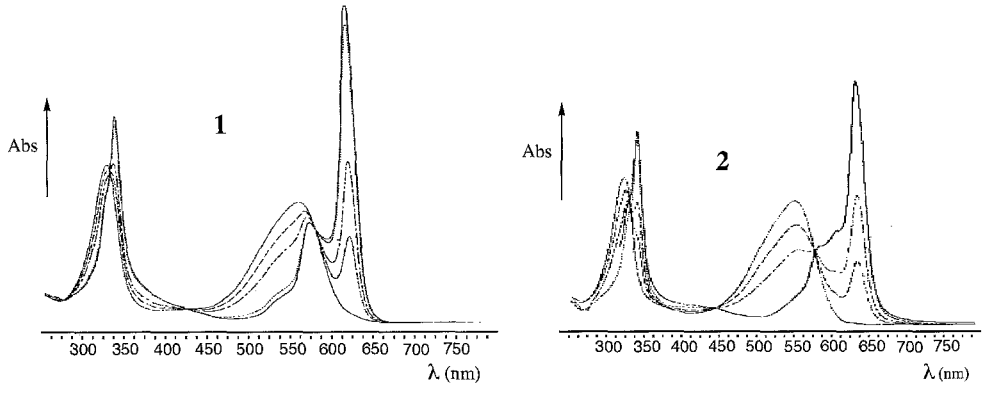


Fig. 2. Examples of the spectrophotometric titration of tripyrrin-1-ones ($2.5\,mol \cdot l^{-1}$) with M(II) acetate in ethanol; A **1** with $Cu(AcO)_2$; B **2** with $Zn(AcO)_2$

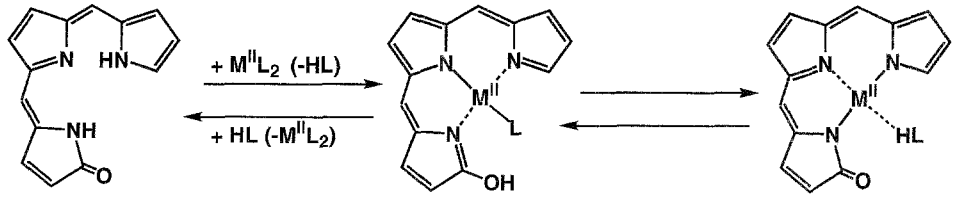
stoichiometry. In the case of **9** and **10** the spectrophotometric titration results in quasi-isosbestic points, but this should be attributed to the presence of the sulfonate of the divalent metal cations which can give rise to dimeric structures *via* the sulfonate group.

The ROESY spectra of the Zn(II) chelates show the expected effects corresponding to the *Z,Z,syn,syn* configuration-conformation of the tripyrrinone structure [6e]. The EPR spectra of the Cu(II) tripyrrinonates are of the same type as those of the 2:1 complexes of dipyrrins [1], *i.e.* the characteristic spectra of d^9 Cu species with the unpaired electron localized at the $d_{x^2-y^2}$ orbital. We therefore assign the same constitutional formula to the Cu(II) chelates as to the Zn chelates on the basis of an expected better tripyrrinone-metal interaction for Cu(II) than for Zn(II); none of the structural data argues against this assumption.

The ^{13}C NMR chemical shift of C1 is about 180 ppm in the case of **7**, **9**, **11**, and **11a** and thus *ca.* 8 ppm higher than the value corresponding to the uncomplexed tripyrrin-1-one, an effect which should be attributed to the electron withdrawing effect exerted by the N–Zn bond. This implies a NH *bis*-deprotonated tripyrrinone and an acetic acid molecule or a molecule of solvent as a second ligand. In the case of the less stable chelate **5**, the ^{13}C chemical shift of C1 is 172 ppm, *i.e.* it is shifted to higher field by about 8 ppm, an effect which is usually attributed to the presence of the hydroximino tautomer in the terminal ring [11, 12]. Furthermore, the ^1H NMR spectrum of **5** confirms this structure by the presence of an exchangeable proton at 7.88 ppm which corresponds to the hydroxyl proton of the hydroximino group [13]. This implies the structure of a monodeprotonated tripyrrinone and an acetate anion as the second ligand for **5**. (see Formula Scheme).

In conclusion, these results indicate that the Cu(II) and Zn(II) chelates are constituted of a divalent metal cation coordinated with one tripyrrin-1-one ligand and with a second ligand (acetic acid or solvent, depending on the preparation method); the number of protons lost during chelation is two. In the case of **6**–**12**, the two protons are abstracted from the tripyrrinone ligand; in the case of **5**, with a tripyrrinone ligand that is more difficult to deprotonate, one proton is abstracted from the tripyrrinone moiety and the other one from the additional ligand.

The structure of **5** suggests that the formation of the chelates **6**–**12** occurs *via* two steps (Scheme 1). First, a monodeprotonated and tautomerized tripyrrinone ligand coordinates the metal by substitution of one of the initial ligands of the metal (*e.g.* acetate anion). This step is similar to that detected for the formation of 1:1 dipyrrin complexes [1]. However, in the case of tripyrrinones the tautomerization of the lactame ring is necessary in order to avoid the steric hindrance between NH group and metal cation. The following prototropic process between the tripyrrinone and the second ligand depends on the relative stabilities of the two types of complexes. Probably only electron-rich tripyrrinones would give the monodeprotonated chelate. In this sense, biliverdins can be considered as tripyrrinones substituted at position 14 by a methylen pyrrolinone ring acting as an electron attracting group.



Scheme 1

The equilibrium between mono and dideprotonated chelate depends on the nature of the second ligand; acetate can act as a bidentate anion which is probably suitable to stabilize **5** relative to the other type of complex.These step-to-step abilities for reversible metal coordination probably account for the efficiency of tripyrrin-1-ones as ion carriers through liquid membranes [6].

The absorption spectrum of Zn complex **5** and monodeprotonated form is similar to that of the dideprotonated chelates **6**–**12**, with very similar λ_{max} values and bathochromic shifts relative to the parent ligand (see Fig. 1). This small dependence of the spectra upon the deprotonation degree suggests that the changes originate from interactions between the d orbitals of the metal and the ligand π system. The quasi-planar π system of the tripyrrinone ligand (parallel to the z axis) can only be perturbed by metal orbitals of appropriate symmetry, *i.e.* d_{xy} and d_{xz}. For the expected geometry of these metal chelates, these metal orbitals are occupied. Assuming a higher energy level for the ligand π system than for the t_{2g} term of the metal, the perturbation would give rise to a bathochromic shift of the ligand transitions as a consequence of the energy increase of the occupied π system. This kind of perturbation would be higher for Cu(II) than for Zn(II) because of the more stable energy level of the Zn orbitals compared to those of Cu.

It should be mentioned that the UV/Vis spectrum of the Mn(III) chelate of **2** supports this suggestion. The *Job* plot of this chelate shows 1:1 stoichiometry *i.e.* a structure corresponding to a dideprotonated tripyrrinone with an acetate anion as additional negatively charged ligand. The UV/Vis spectrum shows the same pattern as those of Fig. 1, but with the low energy absorptions bathochromically shifted with respect to the Cu(II) and Zn(II) chelates (λ_{max}: 645, 612, and 338 nm).

Experimental

Melting points were determined on a Kofler-Reichert micro hotstage 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 Unity (300 MHz) or Varian Gemini (200 MHz); EPR: X band; Bruker EST 300E, magnetic susceptibility measurements: [14] ^{1}H NMR Perkin-Elmer R24B (60 MHz), according to *Evans* instrument. *Job* plots were generated according to the method described in Ref. [1]. Elemental analyses (C, H, N, S) were in accordance with the calculated values.

12,13-Dimethyl-2,3,7,8-tetraethyl-15H,17H-tripyrrin-1-one (**1**, $C_{24}H_{31}N_3O$)

To 456 mg (1.67 mmol) 2,3,7,8-tetraethyl-10*H*-dipyrrin-1-one [15] dissolved in 84 ml diethyl ether saturated with HCl, a solution of 206 mg (1.67 mmol) 3,4-dimethyl-2-formylpyrrole n 6 ml CH_3OH was slowly added (25 min) in an Ar atmosphere, under stirring. After stirring for 30 min the solvent was evaporated *in vacuo*. The residue was dissolved in 70 ml CH_2Cl_2, extracted with 100 ml 5% NH_4OH, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography (Al_2O_3 (II), hexane:CH_2Cl_2 = 2:1) and recrystallized from hexane. 347 mg **1** were obtained (55% yield); m.p.: 131–133 °C; TLC (SiO_2, CH_2Cl_2:CH_3OH = 100:1): R_f = 0.31; MS(+)-FAB (Xe, glycerol): (m/z) = 378 (M + 1), 242 (M–$C_8H_{10}NO$); MS(+)-ES (CH_3OH:H_2O = 1:1): (m/z) = 378 (M + 1); ($CHCl_3$): λ_{max} (ε) = 543 (25300), 323 (32800) nm; UV/Vis ($CuCl_3$): (25300), 323 (32800) nm; (EtOH): λ_{max} (ε) = 542 (33100), 322 (39400) nm; UV/Vis (CH_3OH): λ_{max} (ε) = 541 (27800), 320 (35000) nm; FT-IR (KBr): 1729, 1602, 1287, 1127, 1075 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 9.14 (broad s, 3 × NH), 7.05 (s, HC = pyrrolic), 6.79 (s, HC=, C10), 5.95 (s, HC=, C5), 2.59 (q, J = 7.5 Hz, CH_2CH_3), 2.55 (q, J = 7.5 Hz,

CH_2CH_3), 2.49 (q, $J = 7.5$ Hz, CH_2CH_3), 2.42 (q, $J = 7.5$ Hz, CH_2CH_3), 2.21 (s, CH_3–C13), 2.05 (s, CH_3–C12), 1.23 (t, $J = 7.5$ Hz, CH_2CH_3), 1.19 (t, $J = 7.5$ Hz, CH_2CH_3), 1.17 (t, $J = 7.5$ Hz, CH_2CH_3), 1.15 (t, $J = 7.5$ Hz, CH_2CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT): $\delta = 172.4$ (C=O), 164.6, 148.5, 146.8, 146.4, 142.2, 137.3, 135.0, 130.2, 130.0, 127.5 (CH), 121.8, 117.6 (CH), 98.3 (CH), 18.4 (CH_2), 18.2 (CH_2), 18.2 (CH_2), 17.6 (CH_3), 17.5 (CH_2), 16.2 (CH_3), 15.9 (CH_3), 14.3 (CH_3), 10.5 (CH_3), 9.9 (CH_3) ppm.

12, 14-Dimethyl-2,3,7,8-tetraethyl-15H,17H-tripyrrin-1-one (**2**, $C_{24}H_{31}N_3O$)

To 50 mg (0.18 mmol) 2,3,7,8-tetraethyl-10*H*-dipyrrin-1-one [15] dissolved in 9 ml diethyl ether saturated with HCl, a solution of 23 mg (0.19 mmol) 3,5-dimethyl-2-formylpyrrole in 0.5 ml CH_3OH was slowly added (25 min) in an Ar atmosphere, under stirring. After stirring for 10 min the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2, extracted with 5% NH_4OH, dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography (Al_2O_3 (II), hexane:$CH_2Cl_2 = 2:1$) and recrystallized from hexane. 33.5 mg **2** were obtained (49% yield); m.p.: 122–125 °C; TLC (SiO_2, hexane:$CH_2Cl_2 = 2:1$): $R_f = 0.43$; MS(+)-ES (CH_3OH:$H_2O = 1:1$): $(m/z) = 378$ (M + 1); UV/Vis (EtOH): λ_{max} (ε) = 555 (32100), 325 (41600) nm; FT-IR (KBr): 1698, 1598, 1272, 1227 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 9.22$ (broad s, 3 × NH), 6.77 (s, HC=), 5.96 (s, HC=), 5.91 (s, HC=), 2.58 (q, $J = 7.5$ Hz, CH_2CH_3), 2.54 (q, $J = 7.5$ Hz, CH_2CH_3), 2.50 (q, $J = 7.5$ Hz, CH_2CH_3), 2.43 (s, CH_3), 2.41 (q, $J = 7.5$ Hz, CH_2CH_3), 2.25 (s, CH_3), 1.23 (t, $J = 7.5$ Hz, CH_2CH_3), 1.18 (t, $J = 7.5$ Hz, CH_2CH_3), 1.16 (t, $J = 7.5$ Hz, CH_2CH_3), 1.15 (t, $J = 7.5$ Hz, CH_2CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT). $\delta = 171.7$ (C=O), 162.3, 146.6, 146.0, 145.5, 141.4, 140.6, 136.2, 134.2, 133.4, 129.3 (CH), 112.7, 116.6 (CH), 97.5 (CH), 17.8 (CH_2), 17.7 (CH_2), 17.7 (CH_2), 17.1 (CH_3), 17.0 (CH_2), 15.8 (CH_3), 15.4 (CH_3), 14.0 (CH_3), 13.8 (CH_3), 11.4 (CH_3) ppm.

Sodium 3,4-dimethyl-2-formylpyrrole-5-sulfonate ($C_7H_8NNaO_4S$)

Obtained by sulfonation of 3,4-dimethyl-5-formylpyrrole [13] with concentrated H_2SO_4 following the procedure described in Ref. [3b]. 1 g batches resulted in 47% yields; TLC (SiO_2, CH_2Cl_2:$CH_3OH = 4:1$): $R_f = 0.17$; MS(−)-FAB (Xe, glycerol): $(m/z) = 224$ (M − 1), 202 (M–Na), 122 (M–SO_3Na); UV/Vis (CH_3OH): λ_{max} (ε) = 299 (18100) nm; FT-IR (KBr): 1687, 1667, 1231, 1198 cm^{-1}; ^{1}H NMR (CD_3OD, 200 MHz): $\delta = 9.62$ (s, CHO), 2.27 (s, CH_3), 2.18 (s, CH_3) ppm.

Sodium 2,4-dimethyl-5-formylpyrrole-3-sulfonate ($C_7H_8NNaO_4S$)

Obtained by sulfonation of 2,4-dimethyl-5-formylpyrrole [13] with concentrated H_2SO_4 following the procedure described in Ref. [3b]. 0.5 g batches resulted in 90% yields; TLC (SiO_2, CH_2Cl_2:$CH_3OH = 4:1$): $R_f = 0.17$; MS(−)-FAB (Xe, glycerol): $(m/z) = 202$ (M–Na); UV/Vis (H_2O): λ_{max} (ε) = 299 (18900) nm; FT-IR (KBr): 1665, 1439, 1212, 1196 cm^{-1}; ^{1}H NMR (CD_3OD, 200 MHz): $\delta = 9.51$ (s, CHO), 2.52 (s, CH_3), 2.46 (s, CH_3) ppm.

12,14-Dimethyl-13-sulfo-2,3,7,8-tetraethyl-15H,16H,17H-tripyrrin-1-one (**3a**, $C_{24}H_{31}N_3O_4S$)

3a was obtained according to the method described in Ref. [3b] for similar compounds (condensation of 2,3,7,8-tetraethyl-10*H*-dipyrrin-1-one [13] with sodium 2,4-dimethyl-5-formylpyrrole-3-sulfonate in acidic medium). Purification of the crude product was performed *via* its sodium salt (in the reaction medium, the zwitterionic form is obtained), which was dissolved in water and filtered to eliminate unsoluble organic impurities followed by precipitation with acetic acid. **3a** was further purified by recrystallizaton from methanol dimethylether; 260 mg dipyrrinone batches afforded **3a** in 87% yielded. M.p.: 290 °C (dec); TLC (SiO_2, CH_2Cl_2:$CH_3OH = 5:1$): $R_f = 0.27$; MS(+)-ES (CH_3OH:$H_2O = 1:1$): $(m/z) = 458$ (M + 1), 378 (M + 1-SO_3); MS(−)-ES (CH_3OH:$H_2O = 1:1$): $(m/z) = 456$ (M − 1), 376 (M–SO_3H); UV/Vis (EtOH): λ_{max} (ε) = 580 (48400), 325 (40200) nm; FT-IR (KBr): 1717, 1609, 1275,

1225, 992 cm^{-1}; ^1H NMR (CDOD, 200 MHz): $\delta = 7.22$ (s, HC=, C5), 6.15 (s, HC=, C10), 2.74 (q, $J = 7.5$ Hz, CH_2CH_3), 2.60 (2 × q, $J = 7.5$ Hz, 2 × CH_2CH_3), 2.66 (s, CH_3–C13), 2.52 (s, CH_3–C12), 2.42 (q, $J = 7.5$ Hz,CH_2CH_3), 1.25 (t, $J = 7.5$ Hz, CH_2CH_3), 1.24 (t, $J = 7.5$ Hz, CH_2CH_3), 1.18 (t, $J = 7.5$ Hz, CH_2CH_3), 1.15 (t, $J = 7.5$ Hz, CH_2CH_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): $\delta = 172.7$ (C=O), 152.0, 149.3, 148.8, 146.5, 142.8, 142.5, 135.1, 134.1, 131.9, 130.8, 126.9, 119.7 (CH), 92.9 (CH), 17.2 (CH_2), 16.7 pCH_2), 16.5 (CH_2), 16.1 (CH_2), 15.7 (CH_3), 14.2 (CH_3), 14.1 (CH_3), 13.0 (CH_3), 12.4 (CH_3), 9.9 (CH_3) ppm.

12,13-Dimethyl-14-sulfo-2,3,7,8-tetraethyl-15H,16H,17H-tripyrrin-1-one (**4a**, $C_{24}H_{31}N_3O_4S$)

4a was obtained according to the method described in Ref. [3b] for similar compounds (condensation of 2,3,7,8-tetraethyl-10*H*-dipyrrin-1-one [13] with sodium 3,4-dimethyl-2-formylpyrrole-5-sulfonate in acidic medium 300 mg dipyrrinone batches afforded **4a** in 45% yielded. M.p.: 250 °C (dec); TLC (SiO_2, CH_2Cl_2:CH_3OH = 5:1): $R_f = 0.37$; MS(−)-ES (CH_3OH:H_2O = 1:1): (m/z) = 456 (M − 1), 376 (M–SO_3H); UV/Vis (CH_3OH): λ_{max} (ε) = 579 (50600), 326 (43100) nm; FT-IR (KBr): 1694, 1600, 1223 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 12.41$ (broad s, NH), 11.60 (broad s, NH), 11.23 (broad s, NH), 7.32 (s, HC=, C5), 5.90 (s, HC=, C10), 2.76 (q, $J = 7.5$ Hz, CH_2CH_3), 2.58 (q, $J = 7.5$ Hz, CH_2CH_3), 2.39 (q, $J = 7.5$ Hz, CH_2CH_3), 2.24 (q, $J = 7.5$ Hz, CH_2CH_3), 2.18 (s, CH_3 C13), 2.09 (s, CH_3 C12), 1.31 (t, $J = 7.5$ Hz, CH_2CH_3), 1.21 (t, $J = 7.5$ Hz, CH_2CH_3), 1.12 (t, $J = 7.5$ Hz, CH_2CH_3),0.82 (t, $J = 7.5$ Hz, CH_2CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT): $\delta = 172.7$ (C=O), 152.0, 149.3, 148.8, 146.5, 142.8, 142.5, 135.1, 134.1, 131.9, 130.8, 126.9, 119.7 (CH), 92.9 (CH), 17.2 (CH_2), 16.7 (CH_2), 16.5 (CH_2), 16.1 (CH_3), 15.7 (CH_3), 14.2 (CH_3), 14.1 (CH_3), 13.0 (CH_3), 12.4 (CH_3), 9.9 (CH_3) ppm.

1,15-Dihydro-12,14-dimethyl-1-oxo-2,3,7,8-tetraethyl-17H-tripyrrin-13-sulfonic acid, sodium salt (*3*, $C_{24}H_{30}N_3NaO_4S$)

3 was obtained according to the method described in Ref. [3b] by treatment of 1 mmol **3a** in 200 ml $CHCl_3$ with 100 ml of an aqueous 0.1 *M* $NaHCO_3$ solution in quantitative yield from the organic phase after drying and evaporation. M.p.: 250 °C (dec); TLC (SiO_2, CH_2Cl_2:CH_3OH = 5:1): $R_f = 0.25$; MS(−)-FAB (Xe, glycerol): (m/z) = 456 (M–Na), 376 (M–SO_3Na); UV/Vis (CH_3OH): λ_{max} (ε) = 540 (31700), 322 (37000) nm; UV/Vis ($CHCl_3$): λ_{max} (ε) = 545 (24200), 322 (31800) nm; FT-IR (KBr): 1700, 1605, 1223, 1009 cm^{-1}; ^1H NMR (CD_3OD, 200 MHz): $\delta = 7.02$ (s, HC=, C10), 6.20 (s, HC=, C5), 2.73 (m, 4H, 2 × CH_2CH_3), 2.71 (s, CH_3–C14), 2.63 (q, $J = 7.5$ Hz, CH_2CH_3), 2.55 (s, CH_3), 2.50 (q, $J = 7.5$ Hz, CH_2CH_3), 1.33 (t, $J = 7.5$ Hz, CH_2CH_3), 1.27 (t, $J = 7.5$ Hz, CH_2CH_3), 1.23 (m, 6H, 2 × CH_2CH_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): $\delta = 173.9$ (C=O), 163.4, 148.3, 147.5, 142.8, 141.8, 141.7, 138.2, 135.4, 132.5, 129.3, 128.3, 118.0 (CH), 99.4 (CH), 16.6 (CH_2), 16.4 (CH_2), 16.4 (CH_2), 15.7 (CH_2), 15.5 (CH_3), 14.2 (CH_3), 13.6 (CH_3), 12.1 (CH_3), 12.1 (CH_3), 8.7 (CH_3) ppm.

1,5-Dihydro-12,13-dimethyl-1-oxo-2,3,7,8-tetraethyl-17H-tripyrrin-14-sulfonic acid, sodium salt (**4**, $C_{24}H_{30}N_3NaO_4S$)

4 was obtained according to the method described in Ref. [3b] by treatment of 1 mmol **4a** in 200 ml $CHCl_3$ with 100 ml of an aqueous 0.1 *M*. $NaHCO_3$ solution in quantitative yield from the organic phase after drying and evaporation; it can be recrystallized from $CHCl_3$–diethyl ether. TLC (SiO_2, CH_2Cl_2:CH_3OH = 10:1): $R_f = 0.3$; MS(+)-ES (CH_3OH:H_2O = 1:1): (m/z) = 480 (M + 1), 458 (M + 1-Na), 378 (M + 2H-SO_3Na); MS(−)-ES (CH_3OH:H_2O = 1:1): (m/z) = 456 (M–Na); UV/Vis (CH_3OH) λ_{max} (ε) = 529 (29100), 317 (38800) nm; UV/Vis ($CHCl_3$): λ_{max} (ε) = 546 (27500), 322 (38000) nm; FT-IR (KBr): 1708, 1605, 1221 cm^{-1}; ^1H NMR (CD_3OD, 200 MHz): $\delta = 6.87$ (s, HC=, C10), 6.04 (s, HC=, C5), 2.57 (m, 6H, 3 × CH_2CH_3), 2.34 (q, $J = 7.5$ Hz, CH_2CH_3), 2.17 (s, CH_3), 2.15 (s, CH_3), 1.21 (t, $J = 7.5$ Hz, CH_2CH_3), 1.18 (t, $J = 7.5$ Hz, CH_2CH_3), 1.15 (t, $J = 7.5$ Hz, CH_2CH_3), 1.11 (t, $J = 7.5$ Hz, CH_2CH_3) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT): $\delta = 174.0$ (C=O), 165.0, 150.2, 147.9, 147.7, 142.9,

140.3, 138.8, 135.7, 131.1, 139.4, 121.1, 117.8 (CH), 99.5 (CH), 18.6 (CH_2), 18.5 (CH_2), 18.4 (CH_2), 17.7 (CH_2), 17.5 (CH_3), 16.1 (CH_3), 15.8 (CH_3), 14.1 (CH_3), 9.4 (CH_3), 9.4 (CH_3) ppm.

12,14-Dimethyl-1-hydroxy-2,3,7,8-tetraethyltripyrrinate-η^3,$N^{15,16,17}$-Zn(II) acetate (**5**, $C_{27}H_{33}N_3O_6SZn$)

5 was obtained by mixing stoichiometric amounts of **1** (17 mg (0.045 mmol) in 20 ml CH_3OH) and $Zn(AcO)_2 \cdot 2H_2O$ (9.9 mg (0.045 mmol) in 8 ml CH_3OH). MS(+)-ES (CH_3OH:H_2O = 1:1): (m/z) = 883–881–879 (2M–AcOH–AcO), 444–442–440 (M–AcO); UV/Vis (EtOH): $\lambda_{max}(\varepsilon)$ = 615 (95400), 567 (60500), 334 (58300) nm; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.88 (s, OH), 6.91 (s, HC=, C13), 6.03 (s, HC=, C5), 5.64 (s, HC=, C10), 2.66–2.14 (m = 4 × q, 4 × CH_2CH_3), 2.28 (s, CH_3), 2.08 (s, CH_3–COO), 1.86 (s, CH_3), 1.16 (t, J = 7.5 Hz, CH_2CH_3), 1.03 (t, J = 7.5 Hz, CH_2CH_3), 1.01 (t, J = 7.5 Hz, CH_2CH_3), 0.87 (t, J = 7.5 Hz, CH_2CH_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 181.1 (CH_3COO), 171.6 (C=O), 160.0, 150.9, 145.6, 143.7, 143.0, 138.7, 138.3, 136.8, 133.2, 131.2, 121.6 (CH), 118.2 (CH), 101.4 (CH), 23.2 (CH_3COO), 18.2 (CH_2), 18.1 (CH_2), 17.5 (CH_3), 17.4 (CH_2), 16.9 (CH_2), 16.3 (CH_3), 15.8 (CH_3), 15.1 (CH_3), 13.7 (CH_3), 11.7 (CH_3) ppm.

General procedure for the preparation of compounds **6**–**12**

4 mmol of the respective metal acetate in 20 ml of a mixture water:CH_3OH = 9:1 were extracted with 10 ml CH_2Cl_2 containing 0.06–0.07 mmol of the tripyrrinone. The extraction time depends on the nature of the tripyrrinone. Completion of complexation is indicated by a colour change from red–blue (tripyrrinone) to blue–green (complex). The organic phase was poured through a filtering paper wetted with $CHCl_3$ and subsequently filtered through a nylon filter (Millipore Magna 0.22 μm). The solution was evaporated under vacuum. Yields were quantitative. In some cases, the product could be purified by crystallization. Attempts of chromatographic purification were not successful.

12,14-Dimethyl-2,3,7,8-tetraethyltripyrrinonate-η^3,$N^{15,16,17}$-Cu(II) (**6**, $C_{27}H_{33}N_3O_6SCu$)

The extraction of **6** needs 2 h for completion. Attempts to recrystallize the complex results in partial decomposition. MS(+)-ES (CH_3OH:H_2O = 1:1): (m/z) = 441–439 (M + H–L); UV/Vis (EtOH): $\lambda_{max}(\varepsilon)$ = 622 (63200), 588 sh (22400), 572 sh (22400), 338 (45700) nm; EPR (77 K, CH_3OH): $g_{\parallel}$ = 2.248, $g_{\perp}$ = 2.072, ΔH_{pp} = 116 G.

12,13-Dimethyl-2,3,7,8-tetraethyltripyrrinonate-η^3,$N^{15,16,17}$-Zn(II) (**7**, $C_{27}H_{33}N_3O_6SZn$)

The formation of **7** can be accelerated by the addition of small amounts of NH_4OH. Attempts to recrystallize the product results in partial decomplexation. MS(+)-ES (CH_3OH:H_2O = 1:1): (m/z) = 883–881–879 (2M–2L + H), 821–819–817 (2M–Zn–2L + 3H), 444–442–440 (M–L + H); UV/Vis (CH_3OH): $\lambda_{max}(\varepsilon)$ = 611 (93400), 583 (26000), 562 sh (26300), 335 (56200) nm; FT-IR (KBr): 1617, 1580, 1403, 1389, 1171, 1019 cm^{-1}; ^{1}H NMR (*DMSO*-d_6, 300 MHz): δ = 7.34 (s, CH=, C14), 6.91 (s, HC=, C10), 5.85 (s, HC=, C5), 2.60 (q, J = 7.5 Hz, CH_2CH_3, C8), 2.49 (q, J = 7.5 Hz, CH_2CH_3, C3 or C7), 2.47 (q, J = 7.5 Hz, CH_2CH_3, C7 or C3), 2.25 (q, J = 7.5 Hz, CH_2CH_3, C2), 2.15 (s, CH_3, C12), 1.97 (s, CH_3, C13), 1.78 (s, CH_3COO), 1.11 (t, 6H, J = 7.5 Hz, 2 × CH_2CH_3), 1.08 (t, J = 7.5 Hz, CH_2CH_3), 1.02 (t, J = 7.5 Hz, CH_2CH_3) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz, DEPT): δ = 180.9 (CH_3COO), 180.9 (CO), 151.4, 151.2, 148.2, 146.5, 143.3, 139.7, 137.8, 137.4, 133.7, 133.5, 125.5, 121.1, 103.8, 23.2 (CH_3COO), 17.9, 17.9, 17.6, 17.3, 17.2, 16.4, 15.9, 13.9, 10.1, 9.8 ppm.

12,13-Dimethyl-2,3,7,8-tetraethyltripyrrinonate-η^3,$N^{15,17}$-Cu(II) (**8**, $C_{27}H_{33}N_3O_6SCu$)

Attempts to recrystallize the product results in partial decomplexation MS(+)-ES (CH_3OH:H_2O = 1:1): (m/z) = 501–449 (M + H) UV/Vis (EtOH): 625 (64700), 595 sh (25300), 575 sh (21100), 338

(49300) nm; EPR (77 K, CH_2Cl_2:CH_3OH): $g_{\parallel} = 2.24$, $g_{\perp} = 2.05$, $\Delta H_{pp} = 117$ G; EPR (298 K, solid): $g_{\perp} = 2.12$, $\Delta H_{pp} = 198$ G.

1,15-Dihydro-12,14-dimethyl-1-oxo-2,3,7,8-tetraethyltripyrrin-η^3,$N^{15,16,17}$-zinc(II)-13-sulfonic acid, zinc salt (**9**; $(C_{24}H_{27}N_3O_4SZn)_2Zn\cdot(CH_3COOH)_2$)

The formation of **9** was complete after 3 min. TLC (SiO_2 CH_2Cl_2:CH_3OH = (5:1): $R_f = 0.23$; MS(−)-ES (CH_3OH:H_2O = 1:1): (*m/z*) = 552–520–518 (M–L −0.5Zn); UV/Vis (CH_3OH): $\lambda_{max}(\varepsilon)$ = 614 (63500), 566 (22500), 334 (39400) nm; FT-IR (KBr): 1549, 1457, 1216, 999 cm^{-1}; ^1H NMR (CD_3OD, 300 MHz): $\delta = 7.19$ (s, CH=, C10), 5.82 (s, HC=, C5), 2.69 (q, $J = 7.5$ Hz, CH_2CH_3), 2.50 (s, CH_3–C14), 2.47 (q, $J = 7.5$ Hz, CH_2CH_3), 2.23 (q, $J = 7.5$ Hz, CH_2CH_3), 2.21 (q, $J = 7.5$ Hz, CH_2CH_3), 2.09 (s, CH_3–C12), 1.20 (t, $J = 7.5$ Hz, CH_2CH_3), 1.02 (t, $J = 7.5$ Hz, CH_2CH_3), 0.98 (t, $J = 7.5$ Hz, CH_2CH_3), 0.92 (t, $J = 7.5$ Hz, CH_2CH_3) ppm; ^{13}C NMR (CD_3OD, 75 MHz, DEPT) $\delta = 183.1$ (CO), 157.1, 154.2, 149.8, 145.9, 141.3, 139.5, 136.6, 135.7, 135.2, 130.0, 121.1 (CH), 98.7 (CH), 18.7 (CH_3), 18.5 (CH_2), 18.3 (CH_2), 18.1 (CH_2), 17.7 (CH_2), 17.7 (CH_3), 16.6 (CH_3), 16.3 (CH_3), 14.6 (CH_3), 11.2 (CH_3) ppm.

1,15-Dihydro-12,14-dimethyl-1-oxo-14-sulfo-2,3,7,8-tetraethyltripyrrin-η^3,$N^{15,16,17}$-copper(II)-13-sulfonic acid diacetate, copper salt (**10**, $(C_{24}H_{28}N_3O_4SCu)_2Cu\cdot(CH_3COOH)_2$)

TLC (SiO_2 CH_2Cl_2:CH_3OH = 5:1): $R_f = 0.27$; MS(−)-ES (CH_3OH:H_2O = 1:1): (*m/z*) = 519–517 (M–*L* −0.5Zn); UV/Vis (CH_3OH): $\lambda_{max}(\varepsilon)$ = (62300), 572 (22400), 336 (40200) nm; FT-IR (KBr): 1586, 1214, 1169, 1025, 1003 cm^{-1}; EPR (77 K, CH_3OH): $g_{\parallel} = 2.36$, $g_{\perp} = 2.09$.

1,15-Dihydro-12,13-dimethyl-1-oxo-2,3,7,8-tetraethyltripyrrin-η^3,$N^{15,16,17}$-zinc(II)-14-sulfonic acid, zinc salt (**11**, $C_{24}H_{28}N_3O_4SZn)_2Zn\cdot(CH_3OH)_2$)

The formation at **11** was complete after 3 min. The product could be purified by crystallization from CH_3OH with some drops of H_2O. TLC (SiO_2 without fluorescence indicator, CH_2Cl_2:CH_3OH = (5:1): $R_f = 0.18$; MS(−)-ES (CH_3OH:H_2O = 1:1): (*m/z*) = 1045–1043–1041–1039–1037 (2M–2*L*–H), 522–520–518 (M–*L* −0.5Zn); thermogravimetry (690 °C, air): calc. residue as ZnO: 19.8%, exp. 20.6%; UV/Vis (CH_3OH): $\lambda_{max}(\varepsilon)$ = 613 (55000), 567 (24100), 334 (47500) nm; FT-IR (KBr): 1638, 1588, 1546, 1266, 1221, 1167, 1011, 870 cm^{-1}; ^1H NMR (CD_3OD, 200 MHz): $\delta = 6.99$ (s, CH=), 5.87 (s broad, HC=), 2.68 (q, $J = 7.5$ Hz, CH_2CH_3), 2.57 (q, $J = 7.5$ Hz, CH_2CH_3), 2.31 (q, $J = 7.5$ Hz, CH_2CH_3), 2.15 (s, CH_3), 2.10 (q, $J = 7.5$ Hz, CH_2CH_3), 1.92 (s broad, CH_3), 1.23 (t, $J = 7.5$ Hz, CH_2CH_3), 1.18 (t, $J = 7.5$ Hz, CH_2CH_3), 1.07 (t, $J = 7.5$ Hz, CH_2CH_3), 0.97 (t, $J = 7.5$ Hz, CH_2CH_3) ppm; ^{13}C NMR (CD_3OD, 50 MHz): $\delta = 183.9$ (CO), 159.9, 153.7, 149.5, 148.4, 146.9, 143.5, 136.6, 136.4, 136.3, 136.0, 121.3 (CH), 98.7 (CH), 18.7 (CH_2), 18.6 (CH_2), 18.6 (CH_2), 18.2 (CH_2), 17.7 (CH_3), 16.6 (CH_3), 16.3 (CH_3), 14.6 (CH_3), 10.0 (CH_3), 9.6 (CH_3) ppm.

1,15-Dihydro-12,13-dimethyl-1-oxo-2,3,7,8-tetraethyltripyrrin-η^3,$N^{15,16,17}$-zinc(II)-14-sulfonic acid, sodium salt (**11a**; $C_{24}H_{28}N_3O_4SZnNa$)

11a was obtained by extraction of 15 mg **11** dissolved in 40 ml CH_2Cl_2 with 25 ml of H_2O saturated with NaCl (emulsion is formed). Filtration through a nylon filter (0.22 μm) and washing several times with water affords **11a**. MS(−)-ES (CH_3OH:H_2O = 1:1): (*m/z*) = 522–520–518 (M–L –Na). The product was contaminated with NaCl; however, the element atomic ratios agree with $C_{24}H_{28}N_3S\cdot CH_3O$. UV/Vis ($CH_3OH$): cf. **11**; ^1H NMR (CD_3OD, 300 MHz): $\delta = 6.95$ (s, CH=), 5.89 (s, HC=), 2.65 (q, $J = 7.5$ Hz, CH_2CH_3), 2.51 (q, $J = 7.5$ Hz, CH_2CH_3), 2.33 (q, $J = 7.5$ Hz, CH_2CH_3), 2.17 (s, 6H, 2 × CH_3), 1.20 (t, $J = 7.5$ Hz, CH_2CH_3), 1.17 (t, $J = 7.5$ Hz, CH_2CH_3), 1.16 (t, 6H, $J = 7.5$ Hz,2 × CH_2CH_3), 1.09 (t, $J = 7.5$ Hz, CH_2CH_3) ppm; ^1H NMR (*DMSO*-d_6, 300 MHz): $\delta = 6.90$ (s, CH=, C10), 5.80 (s, HC=, C5), 2.59 (q, $J = 7.5$ Hz, CH_2CH_3), 2.55 (q, $J = 7.5$ Hz, CH_2CH_3), 2.48

(m = 2 × q, 4H, 2 × CH_2CH_3), 2.26 (q, J = 7.5 Hz, CH_2CH_3), 2.12 (s, CH_3, C12), 2.06 (s, CH_3, C13), 1.14–1.02 (m = 4t, 12H, 4 × CH_2CH_3) ppm; ^{13}C NMR (*DMSO*-d_6, 50 MHz DEPT): δ = 181.3 (CO), 157.1, 152.2, 152.2, 147.2, 144.4, 141.0, 134.9, 134.9, 134.3, 133.2, 120.1 (CH), 118.9, 95.9 (CH), 17.7 (CH_3), 17.5 (CH_2), 17.3 (CH_2), 17.1 (CH_2), 17.1 (CH_2), 16.4 (CH_3), 16.2 (CH_3), 14.4 (CH_3), 10.0 (CH_3), 9.9 (CH_3) ppm.

1,15-Dihydro-12,13-dimethyl-1-oxo-2,3,7,8-tetraethyltripyrrin-η^3,$N^{15,16,17}$-copper(II)-14-sulfonic acid diacetate, copper salt (**12**, $(C_{24}H_{28}N_3O_4SCu)_2Cu\cdot(CH_3COOH)_2$)

The complex formation was very fast. The product could be purified by TLC and crystallization from $CHCl_3$ hexane. TLC (SiO_2 without fluorescence indicator, CH_2Cl_2:CH_3OH = 10:1): R_f = 0.4; MS(−)-FAB (Xe, glycerol): (m/z) = 520–518 (M_{mon} + H–L − 0.5Cu); MS(−)-ES (CH_3OH:H_2O = 1:1): (m/z) = 1039–1037–1035 (M_{dim} + H–2L–Cu), 519–517 (M_{mon} − L − 0.5Cu); MS(+)-ES (CH_3OH:H_2O = 1:1): (m/z) = 1041–1039–1037 (M_{dim} − 2L + 2H), 521–519 (M_{mon} + H–L − 0.5Cu); thermogravimetry (150 °C): 9.3% loss corresponding to 2 × CH_3COOH (calc.: 9.9%); UV/Vis (CH_3OH): λ_{max} (ε) = 621 (36400), 572 sh (17100), 337 (36700) nm; UV/Vis ($CHCl_3$): λ_{max} (ε) = 666, 625, 345 nm (intensity ratio: 75:46:100); FT-IR (KBr): 1619, 1580, 1268, 1223, 1160, 876 cm^{-1}; X-ray diffraction: microcrystalline; EPR (77 K, CH_3CN:CH_3OH = 1:1): $g_\parallel$ = 2.31, $g_\perp$ = 2.08; EPR (298 K, solid): $g_\parallel$ = 2.12, ΔH_{pp} = 236 G.

1,15-Dihydro-12,13-dimethyl-1-oxo-2,3,7,8-tetraethyltripyrrin-η^8,$N^{15,16,17}$-copper(II)-14-sulfonic acid, sodium salt (**12a**, $C_{24}H_{27}N_3O_4SCuNa$)

12a was obtained by treatment of 15 mg **12** dissolved in 40 ml CH_2Cl_2 with 25 ml of H_2O saturated with NaCl. TLC (SiO_2, $CHCl_3$:CH_3OH = 10:1): R_f = 0.35; MS(−)-ES (CH_3OH:H_2O = 1:1): (m/z) = 519–517 (M–L–Na); UV/Vis (CH_3OH): λ_{max} (ε) = 623, 572, 337 nm; (100:52:100); UV/Vis ($CHCl_3$): λ_{max} (ε) = 666, 625, 345 nm (77:40:100); EPR (77 K, CH_3OH = 1:1): $g_\parallel$ = 2.23, $g_\perp$ = 2.08; EPR (298 K, CH_3OH); $g_\perp$ = 2.11.

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