U(IV), and, where possible, of Zr(IV) because of their high vapour pressure at reasonable temperatures. Furthermore, the very intriguing series of complexes which can be prepared by stepwise substitution of cp rings by monodentate or bidentate ligands (namely the $U(C_5H_5)_3X$ and $U(C_5H_5)_2X_2$ series) allow to detect variations of electronic structures depending upon electronic prerequisites of the ligand as well as upon geometries.

The series which have been object of study are:

Cyclooctatetraene Complexes [2]
$U(C_8H_8R)_2$ R = $-Si(CH_3)_3$,$-P(t\text{-}but)_2$.

Cyclopentadienyl Complexes
i) $M(C_5H_4R)_4$ M = U, Th; R = H, CH_3 [3].
ii) $M(C_5H_5)_3X$ M = U, Th; X = F, Cl, Br, $-CH_3$, $-OC_2H_5$, $-NCS$, BH_4^- [4].
iii) $M(C_5R_5)_2X_2$ M = U, Th, Zr; R = H, CH_3; X = $-NH_2$, Cl, $-CH_3$, BH_4^- [5, 6].
iv) $M(C_9H_7)_3X$ M = U, Th; X = Cl, Br, $-CH_3$, $-OCH_3$ [7].

All these complexes are of pseudo-tetrahedral geometry.

v) $M(C_5H_5)_2X_2$ M = U; X = carboxylate and dithiocarbammate [8] anions.

These latter complexes are of 'pseudo-octahedral' geometry.

The spectra always show clearly identifiable bands attributable to $5f^{-1}$ ionizations, to suitable symmetry combinations of e_1'' MOs of various cp rings of D_{5h} symmetry and, finally, to ionizations of electrons mainly localized on the $-X$ ligand (when present). As far as $5f^{-1}$ ionizations are concerned, the associated IE's span a wide range and they mostly depend upon the nature of the ligand X. Nevertheless, simple electronegativity arguments do not allow a straightforward correlation. The possible effects due to extra-atomic relaxation terms are also discussed. Finally, the energy dispersion of ionziations of symmetry combinations of cp based MOs seem to be greatly dominated by effects due to interligand repulsion. Furthermore, the trend of intensity variations upon switching from He–I to He–II radiations provides information on the nature of the metal-to-ligand bonding.

Classical Coordination Complexes

In the case of classical coordination complexes, studies spanned series of d and f transition element complexes with an identical ligand array:

i) $M(acac)_4$ M = U, Th, Zr; acac = acetylacetonate anion [9, 10].
ii) $UO_2(acac)_2$ [9, 10].
iii) M(trop) M = U, Th, Zr; trop = tropolonate anion [11].

The most striking result of this comparison is that the spectra, hence many of the bonding characteristics, are so similar.

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Excited-state Properties of Cyclopentadienylytterbium Complexes

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The excited-state properties of species derived from tris(η^5-cyclopentadienyl)ytterbium(III), Cp_3Yb, and from bis(η^5-pentamethylcyclopentadienyl)ytterbium(II), $(Me_5C_5)_2Yb$, have been investigated. Electronic spectra of several adducts of Cp_3Yb have been examined in benzene solution. When added to solutions of this Lewis acid, bases such as Et_3P, pyrrolidine (pl), THF, and tetrahydrothiophene (THT) cause substantial changes in the rich Cp_3Yb absorption spectrum. Titrations reveal that these changes are consistent with the formation of 1:1 adducts whose formation constants, log K_f, range from ~3.5 for THF and THT to ~5.0 for Et_3P and pl. The magnitude of K_f roughly correlates with the position of a visible absorption band previously assigned as a ligand-to-metal charge-transfer (LMCT) transition, and with the gas-phase basicities of the bases employed. Luminescence is observed in the near-IR (~1000–1100 nm), f–f spectral region from Cp_3Yb and its adducts upon excitation into their LMCT bands. Spectral changes accompanying base addition are consistent with 1:1 adduct formation with apparent excited-state adduct formation constants, log K_{app}^*, equal to the corresponding log K_f values within experimental error. The coincidence in K_f and K^*_{app} values probably reflects the excitation conditions employed rather than the establishment of excited-state equilibrium.

Electronic spectra of adducts of $(Me_5C_5)_2Yb$ have been examined in toluene solution. The solid has been isolated as a mono-THF adduct (P. L. Watson, *J. Chem. Soc., Chem. Comm.*, 652 (1980)) and as a mono-Et_2O adduct (R. A. Anderson, *et al.*, *Inorg. Chem.*, *19*, 2999 (1980)), orange and yellow-green compounds, respectively. Toluene solutions retain these colors. The THF adduct exhibits bands at 445, 505, and 790 nm in toluene with absorptivities of ~410, 320, and 190 M^{-1} cm^{-1}, respectively; corresponding values for the Et_2O adduct are 460 and 690 nm with absorptivities of ~410 and 180 M^{-1} cm^{-1}, respectively. Both species are reluctant to add a second equivalent of base to their coordination sphere; a K_f value of ~10 M^{-1} for formation of the bis-THF adduct was measured from spectral changes accompanying titration of the mono-THF adduct with THF. For adducts of $(Me_5C_5)_2Yb$ involving one equivalent of base, the lowest-energy absorption band appears particularly sensitive to the identity of the base, red-shifting as the base is changed from Et_2O to THF to pyridine (λ_{max} ~ 800 nm). The direction of the shift is consistent with an assignment for the band of $Yb \rightarrow \pi^*(Me_5C_5)$, *i.e.*, metal-to-ligand charge transfer (MLCT). Supporting this assignment are photolysis experiments in which irradiation of the THF adduct in toluene, either alone with UV excitation or in a C_6H_5Cl/toluene mixture with visible and near-IR excitation, leads to Yb(III) products with quantum efficiencies of $\sim 10^{-1}$.

The mono-THF adduct emits at 295 K in toluene solution when excited with visible light; the emission band is broad (~90 nm fwhm) with a maximum at 935 nm. Additionally, the adduct exhibits a novel chemiluminescent reaction indicative of the strong reducing power of these Yb(II) species: upon addition of O_2-saturated toluene to a toluene solution of the adduct, a sharp emission band is observed at ~985 nm. This band is also observed in photoluminescence of the product solution and is characteristic of an Yb(III) species. The species and mechanism responsible for the chemiluminescence will be discussed.

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Physico-chemical Studies of Uranyl Fluoride Complexes

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B7

Mössbauer Spectroscopy and X-Ray Diffraction Studies of Neptunium Intermetallics under High Pressure[†]

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The magnetic properties of intermetallic compounds of the light actinides vary from primary local moment behaviour through itinerant electron magnetism to non-magnetic behaviour. A dominant parameter determining the magnetic character is the interatomic separation of the actinide ions which experimentally can be varied by the application of high pressure. To study the microscopic magnetic behaviour we performed Mössbauer experiments on $NpAl_2$, $NpOs_2$, $NpCo_2Si_2$, and NpAs using the 60 keV transition in ^{237}Np. The magnetic hyperfine field B_{hf} and the isomer shift S, which are a measure of the ordered magnetic moment and the s-electron-density at the nucleus, respectively, as well as the magnetic ordering temperatures have been determined at various pressures up to 70 kbar and in the temperature range from 1.6 K to 77 K. In addition, the lattice parameter variation of $NpAl_2$ was measured up to 100 kbar at room temperature by X-ray diffraction.

We obtained the following results:

(i) In the cubic Laves phase compounds $NpAl_2$ and $NpOs_2$ with a Np–Np distance at ambient pressure of 3.371 Å and 3.258 Å, respectively, we observed a strong decrease of B_{hf} and Curie temperature with pressure indicating a progressive delocalization of the 5f electrons. This is markedly confirmed by the isomer shift. In addition, line broadenings are observed which point towards fluctuation phenomena and show that the delocalization process is of a dynamical nature [1–3].

(ii) The X-ray measurements demonstrate an increase of the compressibility of $NpAl_2$ by a factor of 5 when a pressure of 80 kbar is applied. This behaviour further supports the picture of 5f delocalization with reduced atomic volume. A collapse of volume on account of 5f delocalization

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