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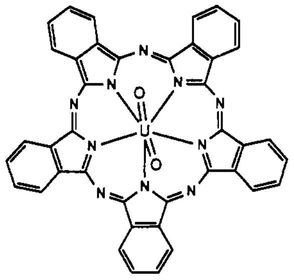
Communications

Synthesis and X-ray Characterization of a Uranyl(VI) Schiff Base Complex Derived from a 2:2 Condensation Product of 3,4-Diethylpyrrole-2,5-dicarbaldehyde and 1,2-Diamino-4,5-dimethoxybenzene

In recent years, considerable effort has been devoted to preparing well-characterized complexes containing the uranyl ion[1-5] and a variety of ligands for this purpose are now known. However, few of these rely on pyrroles for effective metal chelation. Indeed, we are aware of only three uranyl-binding pyrrole-containing systems: Superphthalocyanine (**1**),[3] pentaphyrin (**2**),[4] and sapphyrin (**3**).[5] In each of these ligands, the uranyl(VI) ion is chelated in a saddle-shaped pentagonal planar arrangement, and in the case of sapphyrin, uranyl chelation also induced a chemical modification of the ligand framework.[5] Nonetheless, these results have lead us to consider that it should be possible to make other pyrrole-containing "porphyrin-like" systems, incorporating pentagonal planar or hexagonal planar ligand fields, that might be able to stabilize the formation of uranyl(VI) coordination complexes. In this communication, we wish to report the synthesis and structural characterization of the first hexadentate pyrrole-derived uranyl(VI) Schiff base complex **4**.[6]



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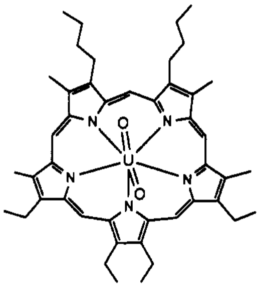

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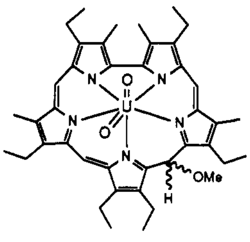

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Ligand synthesis and metal complex preparation are summarized in Scheme I. Here, the key starting material, 3,4-diethylpyrrole-2,5-dicarbaldehyde (**6**),[6-8] was prepared in four steps from starting 3,4-diethylpyrrole by using a modification of the reported synthesis of pyrrole-2,5-dicarbaldehyde.[9] Subsequent metal template condensation in the presence of uranyl nitrate and 4,5-diamino-1,2-dimethoxybenzene (**7**)[10] then gave the uranyl complex **4** in 75% yield.

As an alternative to the above, the metal-free ligand **5**[6,11] could be prepared by an acid-catalyzed condensation.[12] Interestingly, quantitative yields were obtained when nitric acid rather than HCl was used as the acid catalyst. Under these conditions, a protonated

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(1) Uranyl complexes of Schiff base macrocyclic ligands: (a) van Doorn, A. R.; Bos, M.; Harkema, S.; van Eerden, J.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.* **1991**, *56*, 2371–2380 and references within. (b) Nijenhuis, W.; van Doorn, A. R.; Reichwein, A. M.; de Jong, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 3607–3608. (c) Chandra, R. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, *20*, 645–659 and references therein. (d) Casellato, U.; Guerriero, P.; Tamburini, S.; Vigato, P. A.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1990**, 1533–1541 and references therein. (e) Benetollo, F.; Bombieri, G.; De Cola, L.; Polo, A.; Smailes, D. L.; Vallarino, L. M. *Inorg. Chem.* **1989**, *28*, 3447–3452. (f) El-Saied, F. A. *Inorg. Chim. Acta* **1989**, *165*, 147–152. (g) Bullita, F.; Guerriero, S.; Tamburini, S.; Vigato, P. A. *J. Less-Common Met.* **1989**, *153*, 211–218. (h) van Staveren, C. J.; Fenton, D. E.; Reinhoudt, D. N.; van Eerden, J.; Harkema, S. *J. Am. Chem. Soc.* **1987**, *109*, 3456–3458. (i) De Cola, L.; Smailes, D. L.; Vallarino, L. M. *Inorg. Chim. Acta* **1985**, *110*, L1–L2. (j) Casellato, U.; Fregona, D.; Sitran, S.; Tamburini, S.; Vigato, P. A. *Inorg. Chim. Acta* **1985**, *110*, 161–167.

(2) For overviews of macrocyclic Schiff base complexes of lanthanides and actinides, see: (a) Fenton, D. E. *Chem. Soc. Rev.* **1988**, *17*, 69–90. (b) Bombieri, G. *Inorg. Chim. Acta* **1987**, *139*, 21–32.

(3) (a) Day, V. W.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1975**, *97*, 4519–4527. (b) Marks, T. J.; Stojakovic, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 1695–1705. (c) Cuellar, E. A.; Stojakovic, D. R.; Marks, T. *Inorg. Synth.* **1980**, *20*, 97–100. (d) Cuellar, E. A.; Marks, T. J. *Inorg. Chem.* **1981**, *20*, 3766–3770. (e) Marks, T. J.; Stojakovic, D. R. *J. Chem. Soc., Chem. Commun.* **1975**, 28–29.

(4) Burrell, A. K.; Hemmi, G.; Lynch, V.; Sessler, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 4690–4692.

(5) Burrell, A. K.; Cyr, M. J.; Lynch, V.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1710–1713.

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

(7) Well prior to this work Fenton and co-workers prepared a series of macrocycles derived from alkyl-free pyrrole-2,5-dicarbaldehyde and used these to chelate Cu(II) and other cations of the transition series; see: (a) Fenton, D. E.; Moody, R. *J. Chem. Soc., Dalton Trans.* **1987**, 219–220. (b) Adams, H.; Bailey, N. A.; Fenton, D. E.; Moss, S.; Rodriguez de Barbarin, C. O.; Jones, G. *J. Chem. Soc., Dalton Trans.* **1986**, 693–699. (c) Adams, H.; Bailey, N. A.; Fenton, D. E.; Moss, S.; Jones, G. *Inorg. Chim. Acta* **1984**, *83*, L79–L80.

(8) An alternative synthesis of 3,4-diethylpyrrole-2,5-dicarbaldehyde (**6**) has recently been reported by Vogel and co-workers: Vogel, E.; Jux, N.; Rodriguez-Val, E.; Lex, J.; Schmicker, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1387–1390.

(9) Miller, R.; Olsson, K. *Acta Chem. Scand.* **1981**, *B35*, 303–304.

(10) Sessler, J. L.; Mody, T. D.; Ramasamy, R.; Sherry, A. D. *New. J. Chem.*, in press.

(11) The systematic name for macrocyclic ligand **5** is 13,14,27,28-tetraethyl-6,7,20,21-tetramethoxy-3,10,17,24,29,30-hexaazapentacyclo-$[24.2.1.1^{12,15}.0^{4,9}.0^{18,23}]$triaconta-2,4,6,8,10,12,14,16,18,20,22,24,26,28-tetradecaene.

(12) Sessler, J. L.; Johnson, M. J.; Lynch, V. *J. Org. Chem.* **1987**, *52*, 4394–4397.

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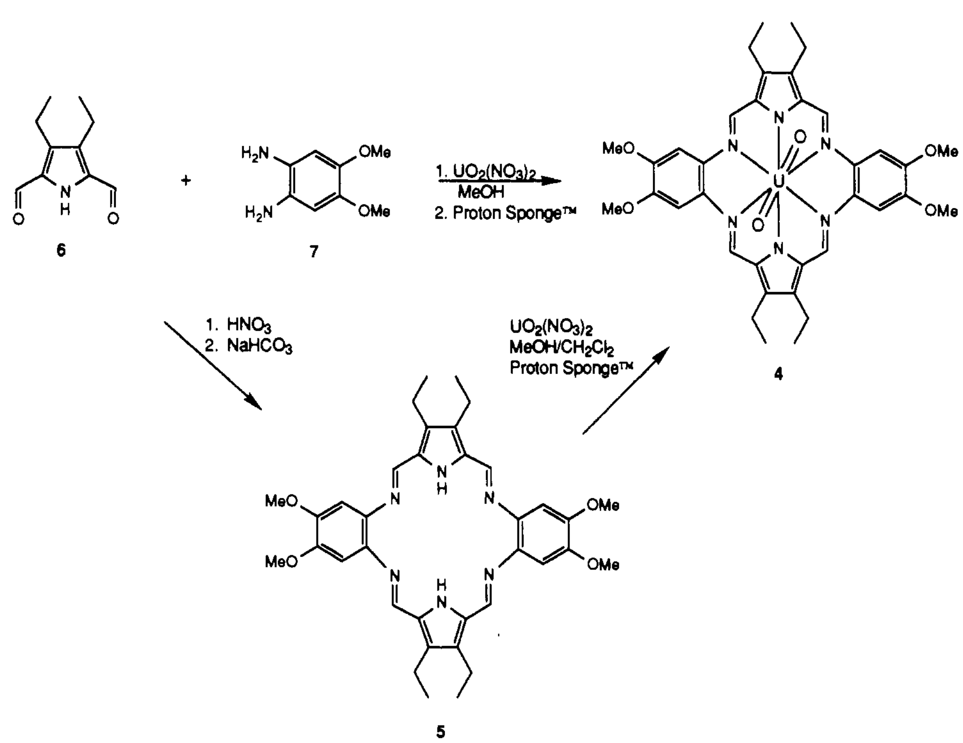
Scheme I



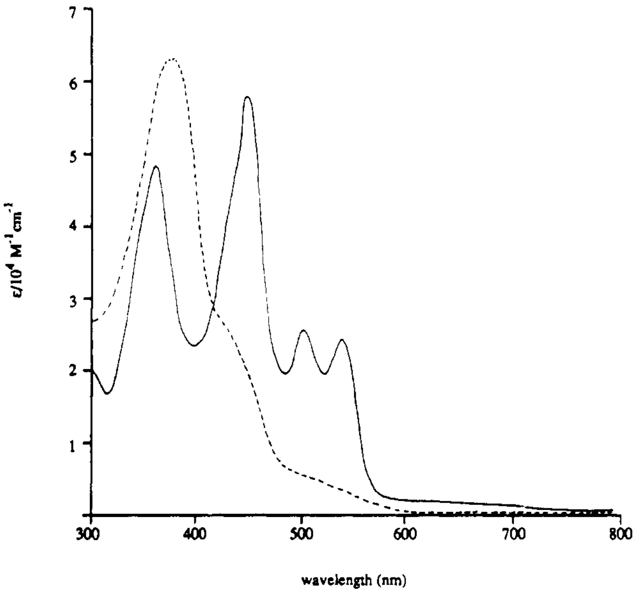


Figure 1. Optical spectra of the metal-free ligand **5** (---) and its corresponding uranyl adduct **4** (—) as recorded in $CHCl_3$ at room temperature.

nitrate salt **5**·$2HNO_3$ precipitated cleanly from the reaction mixture in a few minutes. This interesting result leads us, as an aside, to suggest that these types of Schiff base condensation reactions could be subject to a general "anion template effect", and this is something we are exploring in the context of other related syntheses.[13] In any case, washing **5**·$2HNO_3$ with aqueous $NaHCO_3$ produced the free base **5**, which upon treatment with $UO_2(NO_3)_2$ and *N,N,N′,N′*-tetramethyl-1,8-naphthalenediamine (Proton Sponge) in a 3:1 (v/v) solution of methanol and dichloromethane gave the uranyl chelate **4** in 85% yield. Here, as above, Proton Sponge was added to prevent the formation of **5**·$2HNO_3$.[14] Interestingly, the optical spectrum of this metal-free material **5** is very different from its corresponding uranyl adduct **4** (Figure 1).[6]

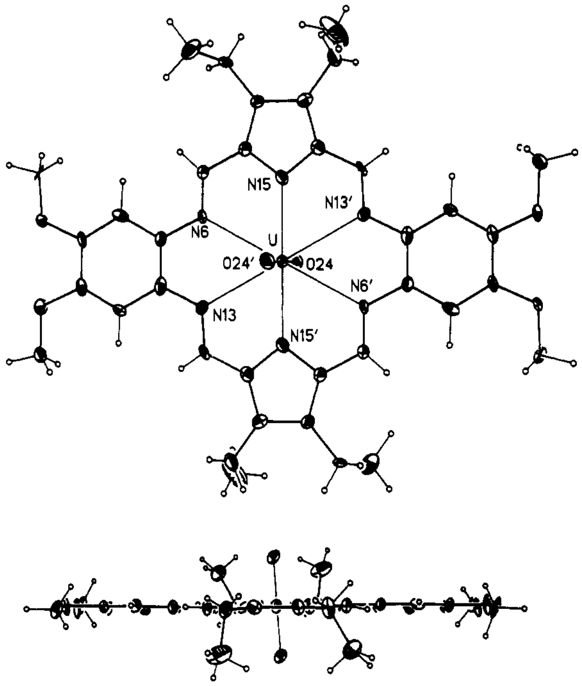


Figure 2. Top: View of **4** showing the hexagonal bipyramidal coordination around uranium. The uranium atom lies on an inversion center at $^1/_2$, $^1/_2$, $^1/_2$. Atoms marked with a prime are related by $1 - x$, $1 - y$, $1 - z$. The thermal ellipsoids are scaled to the 50% probability level, while the hydrogen atoms are scaled to an arbitrary size. Relevant bond angles and distances are given in the text. Bottom: View of **4** showing the planar conformation of the macrocycle. The uranyl group is inclined at an angle of 87° with respect to the macrocycle plane.

Initial characterization of **4** was made by spectroscopic means. The ^1H and ^{13}C NMR spectra of this material were remarkable in their simplicity[6] as would be expected for a very symmetrical structure. In addition the infrared spectrum of **4** showed a single sharp absorption for the uranyl ion (ν_{asym}(U–O) 910 cm^{-1}) and no vibrations that could be assigned to a pyrrole NH stretch or to vibrations of coordinated anions. Taken together, these spectral

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(13) Sessler, J. L.; Mody, T. D.; Ford, D. A.; Lynch, V. *Angew. Chem.*, in press.

(14) In the absence of Proton Sponge, the same reaction conditions produced a mixture of protonated nitrate salt **5**·$2HNO_3$ and **4**.

Table I. Crystallographic Data for $UO_2(C_{36}H_{40}N_6O_4)(CHCl_3)_4$

chem formula	$C_{40}H_{44}N_6O_6Cl_{12}U$	space group	$P2_1/c$ (No. 14)
		T, °C	-100
a, Å	7.790 (4)	λ(Mo Kα), Å	0.7107
b, Å	24.708 (14)	ρ_{calc}, g/cm^3 (-100 °C)	1.82
c, Å	13.167 (8)		
β, deg	100.79 (4)	μ, cm^{-1}	37.90
V, Å^3	2490 (2)	transm coeff	0.5131-0.6765
Z	2	$R(F)$	0.0445
fw	1368.29	$R_w(F)$	0.0466

data are consistent with a neutral complex in which the uranyl ion is coordinated to all six ring nitrogen atoms.

A single-crystal X-ray diffraction analysis of **4**[15] (Table I) reveals that in the solid state the uranyl cation is coordinated to all six nitrogen atoms in a planar fashion. Although not formally aromatic, the complex is remarkably planar. In fact, the maximum deviation from planarity is 0.011 (7) Å for N15 (Figure 2). The structure of complex **4** is thus very different from the saddle-shaped conformations seen in the uranyl chelates of the formally aromatic "expanded porphyrin" ligands **1** and **2**. As a result, in part, of this planarity, the coordination geometry about the uranium atom is hexagonal bipyramidal. The relevant U–N6, U–N13, and U–N15 bond distances are 2.733 (7), 2.748 (7), and 2.418 (7) Å, respectively. The N–U–N angle for adjacent nitrogen atoms is 60.0 (1)° (average), which is equal to the ideal value of 60° for an exact hexagonal arrangement around uranium. The U–O distance is 1.770 (6) Å.[15] Interestingly, the average bond length for C5–N6 and C14–N13 (1.295 (7) Å (average)) is midway in value between those corresponding imine bonds observed for a nonaromatic texaphyrin precursor (1.310 (6) Å (average))[12] and the corresponding aromatic texaphyrin (1.273 (8) Å (average)).[16]

This uranyl complex **4** appears to be quite stable, undergoing no apparent decomposition or demetalation when stirred for several hours in a 5:1 (v/v) solution of chloroform and trifluoroacetic acid. In fact, exposure to these conditions leads solely to protonation (not demetalation) as evidenced by the fact that adding triethylamine serves to regenerate quantitatively the starting complex as determined by both optical spectroscopy and FAB mass spectrometry. In addition, heating complex **4** to 300 °C fails to effect any apparent decomposition as judged by FAB mass spectrometry, optical spectroscopy, and TLC analysis.

Taken together, the present results indicate that relatively simple pyrrole-derived tetraimine systems, such as **5**, can be used to support the formation of planar UO_2^{2+} complexes. Currently, we are exploring further the lanthanide and actinide cation coordination properties of ligand **5** and have preliminary results consistent with La(III), Eu(III), and Gd(III) all being effectively chelated by this system. Further results of these metal chelation studies will be published in due course.

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Supplementary Material Available: Text giving synthetic experimental details for compounds **4**, **5**, **5**·$2HNO_3$, and **6** and X-ray experimental details for **4** and tables of atomic thermal factors, atomic positional parameters, and bond distances and angles for **4** (18 pages); a listing of observed and calculated structure factor amplitudes for **4** (17 pages). Ordering information is given on any current masthead page.

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

Jonathan L. Sessler*
Tarak D. Mody
Vincent Lynch

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[15] (a) Crystallographic summary for **4** [$C_{36}H_{40}N_6O_6U(CHCl_3)_4$]: MW = 1368.29; crystallized as dark green needles from chloroform layered with methanol in the monoclinic space group $P2_1/c$ (No. 14), with a = 7.790 (4) Å, b = 24.708 (14), c = 13.167 (8) Å, β = 100.79 (4)°, V = 2490 (2) Å^3, Z = 2, ρ_{calc} = 1.82 g cm^{-3} (198 K), $F(000)$ = 1340, μ(Mo Kα) = 37.90 cm^{-1}, λ = 0.7107 Å. Data were collected on a Nicolet R3 diffractometer at 198 K, equipped with a Nicolet LT-2 low-temperature device, using the Ω scan technique at 6–12°/min out to a 2θ limit of 50°. A total of 9056 reflections were collected, of which 4416 were unique. The R for averaging symmetry equivalent reflections was equal to 0.046. Data were corrected for Lp effects, decay, and absorption. The structure was solved by the direct methods and refined by full-matrix least-squares using SHELXTL-PLUS.[15b] All H atoms were obtained from the ΔF map and refined with isotropic temperature factors except for those on C8, C14, C16, and C23, which did not refine well and were fixed at $1.2U_{eq}$ of the relevant carbon atom. The macrocycle lies around an inversion center with the uranium atom at $^1/_2$, $^1/_2$, $^1/_2$. A total of 376 parameters were refined to a final R = 0.0445, R_w = 0.0466 and a goodness-of-fit = 1.168 using 3009 reflections having $F > 4\sigma(F)$. Full details of the X-ray experimental procedure are found in the supplementary material. (b) Sheldrick, G. M. SHELXTL-PLUS. Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1987.

[16] Sessler, J. L.; Murai, T.; Lynch, V.; Cyr, M. *J. Am. Chem. Soc.* **1988**, *110*, 5586–5588.