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Synthesis and characterization of double and triple decker uranium porphyrins

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A novel triple decker uranium complex has been prepared by refluxing tetraphenylporphyrin and uranyl acetate in phenol or benzonitrile, and its chemical transformations have been studied.

Double and triple decker porphyrin and phthalocyanine complexes exhibit promising properties such as high stability of neutral and oxidised forms, solubility in organic solvents and ability to self-organization in solid layers. Porphyrin and phthalocyanine complexes of lanthanides and actinides with double and triple decker structures can be used as components of new materials.[1,2]

Four-charged ions of zirconium, hafnium, cerium and actinides, as well as three-charged ions of lanthanides, form double decker porphyrin complexes.[3–6] The Ln(OEP)$_2$ complexes (Ln = Ce$^{\mathrm{IV}}$, Eu$^{\mathrm{III}}$, Nd$^{\mathrm{III}}$ or La$^{\mathrm{III}}$ and OEP is the octaethylporphyrin dianion) were prepared[7] by refluxing H$_2$OEP and the appropriate Ln$^{\mathrm{III}}$(acac)$_3$·xH$_2$O in 1,2,4-trichlorobenzene under an inert atmosphere. The refluxing of the reaction mixture for 20 h led to the formation of the triple decker Eu$_2$(OEP)$_3$ complex in 16% yield along with the corresponding double decker.[8] U$^{\mathrm{IV}}$ and Th$^{\mathrm{IV}}$ double decker complexes were obtained by reactions of H$_2$TPP or H$_2$OEP with diethyl amide metal complexes.[9–11] Triple decker thorium(III) tetraphenylporphyrin was obtained for the first time in 1991.[12]

During the synthesis of uranium tetraphenylporphyrin complexes, we found that the reaction between H$_2$TPP and UO$_2$(AcO)$_2$ in a 1:10 molar ratio in refluxing benzonitrile for 19 h yields two complexes: U$^{\mathrm{IV}}$(TPP)$_2$ and U$_2^{\mathrm{III}}$(TPP)$_3$. H$_2$TPP (196 mg, 0.32 mmol) and UO$_2$(AcO)$_2$ (1240 mg, 3.2 mmol) were added to benzonitrile (20 ml) and refluxed at 195 °C for 19 h. The reaction was monitored by UV-VIS spectroscopy and thin-layer chromatography (TLC). After cooling, the reaction mixture was purified on an Al$_2$O$_3$ column (grade III, basic) using CHCl$_3$. Two fractions were eluted: a red solution of unreacted H$_2$TPP and a purple solution of U$^{\mathrm{IV}}$(TPP)$_2$ and U$_2^{\mathrm{III}}$(TPP)$_3$. The complexes were separated by TLC using benzene–chloroform (1:4). Individual complexes can also be obtained by dissolving the reaction mixture in ethanol after benzonitrile evaporation. The complex U$^{\mathrm{IV}}$(TPP)$_2$ is soluble in ethanol, whereas the complex U$_2^{\mathrm{III}}$(TPP)$_3$ remained in a solid phase. Filtration gives a green-violet solid residue of U$_2^{\mathrm{III}}$(TPP)$_3$ (18% yield). The evaporation of ethanol from the filtrate yields a pink-violet powder of U$^{\mathrm{IV}}$(TPP)$_2$ (14%).

The compounds U$^{\mathrm{IV}}$(TPP)$_2$ and U$_2^{\mathrm{III}}$(TPP)$_3$ are stable in air and have spectral and chemical properties which are consistent with 1:2 and 2:3 uranium/tetraphenylporphyrin ratios. An analogous synthetic procedure in phenol gives double and triple decker uranium tetraphenylporphyrins mixture in 3 h 40 min (a tetraphenylporphyrin band at 516 nm disappeared from the absorption spectrum of the reaction mixture). The yields of U$^{\mathrm{IV}}$(TPP)$_2$ and U$_2^{\mathrm{III}}$(TPP)$_3$ complexes decrease with the time of refluxing. Thus, we report here the first synthesis of the uranium complex with a triple decker structure.[13,†]

The NMR spectrum of the double decker complex agrees with published data for Th$^{\mathrm{IV}}$(TPP)$_2$[9] and Ce$^{\mathrm{IV}}$(TTP)$_2$ (TTP is the tetratolylporphyrin dianion).[4] The assignment of peaks for U$^{\mathrm{IV}}$(TPP)$_2$ is based on integrated intensity ratios and chemical shifts compared with analogous complexes. The NMR spectrum of the triple decker complex shows ten peaks due to ten kinds of protons: two of C$_4$H$_2$N (one inner and two outer macrocycles), two of p-Ph, three of o-Ph and three of m-Ph.

Double decker and triple decker complexes have different UV-VIS and IR spectra. The IR spectra of double and triple decker complexes are more complicated at 700 ($\gamma_{\mathrm{C-H}}$ of benzene rings), 800 ($\gamma_{\mathrm{C-H}}$ of pyrrole rings), 990–1010 ($\delta_{\mathrm{C-H}}$, $\nu_{\mathrm{C-C}}$, $\nu_{\mathrm{C-N}}$ of pyrrole rings) and 1540–1550 cm^{-1} (pyrrole ring stretching) than these of lanthanide monoporphyrinates (X)Ln$^{\mathrm{III}}$TPP.[14] The frequencies of vibrations $\nu_{\mathrm{U-N}}$ [430 and 436 cm^{-1} for U$^{\mathrm{IV}}$(TPP)$_2$ and U$_2^{\mathrm{III}}$(TPP)$_3$, respectively] are higher than $\nu_{\mathrm{Ln-N}}$ (Ln: Sm–Lu, 421–429 cm^{-1}). There are no bands at 212–216 cm^{-1} ($\nu_{\mathrm{M-Cl}}$, M–O) in the spectra of U$^{\mathrm{IV}}$(TPP)$_2$ and U$_2^{\mathrm{III}}$(TPP)$_3$ because of the absence of acidoligands X (Cl or PhO) from the complexes.

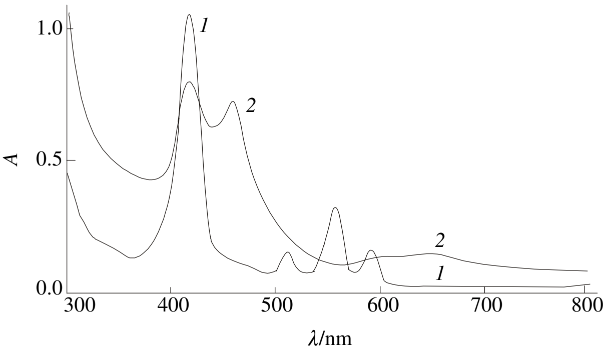


Figure 1 UV-VIS spectra of (*1*) U$^{\mathrm{IV}}$(TPP)$_2$ in ethanol and (*2*) U$_2^{\mathrm{III}}$(TPP)$_3$ in benzene.

The UV-VIS spectra of both of the uranium complexes are shown in Figure 1. A wide low-intensity band at 657.9 nm and an intense band at 462 nm appear in the U$_2^{\mathrm{III}}$(TPP)$_3$ spectrum as compared with (X)Ln$^{\mathrm{III}}$TPP spectra. Similar bands at 668 and 488 nm were found in the Nd$^{\mathrm{III}}$(OEP)$_2$ spectrum.[15] An extra band at 462 nm may be due to a porphyrin-to-uranium(III) charge-transfer transition. This could be connected with the striving of the two uranium atoms [or the neodymium atom in Nd$^{\mathrm{III}}$(OEP)$_2$] with a coordination number of 8 for a stable f^4 ($a_{2u}^1 t_{1u}^3$) configuration in the complex.

The double decker U$^{\mathrm{IV}}$(TPP)$_2$ complex has a 'normal' metalloporphyrin UV-VIS spectrum. Absorption bands in the visible region Q(0,0) are bathochromically shifted as compared to those of (X)Ln$^{\mathrm{III}}$TPP. For example, for (Cl)Lu$^{\mathrm{III}}$TPP, λ_{max} (lg ε) are 585 (3.5), 547 (4.0), 510 (3.6) and 416 (5.5) nm in ethanol.[14]

[†] *U$^{\mathrm{IV}}$(TPP)$_2$*. Electronic absorption spectrum (ethanol), λ_{max}/nm (lg ε): 595.3 (4.03), 556.9 (4.33), 516.0 (4.01), 422.5 (4.84). IR (KBr, ν/cm^{-1}): vibrations of pyrrole rings, 802 [γ(C–H)], 997, 1008 [ν(C–C), δ(C–H), ν(C–N)], 1372, 1388 [ν(C–N)], 1442 [ν(C=N)], 2870, 2930 [ν(C–H)]; vibrations of benzene rings, 706, 724 and 754 [γ(C–H)], 1072 and 1160, 1178 [δ(C–H)], 1527, 1578, 1600 [ν(C=C)], 3050, 3090 [ν(C–H)]; vibrations of U–N bonds, 430. ^{1}H NMR (CDCl$_3$) δ: 8.93 (m, 8H, J_{HH} 10.1 Hz, o-Ph), 8.19 (s, 16H, C$_4$H$_2$N), 7.74 (t, 8H, J_{HH} 7.75 Hz, m-Ph); 7.72 (t, 8H, J_{HH} 7.44 Hz, p-Ph), 7.52 (t, 8H, J_{HH} 6.82 Hz, m-Ph), 6.70 (m, 8H, o-Ph). Found (%): U, 16.1. Calc. for U$^{\mathrm{IV}}$(TPP)$_2$ (%): U, 16.26.

U$_2^{\mathrm{III}}$(TPP)$_3$. Electronic absorption spectrum (benzene), λ_{max}/nm (lg ε): 657.9 (4.40), 599.5 (4.36), 462.1 (5.12), 422.3 (5.16). IR (KBr, ν/cm^{-1}): vibrations of pyrrole rings, 808 [γ(C–H)], 1000, 1016 [ν(C–C), δ(C–H), ν(C–N)], 1375, 1380 [ν(C–N)], 1445 [ν(C=N)], 2875, 2950 [ν(C–H)]; vibrations of benzene rings, 704, 710 and 728 [γ(C–H)], 1080 and 1158, 1185 [δ(C–H)], 1528, 1550, and 1580, 1608 [ν(C=C)], 3070, 3100 [ν(C–H)]; vibrations of U–N bonds, 436. ^{1}H NMR (CDCl$_3$) δ: 9.97 (d), 8.42 (m), 8.24(s), 7.76 (t), 7.74 (t), 7.71 (t), 7.68 (t), 7.49 (t), 7.02 (d), 6.72 (d). Found (%): U, 19.8. Calc. for U$_2^{\mathrm{III}}$(TPP)$_3$ (%): U, 20.57.

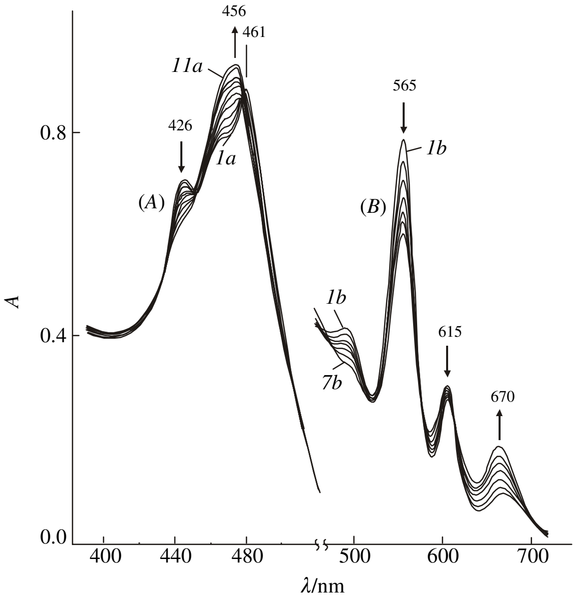
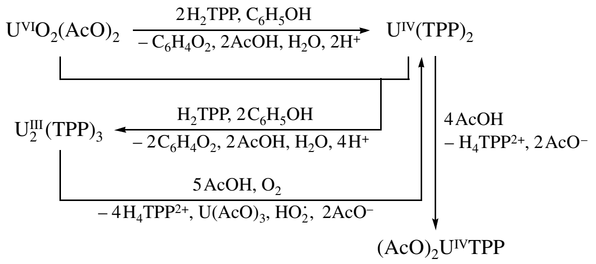


Figure 2 UV-VIS spectra during dissociation of $U_2^{III}(TPP)_3$ [(*A*), in benzene–40% AcOH, 308 K, 0–1 h] and $U^{IV}(TPP)_2$ [(*B*), in ethanol–55% AcOH, 353 K, 0–4 h]. (*1a*) $U_2^{III}(TPP)_3$, (*1b*) $U^{IV}(TPP)_2$, (*11a*) $U^{IV}(TPP)_2 + H_4TPP^{2+}$, (*7b*) $(AcO)_2U^{IV}TPP + H_4TPP^{2+}$.

No band is found between 450 and 500 nm in the spectrum of $U^{IV}(TPP)_2$. Analogous regularities were observed in $Ce^{IV}(OEP)_2$ and $Ce_2^{III}(OEP)_3$ complexes, for which the crystal structures were described.[16] The average Ce–N distance in triple decker $Ce_2^{III}(OEP)_3$ is 2.63 Å, which is considerably larger than the corresponding value in $Ce(OEP)_2$ (2.475 Å), reflecting the fact that the former molecule contains two Ce^{III} ions, whereas the latter molecule contains a smaller Ce^{IV} ion. Buchler *et al.*[16] explained the appearance of wide absorption bands in the region higher than 650 nm in the spectra of metalloporphyrins with two and more macrocycles by resonance interactions of the porphyrin ligands. The corresponding broad bands in the double decker complex $U^{IV}(TPP)_2$ is between 950 and 1000 nm.

Chemical properties of double and triple decker porphyrin complexes are essentially different. The complexes $U^{IV}(TPP)_2$ and $U_2^{III}(TPP)_3$ dissociate with a spectrophotometrically measured rate only in the presence of AcOH in concentrations above 40%. $U^{IV}(TPP)_2$ dissociates in a mixed ethanol–AcOH solvent at 330–350 K, whereas $U_2^{III}(TPP)_3$ dissociates in benzene–AcOH at 300–320 K. The dissociation rate constants of formally first order ($k_{obs}^{298\,K}$) at a 50% AcOH concentration in the above solvents are equal to 10^{-4} and 0.5×10^{-3} s^{-1} for U(TPP)$_2$ and U$_2$(TPP)$_3$, respectively. Taking into account that the reactivity of the complexes changes on going from one mixed solvent to another,[17] it is possible to note an enormous difference in the stability of the double and triple decker complexes. The UV-VIS absorption spectra of $U^{IV}(TPP)_2$ and $U_2^{III}(TPP)_3$ during dissociation (Figure 2) show a series of bands smoothly passing from the spectrum of the initial complex to another form of the complex: $(AcO)_2U^{IV}(TPP)$ and $U^{IV}(TPP)_2$, respectively. The spectra of the reaction mixtures contain additional absorption bands of the free protonated porphyrin H_4TPP^{2+}. The bands at 456 and 670 nm correspond to H_4TPP^{2+}. The reaction products were identified by UV-VIS spectra after extracting the products from the reaction mixture and purifying to remove AcOH traces by column chromatography on Al_2O_3 with $CHCl_3$. The double decker complex band at 516.0 nm (Figure 1) is absent from the absorption spectrum of the dissociation product $(AcO)_2U^{IV}TPP$ (Figure 2). The UV-VIS spectrum of $(AcO)_2U^{IV}TPP$ is in agreement with the spectrum published for $(Cl)_2UTPP$.[11]

The above data suggest the following reaction scheme of mutual transformations of different uranium complex species:



The acidocomplex $(AcO)_2U^{IV}TPP$ was not formed from H_2TPP and $UO_2(AcO)_2$ in benzonitrile, phenol, or imidazole, which is the best medium for the formation of (X)LnTPP complexes. Two complex compounds, $U^{IV}(TPP)_2$ and $U_2^{III}(TPP)_3$, are formed faster in a basic medium (phenol) than in benzonitrile. Phenol, being oxidised to quinone, promotes the reduction of uranium(VI) in initial $U^{VI}O_2(AcO)_2$ to the U^{IV} state, in which uranium cations can coordinate the porphyrin. Transformation of the double decker complex $U^{IV}(TPP)_2$ into the triple decker $U_2^{III}(TPP)_3$ is analogous to the mechanism of formation of similar phthalocyanine complexes.[1]

References

1 C. C. Leznoff and A. B. P. Lever, *Phthalocyanines: Properties and Application*, eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989, 1990, 1992, vols. 1–3.
2 F. Fernandez-Alonso, P. Marovino, A. M. Paoletti, M. Righini and G. Rossi, *Chem. Phys. Lett.*, 2002, **356**, 607.
3 J. W. Buchler, A. De Cian, J. Fisher, P. Hammerschmitt, J. Loffler, B. Scharbert and R. Weiss, *Chem. Ber.*, 1989, **122**, 2219.
4 J. W. Buchler, H. G. Kapellmann, M. Knoff, K. L. Lay and S. Pfeifer, *Naturforsch*., 1983, **38b**, 1339.
5 J. W. Buchler and J. Loffler, *Naturforsch*., 1990, **45b**, 531.
6 J. W. Buchler, P. Hammerschmitt, I. Kaufeld and J. Loffer, *Chem. Ber.*, 1991, **124**, 2151.
7 J. K. Duchowski and D. F. Bocian, *J. Am. Chem. Soc.*, 1990, **112**, 3312.
8 J. W. Buchler, A. De Cian, J. Fisher, M. Kihn-Botilinski and R. Weiss, *Inorg. Chem*., 1988, **27**, 339.
9 G. S. Girolami, S. N. Milam and K. S. Suslick, *J. Am. Chem. Soc*., 1988, **110**, 2011.
10 K. M. Kadish, G. Moninot, Y. Hu, D. Dubois, A. Ibnlfassi, J. M. Barbe and R. Guilard, *J. Am. Chem. Soc*., 1993, **115**, 8153.
11 G. S. Girolami, S. N. Milam and K. S. Suslick, *Inorg. Chem*., 1987, **26**, 343.
12 L. N. Lomova, L. G. Andrianova and B. D. Berezin, *Zh. Neorg. Khim*., 1991, **36**, 641 (*Russ. J. Inorg. Chem*., 1991, **36**, 361).
13 M. O. Senge, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 10.
14 T. N. Lomova and L. G. Andrianova, *Zh. Fiz. Khim*., 2000, **74**, 1587 (*Russ. J. Phys. Chem*., 2000, **74**, 1432).
15 J. W. Buchler and B. Scharbert, *J. Am. Chem. Soc*., 1988, **110**, 4272.
16 J. W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski, H. Paulus and R. Weiss, *J. Am. Chem. Soc*., 1986, **108**, 3652.
17 L. N. Lomova, L. G. Andrianova and B. D. Berezin, *Zh. Neorg. Khim*., 1989, **34**, 2867 (*Russ. J. Inorg. Chem*., 1989, **34**, 1639).

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