Co(II) and Co(III) complexes of *m*-benziphthalocyanine†

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The syntheses and structural elucidations of three different cobalt complexes of *m*-benziphthalocyanine are reported; both Co(II) and Co(III) complexes can be generated, and the ring undergoes partial oxidation upon metalation with $Co(OAc)_2 \cdot 4H_2O$.

The modification of porphyrin by replacing core nitrogen atoms with carbon atoms results in macrocycles with interesting intrinsic electronic properties[1] as well as unusual metal coordination modes.[2] This replacement results in porphyrinoids with the possibility of forming organometallic complexes upon metallation. This area of research accelerated with the discovery of N-confused porphyrin and its unique coordination chemistry.[2] One of the methods for introducing a carbon atom at the core of the macrocycle is to exchange one of the pyrrole rings with a benzene unit. In normal porphyrin, this leads to the formation of benziporphyrin, shown in Fig. 1. The *m*-benziporphyrins were first reported in 1994 by Berlin and Breitmaier[3] and in later years synthetic routes were improved[4] and *meso*-substituted variants were also presented.[5] Although this macrocycle no longer has porphyrin-like aromaticity, a wide variety of interesting metallation chemistry was observed.[5–8]

We have recently begun investigating the metal chemistry of azaporphyrin analogs of core modified porphyrins.[9] The azaporphyrin analog of *m*-benziporphyrin was first synthesized over half a century ago by Elvidge and Golden in their investigations of the synthesis of phthalocyanine analogs using diiminoisoindolene.[10] This family of macrocycles is known collectively as the hemiporphyrazines,[11] and the mono-benzene substituted analog can be designated as a monocarbahemiporphyrazine or *m*-benziphthalocyanine (bzpc). This ring closely resembles *m*-benziporphyrin, except that the *meso* carbons are replaced with nitrogens and the number of internal protons is four rather than two. Although the bzpc macrocycle has been known for decades and is readily synthesized, its metallation chemistry has not been extensively investigated. In this communication, we are reporting the cobalt coordination chemistry of *m*-benziphthalocyanine.

The bzpc macrocycle can be synthesized as described in the literature with moderate yields.[10] Cobalt can be cleanly inserted into the ring by using cobalt carbonyl in a reaction similar to that used for metal insertions into N-confused porphyrin (Scheme 1). The reaction of bzpc with $Co_2(CO)_8$ followed by crystallization under anaerobic conditions resulted in the formation of Co^{II}(bzpc)py complex, **1**.‡ The activation of the internal C–H bond to form a direct Co–C bond is observed with this complex. The Co(II) ion fits well into the coordination core of the macrocycle, forming a slightly distorted square pyramidal complex. The Co–C bond measures 2.0020(15) Å. The equatorial Co–N bond lengths vary between 1.9754(13) Å to 2.0164(12) Å while the axial Co–N distance is 2.1775(13) Å which is shorter than the value of 2.44 Å of the Co(II) porphyrin piperidine complex. But, this is slightly shorter than the distance (2.16 Å) observed in the Co(II) porphyrin 3,5-dimethylpyridine adduct,[12] which suggests that **1** is a similar low spin Co(II) species. The complex is paramagnetic, and as expected the magnetic susceptibility gives $\mu_{eff} = 1.80$ which correlates to a low spin ($S = \frac{1}{2}$) electronic configuration. The ring is tetraanionic, requiring the protonation of two *meso* nitrogen positions for charge balance. These protons are observed in the difference map, and no cations are present in the unit cell.

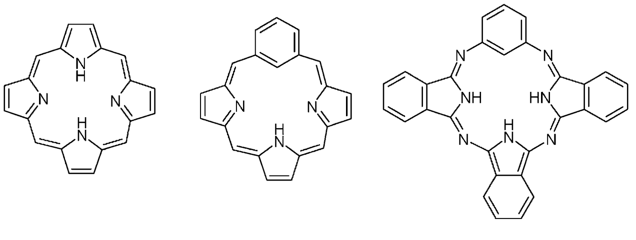
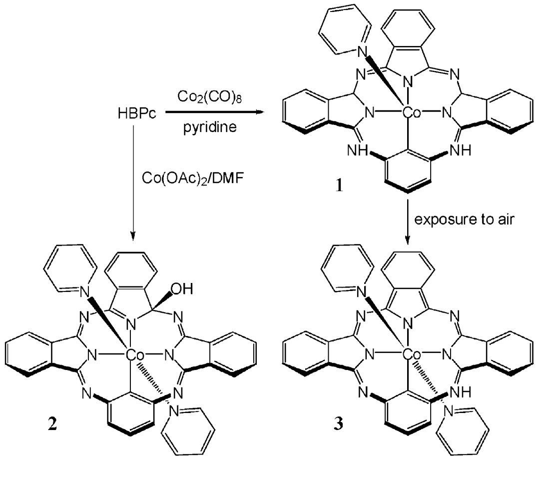


Fig. 1 Normal porphyrin (left), *m*-benziporphyrin (middle) and *m*-benziphthalocyanine (bzpc, right).



Scheme 1 Synthesis of Co^{II}(bzpc)py **1**; Co^{III}(bzpc)py_2 **2** and Co^{III}(bzpcOH)py_2 **3**.

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Fig. 2 The structures of Co^{II}(bzpc)py (**1**), Co^{III}(bzpc)py_2 (**2**), and Co^{III}(bzpcOH)py_2 (**3**) with 50% thermal ellipsoids. Hydrogen atoms except those on the bridging *meso* nitrogens and the alcohol have been omitted for clarity.

This compound can then be oxidized by air in the presence of pyridine to produce the corresponding Co(III) complex, Co^{III}(bzpc)py_2 (**2**). The complex is six coordinate, with an additional pyridine occupying an axial position. The Co–C bond remains intact, but the distances about the metal reflect the increase in oxidation state, with an average 1.97 Å Co–N bond length. The Co–C bond length remains the same as in the Co(II) species, with a distance of 2.000(4) Å. The average axial Co–N bond lengths of 1.98 Å is comparable with the values observed for the N-confused porphyrin complex Co(NCTPP)py_2[13] but is shorter than the distance (2.06 Å) observed for the cationic Co(III) porphyrin piperidine complex.[14] The metal is a diamagnetic Co(III) center, as expected for the geometry and oxidation state. Once again, the macrocycle is tetraanionic, requiring a single proton on a *meso* position for charge balance. As in the Co(II) product, the proton is observed in the difference map and there are no cations in the unit cell.

The Co^{III}(bzpc)$(py)_2$ complex is unstable in solutions after prolonged exposure to air, often demetallating to form organic fragments and paramagnetic cobalt oxides. We believe that this decomposition process occurs through oxidation or hydrolysis of the ligand. Torres and Hanack noted that the lack of aromaticity and iminic nature of these macrocycles can result in ligand decomposition.[11] We were able to observe partial oxidation of the ligand upon metallation of the free base with $Co(OAc)_2 \cdot 4H_2O$ in DMF under aerobic conditions. The resultant product, Co^{III}(bzpcOH)py_2, is precipitated from DMF with the addition of water and recrystallized from pyridine/*p*-xylene. Single crystal X-ray structure elucidation of the molecule shows a hydroxide at an α-carbon position. As a result, the macrocycle deviates from planarity due to the sp^3 hybridized carbon in the ring. This resultant complex is chiral, although the reaction produces a racemic mixtures of the two enantiomers. Similar oxidations have been observed in the phthalocyanines.[15] The cobalt is a low spin +3 metal ion, and the macrocycle is trianionic and no additional protons are observed on the external nitrogen positions. The Co–C distance, 1.958(5) Å, is slightly shorter than the Co–C distance of **2**. The equatorial Co–N distances vary between 1.897(4) and 1.963(4) Å while the axial Co–N distances are 1.979(4) and 1.988(4) Å, the same axial distances as seen in compound **2**.

In conclusion, three different cobalt complexes of *m*-benziphthalocyanine are reported in two oxidations states. The metal can be inserted using either cobalt carbonyl or cobalt acetate; in the latter case oxidation of one of the Schiff base C=N bonds occurs. We are continuing our work on the fundamental metallation chemistry and electrochemistry of the carbaporphyrinoids and their azaporphyrin analogs.

Notes and references

‡ *Crystal data*: for **1–3**: data were collected at 100 K (Bruker KRYOFLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. For $C_{48}H_{39}Co_1N_{10}$ **1**; $M = 814.84$, red block 0.30 × 0.20 × 0.05 mm, monoclinic, space group $P21/n$, $Z = 4$ in a cell of dimensions $a = 15.4472(1)$, $b = 18.5201(2)$, $c = 16.7680(2)$ Å, $\alpha = 90°$, $\beta = 116.181(2)°$, $\gamma = 90°$, $V = 4304.9(7)$ Å^3, $D_c = 1.320$ mg m^{-3}, μ(Mo-Kα) = 0.448 mm^{-1}, $F(000) = 1596$; final R indices on 9370 independent reflections [$I > 2\sigma(I)$]: $R1 = 0.0387$, w$R2 = 0.0992$. For $C_{55}H_{41}Co_1N_{12}$ **2**; $M = 928.93$, green block 0.18 × 0.05 × 0.01 mm, monoclinic, space group $P21/c$, $Z = 4$ in a cell of dimensions $a = 9.9002(2)$, $b = 10.0469(2)$, $c = 44.850(2)$ Å, $\alpha = 90°$, $\beta = 93.700(3)°$, $\gamma = 90°$, $V = 4451.8(1)$ Å^3, $D_c = 1.396$ mg m^{-3}, μ(Mo-Kα) = 0.441 mm^{-1}, $F(000) = 1932$; final R indices on 10627 independent reflections [$I > 2\sigma(I)$]: $R1 = 0.0760$, w$R2 = 0.1626$. For $C_{56}H_{46}Co_1N_9O_1$ **3**; $M = 919.95$, red block 0.28 × 0.18 × 0.08 mm, triclinic, space group $P\bar{1}$, $Z = 2$ in a cell of dimensions $a = 12.5789(1)$, $b = 13.3090(1)$, $c = 15.3136(1)$ Å, $\alpha = 75.7250(1)°$, $\beta = 76.5220(1)°$, $\gamma = 69.3530(1)°$, $V = 2294.6(3)$ Å^3, $D_c = 1.331$ mg m^{-3}, μ(Mo-Kα) = 0.426 mm^{-1}, $F(000) = 960$; final R indices on 8946 independent reflections [$I > 2\sigma(I)$]: $R1 = 0.0946$, w$R2 = 0.2567$. CCDC 641690–641692 For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704815g

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