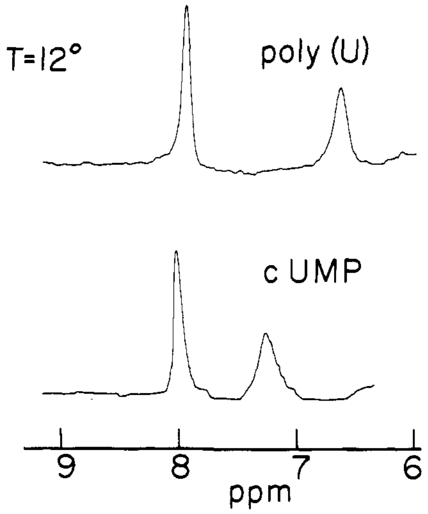

Figure 5. 300-MHz ^{1}H NMR spectra of cUMP and poly(U) in H_2O. The poly(U) sample was dialyzed against 0.1 M NaCl, 10 mM cacodylate buffer at pH 7.0. The pH of the cUMP sample was 5.9.

DNA even though the stacking interactions of DNA are thought to be more energetically favorable.[1,2] The T_m is determined by the relative stabilities of the helical and single-stranded (disordered) states of the nucleic acid. The 2′-OH-phosphate-water bridge is thought to only be present in helical RNA and hence would tend to stabilize the helical state relative to the single-stranded (disordered) state. At this time we tentatively propose that the 2′-OH-water-phosphate bridge is an important, though not the only, factor in the stabilization of the A form of RNA as well as contributing to the greater stability of helical RNA relative to helical DNA.

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Communications to the Editor

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 toward 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 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 5950 Å ESCA spectrometer using monochromatized Al Kα radiation. The charging effects were neutralized by an electron flood gun. Of the compounds we studied, ThPc_2 and UPc_2 had been prepared by Franz Lux, and lanthanide phthalocyanine compounds[11] were synthesized and purified as described in a previous paper.[11b] The powdered samples were stuck on double-stick scotch tape. Each of the samples was internally calibrated to the intense C 1s peak observed in the lowest energy side.[12] The binding energy of the standard peak is assumed to be 284.8 eV. The metal phthalocyanine complexes are extremely stable and we did not observe any visible evidence of decomposition and/or oxidation of the sample.

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

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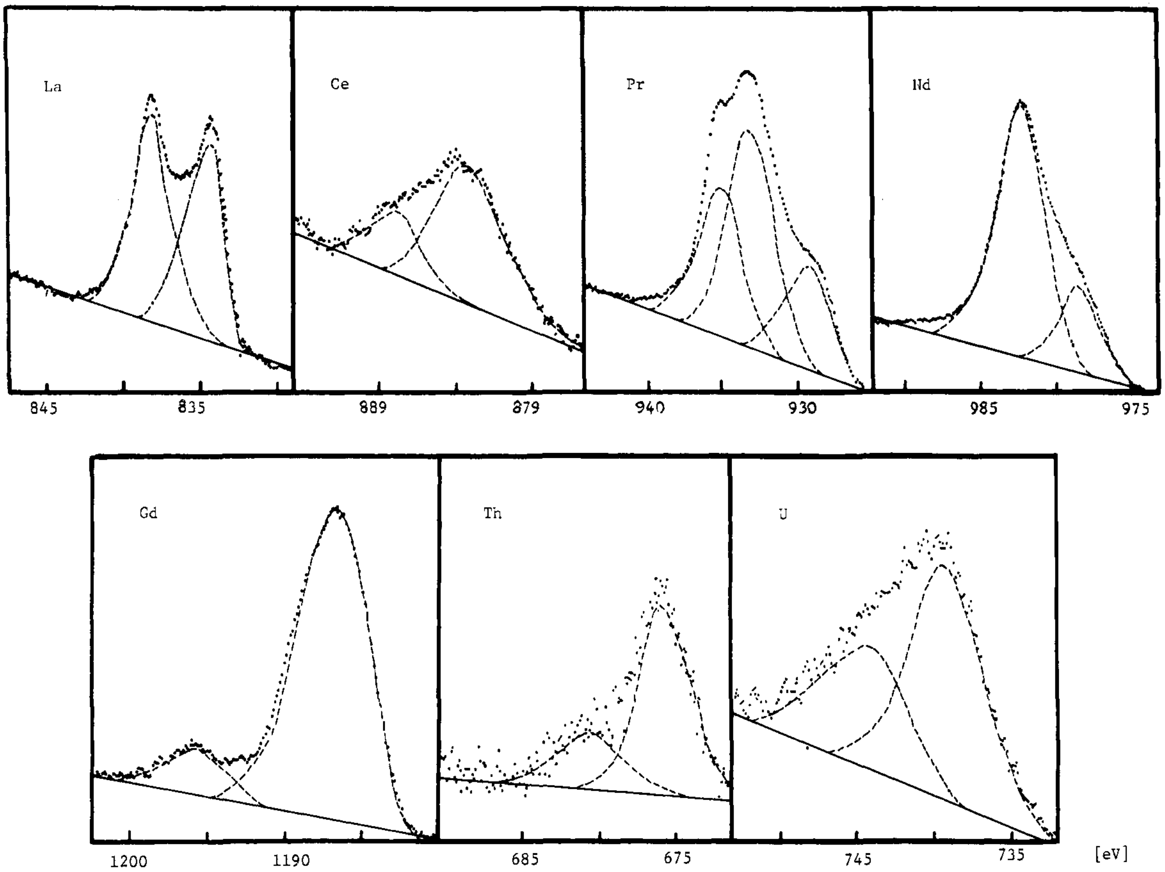

Figure 1. Photoelectron spectra of the Ln3$d_{5/2}$ and An4$d_{5/2}$ levels of H[LnPc$_2$] (Ln = La, Ce, Pr, and Nd) and AnPc$_2$ (An = Th and U). Deconvolution of the satellite structure is given by the dotted lines.

Table I. Binding Energies (*E*) of Ln 3$d_{5/2}$ and An 4$d_{5/2}$ of Diphthalocyanine Complexes, and their Satellite Energies (ΔE) measured from the Parent Peaks (Electronvolts)

compd	binding energy, *E*	satellite energy (ΔE) A	B	C
		3$d_{5/2}$		
H[LaPc$_2$]	834.5		3.9 (1.00)[a]	
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)
		4$d_{5/2}$		
ThPc$_2$	675.8		4.6 (0.30)	
Upc$_2$	739.5		$\simeq$4.9 ($\simeq$0.52)[b]	

[a] Values in parentheses are satellite to main signal intensity ratios (*R*). [b] Note 13.

3$d_{5/2}$ or 4$d_{5/2}$ signal. The binding energies of the main 3$d_{5/2}$ and 4$d_{5/2}$ peaks (*E*) and their satellites (ΔE) are given in Table I, as well as the intensity ratio (*R*) of the satellite to the main line.

The intense satellites at $\simeq$4 eV from each of a principal 3$d_{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 $\rightarrow$ 4f).[3] We observed a similar satellite in *both* Th and U 4$d_{5/2}$ 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.[14] The evidence appears to provide valuable aids for the discussion of satellite origins and electronic structures of f elements. The 3$d_{5/2}$ signal of H[PrPc$_2$] also show a satellite to higher binding energy side. The satellite, however, is not attributable to the L $\rightarrow$ 4f transition owing to its small energy separation, ΔE = 1.7 eV. Moreover, any usual shake-up mechanism fails to explain the presence of shoulders to lower binding energy in Pr and Nd 3$d_{5/2}$ signals. The unique satellite was also observed for trihydroxide compounds of Pr and Nd.[16] The interpretation based on the charging effect can be ruled out because the satellite structure was not affected by the changes in voltage and emission current of the electron flood gun. The satellites may be a feature of multiple splitting caused by 4f unpaired electrons, strong Auger lines of the MV-N67-N67 type[17] or "shake-down" mechanism.[18] 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 $\rightarrow$ 4f (half-occupied in this case) charge-transfer mechanism.[19] However, the relatively large energy separation (ΔE = 9.2 eV) makes rather questionable the application of the L $\rightarrow$ 4f mechanism. In general, half-occupied 4f levels are lower in energy than unoccupied 4f levels, and L $\rightarrow$ 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 3$d_{5/2}$ line to another type of transition such as an intraatomic or 4f $\rightarrow$ L shake-up process.

A puzzling question now arises as to the L $\rightarrow$ f charge-transfer mechanism responsible for the satellites of lanthanide and actinide complexes. The L $\rightarrow$ 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 which relates to multiple splitting of core levels 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.[20,21] Recent MS Xα calculations of LaF$_3$ and CeF$_3$ found a large influx of electrons from the ligands to the 4f shell during core ionization.[22] 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. Owing to the electron flow upon core ionization, the antibonding counterpart ($\phi_M^*(i)$) should gain ligand character in core-ionized state. The strong satellite of the La complex can be explained by the large overlap between these MO's, $\langle \phi_L | \phi_M^*(i) \rangle$ 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 possible 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 $\langle \phi_L | \phi_M^*(i) \rangle$. In the actinide complexes [AnPc$_2$], the ϕ_L orbital must have some 5f admixture even in their ground states. Thus, the electron flow from ligands to 5f levels is not so significant as it is in the lanthanide case. In such a situation, we cannot anticipate either the large overlap $\langle \phi_L | \phi_M^*(i) \rangle$, i.e., strong satellite, or the significant role of half-occupied 5f orbital(s) to reduce shake-up intensity.

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Efficient Trapping of Silylenes through Disilene Intermediates[1]

Sir:

During the course of the study on disilenes, we have found that variously substituted silylenes (**1**) can dimerize efficiently to disilenes (**2**) which are trapped with anthracene. Previously, Margrave and Perry[2] have rationalized results of the reaction of difluorosilylene with acetylene at low temperature in the condensed phase by postulating the existence of tetrafluorodisilene (or diradical), and Conlin and Gaspar[3] have shown recently that dimethylsilylene dimerizes in the gas phase at 600–700 °C to give tetramethyldisilene as an intermediate. Existence of the latter has been evidenced from the reaction product identical with the known rearrangement product found previously in the reaction of disilene.[4]

Cothermolysis of 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**3a**)[5] and anthracene in a sealed tube at 350 °C gave 2,3,5,6-dibenzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**6a**)[4] in 36% yield along with 1,2,3,4-tetraphenylnaphthalene. The formation of **6a** is rationalized most reasonably in terms of the Diels–Alder-type reaction of highly reactive tetramethyldisilene with anthracene, an efficient enephile, as depicted in Scheme I. The phenylmethylsilylene and the diphenylsilylene were also generated similarly from **3b** and **3c** (350 °C, 1 h) and gave **6b** (40% yield) and **6c**[6] (46% yield), respectively, by the reaction with anthracene.

7-Silanorbornadiene is a well-known thermochemical silylene generator[5] and, in fact, on thermolysis of **3a** in the presence of both 2,3-dimethylbutadiene and anthracene, the dimethylsilylene was trapped with the diene affording 1,1,3,4-tetramethyl-1-sila-3-cyclopentene (**7a**)[7] in 36% yield. However, under these conditions, **6a** was not detected in the thermolysate. This fact can be explained well by postulating that the butadiene traps the dimethylsilylene so efficiently that the concentration of the silylene would be too low to undergo dimerization.

Another possible route to **6a** without involving intermediate disilene is a stepwise insertion of the dimethylsilylene into anthracene. Such a route has to involve 2,3,5,6-dibenzo-7,7-dimethyl-7-silabicyclo[2.2.1]hepta-2,5-diene as a direct precursor to **6a**. At this moment, this possibility cannot be excluded completely. However, in carbene chemistry, it is known that only the 1,2 adduct was obtained from the thermal reaction of :CHCO$_2$R with anthracene.[8a,b] Although in some cases, a hypothetical 9,9a adduct of :CH$_2$ and anthracene, that subsequently isomerized to dibenzonorbornadiene, was obtained as a minor product;[8c] in the case of thermally generated silylenes, such adducts of cyclic dienes gave ring-expanded products predominantly rather than rearranged products.[8d,e] The 7-silanorbornadiene system, such as the precursor itself,

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