J. Am. Chem. Soc. **1994,** *116,* 2639-2640

Solitaire Porphyrazines: X-ray Crystal Structure and Spectroscopy of [1,1'-Bis(diphenylphosphino)ferrocene]-[(norphthalocyanine)dithiolato]palladium(II)

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Received November 8, 1993
Revised Manuscript Received January 10, 1994

Star porphyrazines are symmetrical coordination compounds prepared by the peripheral tetra-metalation of porphyrazine octathiolate.[1,2] We now report the first directed synthesis and structural characterization of a related new class of unsymmetrical complexes, solitaire porphyrazines, which are based on a macrocycle endowed with a *single* metal-chelation site at its periphery. The first examples of this novel class of compounds employ a ligand, denoted as a norphthalocyanine dithiolate, that can be viewed as a phthalocyanine (pc), where one of the benzo rings at the periphery is replaced with a dithiolato chelate. Hence, it is capable of coordinating a single exocyclic metal ion in addition to that within the central cavity (Chart 1). In particular, the bimetallic moiety [1,1'-bis(diphenylphosphino)ferrocene]-palladium(II) ((P-P)Pd(II)) has been bound to the dithiolate unit, with M = "H_2" (**9**), Ni (**10**), and Cu (**11**) incorporated in the central cavity.

Solitaire porphyrazines were prepared by the mixed condensation of 1,2-dicyanobenzene (in excess) with the dithiomaleonitrile derivative **1**, using Mg(II) as a template (Scheme 1).[3a] This reaction gave the soluble, protected Mg(norphthalocyanine) derivative **2** (16–18% yield), which had been designed to be easily separated from the insoluble Mg(pc) byproduct.[3] Subsequent demetalation of **2** with trifluoroacetic acid and remetalation with $M(OAc)_2$ (M = Ni(II) or Cu(II)) gave **4** and **5** in nearly quantitiative yields. Reductive debenzylation (Na/NH_3) produced the norphthalocyanine dithiolates **6–8**, which were capped *in situ* with $(P\text{-}P)PdCl_2$ to give **9–11** in 30% yield.

Of the three solitaire porphyrazines, **9** gave the best crystals (CH_2Cl_2/Et_2O), and its X-ray structure is shown in Figure 1. The complex crystallizes in the monoclinic space group *C2/c* with eight macrocycles and eight ordered dichloromethane molecules per unit cell.[4] Interestingly, the macrocycles form slipped stacks, as seen for the parent M(pc), despite the peripheral asymmetry. The macrocyclic ring is essentially planar, and the geometry of the norphthalocyanine portion of **9** is similar to that of pc,[5] with only slight variations seen in the pyrrole containing the fused dithiolene moiety (supplementary material). However, the asymmetry at the periphery is nonetheless apparent at the core in that the internal N–H protons are resolved in the X-ray structure, being localized on pyrrole nitrogens N1 and N3.

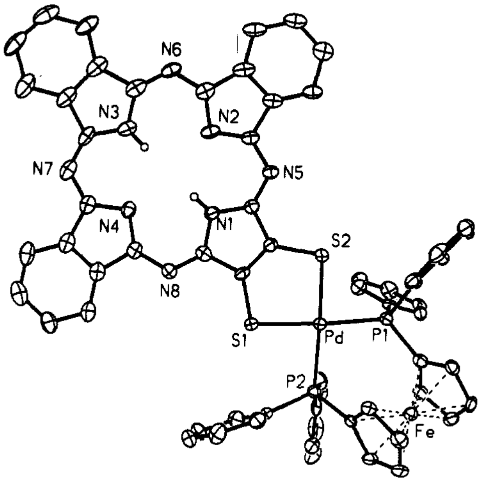
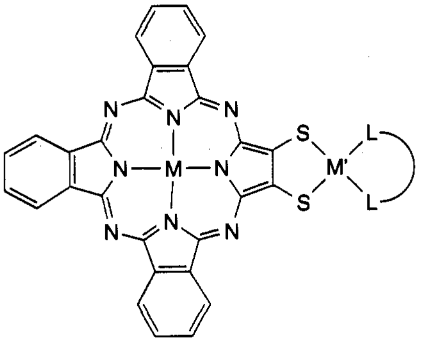
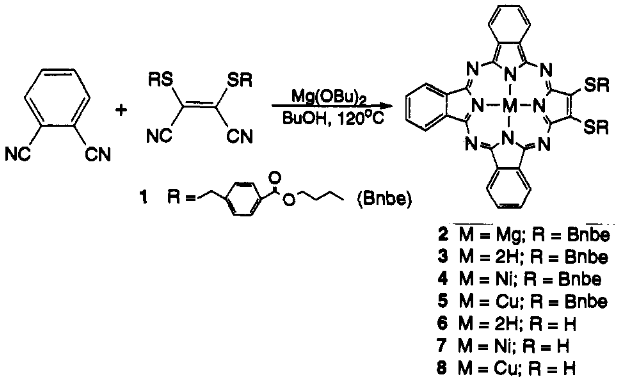


Figure 1. Thermal ellipsoid plot of **9** showing 50% probability ellipsoids. For clarity, the heteroatoms have been labeled and hydrogen atoms have been omitted.

Chart 1



Scheme 1



The four-coordinate palladium ion is chelated by the two "dithiolene" sulfurs and by the two phosphorus atoms of the 1,1'-bis(diphenylphosphino)ferrocene moiety. As seen with the star porphyrazines, tetrametal complexes of nickel porphyrazine octathiolate, $[Ni(pzot)]^{8-}$, the dithiolene unit of **9** adjusts itself in order to chelate the palladium ion by a swing of the C_β–S bond.[1,2] Whereas the C_β–C_β–S bond angle for the unconstrained

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(4) Crystallographic data for $1 \cdot CH_2Cl_2$: monoclinic, $C2/c$, $a = 37.916(7)$ Å, $b = 10.8070(10)$ Å, $c = 29.588(4)$ Å, $\beta = 109.851(11)°$, $V = 11404(3)$ Å^3, $Z = 8$; Siemens P4 diffractometer, $T = 125$ K, Cu Kα radiation, data collected to $2\theta = 112°$. The structure was solved by direct methods, and the data were corrected for absorption effects. Full-matrix least-squares refinement was performed with F^2 on 745 parameters using SHELXL-93 (Sheldrick, G. M. *J. Appl. Crystallogr.*, in preparation), leading to R_w2 for all 7439 unique data of 0.1245. The conventional R1, calculated with 6045 data with $I > 2\sigma(I)$, is 0.0469.

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reference, magnesium octakis(methylthio)porphyrazine, Mg(omtp), is 128.5(35)°,[1b] the same angle in **9** closes to 124.0(7)°. Likewise, the interatomic distance between the sulfurs decreases from 3.53 Å in Mg(omtp) to 3.31 Å in **9**. The Pd–S bond distance for **9** of 2.316(5) Å is similar to the value 2.300 Å seen in (dithiooxalato-*S,S'*)bis(trimethylphosphine)palladium(II).[6a] Likewise, the Pd–P bond distance for **9** is 2.326(4) Å, as compared to the literature value of 2.334 Å.[6] The bond angles around palladium are not all equal for **9**, with S–Pd–S and P–Pd–P angles of 90.6(5)° and 97.9(5)°, respectively. These differ slightly (~3°) from the literature references, probably because the phosphine ligands are different. The ferrocene portion of the diphosphine cap is structurally similar to free ferrocene, and the average Fe–C bond distance of 2.043(6) Å is comparable to the reported value of 2.04(2) Å.[7]

Peripheral asymmetric functionalization of a M(pc) does not cause significant changes in its electronic structure,[3d] whereas removal of one benzo group does.[3a,8] Indeed, a comparison of the visible absorption spectra for **9** and **10** to those for the analogous pc complexes reveals the asymmetry at the macrocycle periphery (Figure 2).[9] The spectrum of Ni(pc) shows an intense "0–0" band at 680 nm with vibronic structure to shorter wavelength, in particular a well-defined vibronic band at 604 nm. This pattern is doubled in the lowered symmetry ($D_{4h} \rightarrow D_{2h}$) of H_2(pc), with the splitting into two "0–0" (Q_x,Q_y) bands[10] at 664 and 688 nm being particularly clear. The reduction from D_{4h} to C_{2v} symmetry in the peripherally functionalized complex **10** has a similar effect; the two visible absorbances of **10** at 598 and 668 nm, where the latter seems to be two overlapping peaks, represent an unresolved version of the visible pattern of H_2(pc) (Figure 2). The enhanced asymmetry of the metal-free macrocycle **9** thus appears to sharpen the pattern of **10** rather than to introduce further splitting. However, the situation may in fact be more complex, as the low-energy vibronic bands at ~590 nm now have almost the same intensity as the "0–0" band at ~725 nm. Electronic structure calculations will address this issue.

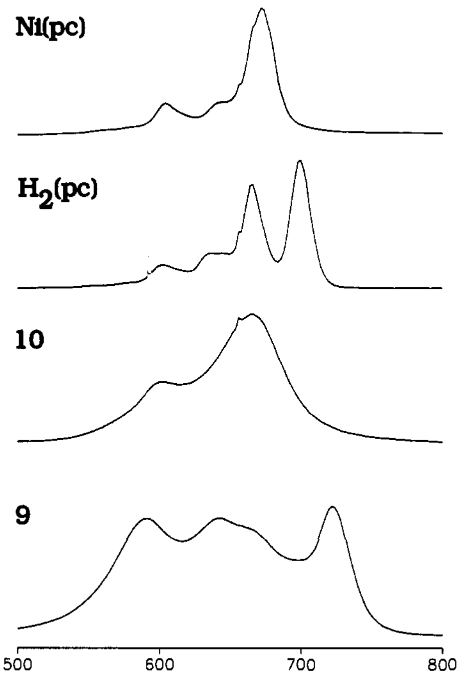

Figure 2. Optical spectra of both metalated and metal-free phthalocyanines (chlorobenzene) and solitaire porphyrazines (dichloromethane, 20 μM).

Star porphyrazines[1,2] and solitaire porphyrazines represent the first in a new family of multimetallic macrocycles being synthesized. In particular, the binucleating ligand system reported here permits the preparation of a wide variety of metal complexes whose novel spectroscopic and magnetic properties will be the subject of future reports.

Acknowledgment. This work was supported by the National Science Foundation (CHE-9107589 and DMR-9119832).

Supplementary Material Available: Figures showing the numbering scheme, displacements from the least-squares plane, and unit cell packing diagrams and tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (15 pages); listing of observed and calculated structure factors (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[9] In addition, complexes **9–11** all display a higher-energy "soret" absorbance at 338 nm, analogous to that at ~345 nm for pc.

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