Axial ligation modulates the electron distribution in helical cobalt complexes derived from octaethylbilindione

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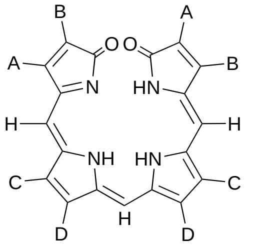
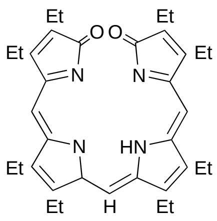
Addition of pyridine to the four-coordinate cobalt(II) complex, [Co^{II}(oebOx)]I$_3$, which shows an EPR spectrum with well resolved Co hyperfine coupling, converts the complex into one with Co^{III}/ligand radical structure and an EPR spectrum with g_z = 1.98, and g_{xy} = 2.02 and no cobalt hyperfine coupling.

Biliverdin 1Xa, **1a**, a product of haem catabolism, has been recently reported to have two interesting physiological activities: antioxidant activity and anti-HIV activity.[1] In order to understand the molecular bases for these activities, we have undertaken the study of redox behaviour of biliverdin analogues and their metal complexes. Octaethylbilindione, **1b**, a symmetrically substituted version of biliverdin 1Xa, forms a series of helical metal complexes with cobalt, nickel and copper in which the electronic structure indicates a significant contribution from a ligand-based free radical.[2–7] Upon treatment with an oxidant (*e.g.* diiodine) **1b** undergoes a facile two-electron oxidation to form **2** which has been isolated in a protonated form.[8] Recently we have shown that the cobalt complex of **1b**, Co(**1b**), undergoes a series of reversible, one-electron redox reactions as shown in eqn. (1).[9] Two members of this series, [Co(**1b**)] **3** and [Co(C$_{35}$H$_{43}$N$_4$O$_2$)]$^+$ **4**$^+$, have been isolated and thoroughly characterized. The electronic structure of four-coordinate **3** has been described in terms of contributions from both the Co^{III}/oeb^{3-} and Co^{II}/oeb$^{\cdot 2-}$ forms, where oeb$^{\cdot 2-}$ is the radical obtained by one-electron oxidation of oeb^{3-}.[4] Complex **4**$^+$ has been isolated as the triiodide salt. In the solid state the Co–I$_3$ distance is long (2.818 Å) and has been interpreted in terms of an ion-paired structure.[9] The structural and magnetic properties of [**4**$^+$]I$_3$ indicate that it is a cobalt(II) complex of the two-electron oxidized ligand **2**, *i.e.* it is [Co^{II}(oebOx)]I$_3$.[9] Here we demonstrate that the electronic structure of [**4**$^+$] is altered by the addition of axial pyridine ligands.



1a A = C = methyl
B = vinyl
D = propionate

1b A = B = C = D = ethyl
(H$_3$oeb)



2 (HoebOx)

$$[Co(\mathbf{1b})]^{2-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Co(\mathbf{1b})]^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \underset{\mathbf{3}}{[Co(\mathbf{1b})]} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \underset{\mathbf{4}}{[Co(\mathbf{1b})]^+} \quad (1)$$

The EPR spectrum of [**4**$^+$]I$_3$, like other cobalt(II) complexes, is sensitive to its environment. At 77 K it shows a rhombic pattern that can be fit with g_1 = 2.42, g_2 = 2.23 and g_3 = 2.01 but hyperfine coupling from cobalt was not resolved.[9] However, in dichloromethane–methanol at 77 K the spectrum shown in Fig. 1(*a*) is obtained. The parallel portion of the spectrum is clearly resolved with g_z = 2.013 and A_z = 89.3 × 10^{-4} cm^{-1}. The perpendicular region is more difficult to interpret because of the dependence of linewidth on both orientation and the quantum number M_I. However, g_x and g_y are estimated at 2.29 with A_x *ca.* 16 × 10^{-4} cm^{-1} and A_y *ca.* 35 × 10^{-4} cm^{-1}. This spectrum is indicative of the formulation of the complex as [Co^{II}(oebOx)]I$_3$. Addition of pyridine to a sample of [**4**$^+$]I$_3$ in MeOH–CH$_2$Cl$_2$ results in the formation of [(py)$_2$Co^{III}(oeb·)]I$_3$, [**5**$^+$]I$_3$, as shown by a marked alteration in the EPR spectrum. The resulting spectrum for a solution frozen at 77 K is shown in Fig. 1(*b*). The new spectrum shows a sharp, slightly anisotropic signal ($g_{x,y}$ = 1.996, g_z = 2.018) near the free electron *g* value. The cobalt hyperfine interaction is also lost. These alterations in the EPR spectrum suggest that a significant rearrangement of the electronic structure of the complex [**4**$^+$]I$_3$ occurs when axial pyridine ligands are present and that the pyridine adduct behaves as if it contains a ligand-based free radical.

Deep purple prisms of [**5**$^+$]I$_3$ may be isolated by dissolving a sample of [**4**$^+$]I$_3$ in pyridine and allowing the solution to stand. The structure of [**5**$^+$]I$_3$ has been determined by X-ray crystallography.‡ A view of the cation, which has crystallographic C_2 symmetry with the rotation axis passing through the cobalt ion and the unique methine carbon atom, is shown in Fig. 2. The cobalt ion is six-coordinate with bonds to the nitrogen atoms of two axial pyridine ligands and the four nitrogen atoms of the helical tetrapyrrole ligand. The Co–N bond distances [Co–N(1) 1.950(5), Co–N(2) 1.956(4) and Co–N(3) 1.997(5) Å] are indicative of the presence of a Co^{III} centre in the complex.[10] The Co–N distances [1.916(7), 1.910(7), 1.926(7) and 1.898(7) Å] in [**4**$^+$]I$_3$ are slightly shorter than the equatorial Co–N distances in [**5**$^+$]I$_3$.[9] However, the pattern of Co–N distances seen for [**5**$^+$]I$_3$ is similar to those of low-spin cobalt(III) porphyrin complexes such as [Co^{III}(ttp)(Him)$_2$]$^+$ (where Him is imidazole

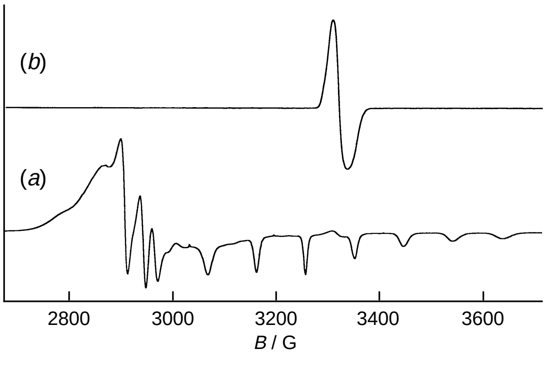


Fig. 1 EPR spectra of frozen solutions at 77 K of (*a*) [Co^{II}(oebOx)]I$_3$ in CH$_2$Cl$_2$–MeOH and (*b*) [Co^{III}(oebO·)(py)$_2$]I$_3$ {obtained by adding py to a CH$_2$Cl$_2$–MeOH solution of [Co^{II}(oebOx)]I$_3$}

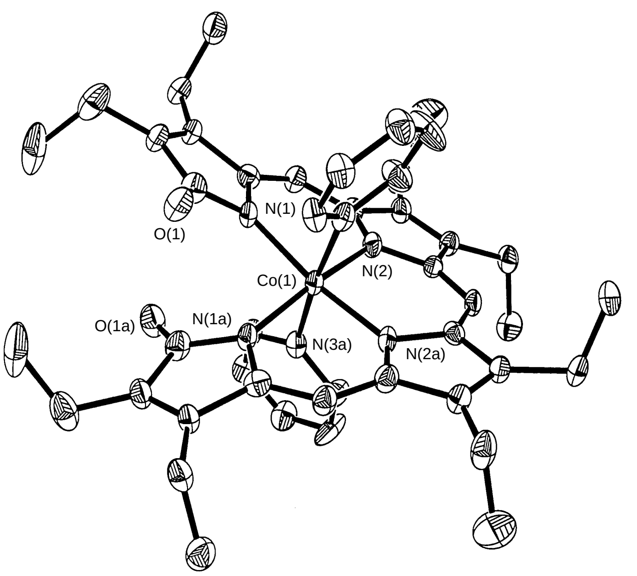


Fig. 2 A perspective view of $[Co(oebO\cdot)py)_2]^+$ with 50% thermal contours for all atoms. Selected bond lengths (Å) and angles (°): Co–N(1) 1.950(5), Co–N(2) 1.956(4), Co–N(3) 1.997(5), C(1)–O 1.216(7); N(1)–Co–N(2) 89.8(2), N(1)–Co–N(3) 85.6(2), N(1)–Co–N(1a) 91.3(3), N(2)–Co–N(3) 94.6(2), N(2)–Co–N(2a) 92.0(3), N(2)–Co–N(1a) 167.2(2), N(3)–Co–N(3a), 174.5(3).

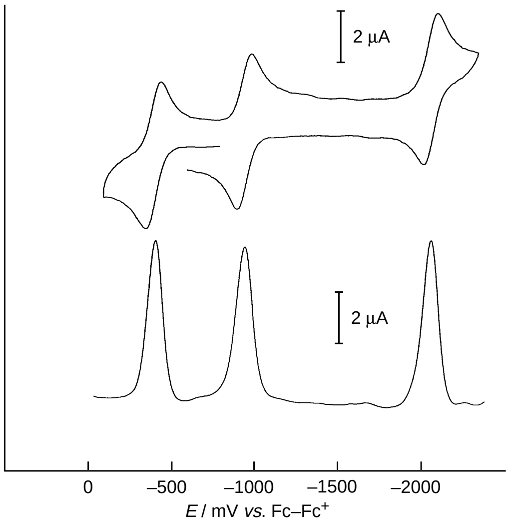


Fig. 3 Cyclic voltammogram and differential pulse voltammogram of Co(oeb) (1.6 mM) in pyridine solution with 0.1 M $NBu^n{}_4ClO_4$ as supporting electrolyte

and ttp is the dianion of tetraphenylporphyrin) which has a Co–$N_{(axial)}$ distance of 1.93(2) Å and an average Co–N_{eq} distance of 1.98(2) Å.[11] In marked contrast, the axial Co–N distances are longer than the in-plane Co–N distances for cobalt(II) porphyrins. For example in $[Co^{II}(oep)(3Me\text{-}py)_2]$ the axial Co–N distance is 2.386(2) Å while the in-plane Co–N distances average 1.992 Å.[12]

$[\mathbf{5}^+]I_3$ dissolves readily in dichloromethane solution to produce a purple solution with λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 290 (46 900), 360 (32 400), 628 (9900). The magnetic moment of a dichloromethane solution of the complex $[\mathbf{5}^+]I_3$ is 2.0(2) μ_B.

Electrochemical studies show that in pyridine solution a four-membered electron transfer series exists for this family of cobalt complexes. Fig. 3 shows cyclic voltammetric and Osteryoung square-wave voltammetric data for Co(oeb) in pyridine solution. One reversible oxidation [at -388 mV with $\Delta E_p = 64(2)$ mV and $w_{1/2} = 112(2)$ mV] and two reversible reductions [at -924 mV with $\Delta E_p = 66(2)$ mV and $w_{1/2} = 118(2)$ mV and at -2046 mV with $\Delta E_p = 66(2)$ mV and $w_{1/2} = 112(2)$ mV] are observed. The reversible nature of these processes suggests that the axial ligation of cobalt does not change during the redox process and previous work has demonstrated spectral changes for Co(oeb) in pyridine as compared to dichloromethane solution that are indicative of axial ligation by pyridine.

The alteration in internal oxidation states in $[Co^{II}(oebOx)]I_3$, $[\mathbf{4}^+]I_3$, and $[Co^{III}(oeb\cdot)(py)_2]I_3$, $[\mathbf{5}^+]I_3$, has some parallels in the valence tautomerization observed for other transition-metal complexes. For example the oxidation of Ni^{II}(porphyrin) is known to yield either $[Ni^{III}(porphyrin)]^+$ or $[Ni^{II}$(porphyrin radical)$]^+$.[13] Cobalt complexes of dioxolene ligands also experience valence tautomerization, Co^{III}(bipy)(semiquinone)(catecholate)/Co^{II}(bipy)(semiquinone).[14] In all these complexes the redox potentials of the ligands and the metal centres are close in energy so that the electron distribution between these components is markedly effected by environmental effects, which in the present case involve the availability of axial ligands.

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Footnotes

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‡ *Crystal data*: purple prisms of $C_{45}H_{53}CoI_3N_6O_2$ obtained by addition of pyridine to a CH_2Cl_2 solution of $[Co^{II}(oepOx)]I_3$ form in the monoclinic space group *C*2/*c* with $a = 14.471(3)$, $b = 17.436(3)$, $c = 19.048(4)$ Å, $\beta = 107.50(2)°$ at 130(2) K with $Z = 4$ with the use of nickel filtered Cu-Kα ($\lambda = 1.541\,78$ Å) radiation. A correction was applied for the 3% decay in two standard reflections that was observed over the course of the data collection. Refinement of 2892 reflections and 259 parameters yielded $wR_2 = 0.093$ for all data and a conventional $R_1 = 0.045$ based on 2499 reflections with $I > 2\sigma(I)$. The largest peak and hole in the final difference map are 0.98 and -1.07 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/456.

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