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# Synthesis, derivatization and structural characterization of octahedral tris(5-phenyl-4,6-dipyrrinato) complexes of cobalt(III) and iron(III)

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### Abstract

The formation of octahedral tris(5-phenyl-4,6-dipyrrinato) complexes of cobalt(III) and iron(III) of *p*-substituted (-H, -CO<sub>2</sub>Me, -NO<sub>2</sub>) 5-phenyl-4,6-dipyrrins is described. The molecular structure of the parent cobalt(III) complex was determined by X-ray crystallography. Crystals of C<sub>45</sub>H<sub>33</sub>N<sub>6</sub>Co·C<sub>3</sub>H<sub>6</sub>O are monoclinic, a = 13.539(2), b = 22.348(2), c = 13.467(1) Å, V = 3882.7(8) Å<sup>3</sup>, Z = 4, space group C2/c. The structure was solved by direct methods and refined by full-matrix least-squares procedures to R = 0.039 and Rw = 0.033 for 2309 reflections with  $I \ge 3\sigma(F^2)$ . These regular octahedral complexes underline the special coordination properties of the 5-phenyl-4,6-dipyrrins as compared to  $\alpha$ ,  $\beta$ -alkyl-substituted dipyrrins for which no such tris-complexes are known. The reduction of the *p*-methoxycarbonyl-substituted Co(III) complex to the corresponding *p*-amino complex and the saponification, chlorination and esterification of the *p*-methoxycarbonyl-substituted Co(III) complex are reported, highlighting the chemical stability of the complexes and their potential to be incorporated into larger structures. (B) 1997 Elsevier Science S.A.

Keywords: 5-Phenyldipyrromethanes; meso-Phenyldipyrrinato complexes; Iron(III) chelates; Cobalt(III) chelates; Crystal structures

#### 1. Introduction

4,6-Dipyrrins, also known as dipyrromethenes, are basic, brightly colored, fully conjugated flat bipyrrolic molecules. Their structure, atom numbering scheme and the formal nomenclature for dipyrrins (1) are shown in Fig. 1. Carbons 1 and 9 are also referred to as  $\alpha$ -carbons, positions 2, 3, 7 and 8 as  $\beta$ -positions and position 5 as the *meso*-position. Their propensity to strongly chelate transition metals has long been recognized [1].

Recently, we [2] and in an independent study, Lindsey's group [3], reported the preparation of 5-phenyl-substituted  $\alpha,\beta$ -unsubstituted dipyrrins such as 3. They were made by DDQ (2,3-dichloro-5,6-dicyano-1,4-quinone) oxidation of the corresponding dipyrromethane 3, for which we [4], based on methods given by Lee and Lindsey [5] or Carell [6], reported large scale procedures of synthesis.

These were the first reports describing dipyrrins and their metal complexes lacking  $\alpha$ - and  $\beta$ -substituents and bearing, at the same time, a *meso*-substituent. Some reports on *meso*-phenyl and at least an  $\alpha$ -substituted [7,8] as well as some

$$\begin{array}{c}3 & 5 & 7\\2 & 4 & 6\\NH & N=\\1 & 10 & 11 & 9 & 1\end{array}$$

4,6-Dipyrrin 2-(2-H-Pyrrol-2-ylidenemethyl)pyrrole Fig. 1. Nomenclature and atom numbering scheme of dipyrrins.

meso- and  $\alpha$ - or  $\beta$ -unsubstituted systems have appeared in the literature [9-11]. Meso-phenyl-substituted dipyrrins have some special properties which have made them objects of several recent studies. Beyond the favorable photophysical characteristics of dipyrrinato BF<sub>2</sub> complexes [3,12], their meso-phenyl groups generally can be derivatized with a wide selection of substituents. This makes these pigments amenable for incorporation into larger structures such as photonic wires [13], optoelectronic gates [14], light-harvesting arrays [3] or other models of the photosynthetic apparatus [9,15]. The lack of any  $\alpha$ -substituent in 3 and thus the lack of unfavorable inter-ligand steric interactions when several ligands chelate one metal, has a pronounced effect on the stereochemistry of the ligands around the metal center [2]. The nickel(II) bis-complex of 3, for example, is, in contrast to the analogous complexes of  $\alpha$ -substituted dipyrrins, close to square planar and thus diamagnetic.

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The bulk of the known structurally characterized tetrahedral [1,16,17] or distorted planar [2,18] dipyrrinato metal structures contain metals chelated by an N4-donor set. Dipyrrinato complexes in which the coordination number of the central metal is higher than four are either mixed ligand systems [19] or where carbonyl oxygens of  $\alpha$ -substituents in bis-dipyrrinato complexes act as additional donors, forming N4O2- and N4O4-donor sets [17,20]. Dipyrrinato tris-chelates (Ne-donor set) are for steric reasons only attainable by  $\alpha$ -unsubstituted dipyrrins. We are aware of only two earlier reports of such complexes, viz the two 1974 reports by Murakami et al. of the tris (3,3',4-trimethyldipyrrinato) complexes of manganese(III) [21] and iron(III) [22]. However, their molecular structures were not determined and, in fact, some spectroscopic properties indicated lesser than octahedral symmetries.

We present here another example in which the lack of interligand steric interactions in *meso*-phenyl dipyrrin ligands distinguishes their coordination properties markedly from those of  $\alpha$ , $\beta$ -alkylated systems, namely their ability to form neutral octahedral dipyrrinato tris-complexes with trivalent metals. We chose cobalt(III) and iron(III) as typical examples. An X-ray single crystal structure analysis of the cobalt(III) complex illustrates their high symmetry and represents the first structurally characterized tris-dipyrrinato chelate, and, in fact, the first report on cobalt(III) dipyrrinato complexes in general. Furthermore, we have been able to demonstrate the functional group interconversion of selected *p*-substituents of cobalt(III) tris-pyrrinato complexes, thereby underlining their stability and potential for incorporation into larger structures.

### 2. Experimental

### 2.1. Materials and instrumentation

Dipyrrins 3 and 5 [2] and [Co(pyridine)<sub>4</sub>Cl<sub>2</sub>]Cl [23] were prepared as previously reported. All other reagents and solvents were purchased and used as received. The silica gel used in flash chromatography was Merck silica gel 60, 230-400 mesh whilst  $R_f$  values were measured on Merck silica TLC aluminum sheets (silica gel 60 F254). Melting points were determined on a Thomas hot stage or Büchi apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AC-200 or AMX-300 instruments. UV-Vis spectra were recorded on an HP8452A photo diode array spectrophotometer (instrumental precision  $\pm 2$  nm) in the solvents indicated. Elemental analyses were performed by Mr P. Borda of the departmental microanalytical laboratory. The high and low resolution mass spectra were obtained by the departmental mass spectrometry service laboratories (G. Eigendorf, Director).

### 2.2. Preparations

#### 2.2.1. 5-(4-Methoxycarbonylphenyl)dipyrromethane (6)

A solution of methyl 4-formylbenzoate (5.55 g, 33.8 mmol) and pyrrole (22.6 ml, 10 equiv.) in toluene (200 ml) was purged with N2 for 30 min before a saturated solution of p-toluenesulfonic acid in warm toluene (1 ml) was added and the mixture heated to reflux for 1.5 h. After cooling, the pale yellow solution was washed with dilute aqueous Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O. The organic phase was dried over anhydrous Na<sub>2</sub>CO<sub>3</sub> and evaporated in vacuo into a brown oil which was charged onto a flash column  $(6 \times 25 \text{ cm}, \text{CHCl}_3)$ . Following residual pyrrole, the main colorless fraction was collected. The combined fractions were evaporated on a rotary evaporator to produce a tan solid in 49% yield (4.65 g). An analytical sample was recrystallized from CHCl<sub>3</sub>/hexane to provide a white powder.  $R_{\rm f}$  (CHCl<sub>3</sub>-silica) = 0.15 (spot stains bright red when fumigated with Br<sub>2</sub>) [24]. M.p. =  $158^{\circ}$ C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz):  $\delta$  3.82 (s, 3H, CH<sub>3</sub>), 5.45 (s, 1H, 5-H), 5.66 (s, 2H), 5.91 (m, 2H), 6.62 (s, 2H), 7.31 (d, J=9 Hz, 2H), 7.87 (d, J=9 Hz, 2H), 10.6 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ 44.4, 52.6, 107.9, 108.9, 118.0, 128.9, 129.1, 130.3, 132.1, 147.9, 167.4. Anal. Calc. for C17H16N2O2: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.45; H, 5.88; N, 9.68%.

#### 2.2.2. 5-(3-Methoxycarbonylphenyl)dipyrromethane

Prepared from methyl 3-formylbenzoate (3.02 g, 18.3 mmol) and pyrrole in 68% yield (3.49 g) as described for the synthesis of **6**. M.p. =  $124-127^{\circ}$ C.  $R_{\rm f}$  (CHCl<sub>3</sub>) = 0.4 (spot stains bright red when fumigated with Br<sub>2</sub>) [24]. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 300 MHz):  $\delta$  3.81 (s, 3H), 5.53 (s, 1H), 5.67 (s, 2H), 5.92 (m, 2H), 6.64 (s, 2H), 7.43 (m, 2H), 7.81 (m, 2H), 10.62 (br s, 2H). <sup>13</sup>CNMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  44.3, 52.8, 107.9, 108.9, 118.0, 128.6, 129.1, 129.9, 130.8, 132.4, 133.4, 143.2, 167.5. *Anal.* Calc. for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.52; H, 5.86; N, 9.98

### 2.2.3. 5-(4-Methoxycarbonylphenyl)-4,6-dipyrrin(7)

Dipyrromethane 6 (1.0 g, 3.57 mmol) was dissolved in CHCl<sub>3</sub> (20 ml). DDQ (891 mg, 1.1 equiv.) dissolved in warm benzene (2 ml) was added and the instantly darkening mixture was gently warmed for 30 min. Et<sub>3</sub>N (1 ml) was then added to the black solution containing precipitated material, resulting in a dark yellow homogenous solution. The solution was passed through a short column (CHCl<sub>3</sub>-silica) and the first bright yellow fraction was collected, reduced to a yellow residue in vacuo and immediately used in the metal complexation experiments.  $R_f$  (CH<sub>2</sub>Cl<sub>2</sub>/2%MeOH-silica) = 0.2-0.3 (bright yellow spot stains slowly pink when fumigated with Br<sub>2</sub>). UV-Vis (MeOH-trace NH<sub>4</sub>OH):  $\lambda_{max}$  360, 472 nm. MS (+EI): m/e 278 (100,  $M^+$ ), 263 (15,  $M^+$  -CH<sub>3</sub>), 219 (60,  $M^+$  -CO<sub>2</sub>CH<sub>3</sub>).

# 2.2.4. Tris(5-phenyl-4,6-dipyrrinato)Co(III)(8)

To a stirred solution of 5-phenyldipyrromethane (111 mg, 0.5 mmol) in CHCl<sub>3</sub>:MeOH (1:1, 10 ml) was added DDQ (113 mg, 1 equiv.) dissolved in warm benzene (2 ml). After TLC examination revealed full consumption of the starting material ( $R_{\rm f}$  (CH<sub>2</sub>Cl<sub>2</sub>:CCl<sub>4</sub>, 1:1) = 0.78) (~1 h), Et<sub>3</sub>N (1 ml) and a solution of [Co(py)<sub>4</sub>Cl<sub>2</sub>]Cl (80 mg, 0.16 mmol) in MeOH (3 ml) were added. The dark mixture was gently warmed for 30 min and then evaporated in vacuo to dryness to produce a black solid. This crude product was charged onto a flash column (15×3 cm, CH<sub>2</sub>Cl<sub>2</sub>). The first bright orange band was collected and evaporated to dryness to produce 8 in 29% yield (based on 2, 35 mg). M.p. = 243°C.  $R_{\rm f}$  $(CH_2Cl_2) = 0.86.$  <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  6.3 (dd, J = 1.2, 4.4 Hz, 2H, 6.40 (s, 2H), 6.72 (dd, J = 1.2, 4.4 Hz, 2H), 7.46 (m, 5H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 118.5, 127.2, 128.1, 130.4, 133.0, 135.7, 138.1, 145.3, 151.7. IR (film on KBr): 1553, 1376, 1338, 1246, 1204, 1032, 994 cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\epsilon$ ): 318 (4.34), 398 (4.26), 466 (4.83), 504 (4.77) nm. LR-MS (+FAB, thioglycerol): m/e 717 (16,  $MH^+$ ), 603 (5,  $M^+ - 2 \times C_6H_5$ ), 497 (68,  $M^+ - C_{15}H_{11}N_2$ ), 278 (43), 220 (35, ligand H<sup>+</sup>). HR-MS (+EI, 220°C): m/e calc. for C<sub>45</sub>H<sub>33</sub>N<sub>6</sub>Co: 716.20984; found: 716.20951. Anal. Calc. for C45H33N6Co: C, 75.40; H, 4.64; N, 11.72. Found: C, 74.91; H, 4.71; N, 11.55%. Slow evaporation of an acetone solution produced 8 as its mono acetone solvate in X-ray quality ruby-red dichroic (red-green) crystals. Anal. Calc. for C45H33N6Co. C<sub>3</sub>H<sub>6</sub>O: C, 74.41; H, 5.07; N, 10.85. Found: C, 74.73; H, 4.90; N, 11.31%.

# 2.2.5. Tris[5-(4-methoxycarbonylphenyl)-4,6-dipyrrinato]Co(III) (10)

The 5-(4-methoxycarbonylphenyl)dipyrrin (7) prepared as described above was dissolved in MeOH (10 ml) and Et<sub>3</sub>N (1 ml). To the heated solution, [Co(py)<sub>4</sub>Cl<sub>2</sub>]Cl (230 mg, 0.54 mmol, 0.15 equiv. based on dipyrromethane 6) was added dropwise over a period of 30 min, until TLC evaluation indicated that all the dipyrrin was consumed. Work-up of the bright orange solution was analogous to that described for 8, albeit with a more polar eluent (CH<sub>2</sub>Cl<sub>2</sub>, then 2%MeOH/ CH2Cl2), to produce 10 as an orange microcrystalline powder in 33% yield (350 mg). M.p.  $\geq 280^{\circ}$ C.  $R_{f}$  (CH<sub>2</sub>Cl<sub>2</sub>) = 0.7 (bright orange spot). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 3.97 (s, 3H), 6.35 (m, 2H), 6.42 (s, 2H), 6.66 (m, 2H), 7.53 (d, J=9 Hz, 2H), 8.10 (d, J=9 Hz, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): 8 52.8, 119.6, 129.0, 130.7, 130.9, 133.4, 135.6, 143.0, 145.3, 152.6, 167.2. IR (KBr): 1721, 1548, 1557, 1378, 1346, 1280, 1249, 1110, 1048, 997, 890, 829, 771, 759, 721 cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (rel. intensities) 270 (sh), 310 (0.45), 400 (0.33), 470 (1.0), 506 (0.85) nm. MS (+FAB, NBA): m/e 891 (8, MH<sup>+</sup>), 613 (10, MH+ - ligand). Anal. Calc. for C51H39N6O6C0: C, 68.76; H, 4.41; N, 9.43. Found: C, 68.47; H, 4.45; N, 9.30%.

### 2.2.6. Tris[5-(3-methoxycarbonylphenyl)dipyrrinato |Co(III)

Prepared in 30% yield and in analytical purity from 5-(3methoxycarbonylphenyl)dipyrromethane according to the procedure descibed for 10.  $R_f$  (CH<sub>2</sub>Cl<sub>2</sub>) = 0.8 (bright orange spot). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  3.95 (s, 3H), 6.34 (m, 2H), 6.39 (m, 2H), 6.65 (m, 2H), 7.52 (m, 1H), 7.64 (m, 1H), 8.21 (m, 2H). IR (KBr): 1724, 1543, 1378, 1345, 1289, 1248, 1202, 1041, 1030, 999, 882, 837, 749, 723, 701 cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (rel. intensities) 270 (sh), 312 (0.45), 400 (0.30), 470 (1.0), 508 (0.85) nm. Anal. Calc. for C<sub>51</sub>H<sub>39</sub>N<sub>6</sub>O<sub>6</sub>Co: C, 68.76; H, 4.41; N, 9.43. Found: C, 68.32; H, 4.41; N, 9.38%.

# 2.2.7. Tris[5-(4-carboxylphenyl)-4,6-dipyrrinato]Co(III) (14)

Ester 10 (200 mg, 0.225 mmol) was suspended in a 1:1 mixture of THF and H2O/4% KOH (10 ml) and the suspension was heated to reflux for 3 h during which time all material went into solution. After cooling, 6 N aqueous HCl was added dropwise until the free acid precipitated as a red solid. This was filtered and dried in vacuo at 60°C to produce the acid in ~90% yield as a red solid (170 mg). Elemental analysis indicated the presence of variant amounts of solvent in this hygroscopic solid.  $R_f$  (CH<sub>2</sub>Cl<sub>2</sub>/5% MeOH-silica) = 0 (bright orange-red spot). <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>):  $\delta 6.38$  (m, 1H), 6.44 (s, 1H), 6.66 (m, 1H), 7.62 (d, J=9) Hz, 1H), 8.20 (d, J = 9 Hz, 1H). IR (KBr): 3440 (br), 1687, 1547, 1390, 1350, 1257, 1035, 994, 883, 766, 720 cm<sup>-1</sup>. MS (EI): m/e 848 ( $M^+$ ). UV-Vis (MeOH/H<sub>2</sub>O 1:1):  $\lambda_{max}$ (rel. intensities) 308 (0.45), 400 (0.33), 468 (1.0), 506 (0.85) nm

# 2.2.8. Tris[5-(4-chlorocarbonylphenyl)-4,6-dipyrrinato]-Co(III) (15)

Acid 14 was dissolved in a little dry THF, oxaloyl chloride and a trace of DMF were added, and the orange solution was warmed for 30 min. TLC of this solution revealed one low polarity streaking orange spot and consumption of all starting material. The mixture was then evaporated to dryness in vacuo to produce an orange film. Alternatively, neat SOCl<sub>2</sub> (followed by evaporation to dryness while small amounts of CCl<sub>4</sub> were added) was used to accomplish the conversion of 14 to 15. The crude acid chloride was immediately used. LR-MS (+EI): m/e 904 ( $M^+$ ). The identity of 15 was also shown by dissolution in MeOH containing Et<sub>3</sub>N, to quantitatively generate the ester 10.

### 2.2.9. Tris[5-(4-nitrophenyl)-4,6-dipyrrinato]Co(III)(9)

Prepared in 38% yield as a brick-red crystalline material from 5-(4-nitropheny!)dipyrromethane according to the general procedure outlined for the preparation of **8**. M.p. > 320°C.  $R_f$  (CH<sub>2</sub>Cl<sub>2</sub>) = 0.82. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta 6.38$  (dd, J = 1.6, 4.6 Hz, 1H), 6.43 (s, 1H), 6.61 (dd, J = 1.6, 4.6 Hz, 1H), 7.62 (d, 8.0 Hz, 1H), 8.32 (d, J = 8.0 Hz, 1H). IR (film on KBr): 1534, 1341, 1243, 1033,

Table 1

994, 889 cm<sup>-1</sup>. UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\epsilon$ ) 306 (4.57), 396 (4.33), 472 (4.73), 508 (4.67) nm. LR-MS (+FAB, NBA): *m/e* 851 (*M*<sup>+</sup>). *Anal.* Calc. for C<sub>45</sub>H<sub>30</sub>N<sub>9</sub>O<sub>6</sub>Co· C<sub>3</sub>H<sub>6</sub>O: C, 63.46; H, 3.99; N, 14.8. Found: C, 63.09; H, 3.77; N, 13.94%.

# 2.2.10. Tris[5-(4-aminophenyl)-4,6-dipyrrinato]Co(III) (13)

The trinitro complex 9 (160 mg,  $1.9 \times 10^{-4}$  mol) dissolved in THF (10 ml) containing Et<sub>3</sub>N (1 drop) was stirred with 10% Pd on carbon (30 mg) while  $H_2$  was bubbled through the solution for 3 h. No starting material could be detected after this time by TLC. The solution was filtered over Celite® and evaporated to dryness in vacuo. The residue was taken up in CHCl<sub>3</sub> and the product was precipitated out by addition of Et2O. The solids were filtered off, washed with a little cold EtOH followed by Et<sub>2</sub>O and were then dried under vacuum at 60°C to provide 13 as a red powder in 78% yield (112 mg).  $R_{\rm f}$  (CH<sub>2</sub>Cl<sub>2</sub>) = 0.1 (orange spot). M.p. ≥ 200°C (dec.). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$ 5.51 (s, 1H), 6.14 (s, 1H), 6.33 (dd, J = 1.5, 4.5 Hz, 1H), 6.64 (d, J = 8 Hz, 1H), 7.77 (dd, J = 1.5, 4.5 Hz, 1H), 7.11(d, J = 8 Hz, 1H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>):  $\delta$  112.5, 118.3, 124.5, 131.8, 132.5, 135.4, 147.7, 149.8, 149.9. IR (KBr): 3456, 3363, 1707, 1618, 1543, 1380, 1344, 1247, 1205, 1043, 1002, 885, 809, 771, 735, 714 cm<sup>-1</sup>. UV-Vis  $(CH_2Cl_2)$ :  $\lambda_{max}$  ( $\epsilon$ ) 394 (4.41), 466 (4.75), 502 (4.66) nm. LR-MS (+FAB, thioglycerol): m/e 762 (30, MH<sup>+</sup>), 528 (M<sup>+</sup>-ligand). Anal. Calc. for C<sub>45</sub>H<sub>36</sub>N<sub>9</sub>Co: C, 70.95; H, 4.76; N, 16.55. Found: C, 70.58; H, 4.66; N, 16.32%,

# 2.2.11. Tris(5-phenyl-4,6-dipyrrinato)Fe(III)(11)

Prepared in 51% yield as dark green crystalline material with a metallic lustre from anhydrous FeCl<sub>3</sub> and **2** by a method similar to the procedure described for **8**. M.p. =286°C.  $R_f$  (CH<sub>2</sub>Cl<sub>2</sub>) = 0.79 (brown spot). IR (film on KBr): 1553, 1378, 1330, 1039, 994, 835 cm<sup>-1</sup>. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  (log  $\epsilon$ ) 316 (4.34), 442 (4.72), 490 (4.59) nm. LR-MS (+EI, thioglycerol): m/e 714 (3.5,  $M^+$ ), 600 (3), 494 (35,  $M^+$  - ligand), 275 (20). Anal. Calc. for C<sub>45</sub>H<sub>33</sub>N<sub>6</sub>Fe: C, 75.73; H, 4.66; N, 11.77. Found: C, 75.92; H, 4.75; N, 11.87%.

# 2.2.12. Tris[5-(4-nitrophenyl)-4,6-dipyrrinato]Fe(III)(12)

Prepared in 53% as dark green microcrystalline material from 5 as described for 11. M.p. > 320°C.  $R_{\rm f}$  (CH<sub>2</sub>Cl<sub>2</sub>) = 0.76 (brown spot). IR (film on KBr): 1552, 1340, 1238, 1040, 994, 822 cm<sup>-1</sup>. UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\rm max}$  (log  $\epsilon$ ) 272 (4.82), 304 (4.70), 448 (4.81), 498 (4.69) nm. LR-MS (+FAB, thioglycerol): m/e 848 (4.2,  $M^+$ ), 584 (2,  $M^+$  – ligand). Anal. Calc. for C<sub>45</sub>H<sub>30</sub>N<sub>9</sub>O<sub>6</sub>Fe · C<sub>3</sub>H<sub>6</sub>O: C, 63.58; H, 3.92; N, 13.91. Found: C, 63.48; H, 3.93; N, 13.91%.

### 2.3. X-ray crystallographic analysis of 8 - acetone

Crystallographic data are summarized in Table 1. The final unit-cell parameters were obtained by least-squares on the

8.C3H6O
C48H39CoN6O
774.81
red, prism
$0.35 \times 0.40 \times 0.45$
monoclinic
C2/c
13.539(2)
22.348(2)
13.467(1)
107.654(9)
3882.7(8)
4
21
1.325
1616
Mo
4.88
0.91-1.00
ω-2θ
$1.25 \pm 0.35 \tan \theta$
32 (up to 8 rescans)
$+h, +k, \pm l$
60
5.2
6017
5786
0.053
2309
266
0.039
0.033
1.59
0.0008
-0.28, 0.35

<sup>a</sup> Rigaku AFC6S diffractometer, takeoff angle 6.0°, aperture 6.0×6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), Mo K $\alpha$  ( $\lambda = 0.71069$ Å) radiation, graphite monochromator,  $\sigma^2(F^2) = [5^2(C+4B)]/Lp^2$ (S=scan speed, C=scan count, B=normalized background count), function minimized  $\Sigma w(|F_o| - |F_c|)^2$  where  $w = 4F_o^2/\sigma^2(F_o^2)$ ,  $R = \Sigma 1|F_o| - |F_c| 1/\Sigma |F_o|$ ,  $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ , and  $GOF = [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$ . Values given for R,  $R_w$  and GOF are based on those reflections with  $l \ge 3\sigma(l)$ .

setting angles for 25 reflections with  $2\theta = 28.5 - 41.8^\circ$ . The intensities of three standard reflections, measured every 200 reflections throughout the data collections decayed uniformly by 5.2%. The data were processed, corrected for Lorentz and polarization effects, decay, and absorption (empirical:  $\psi$ -scans) [25].

The structure was solved by conventional heavy atom methods. The structure analysis was initiated in the centrosymmetric space group C2/c on the basis of the *E*-statistics, this choice being confirmed by subsequent calculations. The metal complex has exact  $C_2$  symmetry. The acetone molecule was modeled as 1:1 disordered about the two-fold axis with the terminal carbon atoms C(26) and C(27) located on the two-fold axis. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed

Table 3

Table 2 Atom coordinates and  $B_{eq}$  (Å<sup>2</sup>) for compound 8-acetone

Atom	x	у	z	B <sub>e4</sub> *
Co(1)	0.5000	0.24994(3)	0.7500	2.73(1)
O(1) <sup>b</sup>	0.4289(5)	0.0350(3)	0.3447(6)	9.6(2)
N(1)	0.5052(2)	0.2528(1)	0.6073(1)	2.86(5)
N(2)	0.6039(2)	0.18703(9)	0.7868(2)	2.86(6)
N(3)	0.3911(2)	0.31020(10)	0.7169(2)	2.72(6)
C(1)	0.4484(2)	0.2881(1)	0.5311(2)	3.36(7)
C(2)	0.4646(2)	0.2751(1)	0.4354(2)	3.57(7)
C(3)	0.5343(2)	0.2291(1)	0.4537(2)	3.28(7)
C(4)	0.5613(2)	0.2152(1)	0.5616(2)	2.88(7)
C(5)	0.6291(2)	0.1709(1)	0.6149(2)	2.80(6)
C(6)	0.6510(2)	0.1583(1)	0.7208(2)	2.88(7)
C(7)	0.7267(2)	0.1181(1)	0.7816(2)	3.45(7)
C(8)	0.7248(2)	0.1222(1)	0.8815(2)	3.49(7)
C(9)	0.6483(2)	0.1647(1)	0.8819(2)	3.41(7)
C(10)	0.6808(2)	0.1331(1)	0.5542(2)	3.31(7)
C(11)	0.7495(3)	0.1568(1)	0.5063(3)	4.44(8)
C(12)	0.7933(3)	0.1211(2)	0.4467(3)	5.6(1)
C(13)	0.7697(3)	0.0610(2)	0.4354(3)	6.1(1)
C(14)	0.7040(3)	0.0368(1)	0.4838(3)	5.7(1)
C(15)	0.6593(3)	0.0725(1)	0.5427(3)	4.54(9)
C(16)	0.2888(2)	0.3004(1)	0.6841(2)	3.39(7)
C(17)	0.2333(2)	0.3542(1)	6.6624(2)	3.55(7)
C(18)	0.3051(2)	0.3993(1)	0.6848(2)	3.29(7)
C(19)	0.4040(2)	0.3722(1)	0.7192(2)	2.83(7)
C(20)	0.5000	0.4008(2)	0.7500	2.82(9)
C(21)	0.5000	0.4677(2)	0.7500	3.1(1)
C(22)	0.4963(3)	0.4991(1)	0.6610(2)	4.71(9)
C(23)	0.4964(3)	0.5613(2)	0.6612(3)	5.5(1)
C(24)	0.5000	0.5914(2)	0.7500	5.5(2)
C(25) b	0.4734(6)	0.0372(4)	0.2841(7)	6.1(3)
C(26)	0.5000	0.0962(3)	0.2500	6.1(2)
C(27)	0.5000	-0.0198(3)	0.2500	8.6(2)

Selected bond lengths (Å) for the compound 8-acetone				
Co(1)-N(1)	1.946(2)			
Co(1)-N(2)	1.944(2)			
Co(1)-N(3)	1.946(2)			
N(1)-C(1)	1.336(3)			
N(1)-C(4)	1.395(3)			
N(2)-C(6)	1.397(3)			
N(2)-C(9)	1.335(3)			
C(1)-C(2)	1,402(4)			
C(2)-C(3)	1.367(4)			
C(3)-C(4)	1.421(4)			
C(4)-C(5)	1.392(4)			
C(5)-C(6)	1.394(4)			
C(5)-C(10)	1.490(4)			
C(6)-C(7)	1.421(3)			
C(7)-C(8)	1.357(4)			
C(8)-C(9)	1.407(4)			

Table 4

Selected bond angles (°) for the compound 8-acetone

N(1)-Co(1)-N(1)'	176.2(2)	
N(1)-Co(1)-N(2)	92.04(9)	
N(1)-Co(1)-N(3)	90.15(9)	
N(2)-Co(1)-N(3)	176.7(1)	
C(1)-N(1)-C(4)	106.3(2)	
N(1)-C(4)-C(3)	108.2(2)	
C(2)-C(3)-C(4)	107.4(2)	
C(1)-C(2)-C(3)	106.4(3)	
N(1)-C(1)-C(2)	111.7(2)	
N(1)-C(4)-C(5)	124.3(2)	
C(3)-C(4)-C(5)	127.5(3)	
C(4)-C(5)-C(6)	125.0(3)	
C(5)-C(6)-C(7)	127.5(3)	
C(6)-C(7)-C(8)	107.5(3)	
C(7)-C(8)-C(9)	106.5(2)	
N(2)-C(9)-C(8)	111.5(3)	
C(6)-N(2)-C(9)	106.2(2)	
N(2)-C(6)-C(7)	108.2(2)	
N(2)-C(6)-C(5)	124.2(2)	
Co(1)-N(2)-C(9)	126.5(2)	
Co(1)-N(2)-C(6)	127.2(2)	
~		

rins is not mandatory for their use as ligands. In fact, isolation and purification of the free base dipyrrins is, due to slow decomposition, difficult [2]. Thus, a simplified procedure involves the one-pot oxidation of the dipyrromethane, basification of the reaction mixture and consecutive metallation of the dipyrrin.



#### <sup>a</sup> $B_{eq} = (8/3) \pi^2 \sum U_{ij} a_i a_j (\mathbf{a}_j \cdot \mathbf{a}_j).$

\* 50% occupancy due to disorder.

in idealized positions (C-H=0.98 Å,  $B_{\rm H}$ =1.2 $B_{\rm bonded \, atom}$ ). A correction for secondary extinction (Zachariasen type 2 isotropic) was applied, the final value of the extinction coefficient being 1.67 (10) × 10<sup>-7</sup> [25]. Neutral atom scattering factors and anomalous dispersion corrections for all atoms were taken from the International Tables for X-Ray Crystallography [26]. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2 and selected bond lengths and angles appear in Tables 3 and 4. See also Section 4.

# 3. Results and discussion

### 3.1. The formation of meso-phenyldipyrrins

The dipyrrins 3, 5 and 7 used in this study were formed by 2,3-dicyano-5,6-dichloro-1,4-quinone (DDQ) oxidation of the corresponding dipyrromethanes 2, 4 and 6 [2,3] (Scheme 1). The dipyrromethanes were synthesized using the general procedures provided by Lee and Lindsey [5] or Carell [6]. However, isolation and purification of the dipyr-

# 3.2. The formation of tris-pyrrinato complexes of Co(III) and Fe(III)

The (distorted) tetrahedral cobalt(II) complexes of both  $\alpha$ - and  $\beta$ -alkyl-substituted dipyrrins have been frequently reported, and in every case they have been described as airstable [1,9,18,27]. Following a general protocol [2], we found that, as expected, a solution of cobalt(II) acetate in methanol yielded an orange precipitate when reacted with meso-phenyldipyrrin (3) and base. Mass spectral analysis indicated the formation of the anticipated product bis(mesophenyldipyrrinato)cobalt(II) (HR-MS (+EI, 200°C): m/e calc. for C<sub>30</sub>H<sub>22</sub>N<sub>4</sub>Co: 497.11765; found: 497.11713). The optical spectrum of a freshly prepared sample showed a clear resemblance to the previously prepared nickel(II), copper(II) and zinc(II) complexes, however, we were unable to purify the product due to its decomposition into orange polar products. Upon standing and open to air, a mixture containing an excess of ligand formed a non-polar orange pigment with a mass corresponding to the oxidized cobalt(III) tris-pyrrinato complex 8 (HR-MS (+EI, 220°C): m/e calc. for C45H33N6Co: 716.20984; found: 716.20951). This suggested the direct use of a relatively labile cobalt(III) salt ([Co<sup>III</sup>- $(py)_4Cl_2$  [Cl) [18] and, in fact, this produced the desired tris-dipyrrinato complexes 8-10, as precipitates, with the dipyrrins 3, 5 and 7. The precipitates were purified by chromatography to produce bright orange crystalline materials. The combined yield for the oxidation of the dipyrromethanes to the dipyrrin and the metal complexation performed as a one-pot synthesis is  $\sim 30\%$  and the reaction can be scaled up to produce 1 g of metal complex per run. Column chromatography is particularly convenient to isolate the metal complexes since they are neutral and generally the least polar component in the reaction mixtures. An excess of metal lowered the yields since this caused the formation of polar orange products which we assume to be mixed ligand systems, containing dipyrrin units as well as acetate, hydroxo-chloro groups or other potential ligands present in the reaction mixture.

Cobalt(III) shows a particular affinity for nitrogen donor atoms, in fact, the preferred oxidation state of cobalt in the presence of nitrogen donor ligands is + III. Examples of this type of complex are profuse [28,29]. In light of this, all of the previously stable cobalt(II) complexes of the N,N-chelating dipyrrins have to be regarded as exceptions to this rule.

It has been noted by Murakami et al. [21,22] that the bulkiness of the  $\alpha$ -substituents in dipyrrinato complexes of iron and manganese determines their preferred oxidation states. Bulky methyl substitution allowed only the formation of bis-dipyrrinato complexes with a tetrahedral conformation, resulting in the formation of divalent metal complexes with a 1:2 metal to ligand molar ratio, while the lack of any substituents at these positions allowed the formation of octahedral 1:3 complexes with a trivalent metal. In other words, the ligand, by allowing or disallowing a certain coordination geometry, stabilizes the metal in the oxidation state which best suits the enforced coordination geometry. This effect of control of the oxidation state brought about by the  $\alpha$ -substituents (or the lack thereof) parallels the effect of control of spin state in the series of nickel(II) bis-dipyrrinato complexes [2].

This rationalization suggests that *meso*-phenyldipyrrins should form stable iron(III) tris-complexes and this is, indeed, observed. Conversely, iron(II) forms only oxidatively unstable bis-dipyrrin complexes and, in the presence of excess ligand, spontaneously forms the iron(III) tris-complexes. Thus, iron(III), as its chloride, readily reacts in methanol and in the presence of base with the dipyrrins 3 and 5 to provide precipitates which, after purification by recrystallization or chromatography, analyze (elemental analysis, mass spectrum) to be of the tris-dipyrrinato structures 11 and 12 (Scheme 2).

# 3.3. Spectroscopic properties of the tris-dipyrrinato complexes of iron(III) and cobalt(III)

The UV-Vis spectra of the cobalt and iron complexes 9 and 12 are shown in (Fig. 2). They resemble those of structurally characterized transition metal bis-complexes of *meso*-phenyldipyrrins [2] and, therefore, it can be assumed that in these tris-complexes the dipyrrin moieties are not distorted but, as expected, flat. Two sets of peaks can be distinguished. The higher energy transitions, which are identical in both *p*-nitro-substituted complexes but which differ strongly with





Fig. 2. UV-Vis spectra (CH2Cl2) of 9 (broken line) and 12 (solid line).

the type of phenyl substituents present, can be attributed to  $\pi - \pi^*$  transitions of the *p*-nitrophenyl group and those between 400 and 540 nm to ligand-to-metal charge transfer and  $\pi - \pi^*$  transitions of the dipyrrinato moiety. The spectrum of 12 is slightly hypsochromically shifted compared to that of the  $\beta$ -alkylated analogue [22]. This is a general trend in the more electron deficient *meso*-phenyldipyrrins [2].

The simple <sup>1</sup>H and <sup>13</sup>C NMR spectra of the diamagnetic cobalt(III) species resemble those of the non-metallated ligands and lay testimony to the assumed high symmetry of the complex. One feature in NMR actually suggests an octahedral structure, namely the particularly large high-field shift of the  $\alpha$ -protons ( $\delta = 6.43$  ppm) of the ligand in, for instance, 9 compared to that of the analogous distorted square planar nickel(II) ( $\delta = 10.83$  ppm) or the tetrahedral zinc(II) biscomplexes ( $\Delta \delta = 7.59$  ppm) [2]. Models demonstrate that in a tetrahedral arrangement the  $\alpha$ -protons of the dipyrrinato units are the furthest away from the opposing pyrrolic ring. A planar arrangement 'overlaps' the protons, which are then subject to a 'double shielding' effect by two aromatic dipyrrinato systems. An octahedral arrangement, however, would 'push' the  $\alpha$ -protons towards a face of a neighboring aromatic unit, thereby affecting the observed deshielding,

Although the spectroscopic evidence is compelling, ultimate proof of the regular octahedral structure could only be provided with a single crystal X-ray structure analysis.

# 3.4. Crystal structure of tris[(5-phenyl)dipyrrinato]Co(III) · acetone

A crystal of 8 (as its acetone solvate) suitable for X-ray crystallography could be grown and its analysis fully establishes the proposed octahedral structure. An ORTEP representation of the molecule is shown in Fig. 3 and relevant experimental data are listed in Table 1. Positional parameters and equivalent isotropic thermal parameters, selected bond lengths and angles are listed in Tables 2-4.

The six coordinating nitrogens in complex 8 form an almost perfect octahedral coordination sphere around the central metal. Complex 8 has exact  $C_2$  symmetry. The distortion from the, perhaps, expected  $C_3$  symmetry is, however, very small. The acetone is 1:1 disordered about the two-fold axis



Fig. 3. Molecular structure of 8 (as its acetone solvate). The acetone and hydrogen atoms were omitted for clarity. Thermal ellipsoids are represented at the 33% probability level.

with the terminal atoms C(26) and C(27) located on the two-fold axis. The *meso*-phenyldipyrrinato ligand molecules are flat and they enclose dihedral angles of only 1.1 and 2.2° off the ideal 90° and the cobalt-nitrogen bond lengths (1.945(2) Å) are, within the experimental uncertainty, equal and within the expected range. The bite angles of the two non-equivalent ligands are 87.25(9) and 92.04(9)°. The trend in the bond length differences of the two pyrrolic  $C_{\alpha}$ - $C_{\beta}$  bond lengths is equivalent to those observed before, and they find the same explanation in the resonance structures involved [2].

The short distance (2.42 Å) from the  $\alpha$ -hydrogens to the nitrogens of the opposing ligands is remarkable, for instance H1 (attached to C1) to N3. As explained above, this short distance is a result of the octahedral arrangement of the ligands and the given length of the metal-nitrogen bond. However, the lack of any appreciable distortion within the ligands, or within the arrangement of the ligands around the central metal to prevent such a close contact, allows speculations about the existence of a stabilizing hydrogen-bond interaction between these atoms. Such weak C-H…N interactions have been described before and are also known to influence solid state structures [30].

## 3.5. Chemical transformations of p-phenyl substituents of tris[(5-phenyl)dipyrrinato]Co(III) complexes

The use cf the tris-dipyrrinato complexes in larger structures such as model systems for certain aspects of the photosynthetic apparatus [3,13-15] or for the construction of larger supramolecular structures [31] requires their simple functionalizations or functional group interconversions. The potential for such reactions has been shown with some example reactions performed on the cobalt(III) complexes (Scheme 2). For instance, the *p*-nitro groups of **9** can be smoothly reduced to produce the *p*-amino-substituted complex 13, without any appreciable reduction of the metal center or loss of chromophore even though free base dipyrrins are known to be susceptible to reduction to the corresponding leuko-compounds [2]. The saponification of the methyl ester 10 produced the free acid 14 which could be converted to the corresponding acid chloride 15. This was directly, for mere demonstration purposes, smoothly converted back to the methyl ester 10. Neither the strongly basic reactions of the ester cleavage nor the harshly acidic conditions of the chlorination affected the complex. This is not entirely unexpected as cobalt(III) complexes have generally high stabilities and are kinetically inert.

# 4. Supplementary material

Tables listing structure factors, anisotropic thermal parameters, hydrogen position parameters, inter-molecular nonbonding contact distances, intramolecular bond distances and angles, least-squares planes and dihedral angles, and views of the unit cell are available from the authors.

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