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The Electronic Structure and Chemical Bonding of $(\eta^5\text{-}C_5H_5)_2LuCl{\cdot}OC_4H_8$: A Localized INDO Study*

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Abstract

A localized INDO study revealed that the monomeric $(\eta^5\text{-}C_5H_5)_2LuCl{\cdot}OC_4H_8$ is covalent in character. The main contribution of the metal to bonding is due to the 5d orbitals while the 4f orbitals are strongly localized. The stability of the monomer may be attributed to the great energy gap between the HOMO and the LUMO and the steric hindrance of the THF group. The possible dimerization of dicyclopentadienyl lanthanide chlorides and the complexing activation of Ln–Cl bond are discussed.

Introduction

For a long time the chemistry of lanthanide compounds, especially of organolanthanides, has been one of the most attractive and promising research fields. The theoretical relationship between the electronic structure and the properties of the compounds has been discussed in a series of papers published by the authors [1–4]. Recently, a $(\eta^5\text{-}C_5H_5)_2LuCl{\cdot}THF$ complex was synthesized and characterized by one of the authors (CQ) [5]. It is interesting to note that the compound is the first and only monomer among the dicyclopentadienyl lanthanide chlorides reported in literature [5]. To compare the electronic structure of the monomer with that of corresponding dimeric species [4], a localized INDO calculation has been carried out in this investigation.

Method and Results

The spin-unrestricted INDO method suitable for lanthanide compounds was used. The program and the parameters involved were published previously [1]. Because of the delocalizability of the canonical molecular orbitals (CMO's) obtained from the INDO calculation, it is difficult to relate them to the conventional concept of the chemical bond. For bridging this gap, the Edmiston–Ruedenberg method was used to transform the CMO's to localized molecular orbitals (LMO's). The details of the procedure were described in ref. 4. The work was performed on a Honeywell DPS 8/52 computer.

The geometrical parameters of the monomer are taken from ref. 5 and shown in Fig. 1. The energy levels, composition and assignment of the occupied LMO's (α-spin only) are listed in Table I. The net atomic charges and the Mulliken population data were also calculated and are presented in Fig. 2 and Table II, respectively. Figures 3a and 3b are the contour maps of the two LMO's corresponding to the Lu–Cl σ bond and the O → Lu dative bond.

Discussion

After the localization transformation it is easier and more reliable to assign the LMO's to the chemical bonds. From Table I it is seen that the 52 LMO's definitely correspond to the 40 chemical bonds and

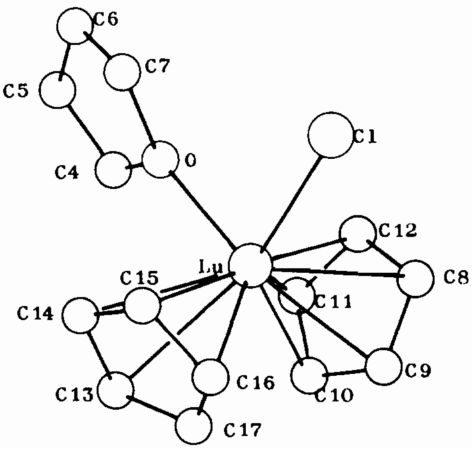

Fig. 1. Molecular structure and atom numbering scheme for $(\eta^5\text{-}C_5H_5)_2LuCl{\cdot}OC_4H_8$ (H atoms are omitted).

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TABLE I. α-Spin Localized Molecular Orbitals of $(\eta^5\text{-}C_5H_5)_2LuCl\cdot OC_4H_8$

No.	E (a.u.)	Main composition (%)	Assignment
1	−1.261	48.8 C13 + 48.0 C14	C13–C14 σ
2	−1.238	48.1 C10 + 48.3 C11	C10–C11 σ
3	−1.222	62.3 O + 31.2 C3	O–C3 σ
4	−1.195	49.4 C8 + 48.8 C12	C8–C12 σ
5	−1.184	66.9 O + 22.7 C5	O–C5 σ
6	−1.15	49.1 C15 + 48.5 C16	C15–C16 σ
7	−1.146	48.8 C8 + 49.1 C9	C8–C9 σ
8	−1.137	50.4 C7 + 48.4 H7	C7–H7 σ
9	−1.136	49.2 C13 + 48.5 C17	C13–C17 σ
10	−1.135	51.5 C7 + 47.2 H7′	C7–H7′ σ
11	−1.135	50.9 C4 + 48.1 H4	C4–H4 σ
12	−1.129	51.2 C4 + 47.7 H4′	C4–H4′ σ
13	−1.126	50.6 C6 + 48.6 C7	C6–C7 σ
14	−1.115	49.2 C11 + 48.7 C12	C11–C12 σ
15	−1.103	49.0 C5 + 49.1 C6	C5–C6 σ
16	−1.098	54.7 C6 + 44.1 H6	C6–H6 σ
17	−1.096	52.8 C5 + 46.7 H5	C5–H5 σ
18	−1.095	53.0 C5 + 46.6 H5′	C5–H5′ σ
19	−1.094	53.0 C6 + 46.6 H6′	C6–H6′ σ
20	−1.088	100.0 4f	4f Lu
21	−1.088	100.0 4f	4f Lu
22	−1.088	100.0 4f	4f Lu
23	−1.088	100.0 4f	4f Lu
24	−1.088	100.0 4f	4f Lu
25	−1.088	100.0 4f	4f Lu
26	−1.088	100.0 4f	4f Lu
27	−1.085	48.2 C14 + 49.6 C15	C14–C15 σ
28	−1.081	85.0 O + 11.5 Lu(5d, 6s)	O → Lu
29	−1.080	48.6 C9 + 49.2 C10	C9–C10 σ
30	−1.071	46.3 C16 + 49.7 C17	C16–C17 σ
31	−1.062	50.0 C4 + 49.2 C5	C4–C5 σ
32	−1.061	48.5 C14 + 49.8 H14	C14–H14 σ
33	−1.054	48.9 C11 + 49.5 H11	C11–H11 σ
34	−1.050	49.4 C10 + 49.0 H10	C10–H10 σ
35	−1.048	49.6 C8 + 48.7 H8	C8–H8 σ
36	−1.048	48.2 C16 + 49.5 H16	C16–H16 σ
37	−1.045	48.5 C17 + 49.7 H17	C17–H17 σ
38	−1.044	49.4 C12 + 48.8 H12	C12–H12 σ
39	−1.044	49.2 C13 + 49.1 H13	C13–H13 σ
40	−1.042	49.5 C9 + 48.8 H9	C9–H9 σ
41	−1.038	49.4 C15 + 48.9 H15	C15–H15 σ
42	−1.023	89.0 O	lone pair on O
43	−0.896	81.3 C(2p) + 6.6 Lu(5d)	C–C π Cp2
44	−0.755	92.3 Cl	lone pair on Cl
45	−0.631	86.9 C(2p) + 7.9 Lu(5d)	C–C π Cp1
46	−0.580	92.3 C(2p) + 6.5 Lu(5d)	C–C π Cp2
47	−0.571	92.6 C(2p) + 5.1 Lu(5d)	C–C π Cp1
48	−0.560	85.4 Cl + 10.0 Lu(5d) + 3.5 Lu(6s)	Lu–Cl σ
49	−0.555	90.2 C(2p) + 7.5 Lu(5d)	C–C π Cp1
50	−0.551	92.9 C(2p) + 6.7 Lu(5d)	C–C π Cp2
51	−0.474	95.7 Cl	lone pair on Cl
52	−0.443	95.3 Cl	lone pair on Cl, HOMO
53	0.153	78.6 Lu(5d)	vacant 5d Lu, LUMO
54	0.206	39.1 Lu(5d) + 27.8 Lu(6p)	vacant 5d and 6p Lu

the 12 lone pairs (on Cl, O and Lu atoms, respectively) in the monomer. In terms of the valence bond theory, the LMO no. 28 is the dative bond from one lone pair on the oxygen atom to the Lu atom while the LMO no. 48 is the Lu–Cl σ bond. The six LMO's nos. 43, 45, 46, 47, 49 and 50 can be considered as

TABLE II. Population Data of $(\eta^5\text{-}C_5H_5)_2LuCl{\cdot}OC_4H_8$

Subshell		Lu				Bond order
		6s	6p	5d	4f	
Orbital population		0.377	0.629	1.452	14.000	–
Overlap population						
Cl	3s	0.099	0.207	0.058	0.000	Lu–Cl
	3p	0.036	0.059	0.198	0.000	0.656
O	2s	0.048	0.066	0.064	0.000	Lu–O
	2p	0.011	0.012	0.113	0.000	0.314
C	2s	0.037	0.079	0.020	0.000	Lu–C
	2p	0.018	0.021	0.079	0.000	0.254

six conjunctive C–C π bonds in the two cyclopentadienyl rings, which are still delocalized on each ring and coordinate to the metal, forming six dative bonds. Therefore, the coordination number of the lutetium atom is eight.

From Table I it is also seen that the LMO's nos. 20–26 are composed of only the 4f atomic orbitals of the Lu and are equal to each other energetically.

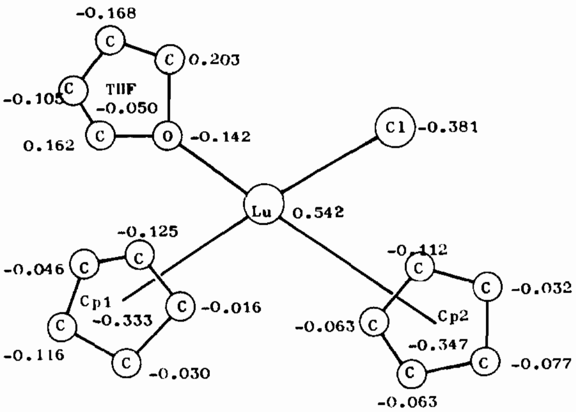

Fig. 2. Net charge distribution of $(\eta^5\text{-}C_5H_5)_2LuCl{\cdot}OC_4H_8$.

Moreover, Table II shows that the overlap populations between the 4f and the other atomic subshells are nearly zero, implying that the 4f orbitals are not perturbed at all during the complex formation and are still atomic in character. The data in Table II confirm the conclusion that the 5d orbitals play a dominant role in bonding interaction. This is fairly consistent with our previous research [1–4].

The net charge on the central metal is 0.542 (Fig. 2), which is far from the value estimated by ionic model, +3. Besides, the bond orders of Lu–Cl and O → Lu have considerable values (Table II), indicating that both of the bonds are covalent in character. The contour maps shown in Fig. 3 schematically describe the covalent nature of the bonds.

For CMO's the energy difference between the HOMO and the LUMO is 0.453 a.u. (0.596 a.u. for LMO's), which is comparable with other lanthanide compounds including chlorine bridged dimers [1–4] and explains the stability of the monomer. Furthermore, it is worth noting that the HOMO is a 3p lone pair on the chlorine atom, while the LUMO is mainly composed of the vacant 5d orbitals of the lutetium atom. The fact suggests the possibility of dimerization of dicyclopentadienyl lanthanide chlorides, which was verified experimentally [5]. The existence of the titled monomeric species may be explained simply by the steric hindrance of the THF group. In fact, a dimer $((\eta^5\text{-}C_5H_5)_2LuCl)_2$ has been observed in benzene solution [5], in which no dative bond can be formed; hence, the expected dimerization occurs. According to the new definition of covalence proposed by one of the authors (GXX) [6], the covalence of Lu in the monomer should be 13, again indicating the covalent unsaturation of the central metal of the monomer.

The bond order of Lu–Cl in the monomer, 0.656, is smaller than that in lanthanide trichlorides, ~0.80 [7], and greater than that in cyclopentadienyl chlorine bridged dimers, ~0.47 [4]. The fact is helpful in explaining the so-called complexing activa-

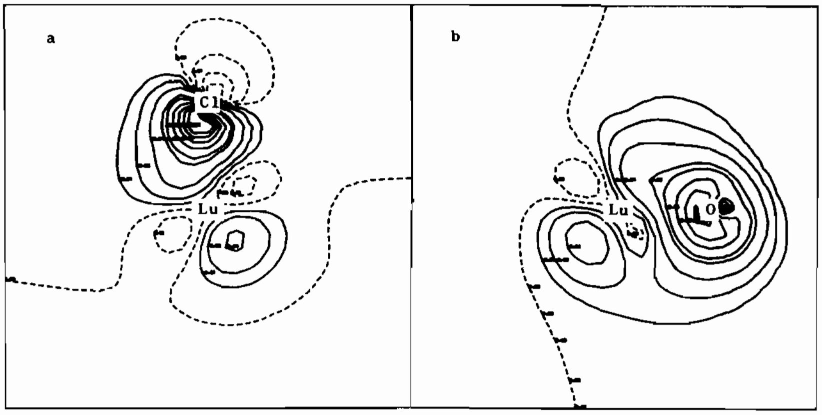

Fig. 3. Localized molecular orbital contour maps of (a) the Lu–Cl bond and (b) the O → Lu bond on the plane Lu–Cl–O.

tion of the Ln–Cl bond observed in experiments [8]. Also, it may be worth noting that the Ln–Cl bond would be effectively weakened when a chlorine bridged dimer is formed.

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