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ELECTRONIC STRUCTURE OF BIS(CYCLOPENTADIENYL) LANTHANIDE
COMPOUNDS: PHOTOELECTRON SPECTRA AND MOLECULAR ORBITAL
CALCULATIONS.

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Gas phase He I and He II photoelectron (p.e.) spectra have been
obtained for $\text{Ln}(\eta\text{-C}_5\text{Me}_5)_2$, where $\text{Ln}=\text{Sm}, \text{Eu}, \text{Yb}$. Bands associated
with ionization of f-electrons are identified for the Sm and Yb
compounds. Ionization energies calculated from quasi-relativistic
XX-SW calculations are in good agreement with the experimental
values. These calculations show the compounds to be highly ionic
in nature, and provide no orbital reason for the established non-
parallel geometry of the rings.

Bis(pentamethylcyclopentadienyl) complexes have been synthesized for Sm, Eu and Yb [1,2] free of any other adduct. Structural investigations on crystalline $\text{Sm}(\eta\text{-C}_5\text{Me}_5)_2$ [1] and gas phase $\text{Yb}(\eta\text{-C}_5\text{Me}_5)_2$ [3] show that the cyclopentadienyl rings are non-parallel with the ring centroid-metal-ring centroid angle being 140° and 156° respectively. Bis(ring) sandwich compounds frequently exhibit a structure with tilted rings due to interaction of metal d-orbitals with further ligands [4], or induced by a metal lone pair as in stannocene [5]. In the case of bis(pentamethylcyclopentadienyl)ytterbium neither one of these explanations can be used to rationalise the observed structure.

Ionizations of f-electrons have proved difficult to identify, for lanthanide complexes partly because of their low ionization cross section with He-I radiation [6,7] and partly because of the tendency for the f ionization energies (i.e.) to lie in the same region as those of the ligand bands [8]. The latter is not so likely when the lanthanide is in a low oxidation state such as the divalent state found for Sm, Eu and Yb. Yet no P.E. studies on Ln(II) molecular complexes have been reported as yet.

We undertook an investigation of the electronic structure of $\text{Ln}(\eta\text{-C}_5\text{Me}_5)_2$, where $\text{Ln}=\text{Sm}$, Eu and Yb , by means of gas phase He I and He II P.E. spectroscopy and quasi-relativistic $\text{X}\alpha\text{-SW}$ calculations [9]. This theoretical method has proved successful in the investigation of bis-annulene compounds of the actinides [10] and lanthanides [10,11].

The calculations were performed on $\text{Yb}(\eta\text{-C}_5\text{H}_5)_2$ and $\text{Eu}(\eta\text{-}$

$C_5H_5)_2$ in the parallel conformation (D_{5d} symmetry) (see Table 1) and, for the Yb complex, in the tilted conformation with distances consistent with the available electron diffraction data [3]. Spin polarization effects in the Eu complex were taken into account in a separate calculation. Slater's transition state procedure was used to compute the i.e. The ring-metal interaction was evaluated by comparison of results for a cluster of two neutral cyclopentadienyl rings with the same muffin-tin geometry as for the Yb complex, with an "empty sphere" present in place of the metal atom [10,12]. The orbital energies calculated for $Yb(\eta-C_5H_5)_2$ (D_{5d}) are shown in Figure 1 alongside those for the empty $(\eta-C_5H_5)_2$ dimer and for the Yb atom.

With respect to $(\eta-C_5H_5)_2$ most levels undergo a uniform 0.7 eV downward shift in the complex and have only a tiny localization in the metal sphere. The occupied levels derived from the $(C_5H_5)_2$ ring π -levels undergo larger shifts and have a larger but still very small localization in the metal sphere (orbital, stabilization with respect to $(\eta-C_5H_5)_2$, metal contribution to the M.O.: $3a_{1g}$, -1.25 eV, 0.077; $3a_{2u}$, -0.88 eV, 0.042; $3e_{1g}$, -1.41 eV, 0.094; $3e_{1u}$, -0.99 eV, 0.055). The induced ranking of the ring π -orbitals is the same as that found in ferrocene [13], however, the amount of metal contribution to these orbitals is much larger in the d-block metallocene, namely 0.16, 0.09, 0.30, and 0.09 respectively. The difference is particularly striking when one takes into account that the radius of the Yb sphere is 10% greater than that of the Fe sphere. Corresponding values for the e_{2g} and e_{2u} of $Ce(\eta-C_8H_8)_2$ are 0.206

and 0.330 respectively. The results from the calculation in C_{2v} symmetry show no significant differences from the D_{5d} results, either in the occupied molecular orbital energies or in the corresponding orbital charge distributions.

The splitting of the f-orbitals found from the calculation is 0.07 eV. This is substantially smaller than the spin-orbit splitting so only the centre of gravity of the Yb manifold is shown in Figure 1. Ionization of the f^6 , f^7 and f^{14} configurations gives rise to a number of ion states, whose related spectral band intensities may be predicted by Cox's rules [14], and whose positions relative to the ground state should be similar to those found from absorption studies on Sm^{3+} , Eu^{3+} and Yb^{3+} . The absorption frequencies associated with f-f transitions in these trivalent cations are fairly insensitive to the chemical environment [15]. The anticipated intensity and energy data are shown diagrammatically as stick spectra superimposed on the experimental spectra in Figure 2.

In the p.e. spectra of $Sm(\eta-C_5Me_5)_2$ and $Yb(\eta-C_5Me_5)_2$ bands (see Figure 2) attributable to part of the f-ionization manifold are clearly visible. They may be distinguished by the significant increase in relative intensity in the He II spectra compared with the He I. In both cases higher lying f-bands will coincide with the ring upper e_1 ionizations, and may not be assigned directly, but only by inference from the position of the ground state. In the case of the p.e. spectrum of $Eu(\eta-C_5Me_5)_2$ (see Figure 2) there is no resolved f-band so the f-ionization can be assumed to form part of the band which stretches from ca. 6 eV to 8 eV.

Comparison of the position of the leading edge of this band with the comparable bands in the p.e. spectra of the Sm and Yb complexes, suggests that the f-ionization lies in the lower i.e. region of this band.

The ionizations from the levels originating in the ring e_1 orbitals form the principal part of the band at 6.5-8 eV in all spectra. In the Yb case the $^2F_{5/2}$ state lies under this band but for Sm and Eu the major part of the profile is free of f-ionization processes, especially in the He I spectra. The p.e. spectra of the d-block decamethylmetallocenes show separate e_{1u} and e_{1g} ionization bands with differing He I/He II intensity ratios [16]. The separation varies along the first transition series (V 0.42 eV; Cr 0.62 eV; Mn 0.69 eV; Fe 0.77 eV) as does the onset of the e_{1u} band (V 7.0 eV; Cr 7.1 eV; Mn 7.1 eV; Fe 7.3 eV). The e_{1g} orbitals have a covalent interaction with the metal $3d_{xz}$ and $3d_{yz}$ orbitals which increases along the first transition series; the e_{1u} orbitals lack a partner of suitable energy and symmetry so the splitting between them increases along the first transition series. The onset of the e_{1u} band reflects the charge on the ring and is lowest for the most ionic member of the series namely $V(\eta-C_5Me_5)_2$. The corresponding lanthanide p.e. band, in contrast, is not split into two. This may in part be due to the lower symmetry as the degeneracy of the e_1 levels are lifted. However in the p.e. spectrum of stannocene two bands are clearly resolved. The lack of structure may also be attributed to the highly ionic nature of this complex. The onset of the ring e_1 ionizations lies considerably lower than those given above (Sm

6.3 eV; Eu 6.3 eV; Yb 6.5 eV) reinforcing the view that the rings are more negatively charged as indicated by the calculations.

Both the calculation and the p.e. spectra concur that within a molecular orbital model no explanation can be given for the observed bent structure of $\text{Yb}(\eta\text{-C}_5\text{Me}_5)_2$. It's ionic nature leads to the expectation of a structure with parallel rings with bending being feasible at practically no energetic expense. For a rationalization of the structure with tilted rings one may have to resort to electrostatic considerations within the polarizable ion model [17]. This model has been used successfully in understanding structural trends in the bent lanthanide dihalides and pyramidal lanthanide trihalide structures. Bending will increase the electrostatic repulsion between the rings but may be overcompensated for by increased attractive interaction between the metal and the rings if forces such as charge-induced dipole and induced dipole-induced dipole are taken into account.

Finally, it should be noted that the first i.e. of the complexes lie in the order $\text{Sm}(\eta\text{-C}_5\text{Me}_5)_2 < \text{Yb}(\eta\text{-C}_5\text{Me}_5)_2 < \text{Eu}(\eta\text{-C}_5\text{Me}_5)_2$. The inferred ease of oxidation is that expected from their electrochemical [18] and chemical behaviour.

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Figure 1. X α -SW valence orbital energies for Yb(η -C₅H₅)₂ for D_{5d} geometry; also shown for comparison are the orbital energies of the empty cluster (C₅H₅)₂ and for the Yb atom. Occupied orbitals are indicated by solid lines, empty ones by dashed lines.

Figure 2. P.E. spectra of Ln(η -C₅Me₅)₂ a) Ln=Sm, He I b) Ln=Sm, He II c) Ln=Eu, He I d) Ln=Eu, He II e) Ln=Yb, He I f) Ln=Yb, He II.

Table 1.

Calculated transition state orbital energies (TSOE) for $\text{Ln}(\eta\text{-C}_5\text{H}_5)_2$, $\text{Ln}=\text{Eu}^{\text{b)}$ and $\text{Yb}^{\text{a)}$; estimated and experimental ionization energies for $\text{Ln}(\eta\text{-C}_5\text{Me}_5)_2$, $\text{Ln}=\text{Sm}$, Eu , and Yb .

Orbital	TSOE		Ionization energies				
	Eu	Yb	Sm	Eu		Yb	
			exp.	est. ^{c)}	exp.	est. ^{c)}	exp.
Ln f	6.60 ^{d)}	6.91 ^{d)}	5.4	5.6	6.3	5.2(J=7/2) 6.5(J=5/2)	6.1
			5.6				
			8.7				
$3e_{1u}$	7.26	7.63	6.8		6.6		
			7.1	5.9	6.9	6.2	7.1
$3e_{1g}$	7.57	7.79	7.3		7.3		
$3a_{2u}$	10.75	11.11	10.6		10.5		10.9
				9.5		9.9	
$3a_{1g}$	11.20	11.61					
$2e_{2u}$	12.29	12.40	11.2		11.6		12.3
				10.9		11.1	
$2e_{1u}$	12.43	12.74	13.5		13.5		14.5
$2a_{2u}$	15.33	15.54		13.8		14.0	
$2a_{1g}$							

a) Calculation with tilted rings (C_{2v} symmetry) b) Spin polarized calculation c) TSOE for ligand levels reduced by 1.5 eV, those for metal levels by 1.0 eV [16]. Only average energies given for adjacent ligand levels d) Average over f manifold e) Spin-orbit splitting taken into account.

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