X-Ray Crystal Structure Analysis of Bisphthalocyaninatouranium(IV)

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Summary The crystal and molecular structure of bisphthalocyaninatouranium(IV), the first complex of an actinide element with the phthalocyaninato-ion, has been determined by *X*-ray diffraction analysis.

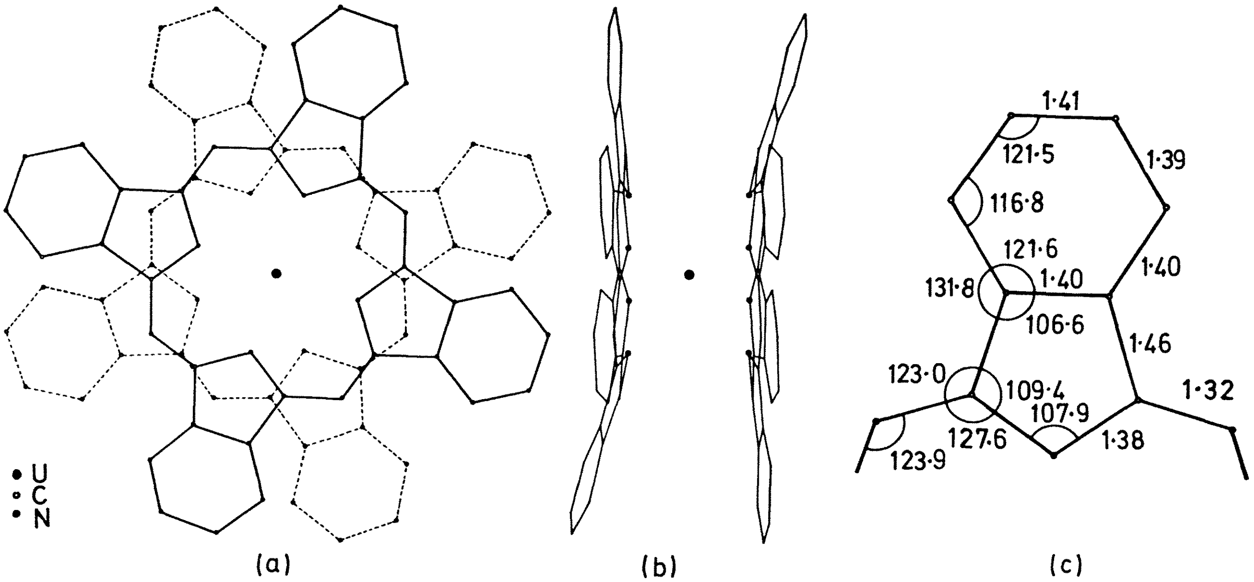
BISPHTHALOCYANINATOURANIUM(IV)[1] ($C_{64}H_{32}N_{16}U$) (**1**) is the first complex of an actinide element with the phthalocyaninato-ion (abbreviated to Pc) whose structure has been solved by *X*-ray diffraction.

A single crystal prepared by sublimation[2] was used for the *X*-ray analysis. *Crystal data*: $a = 18{\cdot}74_1$, $b = 18{\cdot}73_3$, $c = 15{\cdot}61_3$ Å, $\beta = 113{\cdot}6_9°$, $D_m = 1{\cdot}66$ g cm^{-3}, space group $C2/c$, $Z = 4$, $D_c = 1{\cdot}67$ g cm^{-3}. The asymmetric unit contains half a formula unit of (**1**). All reflections with $\theta \leqslant 28°$ were measured on a Siemens single crystal diffractometer using Mo-K_α radiation ($\theta/2\theta$ scan, 5-point measuring procedure, 6032 independent reflections of which 14% were considered unobserved [$I < 2\sigma_I$]).

The position of the uranium atom was deduced from a Patterson synthesis. A difference Fourier synthesis with uranium phases revealed the positions of all light atoms except hydrogen. In addition inspection of this difference Fourier synthesis permitted the exclusion of the alternative non-centrosymmetric space group Cc [one formula unit of (**1**) per asymmetric unit]. The uranium atom lies in a special position on the crystallographic twofold axis by which the two Pc ligands are related to one another.

The structure was refined by full-matrix least-squares first treating all atoms isotropically and then applying an anisotropic temperature factor to the uranium atom. The refinement converged at an R factor of 5·7%, and is being continued using data corrected for absorption.

The Figure (a and b) shows the structure of the molecule. The nitrogen atoms of the pyrrole rings of two Pc systems are in an 8-fold co-ordination around the uranium atom. The four pyrrole nitrogen atoms of each ligand form a square with sides of 2·80 Å. The uranium atom is equidistant from all the pyrrole nitrogen atoms (2·43 Å). The distance of the uranium atom from the planes defined by the pyrrole nitrogen atoms of the two ligands is 1·40$_5$ Å. The Pc ring systems are rotated *ca.* 37° away from a prismatic configuration. The co-ordination around the uranium atom thus deviates significantly (*ca.* 8°) from a square antiprism. The molecule possesses 422 symmetry in a first approximation, only one twofold axis being crystallographic.



(a) (b) (c)

FIGURE. *Molecular structure of bisphthalocyaninatouranium*(IV): (a) *Projection of the molecule onto the plane of the pyrrole nitrogen atoms*; (b) *Projection of the molecule along the crystallographic twofold axis. Only the pyrrole nitrogen atoms are marked.* (c) *Average bond lengths and angles in the Pc ring system. Errors in the average lengths and angles given are* 0·01 Å *and* 0·7°, *respectively.*

The Pc ring system is not planar but saucer-shaped [Figure (b)]. The four pyrrole nitrogen atoms form the base of the saucer which curves away from the uranium atom, owing, primarily, to the bonding of the pyrrole nitrogen atoms to the uranium. The sp^2-orbitals at the N atoms forming σ-bonds to the uranium are thus bent so as to be directed at the uranium atom. Further, the curvature of the Pc ring system leads to a decrease in the van der Waals energy of repulsion between the two ligands. The deviation of the non-uranium-bonded C and N atoms of the 16-membered aromatic core from the plane of the pyrrole N atoms is not uniform. For the C atoms the distances from the reference plane vary from 0·09 to 0·28 Å and for the somewhat more peripheral bridging N atoms from 0·10 to 0·35 Å. This leads to considerable deviations of the Pc system from its optimal 4*mm* symmetry. Thus, for example, the benzene rings make angles of 17·1, 11·4, 6·9, and 6·6° with the pyrrole nitrogen plane although the bond lengths and angles fulfil the above symmetry. Very small changes in bond angle can give rise to considerable conformational changes in the system as a whole. Similar conformations have been reported for SnPc[3] and SnPc$_2$.[4]

The mean bond lengths and angles in the Pc ring system [Figure (c)] do not differ appreciably from those of other metal–Pc complexes, *e.g.* CuPc,[5] PtPc,[6] SnPc,[3] (MnPcPy)$_2$-O,[7] and the metal-free H$_2$Pc.[8] The C–N distances in the inner 16-membered ring differ significantly from one another (1·38 and 1·32 Å), the π-bond order of the C–N (pyrrole) bond being smaller. Similar bonding occurs in the inner ring of the porphyrins.[9] Owing to the annellated 5-membered ring the benzene rings of the isoindole fragments have their symmetry reduced from 6/*mmm* to *mmm*.[3,7] The C–C bonds joining benzene rings to the inner 16-membered ring are 1·46 Å long which suggests a relatively weak interaction between the π-systems of the inner ring and of the benzene rings.

A comparison of this structure with Pc–metal complexes mentioned above indicates that the actinide element uranium does not show any special properties and that the bonding between the ligand (or ligands) and the actinide atom is analogous to that for other metals.

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The following paper was originally published in Chem. Comm., 1971, 187. *Unfortunately the formulae block was omitted, which renders the paper difficult to follow. We are therefore reproducing the paper with the formulae block.*