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Preliminary communication

Synthesis, structural characterisation and dynamic behaviour of pentafulvalenyldilanthanide(II) complexes

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Abstract

A one-step preparation of pentafulvalenyldilanthanide(II) complexes can be performed in good yield by an electron-transfer reaction of ytterbium or samarium metal powders with a pentafulvalene. © 1998 Elsevier Science S.A.

Keywords: Lanthanide; Samarium; Ytterbium; Fulvalene; π-Complex

1. Introduction

The direct synthesis of lanthanide complexes by interaction of the zerovalent metals with an organic precursor is a simple and attractive method which has been used for the preparation of trivalent [1–5] as well as divalent compounds; in the divalent field, two-electron processes have involved either oxidative addition [6–10] or interaction of the metal with an unsaturated organic precursor such as cyclooctatetraene [11] or naphthalene [12]. Ansa-ytterbocenes and samarocenes have likewise been obtained by coupling of a fulvene around ytterbium or samarium [13].

A two-electron transfer of a lanthanide (Ln: Yb or Sm) towards the 10-π electron system of a pentafulvalene (Pf) should give a Pf^{2-} dianion, consisting of two linked 6-π electron Cp^- anions, and a Ln^{2+} cation, which by recombination would yield a pentafulvalenyl sandwich complex incorporating two Ln elements in the +II oxidation state. An interesting coordination compound with two Sm(II) has recently been prepared [14].

2. Results and discussion

The reported results are summarized in Fig. 1. Interaction of Yb and Sm metal powders with the stable tetra(*t*-butyl)pentafulvalene [15] (tPf) in THF afforded dark green (Yb) or dark purple (Sm) solutions.

In the ytterbium case, a microcrystalline 60:40 mixture of two Yb(II) isomers (**1** and **2**) could be isolated (68% yield). The major isomer **1** was obtained by recrystallization in THF-hexane (green crystals, 24% yield). An X-ray crystallographic study revealed that the structure of **1**: $(tPf)_2Yb_2(THF)_2$ had incorporated two Yb atoms in a bis-sandwich complex (Fig. 2). The C–Yb bond distances (264–279 pm) are similar to those found in $(tBu_2Cp)_2Yb(Me_4C_3N_2)$ [16]; the Yb–O distance (245 pm) is normal. No metal–metal bonding interaction is present (Yb–Yb distance = 494 pm). The dihedral angles between the Cp rings ligands (63° and 26°) are different in the two nonplanar tPf ligands, one of these angles is similar to that of $(tPf)Mo_2(CO)_6Me_2$ (65°) [17] and of $(tPf)Tl_2$ (70°) [18]. Along the centroïd(Cp)–centroïd(Cp) axes, the *t*-Bu substituents on both Cp rings of the tPf ligands are eclipsed with the *t*-Bu substituents of the other in a *syn*, *syn* configuration.

The major isomer **1** has a sole pseudo-C_2 axis passing through the middle points of the Cp–Cp bonds. Four NMR signals should thus be observed in **1** for the cyclopentadienyl protons and for the *t*-Bu groups. The higher symmetry of the room temperature ^1H NMR spectrum (two signals for the cyclopentadienyl protons and for the *t*-butyl groups) is attributed to a dynamic process interconverting the two tPf ligands, presumably an oscillating movement around the Cp–Cp bonds, on

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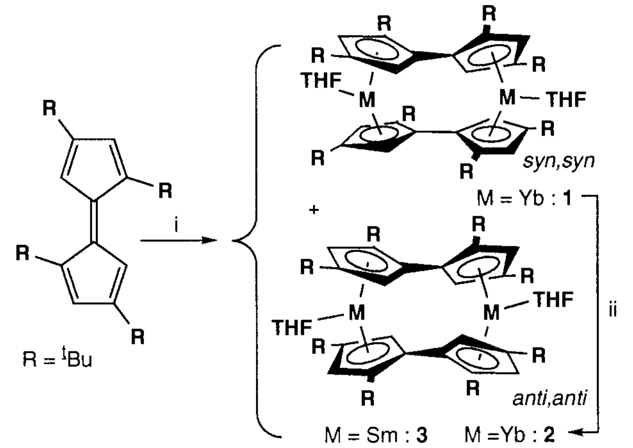

Fig. 1. Synthesis of pentafulvalenyldilanthanide complexes. Reagents and conditions: (i) Yb or Sm (+1 wt.% $HgCl_2$), THF, room temp., 16 h; (ii) 110°C, THF (sealed tube), 2 h.

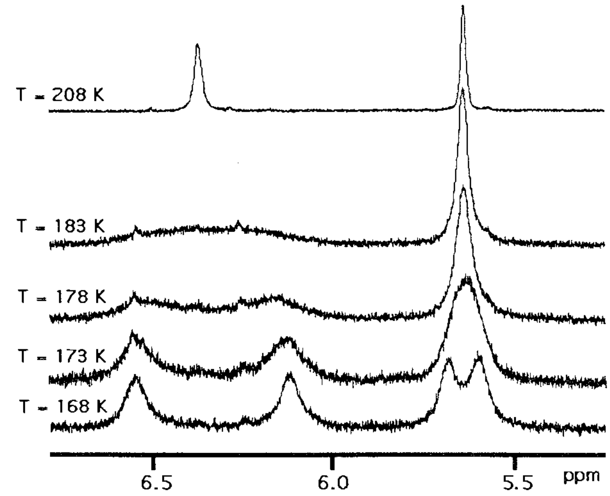

Fig. 3. Variable temperature ^1H NMR spectra of **1** (400 MHz).

the basis of a variable temperature ^1H NMR study (Fig. 3): four cyclopentadienyl resonances were clearly seen at 168 K, decoalescence was also observed for the *t*-butyl groups; the $\Delta G^{\ddagger}$ for this process is equal to 34.4 kJ mol^{-1} at 183 K.

After a few days at room temperature, signals corresponding to **2** appeared in the ^1H NMR spectrum of a solution of **1** in d-8 THF. Heating THF solutions of the crude (**1** + **2**) mixture, or of pure, isolated **1**, yielded pure **2** (deep green crystals, 75% yield). An X-ray study (Fig. 4) showed that the difference between the two isomers **1** and **2** was that in **2**, viewed along a centroïd–centroïd axis, the *t*-Bu substituents of one tPf ligand are eclipsed with the cyclopentadienyl protons of the other in an *anti,anti* configuration. The C–Yb bond distances (267–278 pm), the Yb–O bond distance (244 pm) and the Yb–Yb distance (500 pm) are similar to those found in **1**. The Cp–Cp plane angles of the two tPf ligands are now equal (62°).

The symmetric appearance of the ^1H NMR spectrum of **2** (two signals corresponding to the *t*-butyl groups and two for the cyclopentadienyl protons, even down to 170 K) is consistent with the D_2 symmetry of **2**, where three C_2 axes are present: one passing through the two metals, one through the middle points of the Cp–Cp bonds in the two tPf ligands, and the last one perpendicular to the other two.

No trace of any another isomer such as *anti,syn* could be isolated.

In the samarium case, only the *anti,anti* compound **3** $(tPf)_2Sm_2(THF)_2$ similar to **2** was obtained (purple crystals, 55% yield) after work-up. The C–Sm bond distances (280–290 pm) and the Sm–O bond distance

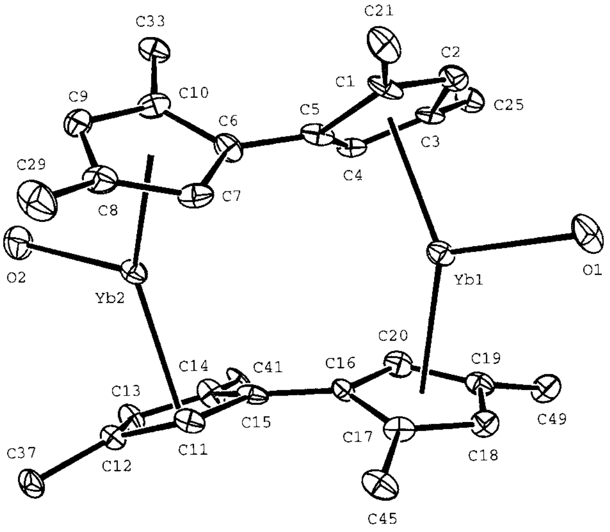

Fig. 2. An ORTEP plot of one molecule of **1** with ellipsoid scaled at 50% probability level, CH_3 and CH_2 groups omitted for reasons of clarity.

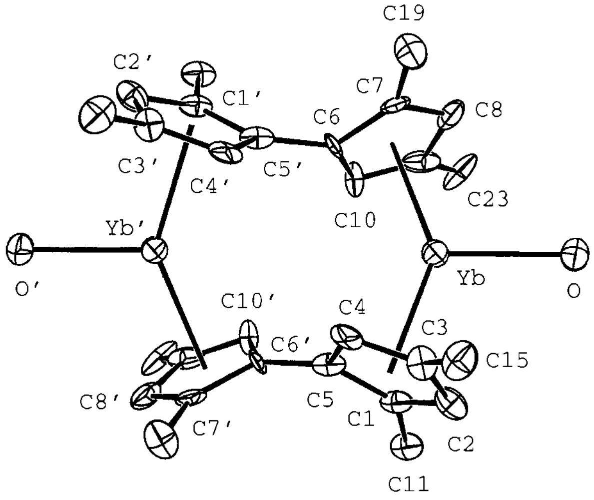

Fig. 4. An ORTEP plot of one molecule of **2** with ellipsoid scaled at 50% probability level, CH_3 and CH_2 groups omitted for reasons of clarity.

(257 pm) are similar to those found in $(tBu_2Cp)_2Sm(THF)$ [19]. The dihedral angles between the Cp rings (62 and 66°) are similar to those found in **2**. Like in **1** and **2**, the Sm–Sm distance (493 pm) precludes any bonding interaction between the two metals.

In summary, the interaction of tPf with Yb or Sm afforded sandwich complexes **1**–**3**. With Yb, both the *syn,syn* and the *anti,anti* isomers **1** (kinetic) and **2** (thermodynamic) were isolated, whereas with Sm, only the *anti,anti* complex **3** could be isolated. Further developments will involve the oxidation chemistry of these compounds.

3. Experimental

3.1. General considerations

All experiments were performed with dry, oxygen free solvents on a vacuum line or under argon in a Braun Labmaster 130 glove box with $[H_2O]$, $[O_2] < 1$ ppm. NMR spectra were recorded in d-8 THF at 293 K at the following frequencies: 200.1 MHz for ^1H and 50.3 MHz for ^{13}C (δ are expressed in ppm from int. Me_4Si, J are in Hz). Micronalyses were performed at the University of Dijon, France, thanks to Mrs. Pascale Desmurs.

3.2. General procedure for the preparation of compounds *1*–*3*

A mixture of tetra(*t*-butyl)pentafulvalene (tPf), Ln powder and $HgCl_2$ (ca. 1 wt.%) was stirred at room temperature in THF for 16 h. The reaction mixture was then evaporated to dryness and the residue extracted into hexane and filtered. The hexane solution was concentrated to a small volume and the resulting crystals were filtered, rinsed with cold hexane and dried under vacuum.

3.3. Preparation of the 60:40 mixture of syn,syn and anti,anti bis(tetra(t-butyl)pentafulvalenyl)bis(tetrahydrofuran)diytterbium (*1* + *2*)

From tPf (1.06 g, 3 mMol) and Yb (0.65 g, 3.7 mMol), a green crystalline powder was obtained (1.21 g, 1.0 mMol, 68%), which consisted of **1** and **2** in a 60:40 mixture.

3.4. Isolation of syn,syn bis(tetra(t-butyl)pentafulvalenyl)bis(tetrahydrofuran)diytterbium (*1*)

A 0.50 g mixture of [**1** + **2**] was dissolved in THF and concentrated to ca. 3 ml whereupon crystals appeared. Hexane (10 ml) was then added with stirring at 0°C and the solution was filtered, rinsed with cold hexane and dried under vacuum, yielding green crystalline **2** (0.12 g, 24%). ^1H NMR: δ 1.25, 1.26 (36H), 1.74 (8H, THF), 3.61 (8H, THF), 5.72 (d, $^4J = 3$, 4H), 6.50 (d, $^4J = 3$, 4H).^{13}C: 33.01 (CMe_3), 33.17 (Me), 33.21 (Me), 33.69 (CMe_3), 106.08, 109.74 (CH), 119.26, 129.72, 131.44 (quat. C).

3.5. Preparation of anti,anti bis(tetra(t-butyl)pentafulvalenyl)bis(tetrahydrofuran)di-ytterbium (*2*)

A 0.39 g of [**1** + **2**] mixture in THF solution (15 ml) was heated in a sealed tube at 110°C for 2 h. Work-up by hexane extraction as above afforded very dark green crystals of **2** (0.29 g, 75%). ^1H NMR: δ 1.07 (18H), 1.23 (18H), 1.74 (8H, THF), 3.61 (8H, THF), 5.65 (d, $^4J = 3$, 4H), 6.53 (d, $^4J = 3$, 4H). ^{13}C (50.3 MHz): $d = 32.70$ (CMe_3), 33.06 (Me), 33.68 (Me), 104.05, 112.96 (CH) 119.93, 130.75, 132.47 (quat. C). One CMe_3 was not observed. Anal (%): Found, C: 60.00; H: 8.49; calc. for $C_{60}H_{96}Yb_2O_2$, C: 60.28; H: 8.09.

3.6. Preparation of anti,anti bis(tetra(t-butyl)pentafulvalenyl)bis(tetrahydrofuran)di-samarium (*3*)

From tPf (0.53 g, 1.5 mMol) and Sm (0.28 g, 1.86 mMol), [**3** hexane] was obtained as a purple crystalline powder (0.50 g, 0.4 mMol, 52%). ^1H NMR: δ −23.1 (4H), 0.94–1.33 (m, 14H, hexane), 1.74 (8H, THF), 3.61 (8H, THF), 11.4 (18H), 15.4 (18H), 40.0 (4H). ^{13}C: −77.8, −32.1, −18.5, −13.9, −3.4 (quat. C), 14.36, 23.45, 32.47 (hexane), 44.9, 64.3 (Me), 94.4, 102.3 (CH). Anal (%): Found, C: 60.66; H: 8.41; calc. for $C_{60}H_{96}Sm_2O_2$, C: 62.66; H: 8.01.

3.7. X-ray experimental

Crystals of **1** and **3** were obtained by slow cooling of hexane solutions of the compounds while **2** was crystallised from diethylether. Data were collected on an Enraf–Nonius CAD4 Diffractometer, using MoKα radiation and a graphite monochromator. The structures were solved by direct methods (SIR92). All atoms were refined anisotropically, except for hydrogen atoms included as fixed contributions to the structure factors. For **1**, $C_{60}H_{96}Yb_2O_2$ at $T = 123$ K, monoclinic, space group $P2_1/a$ (no. 14), $a = 1.9886(3)$ nm, $b = 1.5148(2)$ nm, $c = 1.9955(3)$ nm, $\beta = 92.64(1)°$, $V = 6.004(2)$ nm^3, $Z = 4$, $d_{calc} = 1.249$, $\mu = 31.2$ cm^{-1}, 2θ max = 60°, 6924 reflections with $F^2 > 3\sigma(F^2)$, $R = 0.047$, $w_R = 0.065$, g.o.f = 1.13; for **2**, $C_{60}H_{96}Yb_2O_2$ at $T = 173$ K, orthorhombic, space group Pbcn (no. 60), $a = 1.6125(2)$ nm, $b = 1.9736(3)$ nm, $c = 1.9958(3)$ nm, $V = 6.350(2)$ nm^3, $Z = 4$, $d_{calc} = 1.250$, $\mu = 29.5$ cm^{-1}, 2θ max = 46.9°, 4626 reflections with $F^2 > 3\sigma(F^2)$, $R = 0.059$, $w_R = 0.091$, g.o.f = 1.65; for [**3** · hexane],

$C_{66}H_{110}Sm_2O_2$ at $T = 123$ K, orthorhombic, space group Pbca (no. 61), $a = 1.9624(3)$ nm, $b = 2.1684(3)$ nm, $c = 3.0607(5)$ nm, $V = 13.023(5)$ nm^3, $Z = 8$, $d_{calc} = 1.261$, $\mu = 18.3$ cm^{-1}, 2θ max = 51.8°, 3667 reflections with $F^2 > 3\sigma(F^2)$, $R = 0.074$, $w_R = 0.117$, g.o.f = 0.94. [1]

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[1] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number 100/250.