

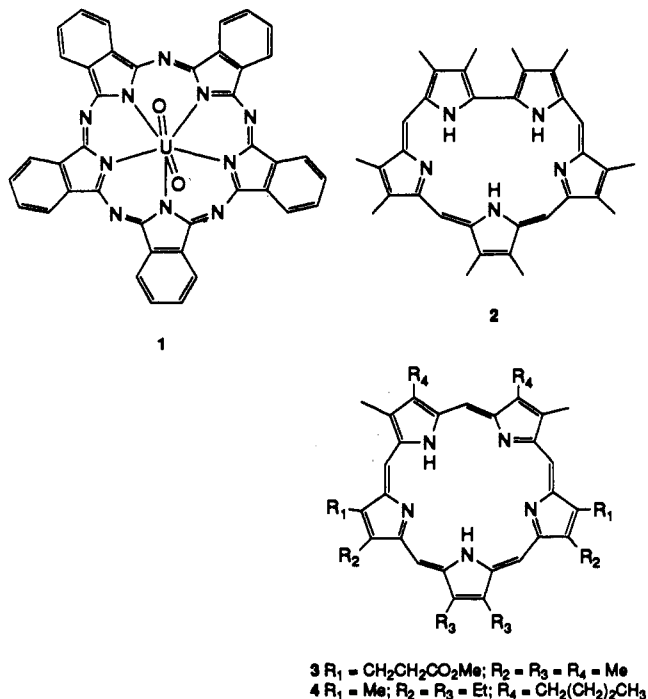
Uranylpentaphyrin: An Actinide Complex of an Expanded Porphyrin

Anthony K. Burrell, Gregory Hemmi, Vincent Lynch, and Jonathan L. Sessler*

Department of Chemistry and Biochemistry
University of Texas at Austin, Austin, Texas 78712

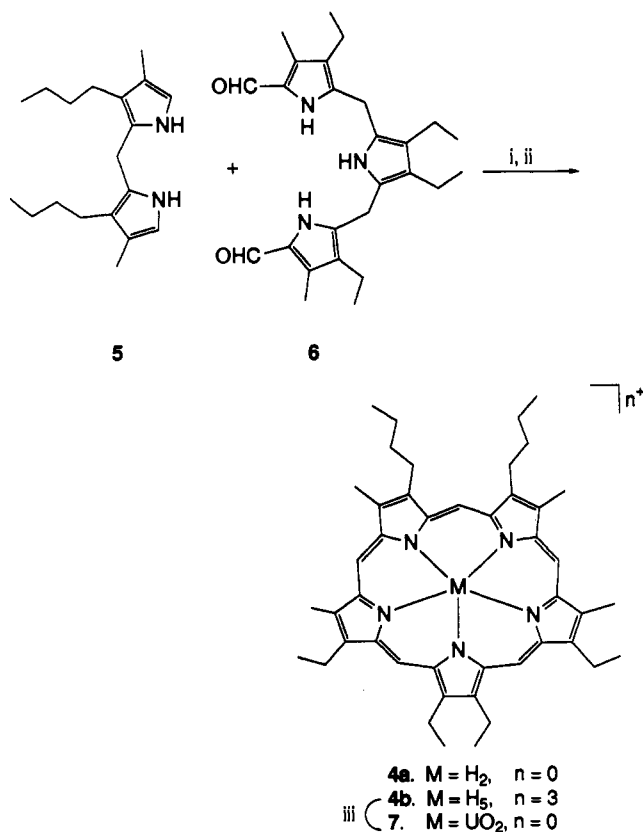
Received April 15, 1991

The porphyrins are among the most versatile of ligands, forming complexes with almost every metal and semimetal in the periodic table.¹ Unfortunately, this rich cation-complexing chemistry is severely limited in the case of the actinides. In fact, to date, no stable uranyl complex has been prepared with any porphyrin or phthalocyanine, although out-of-plane complexes have been characterized structurally with U(IV) and Th(IV).²⁻⁶ Presumably this failure reflects the fact that cations of the early actinides are too large to be accommodated within the ca. 2.0 Å radius porphyrin core⁷ and could, perhaps, indicate that larger "expanded porphyrin"-type ligands might prove more successful in stabilizing 1:1, in-plane, actinide cation complexes. Nonetheless, no generalized actinide binding expanded porphyrin system currently exists. A crystallographically characterized "uranylsuperphthalocyanine" complex, **1**, was obtained as the result of a direct, metal-template condensation between phthalonitrile and UO₂²⁺.⁸



However, the resulting uranyl-ligand conjugate proved unstable

Scheme I*



* Reagents: (i) HBr-AcOH; (ii) chloranil; (iii) UO₂Cl₂/pyridine/*i*-PrOH.

in the presence of acids or other metal salts, reacting to give the corresponding ring-contracted metal-free and metal-containing phthalocyanines, respectively.^{8b} Moreover, the electronically similar saphyrins (e.g., **2**) reportedly failed to form any coordination complexes with uranyl cation.⁹ On the other hand, initial studies¹⁰ of pentaphyrin (**3**)¹¹ led to the suggestion that this particular expanded porphyrin system would, in fact, react with uranyl salts. However, little definitive insight into the nature or composition of the resulting complex(es) was provided in the undissemated report associated with this work.¹⁰ We have, therefore, undertaken a systematic study of the coordination chemistry of pentaphyrins, an interesting class of potentially dianionic, aromatic, pentadentate ligands, and in this communication we report the synthesis and structural characterization of the uranyl chelate of the new decaalkyl pentaphyrin **4**.¹² To the best of our knowledge, this chelate represents the first structurally characterized actinide complex of a pyrrole-derived expanded porphyrin and the first uranyl complex of a porphyrin- or phthalocyanine-like system available in both its free-base and metal-containing forms.

Pentaphyrin (**3**), first reported in 1983 by Gossauer,^{11a} was obtained via an acid-catalyzed oxidative [2 + 3] MacDonald type¹³ condensation between a diformyl tripyrrane and an α -free di-

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(12) The systematic name for pentaphyrin **4** is: 2,23-dibutyl-8,12,13,17-tetraethyl-3,7,18,22-tetramethyl-26,27,28,29,30-pentazahexacyclo-[21.2.1.1^{6,9}.11¹⁴.1^{16,19}.12²⁴]triaconta-1(26),2,4,6(27),7,9,11,13,15,17,19-(29),20,22,24-tetradecaene.

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pyrromethane. Recent advances in both dipyrromethane¹⁴ and tripyrrane¹⁵ syntheses have made these requisite precursors readily available and have led us to consider that the decaalkyl-substituted pentaphyrin **4** should be readily obtainable via a similar [3 + 2] condensation procedure (Scheme I). However, in our hands little or no isolable product was obtained when the critical [3 + 2] condensation was carried out in accord with the procedure of Gossauer.¹¹ On the other hand, yields as high as 65% (vs the 31% reported by Gossauer^{11a}) were routinely obtained when the initial condensation was carried out under rigorously anaerobic conditions. Such an improvement in yield could prove significant, given the attention that these¹⁶ and other similar¹⁷⁻¹⁹ expanded porphyrin systems are now receiving as potential photosensitizers for use in various photodynamic therapy-type applications.

Pentaphyrin **4** is isolated, after column chromatography, as the partly protonated macrocycle and converted to either the free-base form **4a** (λ_{\max} (CHCl₃) = 467 nm; ϵ = 16 000 cm²·mol⁻¹) or the triprotonated species (as the trichloride salt) **4b** (λ_{\max} (CHCl₃) = 462 nm; ϵ = 240 000 cm²·mol⁻¹) by treatment with base or acid, as appropriate.²⁰ Uranyl insertion was effected by dissolving **4b**·3Cl and UO₂Cl₂ in a 1:1 (v/v) solution of pyridine/*i*-PrOH and heating at reflux until a single Soret-like band at 500 nm was obtained in the UV/vis spectrum (ca. 8 h). The resulting product, **7**, was purified by column chromatography to give a dark green solid that is deep ruby red in solution.²⁰ While this product is distinctly different from the unmetallated pentaphyrin **4**, the ¹H NMR spectra of these two materials are remarkably similar, showing in both cases features consistent with an overall C₂ symmetry. This suggests that complex **7** exists in solution either as a highly symmetrical structure with the uranyl cation coordinated in the center of a planar pentaphyrin or as some sort of fluxional (rapidly interconverting) ensemble of distorted structures which on average contain the uranyl cation within the macrocyclic plane.

The single-crystal X-ray structure of **7**²¹ is consistent with the second of these two possibilities. It reveals (Figure 1) that in the solid state the uranyl cation is coordinated in the center of the pentaphyrin but that the macrocycle is distorted from planarity to give a structure reminiscent of that of uranylsuperphthalocyanine.^{8a} In particular, the uranyl cation is located at the center of the saddle-shaped pentaphyrin, with the distortion from planarity being due to the bonding demands of the uranyl cation. The result is an essentially symmetrical pentagonal bipyramidal coordination geometry for the uranium atom with U-N and U-O distances at 2.541 (3) Å and 1.756 (5) Å, respectively.

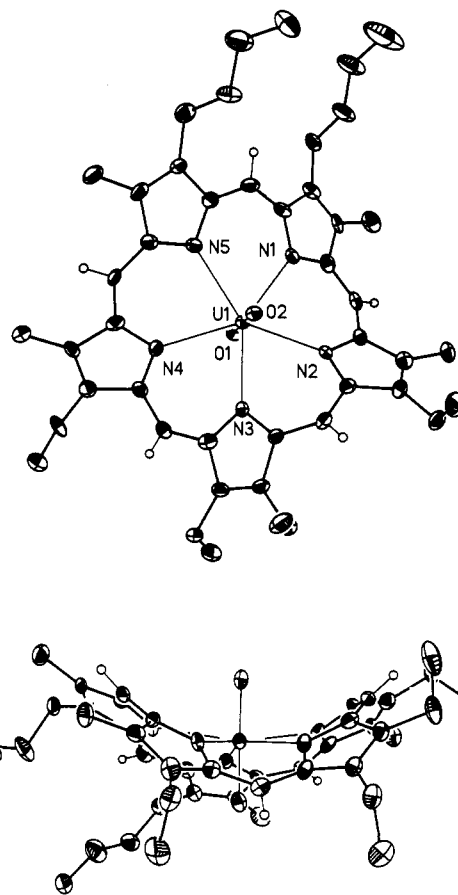


Figure 1. Top: View of **7** showing the nearly pentagonal bipyramidal coordination around uranium. The thermal ellipsoids are scaled to the 30% probability level while the hydrogen atoms are scaled to an arbitrary size. The hydrogen atoms on the alkyl portion of the pentaphyrin have been omitted for clarity. Some relevant bond lengths (Å) are as follows: U1-O1 1.759 (6), U1-O2 1.753 (7), U1-N1 2.566 (8), U1-N2 2.506 (8), U1-N3 2.494 (8), U1-N4 2.543 (8), U1-N5 2.598 (7). The N-U-N angle for adjacent nitrogens is 73.1 (1)° (average) and is only slightly larger than the ideal value of 72° for an exact pentagonal arrangement around uranium. Bottom: View of **7** showing the saddle-like conformation assumed by the pentaphyrin to accommodate the coordination to the uranyl group. The uranium lies in the plane of the nitrogen donors which form a nearly planar arrangement. The maximum deviation from the plane is 0.46 Å for N5.

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(20) Satisfactory spectroscopic and mass spectrometric data were obtained for all new compounds (cf. supplementary material).

(21) Crystals were very dark red blocks obtained by slow evaporation of a pentane solution of **7**. Crystal data: C₄₅H₅₅N₅UO₂, *M*_r = 935.99, monoclinic, space group P2₁/c (No. 14), with *a* = 11.694 (2), *b* = 14.545 (4), *c* = 24.510 (5) Å, β = 100.875 (14)°, *V* = 4094 (2) Å³, *Z* = 4, ρ_{calcd} = 1.52 g·cm⁻³, Mo K α radiation (λ = 0.7107 Å) with a graphite monochromator on a Nicolet R3 diffractometer at -100 °C. A total of 12 044 reflections were measured, of which 6282 were unique (*R*_{int} = 0.030). Data were corrected for Lp effects, decay, and absorption. The structure was solved by the heavy atom method and refined by full-matrix least squares (SHELXTL-Plus). All hydrogen atoms were idealized. The final *R* = 0.0491, with *wR* = 0.0477 and goodness of fit = 1.230 for 531 parameters and 4392 reflections having *F*_o > 4(σ (*F*_o)). The methyl group on C32 is disordered.

Although bearing some structural similarity to the uranyl-superphthalocyanine system, the present uranyl-pentaphyrin **7** differs dramatically in terms of chemistry. First, it is quite soluble in all common organic solvents. Second, it appears considerably more stable, undergoing no apparent decomposition or hydrolysis when, as a dichloromethane solution, it is stirred overnight in the presence of 0.1 M 2,4-pentanedione in pH 10 carbonate buffer. Third, treatment with other metal salts appears to effect neither demetalation nor decomposition whereas subjection to strongly acidic conditions leads only to regeneration of the metal-free species, **4b** (rather than to ring contraction and, e.g., porphyrin formation). Fourth, and perhaps most importantly, because the pentaphyrins may be obtained in both metal-free and metal-containing forms, the preparation of other centrally bound metal complexes can be conceived. Preliminary studies with other metal salts appear promising; spectral evidence consistent with complex formation has been obtained with several lanthanide salts.²² Current efforts, therefore, are being devoted to characterizing these pentaphyrin complexes and to exploring further the general coordination properties of this as yet little studied series of expanded porphyrins.

(22) In the visible spectrum of the putative gadolinium(III) complex, for instance, the Soret-like band appears at 505 nm.

Acknowledgment. Support was provided by an NIH grant (AI 28845), an NSF Presidential Young Investigator Award (1986), an Alfred P. Sloan Foundation Research Fellowship (1989-1991), and a Camille and Henry Dreyfus Foundation Teacher-Scholar Award (1988-1992) to J.L.S. We thank Profs. A. Gossauer and D. Dolphin for providing us with copies of the Ph.D. Dissertation and M.S. Thesis of Dr. H. Rexhausen and Mr. R. E. Danso-Danquah, respectively.

Supplementary Material Available: Synthetic experimental details for compounds **4a**, **4b**, and **7**, X-ray experimental data for **7**, and tables of atomic thermal factors, atomic positional parameters, bond distances, and angles for **7** (22 pages); listing of observed and calculated structure factor amplitudes for **7** (24 pages). Ordering information is given on any current masthead page.

Formation of a Copper-Dioxygen Complex ($\text{Cu}_2\text{-O}_2$) Using Simple Imidazole Ligands

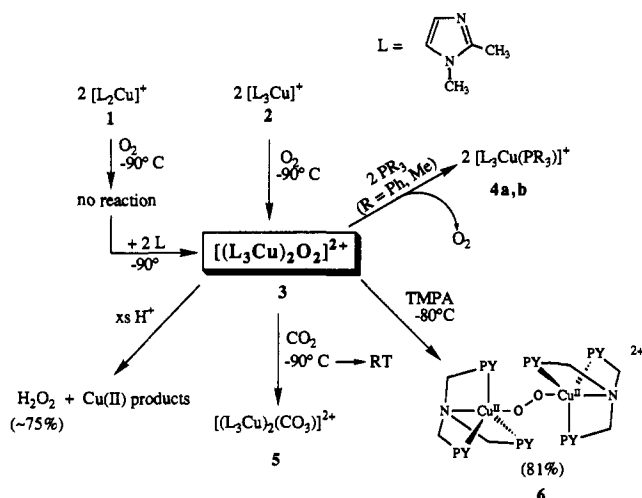
Indrajit Sanyal,[†] Richard W. Strange,[‡]
Ninian J. Blackburn,^{*§} and Kenneth D. Karlin^{*†}

Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218
Daresbury Laboratory, Warrington, WA4 4AD, UK
Department of Chemical and Biological Sciences
Oregon Graduate Institute, Beaverton, Oregon 97006-1999

Received March 21, 1991

Side-chain imidazole ligation (derived from histidine) pervades the active-site chemistry of copper metalloproteins, including the O_2 -carrier hemocyanin (Hc),¹ in addition to copper oxygenases and oxidases.² In bioinorganic modeling studies, there has been considerable recent progress in the characterization of synthetically derived $[\text{Cu}_2\text{-O}_2]$ species,^{2a,3-5} but these systems have generally not utilized imidazole ligands. There is a good deal of interest in polyimidazole copper complexation,^{6,7} and here we report that

Scheme I



a $[\text{Cu}_2\text{-O}_2]$ species can be generated by reaction of O_2 with a mononuclear Cu(I) complex possessing the simple unidentate 1,2-dimethylimidazole (L) ligand.

Following Sorrell's observation that linear two-coordinate Cu(I) complexes (with nitrogen heterocyclic ligands) are unreactive to CO and O_2 ,⁸ we observed a similar phenomenon with $[\text{L}_2\text{Cu}^+](\text{PF}_6)^-$ (**1**).⁹ However, when another equivalent of L is added to form $[\text{L}_3\text{Cu}^+](\text{PF}_6)^-$ (**2**),¹⁰ derived solutions are extremely air sensitive. By then employing low-temperature manipulations that have been successfully applied to copper(I) complexes with aminoalkylpyridine polydentate ligands,^{5,11} we found that oxygenation of **2** at -90°C in CH_2Cl_2 (manometry: $\text{Cu}:\text{O}_2 = 2.06 \pm 0.02$) gave a stable, EPR-silent (77 K), intensely brown colored solution [UV-vis λ_{max} (ϵ , $\text{M}^{-1}\text{cm}^{-1}$), 346 (sh, 2200),¹² 450 (sh, 1450), 500 (1900), and 650 (600) nm], formulated as the peroxo-dicopper(II) complex $[(\text{L}_3\text{Cu})_2(\text{O}_2)]^{2+}$ (**3**) (Scheme I).

Reactivity studies have been found to be useful in characterizing copper-dioxygen complexes,¹³ and here they provide further evidence for the presence of a bound nucleophilic peroxo moiety. Reaction of tertiary phosphines PR_3 ($\text{R} = \text{Ph}, \text{Me}$) displaces the bound O_2 ligand in **3**, as judged by the qualitative detection of dioxygen using pyrogallol,¹¹ and by the isolation of $[\text{L}_3\text{Cu}(\text{PR}_3)]^+$ (**4**).¹⁴ Reaction of **3** with an excess of acid ($\text{HPF}_6\cdot\text{Et}_2\text{O}$, 10 equiv/Cu) generates H_2O_2 in $\sim 75\%$ yield as determined by iodometric titration. Also consistent with a peroxo-metal formulation,^{13a,b} complex **3** undergoes an immediate reaction with CO_2 at low temperature (-90°C), which upon warming produces a carbonato-dicopper(II) complex $[(\text{L}_3\text{Cu})_2(\text{CO}_3)]^{2+}$ (**5**).¹⁵

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(10) $[\text{L}_3\text{Cu}^+](\text{PF}_6)^-$ (**2**): Anal. Calcd for $\text{C}_{11}\text{H}_{24}\text{CuF}_6\text{N}_6\text{P}$: C, 36.24; H, 4.88; N, 16.92. Found: C, 36.67; H, 5.11; N, 16.97. Δ_m (CH_3CN) = $144 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (1:1 electrolyte).

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(14) The reaction of **3** with PPh_3 was slow and yielded $[\text{L}_3\text{Cu}^+(\text{PPh}_3)](\text{PF}_6)^-$ (**4a**) (yield = 67%) with a small amount of OPPh_3 (7%). Anal. Calcd for $\text{C}_{33}\text{H}_{39}\text{CuF}_6\text{N}_6\text{P}_2$: C, 52.16; H, 5.13; N, 11.06. Found: C, 51.51; H, 5.12; N, 10.76. With PMe_3 the reaction of **3** was fast and yielded 81-85% of $[\text{L}_3\text{Cu}^+(\text{PMe}_3)](\text{PF}_6)^-$ (**4b**), which was proved by ^1H NMR.

[†] Johns Hopkins University.

[‡] Daresbury Laboratory.

^{*} Address for correspondence: Professor K. D. Karlin, Dept. of Chemistry, The Johns Hopkins University, Charles and 34th Sts., Baltimore, MD 21218.

[§] Oregon Graduate Institute.

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