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Dicyclopentadienylsamarium complexes with t-butyl substituents in the ring. Crystal and molecular structures of the solvate $(\eta^5\text{-}C_5H_3Bu^t_2)_2Sm \cdot OC_4H_8$ and homoleptic ate complex $[NaSm(\eta^5:\eta^2\text{-}C_5H_4Bu^t)_3 \cdot OC_4H_8]_n$

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Abstract

Interaction of SmI_2 with $C_5H_3Bu^t_2Na$ and $C_5H_4Bu^tNa$ yielded a monosolvate (I) with the formula $(\eta^5\text{-}C_5H_3Bu^t_2)_2Sm \cdot OC_4H_8$ and a homoleptic ate complex (II) with the formula $[NaSm(\eta^5:\eta^2\text{-}C_5H_4Bu^t)_3 \cdot OC_4H_8]_n$. The crystals of I are monoclinic: *a* 11.449(3); *b* 15.305(4); *c* 17.688(5) Å; γ 92.93(2)°; space group $P2_1/n$; $Z = 4$; d_{calcd} 1.24 g/cm³. This compound is monomeric with a pseudotrigonal coordination environment around the Sm atom. The crystals of II are rhombic: *a* 8.969(2); *b* 15.964(4); *c* 21.701(5) Å; space group $Pc2/n$; d_{calcd} 1.30 g/cm³. The lattice of II is built up of planar polymer grids between which crystallizational THF molecules are located.

Introduction

In recent years, study of the complexes of metals that are in the +2 oxidation state [1] has yielded particularly remarkable and striking results in the case of the organometallic chemistry of lanthanoids. The chemical properties of the compounds differ substantially from those displayed by lanthanoidal metallocenes that are in the +3 oxidation state. For example, formation of stable hetero- and homoleptic ate complexes with the formula $Cp'LnX_2ML_n$ [2–5] ($Cp' = C_5H_5$, C_5Me_5, $C_5H_3(SiMe_3)_2$, $C_5H_3Bu^t_2$) and $M = LnCp_4$ [6,7] is characteristic of biscyclopentadienyl-Ln^{3+} derivatives, whereas for Ln^{2+} the structure of only one ate complex with the formula $Li[(C_5Me_5)YbI_2] \cdot 2Et_2O$ [8], and the synthesis of $KSm(C_5H_5)_3$ [9], have been reported.

In the chemistry of low-valent lanthanoid complexes, particular emphasis has up to now been laid on compounds that have a C_5Me_5 ligand whose effect is to decrease the acidity of the compound. This effect might also be achieved by the use of more accessible cyclopentadienyl ligands with bulky t-butyl substituents.

The present communication describes the synthesis of samarocene complexes with t-butylcyclopentadienyl ligands: monosolvate $(\eta^5\text{-}C_5H_3Bu^t_2)_2Sm \cdot OC_4H_8$ (I) and homoleptic ate complex $[NaSm(\eta^5:\eta^2\text{-}C_5H_4Bu^t)_3 \cdot OC_4H_8]_n$ (II), and discusses results of X-ray diffraction studies on them.

Experimental

For the X-ray diffraction study, all synthetic and sampling operations were carried out under vacuum or dry argon.

SmI_2 was prepared as described in ref. 10. t-Butylcyclopentadiene and di-t-butylcyclopentadiene were synthesized as described previously [11] and metallized with sodium amide in liquid ammonia.

$(C_5H_3Bu^t_2)_2Sm \cdot THF$ (I). Complex I was produced by the interaction of SmI_2 and $C_5H_3Bu^t_2Na$ in the ratio 1/2 in THF. $C_5H_3Bu^t_2Na$ (3 g; 15 mmol) in 75 ml of THF was added to SmI_2 (3 g; 7.4 mmol) in 50 ml of THF at room temperature. The solution turned black-brown. The mixture was stirred for 5 h, THF was removed under vacuum, and 100 ml of toluene was added. The dark-violet suspension was stirred for 10 h, the residue was filtered, the sediment was evaporated to an oil and 10 ml of pentane added. After 1 h, the black solution evolved dark-green, nearly black, acicular crystalline solids which were separated from the mother liquor by decantation, washed with cold pentane and evaporated under vacuum (yield ~ 70%). Found: Sm, 26.3. $C_{30}H_{50}SmO$ calcd.: Sm, 26.04%.

$NaSm(C_5H_4Bu^t)_3 \cdot THF$ (II). Complex II was prepared either through the interaction of SmI_2 and $C_5H_4Bu^tNa$ in the ratio 1/3 in THF (Method A) or through that of $(C_5H_4Bu^t)_2Sm \cdot 2THF$ and $C_5H_4Bu^tNa$ in the ratio 1/1 in THF (Method B).

Method A. $C_5H_4Bu^tNa$ (4.8 g; 33.3 mmol) in 100 ml of THF was added to SmI_2 (4.5 g; 11.1 mmol) in 100 ml THF. The red-violet solution was agitated for 5 h, then evaporated to a quarter of its volume, then 50 ml of ether added. The white sediment was filtered off and evaporated to 20 ml and again 100 ml of ether added. After 3 h red-violet crystalline solids were found which were on the walls of the flask, separated from the mother liquor, washed with ether and dried under vacuum (yield 22%)

Method B. $C_5H_4Bu^tNa$ (0.84 g; 5.8 mmol) in 50 ml of THF was added to III (3 g; 5.6 mmol) in 100 ml of THF. The red-violet solution was stirred for 5 h, evaporated to a volume of 20 ml under vacuum, then 100 ml of ether added. The deposited crystals were processed as with Method A (yield 35%). Found: Sm, 24.1; Na, 3.5. $C_{31}H_{47}SmNaO$ calcd.: Sm, 24.27; Na, 3.72%.

$(C_5H_4Bu^t)_2Sm \cdot 2THF$ (III). Complex III was produced via the interaction of SmI_2 and $C_5H_4Bu^tNa$ in the ratio 1/2 in THF.

Table 1

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) in $(C_5H_3Bu^t)_2Sm \cdot THF$ molecule

Atom	*x*	*y*	*z*	*U*
Sm	1261(1)	1664(1)	2332(1)	56(1)
O	1392(11)	3243(7)	2827(7)	80(5)
CT1 [a]	2044(21)	3614(15)	3467(14)	112(11)
CT2	1475(23)	4425(15)	3671(15)	162(14)
CT3	855(24)	4655(17)	3072(17)	169(15)
CT4	782(25)	3921(16)	2511(12)	123(13)
C1	3663(13)	1543(9)	1919(9)	72(6)
C2	3644(13)	1497(10)	2692(9)	69(6)
C3	3076(18)	680(15)	2921(12)	51(9)
C4	2714(15)	257(10)	2270(10)	74(7)
C5	3069(14)	811(12)	1658(9)	81(8)
C6	2971(19)	427(14)	3753(11)	61(9)
C7	2471(31)	1104(21)	4207(14)	199(18)
C8	2172(30)	−368(19)	3827(15)	206(17)
C9	4118(20)	193(20)	4084(14)	152(14)
C10	4174(15)	2179(16)	1396(13)	111(10)
C11	5329(26)	2350(26)	1512(26)	391(28)
C12	3508(38)	2916(22)	1277(25)	337(27)
C13	4197(36)	1862(29)	608(22)	336(29)
C14	−1146(13)	1275(12)	2605(10)	74(7)
C15	−1154(14)	1788(10)	1976(11)	69(7)
C16	−701(14)	1360(11)	1376(8)	65(7)
C17	−378(14)	560(9)	1633(9)	72(7)
C18	−663(16)	494(12)	2417(11)	68(9)
C19	−653(15)	1638(11)	586(10)	81(7)
C20	−1629(22)	1203(16)	126(12)	150(12)
C21	447(22)	1392(17)	145(12)	133(12)
C22	−663(29)	2632(18)	489(12)	204(16)
C23	−1645(17)	1505(19)	3401(13)	120(12)
C24	−2878(27)	1629(29)	3351(17)	267(23)
C25	−935(25)	2099(26)	3816(16)	303(22)
C26	−1911(37)	682(22)	3846(18)	290(24)

[a] T = statistically disordered atoms in a THF molecule.

$C_5H_4Bu^tNa$ (4 g; 27.8 mmol) in 120 ml of THF was added to SmI_2 (5.5 g; 13.5 mmol) in 140 ml of THF. The solution became cherry-red. The mixture was agitated for 4 h, the solvent was removed to 2/3, then 100 ml of ether was added. The resulting white residue was filtered off and the violet-red filtrate was evaporated until nearly dry. The blue-violet sediment was washed with ether and dried under vacuum (yield 58%). Found: Sm, 28.1; C, 58.0; H, 7.7%. $C_{26}H_{42}SmO_2$ calcd.: Sm, 27.98; C, 58.20; H, 7.84%.

The X-ray diffraction study of monocrystals of I and II packed in glass capillary tubes was performed by use of automatic Nicolet *P*3 (I) and Syntex $P\bar{1}$ (II) diffractometers (Mo-K_α irradiation, $\theta/2\theta$ scanning up to $2\theta \leqslant 45$).

Crystals of I were monoclinic: *a* 11.449(3); *b* 15.305(4); *c* 17.688(5) Å; γ 92.93(2)°, *V* 3095(1) $Å^3$; space group $P2_1/n$; $Z = 4$, d_{calcd}, 1.24 g/cm^3. 2043 reflections with $I \geqslant 3\sigma(I)$ were used for calculation.

Table 2

Atom coordinates ($\times 10^4$) and temperature factors (Å$^2 \times 10^3$) in the complex $[NaSm(C_5H_4Bu^t)_3 \cdot THF]_n$

Atom	x	y	z	U
Sm	5158(1)	2500	2260(1)	42(1)
Na	88(10)	817(6)	2644(6)	66(4)
C1	6575(25)	4135(14)	2361(13)	33(9)
C2	6266(32)	4131(20)	1686(17)	45(12)
C3	4686(30)	4115(20)	1653(11)	74(11)
C4	4006(41)	4195(30)	2252(31)	68(24)
C5	5130(51)	4213(21)	2635(19)	79(19)
C6	2059(29)	2575(51)	1997(18)	64(16)
C7	2046(21)	2662(13)	2627(11)	50(10)
C8	2715(43)	1750(29)	2812(20)	83(18)
C9	2944(43)	1223(28)	2370(20)	58(19)
C10	2612(36)	1563(20)	1791(18)	54(14)
C11	7343(40)	4102(26)	1179(15)	46(14)
C12	7198(59)	4980(24)	833(16)	104(20)
C13	7149(41)	3393(36)	753(18)	141(24)
C14	8980(37)	4140(33)	1419(20)	93(19)
C15	2625(37)	1348(18)	1180(21)	109(16)
C16	4028(43)	1730(22)	831(20)	87(17)
C17	1361(47)	1587(32)	708(28)	165(27)
C18	2951(53)	402(27)	1105(14)	117(20)
C19	7397(26)	1771(15)	3064(15)	44(11)
C20	8221(28)	2130(18)	2571(17)	61(13)
C21	7982(37)	1825(20)	2004(15)	71(13)
C22	7100(32)	1046(19)	2157(15)	58(13)
C23	6746(37)	1158(18)	2840(16)	57(13)
C24	7506(86)	1946(41)	3797(30)	85(25)
C25	7802(76)	2289(102)	3798(19)	339(59)
C26	8908(63)	1411(53)	4061(25)	238(39)
C27	6131(51)	1998(45)	4053(22)	229(41)
T1 [a]	8554(121)	8789(90)	244(63)	298(59)
T2	7825(156)	8469(67)	698(56)	328(46)
T3	7178(141)	8625(111)	776(64)	262(74)
T4	7000(138)	9764(87)	524(58)	244(53)
T5	7904(135)	9676(76)	71(46)	210(53)

[a] T = statistically disordered atoms in a THF molecule.

Table 3

Basic interatomic length (Å) and valence angles (°) in the $(C_5H_3Bu^t)_2Sm \cdot THF$ molecule

Bond	d (Å)	Angle	ω (°)
Sm–CpI	2.55	CpI/CpII	52.6
Sm–CpII	2.55	CpISmCpII	132.5
Sm–C_{mean}	2.81(4)	CpISmO	113.4
Sm–O	2.57(1)	CpIISmO	114.1
O–C1T	1.46(3)	CpI/C1–C10	3.7
O–C4T	1.40(3)		
C1T–C2T	1.48(3)	CpI/C3–C6	1.4
C2T–C3T	1.33(4)	CpII/C14–C23	2.3
C3T–C2T	1.50(4)	COC	106.7(15)
		SmOC	129.5(11)
		SmOC	123.8(12)

Table 4

Basic interatomic lengths in the complex $[NaSm(C_5H_4Bu^t)_3\cdot THF]_n$

Bond	*d*	Bond	*d*
Sm–C1	2.91(3)	Na–C1′	3.00(3)
Sm–C2	3.05(3)	Na–C2′	3.24(3)
Sm–C3	2.93(3)	Na–C3′	3.14(3)
Sm–C4	2.90(3)	Na–C4′	2.78(3)
Sm–C5	2.85(3)	Na–C5′	2.63(3)
Sm–C6	2.84(3)	Na–C6′	3.60(3)
Sm–C7	2.91(3)	Na–C7′	3.43(3)
Sm–C8	2.77(3)	Na–C8′	2.81(3)
Sm–C9	2.86(3)	Na–C9′	2.71(3)
Sm–C10	2.91(3)	Na–C10′	3.16(3)
Sm–C19	2.90(3)	Na–C19	3.00(3)
Sm–C20	2.89(3)	Na–C20	2.69(3)
Sm–C21	2.81(3)	Na–C21	2.84(3)
Sm–C22	2.91(3)	Na–C22	2.90(3)
Sm–C23	2.86(3)	Na–C23	3.08(3)
Sm–C_{mean}	2.89	Na–C_{mean}	3.00(26)
Sm–CpI	2.66	Na–CpI′	2.71
Sm–CpII	2.56	Na–CpII′	2.65
Sm–CpIII	2.61	Na–CpIII	2.90
C1–C2	1.49(4)	C9–C10	1.40(4)
C2–C3	1.42(4)	C6–C10	1.75(4)
C3–C4	1.44(4)	C10–C15	1.37(4)
C4–C5	1.31(4)	C19–C20	1.42(4)
C1–C5	1.43(4)	C20–C21	1.33(4)
C2–C11	1.47(4)	C22–C23	1.52(4)
C6–C7	1.37(4)	C22–C23	1.52(4)
C7–C8	1.63(4)	C19–C23	1.24(4)
C8–C9	1.29(4)	C19–C24	1.62(4)

Table 5

Basic valence angles in the complex $[NaSm(C_5H_4Bu^t)_3\cdot THF]_n$

Angle	*ω*	Angle	*ω*
CpISmCpII	122.1	CpI′NaCpII′	122.9
CpISmCpIII	113.4	CpI′NaCpIII	126.9
CpIISmCpIII	123.4	CpII′NaCpIII	109.7
CpI/CpII	68.5	C4′NaC20	121.0
CpII/CpIII	56.1	C4′NaC9	124.9
CpI/CpIII	123.1	C5′NaC8	122.0
C5′NaC21	116.0	C8′NaC21	109.0
C9′NaC20	113.0	C1C2C3	103.6
C2C3C4	112.1	C3C4C5	104.4
C4C5C1	115.6	C5C1C2	103.9
C6C7C8	98.7	C7C8C9	117.3
C8C9C10	112.3	C7C6C10	110.5
C6C10C9	100.9	C19C20C21	117.5
C20C21C22	100.3	C21C22C23	103.1
C22C23C19	112.0	C20C19C23	105.6
SmCpIINa	156.9	NaSmNa1	115.8
SmCpIIINa1	169.8	NaSmNa2	119.1
Na1CpI*Sm1	160.5	Na1SmNa2	121.1
SmNaSm2	115.8	SmNaSm3	119.9
Sm3NaSm2	121.9		

Crystals of II were rhombic: a 8.969(2); b 15.964(4), c 21.701(5) Å; V 3107(1) Å^3; space group $Pc2/n$; d_{calcd}, 1.30 g/cm^3. 1040 reflections with $I \geqslant 3\sigma(I)$ were used for calculation. No correction for absorption was applied for I and II (μ(Mo-K_α) 19.5 and 19.6 cm^{-1}, respectively).

The structures were solved by the Patterson method using a SHELXTL program package and verified by the least-squares method in the anisotropic (isotropic for a I · THF molecule) approximation up to $R = 0.057$ ($R_w = 0.056$) for I and $R = 0.045$ ($R_w = 0.047$) for II. The atomic coordinates are listed in Tables 1 and 2; the main interatomic distances and bond angles are given in Tables 3 and 5.

Results and discussion

The interaction of SmI_2 and sodium t-butylcyclopentadienide in THF provides two different products depending on the ratio of agents. Elemental analysis indicates that samarocene disolvate $(C_5H_4Bu^t)_2Sm \cdot 2THF$ (III) forms when the ratio of Cp′Na to SmI_2 is $1 \leqslant 2$, whereas the compound $NaSm(C_5H_4Bu^t)_3 \cdot THF$ (II) crystallizes from the solution when the ratio is 1/3.

Considering the 1,3-$C_5H_3Bu^t_2$ ligand, reaction involving any ratio of SmI_2 to $C_5H_3Bu^t$ yields only one product, namely the monosolvate $(C_5H_3Bu^t_2)_2Sm \cdot THF$ (I). X-ray analysis of the complex has shown that the compound is monomeric and has a pseudotrigonal coordination environment around the samarium atom (Fig. 1). A similar structure has been disclosed for the complex $(C_5Me_5)_2Yb \cdot THF$ [12], whereas permethylsamarocene tetrahydrofuranate contains two THF molecules [13] as is the case with most other compounds of this type [1.2].

The oxygen atom in molecule I is located almost exactly on the axis of symmetry of the wedge like Cp'_2Sm sandwich. The Sm–O distance (2.57 Å) in I is less than

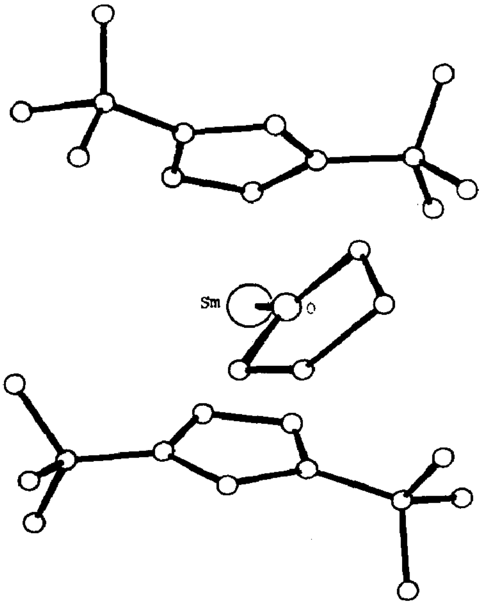

Fig. 1. Molecular structure of the complex $(\eta^5\text{-}C_5H_3Bu^t)_2Sm \cdot OC_4H_8$ (I).

that in $(C_5Me_5)_2Yb \cdot THF$ (2.41 Å) [12], though the covalent radius of the Yb atom is only 0.06 Å smaller than that of the Sm atom. This may be associated with higher Lewis' acidity in Yb than in Sm. The Cp–Sm and C_{mean}–Sm distances for I take on values intermediate between those known for $(C_5Me_5)_2Sm \cdot (THF)_2$ [13] and $(C_5Me_5)_2Sm \cdot DME$ [14], on the one hand, and for $(C_5Me_5)Yb \cdot THF$ [12], on the other.

The cyclopentadienyl ligands in the wedge-like sandwich $(C_5H_3Bu^t_2)_2Sm$ have a distorted conformation similar to that of $[(C_5H_3Bu^t_2)_2Lu(\mu\text{-}X)]_2$, where X is Cl [15] and H [16] and this provides a minimal repulsion between the rings and a molecule in THF. It should be noted that steric stress in the I molecule is slight, as is indicated by lower values of Bu^t-group angles of deflection from the ring planes (Table 3), whereas those in the $(C_5H_3Bu^t_2)_2$ complexes are as high as 12° [15,16]. The CpSmCp angle in I is less than that in $(C_5Me_5)_2Sm \cdot (THF)_2$ [13] and $(C_5Me_5)_2Sm \cdot DME$ [14] (137° and 140°, respectively), which is in good agreement with the fact that a $C_5H_3Bu^t_2$ ligand shows lower donor capacities than does a C_5Me_5 ligand.

Thus, the structure of I is generally typical of compounds of this kind, yet possesses some distinctive features. On the contrary, the structure of $NaSm(C_5H_4Bu^t)_3 \cdot THF$ has proved to be, to a great extent, unexpected.

Proceeding from the stereochemistry of II and the data available in the literature, one might think the compound would be an associate where the Sm atom is in the +2 oxidation state and surrounded by 3 or 4 $C_5H_4Bu^t$ groups and the Na atom, as in the complex $[Na(THF)_2][(Cp_3U)_2(\mu\text{-}H)]$ [17], is solvated with a THF molecule and as well as η-bound to the cyclopentadienyl ligands. An X-ray diffraction study of the compound, however, indicated that its THF molecule was crystallizational rather than solvated. Its minimal contact with the $[NaSmCp'_3]$ molecule (C7 atom) is 3.79 Å.

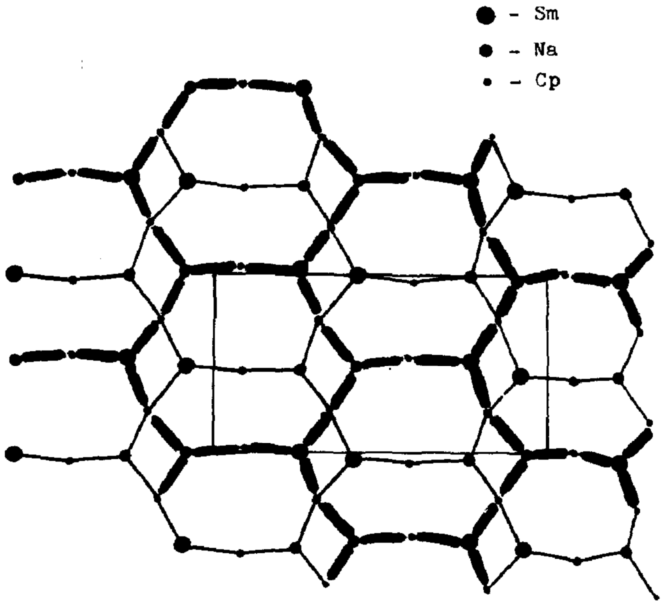

Fig. 2. Crystal lattice of the complex $[NaSm(\eta^5:\eta^2\text{-}C_5H_4Bu^t)_3 \cdot OC_4H_8]_n$ (II).

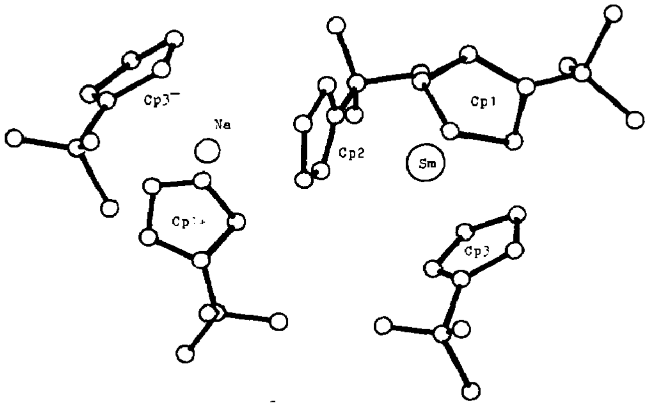

Fig. 3. Structure of the $[SmCp'_3NaCp'_3]$ group in a $[NaSm(\eta^5:\eta^2\text{-}C_5H_4Bu^t)_3 \cdot OC_4H_8]_n$ molecule.

Figure 2 shows that the crystal lattice in II is constructed from planar polymer grids with an identidal period along the *a* axis of 4.48 Å. Representing the cyclopentadienyl ligand as a point (the centres of the C_5 rings are denoted as black circles in Fig. 2), it is evident that the combined packing of $[SmCp'_3]$ anions and Na cations yields distorted hexagons in the layer, the average value of the walls of the hexagons (Sm–Na) being 5.29 Å with Sm–Na' distances of ~ 11.0–11.5 Å. The THF molecules are located above their interstices, as in the cell surrounded by t-butyl substituents. The hexagonal layer is virtually planar: the Sm and Na atoms are ±0.05 Å higher than the root-mean-square plane passing through all the metallic atoms in the layer. The structure of the compound means that it may be possible to synthesize layer insertion compounds like those that are already well-known in the chemistry of graphite.

The structure of the $[SmCp'_3NaCp'_3]$ group in the polymeric molecule of II is given in Fig. 3. The samarium atom is linked with three planar cyclopentadienyl rings in the range of 0.037 Å (Cp'I), 0.030 Å (Cp'II), and 0.068 Å (Cp'III). The quaternary C atoms in the t-butyl groups are slightly (0.20 Å at the most in the Cp'III ring) off the planes for corresponding rings. The ring conformation in the Cp'ISmCp'III and Cp'IISmCp'III wedge-like sandwiches is screened, but the substituents point in opposite directions, whereas that in the Cp'ISmCp'II is distorted, but with the substituents pointing in the same direction.

The Sm atoms are slightly off the plane formed by the centres of three Cp rings. The Sm–C distance in II varies within the range 2.77–3.06 Å (Table 4). The mean Sm–C distance (2.89 Å) in II is slightly larger than that (2.86 Å) found in $(C_5Me_5)_2Sm(THF)_2$ [18] and noticeably larger than those in $(C_5Me_5)_2Sm \cdot DME$ [14], $(C_5Me_5)_2Sm$ [19], and even in $[C_5H_3(SiMe_3)_2]_3Th$ [20] (2.82, 2.79, and 2.80 Å, respectively), though the covalent radii in Sm and Th are virtually equal. This is indicative of higher $Sm–C_5H_4Bu^t$ bond ionicity in II.

As it would be expected, the CpSmCp valence angles in II differ greatly from those typical of dicyclopentadienylsamarium complexes (136–140°) [14,18,19] and they are close to 120° (Table 5).

The coordination of the Na atom in II is brought about at the $C_5H_4Bu^t$ ligand, yet Table 4 indicates that two out of five Na–C distances are much shorter than the others. From this it follows that in addition to electrostatic interaction with the negatively charged cyclopentadienyl ring, the covalent component is fairly significant in this respect. This conclusion is supported by a noticeable alternation of the C–C bonds in the Cp rings (Table 4), a shorter C–C bond corresponding to short Na–C contacts. Thus, the cyclopentadienyl group in II appears as an η^2 ligand in relation to the Na atom.

As follows from the structural findings, the Sm atom in II has a coordination number of 9. Close Cp ligand coordination in two-valent lanthanoids has been found in the polymer complex of ytterbium with the formula $[(C_5H_4Me)_2Yb \cdot THF]_n$ [21]. However, due to solvation of a THF molecule, the Yb atom has a pseudo-tetrahedral environment and coordination number of 10. It is clearly evident that the coordination of 3Cp ligands following the η^5-type is determined by their spatial characteristics and the size of a metallic atom. In fact, complexes with 3 η^5-C_5H_5 groups, for example, a Nd complex, are well known to be typical [22] of a methyl-substituted cyclopentadienyl ligand and Ln^{3+} atoms are found in the cerium subgroup. Moreover, even a bulky ligand such as $C_5H_3(SiMe_3)_2$ provides an η^2-tris-complex with a Th atom ($r_{cov.}$ 1.65 Å) [20]. When the central atom (Sc, Lu) decreases in size, one of three C_5H_5 ligands becomes η^1-coordinated [23]. Steric hindrances produced by such a bulky ligand as C_5Me_5 result in failure of the formation of triscomplexes with η^5-coordination and Ln^{3+} and Ln^{2+} atoms. In the mixed-valence and mixed-ligand complex $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$, the normal ligand C_5H_5 is linked with both the metallic atoms by the $\eta^2 : \eta^5$-type [24]. The $C_5H_4Bu^t$ ligand differs slightly from a monomethyl-substituted ligand in steric characteristics. However, even this is sufficient to alter the basic structure of II as compared with $[(C_5H_4Me)_2Yb \cdot THF]_n$. A di-t-butylcyclopentadienyl ligand is close to permethylcyclopentadiene in its properties, as shown by the identical structures of $(C_5Me_5)_2Yb \cdot THF$ and I. The $C_5H_3Bu^t_2$ ligand seems to be inferior to a C_5Me_5 molecule in donor capacity, but is superior in the steric hindrance produced. This is indicated by the formation of disolvate in the case of $(C_5Me_5)_2Sm \cdot 2THF$ and monosolvate in the case of I.

The complex I is the first representative of a number of homoleptic cyclopentadienyl ate complexes with the general formula $[MCp'_n]^-$ to have its structure described. The Cp'_2M^- metallocene atoms are unstable and are readily degraded to split off Cp'^- [22], but MCp'_4 anions are unlikely to exist for steric reasons. The optimal stability seems to be displayed by MCp'^-_3 complexes, where M is a metal of a group, which exhibits strong acidity. Formation of such complexes is certain to require an optimal size ratio of a ligand and a metal, a complex producer.

The fact that it is easy to prepare complex I shows that such ate complexes may be formed during synthesis of two-valence lanthanide derivatives via salts of cyclopentadienes that are smaller in volume than C_5Me_5. This is undoubtedly to be borne in mind while synthesizing such compounds and, above all, complexes with a normal C_5H_5 ligand, which are themselves to be used as reagents.

References

1 I.P. Beletskaya, G.Z. Suleimanov, Metalloorg. Khim., 1 (1988) 10.
2 W.J. Evans, Adv. Organomet. Chem., 24 (1985) 131.
3 M.F. Lappert, A. Singh, J. Organomet. Chem., 239 (1982) 133.
4 H. Schumann, H. Lanke, E. Hahn, M.J. Heeg, D. Helm, Organometallics, 4 (1985) 321.

5 H. Schumann, S. Nickel, E. Hahn, M.J. Heeg, Organometallics, 4 (1985) 800.
6 H. Schumann, J. Less-Common Met., 112 (1985) 327.
7 K. Jacob, M. Glauz, K. Tittes, K.H. Thiele, Z. Anorg. Allg. Chem., 556 (1988) 170.
8 P. Watson, J. Chem. Soc., Chem. Commun., (1980) 652.
9 G.B. Deacon, G.N. Pain, T.D. Tuong, Polyhedron, 4 (1985) 1149.
10 P. Girarg, J.L. Namy, H.B. Kagan, J. Am. Chem. Soc., 102 (1980) 2693.
11 T. Leigh, J. Chem. Soc., (1964) 3294.
12 T. Don Tilley, R.A. Andersen, A. Zalkin, Inorg. Chem., 19 (1980) 2999.
13 W.J. Evans, J.W. Yrate, H.W. Choi, I. Bloom, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc., 107 (1985) 941.
14 S.J. Swamy, J. Loebel, J. Pickardt, H. Schumann, J. Organomet. Chem., 353 (1988) 27.
15 V.K. Belsky, S.Ya. Knyazhansky, B.M. Bulychev, G.L. Soloveichik, Metalloorg. Khimiya, 2 (1989) 507.
16 S.Ya. Khyazhansky, V.K. Belsky, B.M. Bulychev, G.L. Soloveichik, Metalloorg. Khim., 2 (1989) 570.
17 J.F. Le Marechal, C. Villievs, P. Chaplin, M. Lance, M. Nierlich, J. Vigner, M. Ephritikhine, J. Chem. Soc., Chem. Commun., (1989) 308.
18 W.J. Evans, I. Bloom, W.E. Hunter, J.L. Atwood, J. Am. Chem. Soc., 103 (1981) 6507.
19 W.J. Evans, L.A. Hughes, T.P. Hanusa, J. Am. Chem. Soc., 106 (1984) 4270.
20 P.C. Blake, M.F. Lappert, J.L. Atwood, H. Zhang, J. Chem. Soc. Chem. Commun., (1986) 1148.
21 H.A. Zinnen, J.J. Pluth, W.J. Evans, J. Chem. Soc., Chem. Commun., (1980) 810.
22 J.H. Burns, W.H. Baldwin, F.H. Fink, Inorg. Chem., 13 (1974) 1916.
23 S.H. Eggers, H. Schultze, J. Kopf, R.D. Fischer, Angew. Chem., 98 (1986) 631.
24 W.J. Evans, T.A. Ulibarri, J. Am. Chem. Soc., 109 (1987) 4292.