

Structure of (Acetonitrile- d_3)tris(η^5 -cyclopentadienyl)samarium

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Abstract. $[\text{Sm}(\text{C}_5\text{H}_5)_3\text{NCCD}_3]$, $M_r = 389.69$, orthorhombic, $Pnma$, $a = 19.501(6)$, $b = 9.645(5)$, $c = 8.223(4)$ Å, $V = 1547(2)$ Å³, $Z = 4$, $D_x = 1.67$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 37.973$ cm⁻¹, $F(000) = 756$, $T = 295(1)$ K, $R = 0.036$ for 767 reflections [$I > 3\sigma(I)$]. The samarium displays pseudo-tetrahedral geometry *via* coordination to three cyclopentadienyl rings and one σ -bonded acetonitrile ligand. The molecule as a whole exhibits imposed C_s symmetry. The Sm—N bond nature and strength are similar for all $\text{Ln}(\text{C}_5\text{H}_5)_3\text{NC}-R$ ($R = \text{alkyl}$) complexes.

Introduction. Molecular and crystal structures of a number of 1:1 adducts of the strongly Lewis-acidic organolanthanoid complexes $\text{Ln}(\text{C}_5\text{H}_5)_3$, with different bases, have been reported in the literature: $(\text{C}_5\text{H}_5)_3\text{Pr}(\text{CN}-\text{C}-\text{C}_6\text{H}_{11})$ (Burns & Baldwin, 1976), $[(\text{C}_5\text{H}_5)_3\text{Yb}]_2(\mu\text{-pyrazine})$ (Baker & Raymond, 1977), $(\text{C}_5\text{H}_5)_3\text{M}(\text{THF})$ ($M = \text{Y, La, Nd, Sm, Gd}$ or Lu) (Rogers, Atwood, Emad, Sikora & Raush, 1981; Rogers, Bynum & Atwood, 1980; Benetollo, Bombieri, Bisi Castellani, John & Fisher 1984; Ni, Deng & Qian, 1985; Deacon, Koplick & Tuong, 1984), $(\text{C}_5\text{H}_5)_3\text{M}(\text{py})$ ($M = \text{Sm}$ and Nd) (Deacon, Gatehouse, Platts & Wilkinson, 1987), $(\text{C}_5\text{H}_5)_3\text{-La}(\text{NC}-\text{CH}_2-\text{CH}_3)$ (Spirlet, Rebizant, Apostolidis & Kanellakopoulos, 1987).

The structures of $\text{Ln}(\text{C}_5\text{H}_5)_3$ complexes usually exhibit polymeric chain arrangements. The coordination of the Ln atoms is pseudo-tetrahedral, the Ln atoms being bonded to two pentahapto- and to one monohapto- or bihapto-cyclopentadienyl rings (Rebizant, Apostolidis, Spirlet & Kanellakopoulos, 1988). Upon addition of a Lewis base, the bridging bonds are broken up and the completion of the coordination sphere of the Ln atom is achieved by adduct formation. So far, no crystal structure has been reported for a lanthanide tricyclopentadienyl

1:1 adduct with the acetonitrile ligand. A deuterated acetonitrile solution allowed us to obtain single crystals of the samarium derivative, whose crystal structure is reported here.

Experimental. The compound was synthesized by stoichiometric reaction of tris(cyclopentadienyl)samarium with CD_3CN in *n*-pentane at room temperature. Recrystallization from CD_3CN afforded single crystals. A selected specimen ($0.20 \times 0.25 \times 0.25$ mm) was sealed in a thin-walled glass capillary under an inert atmosphere. Enraf-Nonius CAD-4 X-ray diffractometer, graphite-monochromated $\text{Mo } K\alpha$ radiation using $\theta-2\theta$ scans. Cell parameters were refined by least squares from angle data of 25 reflections in the range $9 < 2\theta < 20^\circ$. The space group was established from systematic absences. Data were collected in the ranges $2 < 2\theta < 24^\circ$, $h = -10 \rightarrow 0$, $k = 0 \rightarrow 12$, $l = 0 \rightarrow 24$; 2676 reflections were collected, corresponding to 1442 unique reflections, 767 with $I > 3\sigma(I)$ were used in refinement. Intensities of three standard reflections measured at 30 min intervals showed no deviations from mean. Intensities were corrected for Lorentz-polarization effects; empirical absorption corrections using the program *DIFABS* (Walker & Stuart, 1983), transmission coefficients min. 0.9792 and max. 1.0624. The structure was solved by direct methods and refined by full-matrix least-squares techniques which minimized $\sum w(\Delta F)^2$, $w = 1/[\sigma(F_o)]^2$ with $\sigma(F_o) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I) + (AI)^2]^{1/2}/Lp$, where A , the ignorance factor, is 0.07. Anisotropic thermal parameters for non-H atoms; cyclopentadienyl H atoms in calculated positions included in final structure factor calculation with B_{iso} between 7.0 and 9.0 Å². Acetonitrile- d_3 D atoms were not included in the refinement. A secondary-extinction coefficient refined to a value of $g = 1.225 \times 10^{-7} \{F_c = F_o/[1 + g(F_o^2)Lp]\}$. $R = 0.036$, $wR = 0.047$, $S = 1.239$, $(\Delta/\sigma)_{\text{max}} = 0.03$, $\Delta\rho$ in final difference Fourier map within $+1.705$ and -1.182 e Å⁻³. Atomic scattering

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factors and anomalous-dispersion terms were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf-Nonius (1986) *SDP* programs were used.

Discussion. Table 1 contains final atomic positional parameters for the non-H atoms. Selected distances and angles are reported in Table 2.* The molecular structure is presented in Fig. 1. Atoms designated by numbers only are C atoms. H atoms have been omitted to simplify the drawing.

The Sm ion is pentahapto covalently bonded to three planar cyclopentadienyl groups and to one acetonitrile N atom to provide a formal coordination number of ten (each η^5 -C₅H₅ ligand being considered as a donor of three electron pairs). The stereochemistry is similar to that observed in other (C₅H₅)₃LnX (X = unidentate ligand) complexes with ring centroid–metal–ring centroid angles in the range 110 to 120°, as in the compounds cited in the *Introduction*. In the present case, the pseudo-tetrahedral coordination polyhedron has imposed C_s symmetry, the Sm atom, the acetonitrile molecule and one C atom of one cyclopentadienyl ring lying on a mirror plane.

The Sm—C distances average 2.74 (1) Å, in agreement with the values reported for the pentahapto Sm—C bond lengths in Sm(C₅H₅)₃ (Wong, Lee & Lee, 1969). They also compare favorably with the distances previously reported for several pentahapto-cyclopentadienyl samarium complexes (Rogers *et al.*, 1981; Deacon *et al.*, 1987). C—C bond lengths and C—C—C bond angles in each C₅ ring agree with known values.

Subtraction of the ionic radius, 1.17 Å, of ten-coordinated samarium (Shannon, 1976; Raymond & Eigenbrot, 1980) from the Sm—N bond length gives a value of 1.36 Å, significantly shorter than the corresponding values (1.40 to 1.52 Å) calculated for a series of organolanthanoid complexes with nitrogen-donor ligands (Deacon *et al.*, 1987). Subtraction of the relevant ionic radii from the metal–nitrogen bond lengths in (C₅H₅)₃La(NCCH₂CH₃) and in (C₅H₅)₃Yb(NCCH₂CH₃) (Spirlet *et al.*, 1987) gives 1.35 and 1.31 Å respectively. Thus identical metal–nitrogen bonding is observed for 1:1 adducts of Ln(C₅H₅)₃ with aliphatic nitrile ligands. Ln—N bonds are significantly weaker in the corresponding 1:2 adducts (Deacon *et al.*, 1987; Spirlet *et al.*, 1987) as well as in 1:1 adducts with the pyridine ligand (Deacon *et al.*, 1987; Spirlet *et al.*, 1987).

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, C—C and N≡C bond lengths, and C—C—C and N≡C—C bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53151 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$B_{\text{eq}} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B _{eq} (Å ²)
Sm	0.39061 (4)	0.25000	0.21502 (8)	3.46 (1)
C(1)	0.3734 (7)	-0.035 (1)	0.237 (1)	7.4 (4)
C(2)	0.4213 (6)	-0.002 (1)	0.352 (2)	6.3 (3)
C(3)	0.3868 (7)	0.074 (1)	0.470 (1)	8.0 (3)
C(4)	0.3175 (7)	0.087 (1)	0.422 (1)	7.6 (3)
C(5)	0.3109 (7)	0.021 (1)	0.278 (2)	7.8 (4)
C(6)	0.456 (1)	0.250	-0.086 (2)	6.8 (5)
C(7)	0.4192 (8)	0.137 (2)	-0.085 (1)	9.1 (4)
C(8)	0.3456 (6)	0.181 (2)	-0.089 (1)	11.6 (7)
N	0.5177 (6)	0.250	0.276 (1)	5.2 (3)
C(9)	0.5752 (9)	0.250	0.316 (2)	5.2 (4)
C(10)	0.6473 (6)	0.250	0.367 (3)	6.0 (4)

Table 2. *Selected distances (Å) and angles (°) in [Sm(C₅H₅)₃NCCD₃]*

Standard deviations are given in parentheses.

(a) Interatomic bond distances and angles

Sm—C(1)	2.77 (1)	N—Sm—Rc1*	97.6 (5)
Sm—C(2)	2.74 (1)	N—sm—Rc2*	98.4 (5)
Sm—C(3)	2.70 (1)	Rc1—Sm—Rc1'	119.0 (5)
Sm—C(4)	2.72 (1)	Rc1—Sm—Rc2	117.7 (5)
Sm—C(5)	2.75 (1)	Sm—N—C(9)	175 (1)
Sm—C(6)	2.79 (2)	N—C(9)—C(10)	180 (2)
Sm—C(7)	2.76 (1)		
Sm—C(8)	2.73 (1)		
Sm—N	2.53 (1)		

(b) Short intermolecular contacts (< 3.4 Å)

C(1)···C(7)	3.25 (2)	C(2)···N	3.13 (2)
C(3)···C(3')	3.39 (3)	C(6)···N	3.21 (2)
C(4)···C(4')	3.15 (2)		

(c) Short intermolecular contacts (< 3.7 Å)

C(2)···C(9 ⁱⁱ)	3.63 (2)	C(3)···C(9 ⁱⁱ)	3.66 (2)
C(2)···C(10 ⁱⁱ)	3.59 (2)	C(3)···C(10 ⁱⁱ)	3.46 (1)

Symmetry code: (i) x, 0.5 - y, z; (ii) 1 - x, -y, 1 - z.

* Rc1 denotes the centroid of ring 1 [C(1), C(2), C(3), C(4), C(5)]; Rc2 the centroid of ring 2 [C(6), C(7), C(8), C(7'), C(8')].

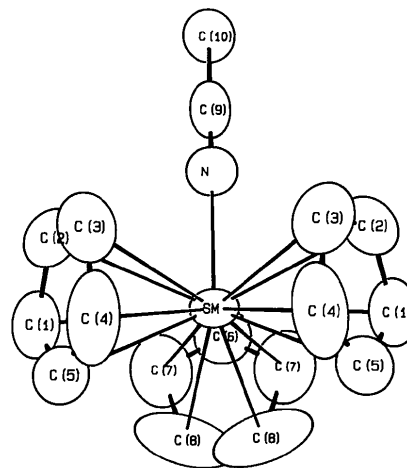


Fig. 1. The molecular structure. Thermal ellipsoids are at the 50% probability level.

A significant feature observed in $\text{Sm}(\text{C}_5\text{H}_5)_3\text{NCCD}_3$ is the deviation from linearity of the $\text{Sm}-\text{N}=\text{C}$ arrangement: there is a bending of about 5° between the $\text{Sm}-\text{N}$ bond and the linear acetonitrile ligand as shown by the $\text{Sm}-\text{N}\equiv\text{C}$ angle (Table 2). Analogous deviations are displayed by the propionitrile derivative $(\text{C}_5\text{H}_5)_3\text{M}(\text{py})$ ($M = \text{Sm}, \text{Nd}$) (Deacon *et al.*, 1987). The deviations could result from steric hindrance in the unit-cell packing since there are some short intermolecular contacts (Table 2), less than 3.7 \AA (Pauling, 1960; Raymond & Eigenbrot, 1980), involving the acetonitrile C atoms and the cyclopentadienyl rings in $\text{Sm}(\text{C}_5\text{H}_5)_3\text{NCCD}_3$, and also in the $\text{Ln}(\text{C}_5\text{H}_5)_3\text{NCCH}_2\text{CH}_3$ complex (Spirlet *et al.*, 1987). It should be noted, nevertheless, that a nearly linear $\text{Pr}-\text{C}\equiv\text{N}$ arrangement has been observed in the isocyanide complex $(\text{C}_5\text{H}_5)_3\text{Pr}(\text{CN}-\text{C}-\text{C}_6\text{H}_{11})$ (Burns & Baldwin, 1976).

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Structure of a Dipotassium Tetraiodomercurate(II) Salt with Dibenzo-18-crown-6

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Abstract. Bis[(dibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadeca-2,11-diene)potassium] tetraiodomercurate(II) hemiethanol solvate, $[\text{K}(\text{C}_{20}\text{H}_{24}\text{O}_6)]_2\text{[HgI}_4\text{]}\cdot 1/2\text{C}_2\text{H}_5\text{OH}$, $M_r = 1507.2$, triclinic, $P\bar{1}$, $a = 11.994$ (4), $b = 14.999$ (5), $c = 17.051$ (6) \AA , $\alpha = 63.43$ (2), $\beta = 77.91$ (3), $\gamma = 68.46$ (3) $^\circ$, $U = 2548$ (1) \AA^3 , $Z = 2$, $D_m = 1.93$ (3), $D_x = 1.96 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$, $\mu = 56.3 \text{ cm}^{-1}$, $F(000) = 1446$, $T = 150 \text{ K}$, final $R = 0.049$ for 6154 [$I > 3\sigma(I)$] independent observed reflections. The structure of the molecule essentially consists of two potassium-crown ether cations linked through a central tetrahedral tetraiodomercurate anion with $\text{K}\cdots\text{I}$ distances of 3.520 (3) and 3.474 (3) \AA . Both the potassium ions are thus seven coordinate (six O atoms from the crown ether and one I atom from the anion). The

average $\text{K}\cdots\text{O}$ distances are 2.743 \AA in both complex cations.

Introduction. Many compounds containing the $[\text{K-DB18C6}]^+$ cation (as well as the $[\text{K-18C6}]^+$ cation) have been prepared and characterized, partly because potassium forms the most stable complex cation with crown ethers with six O atoms (Dobler, 1981). However, relatively few structures of these compounds have been reported. Those reported include the iodide (Hilgenfeld & Saenger, 1981), a series of aluminates (Atwood, Hunter, Rogers & Weeks, 1985; Zaworotko, Reid & Atwood, 1985), a complex chromium anion (Wink, Fox & Cooper, 1985), a cobaltate(II) (Fan, Zhang, Wang, Zhang & Han, 1985) and two mercurate(II) complexes (Mok,