Racemic iron(III) and cobalt(III) complexes containing a new pentadentate "helmet" phthalocyaninato ligand†

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Solvothermal reactions of iron(II) acetate tetrahydrate and cobalt(II) acetate tetrahydrate with 1,2-dicyanobenzene in methanol solution result in the formation of racemic six-coordinate iron(III) and cobalt(III) complexes, respectively, with a new bicyclic pentadentate 14,28-[1,3-diiminoisoindolinato]phthalocyaninato ligand.

The coordination chemistry of phthalocyanine and phthalocyanine-like ligands has long been an area of active investigation, largely due to an impressive and diverse array of optical, electronic, photochemical, magnetic, and catalytic properties.[1] Although numerous substituted phthalocyaninato complexes are known, few fully characterized examples in which the inner ring of the ligand has been modified from the parent phthalocyanine, resulting in a non-planar ligand, have been reported.[2–6] To our knowledge, two of these represent the only structurally characterized examples in which two positions on the inner ring of a phthalocyanine complex are bridged by a metal-coordinating group resulting in a bicyclic ligand with additional coordinating nitrogen atoms. These complexes, bearing ligands that are well-described as either two phthalocyaninato ions sharing one common half or as a phthalocyaninato complex in which positions 14 and 28 are bridged by a 3,3′-iminobis(1-isoindolylideneamino) unit, are {14,28-[3,3′-iminobis(1-isoindolylideneamino)]phthalocyaninato}gadolinium(III),[3] and {14,28-[3,3′-iminobis(1-isoindolylideneamino)]phthalocyaninato}thallium(III).[4]

We now report the syntheses (as racemic mixtures) and X-ray crystal structures‡ of two unprecedented chiral metal complexes bearing a bicyclic pentadentate "helmet phthalocyaninato" ligand in which the inner ring of the ligand is bridged at the 14 and 28 positions by a (deprotonated) 1,3-diiminoisoindolino group. A line drawing showing this new ligand coordinated to a generic hexacoordinate metal atom is presented in Fig. 1. Syntheses of these products have been accomplished through adaptation of a standard metallophthalocyanine synthetic procedure that involves reaction of a metal source with phthalodinitrile (1,2-dicyanobenzene). Specifically, we have observed that reactions of iron(II) acetate tetrahydrate with 1,2-dicyanobenzene at 130 °C in

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† Electronic supplementary information (ESI) available: Synthesis, purification, and spectroscopic characterization for **1** and **2** and 3-dimensional structures for the metal complexes in **1**, **2** and 4-hydroxypyridine(diiPc)iron(III) viewable with the CHIME plug-in. See DOI: 10.1039/b606537f

methanol result in mixtures from which L(14,28-[1,3-diiminoisoindolinato]phthalocyaninato)iron(III) dimethanol solvate (**1**), where L is either methanol or water, can be obtained. Reactions of cobalt(II) acetate tetrahydrate with 1,2-dicyanobenzene at 70 °C produce methanol(14,28-[1,3-diiminoisoindolinato]phthalocyaninato)cobalt(III) dimethanol solvate (**2**), These reactions are represented in general form in eqn (1), where M represents either iron or cobalt, diiPc represents the 14,28-[1,3-diiminoisoindolinato]phthalocyaninato ligand, and L represents the ligands that complete the coordination spheres of the metals. In both cases the metal is oxidized from the +2 to the +3 state.

$$M(II)(OAc)_2 + 6(CN)_2C_6H_4 \rightarrow$$
$$L(diiPc)M(III) + \text{by-products} \quad (1)$$
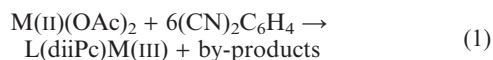
The crystallographically-determined structure of the iron complex in **1**, bearing a resemblance to the heme structure, is shown in Fig. 2, where the ligand L completing the coordination sphere of the metal is shown as the 81% occupied methanol. The X-ray structure of the metal complex in **2** is analogous to that seen in **1**. The isolated yields are 22.0–22.5% for **1** and 7.2% for **2**.

Other than the non-planarity of the diiPc ligands in **1** and **2** induced by the presence of bridgehead carbons at the 14 and 28 positions, other structural features in the complexes are typical for metal complexes bearing phthalocyanine and phthalocyanine-like ligands. The UV-VIS spectra of complexes **1** and **2** bear an important similarity to those observed for the alkoxy-modified nickel complexes bearing ligands substituted at the 14 and 28 positions[6] in that the Q-band present in the spectra of unmodified
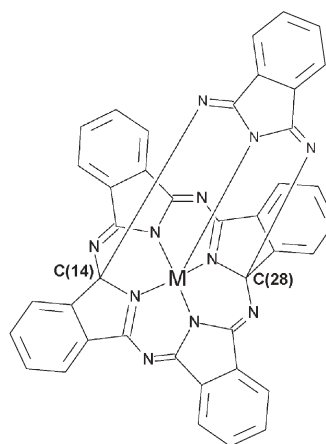

Fig. 1 A line drawing showing an "exploded view" of the new "helmet" phthalocyaninato ligand coordinated to a metal atom.
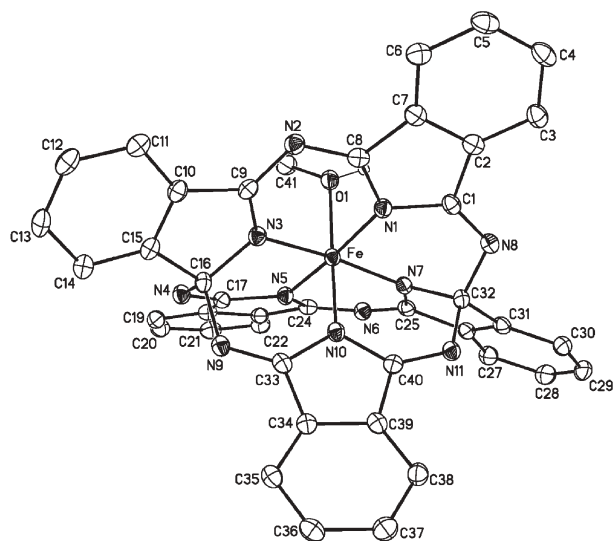
Fig. 2 The crystallographically determined structure of the iron complex in **1**; all H atoms are excluded except for the hydroxo hydrogen atom. Ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) for **1**: Fe–N(1), 1.9060(13); Fe–N(3), 1.8700(13); Fe–N(5), 1.9032(13); Fe–N(7), 1.8728(13); Fe–N(10), 1.8656(13); Fe–O(1), 1.9999(11); N(3)–C(16), 1.4708(19); N(4)–C(16), 1.4664(19); N(9)–C(16), 1.485(2); C(15)–C(16), 1.526(2); N(7)–C(32), 1.4719(19); N(8)–C(32), 1.4643(19); N(11)–C(32), 1.4822(19); C(31)–C(32), 1.526(2); N(1)–Fe–N(3), 89.78(5); N(3)–Fe–N(5), 90.62(5), N(5)–Fe–N(7), 89.66(5); N(7)–Fe–N(1), 90.56(5); N(10)–Fe–N(1), 92.58(5); N(10)–Fe–N(3), 86.72(6); N(10)–Fe–N(5), 92.88(5); N(10)–Fe–N(7), 86.76(5); O(1)–Fe–N(1), 85.19(5); O(1)–Fe–N(3), 92.84(5); O(1)–Fe–N(5), 89.35(5); O(1)–Fe–N(7), 93.68(5); O(1)–Fe–N(10), 177.73(5); N(1)–Fe–N(5), 174.54(6); N(3)–Fe–N(7), 173.48(6); N(3)–C(16)–C(15), 101.92(12); N(3)–C(16)–N(4), 114.39(12); N(3)–C(16)–N(9), 110.99(12); N(4)–C(16)–N(9), 109.15(12); N(4)–C(16)–C(15), 112.23(12); C(15)–C(16)–N(9), 107.84(12); N(8)–C(32)–C(31), 113.05(12); N(8)–C(32)–N(7), 114.07(12); N(8)–C(32)–N(11), 108.67(12); N(11)–C(32)–N(7), 111.32(12); N(11)–C(32)–C(31), 107.23(12); C(31)–C(32)–N(7), 102.23(12).

phthalocyaninato complexes is absent, undoubtedly due to the interruption of conjugation in the macrocyclic ring. Specific electronic spectral data for **1** are: $\lambda_{max}(CH_2Cl_2)$/nm 230 (ε/dm^3 mol^{-1} cm^{-1} 60 000), 263.5sh, 414(10 000), 443.0sh, 530.5 (2 600), 574.5sh and 620.5sh. For **2**: $\lambda_{max}(CH_2Cl_2)$/nm 234.0 (ε/dm^3 mol^{-1} cm^{-1} 66 200), 250.0sh, 318.5 (22 300) and 472.0 (2 770). Based upon these spectra and the lack of complete conjugation, the diiPc ligand is in some respects more accurately described as phthalocyanine-like than as a phthalocyaninato ligand, the latter retaining its relevance as a structural descriptor.

The formation of the helmet-shaped capped phthalocyaninato ligand itself in compounds **1** and **2** is interesting in several respects. First, it is formed in one pot in what can truly be described as a template synthesis. Although proceeding under nearly identical reaction conditions to those employed in the formation of the alkoxy-modified phthalocyaninato nickel(II) complexes described earlier,[6] a completely different modified phthalocyaninato ligand forms. While it is not at all surprising that iron and cobalt would form six-coordinate complexes, a search of the Cambridge Structural Database[7] reveals that all structurally characterized hexacoordinate phthalocyaninato complexes of these metals consist of a tetradentate phthalocyaninato ligand with two

separate axial ligands completing the coordination sphere.[7] The observation that solvothermal reactions of iron and cobalt acetate starting materials with 1,2-dicyanobenzene result in the formation of **1** and **2**, rather than only planar phthalocyaninato complexes of Fe and Co, likely owes much to the relatively low reaction temperatures, in contrast to the usual conditions employed in metallophthalocyanine syntheses. While we do not know the mechanism of formation of **1** and **2**, it is possible that it could proceed through intermediate species analogous to the alkoxy-modified nickel complexes, given the similarity of the synthetic conditions. It is also interesting to note that the formation of complexes **1** and **2** does not occur if metals in the +3 oxidation state are employed as starting materials in place of Fe(II) or Co(II) acetate complexes, suggesting that the formation of the diiPc ligand requires a concomitant one-electron oxidation of the metal to which it coordinates. In contrast to the alkoxy-modified phthalocyaninato nickel(II) complexes,[6] neither **1** nor **2** are observed to decompose to PcFe or PcCo when authentic samples are subjected to the conditions under which they are synthesized. Further, treatment of PcCo with 1,2-dicyanobenzene at 70 °C in methanol does not result in the formation of **2**. These observations indicate that PcCo and **2** are formed in competing reactions.

The chirality of **1** and **2** is of interest as these are members of a relatively small group of phthalocyaninato complexes in which chirality results from factors other than peripheral substitution of the Pc ring.[8] Of note is the fact that the axial ligands that complete the coordination sphere in **1** and **2** appear to be labile, as the metal complexes in both remain completely adsorbed at the top of a silica gel column as non-Lewis base solvents are eluted, suggesting ligand loss and chemisorption. Compounds **1** and **2** move down the column only upon the addition of methanol. Further, reactions of **1** with 4-hydroxypyridine in dichloromethane solution result in the formation of a derivative that has not yet been fully purified and characterized, but that X-ray crystallography has conclusively established as 4-hydroxypyridine(diiPc)iron(III), which possesses a structure analogous to both **1** and **2**. This result presents the possibility that diastereomers may be prepared and separated by coordinating a chiral ligand to a (diiPc)iron(III) [or (diiPc)cobalt(III)] complex. Efforts in this direction are currently underway in our laboratory. The complete crystallographic details, metal coordination features, and chemical behaviour of the complexes presented in this manuscript will be discussed in a forthcoming full paper.

Notes and references

Crystal data for **2**: $C_{43}H_{32}CoN_{11}O_3$ $M = 809.73$, monoclinic, space group = $P2_1/n$, $a = 14.9142(7)$, $b = 13.6308(7)$, $c = 18.7876(9)$ Å, $\beta = 109.995(1)°$, $V = 3589.2(3)$ Å^3, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.539$ mm^{-1}, $T = 100(2)$ K. The structure, refined on F^2, converged for 29092 reflections (7332 unique, $R_{\text{int}} = 0.0291$) to give $R_1 = 0.0384$ and w$R_2 = 0.1019$ for all reflections for which $I > 2\sigma(I)$ and goodness-of-fit = 1.028. CCDC 606957. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606537f

Crystal data for 4-hydroxypyridine(diiPc)iron(III)·1.5(ethyl acetate): $C_{51}H_{37}FeN_{12}O_4$ $M = 937.78$, monoclinic, space group = $C2/c$, $a = 22.597(2)$, $b = 21.775(2)$, $c = 19.6275(15)$ Å, $\beta = 107.0650(10)°$, $V = 9232.4(15)$ Å^3, $Z = 8$, $\mu(\text{Mo-K}\alpha) = 0.387$ mm^{-1}, $T = 100(2)$ K. The structure, refined on F^2, converged for 47453 reflections (9488 unique, $R_{\text{int}} = 0.0338$) to give $R_1 = 0.0355$ and w$R_2 = 0.0966$ for all reflections for which $I > 2\sigma(I)$ and goodness-of-fit = 1.088. The PLATON SQUEEZE option was used to remove disordered solvent.[9] CCDC 606959. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606537f

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