Supporting Information

Elucidation of the extraordinary 4-membered pyrrole ring-contracted azeteoporphyrinoid as an intermediate in chlorin oxidation

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1) Experimental Section:

Materials and General Procedures. All of the chemicals and solvents were obtained from Aldrich. The products were purified by flash chromatography using silica gel (200-400 mesh). UV – Visible spectra were obtained using Perkin Elmer Lamba 19 spectrophotometer using UVWinlab software. ^{1}H-NMR spectra were recorded on VXR 400 MHz or Gem 300 MHz NMR spectrometer and referenced to the proton resonances resulting from incomplete deuteration of NMR solvents. IR spectra were recorded from KBr pellets on a Nicolet 510P FT IR spectrometer. MALDI-TOF, EI-HRMS, and ESI data were obtained on Bruker Biglex III MALDI-TOF, Thermo Finnigan MAT 95 XP high resolution, and MAT 95XP mass spectrometers, respectively.

The starting materials**, 1Ni and 1Cu** were synthesized following standard literature procedures.[1,2]

General procedure:

Dioxochlorin **1M** (M = Ni, Cu) was dissolved in chlorobenzene and benzeneselenic anhydride (BSA, 70% wt/wt) was added. The resulting mixture was heated under reflux for several hours and the reaction was monitored by TLC (dichloromethane/hexanes 1:1). The reaction mixture was then cooled to ambient temperature, the solvent was removed under reduced pressure, and the residue was purified on a Si-Gel column with dichloromethane/hexanes (2:1) as eluent. The reported yields refer to isolated material following column chromatography.

(2-oxo-4,9,14,19-tetraphenylazetchlorinato)nickel(II) (3Ni) and (5,10,15,20-tetraphenyl-porpholactonato)nickel(II) (4Ni):

Following the general procedure above, **1Ni** (I: 20.0 mg (0.028 mmol), II: 35.0 mg (0.099 mmol)) and BSA (I: 58.0 mg, 4 equiv., II: 152.0 mg 6 equiv.) in chlorobenzene (5 ml) were stirred and refluxed for 14 h (I) and 9 h (II). Yield: I: 3.6 mg (18%) **3Ni**; 2.7 mg (14%) **4Ni**; II: 6.5 mg (19%) **3Ni**; 12.0 mg (35%) **4Ni**.

Characterization of **3Ni**:

UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 698 (3.86), 663 (3.94), 579 (3.88), 435 (4.65), 384 (4.85); IR (cm^{-1}): 3439, 1828,[3] 1789, 1597, 1566, 1545, 1510, 1450, 1440, 1384, 1362, 1342, 1233, 1154, 1102, 1074, 1055, 1018, 1005, 832, 799, 758, 694; ^1H NMR ($CDCl_3$): δ 8.40-8.33 (dd, 4H, β-pyrrolic H), 8.12 (s, 2H, β-pyrrolic H), 7.94-7.88 (m, 8H, meso-ArH), 7.71-7.55 (m, 12H, meso-ArH); MALDI TOF m/z 672 (M); EI-HRMS Calcd. for $C_{43}H_{26}N_4ONi$ (MH^+): 673.1533, Found: 673.1533.

Characterization of **4Ni**:

UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 586 (4.47), 544 (3.98), 416 (5.23); IR (cm^{-1}): 1775, 1597, 1544, 1440, 1368, 1343, 1301, 1214, 1155, 1069, 1005, 927, 831, 795, 770; 745, 722, 694, 673, 503, 445; ^1H NMR ($CDCl_3$): δ 8.61-8.59 (d, 1H, β-pyrrolic H), 8.56-8.46 (m, 4H, β-pyrrolic H), 8.40-8.37 (d, 1H, β-pyrrolic H), 7.96-7.90 (m, 6H, meso-ArH), 7.82-7.79 (m, 2H, meso-ArH), 7.72-7.66 (m, 12H, meso-ArH; MALDI TOF m/z 688 (M); EI-HRMS Calcd. for $C_{43}H_{26}N_4O_2Ni$ (MH^+): 689.1482, Found: 689.1492.

(2-oxo-4,9,14,19-tetraphenylazetchlorinato)copper(II) (3Cu) and (5,10,15,20-tetraphenyl-porpholactonato)copper(II) (4Cu):

Following the general procedure previously described, **1Cu** (I: 40 mg (0.057 mmol), II: 40 mg (0.057 mmol, III: 40 mg (0.057 mmol), IV: 40 mg (0.057 mmol)) and BSA (I: 58 mg, 2 equiv., II: 117.0 mg 4 equiv., III: 117.0 mg, 4 equiv., IV: 234 mg, 8 equiv.) in chlorobenzene (5 ml) were stirred and refluxed for 22 h (I), 18 h (II), 8 h (III), and 5 h (IV), respectively. Yield: I: 3.0 mg (8%) **3Cu**; 10.5 mg (27%) **4Cu**; II: traces of **3Cu**; 29.6 mg (75%) **4Cu**, III: 2.8 mg (7%) **3Cu**; 27.5 mg (70%) **4Cu**; IV: 2.5 mg (6%) **3Cu**; 32.3 mg (82%) **4Cu**.

Characterization of **3Cu**:

UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 711 (3.96), 661 (3.96), 581 (3.85), 436 (4.76), 417 (4.64), 376 (4.78); IR (cm^{-1}): 3431, 1816,[3] 1788, 1653, 1596, 1575, 1544, 1521, 1499, 1456, 1435, 1384, 1349, 1335, 1232, 1155, 1115, 1073, 1023, 1014, 929, 847, 831, 793, 749, 723, 695, 674, 641, 575, 555, 504; ESI m/z 677.3 (M); EI-HRMS Calcd. for $C_{43}H_{26}N_4OCu$ (M^+): 677.1397, Found: 677.1395.

Characterization of **4Cu**:

UV-Vis (CH_2Cl_2): λ_{max} (lg ε) = 595 (4.52), 549 (4.10), 418 (5.57); IR (cm^{-1}): 1770, 1545, 1501, 1440, 1357, 1343, 1299, 1213, 1156, 1067, 1003, 995, 926, 889, 844, 830, 796, 771, 750, 720, 697, 685; 662, 620, 545, 516, 444; ESI m/z 693 (MH^+); EI-HRMS Calcd. for $C_{43}H_{26}N_4O_2Cu$ (MH^+): 694.1425, Found: 694.1436.

2) X-Ray Crystallography:

Crystals suitable for X-ray diffraction studies were obtained from slow vapor diffusion of diethylether into CH_2Cl_2. All crystallographic data were collected on a SMART Platform CCD (Bruker) equipped with a low temperature device. The intensity data were corrected for absorption (SADABS).[4] Final cell constants were calculated from 2599 (for **3Cu**), 4144 (for **4Cu**), 8991 (for **3Ni**), and 2022 (for **4Ni**) strong reflections from the dataset (SAINT).[5] The structures were solved using direct methods (SIR92[6] for **3Cu**, **4Cu, 3Ni** and SIR2004[7] for **4Ni**) and refined by full-matrix least-square/difference Fourier cycles.[8] All non-hydrogen positions were refined anisotropically. All hydrogen atoms were refined relative isotropic displacement parameters. Disorder was found for all structures and refined with sets of appropriate restraints and constraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication data CCDC-615720 (**3Cu**), -615719 (**4Cu**), CCDC-617061 (**3Ni**), -617062 (**4Ni**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

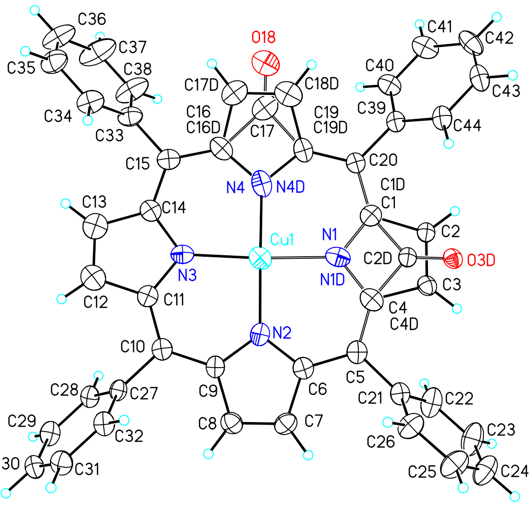

Figure 1S.: ORTEP plot for **3Cu** at 50% probability, disorder shown.

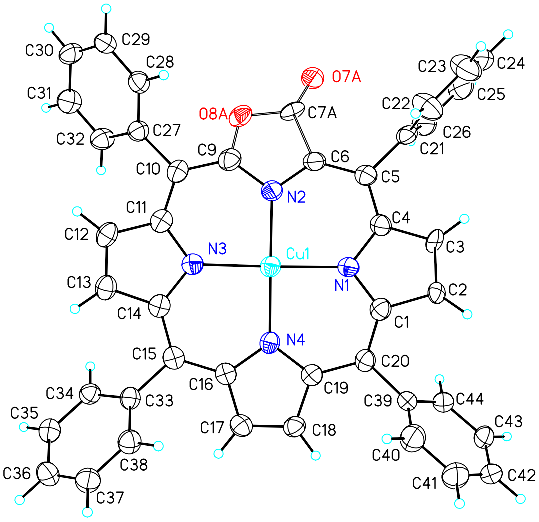

Figure 2S.: ORTEP plot of **4Cu** at 50% probability. Solvent and disorder omitted for clarity.

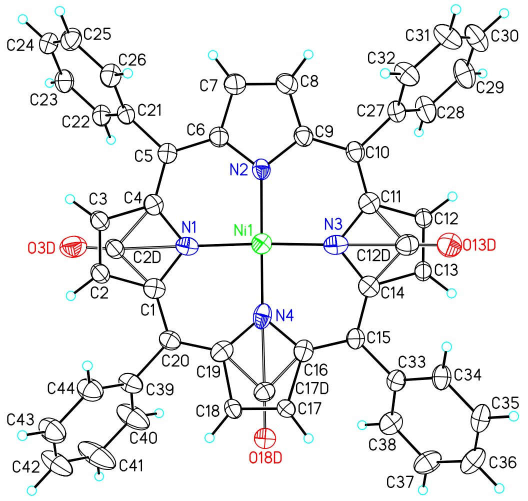

Figure 3S.: ORTEP plot for **3Ni** at 50% probability, disorder shown.

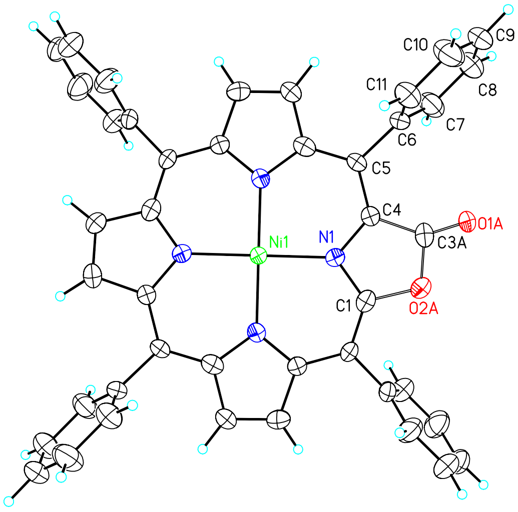

Figure 4S.: ORTEP plot of **4Ni** at 50% probability. Disorder omitted for clarity.

3) References:

1. M. J. Crossley, P. L. Burn, S. J. Langford, S. M. Pyke, and A. G. Stark; *J. Chem. Soc. Chem. Commun.,* **1991**, 1567-1568.
2. H. W. Daniell, S. C. Williams, H. A. Jenkins, and C. Brueckner; *Tetrahedron Lett.,* **2003**, 44, 4045-4049.
3. For azetporphyrinoids **3Ni** and **3Cu**, two ν_{CO} features (~2:1) are observed, separated by ~30 cm^{-1}, in both solid and solution IR spectra. Repeated analytical evaluation demonstrates the high purity of the compound, suggesting that these features may derive from Fermi resonance with a low energy vibration of the macrocycle, or a combination mode involving ν_{CN} of the 4-membered ring. The lack of an observable temperature-dependence to the intensities of these vibrations guides the explanation away from a dynamic process (*e.g.* ring-opening). Assignment of these features will be discussed in detail in a future manuscript.
4. An empirical correction for absorption anisotropy, R. Blessing, *Acta Cryst.* **A51**, 33 (1995).
5. SAINT, Bruker Analytical X-Ray Systems, Madison, WI, current version.
6. SIR-92, A. Altomare; G. Cascarno; C. Giacovazzo; A. Gualardi; *J. Appl. Cryst.* **26**, 343 (1993).
7. Sir2004, A Program for Atomatic Solution and Refinement of Crystal Structure. M. C. Burla, R. caliandro,M. Carnalli, B. Carrozzini, G. L. Cascarano, L. De Caro,C. Giacovazzo, G. Polidori, R. Sagna. version 1.0 (2004).
8. SHELXTL V5.10, Bruker Analytical X-Ray Systems, Madison, WI