Synthesis, Fluxional Behaviour in Solution and Crystal Structure of the Organolanthanide Complexes $[Ln(C_5H_4CH_2CH_2OMe)_2(thf)][Co(CO)_4]$ (Ln = Sm or Yb, thf = tetrahydrofuran)†

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The $[Ln(C_5H_4CH_2CH_2OMe)_2(thf)]^+$ cations (Ln = Sm **1** or Yb **2**, thf = tetrahydrofuran) which represent the first examples of organolanthanide cationic complexes with $[Co(CO)_4]^-$ as anion, have been synthesised by metathesis of $[Ln(C_5H_4CH_2CH_2OMe)_2I]$ with $K[Co(CO)_4]$ or by one-electron oxidation of divalent $[Ln(C_5H_4CH_2CH_2OMe)_2(thf)]$ with $[Co_2(CO)_8]$. The crystal structure of complex **2** has been determined: space group $P2_12_12$, a = 10.700(3), b = 11.509(4), c = 10.381(4) Å, Z = 2. Least-squares refinement led to convergence with R = 0.040, R' = 0.047. It exists as discrete cations and anions with no Ln–OC–Co linkage. The samarium analogue **1** is isostructural. Variable-temperature NMR studies indicated that, at low temperature, the spectra of complex **1** are in good accordance with the structure in the solid state. At high temperature the two ether chains of **2** remain co-ordinated on the metal.

The chemistry of cationic compounds of early d-block transition metals and actinide elements has received much attention.[1–6] This interest arises from the suggestions that such cationic species play a major role in the polymerization of olefins by Ziegler–Natta and Kaminsky-type catalyst systems. However, cationic organolanthanide chemistry is much less developed and few such species have been reported and structurally characterized, *e.g.* $[Sm(\eta\text{-}C_5Me_5)_2(thf)_2][BPh_4]$ (thf = tetrahydrofuran),[7] $[Ce(\eta\text{-}C_5Me_5)_2(thf)_2][BPh_4]$,[8] $[La(\eta\text{-}C_5Me_5)_2[CH(SiMe_3)_2](thf)_3][BPh_4]$,[9] $[La\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(NCMe)(dme)][BPh_4]\cdot 0.5dme$[10] (dme = dimethoxyethane) and $[Sm(\eta\text{-}C_5Me_5)_2(N_2H_4)][BPh_4]$.[11] All these cationic compounds contain the same non-co-ordinating BPh_4^- anion.

Many f metal–actinide[12] and –lanthanide acid–base complexes with bridging carbonyl groups have been reported.[13–21] All these complexes present a Ln–CO–M interaction in which the metal carbonyl acts as a Lewis base. In contrast, the complex $[SmI_2(thf)_5][Co(CO)_4]$ containing discrete $[SmI_2(thf)_5]^+$ cations and $[Co(CO)_4]^-$ anions has been described as 'the first structure of a transition metal carbonyl compound reduced by a divalent lanthanide in which isocarbonyl linkages are not found'.[21] In this complex, the presence of five thf ligands seemed to impede the Sm–OC–Co 'isocarbonyl' linkage formation. Suitable crystals of this pentasolvate have been obtained from a thf-saturated solution of $[SmI_2(thf)_4][Co(CO)_4]$.[21] Similar behaviour has been reported for chloro derivatives of lanthanum, ytterbium and lutetium.[22] We thought that Ln–CO–M isocarbonyl linkages might also be avoided by using a donor cyclopentadienyl chelating ligand, $MeOCH_2CH_2C_5H_4$, and tried to synthesise cationic organolanthanide complexes with $[Co(CO)_4]^-$ as counter ion by reaction of $[Ln(C_5H_4CH_2CH_2OMe)_2I]$ and $K[Co(CO)_4]$ or by one-electron oxidation of divalent organolanthanide complexes with $[Co_2(CO)_8]$. We report here the synthesis, structure and variable-temperature NMR study of the complexes $[Ln(C_5H_4CH_2CH_2OMe)_2(thf)][Co(CO)_4]$ (Ln = Sm or Yb).

Experimental

All operations were performed under prepurified argon by use of Schlenk techniques or in a glove-box. All solvents were refluxed over sodium–benzophenone and distilled under argon immediately before use. The compounds $[Ln(C_5H_4CH_2CH_2OMe)_2I]$ (Ln = Sm or Yb),[23,24] $[Ln(C_5H_4CH_2CH_2OMe)_2(thf)]$[25] and $K[Co(CO)_4]$[26] were prepared by published procedures; $[Co_2(CO)_8]$ (Aldrich) was used without further purification. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer in Nujol or Fluorolube mulls, on CsI discs; the samples were prepared in an argon-filled glove-box. Proton NMR spectra were recorded on a Bruker AC 200 spectrometer with positive fields being downfield from the external standard $SiMe_4$. The solvent $[^2H_8]$thf was dried over Na/K alloy and degassed by freeze–thaw cycles on a vacuum line; C_6D_6 was dried over sodium sand and stored on 4 Å molecular sieves. Samples were stored in sealed tubes.

Preparations.—$[Sm(C_5H_4CH_2CH_2OMe)_2(thf)][Co(CO)_4]$ **1**. A mixture of $[Sm(C_5H_4CH_2CH_2OMe)_2I]$ (0.953 g, 1.822 mmol) and $K[Co(CO)_4]$ (0.383 g, 1.822 mmol) in dry thf (50 cm^3) was stirred at room temperature for 24 h. The suspension was centrifuged to remove solids, the volume of the yellow filtrate reduced in vacuum to *ca.* 20 cm^3 and toluene (4 cm^3) was added. The clear solution produced yellow crystals of complex **1** (0.72 g, yield 62%), m.p. 148 °C (decomp.).

Alternatively, $[Co_2(CO)_8]$ (0.359 g, 1.05 mmol) was dissolved in thf (*ca.* 10 cm^3) and slowly added to a flask containing $[Sm(C_5H_4CH_2CH_2OMe)_2(thf)]$ (0.832 g, 2.10 mmol) in thf (30 cm^3) in the dark at 0 °C. The resulting solution was then stirred for 4 h at room temperature, yielding a light brown solution. The solvent volume was slowly reduced in vacuum to *ca.* 20

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

cm^3. After storage overnight at room temperature, the clear solution produced yellow crystals of complex **1** (0.78 g, 58% yield), m.p. 148 °C (decomp.). ^{1}H NMR ([^{2}H$_8$]thf, 297 K): δ 1.3 (d, 3 H, *J* 10, OCH$_3$), 3.2 (2 H, *J* 25, OCH$_2$), 4.2 (2 H, *J* 25, CH$_2$), 7.1 (2 H, *J* 40, $C_5H_4CH_2CH_2OMe$) and 10.2 (2 H, *J* 140 Hz, $C_5H_4CH_2CH_2OMe$). IR: 2067w, 2022w, 2003w, 1872s (br), 1056m, 1043m, 992w, 809m, 794m, 722w, 552m, 385w and 261w cm^{-1}.

[Yb($C_5H_4CH_2CH_2OMe$)$_2$(thf)][Co(CO)$_4$] **2**. This complex was prepared similarly from either [Yb($C_5H_4CH_2CH_2OMe$)$_2$I] or [Yb($C_5H_4CH_2CH_2OMe$)$_2$ (thf)] in 65 and 55% yield respectively, as red crystals, m.p. 112 °C (decomp.). For ^{1}H NMR data see Table 5. IR: 2021m, 1975w, 1873s (br), 1044m, 1005m, 965m, 858m, 803m, 721w, 552s, 390w and 257w cm^{-1}.

Satisfactory elemental analyses could not be obtained for these complexes [*e.g.* Found: C, 44.00; H, 4.30; Co, 8.00 (by difference); Sm, 19.40. Calc. for $C_{24}H_{30}CoO_7Sm$: C, 45.05; H, 4.70; Co, 9.25; Sm, 23.50%].

Crystal Structure Analysis of [Yb($C_5H_4CH_2CH_2OMe$)$_2$(thf)][Co(CO)$_4$] **2**.—A red crystal of complex **2** of approximate dimensions 0.40 × 0.30 × 0.15 mm was sealed in a thin-walled glass capillary filled with argon. The lattice parameters were determined and intensity measurements done on a Rigaku AFC5R diffractometer using Mo-Kα radiation (graphite monochromated, λ 0.710 69 Å). All 1618 data were corrected for Lorentz, polarization and absorption effects. A careful examination of a preliminary data set revealed the systematic extinctions *h*00 for $h = 2n + 1$ and 0*k*0 for $k = 2n + 1$; the space group $P2_12_12$ is uniquely defined (Table 2).

The structure was solved by direct methods (MITHRIL)[27] and refined by full-matrix least-squares techniques. Hydrogen-atom contributions were included using a riding model with d(C–H) = 0.96 Å and B_{iso} fixed at 1.3B_{iso} of the carbon atoms bearing them. Refinement of positional and anisotropic thermal parameters [Yb, O(2) and Co atoms lie on special positions, so U_{13}, U_{23} set to zero for these atoms] led to convergence with $R = 0.040$, $R' = 0.047$ and goodness of fit = 1.22 for 151 variables refined against those 1192 data with $I > 3\sigma(I)$. A final Fourier difference map was devoid of significant features, maximum of 0.70 e Å^{-3}. The final values of the positional parameters are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The use of 2-methoxyethylcyclopentadienyl as a ligand[28] for organolanthanides has been developed by the Shanghai group since 1989. This easily synthesised compound obviously possesses the properties of a Lewis base. The formation of an intramolecular co-ordination bond between the oxygen atom of the chain and a metal centre takes place affording a stable five-membered metallacycle. Both the increase of the co-ordination number of the metal and of the steric bulk effect enhance significantly the stability of the organolanthanide complexes.[24–26,28,29] Like the well known C_5Me_5 and C_5H_3(SiMe$_3$)$_2$-1,3, the present ligand enhances both the solubility and crystallinity of the complexes.

Synthesis of [Ln($C_5H_4CH_2CH_2OMe$)$_2$(thf)][Co(CO)$_4$].—These compounds were obtained in two ways: (*a*) the reaction of [Ln($C_5H_4CH_2CH_2OMe$)$_2$I] in thf solution with 1 equivalent of K[Co(CO)$_4$] at room temperature affords the novel cationic organolanthanide complexes **1** (Ln = Sm) and **2** (Ln = Yb) in 62 and 65% yield respectively; (*b*) the one-electron oxidation of [Ln($C_5H_4CH_2CH_2OMe$)$_2$(thf)] with [Co$_2$(CO)$_8$] in thf solution in the dark for 5 h affords crystals of **1** and **2** in 58 and 55% yield respectively. As expected for ionic molecules, the two complexes are essentially insoluble in aromatic and aliphatic solvents and poorly soluble in thf, especially **2**. Satisfactory elemental analyses could not be obtained, but the complexes were unambiguously identified by spectroscopic analysis and by determination of their crystal structures.

IR Spectra.—The IR data for **1** and **2** and related compounds are listed in Table 1. The C–O stretching frequencies for **2** are very similar to values reported for compounds [NR$_3$H][Co(CO)$_4$]$^-$.[30] This indicated that no bridging carbonyl groups are present; use of $MeOCH_2CH_2C_5H_4$ as a ligand means that the oxygen atom of the chain acts as a Lewis base and co-ordinates to the metal precluding M–CO–Ln interactions and affording cationic organolanthanide complexes without isocarbonyl linkage.

It is well known that lanthanide complexes act as Lewis acids towards metal carbonyls to form acid–base complexes with bridging carbonyl groups.[12,13,15] In these complexes the Ln–OC interaction tends to reduce the CO stretching frequency, *e.g.* in [(η-C_5Me_5)$_2$Yb(OC)Co(CO)$_3$][13a] the corresponding wavenumber is lowered by 112 cm^{-1} relative to that found for **2**.

Crystal Structure.—Suitable single crystals of complex **2** were obtained by crystallization from thf–toluene (5:1). The structure is shown in Fig. 1, crystallographic data in Table 2, atomic coordinates in Table 3 and selected bond distances and angles in Table 4. In accordance with the infrared data, **2** exists as discrete [Ln($C_5H_4CH_2CH_2OMe$)$_2$(thf)]$^+$ cations and [Co(CO)$_4$]$^-$ anions. The anion has normal distances and angles[21] and is well separated from the cation. The cation adopts a very distorted trigonal-bipyramidal structure with the two oxygen atoms of the chain on the axis of the trigonal pyramid.

The ytterbium and O(2) atoms lie on a two-fold axis ($\frac{1}{2}$,0,*z*) and the Co atom occupies a special position ($\frac{1}{2}$,$\frac{1}{2}$,*z*), so the overall molecular symmetries of the cation and of the anion are C_2. The centroid(1)–Yb–centroid(2) angle of 126.0° is comparable to those of 127.1 and 128.4(2)° in [Yb($C_5H_4CH_2CH_2OMe$)$_2$I] **3**[23] and [Yb($C_5H_4CH_2CH_2OMe$)$_2$(thf)][25] respectively. However it is smaller than the analogous angle 139.4(7)° in [(η-C_5Me_5)$_2$Yb(OC)Co(CO)$_3$(thf)].[13a] The average Yb–C (ring) bond length of 2.57(2) Å is similar to those found in the trivalent species [(η-C_5Me_5)$_2$Yb(OC)Co(CO)$_3$(thf)] [2.596(2) Å] and **3** (2.596 Å) but significantly shorter than that found in the divalent species, [Yb($C_5H_4CH_2CH_2OMe$)$_2$-

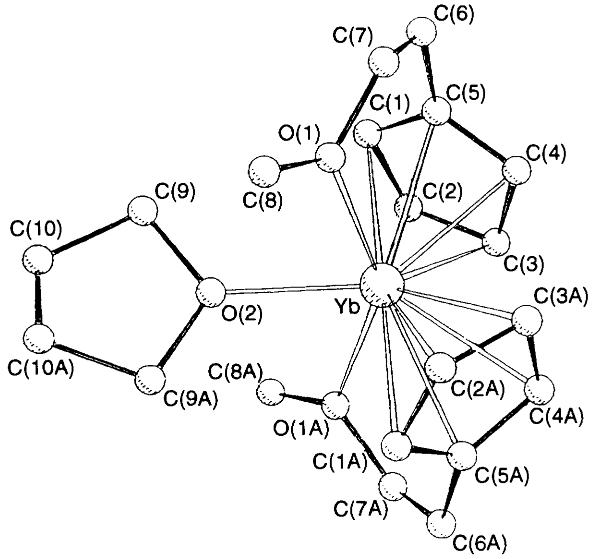


Fig. 1 Structural representation of the cationic part of complex **2**. Hydrogen atoms are omitted

Table 1 Infrared spectral data

Complex	Medium	$\tilde{\nu}$(CO)/cm^{-1}	Ref.
$[Sm(C_5H_4CH_2CH_2OMe)_2(thf)][Co(CO)_4]$	Nujol	2067w, 2022w, 2003w, 1872s (br)	This work
$[Yb(C_5H_4CH_2CH_2OMe)_2(thf)][Co(CO)_4]$	Nujol	2021w, 1975w, 1873s (br)	This work
$[NMe_3H][Co(CO)_4]$	Toluene	2015w, 1943s, 1899vs	30
$[NEt_3H][Co(CO)_4]$	Toluene	2015w, 1931s, 1895vs	30
$[SmI_2(thf)_4][Co(CO)_4]$	KBr	1930–1840s (br), 1783s	21
$[Sm(\eta\text{-}C_5Me_5)(thf)][Co(CO)_4]$	Nujol	2025s, 1950s, 1920w, 1860 (br), 1785 (br)	21
$[(\eta\text{-}C_5Me_5)_2Yb(OC)Co(CO)_3(thf)]$	Nujol	2023w, 1973w, 1939s, 1917s, 1823w, 1798m (sh), 1761s	13
$[(\eta\text{-}C_5Me_5)_2Yb(OC)_2Mn(CO)_3]$	Nujol	1965s, 1937 (sh), 1928 (sh), 1822m, 1840s, 1775s	14
$[(\eta\text{-}C_5Me_5)_2Yb(OC)_2Re(CO)_3]$	Nujol	1982 (sh), 1972s, 1950s, 1945 (sh), 1785 (sh), 1770 (sh), 1750s (br)	14

Table 2 Crystal data, data collection and refinement for complex **2**

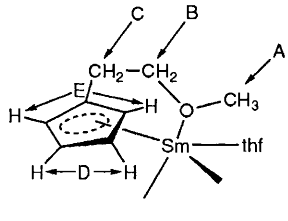
Formula	$C_{24}H_{30}CoO_7Yb$
M	662.47
Crystal system	Orthorhombic
Space group	$P2_12_12$ (no. 18)
a/Å	10.700(3)
b/Å	11.509(4)
c/Å	10.381(4)
U/Å^3	1278.4(7)
Z	2
D_c/g cm^{-3}	1.72
Diffractometer	Rigaku AFC5R
T/K	298
hkl ranges	0–13, 0–14, 0–12
Scan type	2θ–ω
Scan speed/° min^{-1}	16.0
2θ range/°	3–54
μ(Mo-Kα)/mm^{-1}	4.311
Reflections collected	1648
Independent reflections	1618

Table 3 Atomic positional parameters for complex **2**

Atom	*x*	*y*	*z*
Yb	$\frac{1}{2}$	0	0.126 80(6)
O(1)	0.692(1)	−0.092(1)	0.191(1)
O(2)	$\frac{1}{2}$	0	0.350 1(9)
C(1)	0.653(2)	0.172(2)	0.128(2)
C(2)	0.538(2)	0.215(2)	0.073(2)
C(3)	0.500(4)	0.165(2)	0.040(2)
C(4)	0.616(2)	0.093(2)	0.062(2)
C(5)	0.697(2)	0.101(2)	0.040(2)
C(6)	0.819(2)	0.022(5)	0.063(4)
C(7)	0.803(3)	−0.072(2)	0.119(4)
C(8)	0.704(2)	−0.187(2)	0.276(2)
C(9)	0.591(2)	0.064(2)	0.433(2)
C(10)	0.539(7)	0.042(3)	0.568(2)
Co	$\frac{1}{2}$	$\frac{1}{2}$	0.454 8(3)
O(O1)	0.422(2)	0.314(2)	0.614(2)
C(O1)	0.453(2)	0.389(2)	0.548(2)
O(O2)	0.705(3)	0.427(3)	0.300(3)
C(O2)	0.622(3)	0.457(3)	0.365(3)

(thf)] (2.737 Å)[25] and $[Yb(\eta\text{-}C_5Me_5)_2(NC_5H_5)_2]$ [2.742(7) Å][31] because the ionic radius of Yb^{II} is *ca.* 0.16 Å larger than that of Yb^{III}. This difference in ionic radii explains why the Yb–O(2) bond length of 2.32(1) Å is shorter than that found in $[Yb(C_5H_4CH_2CH_2OMe)_2(thf)]$, 2.496(4) Å. However, it is close to those found in $[(\eta\text{-}C_5Me_5)_2Yb(OC)Co(CO)_3(thf)]$ [2.335(2) Å]. The C–O bond length of 1.15(2) Å is equal to those of terminal CO and *ca.* 0.05 Å smaller than that of bridging CO in $[(\eta\text{-}C_5Me_5)_2Yb(OC)Co(CO)_3(thf)]$ (Table 4).

A yellow crystal of complex **1** also obtained by slow crystallization from thf–toluene (5:1) was found to be isostructural with **2**: orthorhombic, space group $P2_12_12$, a = 10.807(3), b = 11.603(3), c = 10.482(3) Å, U = 1314.4(6) Å^3, Z = 2.



^{1}H *NMR Spectra.*—The ytterbium complex **2** is very poorly soluble in [$^2H_8$]thf: at room temperature (297 K) the spectrum shows only one paramagnetic well resolved signal (δ 50.0). At 333 K three sharp signals of relative intensity 3:2:2 and two broad signals of intensity *ca.* 2 were recorded. These were attributed to the protons of the chain and of the ring respectively by comparison with the spectrum of **3**, recorded in C_6D_6 (Table 5).

The chemical shifts of the chain protons CH_3OCH_2 are in the same range for complexes **2** and **3**. The latter, which does not contain any co-ordinated thf, obviously exists in C_6D_6 solution as a five-co-ordinated complex with the two oxygen atoms of the chain ligated to the metal as found in the solid state.[24] Such a conformation should lead to a more complicated spectrum (nine signals, see below), but rapid intramolecular exchange, probably by Berry pseudo-rotation, which is very common for five-co-ordinated species, leads to an averaged spectrum (five signals). In [$^2H_8$]thf solution the chemical shifts of **3** are unchanged but the signals sharpen. This suggests that in a co-ordinating solvent the chains remain bonded to the metal and that the contribution of a six-co-ordinated species $[Yb(C_5H_4CH_2CH_2OMe)_2I(thf)]$ to the exchange process cannot be precluded. Complex **2** very likely has the same structure without any chain–solvent competition.

The spectrum of the more soluble samarium complex **1** recorded at 297 K shows five signals of relative intensity 3:2:2:2:2 at δ 1.3(A), 3.2(B), 4.2(C), 7.1(D) and 10.2(E). The last signal is broadened ($w_{\frac{1}{2}}$ = 180 Hz). A variable-temperature NMR study in the range 193–333 K revealed interesting changes which were all reversible. At 193 K, in addition to the well resolved thf signals at δ 1.7 and 3.5, and to the weak signals of very small amounts of free $C_5H_5CH_2CH_2OMe$, nine signals (A, B_1, B_2, C_1, C_2, D_1, D_2, E_1, E_2) were recorded. As the temperature was raised A remained unchanged, B_1 and B_2 and C_1 and C_2 coalesced into B and C at *ca.* 257 K, D_1 and D_2 into D at 263 K and E_1 and E_2 also coalesced at 273 K. This higher temperature of coalescence is due to a greater difference in chemical shifts. After heating all the signals sharpened and at 333 K A appeared as a singlet, B and C as poorly resolved triplets whereas E($w_{\frac{1}{2}}$ = 50 Hz) remained slightly more broadened than D ($w_{\frac{1}{2}}$ = 20 Hz).

After analysis of the complete set of spectra and decoupling experiments, all the signals were assigned: A to CH_3, B (B_1 and B_2), C (C_1 and C_2) respectively to β- and α-CH_2 of the chain, D (D_1 and D_2) and E (E_1 and E_2) to the cyclopentadienyl ring protons. In the range 193–253 K signals E_1 and E_2 exhibit a large difference in chemical shifts of *ca.* 8 ppm. These two

Table 4 Comparison of selected bond distances (Å) for complex **2**[a] and some bis(cyclopentadienyl)ytterbium complexes

Bond	[Yb($C_5H_4CH_2CH_2OMe)_2$-(thf)]$^+$ **2**	[(η-$C_5Me_5)_2$Yb(OC)Co-(CO)$_3$(thf)]	[Yb($C_5H_4CH_2CH_2$-OMe)$_2$I] **3**	[Yb($C_5H_4CH_2CH_2OMe)_2$-(thf)]
Yb–O(1)	2.41(1)		2.450	2.564(3)
Yb–O(2)	2.32(1)	2.335(2)		2.496(4)
Yb–C (ring)	2.57(2)	2.596(2)	2.596	2.737
Yb–centroid	2.288	2.302(10)	2.334	2.440(4)
Yb–O(bridging CO)		2.258(2)		
Co–C	1.68(2)	1.70(3)[b] 1.77(3)[c]		
O–C	1.15(2)[d]	1.14(2)[b] 1.19(3)[c]		
Ref.	This work	12	23	25

[a] Selected bond angles (°): centroid (1)–Yb–centroid (2). [b] Terminal. [c] Bridging 126.0, O(1)–Yb–O(1A) 147.8(5), O(1)–Yb–O(2) 73.9. [d] Average value.

Table 5 Proton NMR data for complexes **2** and **3**

Complex	Conditions	Chain $CH_3OCH_2CH_2$			Ring	
2	[$^2H_8$]thf, 297 K	50.0 (100)*	—	—	—	—
	[$^2H_8$]thf, 333 K	43.1 (100)	23.8 (200)	−11 (150)	−16 (1800)	−41 (800)
3	[$^2H_8$]thf, 297 K	72.7 (100)	53.6 (100)	7.0 (100)	−3.0 (200)	−82 (600)
	C_6D_6, 297 K	73.8 (100)	53.2 (400)	6.5 (400)	−3.0 (400)	−83 (3500)

* $W_{\frac{1}{2}}$ in Hz.

signals, and therefore E, could be assigned to the α and α′ ring protons whereas D_1 and D_2 ($\Delta\delta = 3$ ppm) and D were assigned to the β and β′ protons. In the same way the differences in chemical shifts were *ca.* 1.5 ppm for the α methylenic proton signals (C_1 and C_2) and *ca.* 0.5 ppm for the β protons (B_1 and B_2). In the range 193–333 K the chemical shifts of the signals of the methylenic protons decrease in accordance with a normal Curie–Weiss law, whereas those of the cyclopentadienyl proton increase following a reverse Curie–Weiss law (Fig. 2). This behaviour has also been observed in the cyclopentadienyllanthanide series.[32]

At low temperature the observed spectra are in good accord with the solid-state geometry (both CH_3 groups are equivalent whereas the two protons of α- and β-CH_2 groups and also the α, α′ and β, β′ cyclopentadienyl protons are inequivalent). The structure is stable or the exchange processes are slow. Upon raising the temperature the exchanges became faster and at room temperature Berry pseudo-rotation can occur or co-ordination of one or two molecules of thf with concomitant deco-ordination of the chain followed by rotation of the cyclopentadienyl rings. It is noteworthy that the signals of the co-ordinated CH_3OCH_2 moiety show very weak chemical shifts, close to their diamagnetic position. This is not surprising: it has been previously reported that in samarium complexes containing one or two thf the chemical shifts of the OCH_2 signals of co-ordinated thf, recorded in benzene or toluene solution, were also very close to the diamagnetic position,[32,33] but this does not allow us to establish the average mechanism. Nevertheless, in a co-ordinating solvent such as thf the major exchange process might be chain–solvent competition: for the larger early samarium, the intramolecular chelation is expected to be weaker than for the smaller late ytterbium ion; the former ion is also more accessible for the additional co-ordination of thf molecules.

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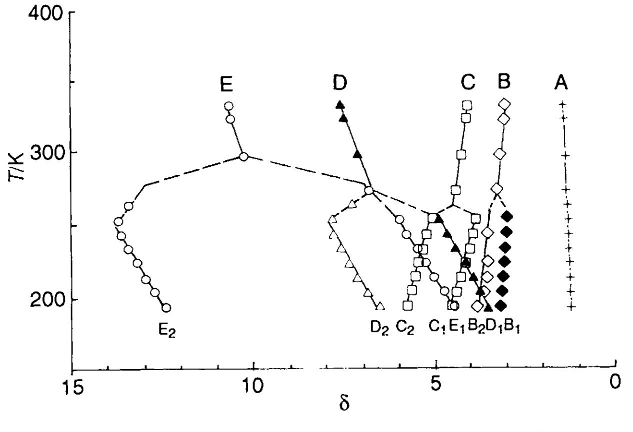

Fig. 2 Variation of the chemical shifts of the signals of complex **1** *versus* temperature in [$^2H_8$]thf

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