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Preparation and Characterization of the First Triscyclopentadienyl Lanthanoid Complexes Containing Two Aliphatic Nitrile Ligands: Crystal and Molecular Structures of the Isomorphous Compounds *Trans*-bis(acetonitrile)tris(η^5-cyclopentadienyl)lanthanoid(III) (Ln = La, Ce, Pr). A successful Confirmation of the 'Solid Angle Sum Rule'

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Abstract

Systematic studies to arrive at some first examples of the sterically congested complex type $Cp_3Ln(NCR)_2$ ($Cp = \eta^5-C_5H_5$, Ln = lanthanoid element) resulted in the preparation and detailed spectroscopic characterization of analytically pure representatives of this type with Ln = La, Ce and Pr, but not with Nd (R = CH_3, and C_2H_5 for Ln = La only). The crystal and molecular structures of representatives of the isomorphous series $Cp_3Ln(NCCH_3)_2$, (Ln = La, Ce, Pr) were determined from three-dimensional X-ray diffraction data. The compounds crystallize in the orthorhombic space group *Pnca* (standard group *Pbcn*) with: a = 14.940(3), b = 14.074(3), c = 8.596(2) Å, Z = 4, R = 0.070, Rw = 0.079 for 1633 intensity data (La derivative, **I**); a = 14.906(3), b = 13.974(3), c = 8.502(2) Å, R = 0.041, Rw = 0.047 for 1378 intensity data (Ce derivative, **VII**); a = 14.936(3), b = 13.986(3), c = 8.498(2) Å, R = 0.031 for 1372 intensity data (Pr derivative, **IX**).

According to the X-ray crystallographic results, the novel complexes are trigonal bipyramidally coordinated with three η^5-bonded Cp rings in the equatorial plane (Ln–ring centre distances 2.62, 2.64 for La, 2.58, 2.59 Å for Ce and 2.57, 2.57 Å for Pr and two acetonitrile groups in the axial positions (Ln–N 2.785 for La, 2.749 for Ce, 2.752 for Pr). The range of the distances in the three derivatives is in agreement with the trend in the crystal radii along the lanthanoid series. Pure 1:2 adducts involving any alkyl group larger than R = C_2H_5 could not be isolated. The relative stabilities of the novel $Cp_3Ln(NCR)_2$ systems, with respect to the decreasing ionic radius (*i.e.* from La to Nd) and to the variable space demanded by the group R, are in excellent accord with independent expectations based on the recently developed cone packing model ('SAS-rule') for f-element organometallics.

Introduction

Although the strongly Lewis-acidic organolanthanoid complexes Cp_3Ln (Ln = La–Lu, $Cp = \eta^5-C_5H_5$) form readily 1:1 adducts Cp_3LnL with numerous monodentate Lewis bases [1], L, including aliphatic isocyanides [2]†, reports on corresponding adducts involving a formally isoelectronic aliphatic nitrile

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†In view of the recently established molecular structure of the complex $Cp_3Y{\cdot}THF$ (Ref. 3) also the non-lanthanoid complex $Cp_3Y{\cdot}CNC_6H_{11}$ (Ref. 2b) is expected to be isostructural with the corresponding Ln-complexes.

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TABLE I. Comparison of the $\Delta\nu$(CN)-Values (in cm^{-1}) of Various $Cp_2MX\cdot L$-systems with L = Isocyanide or Nitrile.

M	L	X	$\Delta\nu$(CN)	Ref.
Yb	CNC_6H_{11}	Cp	67	4a,b
Sm	CNC_6H_{11}	Cp	66	2a
Ce	CNC_6H_{11}	Cp	61	this work
Yb	CNC_6H_{11}	Br	66	4b
Yb	CNC_6H_{11}	Cl	63	4a,b
Yb	CNC_6H_{11}	F	59	4b
Ti	o-$CH_3C_6H_4NC$	Cl	20	5
Yb	p-$CH_3C_6H_4CN$	Cp	20	4a
Yb	p-$CH_3C_6H_4CN$	Cl	29	4a
Ho	CH_3CN	Cp	14	this work
Ho	CH_3CN	Cl	25	4a
Sm	CH_3CN	Cp	8	this work
Sm	CH_3CN	Cl	20	4a
Ce	CH_3CN	Cp	12	this work
Ti	CH_3CN	Cl	20	5

are still relatively scarce [4]. Actually, while the isocyanide complexes Cp_3LnCNR (R = cyclohexyl) remain thermally stable up to about 240 °C, displaying sharp melting points between *ca.* 140 and 170 °C and subliming *in vacuo* (150–170 °C) without notable decomposition [2b], the so far most extensively studied nitrile adduct $Cp_3YbNCCH_3$ [4] between 214 and 223 °C becomes a green liquid which is likely to contain the adduct in a partially dissociated state. All corresponding 1:1 adducts $Cp_3LnNCCH_3$ so far studied are non-volatile, the only sublimation products observed being the base-free complexes Cp_3Ln.

In accordance with the expectation of a pure L → Ln σ-donor bond, the ν(CN) absorptions of all adducts occur at higher wave numbers ($\Delta\nu(CN) > 0$) than for the free Lewis bases, the notably stronger coordination of the isocyanide ligand being reflected by considerably larger $\Delta\nu$(CN) values. In Table I some representative $\Delta\nu$(CN) values of various adducts of the general type $Cp_2MX\cdot L$ are compared where X is either a Cp or halide ligand, and L either isocyanide or nitrile. Apparently, the variation of $\Delta\nu$(CN) is primarily governed by the more pronounced 'softness' [6] of the Lewis base $R-N\equiv C$: as compared with $R-C\equiv N$: but – to a somewhat lesser extent – also by the relative 'softness' of the Lewis acidic Cp_2MX moiety.

Considering, hence, the relatively less favourable combination of a 'soft' acid Cp_3Ln with a 'hard' base $R-C\equiv N$:, it is expected that the comparatively weak Ln–N bonds would be reflected by rather large Ln–N bond distances. In view of *e.g.* d(Pr–O) = 2.56 Å in $Cp_3Pr(THF)$ [7], d(Pr–C) = 2.68 Å in $Cp_3PrCNC_6H_{11}$ [8], and d(Nd–N) = 2.69 Å in the cationic complex $[(tren)_2NdNCCH_3]^+$*, respectively, d(Pr–N) of the uncharged complex $Cp_3PrNCCH_3$ may be assumed to slightly exceed 2.70 Å. Nitrile molecules carrying moderately space-demanding aliphatic groups R are therefore expected to require particularly small fractions of the total coordination sphere of a Ln^{3+} ion and might, hence, serve as promising 'probe ligands' to explore the availability even of relatively small gaps occasionally left between larger primary ligands in sterically saturated complexes.

In organolanthanoid chemistry, one rather challenging problem to date concerns the question on the optimal conditions to verify 1:2 adducts of the general composition $[Cp_3LnLL']^{\pm 0}$ which would formally correspond to the recently developed class of trigonal bipyramidal organoactinoid complexes $[Cp_3{}^fM(IV)XY]^q$ (^fM = U to Pu, X and Y = monodentate uncharged or anionic ligands; q = +1, 0 or −1 [10]) where the metal ion adopts the rather high formal coordination number 11. As a result of various initially unsuccessful experiments involving mainly Ln = Pr and various ligands (L) different from nitriles [4c], the present study has mainly been focused on the spatially more expanded Ln^{3+} ions La^{3+} and Ce^{3+} and to some aliphatic nitriles involving particularly small groups R.

General Properties of and Access to $Cp_3Ln(NCR)_2$ Systems

For the successful preparation of $Cp_3Ln(NCR)_2$ systems, the five slightly different routes as depicted in Scheme 1 (*i.e.* routes 1b, 2, 3b, 3c and 4) have so far been adopted. While route 1a leads, like route 3a, only to the corresponding 1:1 adducts, route 2 has so far been investigated for Ln = La and R' = C_2H_5, n-C_3H_7 and i-C_3H_7 (R = CH_3), and proved to be successful only with R' = C_2H_5. Application of n-butyronitrile has, after drying *in vacuo*, yielded the completely CH_3CN-free 1:1 adduct $Cp_3LaNCC_3H_7$ while the corresponding reaction with isobutyronitrile leads, according to both ^1H NMR spectroscopic and analytical results, to mixtures of the 1:1 adduct and Cp_3La along with traces of the starting material and/or the mixed-ligand system $Cp_3La(NCCH_3)(NC$-i-$C_3H_7)$. $Cp_3La(NCCH_3)$ turns out to be virtually insoluble even in warm benzene or toluene. Moreover, unlike *e.g.* $Cp_3LaCNC_6H_{11}$ and $Cp_3Ln(NCCH_3)$ with Ln = Tb or Yb, $Cp_3La(NCCH_3)$ cannot be extracted with n-pentane.

Routes 3b, 3c and 4 have also been modified by adopting $NCCD_3$ (*vide infra*). The expected

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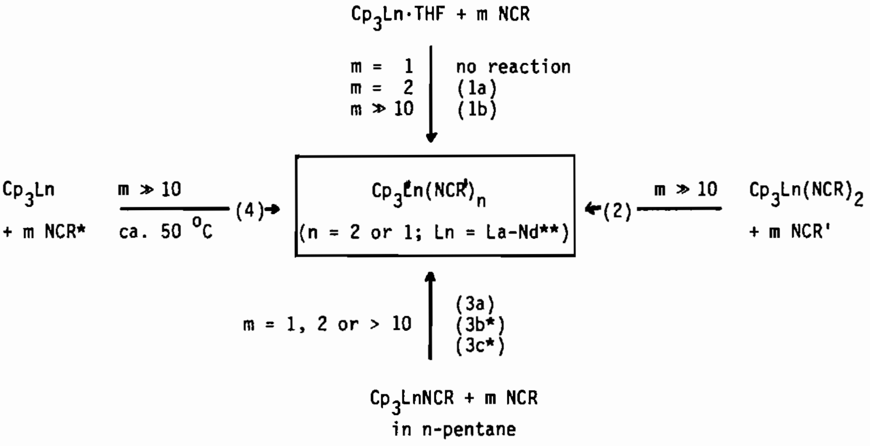
*'tren' = $N(CH_2CH_2NH_2)_3$, counter-anion: ClO_4^-, $\Delta\nu$(CN) = 8 cm^{-1} [9].



Scheme 1. Various preparative routes leading quantitatively to $Cp_3Ln(NCR')_2$ systems ($R = CH_3$, $R' = C_2H_5$). *: pathways also adopted for $NCCD_3$; **: with Ln = Nd, quantitative formation of 1:2 adduct uncertain. Reactions (1a) and (3a) lead only to the 1:1 adduct.

gradual attenuation of the chemical stability of the 1:2 adducts (owing to increasing steric congestion as the ionic radius of Ln decreases) is reflected by the experience that only pathways 4 and 3c (which turn out superior to 3b and 1b) are applicable to produce $Cp_3Pr(NCCH_3)_2$ and even $Cp_3Nd(NCCH_3)_2$. Even after careful drying, however, the latter product turns out to be a mixture of the 1:2 and 1:1 adducts. Routes 3 and 4 are particularly suitable to arrive at single crystals.

The majority of the new products obtained have been fully specified by their elemental analyses (Table II) as well as by infra-red and ^1H NMR spectroscopy (*vide infra*). For a better judgement of the

TABLE II. Calculated and Experimentally Found Elemental Analyses.

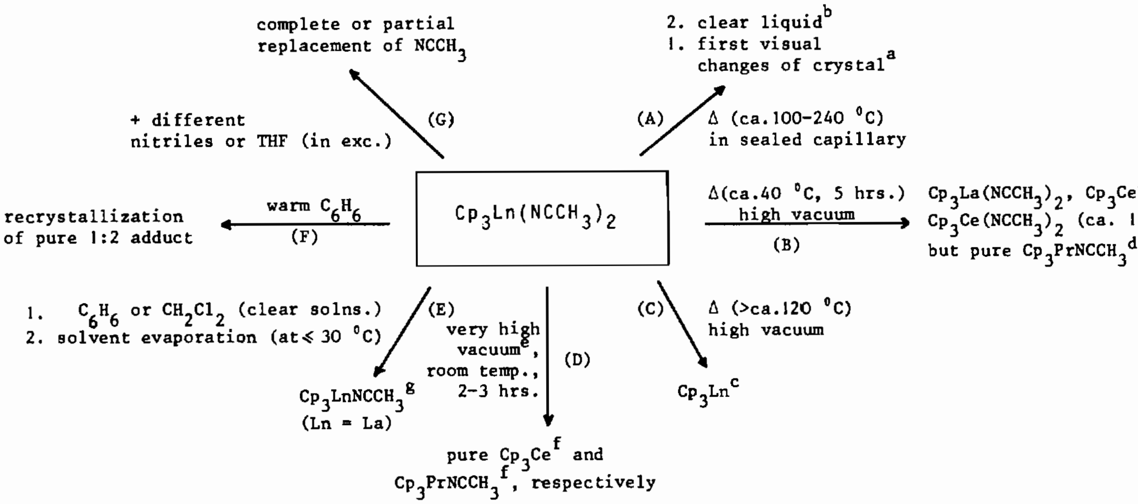
Product/ Procedure[a]	R	Ln	RCN:Ln		C	H	N	Ln
	CH_3	La	1:1	(calc.)	54.42	4.83	3.73	37.02
1b	CH_3	La		(found)	54.26	4.90		37.34
	CH_3	La	1:2	(calc.)	54.82	5.08	6.73	33.37
I /1a	CH_3	La		(found)	54.96	5.17	6.70	33.19
	C_2H_5	La	1:1	(calc.)	55.54	5.18	3.60	35.68
1b	C_2H_5	La		(found)	55.50	5.15	3.65	34.95
	C_2H_5	La	1:2	(calc.)	56.76	5.67	6.31	31.26
II /2	C_2H_5	La		(found)	56.39	5.57	5.98	32.17[b]
	$n\text{-}C_3H_7$	La	1:1	(calc.)	56.58	5.50	3.47	34.44
	$n\text{-}C_3H_7$	La	1:2	(calc.)	58.48	6.19	5.93	29.40
III /2	$n\text{-}C_3H_7$	La		(found)	56.43	5.43	3.55	[c]
IV /2	$i\text{-}C_3H_7$	La		(found)	52.06	5.00	2.73	[c]
	CH_3	Ce	1:1	(calc.)	54.24	4.82	3.72	37.22
V /3a	CH_3	Ce		(found)	54.20	4.90	3.80	37.12
	CH_3	Ce	1:1,5	(calc.)	54.46	4.95	5.29	35.39
VI /3b[d]	CH_3	Ce		(found)	54.39	4.74	5.27	35.65
	CH_3	Ce	1:2	(calc.)	54.66	5.07	6.11	33.56
VII /3b	CH_3	Ce		(found)	54.59	4.98	6.66	33.60
VII /4	CH_3	Ce		(found)	54.65	4.99	6.73	33.43
	CH_3	Pr	1:1	(calc.)	54.13	4.81	3.71	37.35
VIII /3a	CH_3	Pr		(found)	54.12	4.76	3.80	37.39
	CH_3	Pr	1:2	(calc.)	54.56	5.06	6.97	33.69
IX /4	CH_3	Pr		(found)	54.75	4.84	6.80	33.63

(continued overleaf)

TABLE II. *(continued)*

Product/ Procedure[a]	R	Ln	RCN:Ln		C	H	N	Ln
	$C(CH_3)_3$	Pr	1:1	(calc.)	57.29	5.77	3.34	33.60
X /1b	$C(CH_3)_3$	Pr		(found)	55.37	5.75	3.15	c
	CH_3	Sm	1:1	(calc.)	52.79	4.69	3.62	38.89
XI /1b	CH_3	Sm		(found)	52.90	4.72	3.55	c

[a] Adopting the designations of Schemes 1 and 2, respectively. [b] Sample obtained according to eqn. 1. [c] Metal analysis not performed. [d] Obtained by procedure B of Scheme 2.



Scheme 2. Various properties of $Cp_3Ln(NCR)_2$ systems (R = predominantly CH_3). (A) For La at *ca.* 162 °C, Ce at *ca.* 115 °C, and Pr at 170 °C; (B) for La at 218–220 °C (melt turns yellow at 250 °C), Ce at 224 °C (brown), and Pr at 238 °C; (C) by sublimation; (D) also confirmed by full elemental analyses; (E) inside the effectively evacuated (Faraday) magnetic balance; (F) composition confirmed by quantitative determination of weight loss, magnetic susceptibility studies and IR spectroscopy; (G) determined by IR spectroscopy.

analytical data, a few 1:1 adducts are also included in Table II*. In this Table all new complexes have also been individually numbered.

A survey over the general chemical behaviour of most $Cp_3Ln(NCR)_2$ systems is given in Scheme 2. While procedure C turns out to show very similar results for the 1:2 and 1:1 adducts (with $NCCH_3$), procedure B reflects nicely the stepwise decline of stability of the 1:2 adducts as the ionic radius of Ln^{3+} is decreased from La to Pr. The formation of pure Cp_3Ce under procedure D was unexpected. Somewhat surprisingly, the 1:2 adducts seem to melt without clear evidence of decomposition, while the corresponding 1:1 adducts give rise to notable colour changes before $NCCH_3$ is released and/or the crystals are virtually molten. The initially white 1:1 adduct $Cp_3La(NCCH_3)$ turns black already at *ca.* 95 °C whereas the corresponding adducts with CNC_6H_{11} or THF remain unchanged up to *ca.* 150 and 360 °C. Another interesting observation is that the two almost equally chocolate-brown Ce-complexes **V** and **VI** dissolve in acetonitrile reversibly with a surprisingly light colour, while the corresponding (still undecomposed) solutions in CD_2Cl_2 are essentially opaque. The formation of the 1:1 adduct by procedure E does not necessarily imply that complete dissociation of the dissolved 1:2 adduct occurs prior to solvent removal. Hence, procedure E does not rule out procedure F. At least the 1:2 adduct $Cp_3La(CNC_2H_5)_2$ withstands procedure E although the ^1H NMR spectrum of this complex in CD_2Cl_2 solution (*vide infra*) cannot unambiguously be understood in terms of a completely undissociated species.

Spectroscopic Properties

As neither of the 1:1 and 1:2 adducts of Cp_3-Ln with $NCCH_3$ (with the possible exception of

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*A systematic survey over the 1:1 adducts $Cp_3LnNCCH_3$ (Ln = La to Lu) will be published separately.

TABLE III. Survey of Characteristic Absorptions in the Infrared Range (700–3200 cm^{-1}) of Samples in KBr pellets (Exception: Uncoordinated Nitriles).

Band Nr.	Type of vibration[a]	Free base: CH_3CN or CD_3CN	$Cp_3Ln(NCCH_3)$			$Cp_3Ln(NCCH_3)_2$			$Cp_3Ln(NCCD_3)_2$	
			La	Ce	Pr	La	Ce	Pr	La	Ce
1						3106.0	3107.0	3107.0	3101.0	3104.0
2			3093.0	3095.0	3096.0	3091.0	3092.0	3094.0		3093.0
3	ν(CH) of Cp		3086.0	3087.0	3088.0	3079.0	3081.0	3081.0	3084.0	
4			3075.0	3077.0	3078.0				3071.0	3080.0
5			3066.0	3066.0	3067.0					
6	$\nu(CH)_{as}$ of CH_3	3007.0	2987.0[c]	2987.0[c]	2987.0[c]	2981.0	2981.0	2981.0		
7	$\nu(CH)_s$ of CH_3	2949.0	2923.0	2923.0	2923.0	2925.0	2926.0	2926.0		
8	$(\nu_3 + \nu_4)$-comb.[b]	2295.3	2295.6	2295.0	2295.3	2299.8	2299.5	2299.0	–	–
9	ν(CN)	2255.0/2260.6	2267.0	2266.6	2266.7	2266.2	2266.0	2265.9	2275.9	2275.0
10	$\nu(CD)_{as}$ of CD_3	2259.0							2231.7	2232.0
11		2236.0							2200.5	2201.0
12	4f–4f-transitions[d]	–					2170.0			2170.8
13		–					2130.0			2129.4
14	$\nu(CD)_s$ of CD_3	2115.0							2102.2	2103.5
15			1442.0	1441.0	1442.0	1441.0	1438.0	1441.0	1442.0	1443.0
16	ν(CC) of Cp					1409.0	1405.0	1407.0		
17	δ(CH) of CH_3	1378.0	1366.2	1367.0	1367.0	1370.0	1369.5	1369.0		
18			1062.0	1062.0	1063.0	1065.0	1064.0	1064.0	1063.0	1061.0
19	$\delta(CH)_{\parallel}$ of Cp		1054.0	1054.0	1053.0	1020.0	1020.0	1020.0	1020.0	1020.0
20			1014.0	1013.0	1014.0	1011.0	1011.0	1011.0	1010.0	1009.0
21	ν(CC) of nitrile	917.9/823.0	927.5	926.0	926.0	929.0	928.5	928.0	842.0	842.0
22			795.0	797.0	796.0	777.0	777.0	780.0	774.0	778.0
23	$\delta(CH)_{\perp}$ of Cp		760.0	770.0	764.0	760.0	760.0	760.0	758.0	760.0
24			743.0	745.0	746.0					

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[a] For an appropriate assignment of the various vibrations of CH_3CN and CD_3CN, see Refs. [17] and [18]. [b] Caused by Fermi resonance of bands nr. 17 and 21. [c] Rather weak and broad. [d] Assumption (see text).

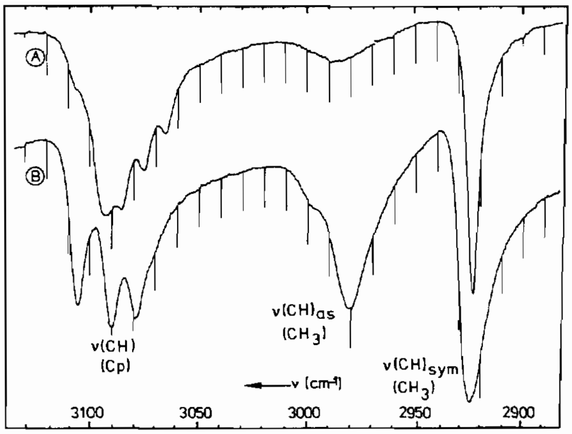

Fig. 1. Infrared spectra of $Cp_3La(NCCH_3)$ (A) and $Cp_3La(NCCH_3)_2$ (B) between 2880 and 3130 cm^{-1} (slow scans and expanded ν-scale).

Ln = Nd) appears to lose the nitrile ligand under the common conditions of the preparation of optimally transparent KBr-pellets, infrared spectroscopy turns out to be a highly informative technique of instrumental analysis. According to Table III, which gives a survey over the absorptions of complexes of the types $Cp_3Ln(NCCH_3)$, $Cp_3Ln(NCCH_3)_2$ and $Cp_3Ln(NCCD_3)_2$ between 730 and 3200 cm^{-1}, characteristic differences between the corresponding 1:1 and 1:2 adducts are apparent for practically all types of vibration except for the ν(CN), δ(CH) and ν(CC) modes of the coordinated nitriles. The positions of the latter three modes differ, however, from those of the uncoordinated nitrile, the notable decrease and increase, respectively, of δ(CH) and ν(CC) suggesting non-negligible interaction between the CH_3 group and the NC triple bond via hyperconjugation. The weakening of the CH bonds is also demonstrated by the lowering of the ν(CH) and ν(CD) frequencies, respectively (*i.e.* of bands nr. 6, 7, 10 and 14 in Table III) on complexation of the nitrile. Surprisingly, the corresponding changes in wave numbers of the bands nr. 6, 7, 10, 14, 17 and 21 match, or even exceed, that of band nr. 9 (ν(CN)) in magnitude.

While Δν(CN) of the three 1:2 adducts **I**, **VII** and **IX** turns out to be ⩽11 cm^{-1}, Δν(CN) of the two hexadeuterated homologues **I**-d_6 and **VII**-d_6 is significantly higher (*ca.* 15 cm^{-1}). For the undeuterated 1:2 adduct **II** (R = C_2H_5), Δν(CN) even amounts to 17 cm^{-1}, which matches those values of the nitrile-deficient samples **III** and **IV** (16 and 18 cm^{-1}, respectively). It should be recalled that Δν(CN) of the formerly investigated, sterically less congested adducts $LnCl_3(NCCH_3)_n$ (n = 1 or 2) range between 20 and 40 cm^{-1} [11]. The frequency of the ν(CC) vibration of coordinated $NCCH_3$, which is known to increase notably when ν(CN) increases [15, 16], exceeds for all complexes listed in Table III the value of free $NCCH_3$ by 6–10 cm^{-1}. The Raman spectra of the two uncoloured complexes **I** and **II** turned out too strongly perturbed by luminescence to show the ν(CN) absorptions.

As is also illustrated by Fig. 1, the ν(CH) vibrations of the 1:1 and 1:2 adducts with $NCCH_3$ display somewhat different fine structures. While that of the former composition is not likely to be caused by intramolecular steric congestion, the ν(CH) fine structure of the 1:2 adduct might be suspected to reflect the non-equivalence of all three Cp ligands within the strongly congested complex, which feature is likewise supported by the X-ray crystallographic results (*vide infra*). Surprisingly, the ν(CH) spectral pattern of the Cp ligands of **II** resembles more that of the 1:1 adducts (with $NCCH_3$) than that of the corresponding 1:2 adducts. Furthermore, **II** displays only one $\delta(CH)_{\parallel}$-band (at 1012, and not at 1020 cm^{-1}), while three $\delta(CH)_{\perp}$ bands appear (at 770, 760 and 745 cm^{-1}).

Expectedly, replacement of $NCCH_3$ by $NCCD_3$ makes the combination band 8 disappear (as the conditions of Fermi resonance are no longer met), and displaces bands 6 and 7 to lower wave numbers (*i.e.* to 10 and 14), but there is no evidence of a H/D exchange between the nitrile and the Cp ligands.

As is evident from both Table III and Figs. 2 and 3, the two 1:2 adducts of Ce give rise to two additional absorptions between 2100 and 2200 cm^{-1}

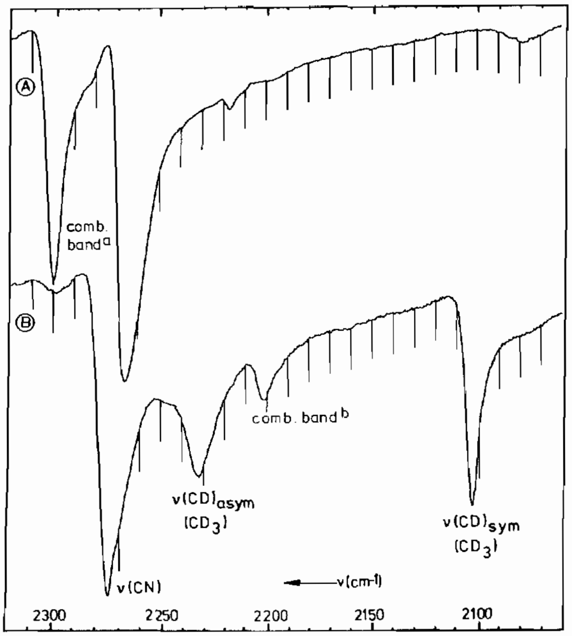

Fig. 2. Infrared spectra of $Cp_3La(NCCH_3)_2$ (A) and $Cp_3La(NCCD_3)_2$ (B) between 2060 and 2320 cm^{-1} (slow scans and expanded ν-scale); a: band nr. 8; b: band nr. 11 of Table III.

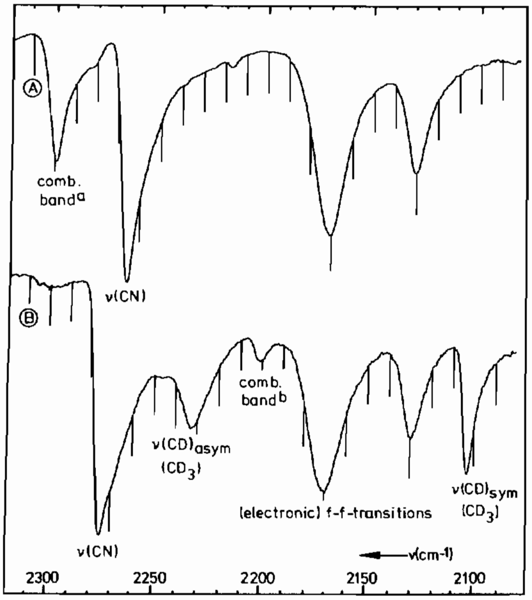

Fig. 3. Infrared spectra of $Cp_3Ce(NCCH_3)_2$ (A) and $Cp_3Ce(NCCD_3)_2$ (B) between 2080 and 2320 cm^{-1} (slow scans and expanded ν-scale); a: band nr. 8; b: band nr. 11 of Table III.

which are absent in the infrared spectra of the corresponding La and Pr complexes. In addition to bands 10 and 14, the IR spectra of the Ce complexes **VII**, **VII**-d_6 and **VI** display between 2000 and 200 cm^{-1} at least two further absorptions, at 1712 and between 510 and 550 cm^{-1}, respectively (the latter one being unusually broad and accompanied by some considerably weaker satellites around 605 and 440 cm^{-1}). These absorptions are all absent in the spectra of the homologous La and Pr complexes **I**, **I**-d_6, **IX** and **IX**-d_6, and even in the spectrum of the pure Ce complex **V**, with but one $NCCH_3$ ligand. Although it would appear tempting to ascribe bands 10 and 14 likewise to ν(CN) modes of nitrile ligands whose CN triple bonds would have been weakened for some unknown reason, both the strictly isostructural nature of the La and Ce complexes **I** and **VII** (as proved by the X-ray crystallographic results, *vide infra*) and the well-known uncapability of $4f^q$-configurated metal ions to give rise to notable $f_\pi \rightarrow ligand_{\pi*}$ back-bonding contributions strongly advocate an alternative explanation of the extra absorptions.

In view of the common experience that predominantly low-lying (f–f) crystal field (CF) transitions of lanthanoid complexes do not become observable until the temperature is lowered [12], while some Ce(III) compounds have been reported to display single CF-transitions even at room temperature [13, 14], it appears justified to tentatively ascribe at least some of the extra absorptions of the complexes **VII** and **VII**-d_6 to unusually intense transitions of a purely electronic origin. As early as 1965, Pappalardo had observed essentially for relatively broad 'extra bands' at 2120, 2220, 2310 and 2410 in the room temperature IR spectrum of solid Cp_3Ce, and ascribed them to transitions between CF-states of the manifolds $^2F_{5/2}$ and $^2F_{7/2}$ of the Ce(III) ion [13]. Most recently, Amberger estimated the energies of all CF-levels of a representative $Cp_3Ce \cdot L$ system using the same CF-parameter set as deduced for the related $Cp_3Pr \cdot L$ system on the basis of combined NIR/VIS- and MCD-spectroscopic studies [19] arriving at E = 0, 89, 514, 2179, 2274, 2484 and 3481 cm^{-1} [12]. At least the two values of 514 and 2179 cm^{-1} lie close to the experimentally observed absorptions of the complexes **VII** and **VII**-d_6 at *ca.* 530 and 2170 cm^{-1}. While magnetochemical studies of the electronic structure of **VII** and **IX** have so far been hampered by the complete loss of nitrile within the effectively evacuated magnetic balance (see procedure D of Scheme 2) low-temperature IR investigations would appear promising to provide supplementary experimental data.

^{1}H NMR spectra have been studied both of the diamagnetic La complexes **I**–**IV** (Table IV) and of the paramagnetic products **V**–**VII** and **X**–**XI** containing Ce, Pr, and Sm (Table V). According to Table IV, the chemical shifts of the Cp ring protons are only weakly affected by a solvent change (from CD_2Cl_2 to C_6D_6), while the resonances of the coordinated nitrile experience high-field shifts of the order of 1.5 ppm. The quantity $\Delta\delta = \delta(\text{complex}) - \delta(\text{free ligand})$ of the nitriles is substantially negative in benzene, but weakly positive in CD_2Cl_2 or $CHCl_3$ solution. The larger $|\Delta\delta|$ values in C_6D_6 suggest strong La-to-nitrile bonding in aromatic hydrocarbon solvents. Both pure **I** and mixtures of **I** and additional CH_3CN (in CD_2Cl_2) display but one methyl proton singlet down to -80 °C. Complex **II** and the 1:1 adduct $Cp_3La(NCC_2H_5)$ show for their C_2H_5 group(s) a resonance pattern of higher order very reminiscent of that of the spectrum of free NCC_2H_5.

Between 305 and 209 K the paramagnetic 1:1 adduct (Ln = Ce) gives rise to Cp proton resonances very similar to those reported for the adduct $Cp_3CeCNC_6H_{11}$ [2d]. Likewise, the methyl proton shift of **V** lies fairly close to the shift of the H_α atom of Ce-coordinated CNC_6H_{11}. A corresponding behaviour was observed for the pair of 1:1 adducts involving Ln = Pr with L = $NCCH_3$ and CNC_6H_{11}, respectively [19]. On the basis of these findings, the ^{1}H NMR spectra of the two 1:2 adducts **VII** and **IX** (dissolved in CD_2Cl_2, see Table V) must be interpreted in terms of rapidly equilibrating mixtures of the 1:1 adducts and an equimolar amount of free nitrile (eqn. 1):

TABLE IV. ^1H NMR Data (Room Temperature) of Various Diamagnetic Systems $Cp_3La(NCR)_n$.

Sample	Protons of Group	Proton Resonances (δ in ppm)			Δδ/ppm of nitrile[f]	
		CD_2Cl_2	C_6D_6		CD_2Cl_2	C_6D_6
$Cp_3La(NCCH_3)_2$ (I)	C_5H_5	5.97 s	6.17 s	(15 H)		
	CH_3	2.12 s	0.49 s	(6 H)	0.14	−0.81
'$Cp_3La(NCC_2H_5)$'[a]	C_5H_5	5.96 s	6.17 s	(15 H)		
	CH_2	2.61 m	1.01 m[a]	(2 H)	0.23	−0.66
	CH_3	1.43 m	0.29 m[a]	(3 H)	0.13	−0.45
$Cp_3La(NCC_2H_5)_2$ (II)	C_5H_5	5.98 s	6.18 s	(15 H)		
	CH_2	2.53 q[b]	1.10 m[a]	(4 H)	0.15	−0.57
	CH_3	1.38 t[b]	0.34 m[a]	(6 H)	0.08	−0.40
$Cp_3La(NC\text{-}n\text{-}C_3H_7)_n$ (III)	C_5H_5	5.97 s		(15 H)		
	α-CH_2	2.52 t[c]		(2–4 H)[g]		
	β-CH_2	1.81 sext.[d]		(2–4 H)[g]		
	CH_3	1.17 t[d]		(3–6 H)[g]		
$Cp_3La(NC\text{-}i\text{-}C_3H_7)_n$ (IV)	C_5H_5	5.97 s		(*ca.* 20 H)		
	CH	2.97 sept.		(1 H)		
	CH_3	1.43 d[e]		(6 H)		
	CH_3[h]	2.11 s		(*ca.* 3 H)		

[a] See text and Fig. 4. [b] J = 7.7 Hz. [c] J = 7.0 Hz. [d] J = 6.6 Hz. [e] J = 7.7 Hz. [f] δ(complex) – δ(free nitrile). [g] Virtually unchanged resonance positions for 1:1 and 1:2 composition. [h] Most probably of unreacted I.

TABLE V. ^1H NMR Data (δ) of some Paramagnetic Adducts $Cp_3Ln(NCR)_n$ (Ln = Ce, Pr or Sm; n = 1 or 2) Dissolved in CD_2Cl_2 (values of solution in toluene-d_8 in parentheses).

T/K	$Cp_3Ce(NCCH_3)_2$		$Cp_3Ce(NCCH_3)$		$Cp_3Pr(NCCH_3)_2$		$Cp_3Pr(NCCH_3)$		$Cp_3PrNCC(CH_3)_3$[a]	
	δ(Cp)	δ(CH_3)	δ(Cp)	δ(CH_3)	δ(Cp)	δ(CH_3)	δ(Cp)	δ(CH_3)	δ(Cp)	δ(CH_3)
305	8.0	−1.1	8.3	−5.0	14.7	−7.1[b]	14.4(14.4)	−25.6(−22.3)	15.1	−12.5
270	8.2	−1.8	8.1	−5.9	17.0	−8.5	16.5(16.8)	−31.1(−19.7)	17.0	−14.6
250	8.2	−2.0	8.1	−6.4	18.2	−9.7	17.8(18.1)	−33.5(−15.0)	18.6	−16.4
230	8.5	−2.3	8.1	−6.8	20.1	−11.0	19.5(17.5)	−37.1(−11.2)	20.4	−18.4
210	8.3	−2.5	8.0	−7.4	22.0	−11.4	21.2	−41.2	22.3	−20.8
200			7.9	−7.6	23.2	−12.2[c]			23.4	−22.5

[a] Solvent toluene-d_8. [b] Line width 14.2 Hz. [c] Line width 47.5 Hz.

$$Cp_3Ln(NCCH_3)_2 \xrightleftharpoons{CD_2Cl_2} Cp_3Ln(NCCH_3) + NCCH_3{*}$$

$$\xrightleftharpoons{CD_2Cl_2} Cp_3Ln(NCCH_3{*}) + NCCH_3 \qquad (1)$$

This view is further supported by the specific temperature dependence of the two singular δ(Cp) and δ(CH_3) resonances of product **VI** which is assumed to be a 1:1 mixture of **V** and **VII** (see Table II). The apparent tendency of **VII** and **IX** to completely dissociate in CD_2Cl_2 into **VI** and **X**, respectively, and free $NCCH_3$ also casts some doubt on the stability of the 1:2 complexes of La when dissolved in CH_2Cl_2. Yet, complex **II** appears to be the only 1:2 adduct that can be recovered from a CH_2Cl_2 solution after solvent evaporation without any loss of the nitrile.

While the proton resonances of complex **VIII** dissolved in CD_2Cl_2 give rise between 200 and 300 K to strictly linear δ-*vs.*-T^{-1} plots, a fairly different behaviour is observed for a toluene-d_8 solution (Table V). In view of the actual formation of **IX** in the presence of excess nitrile, a rapid equilibration of **VIII**, **IX** and $[Cp_3Pr]_n$ cannot be fully excluded. Solutions of complex **X** in toluene-d_8 on the other hand give rise to linear δ-*vs.*-T^{-1} plots.

Some first attempts to detect on saturated solutions of **I** and **II** in CH_2Cl_2/CD_2Cl_2 a resonance of the nucleus ^{139}La were successful (δ = −700 ± 20 and −670 ± 20 ppm, respectively; standard: aqueous solution of $La(NO_3)_3$). While these data refer to the first ^{139}La resonance of organolanthanum complexes, and correspond to the outermost high-field shifts so far observed in ^{139}La NMR spectroscopy [20], the two samples have most probably involved the 1:1 adducts $Cp_3La(NCR)$ rather than the starting complex **I** or **II**.

Applicability of the Solid Angle Sum (SAS) Rule

In 1982 Bagnall and Li suggested that the degree of steric saturation of the ligand sphere of organouranium(IV) complexes could be favourably accounted for by the sum of all ligand solid angles (SAS) as spanned on the surface of a unit sphere around the metal ion [21]. It was demonstrated that practically all structurally investigated complexes $[Cp_3UXY]^q$ of trigonal bipyramidal configuration [10] display SAS-values very close to 0.81, which value had been attributed to optimal steric saturation in organouranium(IV) compounds [26]. Most recently, a systematic analysis of the majority of so far structurally examined organolanthanoid(III) systems has shown that for this class of complexes optimal steric saturation is arrived at the significantly smaller SAS value of 0.72 [22].

The 'solid angle sum rule' would thus predict that sterically non-overcrowded, and hence chemically sufficiently stable, organolanthanoids of the trigonal bipyramidal complex type $Cp_3Ln(NCR)_2$ are not expected until the radius of the central Ln^{3+} ion is increased by some 15% with respect to the ionic radius of U^{4+}. In view of $r(U^{4+}) \approx r(Ho^{3+})$ and $r(Er^{3+})$ [23], an optimal SAS value of 0.72 should correspond to $r(La^{3+})$. To overcome the fact that the $r(Ln^{3+})$ values of all fourteen lanthanoids are different, it has been suggested [22] that the SAS value of any $Cp_nLn^{III}X_pY_q$ system can be favourably approximated by eqn. 2 in which SAF (Lig.) stands for a constant 'solid angle factor' ($SA/4\pi$) of each individual ligand, and $\rho(Ln)$ for

$$SAS = nSAF(Cp) + pSAF(X) + qSAF(Y) + \rho(Ln) \qquad (2)$$

an essentially empirical 'correction' term accounting for the non-constancy of $r(Ln)$. According to Fig. 4, $\rho(Ln)$ has arbitrarily been scaled to $\rho(Eu) = 0$. Adopting, on the basis of eqn. 2, the representative SAF values of 0.215, 0.140 and 0.085 for the ligands Cp^-, Cl^- and $NCCH_3$ respectively (Table VI), the essentially linear SAS(Ln)-*vs.*r(Ln) plots of three fundamental classes of organolanthanoid(III) complexes are presented in Fig. 5. Inclusion of some further important classes of complexes would readily indicate that steric congestion clearly increases in the order:

$$Cp_2LnX < Cp_3Ln < Cp_2LnXL_2 < Cp_3LnL < \\ < CpLnX_2L_3 < Cp_3LnL_2 \qquad (3)$$

stating that mononuclear complexes of the type Cp_2LnX would match the 'region of reasonable steric saturation' (SAS: 0.72 ± 0.10) only in cases of very

TABLE VI. Survey of some Representative Metal-to-Ligand Distances and the Corresponding SAF- and FA-Values for $r(Ln^{3+})$ = 0.95 Å.

Ligand X	M–X distance given (in Å)	Solid angle factor SAF	Fan angle FA (°)
$NCCH_3$	2.70	0.085	33
CH_3^-	2.50[a]	0.130	43
Cl^-	2.50	0.140	45
$(\eta^5\text{-}C_5H_5)^-$	2.42[b]	0.215	55

[a] Terminal CH_3-ligand. [b] For metal-to-ring centre.

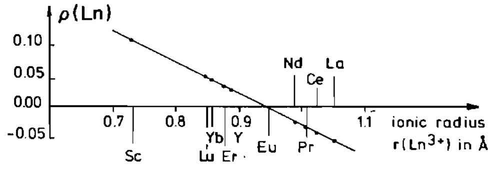

Fig. 4. Graphic representation of the variation of the empiric correction term $\rho(Ln)$ of eqn. 3 as a function of the ionic radius $r(Ln^{3+})$ including Sc^{3+}.

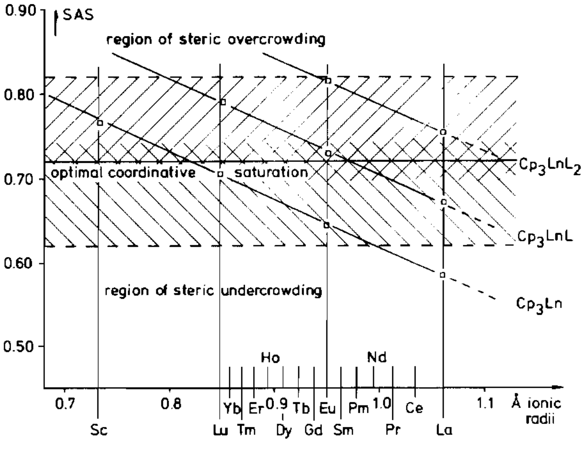

Fig. 5. SAS-*vs.*-$r(Ln^{3+})$ plots for the three representative classes of cyclopentadienyl complexes: Cp_3Ln, $Cp_3Ln\text{-}NCCH_3$ and $Cp_3Ln(\textit{trans-})(NCCH_3)_2$. Optimal SAS-value: 0.72 ± 0.1.

small ionic radii and/or larger SAF(X) values, whereas the reverse is expected for the complex type Cp_3-LnL_2. In fact, recent X-ray crystallographic studies [24] * have confirmed that the representatives of the class of the base-free Cp_3Ln-complexes with (predicted for isolated molecules) SAS values $\leqslant 0.62$ tend in fact to arrive at larger (experimental) SAS values as a result of the formation of polymers involving one bridging Cp ligand per metal ion.

Pseudo-tetrahedral geometry has been assumed for all Cp_3LnL systems, and trigonal bipyramidal coordination for all Cp_3LnL_2 systems. While the former type in accordance with Fig. 5 is known to be verified with all Ln elements [1], the latter type is predicted to avoid critical steric overcrowding only for the elements La–Nd. As the deviation of any individual SAS-value from the 'optimal value' of 0.72 may somehow reflect the relative thermodynamic stability of the system in question, it is worthwhile noting that only for Ln = La $|SAS - 0.72|$ does the difference turn out to become equal for the Cp_3LnL- and Cp_3LnL_2-type adducts, again suggesting comparable chemical stability only for the largest Ln^{3+} ion.

In view of the conceptual simplicity of eqn. 2, no differentiation has been attempted in this study between the standard CAF's of terminal and bridging Cl-ligands, and of $NCCH_3$ in the presence or absence of another $NCCH_3$ ligand, respectively.

One quite essential refinement of the SAS approach would, however, involve the consideration of the potential influence of the size of ligand groups lying more remote from the metal ion than *e.g.* the N-atom of the nitrile or the H-atoms of the Cp ligands (*i.e.* of so-called second-order contributions to SAS). It is expected that the different reactivity of $Cp_3La{\cdot}THF$ with some nitriles NCR (R = C_2H_5, n-C_3H_7 and i-C_3H_7; *vide supra*) reflects the significance of such second-order terms.

The magnitude of ligand fan angles, FA [21], spanned along various spatial directions may be essential for the verification of a distinct structure. Thus, a potential Cp_3LnL_2-system with two nitriles in a *cis*-position can readily be ruled out as the largest hole of a closest-packed Cp_3Ln-moiety offers a FA of 53° while a FA of no less than 33° is required by each nitrile ligand. Similarly the two main FA's of (to second order) 47.5° and 34.0° of a THF ligand (Fig. 6) do not allow a 1:2 stoichiometry with this ligand since a Cp_3Ln-system with three planar ring normals can offer two equivalent holes of FA's not larger than 35°, although the (first order) CAF of THF is comparable to that of the nitrile.

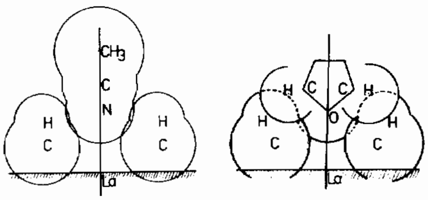

Fig. 6. Schematic view of critically overlapping van der Waals radii of ligand atoms in trigonal bipyramidal Cp_3-$La(NCCH_3)_2$ (a) and (fictitious) $Cp_3La(THF)_2$ (b). The five-membered ring in (b) depicts the C_4O-framework of THF (assumed bond lengths and angles, (a): La–N 2.78, La–Cent 2.55, N–C 1.15, C–C 1.48 Å; (b) La–O 2.57; La–Cent 2.55; O–C 1.46; C–C(THF) 1.42; C–H(THF) 1.1 Å; COC 104; CCO 109; HCH 109°).

The successful preparation of analytically pure examples of the novel complex type $Cp_3Ln(NCR)_2$ with Ln = La, Ce and Pr, but so far not fully convincingly with Nd, and the experimentally clearly supported maximum stability of the La complex (see preceding sections), are in excellent accord with the predictions of the SAS rule. Alternatively, this agreement may be considered as being an encouraging confirmation of the applicability of the SAS rule on f-element organometallics in general.

X-Ray Crystallographic Results**

X-ray crystallographic studies have been carried out on suitable single crystals of the three homologues $Cp_3Ln(NCCH_3)_2$, **I** (Ln = La), **VII** (Ln = Ce) and **IX** (Ln = Pr). Expectedly, the molecular structure of **I**, **VII** and **IX** is essentially trigonal bipyramidal (Fig. 7), significant common features being a statistic disposition of Cp ring B as dictated by the presence of a binary crystallographic axis (one of the two alternative orientations of ring B is indicated in Fig. 7 by asterisks, while the ring H-atoms have been omitted for clarity), and a pronounced bending of the two axial $NCCH_3$ ligands towards ring B (see Fig. 8).

Relevant interatomic distances and bond angles are listed in Table VII. Figure 9 presents a view of the unit cell content showing that between close-lying molecules only normal van der Waals forces are operative. The central Ln^{3+} ion may be assumed to be either formally eleven-coordinated (if each η^5-Cp ligand is considered as a donor of three electron pairs), or as simply five-coordinated by the centres (Cent) of the three equatorially oriented Cp ligands and the two equivalent, axial MeCN

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*X-ray structures of base-free Cp_3Ln complexes with Ln = Nd, Sm, Er and Tm have likewise been completed [4c, 24b].

The X-ray results lead to the following experimental SAS-values: **I (La) 0.751, **VII** (Ce) 0.766 and **IX** (Pr) 0.768.

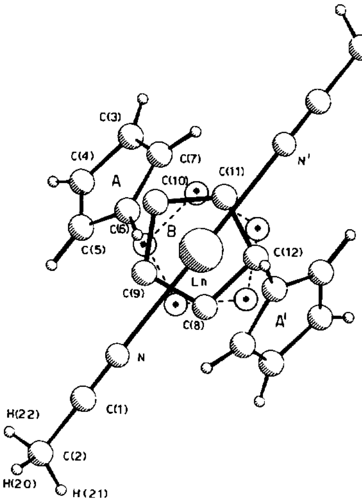

Fig. 7. View down *c* of the $Cp_3Ln(NCCH_3)_2$ molecule: PLUTO-plot; primed atoms are symmetry-related to the unprimed ones through the binary axis; asterisks indicate the alternative orientation of ring B (the H-positions of which have been omitted for clarity).

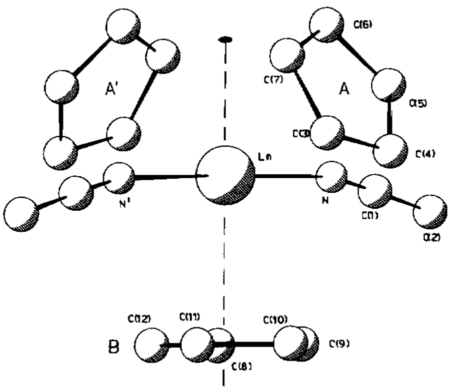

Fig. 8. View of the $Cp_3Ln(NCCH_3)_2$ molecule down *a*; the binary axis is depicted as a dotted line; only one position of ring B is shown.

ligands (trigonal bipyramidal coordination or pseudo-D_{3h} symmetry). The average of the Cent–U–Cent angles is 120°, and that of the Cent-Ln–N angles 90°.

TABLE VII. Selected Bond Lengths (Å) and Bond Angles (°) of the Compounds I, VII and IX.

	(La) I	(Ce) VII	(Pr) IX
M–N	2.785(8)	2.749(6)	2.752(6)
N–C(1)	1.125(12)	1.126(8)	1.141(8)
C(1)–C(2)	1.453(14)	1.453(8)	1.452(9)
Ring A			
M–C(3)	2.86(1)	2.822(6)	2.809(7)
M–C(4)	2.88(1)	2.847(5)	2.831(7)
M–C(5)	2.89(1)	2.863(6)	2.843(8)
M–C(6)	2.90(1)	2.849(5)	2.835(7)
M–C(7)	2.87(1)	2.837(5)	2.802(7)
$M–C_{av.}$	2.88	2.84	2.82
$C–C_{av.}$	1.39	1.40	1.38
$C–C–C_{av.}$	108.0	108.0	108.0
Ring B			
M–C(8)	2.85(2)	2.82(1)	2.84(2)
M–C(9)	2.92(2)	2.83(1)	2.86(2)
M–C(10)	2.94(2)	2.89(1)	2.89(1)
M–C(11)	2.92(2)	2.88(1)	2.83(2)
M–C(12)	2.87(2)	2.84(2)	2.81(2)
$M–C_{av.}$	2.90	2.85	2.85
$C–C_{av.}$	1.41	1.42	1.43
$C–C–C_{av.}$	108.0	108.0	108.0
M–Cent. A	2.62	2.58	2.57
M–Cent. B	2.64	2.59	2.57
N–Cent. A	3.81	3.81	3.79
N–Cent. B	3.83	3.75	3.74
M–N–C(1)	168.7(7)	169.5(4)	169.5(5)
N–M–N'	178.4(8)	178.3(1)	178.6(2)

(continued overleaf)

TABLE VII. *(continued)*

	(La) I	(Ce) VII	(Pr) IX
N–C(1)–C(2)	178.9(10)	178.9(6)	178.6(8)
Cent. A–M–N	89.5(7)	91.1(1)	90.7(1)
Cent. B–M–N	89.7(8)	89.0(1)	89.0(1)
Cent. A–M–Cent. B	122.9(4)	122.5(1)	122.1(1)
Cent. A–M–Cent. A′	120.0(4)	120.2(1)	120.1(1)
Ionic radii Å (Sinha 1976)	1.061	1.034	1.013

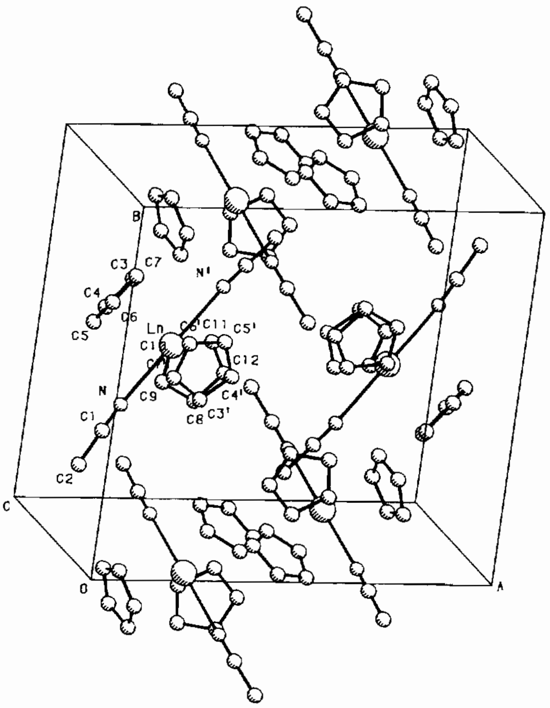

Fig. 9. A perspective view of the unit cell content of Cp_3-$Ln(NCCH_3)_2$ (only one position of ring B is shown).

TABLE VIII. Significant Intramolecular Contacts (<3.6 Å) of the Three Complexes I, VII and IX.[a]

	(La) I	(Ce) VII	(Pr) IX
N•••C(5)	3.15(1)	3.08(1)	3.06(1)
N•••C(3)′	3.25(1)	3.21(1)	3.22(1)
N•••C(7)′	3.23(1)	3.17(1)	3.16(1)
C(1)′•••C(11)	3.60(2)	3.60(2)	3.58(2)
N•••C(8)	3.37(2)	3.26(1)	3.26(2)
N•••C(9)	3.18(2)	3.08(1)	3.10(2)
N′•••C(11)	3.05(2)	3.06(2)	3.01(2)
N′•••C(12)	3.49(2)	3.51(2)	3.49(2)
Cent A•••Cent A′	4.54	4.48	4.45
Cent A•••Cent B	4.62	4.53	4.50

[a] Primed atoms are at ½ – x, 1 – y, z.

However, the two axial MeCN ligands are not colinear with the N–Ln–N′ (179°) arrangement in the three derivatives.

The value of the Ln–N–C(1) angle is 169° in I and 170° in VII and IX, the bending being towards the disordered B ring. In the corresponding cationic complex $[Cp_3U(NCCH_3)_2]^+$ [10a] the U–N–C angles average 174°(3), and in the uncharged compound $Cp_3U(NCS)(NCCH_3)$ 175°(1) [10b]. In view of the absence of any short (d < 4.0 Å) intermolecular distances between nitrile atoms of neighboured molecules in the unit cell, the significant bending of the two nitriles towards ring B might be due to some intramolecular constraints. Actually, the relationship Cent(A)–Cent(A′) < Cent(A)–Cent(B) (see Table VIII) suggests more steric congestion around the rings A and A′, in spite of almost equal Cent (A)–Ln and Cent(B)–Ln bond distances (see Table VII). Moreover, the N-atoms lie closer to a number of atoms of ring B rather than of A and A′*. In addition, the distance C(1)•••C(11) turns out to be the only intramolecular 'non-bonding contact' (see Table VIII) that is significantly shorter than the sum of the van der Waals radii. This feature suggests that weak asymmetric (with respect to the trigonal molecular axis) interactions between the $NCCH_3$ ligand and the Cp ligands (in favour of ring B) might be operative and could also be responsible for the bending of the nitrile towards ring B.

There are no significant differences between the distances Ln–Cent(A) and Ln–Cent(B) (see Table VII), but along the series La, Ce, Pr the

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*N–C(ring) contacts of a similar magnitude (*i.e.* 3.0 ± 0.1 Å) have also been observed on some $[Cp_3UX(NCCH_3)]^q$-systems [10] and, most recently, for the cationic component of the species $[(Ind)UBr_2(NCCH_3)_4]_2[UBr_6]$ (Ind = indenyl [25]).

shortening of both distances is in good agreement with the variation of the standard ionic radii [23]. Likewise, the variation of the average Ln–C distances (ranging from 2.90 to 2.82 Å as Ln changes from La to Pr) compares well with $(U–C)_{ave}$ of the cation $[Cp_3U(NCCH_3)_2]^+$ (2.74 Å [10a]) on the basis of the standard ionic radii. On the other hand, a comparison of the Ln–N bond distances with the corresponding U–N distances of the cationic complex (Pr–N = 2.752; U–N = 2.60 Å; Δ = 0.15 Å) would suggest a significant relative elongation of the Ln–N distance, while virtually a reverse situation would hold after comparison with U–N of the uncharged complex $Cp_3U(NCS)(NCCH_3)$ (U–N = 2.678 Å [10b]; Δ = 0.074 Å) in view of $r(U^{4+})-r(Pr^{3+}) \approx 0.127$ Å [23]. Owing to most recent evidence, even the rather short U–N distance of $[Cp_3U(NCCH_3)_2]^+$ may be considered as somewhat elongated relative to sterically less congested organouranium(IV) cations [25]* containing $NCCH_3$ ligands.

A comparison of the structural data of $Cp_3Pr(NCCH_3)_2$ with those of the pseudo-tetrahedral complex $Cp_3PrCNC_6H_{11}$ ($Pr–C(Cp)_{ave}$ = 2.78 Å; Pr–C(N) = 2.65(1) Å [8]) reveals that the addition of a second neutral ligand to the ψ-T_d complex causes a significant lengthening of the $Pr–C(Cp)_{ave}$ distance (*cf.* to 2.84 Å), and hence most probably also of the Pr–N distance. A similar bond lengthening is also apparent from a comparison of $Cp_3La{\cdot}THF$ [3] with $Cp_3La(NCCH_3)_2$ where the $La–C(Cp)_{ave}$ values are 2.82 and 2.89 Å, respectively. This feature contrasts with the behaviour of organouranium(IV) complexes where the addition of a fifth ligand to a ψ-T_d-system Cp_3UX (X = halide or pseudohalide) is not accompanied by a significant increase of the U–C(Cp) and U–X bond distances [10].

The Pr–C(isocyanide) distance of 2.65 Å as found in the 1:1 adduct $Cp_3PrCNC_6H_{11}$ [8] corresponds to such a large SAF value that, in accordance with our observation, a 1:2 adduct is predicted to be unstable. Chemically stable 1:2 adducts would apparently require an isocyanide ligand capable to very flexibly expand its bond distance to the metal ion by at least 0.5 Å. Experiments to overcome this serious difficulty by combining *e.g.* Cp_3La with one nitrile and one isocyanide, or, alternatively, one nitrile and one N-bonded $NCBH_3$ anion**, are in progress.

Experimental

All operations were carried out under inert gas atmosphere (usually N_2) adopting throughout carefully absoluted organic solvents and reactants. Infrared spectra of high resolution were measured with a Perkin Elmer 283 grating spectrometer, survey spectra with a PE 577 model. ^1H NMR spectra were taken on a Bruker WP 80 SY instrument equipped with a variable-temperature device, the tentative ^{139}La NMR studies on a Bruker SWL 3-100 wide line instrument, and the Raman scans on a Cary 82 spectrometer (using the red He/Ne laser source). The majority of the elemental analyses (data of Table II except those signified by an asterisk) were carried out by DORNIS u. KOLBE, Mikroanalytisches Laboratorium, Mülheim/Ruhr (F.R.G.). Identical samples simultaneously analyzed on a Carlo-Erba Instrument (Hamburg) gave usually rise to unsatisfactorily low C-values.

Preparation of I

A mixture of anhydrous $LaCl_3$ (1.5 g, 6.1 mmol) and KC_5H_5 (1.90 g, 18.2 mmol) dissolved in 25 ml THF was stirred over 72 h at room temperature. From the washed (2–5 ml THF) filtrate, about 1 g of crude $Cp_3La{\cdot}THF$ was isolated after solvent evaporation and drying (4 h, *ca.* 50 °C). 1 g of the crude $Cp_3La{\cdot}THF$ was subsequently stirred overnight in 15 ml of pure CH_3CN. After solvent evaporation the reaction with CH_3CN was repeated for two more times. Finally, the practically dry product was dissolved in CH_2Cl_2; after filtration and solvent removal the residue was dried at *ca.* 30 °C for several hours (yield of **I**: *ca.* 20%, based on $LaCl_3$).

Preparation of II

Product **I** (0.3 g, 0.721 mmol) was added to 10 ml of absolute NCC_2H_5 and stirred overnight at room temperature. After filtration the solid residue was dissolved in CH_2Cl_2; the product obtained after subsequent filtration and solvent evaporation was suspended in 3 ml of NCC_2H_5 and stirred for 4 h. Solvent evaporation and drying over 6 h afforded finally pure **II** in a yield of 70%.

Preparation of $Cp_3La{\cdot}NCCH_3$

After addition of 25 ml of n-pentane to 0.8925 g (2.67 mmol) of base-free Cp_3La (Ar atmosphere), the equimolar amount of 0.140 ml (0.1096 g, 2.67 mmol) $NCCH_3$ was dropwise pipetted to this suspension. The suspended Cp_3La was observed to swell instantaneously. After stirring overnight at room temperature and complete solvent evaporation, a white, air-sensitive powder remained. Yield: 1.892 g, 95%. Traces of non-reacted Cp_3La can be separated by extraction with n-pentane. Complex **I** can be prepared in essentially the same way. Starting

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*The U–N distances of the throughout equatorially bonded $NCCH_3$-ligands in $[(Ind)UBr_2(NCCH_3)_4]_2[UBr_6]$ range between 2.53 and 2.57 Å and turn out even shorter than in the $[Cp_3U(NCCH_3)_2]^+$ cation [10a].

**Assumed bond lengths and angles, (a): La–N 2.78, La–Cent 2.55, N–C 1.15, C–C 1.48 Å; (b) La–O 2.57; La–Cent 2.55; O–C 1.46; C–C(THF) 1.42; C–H(THF) 1.1 Å; COC 104; CCO 109; HCH 109°.

TABLE IX. Summary of Crystal Data Collection.

Compound	$Cp_3La(NCCH_3)_2$ **(I)**	$Cp_3Ce(NCCH_3)_2$ **(VII)**	$Cp_3Pr(NCCH_3)_2$ **(IX)**
Diffractometer type	Syntex $P2_1$	Philips Pw 1100	Philips Pw 1100
Formula	$C_{19}H_{21}N_2La$	$C_{19}H_{21}N_2Ce$	$C_{19}H_{21}N_2Pr$
Molecular weight	416.3	417.5	418.3
Crystal colour	white	orange brown	orange[a]
Habit	prismatic	prismatic	prismatic
Crystal size/mm	0.18 × 0.24 × 0.85	0.12 × 0.20 × 1.20	0.28 × 0.32 × 0.90
Space group	*Pnca*	*Pnca*	*Pnca*
Crystal system	orthorhombic	orthorhombic	orthorhombic
a/Å	14.940(3)	14.906(3)	14.936(3)
b/Å	14.074(3)	13.974(3)	13.986(3)
c/Å	8.596(2)	8.502(2)	8.498(2)
U/Å^3	1807.4	1770.9	1775.2
Z	4	4	4
D_c/g cm^{-3}	1.53	1.57	1.56
F(000)	824	828	832
Radiation (λ/Å)	[graphite-monochromated MoK$_\alpha$ (0.7107)]		
μ/cm^{-1}	22.01	24.08	25.94
Reflections measured	2653	2441	2447
Temperature/K	293	293	293
scan method	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan speed/°	b	1.80	1.80
scan width/°	$[2\theta(\text{Mo-K}_{\alpha1}) - 1.0] \rightarrow [2\theta(\text{Mo-K}_{\alpha2}) + 1.0]$	1.50	1.20
Background counts (s)	c	20	20
2θ max/°	60	56	56
σ limit $[I \geqslant n\sigma(I)]$	n = 3	n = 3	n = 3
Unique observed reflections	1633	1378	1372
Weighting scheme w	$1.6071[\sigma^2(F_o) + 0.001(F_o)^2]^{-1}$	$1.0[\sigma^2(F_o) + 0.002973(F_o)^2]^{-1}$	1.0
R $(R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert)$	0.0705	0.0406	0.031
R_w $(R_w = \Sigma w^{1/2}(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma w^{1/2}\lvert F_o\rvert)$	0.0786	0.0467	

[a] Colour changes from grass green to orange in Lindemann capillary after X-ray irradiation. [b] Linear variable between 6.0°/min for 150 counts/s or less and 29.3°/min for 2500 counts/s or more. [c] Stationary-crystal, stationary-counter at beginning and end of each scan, each for one-fourth of the time taken for the scan.

materials: 0.9238 g (2.76 mmol) Cp_3La and 0.280 ml (5.52 mmol) CH_3CN. Yield: 1.002 g, 87%.

Preparation of $Cp_3Ln \cdot NCCH_3$ (Ln = Pr or Sm)

About 0.3 g of base-free (sublimed) Cp_3Ln was dissolved in *ca.* 15 ml of $NCCH_3$. The solution was stirred for 4 h. After solvent evaporation and vacuum drying (*ca.* 30–40 °C; 6 h), the pure adducts were obtained in almost quantitative yields.

X-ray Measurement and Structure Determination

The crystal and refinement data are compiled in Table IX. Crystals of $Cp_3La(NCCH_3)_2$ **I**, $Cp_3Ce(NCCH_3)_2$ **VII** and $Cp_3Pr(NCCH_3)_2$ **IX** had the form of irregular prism and were mounted in 0.3 mm Lindemann glass capillaries. Unit cell parameters were determined on the basis of 25 strong reflections. The intensities of two standard reflections, monitored at 180 reflection intervals, showed no fluctuations larger than those expected from Poisson statistics. Intensity data were corrected for Lorentz polarization effects, and (for compounds **VII** and **IX**) for absorption following the method of North *et al.* [27]. The structures were solved using three-dimensional Patterson and Fourier techniques, and refined by full matrix least-squares minimizing of the function $\Sigma w|\Delta F|^2$. The three compounds **I**, **VII** and **IX** are isostructural and present therefore the same peculiarities.

In fact, the systematic absences were consistent with the space group *Pnca* (standard group *Pbcn*), and according to the calculated density, there are four molecules per unit cell. This means that the molecules could possess crystallographic symmetry elements like a binary axis or an inversion centre. The vector distribution of the Patterson map suggests that the metal atoms are in the special positions *c* on the binary axis, suggesting that one cyclopentadienyl ring has a statistic distribution. This hypothesis was confirmed by a difference Fourier map calculated with the heavy atom contribution only, which showed a disordered distribution along the binary axis of one ring, hereafter indicated by *B*. This disorder was interpreted considering the five independent carbon atoms C(8), C(9), C(10), C(11) and C(12) statistically distributed over two positions having the site occupancy factor 0.5 (see Fig. 7). The asymmetric unit in the cell is then constituted by one half of a lanthanoid atom, one A ring, 50% of a B ring and one $NCCH_3$ ligand.

This model was refined for **I** including all non-hydrogen atoms with anisotropic thermal parameters. The hydrogen atoms were introduced at the idealized calculated positions (C–H: 0.96 Å), the methyl hydrogens were refined as rigid groups. The common isotropic thermal parameter for hydrogen atoms was U = 0.05 Å^2. For **VII** and **IX** the refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms except those belonging to the disordered ring B, which had to be refined isotropically. The idealized hydrogen atom positions (C–H: 0.98 Å) were calculated and introduced only for the $NCCH_3$ group and for the ordered Cp ring with a common isotropic thermal parameter U = 0.06 Å^2.

In the three refinements the weighting scheme used showed reasonable consistency in a test of $w\Delta^2$ for data sectioned with respect both to F_o and to $(\lambda^{-1} \sin\theta)$. Neutral scattering factors for the atoms were from Ref. [28]. The real ($\Delta f'$) and imaginary ($\Delta f''$) corrections for anomalous dispersion in case of La, Ce and Pr were included in the structure factor calculations. Data processing and computation were carried out using the SHELX 76 program package [29]. Final positional parameters, for the three compounds are presented in Table X*.

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*Thermal parameters, observed and calculated structure factors (×10^3) for the compounds are available as supplementary material (Table XI).

TABLE X. Atomic Coordinates ($\times10^4$) with e.s.d.s in Parentheses[a]; Hydrogen Positions ($\times10^3$).

Atom	*x*	*y*	*z*	Hydrogen	*x*	*y*	*z*
(a) $Cp_3La(NCCH_3)_2$ (I)							
La	2500	5000	5991(1)				
N	1425(6)	3384(6)	5938(9)				
C(1)	1003(6)	2744(6)	5660(10)				
C(2)	444(8)	1929(7)	5291(12)	H(20)	24	163	623
				H(21)	−79	149	470
				H(22)	−8	214	469
C(3)	1450(7)	6634(7)	6731(12)	H(3)	159	719	610
C(4)	806(7)	5934(7)	6412(12)	H(4)	43	592	547
C(5)	820(7)	5274(7)	7598(12)	H(5)	43	470	766
C(6)	1456(7)	5552(8)	8687(10)	H(6)	160	522	965
C(7)	1844(7)	6386(7)	8157(12)	H(7)	232	675	868
C(8)	2615(15)	4250(15)	2917(22)	H(8)	278	357	291
C(9)	1762(17)	4627(14)	2911(22)	H(9)	120	426	291
C(10)	1827(14)	5633(16)	2945(20)	H(10)	133	607	293
C(11)	2738(15)	5852(18)	2920(26)	H(11)	299	650	294
C(12)	3248(15)	4997(17)	2919(18)	H(12)	388	495	293
(b) $Cp_3Ce(NCCH_3)_2$ (VII)							
Ce	2500	5000	5984.3(4)				
N	1433(4)	3396(4)	5937(5)				
C(1)	1000(3)	2755(4)	5677(6)				
C(2)	442(4)	1932(4)	5310(7)	H(20)	−18	199	564
				H(21)	70	134	574
				H(22)	47	191	416
C(3)	1460(4)	6627(4)	6719(6)	H(3)	160	718	606
C(4)	810(3)	5919(4)	6375(7)	H(4)	41	591	546
C(5)	830(4)	5245(4)	7599(8)	H(5)	47	466	767
C(6)	1467(4)	5544(4)	8658(6)	H(6)	162	522	964
C(7)	1863(3)	6387(4)	8149(6)	H(7)	234	675	868
C(8)	2581(9)	4187(10)	2947(15)				
C(9)	1724(7)	4656(11)	3004(12)				
C(10)	1829(9)	5652(11)	2982(13)				
C(11)	2797(14)	5785(10)	2890(15)				
C(12)	3233(12)	4943(12)	2902(17)				
(c) $Cp_3Pr(NCCH_3)_2$ (IX)							
Pr	2500	5000	5981.1(4)				
N	1423(4)	3404(4)	5942(7)				
C(1)	985(4)	2755(4)	5681(8)				
C(2)	429(6)	1934(5)	5308(11)	H(20)	12	168	624
				H(21)	73	141	476
				H(22)	−1	223	460
C(3)	1469(5)	6618(5)	6725(8)	H(3)	161	718	608
C(4)	828(5)	5920(5)	6394(9)	H(4)	44	591	547
C(5)	844(5)	5257(5)	7576(9)	H(5)	46	469	765
C(6)	1470(5)	5529(5)	8645(8)	H(6)	162	519	962
C(7)	1871(5)	6370(5)	8117(9)	H(7)	235	672	865
C(8)	2587(13)	4162(11)	2942(19)				
C(9)	1737(10)	4629(12)	2957(18)				
C(10)	1849(10)	5669(11)	2971(17)				
C(11)	2789(14)	5789(13)	2959(22)				
C(12)	3254(10)	4926(15)	2950(18)				

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[a] In the three compounds the occupancy factors for C(8)–C(12) rings are 0.5.

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