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⑥ Satellite Structures in the ESCA Spectra of Diphthalocyaninato-Lanthanides(III) and -Actinides(IV).

by

⑩ K. Tatsumi, K. Kasuga ~~and~~ M. Tsutsui

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Satellite structures of Ln $3d_{5/2}$ and An $4d_{5/2}$ photoelectron lines have been investigated for a number of diphthalocyaninato-lanthanide(III) and -actinide (IV) complexes. Ligand → f shake-up satellites were not observed in Pr, Nd, and Gd complexes, while La, Ce, Th and U complexes showed strong shake-up peaks. A new interpretation is put forward to explain the sharp variation in intensity observed throughout the lanthanide and actinide series.

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K. Tatsumi, K. Kasuga and M. Tsutsui*

Department of Chemistry
Texas A&M University
College Station, Texas 77843

Abstract: Satellite structures of Ln $3d_{5/2}$ and An $4d_{5/2}$ photoelectron lines have been investigated for a number of diphthalocyaninato-lanthanide(III) and -actinide(IV) complexes. Ligand → f shake-up satellites were not observed in Pr, Nd, and Gd complexes, while La, Ce, Th, and U complexes showed strong shake-up peaks. A new interpretation is put forward to explain the sharp variation in intensity observed throughout the lanthanide and actinide series.

Satellite Structures in the ESCA Spectra of Diphthalocyaninato-Lanthanides(III) and -Actinides(IV)

Sir: Recently, X-ray photoelectron spectroscopy (ESCA) has been successfully applied to the study on the electronic structure of f-transition metal complexes.[1,2] Special attention has been directed towards the satellites observed in the Ln 3d and An 4f photoelectron lines, since they are a potential source of information on the nature of bonding.[3-10] Some attempts have been made to understand these particular satellites, though most of the suggested mechanisms are unsatisfactory by themselves to explain the sharp variation in intensity throughout the Ln and An series. Coherent explanation for the satellite origin is now essential to the proper understanding of the electronic structure of f-elements. In view of the interest in satellite structure, we have investigated ESCA spectra of a series of diphthalocyaninato-lanthanides ($H[LnPc_2]$ (Ln=La, Ce, Pr, Nd, and Gd) and -actinides $AnPc_2$ (An=Th and U). In particular, the satellites accompanying lanthanide $3d_{5/2}$ and actinide $4d_{5/2}$ signals have been examined.

We wish to report here findings of our satellite measurements and a new approach to interpret the satellite structure. This approach is based on a hypothesis that half-occupied f orbitals play an important role in the striking change of the satellite intensity throughout the f-transition metal series.

All spectra reported here were measured on a Hewlett-Packard 5950A ESCA spectrometer using monochromatized Al K_α radiation. The charging effects were neutralized by an electron flood gun. Each of the samples was internally calibrated to the intense C 1s photopeak observed in the lowest energy side.[11] The binding energy of the standard peak is assumed to be 284.8 eV.

Figure 1 shows the observed lanthanide $3d_{5/2}$ and actinide $4d_{5/2}$ spectra of the diphthalocyaninato complexes. Each of the spectra reveals additional structure adjacent to the normal $3d_{5/2}$ or $4d_{5/2}$ signal. The binding energies of the main $3d_{5/2}$ and $4d_{5/2}$ peaks (E) and their satellites (ΔE) are given in Table 1, as well as the intensity ratio (R) of the satellite to the main line. (Figure 1) (Table I)

The intense satellites at ≃ 4 eV from each of a principal $3d_{5/2}$ levels in La(III) and Ce(III) complexes are favorably assigned to charge-transfer shake-up from ligand to empty 4f orbital(s) (L → 4f).[3] We observed a similar satellite in *both* Th and U $4d_{5/2}$ photopeaks of $ThPc_2$ and UPc_2 respectively, in opposition to the common belief that the 4d level in Th(IV) compounds is satellite-free.[13] The evidence appears to provide valuable aids for the discussion of satellite origins and electronic structures of f-elements. The $3d_{5/2}$ signal of $H[PrPc_2]$ also show a satellite to higher binding energy side. The satellite, however, is not attributable to the L → 4f transition due to its small energy-separation ΔE= 1.7 eV. Moreover, the L → 4f transition fails to explain the presence of shoulders to lower binding energy in Pr and Nd $3d_{5/2}$ signals. These satellites[14] may be either a feature of multiple splitting caused by 4f unpaired electrons or strong Auger lines of the MV-N67-N67 type.[15] The weak satellite at 9.2 eV from the principal line in the Gd(III) ($4f^7$) complex might again provide an argument in favor of a L → 4f (half-occupied in this case) charge-transfer mechanism.[16] However, the relatively large energy-separation (ΔE = 9.2 eV) makes rather questionable the application of the L → 4f mechanism. In general, half occupied 4f levels are lower in energy than unoccupied 4f levels, and L → 4f transition energy of the Gd(III) complex, even if the transition occurs, must be smaller than that of the La or Ce analogue. We might ascribe the satellite in the Gd $3d_{5/2}$ line to another type of transition such as an intraatomic or 4f → L shake-up process.

A puzzling question now arises as to the L → f charge-transfer mechanism responsible for the satellites of lanthanide and actinide complexes. The L → 4f shake-up satellite was not observed in Pr(III) (f^2) and Nd(III) (f^3) complexes which have sufficient vacant f orbitals to receive electrons from ligands, whereas La(III) (f^0) and Ce(III) (f^1) complexes reveal strong satellites. In actinide, on the other hand, *both* Th(IV)(f^0) and U(IV)(f^2) complexes have a propensity to show the satellites.

It is tempting to relate the shake-up intensity to covalency of the M-L bonding, i.e., the more covalent the bonding, the more intense the satellite.[5] However, the satellite of H[$LnPc_2$] is much more intense than that of $ThPc_2$, though the latter complex must have more covalent character in M-L bonding than the former. Magnetism of the compounds also cannot interpret this puzzling question.

Let us now point out that adiabatic relaxation upon the core-hole creation is a crucial factor governing the satellite intensity observed.[17,18] Recent MS X_α calculations of LaF_3 and CeF_3 found a large influx of electrons from the ligands to the 4f shell during core ionization.[19] In the ground state of the lanthanide complexes H[$LnPc_2$], an occupied molecular orbital (ϕ_L), which is localized on the ligands, is expected to have only small amount of metal 4f admixture. The antibonding counterpart (ϕ_M^*) of the occupied orbital is then essentially 4f orbital. Due to the electron flow upon core-ionization, the antibonding counterpart should gain ligand character in core-ionized state ($\phi_M^*(i)$). The strong satellite of the La complex can be explained by the large overlap between these MOs, $<\phi_L|\phi_M^*(i)>$ under the sudden approximation. The presence of half occupied 4f orbital(s) appears to cause a decrease in shake-up intensity of H[CePc$_2$] and a vanishing of the shake-up of H[PrPc$_2$] and H[NdPc$_2$]. This is likely because the half occupied 4f orbital(s) can receive electrons, instead of vacant 4f orbitals, from ligand orbitals upon core-ionization. The reduced electron flow to the half-filled 4f level results in considerable diminution of ligand character in ϕ_M^* orbital and consequently a much smaller overlap $<\phi_L|\phi_M^*(i)>$ In the actinide complexes [AnPc$_2$], ϕ_L orbital must have some 5f admixture even in theirground states. Thus, the electron flow from ligands to 5f levels is not as significant as it is in the lanthanide case. In such a situation, we cannot anticipate either the large overlap $<\phi_L|\phi_M^*(i)>$, i.e., strong satellite, or the significant role of half-occupied 5f orbital(s) to reduce shake-up intensity. Detailed description of the interpretation will be given in a forthcoming paper.[20]

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K. Tatsumi[21], K. Kasuga, and M. Tsutsui*

Department of Chemistry
Texas A&M University
College Station, Texas 77843

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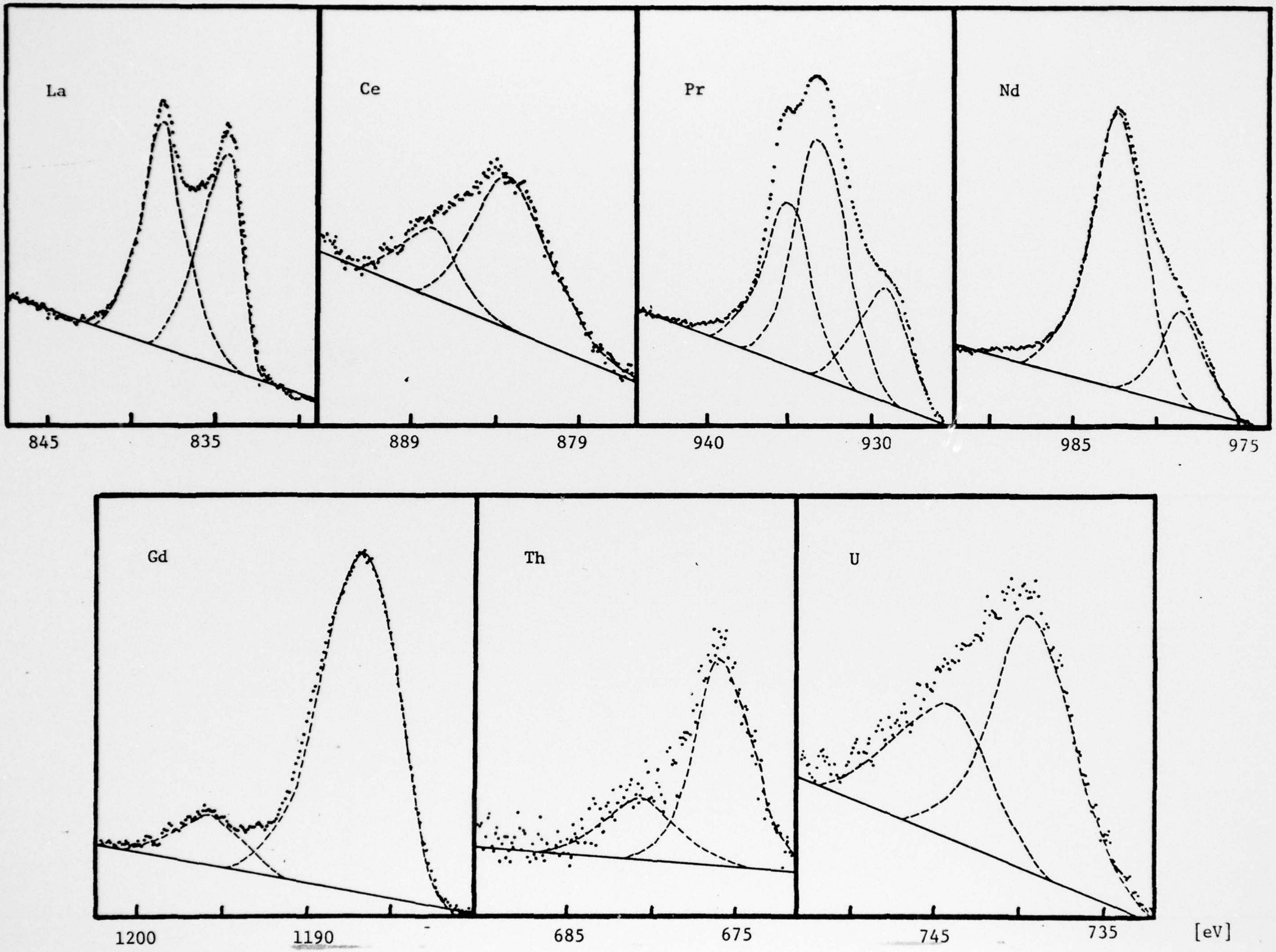
Table I. Binding Energies (E) of Ln 3d5/2 and An 4d5/2 of Diphthalocyanine Complexes, and their Satellite Energies (ΔE) measured from the Parent Peaks (eV).

		Satellite Energy (ΔE)		
Compound	Binding Energy (E)	A	B	C
	$3d_{5/2}$			
$H[LaPc_2]$	834.5	------	3.9(1.00)*	------
$H[CePc_2]$	883.6	------	4.2(0.46)	------
$H[PrPc_2]$	933.5	-4.2(0.46) 1.7(0.68)	------	------
$H[NdPc_2]$	982.4	-3.7(0.34)	------	------
$H[GdPc_2]$	1186.7	------	------	9.2(0.15)
	$4d_{5/2}$			
$ThPc_2$	675.8	------	4.6(0.30)	------
UPc_2	739.5	------	≃4.9(≃0.52)	------

* Values in parentheses are satellite-to-main signal intensity ratios (R).

Figure Caption

Figure 1. Photoelectron spectra of the Ln3$d_{5/2}$ and An4$d_{5/2}$ levels of H[LnPc$_2$] (Ln = La, Ce, Pr, and Nd) and AnPc$_2$ (An=Th and U). Deconvolution of the satellite structure is given by the dotted lines.


La
Ce
Pr
Nd
845
835
889
879
940
930
985
975
Gd
Th
U
1200
1190
685
675
745
735
[eV]

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