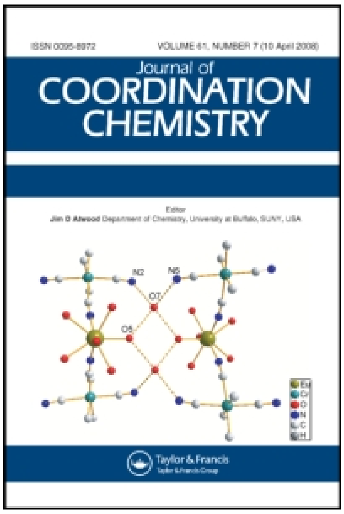

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Covalency in Actinide 5f Compounds: The ESCA of Diphtalocyaninato-Uranium(IV) and -Thorium(IV)

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To cite this Article Dubois, Ronald , Carver, James C. , Tsutsui, Minoru and Lux, Franz(1976) 'Covalency in Actinide 5f Compounds: The ESCA of Diphtalocyaninato-Uranium(IV) and -Thorium(IV)', Journal of Coordination Chemistry, 6: 2, 123 — 125

To link to this Article: DOI: 10.1080/00958977608079896
URL: http://dx.doi.org/10.1080/00958977608079896

J. Coord. Chem.
1976, vol. 6, pp. 123–125

SHORT COMMUNICATION
Covalency in Actinide 5f Compounds: The ESCA of Diphtalocyanato-Uranium(IV) and -Thorium(IV)

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(*Received June 21, 1976*)

The nature of the bonding in both UPc$_2$ and ThPc$_2$ (Pc = phthalocyaninato ion) has been studied by x-ray photoelectron spectroscopy. While the ESCA spectrum of each of the U(4f) levels reveals two electron 'shake-up' satellites characteristic of 5f-orbital participation in bonding, i.e. covalency, the corresponding Th(4f) levels do not. 'shake-up' satellite photopeaks observed in the U(4f) spectra probably arise from electron charge-transfer from molecular orbitals of both metal and ligand character to the corresponding anti-bonding molecular orbitals.

Sir:

Since 1968, when Streitwieser *et al.*,[1] first reported the successful synthesis of bis(cyclooctatetraene) uranium(IV), U(COT)$_2$ [I], numerous investigations have been directed towards elucidating the nature of the interaction between the actinides' 5f-orbitals and the bonding orbitals of various sigma and pi bonded ligands.[2–9] While most studies of organoactinide compounds have involved either NMR[5–8] or magnetic susceptibility measurements,[5,7,9] few if any have reported the use of x-ray photoelectron spectroscopy (ESCA) to probe for covalency in these f-orbital compounds. We have investigated the ESCA spectra of both diphthalocyaninato-uranium(IV)[II] and -thorium(IV)[10] [III] and wish to report evidence of f-orbital participation in bonding in the uranium derivative.

Examination of the carbon (1s) ESCA spectra of both UPc$_2$ and ThPc$_2$ revealed three photopeaks at approximately 284.3(.85), 285.6(1.45) and 287.6(.85)[11] ev of relative areas 0.58:0.38:0.04 respectively. The third low intensity photopeak located at 287.6 eV is assigned to electron "shake-up"[12] arising from the photoionization of core (1s) electrons of carbon atoms accompanied by the simultaneous excitation of a valence to an upper vacant energy level. Such satellite structure has been reported in the ESCA spectra of both H$_2$Pc and CuPc [13] and is dependent on the availability of low lying π^* empty orbitals on the ligand.

The nitrogen (1s) region of both UPc$_2$ and ThPc$_2$ reveals a single sharp photopeak at 398.6(.92)[11] eV (399. 1 eV if 284.8 eV is assumed to be the binding energy of the carbon (1s) reference peak[14]) which exhibits satellite structure separated from the main peak by 1.4 eV, similar to that observed in the carbon (1s) region. These values are consistent with those reported by Niwa *et al.*,[16] for various transition metal phthalocyaninato complexes and indicates that the coordination of two Pc ions to either U(IV) or Th(IV) differs little from coordination to the corresponding transition metal ions.

Examination of the U(4f) regions revealed in addition to the two normal photopeaks (U($4f_{7/2}$) and U($4f_{5/2}$)) two additional electron "shake-up" satellite peaks located at higher binding energies from each of the normal photopeaks. These satellite peaks probably arise from electron charge-transfer from the valence band to vacant upper energy levels. While both the U($4f_{7/2}$) and U($4f_{5/2}$) photo-peaks exhibit satellite structure, accurate deconvolution[17] of the U($4f_{5/2}$) level was hampered by its close proximity to the nitrogen (1s) peak of the Pc ions. This problem was not encountered with the U($4f_{7/2}$) satellite structure.

Deconvolution of the U($4f_{7/2}$) region resulted in a main peak at 379.9(.90) eV and two satellite photopeaks at 380.5(1.9) and 384.3(4.0) eV. These photo-

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peaks have been tentatively assigned to electron charge-transfer transitions ($L \rightarrow M$) from molecular orbitals of predominately ligand character to the corresponding antibonding molecular orbitals of predominately metal character. These assignments are supported by the observed FWHM of each satellite peak and our examination of the valence region of UPc_2.[18]

The observed ratio of the areas of the satellite peak located at 380.5 eV to the main photopeak at 379.9 eV was about 1.2 to 1 in poor agreement with the 1 to 5 ratio observed for the analogous U(4f) satellite peak observed in $RbUO_2(NO_3)_3$.[19] Since the extent of overlap is tied fundamentally to the effect of creating an inner shell vacancy, electron "shake-up" transitions are often enhanced if the transition energies are lowered and the electrons in the initial and final state orbitals tend to occupy the same space.[12a] Thus, the increased ratio observed in UPc_2 might be indicative of the greater overlap and hence covalency between the U(5f) orbitals and the bonding orbitals of the Pc ligands.

Although no molecular orbital calculation on UPc_2 has yet been attempted, the spatial orientations of the U(5f) orbitals in UPc_2 should not differ appreciably from that observed in $U(COT)_2$ where the predominant U(5f)-E_{2u} molecular orbital was calculated to contain approximately 22% ligand character,[9] Fig. 1. Thus the U(5f) orbitals of UPc_2 should play a significant role in bonding.

The Th(4f) region revealed two photopeaks at 334.5(1.0) and 343.8(1.0) eV. These peaks have been assigned to the Th($4f_{7/2}$) and Th($4f_{5/2}$) levels, respectively. Unlike its uranium analog, these photopeaks do *not* show any satellite structure characteristic of electron "shake-up" transitions. Similar results have been reported by Jϕrgensen and Berthou[19] for Th(IV) compounds.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support of the Robert A. Welch Foundation (Grant No. A-240), the Office of Naval Research, and NSF Grant No. Gp-41563 under which the ESCA spectrometer was purchased; and to Dr. Paul Roling for many stimulating and informative discussions.

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11. The first number is the binding energy in eV relative to the $Au(4f_{7/2})$ = 83.8 eV line, and the second number in parentheses is the lines full-width at half-maximum (FWHM) in ev.
12. For a current review of electron "shake-up" theory, see: (a) G. A. Vernon, G. Stucky and T. A. Carlson, *Inorg. Chem.*, **15**, 278 (1976).
    (b) M. A. Brisk and A. D. Baker, *J. Electron Spectrosc.*, **7**, 197 (1975).
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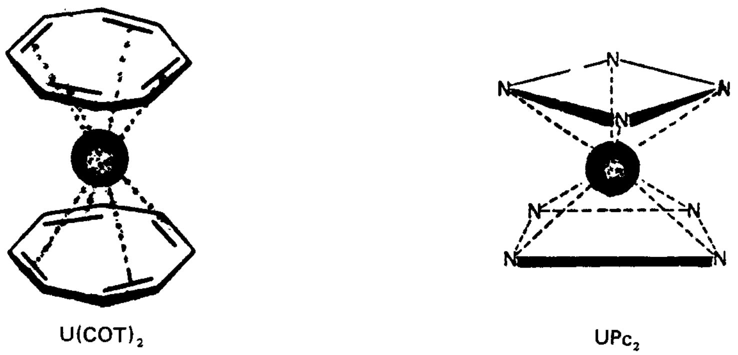
14. Some authors have questioned the use of sublimed gold as a calibrant for ESCA Spectroscopy, reference 15. Because of this, Y. Niwa *et al.* have assigned the carbon (1s) standard peak to 284.8 eV and used it as a calibrant.



$U(COT)_2$ UPc_2

FIGURE 1 Coordination geometries of $U(COT)_2$ [I] and UPc_2 [II]

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18. While a thorough discussion of the quantum mechanical arguments in support of our assignments is not feasible in this communication, these factors will be discussed in a subsequent paper where the valence regions of both $ThPc_2$ and UPc_2 and UPc_2 will be reported.
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