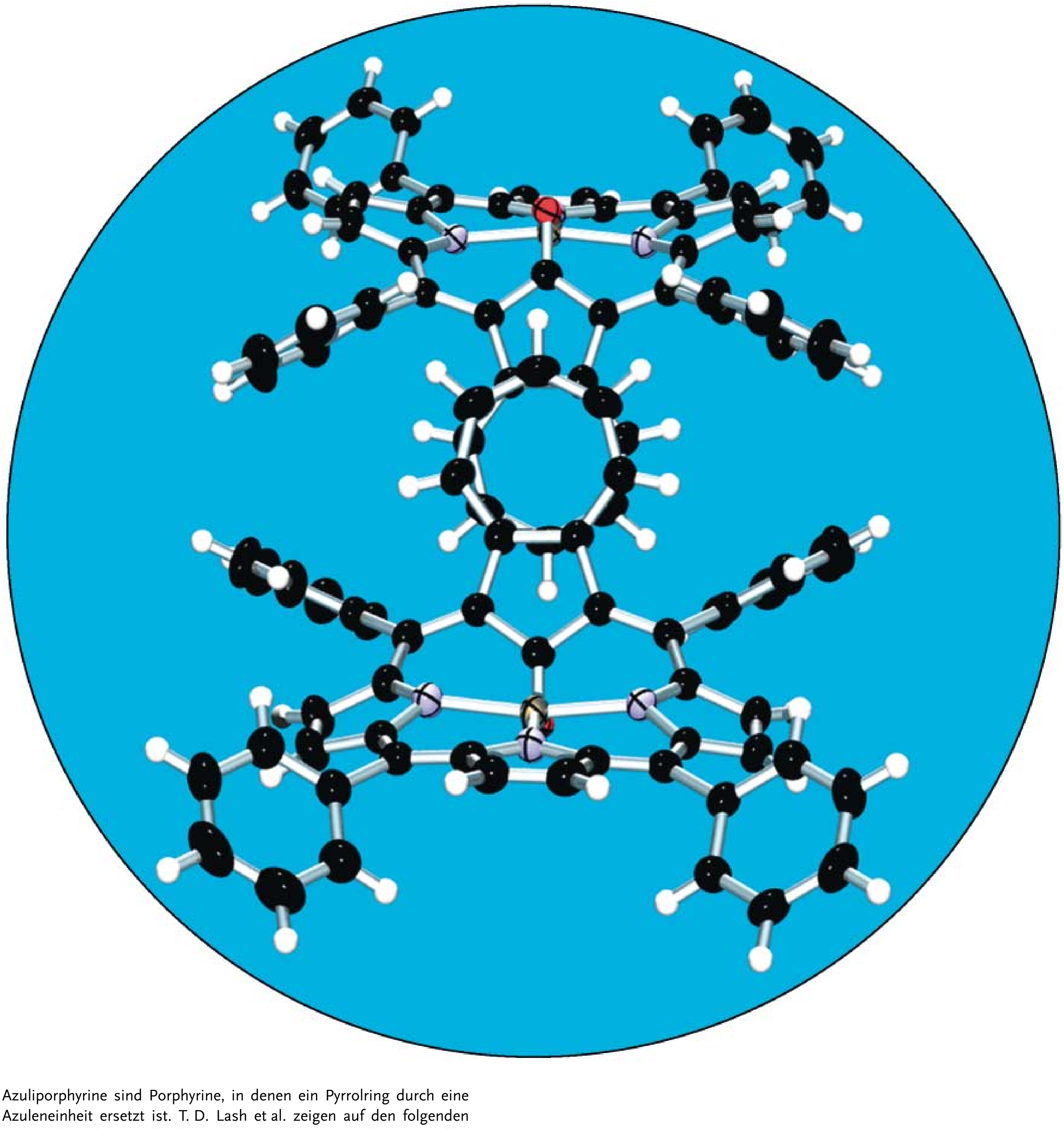
Zuschriften



Azuliporphyrine sind Porphyrine, in denen ein Pyrrolring durch eine Azuleneinheit ersetzt ist. T. D. Lash et al. zeigen auf den folgenden Seiten, dass diese Verbindungen eine einzigartige oxidative Metallierung mit Kupfer(II)-acetat eingehen. Dabei entstehen 21-Oxyazuliporphyrine, Porphyrinoidliganden mit einer internen Carbonylgruppe.

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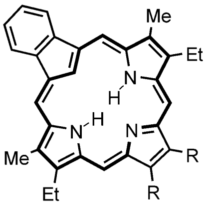
Porphyrin Oxidation

Oxidative Metalation of Azuliporphyrins with Copper(II) Salts: Formation of a Porphyrin Analogue System with a Unique Fully Conjugated Nonaromatic Azulene Subunit[**]

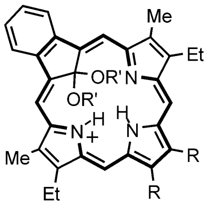
Denise A. Colby, Gregory M. Ferrence, and
*Timothy D. Lash**

Carbaporphyrinoids are porphyrin analogues where one or more of the pyrrole subunits has been replaced by carbocyclic rings such as indene or azulene.[1,2] These systems often exhibit unusual spectroscopic and physical properties[3] and may show varying degrees of aromatic character.[4,5] A particularly promising aspect of carbaporphyrinoid chemistry has been the generation of organometallic derivatives using late-transition-block metals such as nickel, palladium, platinum,[6] and silver.[7] However, some attempts at metalation chemistry resulted in the formation of unexpected oxidation products instead.

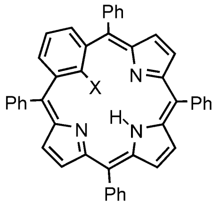
Benzocarbaporphyrins **1** were shown to react with ferric chloride in the presence of various alcohols to afford the benzo[18]annulene ketals **2** in excellent yields,[3] while more recently reaction of nonaromatic tetraphenylbenziporphyrin **3a** with silver(I) acetate was shown to afford the 22-acetoxy derivative **3b**.[8] Our recent studies have focused on the synthesis and chemistry of azuliporphyrins **4** and **5**—carbaporphyrinoids that show intermediary aromatic characteristics.[9–12] Azuliporphyrins react with nickel(II), palladium(II), or platinum(II) salts under mild conditions to afford the corresponding organometallic derivatives (for example, **6**–**8**).[6] We now report that azuliporphyrins **5** give an unusual oxidative metalation with copper(II) acetate to form a new porphyrinoid ligand system with highly modified spectroscopic properties.



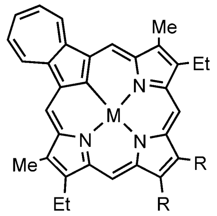
1 R = Et or Ph



2 R' = Me, Et, *i*Pr, etc.



3 a. X = H; b. X = OAc



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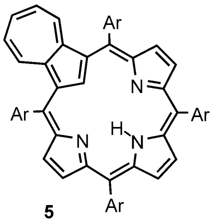
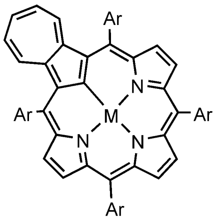
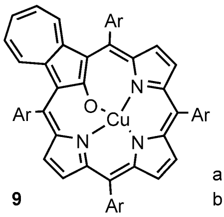


5
a. Ar = Ph
b. Ar = p-ClC$_6$H$_4$



6 M = Ni **7** M = Pd
8 M = Pt **10** M = Cu



9
a. Ar = Ph
b. Ar = p-ClC$_6$H$_4$

Tetraphenylazuliporphyrin **5a**[11,12] reacted with copper(II) acetate in DMF or pyridine at room temperature over a period of 5–10 minutes to afford the green crystalline product **9a** in a 30% yield. Tetrakis(4-chlorophenyl)azuliporphyrin **5b** afforded a similar product **9b** under these conditions. The UV/Vis spectra for **9** were ill-defined with three medium absorptions between 350 and 520 nm. We had anticipated that these derivatives corresponded to the copper(II) complexes **10**. However, high-resolution mass spectrometric analysis demonstrated that an oxygen atom had been incorporated in addition to the copper ion. The electron paramagnetic resonance spectrum for **9a** showed that the metal was present in the copper(II) oxidation state and was coordinated to all three nitrogen atoms. Furuta et al. have shown that N-confused porphyrins react with copper(II) acetate under aerobic conditions to give copper(II) tripyrrinone derivatives where the "confused" ring has been degraded.[13,14] However, our data is consistent with the retention of the full carbaporphyrinoid ring skeleton and the product must therefore differ considerably from the products formed in the study of Furuta et al. The paramagnetic complex cannot be analyzed by NMR spectroscopy, so crystals of **9a** were used for X-ray diffraction analysis. The data obtained demonstrated that a regioselective oxidation of **5a** had occurred at the internal carbon atom to give the copper(II) chelate **9a**.[15]

The most striking features of structure **9a** are the presence of an oxygen atom between C(21) and the copper center as well as the dramatic 52.96(3)° dihedral angle between azulene and the mean [18]annulene plane (Figure 1).[16] The latter can be clearly attributed to the steric requirements imposed by the oxygen atom bridging C21 and Cu. Although this is a

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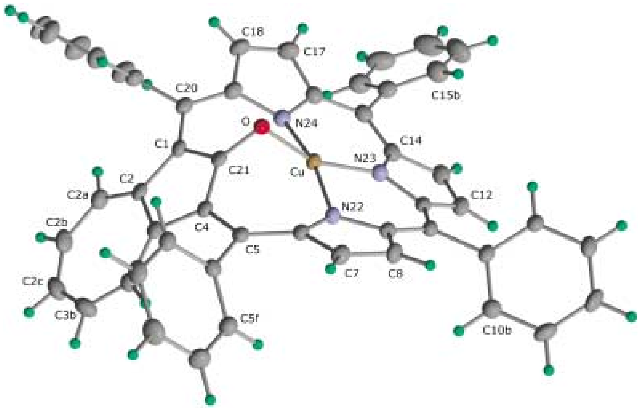
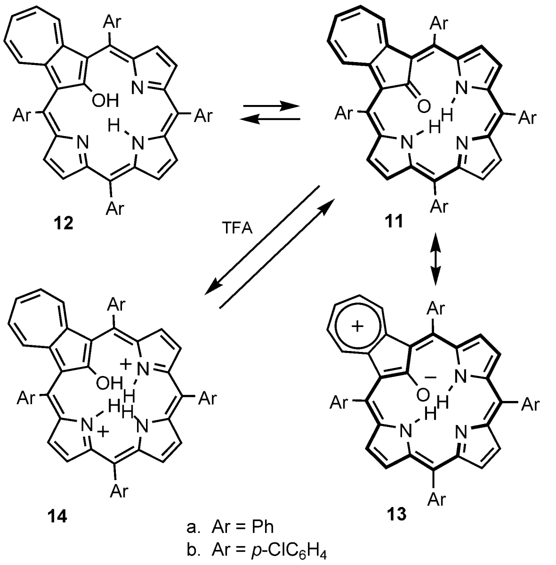


Figure 1. RASTEP drawing (50% probability level) of **9a**, with hydrogen atoms drawn arbitrarily small. Selected bond lengths [Å] and angles [°]: C21-O 1.302(3), C21-Cu 2.474(2), Cu-N23 1.911(2), Cu-O 1.938(2), Cu-N22 1.990(2), Cu-N24 2.003(2); C(21)-O-Cu 97.6(1), N23-Cu-O 157.22(8), N23-Cu-N22 93.56(8), O-Cu-N22 88.05(7), N23-Cu-N24 93.28(8), O-Cu-N24 89.02(8), N22-Cu-N24 168.90(8), N23-Cu-C21 171.33(8), O-Cu-C21 31.44(7), N22-Cu-C21 86.20(8), N24-Cu-C21 85.72(8), O-C21-C1 125(2), O-C21-C4 125.0(2), C1-C21-C4 109.7(2), O-C21-Cu 50.9(1), C1-C21-Cu 112.3(2), C4-C21-Cu 111.9(2), N23-Cu-O-C21 179.5(2).

unique structure, there is some resemblance to nickel(II) and copper(II) octaethylporphyrin *N*-oxides.[15,17] The remainder of the bonding parameters observed in **9a** appear to be routine. The C21–O and Cu–O separations of 1.302(3) and 1.938(2) Å, respectively, are typical for C-O-Cu^{2+} interactions, and the remainder of the macrocycle is distorted from planarity to a lesser extent, as demonstrated by the dihedral angles between the pyrrole rings and the mean [18]annulene plane of 15.8(1), 17.8(1), and 14.3(1)°.

Treatment of **9a** or **9b** with 10% trifluoroacetic acid (TFA)/chloroform afforded excellent yields of the corresponding demetalated 21-oxyazuliporphyrins **11**. The UV/Vis spectrum for free base **11a** showed a strong Soret-like band at 478 nm as well as three weaker absorptions at 554, 603, and 673 nm (Figure 2B). The protonated system formed in 1% TFA/$CHCl_3$ (Scheme 1) exhibited a Soret-like band at 480 nm and a broad far-red absorption centered at 837 nm. Despite the porphyrin-like features of the UV/Vis spectra, the ^1H NMR spectrum of **11a** in $CDCl_3$ showed no evidence of significant aromatic character (Figure 2A). Unlike the azuliporphyrin precursor, in which the cycloheptatrienyl protons resonate between $\delta = 6.9$ and 7.7 ppm, the external azulene protons in **11a** are shifted atypically upfield and resonate at $\delta = 5.16$ (2H, d), 5.38 (1H, t), and 5.69 ppm (2H, t). This observation strongly implies that the aromatic character of the azulene unit has been lost. On the other hand, the pyrrolic protons are only shifted upfield by approximately 0.1 ppm relative to the free base of **5a**. Demetalation of **9** could give rise to 21-hydroxyazuliporphyrins **12** or the corresponding keto tautomers **11**. The data is not consistent with **12**, and keto tautomers are generally favored when this type of situation arises in porphyrinoid systems.[3b,18] The ^{13}C NMR data show a carbonyl group at $\delta = 162.8$ ppm, while the IR spectrum of **11a** shows a strong carbonyl absorption at 1524 cm^{-1}. These data suggest that the carbonyl moiety is highly polarized, although strong hydrogen-bonding interactions undoubtedly contribute to the low frequency value observed for the carbonyl stretch. Several delocalization pathways are feasible



Scheme 1. Tautomers, resonance contributors, and protonated forms of tetraaryloxyazuliporphyrins **11**.

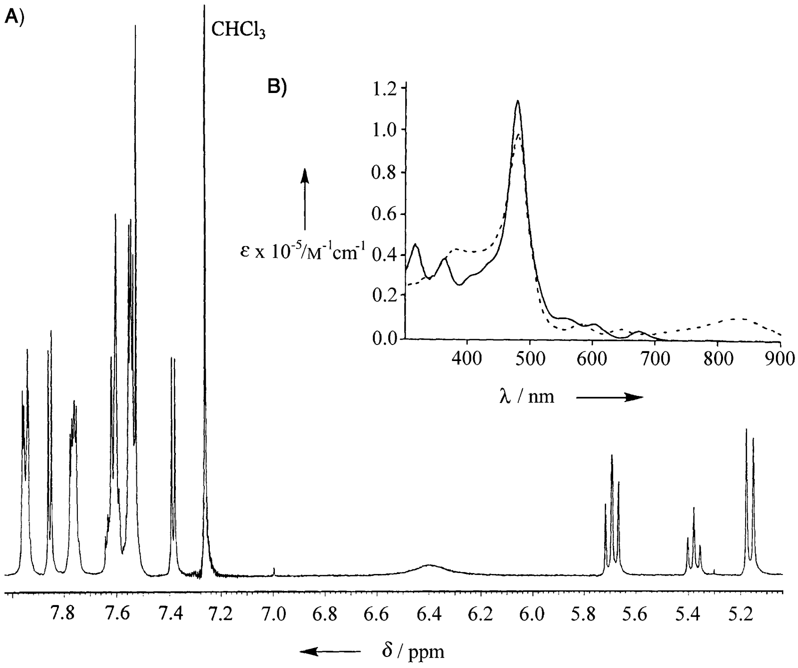


Figure 2. A) 400 MHz ^1H NMR spectrum of tetraphenyloxyazuliporphyrin **11a** showing the atypically upfield-shifted resonances for the external azulene protons between 5.1 and 5.7 ppm. B) UV/Vis spectra of ketone **11a** in 1% $Et_3N/CHCl_3$ (bold line, free base) and 1% TFA/$CHCl_3$ (dotted line, dication **14a**).

for porphyrinoids **11**. The ketone structure has a 24π-electron pathway, and in principle could possess antiaromatic character; however, the upfield shifts seen in the ^{1}H NMR spectra of **11** fall considerably short of the values expected for a species with a paratropic ring current. Alternatively, dipolar resonance contributors such as **13** would provide a porphyrin-like 18π-electron delocalization pathway instead. The latter cannot be a dominant canonical form as the seven-membered ring does not have tropylium ion characteristics as evident from the observed ^{1}H NMR resonances. The unique spectroscopic characteristics of the oxyazuliporphyrin system must arise from a combination of factors and will require more detailed investigation. The ^{1}H NMR spectrum of the corresponding dication **14** in TFA/CDCl$_3$ shows significant diatropic character. The NH protons resonate upfield at $\delta = -0.2$ (1 H) and 3.11 ppm (2 H), compared to 6.40 ppm for **11**, while the pyrrolic protons show up at approximately 0.5 ppm further downfield than those of the free base. In addition, the azulene protons no longer gave abnormal upfield resonances. It would be expected that protonation would favor a species that resembles the aromatic resonance form **13**. Unfortunately, as with the azuliporphyrins **5**,[11,12] the ^{1}H NMR spectra for the dications are considerably broadened, most likely because of restricted conformational mobility in these crowded structures.

The origin of the oxygen atom in **9** remains to be determined. Mass spectrometric analysis of reactions carried out in the presence of ^{18}O labeled water showed that no ^{18}O was incorporated into the copper(II) complex. In addition, acetate was ruled out as the source of the oxygen because the same complex was formed using CuCl$_2$ instead of Cu(OAc)$_2$, albeit in lower yields.[19] However, our results demonstrate that the azuliporphyrin system holds new and surprising chemical properties and further work in this area is underway. In particular, we have found that oxyazuliporphyrins **11** show some promise as macrocyclic ligands and we have generated stable complexes of **11a** with nickel(II), palladium(II) and platinum(II), cations.

Experimental Section

9a: Cu(OAc)$_2$·H$_2$O (230 mg, 1.16 mmol) (OAc = acetate) was added to a solution of **5a** (64.4 mg, 0.0954 mmol) in pyridine (65 mL) and the resulting mixture stirred under an atmosphere of nitrogen for 5 min. The mixture was diluted with chloroform (60 mL), washed with water (150 mL), and dried over sodium sulfate. The solvents were removed under reduced pressure and the residue purified by column chromatography on Grade 3 alumina eluting with 20% hexanes/dichloromethane. The product was collected as a red fraction. Recrystallization from chloroform-hexanes gave **9a** (21.3 mg, 0.0283 mmol, 30%) as shiny dark-green crystals, m.p. > 350 °C. UV/Vis (CHCl$_3$): λ_{max} ($\log\varepsilon$) = 362 (4.57), 415 (4.62), 508 (4.77), 634 (3.90), 669 nm (3.69); HRMS (EI): calcd for C$_{50}$H$_{31}$CuN$_3$O: *m/z* 752.1763; found: 752.1760; elemental analysis (%) calcd for C$_{50}$H$_{31}$CuN$_3$O·0.4CHCl$_3$: C 75.56, H 3.95, N 5.24; found: C 75.46, H 4.14, N 5.26.

21-Oxyazuliporphyrin **11a**: Copper(II) complex **9a** (49.1 mg, 0.0652 mmol) was stirred with 10% TFA/chloroform (50 mL) for 15 min at room temperature. The mixture was washed with water and 5% sodium bicarbonate solution, dried over sodium sulfate, and evaporated to dryness. The residue was purified by column chromatography on Grade 3 alumina eluting with 50% CH$_2$Cl$_2$/CHCl$_3$. The demetalated product eluted as a purple band. Recrystallization from CHCl$_3$/hexanes afforded **11a** (40.9 mg, 0.0592 mmol, 91%) as shiny green crystals, m.p. 321–322 °C (decomp). UV/Vis (1% Et$_3$N/CHCl$_3$): λ_{max} ($\log\varepsilon$) = 318 (4.66), 363 (4.59), 478 (5.06), 554 (4.03), 603 (3.89), 673 nm (3.64); UV/Vis (1% TFA/CHCl$_3$): λ_{max} ($\log\varepsilon$) = 312 (4.42), 337 (4.48), 380 (4.64), 480 (4.99), 579 (3.88), 643 (3.69), 837 nm (4.05); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 5.16$ (2 H, d, $J = 10.4$ Hz), 5.38 (1 H, t, $J = 9.6$ Hz), 5.69 (2 H, t, $J = 10.2$ Hz), 6.40 (2 H, br s), 7.38 (2 H, d, $J = 4.8$ Hz), 7.52 (2 H, s), 7.53–7.56 (6 H, m), 7.59–7.64 (6 H, m), 7.75–7.78 (4 H, m), 7.85 (2 H, d, $J = 4.8$ Hz), 7.93–7.97 ppm (4 H, m); ^{1}H NMR (400 MHz, TFA/CHCl$_3$, dication): $\delta = -0.23$ (1 H, br s), 3.11 (2 H, v br s), 7.26–7.36 (5 H, m), 7.78–7.83 (8 H, m), 7.90–7.96 (6 H, m), 8.05–8.10 (4 H, m), 8.25 (2 H, s), 8.30 (2 H, br d), 8.32–8.38 ppm (4 H, m); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 118.1$, 125.8, 126.5, 127.4, 127.6, 128.4, 129.4, 131.0, 131.4, 131.7, 133.5, 134.5, 135.1, 139.5, 140.5, 141.3, 141.6, 144.8, 150.8, 162.8 ppm; HRMS (FAB): calcd for C$_{50}$H$_{33}$N$_3$O + H: *m/z* 692.2702; found: 692.2701; elemental analysis (%) calcd for C$_{50}$H$_{33}$N$_3$O·CHCl$_3$: C 75.51, H 4.22, N 5.18; found: C 75.01, H 4.29, N 5.20.

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Keywords: aromaticity · azulenes · copper · oxidation · porphyrinoids

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reported in this communication; see C.-H. Hung, W.-C. Chen, G.-H. Lee, S.-M. Peng, *Chem. Commun.* **2002**, 1516–1517.

[16] Crystal data for **9a** ($C_{50}H_{31}CuN_3O$): $M_r = 753.32$, $T = 193(2)$ K, green block, approximate dimensions $0.42 \times 0.12 \times 0.09$ mm^3, monoclinic, space group $P\bar{1}$ (No. 2), $a = 9.374(1)$, $b = 13.750(2)$, $c = 14.681(2)$ Å, $\alpha = 67.209(2)$, $\beta = 87.286(2)$, $\gamma = 86.332(2)°$, $V = 1740.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.437$ Mg m^{-3}, $\mu = 0.674$ mm^{-1}, $\lambda_{(Mo-K\alpha)} = 0.71073$ Å, $2\Theta_{max} = 52.76°$, 9418 measured reflections, 6948 independent reflections, 496 refined parameters, GOF = 1.022, $R_1 = 0.042$ and $wR_2 = 0.104$ ($F_o^2 > 2\sigma(F_o^2)$), $R_1 = 0.057$ and $wR_2 = 0.110$ (for all data), max./min. residual electron density 0.679/−0.369 e Å^{-3}. Data collection and analysis were performed using standard techniques.[6b] CCDC-222542 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[19] Following the initial submission of this paper, we performed the oxidative metalation of **5a** with $Cu(OAc)_2$ in the presence of $^{18}O_2$. EI-MS shows substantial incorporation of the heavy isotope into the copper complex **9a**. This result demonstrates that the oxygen atom is derived from traces of molecular oxygen. The authors thank Professor C. D. Stevenson for her help in this isotope labeling study and Dr. S. L. Mullen, University of Illinois at Urbana-Champaign, for providing the mass spectrometry data.