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A Photoelectron Study of Pentavalent Uranium Imido Complexes

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There is currently considerable interest in the synthesis and characterization of complexes containing multiple bonds between uranium and first row elements [1–3]. Uranium–carbon multiple bonds have been described as primarily ionic on the basis of U=C distances, although there is mention of considerable π-overlap between uranium and carbon in $(\eta\text{-}C_5H_5)_3U{=}CHP(Ph)_2Me$ [4]. In the two reported structural characterizations of uranium imido complexes, the U–N–R groups were found to be distorted from an ideally linear geometry [3]. These bent U–N–C angles could result from simple crystal packing forces (the reason given for the linear and bent imido functionalities in $OsO_2(NCMe_3)_2$) [5]. Alternatively, the distortion may have an electronic origin.

The uranium(V) imido complexes $(MeC_5H_4)_3U{=}NR$ ($R = CMe_3$, $SiMe_3$, Ph) and $[(Me_3Si)_2N]_3U{=}NSiMe_3$ have been examined by gas phase He I and He II photoelectron (PE) spectroscopy in order to elucidate the nature of U=X multiple bonding.

Experimental

The compounds were prepared according to literature methods [6]. PE spectra were obtained using a PES Laboratories 0078 spectrometer fitted with a Helectros lamp giving both He I and He II radiation. The spectra were referenced relative to the He self-ionization band, with xenon and nitrogen calibration gases to determine the scaling factor. Ionization potential (IP) values are correct to within 0.05 eV.

Results and Discussion

The f-orbital ionization energies (IE) were readily identified by the large relative cross-section increase of the f-band upon switching from He I to He II radiation [7] (see Fig. 1).

In the cyclopentadienyl complexes, both the N-π and f-electron band energies are found to be substantially influenced by the imido R substituent. The f-electron IE values of 5.97 eV ($R = CMe_3$), 6.32 eV ($R = C_6H_5$) and 6.45 eV ($R = SiMe_3$) establish the relative electron-withdrawing ability of the imido groups to be $NSiMe_3 > NC_6H_5 > NCMe_3$. The stabilizing nature of the trimethylsilyl group attached to anionic ligands has been noted previously [8], in contrast to the usual description of $SiMe_3$ as an electron-donating substituent in organic chemistry [9]. In analogous $Me_3P{=}NR$ complexes, the $SiMe_3$ substituent was also found to stabilize the N-π band relative to Ph or CMe_3 by 1.25 eV and 0.74 eV respectively [8d]. The large destabilization of the N-π band by the phenyl group is also observed in the uranium imido complexes. The N-π band was observed at 6.97 eV in the phenylimido complex; in the two other cyclopentadienyl (Cp) complexes this band could not be unambiguously assigned, as it apparently overlapped with the Cp-π bands (adiabatic IE 7.37 eV).

A number of observations can be obtained from the spectra of $[(Me_3Si)_2N]_3U{=}NSiMe_3$. First, the metal IE value (6.88 eV) is higher than that in $(MeC_5H_4)_3U{=}NSiMe_3$ (6.45 eV), thus the η^5-MeC_5H_4 is more electron-donating than the monodentate silylamide. This may offer an explanation as to why $(Me_3SiC_5H_4)U(III)$ forms a weak coordination complex with CO, whereas $[(Me_3Si)_2N]_3U$ does not [10, 11].

The N-π band of the imido substituent has been assigned in the silylamide complex at 8.14 eV, significantly lower in energy than the band assigned to the amido N-π electrons at 8.74 eV. This is substantially higher than that found in the phenylimido complex, again supporting the contention that the $SiMe_3$ functionality is withdrawing electron density from the nitrogen dianion. The severe destabilization of the N-π band in the phenylimido complex is presumably due to a repulsive interaction with the phenyl π orbitals, and may account for the observed differences in geometry between $(MeC_5H_4)_3U{=}NPh$ (U–N–C = 167°) [3b] and $[(Me_3Si)_2N]_3U{=}NSiMe_3$ (U–N–Si = 180° [12]. This repulsive interaction would also account for the observation that while the magnitudes of the metal IE values in the cyclopentadienyl complexes are in the order $NSiMe_3 > NC_6H_5 > NCMe_3$, those of the N-$\pi$ ionizations are in the order $NC_6H_5 < NSiMe_3$ or $NCMe_3$.

Finally, we note the increase in both the metal and amido N-π IE values relative to those in the trivalent uranium complex [11] $[(Me_3Si)_2N]_3U$. This implies that as the oxidation state of the metal is increased, there is a distinct polarization of the amido nitrogen

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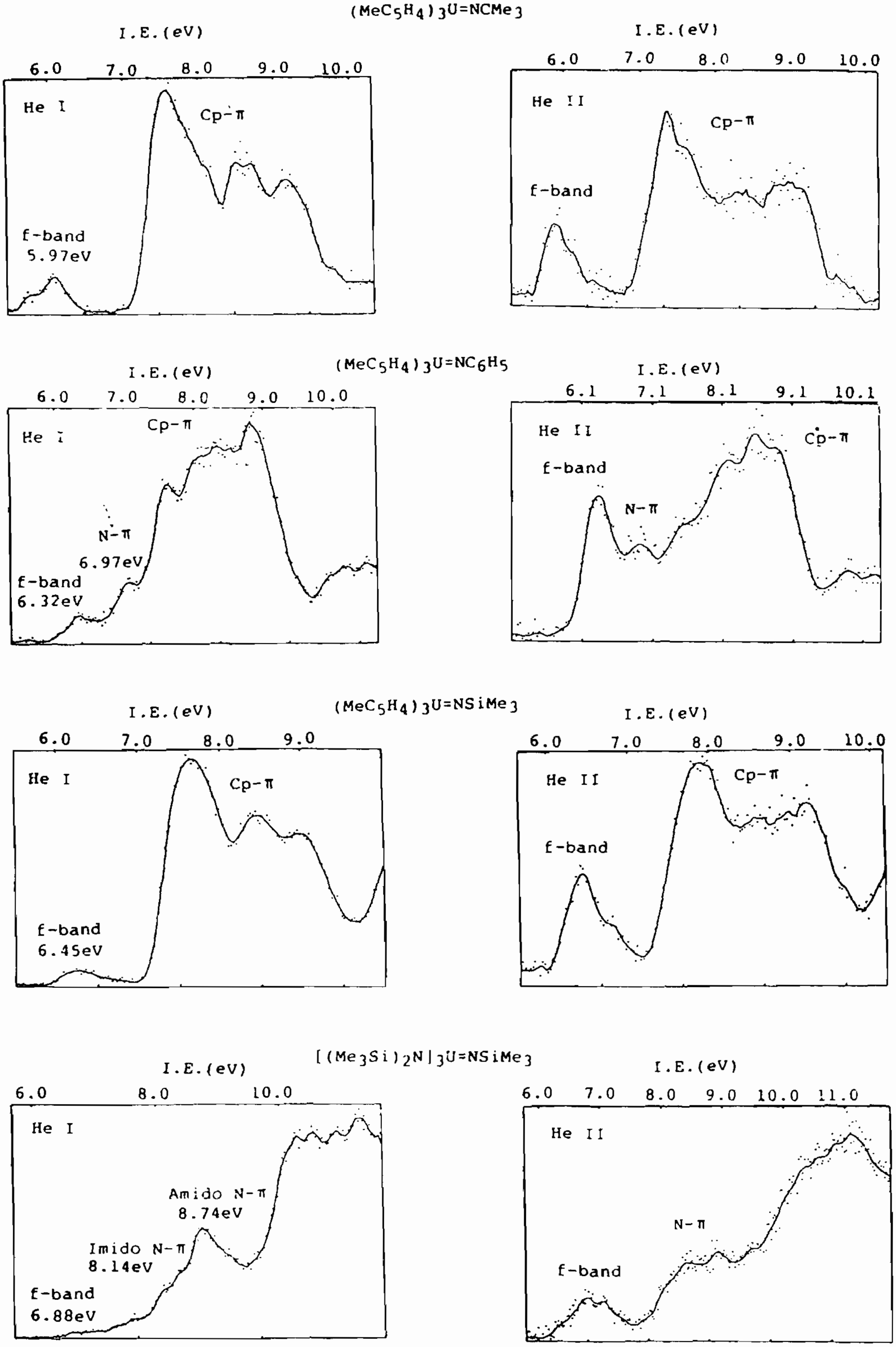

Fig. 1. He I and He II PE spectra of $(MeC_5H_4)_3U{=}NR$, (R = CMe_3, $SiMe_3$, C_6H_5) and $[(Me_3Si)_2N]_3U{=}NSiMe_3$.

π electrons toward the metal, away from the silicon d-orbitals. The width of the f-band in both the U(III) and U(IV) amido complexes is far greater than that observed for any $(\eta\text{-}C_5H_5)_3U$(IV or V) complexes. Thus, in the silylamide complexes, the less sterically congested metal coordination sphere is still capable of reorganizing upon ionization, and variation of U—N distances with metal oxidation state is expected to be greater than that observed for U—Cp distances.

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