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Dianionic and trianionic macrocycles in cobalt N-confused porphyrin complexes†

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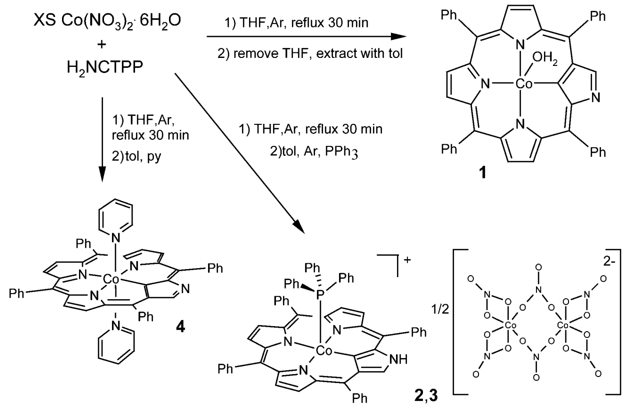
We report the syntheses of cobalt N-confused porphyrins; this work completes the series of the late first-row transition metals that have been incorporated into the core of N-confused porphyrin, and in these compounds the macrocycles can act as either a −2 or −3 anion.

Over the last decade, the synthesis and metallation chemistries of porphyrin analogues and isomers have exploded as fields.[1] One of these isomers, N-confused porphyrin, is a tetrapyrrolic macrocycle with an inverted pyrrole ring.[2] This results in a peripheral nitrogen atom along with an internal carbon that can form organometallic bonds with transition metals. To date, all of the late first-row transition metals from manganese to zinc have been incorporated into the core of N-confused porphyrin with the exception of cobalt.[3] Herein, the syntheses of several Co N-confused porphyrins are reported, completing the above series of N-confused porphyrin complexes. In these compounds, the internal carbon is activated and forms a Co–C bond, and the macrocycle can act as either a −2 or a −3 ligand.

Co(NCTPP)(H_2O) (**1**) was generated by heating a H_2NCTPP solution in THF under anaerobic conditions with an excess of $Co(NO_3)_2{\cdot}6H_2O$ (Scheme 1). As the reaction progresses, the solution gradually turns from brown to greenish over 30 min. Removal of the THF and extraction with toluene followed by filtration to remove impurities gives a quantitative yield of **1**. Species **1** has a broad absorbance near 460 nm and Q-bands ranging from 550 to 700 nm. Crystallization by slow evaporation of toluene results in the isolation of single crystals and the structure of **1**‡ shows a disordered axially coordinating water molecule (Fig. 1(a)). Support for an axial water *vs.* a hydroxide can be made by comparing the Co^{III}–O bond length in a CoTPP water complex (1.98 Å)[4] as compared to a shorter bond length (1.92 Å) in a methoxide complex.[5] As in the nickel complexes, the internal CH is broken and the carbon atom coordinates to the metal center. The lack of an observable proton on the external nitrogen results in a Co^{III} oxidation state assignment. This species decomposes in the presence of air.



Scheme 1 Syntheses of Co(NCTPP) complexes.

If the reaction to produce **1** is followed by the introduction of triphenylphosphine in toluene, the solution changes color to red and a new species (**2**) appears (Scheme 1). In **2**, the Soret band blue shifts to 428 nm and the Q bands shift to 478 and 551 nm. Crystals of **2** were grown from toluene–heptanes, and the elucidated structure‡ shows that the cobalt is five-coordinate with a phosphine axial ligand (Fig. 1(b)). The porphyrin macrocycle is saddle-shaped and the axial phosphine is at an angle of 85.6° from the plane of the four porphyrin core atoms. With regard to the oxidation state assignment of the metal, the environment is similar to that of the recently reported cobalt corrole and corrolazine complexes, which also stabilize a Co^{III} and exhibit complete deprotonation of the core.[6,7] Unlike compound **1**, the external nitrogen in the structure is protonated, which indicates that the macrocycle is acting as a −2 anion and is similar to the externally protonated tautomer observed in the nickel adduct.[2] Evidence for this is seen in the ^1H NMR spectrum of **2**, which shows a NH resonance at 12.11 ppm. This chemical shift is similar to the nickel complex of NCTTP with an external NH resonance at 10.03 ppm.[2] The IR spectrum shows a broad band at 3250 cm^{-1} indicative of a N–H stretching vibration. Also, in contrast to **1**, this species is stable in air.

Within the unit cell of **2** is a novel bimetallic dimer, $[Co_2(NO_3)_4(\mu\text{-}NO_3)_2]^{2-}$, that acts as an anion for the cobalt N-confused porphyrin complex (Fig. 2). The dimer lies on an inversion center in the unit cell. Each metal center exhibits an octahedral geometry, with four terminal bidentate nitrates and two bridging nitrates between the cobalt ions. We can assign the

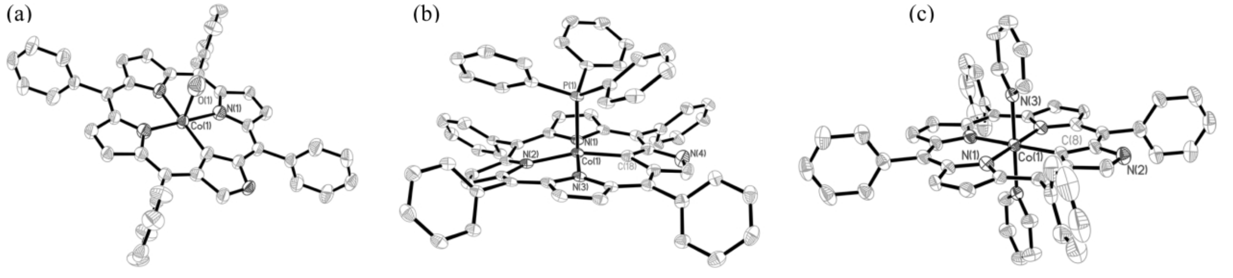


Fig. 1 The structures of (a) Co(NCTPP)(H_2O) (**1**), (b) Co(NCTPP)(PPh_3) (**2**), (c) Co(NCTPP)($py)_2$ (**4**). Selected bond lengths (Å) for: **1**: Co(1)–N(1), 1.999(8); Co(1)–O(1), 2.12(3); **2**: Co(1)–N(1), 1.982(4); Co(1)–N(2), 1.972(4); Co(1)–N(3), 1.982(4); Co(1)–C(18), 1.903(5); Co(1)–P(1), 2.2249(16); **4**: Co(1)–N(1), 1.978(3); Co(1)–C(8), 1.993(3); Co(1)–N(3), 1.982(3). The thermal ellipsoids were scaled to 30% probability for **1** and 50% for **2** and **4**, respectively. Hydrogen atoms have been omitted for clarity. Due to the disorder of the nitrogen atom at the confused pyrrole ring and high symmetry of the crystal, one of eight possible orientations is shown for **1** and **4**.

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† Electronic supplementary information (ESI) available: Absorption spectra for **1**, **2** and **4**. See http://www.rsc.org/suppdata/cc/b4/b404261a/

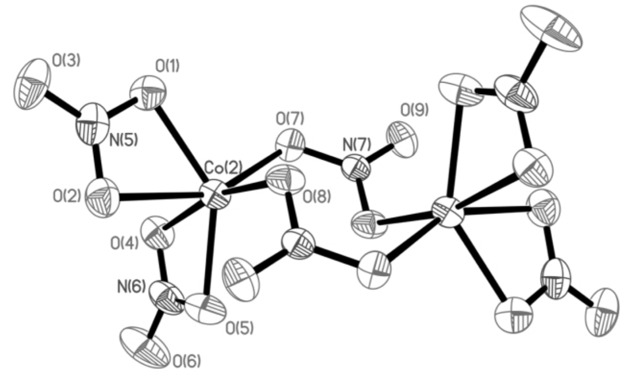

Fig. 2 The structure of $Co_2(NO_3)_4(\mu\text{-}NO_3)_2^{2-}$ anion in **2** with 50% thermal ellipsoids. Selected bond lengths (Å) for the anion in **2**: Co(1)–O(1), 2.094(5); Co(1)–O(2), 2.178(5); Co(1)–O(4), 2.180(4); Co(1)–O(5), 2.043(5); Co(1)–O(7), 2.061(4); Co(1)–O(8), 2.084(4);

oxidation state of the metal in this anion based on the bond distances about the cobalt center; all of the Co–O bonds in this dimer are longer than 2.04 Å, which is in the range for Co^{II}–O bonds in nitrate complexes (2.05 and 2.69 Å).[8] The Co–O bond distances in this anion are also much longer than the Co^{III}–O bonds (1.97 Å) in $Co(NO_3)_3$.[9] With this anion, complete deprotonation of the core of the porphyrin, and the presence of an external nitrogen, the Co(NCTPP)(PPh_3) is cationic and the metal is in the +3 oxidation state. The ^1H NMR resonances in **2** do not exhibit paramagnetic shifts, but are broadened due to the presence of unpaired electron density of the $[Co_2(NO_3)_4(\mu\text{-}NO_3)_2]^{2-}$ dimer anion. A second crystal form of **2** (species **3**‡) can be generated by extracting with CH_2Cl_2 instead of toluene and layering with heptanes; the only difference between the two structures is the identity of the solvent in the void space in the unit cell.

If **1** is dissolved in pyridine, a third absorbance spectrum is produced (species **4**) that exhibits a sharp Soret at 462 and Q bands at 555, 736 and 808 nm (Scheme 1). Crystallization of species **4** from pyridine/heptanes results in the isolation of **4**,‡ a bis-pyridine complex (Fig. 1(c)), where the metal centers lie on individual inversion centers. As in the analogous manganese complex, the metal center is six-coordinate with two coordinating pyridine ligands. Unlike the Mn(NCTPP)(py)$_2$, the axial pyridines are at an angle of nearly 90° from the plane of the 24-atom porphine ring.[10] The axially bound pyridines are similar in orientation to those in the cobalt pentafluorophenyl corrole adduct, with a dihedral angle of zero,[6] as compared to a 90° dihedral angle found in cobalt complexes of octaalkyl corrole and corrolazine.[7] Unlike the Co(NCTPP)(PPh_3) complexes, the external nitrogen is deprotonated with no external NH resonance observed in the ^1H NMR spectrum and no anion is present in the unit cell, therefore the NCTPP motorcycle is acting as a -3 anion in this structure. Further support of the Co^{III} oxidation state is found in the axial Co–N bond lengths of 1.982 Å, which is similar in the length (2.060 Å) to the cationic Co^{III} porphyrin piperidine complex and much shorter than the Co–N length of 2.436 Å in the Co^{II} porphyrin complex with piperidine.[11,12]

This study completes the series of late first-row transition metals that have been bound to the core of N-confused porphyrin. We can now start a full comparison of how this macrocycle stabilizes a variety of oxidation states in transition metals. Continued work will focus on the redox chemistry of cobalt N-confused porphyrins and on the catalytic chemistry of this family of metallomacrocycle.

Notes and references

‡ *Crystal data*: for **1**: data were collected at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. $CoC_{44}H_{30}N_4O$ **1**; $M = 689.65$, black needle $0.5 \times 0.05 \times 0.05$ mm, tetragonal, space group $I4/m$, $Z = 2$ in a cell of dimensions $a = 13.368(4)$, $c = 9.647(6)$ Å, $V = 1724.0(14)$ Å^3, $D_c = 1.329$ Mg m^{-3}, μ(Mo-Kα) = 0.539 mm^{-1}, $F(000) = 714$; final R indices on 815 independent reflections [$I > 2\sigma(I)$]: $R_1 = 0.0908$, $wR_2 = 0.2302$. For **2**; data were collected at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. $Co_2C_{69}H_{51}N_7O_9P$ **2**, $M = 1271.00$, green–black block $0.37 \times 0.15 \times 0.12$ mm, triclinic, space group $P\bar{1}$, $Z = 2$ in a cell of dimensions $a = 14.5294(19)$, $b = 15.1545(19)$, $c = 15.400(2)$ Å, $\alpha = 70.304(2)$, $\beta = 63.161(2)$, $\gamma = 73.503(2)°$, $V = 2813.3(6)$ Å^3, $D_c = 1.500$ Mg m^{-3}, μ(Mo-Kα) = 0.689 mm^{-1}, $F(000) = 1310$, final R indices on 10936 independent reflections [$I > 2\sigma(I)$]: $R_1 = 0.0736$, $wR_2 = 0.1883$. For **3**: data were collected at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. $Co_2C_{63}H_{45}N_7O_9PCl_2$ **3**; $M = 1348.72$, black plate $1.60 \times 0.47 \times 0.09$ mm, triclinic, space group $P\bar{1}$, $Z = 2$ in a cell of dimensions $a = 12.103(3)$, $b = 16.031(4)$, $c = 16.390(4)$ Å, $\alpha = 91.296(4)$, $\beta = 102.294(4)$, $\gamma = 73.503(4)°$, $V = 2911.2(12)$ Å^3, $D_c = 1.539$ Mg m^{-3}, μ(Mo-Kα) = 0.848 mm^{-1}, $F(000) = 1378$, final R indices on 11319 independent reflections [$I > 2\sigma(I)$]: $R_1 = 0.0640$, $wR_2 = 0.1743$. For **4**: data were collected at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system. $CoC_{54}H_{38}N_6$ **4**; $M = 908.93$, red plate $0.5 \times 0.3 \times 0.1$ mm, triclinic, space group $P\bar{1}$, $Z = 2$ in a cell of dimensions $a = 10.664(3)$, $b = 14.584(4)$, $c = 16.371(5)$ Å, $\alpha = 112.333(4)$, $\beta = 96.324(5)$, $\gamma = 91.474(5)°$, $V = 2334.4(12)$ Å^3, $D_c = 1.293$ Mg m^{-3}, μ(Mo-Kα) = 0.416 mm^{-1}, $F(000) = 946$, final R indices on 9037 independent reflections [$I > 2\sigma(I)$]: $R_1 = 0.0808$, $wR_2 = 0.2210$. CCDC 234035–234038. See http://www.rsc.org/suppdata/cc/b4/b404261a/ for crystallographic data in CIF or other electronic format.

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