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Structure of Tris(η^5-cyclopentadienyl)bis(propiononitrile)lanthanum(III)

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Abstract. $[La(C_5H_5)_3(C_3H_5N)_2]$, $M_r = 444{\cdot}36$, monoclinic, $C2/c$, $a = 14{\cdot}988\,(5)$, $b = 8{\cdot}448\,(3)$, $c = 31{\cdot}893\,(6)$ Å, $\beta = 94{\cdot}25\,(4)°$, $V = 4027\,(4)$ Å^3, $Z = 8$, $D_x = 1{\cdot}466$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 21{\cdot}328$ cm^{-1}, $F(000) = 1776$, $T = 295\,(1)$ K, $R = 0{\cdot}04$ for 1775 observed reflections. The La ion has trigonal bipyramidal coordination geometry with three η^5-bonded cyclopentadienyl rings, the centres of which define the equatorial plane of the bipyramid, and two propiononitrile groups in axial positions.

Introduction. Tricyclopentadienides of lanthanide and actinide elements readily form adducts with uncharged Lewis bases (Marks & Ernst, 1982). Up to now, the 1:1 adducts, $M\text{Cp}_3X$ (Cp = C_5H_5), have been most studied. Their usual coordination geometry is a flattened tetrahedron (Baker & Raymond, 1977). Among the 1:2 adducts, $M\text{Cp}_3X_2$, complete structural information is only available for a few complexes: $[\text{UCp}_3(\text{NCS})(\text{NCCH}_3)]$ (Fischer, Klähne & Kopf, 1978), $[\text{UCp}_3(\text{NCS})_2]^-$ (Bombieri, Benetollo, Bagnall & Plews, 1983), $[\text{UCp}_3(\text{NCCH}_3)_2]^+$ (Bombieri, Benetollo, Klähne & Fischer, 1983), $[\text{LaCp}_3(\text{NCCH}_3)_2]$ (Xing-Fu, Eggers, Kopf, Jahn, Fischer, Apostolidis, Kanellakopulos, Benetollo, Polo & Bombieri, 1985). They all present a trigonal bipyramidal coordination geometry. The present structure analysis provides a novel example of a 1:2 adduct of a lanthanoid tricyclopentadienide with an aliphatic nitrile.

Experimental. The title compound was prepared by the reaction of $[La(C_5H_5)_3]$ with an excess of CH_3CH_2CN. Recrystallization from this solvent afforded prismatic single crystals suitable for X-ray analysis. The complex being air sensitive, crystals were sealed in thin-walled glass capillaries under N_2. The specimen selected for measurements was $0{\cdot}3 \times 0{\cdot}2 \times 0{\cdot}2$ mm. Intensity data recorded on an Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell parameters refined by least squares from angle data of 25 reflections. Systematic absences consistent with space groups Cc and $C2/c$. 5929 unique reflections measured (θ–2θ scan mode) in range $4 \leq 2\theta \leq 45°$.

Intensities of three standard reflections measured at 30 min intervals showed no significant deviations from mean. Intensities corrected for Lorentz–polarization effects; empirical absorption corrections (transmission factors 96·14 to 99·99%). Structure solved by direct methods and Fourier techniques that established unequivocally space group $C2/c$. Full-matrix least-squares refinement minimizing $\sum(\Delta F)^2$. Last cycles of refinement with $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, on 1775 independent reflections with $F^2 \geq 3\sigma(F^2)$, index range $h\,0/+16$, $k\,0/+9$, $l\,-32/+32$. Anisotropic thermal parameters for non-H atoms; H atoms in calculated positions included in final structure-factor calculation with $B_{\text{iso}} = 7{\cdot}0$ Å^2. A secondary-extinction coefficient refined to a value of $g = 4{\cdot}3 \times 10^{-7}$ {with $F_c = F_c/[1+g(F_c)^2\text{Lp}]$}. $R = 0{\cdot}040$, $wR = 0{\cdot}055$, $S = 1{\cdot}376$, $(\Delta/\sigma)_{\max} = 0{\cdot}02$, $\Delta\rho$ in final difference Fourier map within $+0{\cdot}914$ and $-0{\cdot}882$ e Å^{-3}. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1983) *SDP-plus* programs.

Discussion. Table 1* contains final atomic positional parameters for the non-H atoms. Selected distances and angles are listed in Table 2. The molecular structure is illustrated in Fig. 1.

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[*] Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, C—C, N—C bond lengths and C—C—C bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44275 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic positional and isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

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

	x	*y*	*z*	B_{eq}
La	0·49224 (3)	0·04370 (6)	0·12454 (2)	3·05 (1)
Ring 1				
C(1)	0·3655 (7)	0·250 (1)	0·1591 (3)	5·9 (3)
C(2)	0·3151 (6)	0·122 (2)	0·1418 (3)	6·7 (3)
C(3)	0·3355 (6)	−0·010 (1)	0·1685 (4)	6·0 (3)
C(4)	0·3986 (6)	0·038 (1)	0·2004 (3)	5·9 (3)
C(5)	0·4170 (7)	0·197 (1)	0·1943 (3)	6·4 (3)
Ring 2				
C(6)	0·4353 (7)	−0·117 (1)	0·0485 (3)	6·0 (3)
C(7)	0·3912 (7)	−0·194 (1)	0·0778 (3)	6·0 (3)
C(8)	0·4544 (8)	−0·280 (1)	0·1038 (3)	6·6 (3)
C(9)	0·5414 (7)	−0·252 (1)	0·0905 (3)	6·4 (3)
C(10)	0·5279 (8)	−0·149 (1)	0·0548 (3)	7·0 (3)
Ring 3				
C(11)	0·6440 (7)	0·191 (2)	0·1654 (5)	10·6 (4)
C(12)	0·6017 (8)	0·316 (2)	0·1478 (4)	8·9 (4)
C(13)	0·6048 (7)	0·307 (1)	0·1057 (4)	7·9 (3)
C(14)	0·6458 (8)	0·176 (2)	0·0900 (3)	9·6 (4)
C(15)	0·6792 (6)	0·094 (1)	0·1321 (7)	12·6 (6)
Propiononitrile ligands				
N(1)	0·5718 (5)	−0·153 (1)	0·1855 (3)	5·7 (2)
C(16)	0·6194 (6)	−0·222 (1)	0·2062 (3)	5·6 (3)
C(17)	0·6852 (6)	−0·310 (1)	0·2355 (3)	6·3 (3)
C(18)	0·6385 (9)	−0·425 (2)	0·2597 (4)	8·5 (4)
N(2)	0·4200 (5)	0·244 (1)	0·0627 (3)	5·8 (2)
C(19)	0·4024 (6)	0·345 (1)	0·0397 (3)	5·0 (2)
C(20)	0·3849 (8)	0·475 (1)	0·0089 (4)	6·5 (3)
C(21)	0·2873 (8)	0·485 (2)	−0·0033 (5)	9·5 (4)

Table 2. *Selected distances* (Å) *and angles* (°) *in* $[La(C_5H_5)_3(NCCH_2CH_3)_2]$

Standard deviations are given in parentheses.

(*a*) Intramolecular bond distances and angles

La–C(1)	2·858 (9)	N(1)–La–Rc1*	91·4 (2)
La–C(2)	2·829 (9)	N(1)–La–Rc2*	89·1 (2)
La–C(3)	2·860 (9)	N(1)–La–Rc3*	89·7 (2)
La–C(4)	2·89 (1)	N(2)–La–Rc1	90·5 (2)
La–C(5)	2·88 (1)	N(2)–La–Rc2	91·3 (2)
La–C(6)	2·86 (1)	N(2)–La–Rc3	88·0 (2)
La–C(7)	2·867 (9)	Rc1–La–Rc2	119·3 (4)
La–C(8)	2·86 (1)	Rc1–La–Rc3	117·9 (4)
La–C(9)	2·846 (9)	Rc2–La–Rc3	122·9 (4)
La–C(10)	2·84 (1)	N(1)–La–N(2)	177·5 (2)
La–C(11)	2·83 (1)	La–N(1)–C(16)	165·4 (9)
La–C(12)	2·89 (1)	La–N(2)–C(19)	167·4 (8)
La–C(13)	2·88 (1)		
La–C(14)	2·85 (1)	N(1)≡C(16)–C(17)	177 (1)
La–C(15)	2·83 (1)	N(2)≡C(19)–C(20)	177 (1)
La–N(1)	2·759 (9)		
La–N(2)	2·756 (9)		

(*b*) Short intra- or intermolecular contacts (< 3·7 Å)

C(3)···C(17^{i})	3·63 (1)	C(7)···C(20^{iii})	3·55 (1)
C(4)···C(17^{i})	3·69 (1)	C(10)···C(19^{iv})	3·66 (1)
C(5)···C(18^{ii})	3·64 (2)	C(20)···C(20^{v})	3·56 (3)

Symmetry code: (i) 0·5+*x*, 0·5+*y*, *z*; (ii) 1−*x*, *y*+1, 0·5−*z*; (iii) *x*, *y*−1, *z*; (iv) 1−*x*, −*y*, −*z*; (v) 1−*x*, 1−*y*, −*z*.

* Rc1 denotes centroid of ring 1 [C(1), C(2), C(3), C(4), C(5)]; Rc2 centroid of ring 2 [C(6), C(7), C(8), C(9), C(10)]; Rc3 centroid of ring 3 [C(11), C(12), C(13), C(14), C(15)].

In $[La(C_5H_5)_3(NCCH_2CH_3)_2]$, the coordination geometry of the La atom is, as expected, trigonal bipyramidal with a pseudo-symmetry of D_{3h} for the La-atom site. The three cyclopentadienyl rings, pentahapto covalently bonded to the lanthanum, occupy the equatorial plane. The two nitrogen-bonded propiononitrile ligands occupy the *trans* diaxial positions. The average ring-centroid–La–ring-centroid angle is 120·0° and the average ring-centroid–La–N angle is 90·0°.

If each η^5-cyclopentadienyl is considered as a donor of three electron pairs, the La^{3+} ion in this complex appears to be eleven coordinated. The averaged La–C distance of 2·86 (1) Å compares favourably with the distances reported for several cyclopentadienyl complexes (Rogers, Atwood, Emad, Sikora & Rausch, 1981; Xing-Fu *et al.*, 1985). The La–N bond lengths are in agreement with the distance of 2·785 (8) Å observed in the corresponding acetonitrile complex $[La(C_5H_5)_3(NCCH_3)_2]$ (Xing-Fu *et al.*, 1985). A significant feature observed here is the deviation from linearity of the La–N≡C–CH$_2$CH$_3$ arrangements as shown by the La–N≡C angles reported in Table 1. A bend of about 14° is observed for the two axial ligands toward one cyclopentadienyl ligand (ring 3). Since there are some short (< 3·7 Å) intermolecular distances between neighbouring molecules (Table 2) these bends may be due to steric hindrance. Nevertheless, it should be noted that similar bends are reported for the acetonitrile derivative too (Xing-Fu *et al.*, 1985), although a nearly linear Ln–C≡N–*R* arrangement has been observed in one isocyanide complex of praseodymium (Burns, 1976).

The large thermal motion exhibited by ring 3 C atoms suggests that it may show some rotational

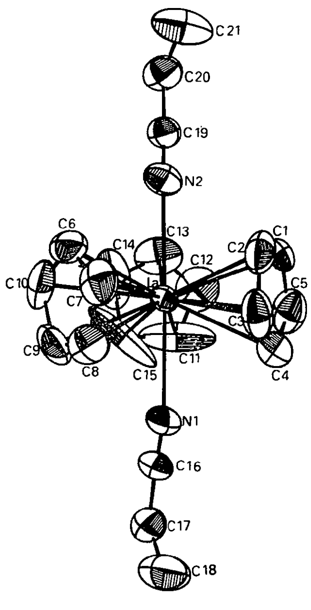

Fig. 1. Molecular structure of $[LaCp_3(NCCH_2CH_3)_2]$.

disorder. This would explain the large range of its C—C bond lengths and C—C—C angles. This feature has already been observed for some cyclopentadienyl complexes (Rogers *et al.*, 1981).

Refinement of a disordered model including two different orientations for ring 3 gave less acceptable agreement factors. Another method of refinement treating ring 3 as a rigid group did not succeed either.

References

BAKER, E. C. & RAYMOND, K. N. (1977). *Inorg. Chem.* **16**, 2710–2715.
BOMBIERI, G., BENETOLLO, F., BAGNALL, K. W. & PLEWS, J. (1983). *J. Chem. Soc. Dalton Trans.* pp. 45–49.
BOMBIERI, G., BENETOLLO, F., KLÄHNE, E. & FISCHER, R. D. (1983). *J. Chem. Soc. Dalton Trans.* pp. 1115–1121.
BURNS, J. H. (1976). *J. Organomet. Chem.* **120**, 361–368.
Enraf–Nonius (1983). *Structure Determination Package; SDP Users Guide.* Version 1.1. Enraf–Nonius, Delft, The Netherlands.
FISCHER, R. D., KLÄHNE, E. & KOPF, J. (1978). *Z. Naturforsch. Teil B*, **33**, 1393–1396.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
MARKS, T. J. & ERNST, R. D. (1982). In *Comprehensive Organometallic Chemistry*, edited by G. WILKINSON, F. G. A. STONE & E. W. ABEL, Vol. 3, Ch. 21. Oxford: Pergamon Press.
ROGERS, R. D., ATWOOD, J. L., EMAD, A., SIKORA, D. J. & RAUSCH, M. D. (1981). *J. Organomet. Chem.* **216**, 383–392.
XING-FU, L., EGGERS, S., KOPF, J., JAHN, W., FISCHER, R. D., APOSTOLIDIS, C., KANELLAKOPULOS, B., BENETOLLO, F., POLO, A. & BOMBIERI, G. (1985). *Inorg. Chim. Acta*, **100**, 183–199.

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Dichloro(thiosemicarbazide)cadmium(II) Monohydrate

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Abstract. $[CdCl_2(CH_5N_3S)].H_2O$, $M_r = 292{\cdot}46$, monoclinic, Cc, $a = 10{\cdot}135\,(4)$, $b = 13{\cdot}961\,(7)$, $c = 6{\cdot}887\,(3)$ Å, $\beta = 124{\cdot}05\,(6)°$, $V = 807{\cdot}4$ Å^3, $Z = 4$, $D_x = 2{\cdot}406$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 35$ cm^{-1}, $T = 293$ K, $R = 0{\cdot}027$ for 692 independent significant reflections. The structure is polymeric, the first such known with the ligand *cis* and bidentate. Each Cd is octahedrally coordinated. The central plane contains the thiosemicarbazide ligand, bonded to Cd through S and N(3) to give a five-membered ring, and two Cl atoms, Cd—Cl, 2·489 (4) and 2·633 (4) Å; Cd—S, 2·583 (3) Å; Cd—N 2·42 (1) Å. The coordination sphere is completed by a Cl from the plane above and an S from the plane below, Cd—Cl, 2·663 (5) Å; Cd—S, 2·919 (5) Å. The water molecule is not part of the coordination sphere, but is involved with it in five separate hydrogen bonds, acting as an acceptor from N(2) and N(3) in two adjacent thiosemicarbazides, as a single donor to one Cl atom, and as a shared donor to two other Cl.

Introduction. Thiosemicarbazide, a well known chelating agent, is used to characterize aldehydes, ketones, and polysaccharides. Some thiosemicarbazide derivatives are potential anti-tumor and anti-hypertensive agents, and others are active against influenza, protozoa, and smallpox (Gowda & Mahadevappa, 1977; Pillai, Nandi & Levinson, 1977). These authors attribute this biological activity to the ability of thiosemicarbazide to chelate trace metals. Thus, thiosemicarbazide is also used as a masking agent to minimize interferences from metals such as copper, nickel, and platinum in the determination of arsenic by atomic absorption methods (Kirkbright & Taddia, 1978). The conformational preferences of thiosemicarbazide in metal-complex formation are therefore of some interest. The majority of its metal complexes are discrete monomeric units in which the ligand has a *cis* conformation and is bidentate, bonding through S and the hydrazinic N atoms (Cavalca, Nardelli & Branchi, 1960; Cavalca, Nardelli & Fava, 1962;

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