

Synthesis and characterization of Eu(II) and Sm(II) complexes containing the cyclopentadienylvanadionaphthalene anion.

Molecular structure of $[(C_5H_5)V(C_{10}H_8)]_2Eu(THF)(DME)$ and $[(C_5H_5)V(C_{10}H_8)Eu(C_5H_5)(THF)]_n^{1,2}$

Igor L. Fedushkin^a, Vladimir K. Nevodchikov^a, Vladimir K. Cherkasov^a,
Mikhail N. Bochkarev^{a,*}, Herbert Schumann^{b,*}, Frank Girgsdies^b, Frank H. Görlitz^b,
Gabriele Kociok-Köhn^b, Joachim Pickardt^b

^a Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina 49, 603600 Nizhny Novgorod GSP-445, Russia

^b Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, D-10623 Berlin, Germany

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Abstract

The reaction of $LnI_2(DME)_3$ with an equimolar mixture of $K(C_5H_5)$ and $K(C_5H_5)V(C_{10}H_8)$ in DME followed by treatment with THF results in the formation of the tetradecker bimetallic complexes $[(C_5H_5)V(C_{10}H_8)]_2Ln(THF)(DME)$ with $Ln = Eu$ (1) and Sm (2). Removal of the solvent and subsequent addition of THF leads to coordination polymers $[(C_5H_5)V(C_{10}H_8)Ln(C_5H_5)(THF)]_n$ with $Ln = Eu$ (3) and Sm (4). These novel complexes have been characterized by IR spectroscopy and the europium derivatives by X-ray crystallography. 1 is triclinic, space group $P1$ (No. 2), $Z = 2$, with $a = 1203.6(4)$, $b = 1230.8(6)$, $c = 1140.8(3)$ pm, $\alpha = 91.37(4)$, $\beta = 97.14(3)$, $\gamma = 100.44(3)^\circ$. The structure was refined to $R = 0.026$ for 3027 observed reflections ($F_o > 3\sigma(F_o)$). It shows two $(C_5H_5)Eu(C_{10}H_8)$ sandwich units η^6 -bonded to Eu via one six membered ring of the naphthalene with an additional THF and DME coordinated to europium. 3 is monoclinic, space group $C2/c$ (No. 15), $Z = 8$, with $a = 1916.0(3)$, $b = 1330.4(3)$, $c = 1765.3(4)$ pm, and $\beta = 90.17(2)^\circ$. The structure was refined to $R = 0.032$ for 2734 observed reflections ($F_o > 4\sigma(F_o)$). It forms infinite polymeric zig-zag chains consisting of $(C_5H_5)Eu$ units, in which the europium atoms are coordinated by an additional THF and $(C_5H_5)V(C_{10}H_8)$ units which are each bonded η^2 via a naphthalene.

Keywords: Europium; Samarium; Vanadium; Cyclopentadienyl complexes; Naphthalene complexes; X-ray structure

1. Introduction

Main group, transition metal and f-element complexes with bridging arene ligands have received considerable attention because of their interesting and varying bonding modes. Among them are several types of binuclear organometallic compounds containing the μ_2 -naphthalene ligand. There are known several com-

plexes with lithium [2], lanthanum [3] and europium [3], in which the μ_2 -naphthalene dianion is coordinated via a slipped 'inverse-sandwich' structure for which π -bonding as well as ionic interactions have been suggested. A slipped triple-decker sandwich structure with an η^6 - π -bonded neutral μ_2 -bridging naphthalene ligand is found in a number of d-block transition metal complexes, such as $(C_5H_5)Fe(\mu_2-C_{10}H_8)Fe(C_5H_5)$ [4], $(C_5Me_5)M(\mu_2-C_{10}H_8)M(C_5Me_5)$, ($M = Cr, V$) [5], $(C_5H_5)V(\mu_2-C_{10}H_8)V(C_5H_5)$ [6] and $(C_6H_6)Cr(\mu_2-C_{10}H_8)Cr(C_6H_6)$ [7]. A different μ_2 -bridging naphthalene coordination has been found in $(C_6H_6)Ru(\mu_2-\eta^4:\eta^6-C_{10}H_8)Cr(CO)_3$ [8] and $[(Me_2CH)_2P(CH_2)_3P(CHMe_2)_2]Co(H)-(\mu_2-\eta^4:\eta^6-C_{10}H_8)V(C_5H_5)$ [5] with a bent naphthalene system η^4 -coordinating to Ru or Co

¹ Part 102 of the series Organometallic Compounds of the Lanthanides. See Ref. [1] for Part 101.

² Dedicated to Professor J. Müller on the occasion of his 60th birthday.

* Corresponding author.

and η^6 -coordinating via the π -system of the second six membered ring to Cr or V. Heterometallic ionic complexes with a neutral naphthalene bridge between an alkali metal cation and an organotransition metal ion like $K(\mu_2-C_{10}H_8)V(C_5H_5)$ were reported by Jonas [4], but no X-ray structural analyses were given. Their structures were compared with that of the benzene analogue complex $(TMED)Li(\mu_2-C_6H_6)V(C_5H_5)$ [9].

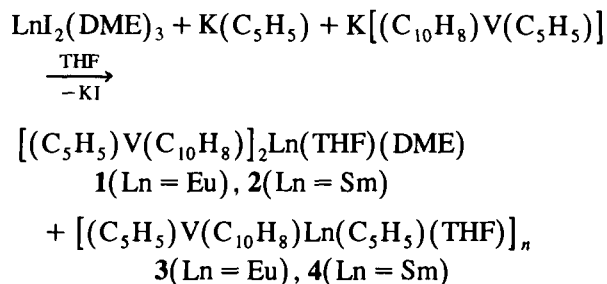
Recently we reported the synthesis and X-ray structural determination of the first heterobimetallic organolanthanide complex $[(C_5H_5)V(\mu_2-C_{10}H_8)Yb(C_5H_5)(THF)]_n$ [10] (THF = tetrahydrofuran). The geometry of this complex, its magnetic moment and the ESR spectrum suggest the double character of the bonding: an electrostatic interaction between the sandwich anion $[(C_5H_5)V(C_{10}H_8)]^-$ (in which the negative charge is localized mainly on the vanadium atom) and the $[(C_5H_5)Yb]^+$ cation, and an η^2 - π -interaction between the ytterbium atom and the neutral naphthalene ligand. The unusual arrangement of this compound, as well as our unsuccessful attempts to obtain the symmetric derivative $[(C_5H_5)V(C_{10}H_8)]_2Yb$, prompted us to synthesize the analogous complexes of other rare earth elements and to investigate their structures. This paper reports the preparation and characterization of some new vanadium–naphthalene–europium and vanadium–naphthalene–samarium complexes.

2. Results and discussion

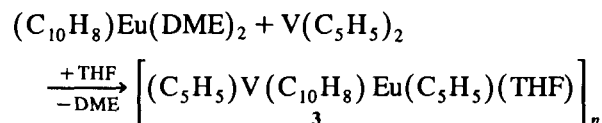
To synthesize the desired compounds it seemed reasonable to use previously reported reactions for the preparation of $[(C_5H_5)V(C_{10}H_8)Yb(C_5H_5)(THF)]_n$ [10]. However, the interaction of $(C_5H_5)_2V$ with the reduction products of either LaI_3 or GdI_3 with alkali metal naphthalenides, as well as the reaction of LaI_3 or GdI_3 with a mixture of $K(C_5H_5)$ and $K[(C_{10}H_8)V(C_5H_5)]$ gave no isolable organolanthanide compound which could be characterized. Intractable mixtures of solid products have also been obtained by reacting $EuI_2(THF)_2$ and $SmI_2(THF)_2$ with the same reagents in THF.

$EuI_2(DME)_3$ and $SmI_2(DME)_3$ (DME = dimethoxyethane) react with a mixture of $K(C_5H_5)$ and $K[(C_{10}H_8)V(C_5H_5)]$, prepared in situ [11], in DME to form two different reaction products, depending on the method of isolation. If the reaction mixture was filtered from the precipitated KI, concentrated to 10 to 15 ml by evaporation in vacuum and a mixture of THF and hexane added, $[(C_5H_5)V(C_{10}H_8)]_2Ln(THF)(DME)$ with $Ln = Eu$ (**1**) and Sm (**2**) could be isolated in reasonable yields. The coordination polymers $[(C_5H_5)V(C_{10}H_8)-Eu(C_5H_5)(THF)]_n$ (**3**) and $[(C_5H_5)V(C_{10}H_8)Sm(C_5H_5)(THF)]_n$ (**4**) could be isolated from the same reac-

tion after complete evaporation of the filtered DME solution and dissolving the dark waxy residues in THF. The black polymers **3** and **4** crystallized after 2 days in very low yields:



The reaction of naphthaleneeuropium $(C_{10}H_8)Eu(DME)_2$ with equimolar amounts of dicyclopentadienylvanadium in THF–DME also results in the formation of **3**; but now in better yields:



The air sensitive compounds **3** and **4** are only slightly soluble in common organic solvents, in contrast to **1** and **2** which dissolve easily in THF, DME and benzene. Upon heating the complexes **1** and **2** melt with decomposition above 110 °C, whereas the black crystals **3** and **4** do not change their shape or color up to 360 °C, but lose coordinated THF above 150 °C.

All four complexes are paramagnetic. The magnitudes of the magnetic moments of the europium derivatives (8.1 BM for **1** and 7.86 BM for **3**) are close to average values for other organoeuropium(II) complexes (7.8 BM [12]). For **4**, $\mu_{eff} = 3.78$ BM is characteristic for Sm(II) derivatives (3.6 BM [12]). The IR spectra of **3** and **4** are identical and coincide with the IR spectrum of $[(C_5H_5)V(C_{10}H_8)Yb(C_5H_5)(THF)]_n$ [9]. A similar set of absorption bands is also observed for the symmetrical complexes **1** and **2**.

The DME solution of **1** shows an intensive ESR signal of a 17 electron d^5 complex of V(0), an octet with $g_{eff} = 2.00$ and $A_i = 4.5$ mT (Fig. 1(a)). A similar spectrum (8 lines with $g_{eff} = 1.982$ and $A_i = 4.47$ mT; anisotropic: axial symmetry of the g and T tensors, $g_{||} = 2.0$, $g_{\perp} = 1.973$, $A_{par} \cong 0$ mT, $A_{\perp} = 7.46$ mT) has been observed for the analogous quasi-polymeric ytterbium complex $[(C_5H_5)V(C_{10}H_8)Yb(C_5H_5)(THF)]_n$ in THF and has been attributed to the anion $[(C_5H_5)V(C_{10}H_8)]^-$ [10]. The poor solubility of **3** does not allow the observation of ESR signals in either THF or DME.

Crystalline **3** and $[(C_5H_5)V(C_{10}H_8)Yb(C_5H_5)(THF)]_n$ display ESR signals which can also be attributed to vanadium(0) with the parameters $\Delta H = 70$ mT, $g_{eff} = 2.05$ and $\Delta H = 7$ mT, $g_{eff} = 2.08$ respectively. The significant broadening of the first of them is

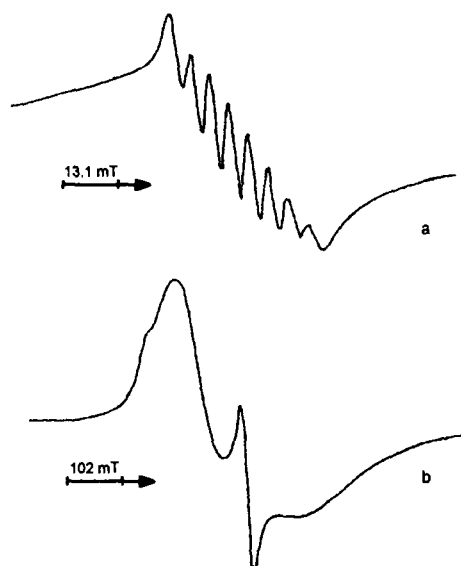


Fig. 1. ESR spectra of **1** at 293 K (a) in DME solution and (b) in the solid state.

probably caused by the paramagnetism of the europium atom. A quite different spectrum is observed for solid **1** (Fig. 1(b)). It exhibits an intensive broad singlet with the parameters $g_{\text{eff}} = 2.65$, $g_{\parallel} = 1.60$ and $g_{\perp} = 3.19$. Since these parameters differ essentially from those of vanadium d^5 , from the radical anion of naphthalene and from the spectrum of europium(II) [13,14], we suppose that Eu(0) atoms are responsible for this ESR spectrum. Solid **2** and **4** also give ESR spectra, which could not be interpreted by us because of their shape and parameters.

3. Molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-C}_{10}\text{H}_8)]_2\text{Eu}(\text{THF})(\text{DME})$ (**1**) and $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\mu_2\text{-}\eta^6\text{:}\eta^2\text{-C}_{10}\text{H}_8)\text{Eu}(\text{THF})(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_5)]_n$ (**3**)

In the solid state **1** crystallizes in discrete monomer units (Fig. 2). The trinuclear complex consists of two

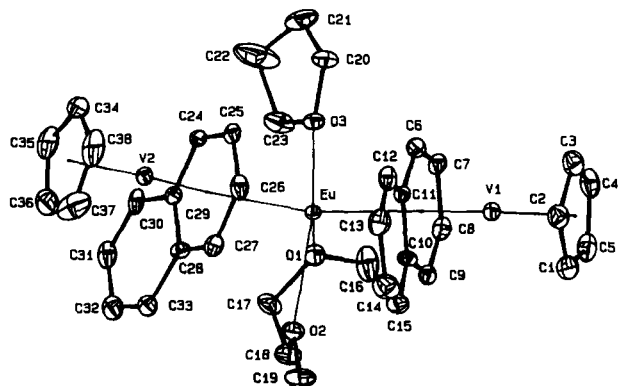


Fig. 2. ORTEP [15] projection of one molecule of $[(\text{C}_5\text{H}_5)\text{V}(\text{C}_{10}\text{H}_8)_2\text{Eu}(\text{THF})(\text{DME})]$ (**1**) with the numbering scheme. Hydrogen atoms are excluded for clarity.

Table 1

Selected bond distance in $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-C}_{10}\text{H}_8)]_2\text{Eu}(\text{THF})(\text{DME})$ (**1**) (estimated standard deviations in the last significant figures are given in parentheses)

	Bond distance (pm)	Bond distance (pm)	
Eu–O(1)	262.9(3)	V(1)–C(6)	215.3(5)
Eu–O(2)	266.5(3)	V(1)–C(7)	212.4(5)
Eu–O(3)	259.2(3)	V(1)–C(8)	211.9(5)
Eu–C(6)	293.3(4)	V(1)–C(9)	212.5(5)
Eu–C(7)	288.4(5)	V(1)–C(10)	215.5(5)
Eu–C(8)	284.5(5)	V(1)–C(11)	215.8(5)
Eu–C(9)	289.5(5)	V(1)–Cp(1) ^a	158.6(2)
Eu–C(10)	299.0(5)	V(2)–C(24)	213.2(5)
Eu–C(11)	301.9(4)	V(2)–C(25)	213.9(5)
Eu–Cp(1) ^a	255.0(2)	V(2)–C(26)	212.1(5)
Eu–C(24)	298.6(5)	V(2)–C(27)	213.5(5)
Eu–C(25)	287.2(5)	V(2)–C(28)	215.4(5)
Eu–C(26)	286.1(5)	V(2)–C(29)	218.4(5)
Eu–C(27)	294.9(5)	V(2)–Cp(2) ^a	159.4(2)
Eu–C(28)	308.4(5)	V(2)–C(34)	225.2(5)
Eu–C(29)	306.8(4)	V(2)–C(35)	222.4(6)
Eu–Cp(2) ^a	260.1(2)	V(2)–C(36)	222.5(7)
V(1)–C(1)	222.1(7)	V(2)–C(37)	224.3(7)
V(1)–C(2)	224.0(5)	V(2)–C(38)	225.9(6)
V(1)–C(3)	225.5(5)	V(2)–Cp(4) ^a	190.8(3)
V(1)–C(4)	225.1(6)		
V(1)–C(5)	223.0(6)		
V(1)–Cp(3) ^a	189.7(3)		

^a Cp(1) is the centroid of the ring C(6)–C(11), Cp(2) of C(24)–C(29), etc.

$[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\eta^6\text{-C}_{10}\text{H}_8)]$ sandwiches, bonded η^6 to the europium atom via the naphthalene bridges. Additionally, one THF and one DME molecule are coordinated to the Eu. The angle V–Eu–V is 126° . The naphthalene ligands remain planar. The distances of the europium atom to the carbon atoms of both η^6 -coordinating rings are in the ranges 284.5 and 301.9 pm with an average of 292.7 pm for C(6) to C(11), and 286.1 and 308.4 pm with an average of 297.0 pm for C(24) to C(29). This is noticeably longer than the comparable Gd–C(η^6) bonds in the bis(arene) complex $[1,3,5\text{-}(\text{t-Bu})_3\text{C}_6\text{H}_3]_2\text{Gd}$ (263 pm) [16] or the Eu–C(η^5) distances in $(\text{C}_5\text{Me}_5)_2\text{Eu}$ (279 pm) [17]. However, they are very close to the Ln–C(η^6) bonds in $(\text{C}_6\text{H}_6)\text{Ln}(\text{AlCl}_4)_3$ (293 pm for Ln = Nd and 291 pm for Ln = Sm) [18]. The C–C bonds in the naphthalene ring coordinated to europium are elongated and equalized compared with free naphthalene. These C–C distances are in the range 142 and 146 pm and close to those in $(\text{C}_5\text{H}_5)\text{V}(\mu_2\text{-C}_{10}\text{H}_8)\text{V}(\text{C}_5\text{H}_5)$ (139.7 to 146.8 pm) [6], $(\text{C}_6\text{H}_6)\text{Cr}(\mu_2\text{-C}_{10}\text{H}_8)\text{Cr}(\text{C}_6\text{H}_6)$ (138.8 to 146.6 pm) [7] and $[(\text{C}_5\text{H}_5)\text{V}(\mu_2\text{-C}_{10}\text{H}_8)\text{Yb}(\text{C}_5\text{H}_5)(\text{THF})]_n$ (143 to 145 pm) [10]. The arrangement of the $[(\text{C}_5\text{H}_5)\text{V}(\text{C}_{10}\text{H}_8)]$ fragments does not differ essentially from that found in $[(\text{C}_5\text{H}_5)\text{V}(\mu_2\text{-C}_{10}\text{H}_8)\text{V}(\text{C}_5\text{H}_5)]$ and $[(\text{C}_5\text{H}_5)\text{V}(\mu_2\text{-C}_{10}\text{H}_8)\text{Yb}(\text{C}_5\text{H}_5)(\text{THF})]_n$. The oxygen atoms of THF and DME lie on the bisectorial plane of the V–Eu–V

Table 2

Selected bond angles in $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-C}_{10}\text{H}_8)_2\text{Eu}(\text{THF})(\text{DME})]_n$ (**1**) (estimated standard deviations in the last significant figures are given in parentheses)

Bond angle (deg)		Bond angle (deg)	
O(1)–Eu–Cp(1)	109.59(9)	Cp(1)–Eu–Cp(2)	132.35(6)
O(1)–Eu–Cp(2)	117.60(9)	Cp(1)–Eu–Cp(3)	177.61(14)
O(2)–Eu–Cp(1)	101.88(9)	Cp(2)–Eu–Cp(4)	175.98(15)
O(2)–Eu–Cp(4)	94.26(9)	Eu–Cp(1)–V(1)	175.35(12)
O(3)–Eu–Cp(1)	102.90(9)	Eu–Cp(2)–V(2)	173.79(12)
O(3)–Eu–Cp(2)	98.13(9)		

angle. Selected bond distances and angles for **1** are given in Tables 1 and 2.

The X-ray crystal structure analysis for **3**, shows a structure very close to that of its ytterbium analogue $[(\text{C}_5\text{H}_5)\text{V}(\mu_2\text{-C}_{10}\text{H}_8)\text{Yb}(\text{C}_5\text{H}_5)(\text{THF})]_n$ [10]. It is a polymer, built from infinite zig-zag chains formed by the $[\text{Eu}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_5)]$ units. Each europium atom of this chain is further coordinated η^2 by the naphthalene of one $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\eta^6\text{-C}_{10}\text{H}_8)]$ unit and by the oxygen atom of one THF (Fig. 3). The two shortest Eu–C_(naphthalene) distances (286.9(8) and 282.8(8) pm) are close to those in the ytterbium analogue (263 and 287 pm) and are in the range of the corresponding Eu–C bonds in **1**. The geometry of the $[(\text{C}_5\text{H}_5)\text{V}(\text{C}_{10}\text{H}_8)]$ fragment (angle $(\text{C}_{10}\text{H}_8)_{(\text{centroid})}\text{-V-Cp}_{(\text{centroid})} = 178.8(2)^\circ$, distance $\text{V-C}_{10}\text{H}_8_{(\text{centroid})} = 190.2(4)$, distance $\text{V-Cp}_{(\text{centroid})} = 159.2(3)$ pm) is practically the same as found in the ytterbium analogue [10]. Selected bond distances and angles for **3** are given in Tables 3 and 4.

4. Experimental

The complexes described below are extremely sensitive to moisture and air. Therefore, both the synthesis

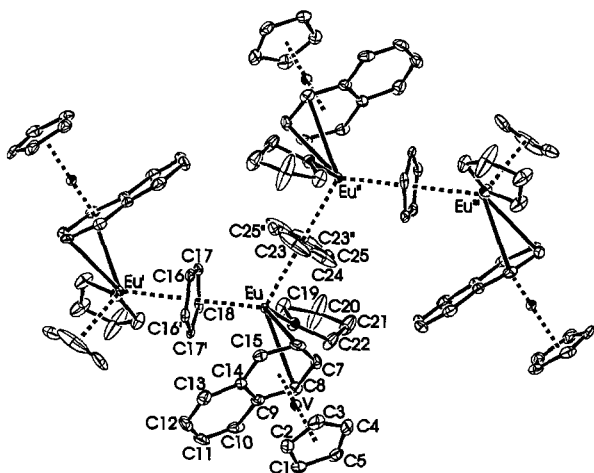


Fig. 3. ORTEP [15] projection of one molecule of $[(\text{C}_5\text{H}_5)\text{V}(\text{C}_{10}\text{H}_8)\text{Eu}(\text{C}_5\text{H}_5)(\text{THF})]_n$ (**3**) with the numbering scheme. Hydrogen atoms are excluded for clarity.

Table 3

Selected bond distances in $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\mu_2\text{-}\eta^6\text{:}\eta^2\text{-C}_{10}\text{H}_8)\text{Eu}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_5)(\text{THF})]_n$ (**3**) (estimated standard deviations in the last significant figures are given in parentheses)

Bond distance (pm)		Bond distance (pm)	
Eu–O(1)	255.8(5)	V–C(1)	224.5(8)
Eu–C(6)	286.9(8)	V–C(2)	224.0(9)
Eu–C(7)	282.8(8)	V–C(3)	222.9(10)
Eu–C(8)	303.7(8)	V–C(4)	226.0(10)
Eu–C(9)	330.8(8)	V–C(5)	225.0(8)
Eu–C(14)	334.4(8)	V–Cp(3)	190 (1)
Eu–C(15)	309.8(8)	V–C(6)	210.5(8)
Eu–C(16)	288.2(8)	V–C(7)	211.6(8)
Eu–C(17)	290.7(8)	V–C(8)	213.9(8)
Eu–C(18)	289.6(5)	V–C(9)	218.5(8)
Eu–Cp(1)	262.7(8)	V–C(14)	215.6(7)
Eu–Cp(2)	265 (1)	V–C(15)	215.4(8)
		V–Cp(4)	159.2(8)

and subsequent manipulation of these compounds were conducted in vacuum lines with rigorous exclusion of air and water using Schlenk techniques. THF and DME were distilled from sodium benzophenone ketyl. $(\text{C}_5\text{H}_5)_2\text{V}$ was prepared by a literature procedure [19] and converted to an equimolar mixture of $\text{K}(\text{C}_5\text{H}_5)$ and $\text{K}[(\text{C}_{10}\text{H}_8)\text{V}(\text{C}_5\text{H}_5)]$ by reaction with $\text{K}(\text{C}_{10}\text{H}_8)$ in situ in THF or DME [11]. $\text{EuI}_2(\text{THF})_2$ was prepared from excess Eu powder and CH_2I_2 in THF solution. The purity was determined by iodine analysis. $\text{SmI}_2(\text{THF})_2$ was obtained analogously. $\text{EuI}_2(\text{DME})_3$ and $\text{SmI}_2(\text{DME})_3$ were prepared by refluxing $\text{LnI}_2(\text{THF})_3$ ($\text{Ln} = \text{Eu}, \text{Sm}$) with DME. $(\text{C}_{10}\text{H}_8)\text{Eu}(\text{DME})_2$ was synthesized from EuI_2 and $\text{Na}(\text{C}_{10}\text{H}_8)$ using the literature procedure [20]. IR spectra were recorded as Nujol mulls with a Perkin–Elmer 577 spectrometer, the ESR spectra using a Bruker ER 200D-1SRC spectrometer (9.35 MHz) and the magnetic susceptibility measurements were carried out by a previously published procedure [21].

4.1. $[(\text{C}_5\text{H}_5)\text{V}(\text{C}_{10}\text{H}_8)]_2\text{Eu}(\text{THF})(\text{DME})$ (**1**)

$\text{EuI}_2(\text{DME})_3$ (3.61 g, 5.36 mmol) was placed in a Schlenk tube and 10 ml of DME was added with vigorous stirring. An equimolar mixture of $\text{K}(\text{C}_5\text{H}_5)$ and $\text{K}[(\text{C}_{10}\text{H}_8)\text{V}(\text{C}_5\text{H}_5)]$, obtained in situ from 0.75 g (4.14 mmol) of $(\text{C}_5\text{H}_5)_2\text{V}$ and $\text{K}(\text{C}_{10}\text{H}_8)$ (prepared in

Table 4

Selected bond angles in $[(\eta^5\text{-C}_5\text{H}_5)\text{V}(\mu_2\text{-}\eta^6\text{:}\eta^2\text{-C}_{10}\text{H}_8)\text{Eu}(\mu_2\text{-}\eta^5\text{:}\eta^5\text{-C}_5\text{H}_5)(\text{THF})]_n$ (**3**) (estimated standard deviations in the last significant figures are given in parentheses)

Bond angle (deg)		Bond angle (deg)	
O(1)–Eu–C(6)	115.8(2)	O(1)–Eu–Cp(2)	96.0(4)
O(1)–Eu–C(7)	86.3(2)	Eu–Cp(1)–Eu'	178.9(2)
O(1)–Eu–C(8)	75.1(2)	Cp(3)–V–Cp(4)	178.8(2)
O(1)–Eu–Cp(1)	103.2(2)		

situ from 0.32 g (8.2 mmol) of K and 1.06 g (8.28 mmol) of $C_{10}H_8$ in 50 ml of DME), was added. The color of the solution changed rapidly from brownish-green to red-brown and a pale solid was formed. After 15 min of stirring, the mixture was centrifuged, decanted from the pale precipitate and the solvent was reduced to 10–15 ml by evaporation in vacuum. Addition of 5 ml of THF and 20 ml of hexane with vigorous stirring resulted in the precipitation of 1.07 g (65%) dark crystals of **1**, m.p. 113–116 °C (decomp.). IR (CsI, cm^{-1}): 1320 (s), 1240 (w), 1200 (w), 1180 (w), 1170 (w), 1105 (m), 1095 (s), 1060 (s), 1030 (m), 1015 (w), 995 (m), 980 (m), 945 (s), 875 (m), 860 (s), 780 (s), 760 (m), 730 (s), 705 (w), 615 (s), 530 (m), 470 (w), 430 (m), 405 (w), 365 (m). Magnetic susceptibility: $\chi_M(293\text{ K}) = 27844 \times 10^{-6}$ cgsu, $\mu_{eff} = 8.1$ BM. ESR (DME, 25 °C): 8 lines, $g_i = 2.00$, $A_i = 4.5$ mT. Anal. Found: C, 57.66; H, 5.85. $C_{38}H_{44}EuO_3V_2$ (**1**). Calc.: C, 56.92; H, 5.53%.

4.2. $[(C_5H_5)V(C_{10}H_8)]_2Sm(THF)(DME)$ (**2**)

The same procedure as given for **1**, using (4.53 g, 6.71 mmol) of $SmI_2(DME)_3$, 1.3 g (10 mmol) of $C_{10}H_8$, 0.39 g (10 mmol) of K and 0.9 g (4.78 mmol) of $(C_5H_5)_2V$, resulted in the isolation of 1.38 g (72%) of dark crystals of **2**, m.p. 110–115 °C (decomp.). IR (CsI, cm^{-1}): 1315 (s), 1240 (w), 1200 (w), 1180 (w), 1170 (w), 1105 (m), 1095 (s), 1060 (s), 1030 (m), 1015 (w), 995 (m), 980 (m), 945 (s), 875 (m), 860 (s), 780 (s), 760 (m), 730 (s), 705 (w), 615 (s), 530 (m), 470 (w), 430 (m), 405 (w), 365 (m). Anal. Found: C, 56.85; H, 6.06. $C_{38}H_{44}O_3SmV_2$ (**2**). Calc.: C, 56.98; H, 5.54%.

4.3. $[(C_5H_5)V(C_{10}H_8)Eu(C_5H_5)(THF)]_n(THF)_{n/2}$ (**3**)

(a) The same procedure as given for **1**, using (4.42 g, 6.54 mmol) of $EuI_2(DME)_3$, 1.45 g (11.32 mmol) of $C_{10}H_8$, 0.43 g (11.02 mmol) of K and 1.0 g (5.52 mmol) of $(C_5H_5)_2V$, resulted in a red-brown solution which was centrifuged and decanted from a pale precipitate. The solvent was removed from this solution in vacuum and 10 ml of THF was added to the dark waxy residue. After keeping this THF solution for 2 days at room temperature a black microcrystalline solid was precipitated, which was isolated and dried in vacuum. Yield: 0.45 g (14%) of **3**. IR (CsI, cm^{-1}): 1320 (s), 1170 (m), 1060 (m), 1030 (s), 995 (s), 980 (w), 940 (s), 910 (w), 875 (m), 800 (s), 780 (s), 760 (s), 730 (s), 710 (s), 615 (w), 530 (m), 435 (m), 400 (w), 360 (w). Magnetic susceptibility: $\chi_M(293\text{ K}) = 26146 \times 10^{-6}$ cgsu, $\mu_{eff} = 7.86$ BM. Anal. Found: C, 54.45; H, 5.66. $C_{26}H_{30}EuO_{1.5}V$ (**3**). Calc.: C, 54.92; H, 5.32%.

(b) $(C_5H_5)_2V$, (1.31 g, 7.2 mmol) was added to a suspension of $C_{10}H_8Eu(DME)_2$ (4.69 g, 10.25 mmol) in 25 ml of DME and the reaction mixture was stirred

Table 5

Crystal data and details for $[(\eta^5-C_5H_5)V(\mu_2-\eta^6:\eta^6-C_{10}H_8)]_2Eu(THF)(DME)$ (**1**) and $[(\eta^5-C_5H_5)V(\mu_2-\eta^6:\eta^2-C_{10}H_8)Eu(\mu_2\eta^5:\eta^5-C_5H_5)(THF)]_n$ (**3**)

	1	3
Formula	$C_{38}H_{44}O_3EuV_2$	$C_{28}H_{34}O_2EuV$
<i>a</i> (pm)	1203.6(4)	1916.0(3)
<i>b</i> (pm)	1230.8(6)	1330.4(3)
<i>c</i> (pm)	1140.8(3)	1765.3(4)
α (deg)	91.37(4)	90
β (deg)	97.14(3)	90.17(2)
γ (deg)	100.44(3)	90
$V \times 10^6$ pm ³	1647(1)	4499.7(15)
<i>Z</i>	2	8
Space group	<i>P1</i> (No. 2)	<i>C2/c</i> (No. 15)
ρ_{calc} (g cm ⁻³)	1.61	1.70
μ (cm ⁻¹)	23.3	31.9
Unique reflections	3222	5054
Observed refl. [$F_o > 3\sigma(F_o)$]	3055	2734 ($> 4\sigma(F_o)$)
R^a	0.0260	0.032
R_w^b	0.0315	

$$^a R = \sum |\Delta F| / \sum |F_o|; \quad ^b R_w = [\sum w^{1/2} |\Delta F| / \sum w^{1/2} |F_o|]$$

for 1 h. The color of the solution turned from black to dark red-brown. After centrifugation and decantation of the solution, the DME was removed in vacuum and 5 ml of THF was added to the residue. This resulted in the isolation of 1.53 g (37%) of black crystals of **3**. The IR spectrum is identical to that of the compound isolated after using route (a).

4.4. $[(C_5H_5)V(C_{10}H_8)Sm(C_5H_5)(THF)]_n(THF)_{n/2}$ (**4**)

The same procedure as given for **3**, using (8.81 g, 13.05 mmol) of $SmI_2(DME)_3$, 2.7 g (121.09 mmol) of $C_{10}H_8$, 0.81 g (20.51 mmol) of K and 1.89 g (10.44 mmol) of $(C_5H_5)_2V$, resulted in 0.47 g (8%) of black microcrystals of **4**. IR (KBr, cm^{-1}): 1320 (s), 1170 (m), 1100 (m), 1060 (m), 1030 (s), 995 (s), 980 (w), 940 (s), 910 (w), 875 (m), 800 (s), 780 (s), 760 (s), 730 (s), 710 (s), 615 (w), 540 (m), 435 (m), 400 (w), 360 (w). Magnetic susceptibility: $\chi_M(23\text{ K}) = 6198 \times 10^{-6}$ cgsu, $\mu_{eff} = 3.78$ BM. Anal. Found: C, 54.89; H, 5.83. $C_{26}H_{30}O_{1.5}SmV$ (**4**). Calc.: C, 55.01; H, 5.33%.

4.5. X-ray crystal structure determination of **1** and **3**

Crystal data and other details of the structure determination are collected in Table 5. The crystals were selected using a modified device, similar to that of Veith and Bärninghausen [22]. The crystals were mounted on a glass fiber and transferred to an Enraf-Nonius CAD 4 four circle diffractometer (ω - 2θ scan, $\lambda = 0.71069$ Å) equipped with a low temperature device. The measurements were performed at 150 K. The

raw data were corrected for Lorentz and polarization effects. Absorption correction was carried out using the empirical method DIFABS [23]. Structure solution and refinement were carried out with the SHELXS-86 [24] and SHELXL-93 [25] software respectively. The refinement method was full-matrix least squares on F^2 . The older SHELX-76 [26] program was also used to prepare the data for DIFABS. The input files for the SHELX programs were prepared with the program UTILITY [27]. All non-hydrogen atoms were refined with anisotropic temperature factors. The positions of the hydrogen atoms were calculated with fixed isotropic temperature factors ($U_{\text{iso}} = 0.08 \text{ \AA}^2$). In **3**, one cyclopentadienyl ring (C(23)–C(25)') and the THF molecule are disordered. Further details of the structure investigation is available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH D-76344 Eggenstein-Leopoldshafen, Germany, upon quoting the depository numbers (CSD 59053 for **1**, and CSD 404053 for **3**), the authors names, and the full citation of the journal.

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