

Study of rare-earth π -complexes by means of Voronoi–Dirichlet polyhedra

O. A. Blatova, V. A. Blatov* and
V. N. Serezhkin

Samara State University, Ac. Pavlov St. 1,
443011 Samara, Russia

Correspondence e-mail: blatov@ssu.samara.ru

An investigation of 135 π -complexes of rare-earth atoms (Ln) was carried out with Voronoi–Dirichlet polyhedra. A novel method for the evaluation of the sizes of polyatomic ligands and steric effects in the structure of organometallic compounds was developed. The dependence of the domain size for Ln atoms on their nature, coordinating number and oxidation state was studied. The reasons for the occurrence of agostic Ln–H contacts were considered with a geometrical–topological analysis.

Received 14 December 2000

Accepted 13 February 2001

1. Introduction

The first cyclopentadienyl complexes of rare-earth atoms were obtained ~50 years ago (Wilkinson & Birmingham, 1954). During this time many methods for the synthesis of π -complexes of *d*- and *f*-elements were developed and crystal structures were studied of more than 900 compounds including Ln atoms (Ln = Sc–Lu; Cambridge Structural Database, 2000), whereas their detailed crystal-chemical classification has not been made. This investigation is the first attempt of a systematical search for crystal structure regularities in this group of compounds using the methods of geometrical–topological crystal-chemical analysis based on the representation of an atom in a crystal field as its Voronoi–Dirichlet polyhedron (VDP). Lately, interest in applying VDPs for the analysis of various classes of inorganic (Thomas, 1996; Christensen & Thomas, 1999) and organic (Pere-sypkina & Blatov, 2000) compounds has increased, because in many cases this method produces additional information on crystal structure. As was recently shown by Blatov, Shevchenko & Serezhkin (1999), a number of VDP characteristics have clear physical meaning and substantially expand the list of atomic descriptors used in crystal-chemical analysis. In particular, one can assume that a VDP is a geometrical image of an atom or of its domain in a crystal field. Therefore, the VDP volume (V_{VDP}) is approximately equal to atomic volume and the radius of the spherical domain (R_{sd}), which is equal to the radius of a sphere of V_{VDP} volume, may be considered as the atomic crystal-chemical radius irrespective of the nature of the interatomic bonds. Although this approximation is more

Table 1

The main groups of the complexes studied.

The most typical ligands are selected: cyclopentadienyl (Cp), cyclooctatetraenyl (COT) and their derivatives (Cp', COT'). Other typical ligands are also given in the final column.

No	Compound composition	Ln atoms	Ligands (<i>L</i>)
(I)	Ln(Cp') ₃	All, except Pm, Eu and Ho	–
(II)	Ln(Cp') ₂	Sm, Eu	–
(III)	Ln(Cp') _{<i>n</i>} L _{<i>m</i>} , <i>n</i> = 1, 2; <i>m</i> = 1, 2, 3	Sc, Y, La, Ce, Nd, Sm, Gd, Tb, Er, Yb, Lu	CH(Si(Me) ₃) ₂ , alkyls, benzene derivatives, polyenes, alkynes, phosphines
(IV)	(Cp') ₂ Ln–L–Ln(Cp') ₂	La, Ce, Sm, Yb	Cp, COT, polyenes
(V)	Ln(COT') ₂	Ce, Nd, Sm, Er, Yb	–
(VI)	Ln(COT)L	Sm, Tb, Lu	Cp', CH(Si(Me) ₃) ₂
(VII)	LnL ₃	La, Pr, Nd	Indenyl
(VIII)	LnL ₃	Nd, Gd, Tb, Lu	2,4-Dimethylpentadienyl

approximate than the representation of an atom as a polyhedral domain confined by zero-flux surfaces in the vector field of the gradient of electron density (Bader, 1990), it is especially effective for the study of complex structures where Bader's method cannot be used due to technical problems.

As in Bader's method, a VDP face may be considered as a contact between two atomic domains. At the same time it corresponds to a chemical bond with only the following additional conditions (Blatov, Pogilyakova & Serezhkin, 1999):

(i) The solid angle of an *i*th VDP face (Ω_i) must be larger than the typical error of its determination ($\sim 1.5\%$ of the total solid angle of 4π steradian).

(ii) The VDP face must be 'major', *i.e.* contacting atoms must be 'direct' neighbours; the segment between them must intersect this face. Other VDP faces are called 'minor' and correspond to chemical interactions being absent between atoms.

The value of the normalized second moment of inertia of VDP (G_3) is used to estimate the sphericity of the atomic coordination shell, because the sphere has the smallest value, $G_3 = 0.0769670$, among all three-dimensional solids. The essential positive shift of the central atom from the VDP centroid (D_A) indicates the spatial anisotropy of an atomic domain mostly caused by a lone electron pair near the atom.

2. Experimental

The original crystal structure information on 823 π -complexes containing Ln atoms was taken from the Cambridge Structural Database (2000) by means of the *TOPOS* program package (Blatov, Shevchenko & Serezhkin, 1999). All compounds were taken into account whose crystal structures had no disordered atoms and were completely determined (occasionally, without allocating H atoms). In this study we have investigated in detail the compounds where Ln atoms were immediately bonded with only C atoms. Most of such compounds (118 of

Table 2

Comparison of VDP characteristics for 2335 H atoms allocated by structure experiment or by calculation.

Method of determination	V_{VDP} (Å ³)	R_{sd} (Å)	G_3	D_A (Å)	Distances H–H (Å)	
					$\langle R \rangle$	$R_{\text{min}}-R_{\text{max}}$
Experiment	12.2 (1.7)	1.42 (7)	0.103 (5)	0.5 (1)	3.01 (49)	1.13–5.87
Calculation with <i>HSite</i>	11.9 (1.7)	1.41 (7)	0.099 (4)	0.4 (1)	2.92 (51)	1.30–5.43

135) can be divided into the groups listed in Table 1 according to their chemical and stoichiometric composition.

3. Methods of analysis of rare-earth π -complexes with Voronoi–Dirichlet polyhedra

3.1. The program *HSite*

As the positions of the H atoms were not determined in many compounds we have developed the computer program *HSite* for the calculation of the coordinates of H atoms connected to *X* atoms ($X = \text{C, N, O, Si, P, S, Ge, As, Se}$) depending on their nature, hybridization type and arrangement of other atoms directly non-bonded with the *X* atoms. In comparison with known similar programs it has some additional features:

(i) In the determination of the hybridization type of an atom *X* the $M \cdots X$ contacts were taken into account and the type (σ or π) of bond for $M \cdots X$ was searched.

(ii) During the generation of H atoms in groups with rotational degrees of freedom (for example, in methyl substituents of a cyclopentadienyl ring), the search for an optimal orientation of the group was fulfilled depending on the arrangement and size of the surrounding atoms. In turn, the sizes of these atoms were approximated by their R_{sd} values. In the determination of the optimal orientation the effects of repulsion in H–H contacts were considered and the possibility of the appearance of hydrogen bonds $\text{O(N)} \cdots \text{H} - \text{O(N)}$ was taken into account.

To evaluate the efficacy of the program *HSite* the positions of 2335 H atoms in 54 completely solved crystal structures of the sample were redetermined. The values of the VDP characteristics for H atoms and average distances $R(\text{H} \cdots \text{H})$ were determined for $\sim 15\,000$ 'direct' $\text{H} \cdots \text{H}$ contacts calculated from the data of structural experiments or according to the results generated with the program *HSite*, which are equal within standard deviations for both individual compounds and the sample as a whole (Table 2).

3.2. Computer identification of atomic bonds

One of the problems which becomes apparent in the study of these compounds is the lack of strict crystal-chemical criteria in the search for Ln–*X* chemical bonds, where *X* is an atom of an organic ligand. Usually in the identification of interatomic bonds the appropriate distances are compared with the sum of the corresponding atomic crystal-chemical

radii, but the tables of such radii for heterodesmic coordination and organometallic compounds have not yet been generated. In particular, it is known (Deacon & Shen, 1996) that in the complexes considered the distances $R(\text{Ln}-\text{C}) < 2.85 \text{ \AA}$ correspond to strong σ or π interactions, but at larger interatomic distances the existence or absence of a bond is a controversial point. For instance, in bis(η^5 -methylcyclopentadienyl)-(2,6-bis(2,4,6-trimethylphenyl)phenyl)ytterbium (GOCJUD) the distance $\text{Yb}-\text{C}(7)$ (Fig. 1) is 3.2 \AA and it is unclear whether this contact should be considered as a bond. Hereafter, the refcodes of compounds in the Cambridge Structural Database are given in parentheses.

Recently (Serezhkin *et al.*, 1997), the method of intersecting spheres was proposed for determining chemical bonds of any type. Within the scope of this method the existence of interatomic contacts is determined as a result of calculating the number of overlapping pairs of internal and external spheres circumscribed around the center of each atom of the pair. Normally, the internal and external spheres have the radii equal to atomic Slater's radius (r_s) and to R_{sd} , respectively. If more than one pair of such spheres intersect each other then a contact is assumed to be a chemical bond and is considered in the determination of atomic coordination number (CN). The efficiency of this method was confirmed by studying several dozens of compounds with different chemical nature (Serezhkin *et al.*, 1997).

In fact, the method of intersecting spheres assumes the shape of an atomic domain to be practically spherical in the crystal structure. This assumption is not correct for the compounds considered here, as in this case the atomic domains in organic ligands usually are ellipsoidal, not spherical (Fig. 2), that is also illustrated by a high average value, $G_3 = 0.11$ (1), for 4017 VDPs of the C atoms in the complexes.

To take into account the shape anisotropy of atomic domains Peresypkina & Blatov (2000) have improved the method of intersecting spheres with the so-called method of spherical sectors. In this method the sphere of R_{sd} radius is replaced with a set of spherical sectors corresponding to separate interatomic contacts, the number of which is equal to

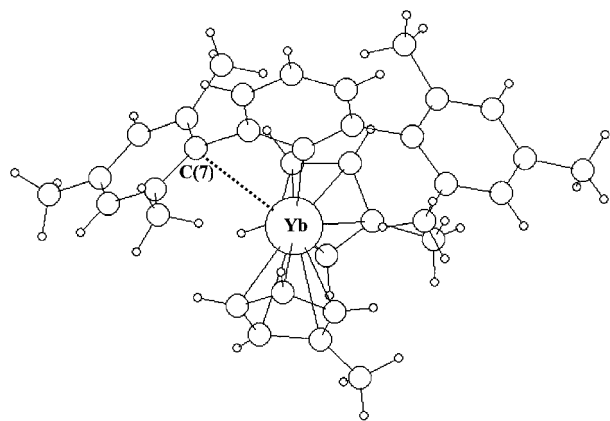


Figure 1
Molecular structure of bis(η^5 -methylcyclopentadienyl)-(2,6-bis(2,4,6-trimethylphenyl)phenyl)ytterbium (GOCJUD). The contact $\text{Yb}\cdots\text{C}(7)$ is marked by a dotted line.

the number of 'major' faces of an atomic VDP. The radius (r_{sec}) of each sector is determined by the formula

$$V_p = (1/3)\Omega r_{\text{sec}}^3, \quad (1)$$

where V_p and Ω are the volume and solid angle of a pyramid with basal VDP face corresponding to interatomic contacts and with the VDP atom in the top. Within the scope of this method an internal Slater's sphere corresponds to the maximum electronic density in a valent atomic shell and the sector surface determines the boundary of the atom in a crystal field in the direction of the atomic contact.

We have used this method for the investigation of π -complexes of rare-earth atoms and the results obtained confirm its accuracy. Only in two out of 135 compounds do the CNs differ from the values given by the authors of the original papers: in tetrakis(μ_2 - σ^1, η^5 -methylcyclopentadienyl)-tetrakis(η^5 -methylcyclopentadienyl)praseodymium (NIJFOB) and in *catena*(μ_2 - η^5, η^3 -1,3-bis(trimethylsilyl)cyclopentadienyl)-(μ_2 - η^5 -1,3-bis(trimethylsilyl)cyclopentadienyl)-bis(η^5 -1,3-bis(trimethylsilyl)cyclopentadienyl)dieuropium (YAMNIJ). Hereafter, the CN of a Ln atom is considered as the total number of atoms of a ligand (L) taking part in valent interactions $\text{Ln}-\text{L}$, unlike efficient CN (Schumann *et al.*, 1995). The authors (Xi-Geng *et al.*, 1997; Hitchcock *et al.*, 1992) have described the complex NIJFOB as a tetramer and the complex YAMNIJ as a polymeric chain, and in both structures the Ln atoms are connected with bridging cyclopentadienyl rings. The calculation using the method of spherical sectors gives the structures as consisting of monomers and dimers, respectively. Note that in these crystal structures the positions of the H atoms have not been determined and the authors of the original papers have assumed the existence of σ -bonds

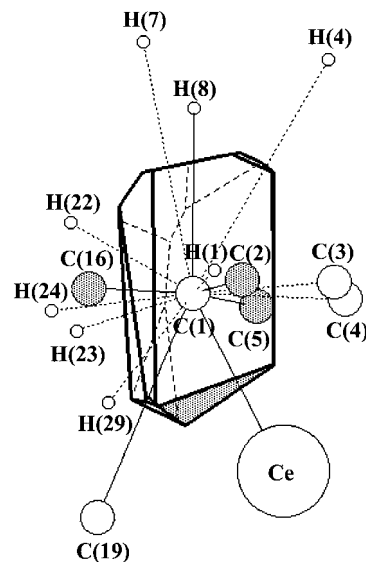


Figure 2
The VDP of the C(1) atom of a cyclopentadienyl ring in the crystal structure of tris(η^5 -methylcyclopentadienyl)-(*tert*-butylisocyanide)cerium (KEDCAX). The C atoms C(2) and C(5) of the ring, C(16) of a methyl group and the VDP face corresponding to the contact $\text{Ce}-\text{C}(1)$ are shaded. 'Indirect' contacts are shown by dotted lines. $G_3 = 0.111$.

Table 3

Sizes of C and H atoms in organic ligands.

The hybridization of C atoms and the composition of their atomic environments are given in parentheses.

Atom	No. of compounds	No. of atoms	$V_{\text{VDP}} (\text{\AA}^3)$	$R_{\text{sd}} (\text{\AA})$
C(sp^3 , C ₄)	17	41	5.2 (2)	1.07 (2)
C(sp^3 , HC ₃)	6	35	4.5 (2)	1.03 (2)
C(sp^3 , H ₂ C ₂)	25	111	3.3 (3)	0.92 (3)
C(sp^3 , H ₃ C)	91	948	2.6 (4)	0.85 (4)
C(sp^3 , H ₃ Si)	30	357	3.3 (4)	0.92 (4)
C(sp^2 , C ₃)	94	866	7.6 (4)	1.22 (2)
C(sp^2 , HC ₂)	103	1269	6.6 (5)	1.16 (3)
C(sp^2 , H ₂ C)	15	60	5.6 (6)	1.10 (4)
C(sp^2 , C ₂ Si)	18	77	9.7 (5)	1.32 (2)
C(sp , C ₂)	14	21	11.2 (9)	1.39 (4)
H (C)	135	6089	12 (2)	1.42 (7)

between complexing atoms and C atoms of the cyclopentadienyl rings, taking into account the rather short contacts $R[\text{Pr}(1)-\text{C}(28)] = 3.02 \text{ \AA}$, $R[\text{Pr}(2)-\text{C}(16)] = 2.99 \text{ \AA}$ in NIJFOB and $R[\text{Eu}(2)-\text{C}(40)] = 3.09 \text{ \AA}$ in YAMNII. However, after allocating hydrogen positions using *HSite* the calculation of VDPs denies the above-mentioned bonds because the atomic domains of the H atoms dislodge the domains of the Ln and C atoms.

3.3. Estimation of ligand sizes and steric effects

To analyze the ligands bonded with Ln atoms we use the integral characteristics of the corresponding molecular VDPs widely applied in the investigation of organic crystals (Pereyapkina & Blatov, 2000). Note that molecular VDP is a union of the VDPs of the atoms forming the molecule (ligand). The calculations performed for 135 Ln complexes (Table 3) indicate, within error accepted for the structural experiment (5–6% for non-H atoms), the constancy of the sizes of atoms in organic ligands, under the condition of similarity for their hybridization and environment. Taking into account this fact the ligand volume V_L can be calculated as the sum of VDP volumes of all atoms Z_i of the ligand:

$$V_L = \sum_i V_{\text{VDP}}(Z_i). \quad (2)$$

For instance, according to (2) and Table 3, $V_L(\text{C}_5\text{H}_5) = 5(6.6 + 12) = 93 \text{ \AA}^3$, which is in good agreement with average values for the cyclopentadienyl ligand from Table 4. It is interesting to note that the volume of all π -ligands showing different types of coordination (cyclopentadienyl, methylcyclopentadienyl, dimethylpentadienyl and cyclooctatetraenyl; Table 4) is practically independent of their coordination type.

Blatov *et al.* (1995) have proposed the use of the solid angle Ω value, which corresponds to a VDP face separating atomic domains, to estimate the bond strength between a pair of atoms. In this study we use the ligand solid angle Ω_L :

$$\Omega_L = \sum_i \Omega(\text{Ln}-Z_i), \quad (3)$$

where $\Omega(\text{Ln}-Z_i)$ are the values of the solid angles of VDP faces corresponding to all $\text{Ln}-Z_i$ contacts with the partici-

pation of the donor ligand atoms. Analysis of all the ligands in the complexes considered show that the value Ω_L expressed in per cent of 4π sr varies insignificantly and is practically independent of the nature of the complexing atom at a given ligand coordination type (Table 4). However, the change of ligand coordination type can strongly influence Ω_L if the degree of screening complexing atom by ligand changes. For instance, Ω_L for 2,4-dimethylpentadienyl at coordination η^5 is nearly three times more than at η^2 (Table 4).

Since the sum of the solid angles of all the ligands in a complex characterizes the degree of filling of the coordination sphere around the central atom, average values of Ω_L listed in Table 4 can be used for the estimation of existence probability for such a complex. Note that Tolman (1970) and Zacharov *et al.* (1990) have also used for this purpose the solid angle with the top in the central atom embracing the ligand, the atoms of which were represented as van der Waals spheres. Generally, the values of Ω_L obtained by the aforesaid method have the same order as the values given by Zacharov *et al.* (1990). For example, according to Zacharov *et al.* (1990) Ω_L ranges from 21 to 30% for 12 compounds containing cyclopentadienyl ions with the coordination type η^5 , which is in agreement with Table 4. In most cases, both methods of the estimation of the screening degree of the central atom by ligand allow one to make similar conclusions about the stability of the complexes. Thus, if the sum of Ω_L ($\Omega_{L\Sigma}$) for all ligands in a complex is more than 100% then the complex should be unstable due to steric effects. For instance, the compound $\text{Ln}(\text{Cp})_4$ cannot exist because in this case $\Omega_{L\Sigma} = 28.2 \times 4 = 112.8\%$. If the value of $\Omega_{L\Sigma}$ is significantly less than 100%, the complexing atom tends to form additional bonds which also result in the compound being unstable. Thus, the isolated groups $\text{Ln}(\text{Cp})_2$ cannot exist in the structure of a crystal because $\Omega_{L\Sigma} = 28.2 \times 2 = 56.4\%$.

At the same time, in contrast to the approach of Tolman (1970) and Zacharov *et al.* (1990), the VDP method of Ω_L and $\Omega_{L\Sigma}$ calculation is more universal because it does not require any values of van der Waals or other radii and allows one to investigate molecular ligands containing any atom (including van der Waals radii which are unknown or determined inaccurately). Moreover, the use of molecular VDPs for the estimation of ligand sizes allows the consideration of both ligand orientation to the complexing atom and the factor of its crystal environment (arrangement of neighbouring ligands and complex groups).

4. Results and discussion

4.1. Domains of rare-earth atoms

In the compounds studied CNs of Ln atoms by C atoms widely range from 4 to 17. At the same time, the data obtained indicate that V_{VDP} of Ln atoms is independent of their CNs, while the range of distances $\text{Ln}-\text{C}$ is rather wide (Tables 5 and 6). Thus, Table 6 shows that V_{VDP} of Nd(+3), Sm(+2) or Sm(+3) atoms is constant within error at all CNs, except 15,

Table 4

Ligand characteristics.

If ligands are connected with several complexing atoms by different ways Ω_L values are given for each coordination type by way of an increase in its dentation to be separated by plus. For instance, for coordination type η^2, η^5 , two numbers are given for η^2 and η^5 coordination, respectively.

Ligand	Coordination type	No. of compounds	No. of ligands	$V_{\text{VDP}} (\text{\AA}^3)$	$R_{\text{sd}} (\text{\AA})$	Ω (%)
CH ₂ (methylene)	μ_2	1	1	32.5	1.98	12.5 (7)
CH ₃ (methyl)	σ^2	6	7	39 (3)	2.10 (5)	8.4 (1.2)
	σ^1	1	3	47 (2)	2.23 (4)	14.2 (4)
	η^2	1	1	96.1	2.84	14.2
C ₄ H ₆ (butyne)	η^3	1	2	104 (2)	2.92 (2)	26.8 (2)
C ₄ H ₇ (butenyl)	σ^1	1	2	164 (6)	3.40 (4)	14.0 (4)
C ₄ H ₁₁ Si (trimethylsilyl)	σ^2	1	1	174.6	3.47	17.4
C ₄ H ₁₂ Al (tetramethylaluminium)	η^5	20	54	96 (4)	2.84 (4)	28.2 (1.9)
C ₅ H ₅ (cyclopentadienyl)	$\mu_2-\sigma^1, \eta^5$	5	8	96 (3)	2.83 (3)	7.7 (1.4)+ 22.2 (1.7)
	$\mu_2-\eta^2, \eta^5$	3	3	96 (5)	2.84 (5)	9.5 (1.7)+ 23.5 (4.7)
	σ^1	1	1	150.9	3.30	13.5
C ₅ H ₉ N (<i>tert</i> -butylisocyanide)	η^6	1	3	109 (3)	2.96 (3)	14.2 (1)
C ₆ H ₅ (phenyl)	$\mu_2-\sigma^1, \eta^2, \sigma^1, \eta^2$	1	1	124.9	3.10	25.4 (2)
C ₆ H ₆ (hexa-2,3,4-triene)	η^5	5	22	124 (5)	3.09 (4)	27.4 (1.9)
C ₆ H ₇ (methylcyclopentadienyl)	$\mu_2-\sigma^1, \eta^5$	1	1	124.7	3.10	4.9
						+25.7
						26.4
C ₆ H ₈ (hexa-1,4-diene)	$\mu_2-\eta^3, \eta^3$	1	1	135.2	3.18	26.4
C ₆ H ₉ (3,3-dimethyl-1-butynyl)	σ^2	1	1	151.7	3.31	15.9 (2)
C ₇ H ₉ (1,3-dimethylcyclopentadienyl)	η^5	1	2	150 (1)	3.30 (1)	29.3
C ₇ H ₁₁ (2,5-dimethylpentadienyl)	η^5	4	12	164 (10)	3.39 (7)	32 (3)
	η^2	1	1	158.0	3.35	11.3
	η^5	5	9	242 (4)	3.86 (5)	30.6 (3.4)
C ₇ H ₁₁ (ethyltetramethylcyclopentadienyl)	σ^1	3	4	180 (2)	3.50 (2)	14.1 (1.0)
C ₇ H ₁₂ N ₂ (tetramethylimidazol-2-idene)	σ^1	16	25	274 (8)	4.03 (4)	13.7 (1.4)
C ₇ H ₁₉ Si ₂ (bis(trimethylsilyl)methyl)	μ_2	4	7	142 (2)	3.24 (2)	14.8 (1.3)
C ₈ H ₅ (phenylethylidene)	$\mu_2-\eta^2, \eta^4$	1	1	149.7	3.29	10.9
C ₈ H ₈ (styrolene)						+15.7
						54.8 (2.7)
						47.5 (3.4)
C ₈ H ₈ (cyclooctatetraenyl)	η^8	7	9	152 (2)	3.31 (1)	54.8 (2.7)
C ₈ H ₁₂ (octa-1,6-diene)	$\mu_2-\eta^8, \eta^8$	3	4	148 (2)	3.29 (2)	47.5 (3.4)
	$\mu_2-\eta^3, \eta^3$	1	1	174.7	34.7	25.2 (4)
	σ^2	1	3	259 (3)	3.95 (2)	23.8 (9)
C ₈ H ₁₈ Al (ethylidene-ethylaluminium)	η^5	1	4	222 (6)	3.76 (4)	29.4 (4)
C ₈ H ₁₃ Si (trimethylsilylcyclopentadienyl)	η^5	6	11	200 (6)	3.63 (4)	28.9 (2.3)
C ₉ H ₁₃ (<i>tert</i> -butylcyclopentadienyl)	η^5	4	5	194 (8)	3.59 (5)	31.2 (4.1)
C ₉ H ₁₃ (tetramethylcyclopentadienyl)	$\mu_2-\sigma^1, \eta^5$	1	2	200.5	3.63	14.6
C ₁₀ H ₁₄ (2,3,4,5-tetramethyl-1-methylenecyclopentadienyl)						+32.9
						30.0 (2.2)
						28.5 (1.1)
C ₁₀ H ₁₅ (pentamethylcyclopentadienyl)	η^5	46	107	227 (7)	3.78 (4)	30.0 (2.2)
C ₁₁ H ₁₅ (4-methyl-1,2-pentamethylenecyclopentadienyl)	η^5	1	3	223 (2)	3.76 (1)	28.5 (1.1)
C ₁₁ H ₂₁ Si ₂ [bis(trimethylsilyl)cyclopentadienyl]	η^5	7	18	333 (9)	4.38 (4)	29.4 (2.7)
C ₁₂ H ₁₈ (hexamethylbenzene)	η^6	2	2	264 (2)	3.98 (1)	23.3
C ₁₂ H ₁₈ (tetramethyloctatriene)	$\mu_2-\eta^3, \eta^3$	2	2	264 (2)	3.98 (1)	23.3 (1)
C ₁₂ H ₂₁ (2- <i>tert</i> -butyl-5,5-dimethylhexa-1,3-dien-3-yl)	σ^1	1	1	239.0	4.08	10.8
C ₁₃ H ₂₁ [di(<i>tert</i> -butyl)cyclopentadienyl]	η^5	6	14	308 (10)	4.19 (5)	28.0 (3.0)
C ₁₄ H ₁₀ (9,10-dihydroanthracene-9,10-diyl)	σ^2	1	1	223.2	3.76	24.4
C ₁₄ H ₁₅ P (methylphenylphosphinomethyl)	σ^1	3	3	306 (12)	4.18 (5)	11.2 (2)
C ₁₄ H ₂₂ (2,4,7,9-tetramethyldeca-1,3,8-trienyl)	η^3, η^5	1	1	306.6	4.18	60.8
C ₁₄ H ₂₄ Si ₂ [bis(trimethylsilyl)cyclooctatetraene]	η^8	1	2	386 (10)	4.52(4)	44.1
C ₁₆ H ₁₀ (1,4-diphenylbutadiene)	$\mu_2-\eta^2, \eta^2$	1	1	268.7	4.00	23.7
C ₁₇ H ₃₂ Si ₃ [tris(trimethylsilyl)cyclooctatetraene]	η^8	1	2	513 (9)	4.96 (3)	50.0
C ₁₈ H ₃₀ (1,3,5-tri- <i>tert</i> -butylbenzene)	η^6	1	1	423.1	4.65	38.2
C ₁₉ H ₁₆ P [2-(diphenylmethylenephosphoranyl)phenyl]	σ^2	1	1	349.6	4.37	28.4
C ₂₀ H ₁₈ (1,8-diphenylocta-3,4,5-trien-3,6-diyl)	$\mu_2-\sigma^1, \eta^2, \sigma^1, \eta^2$	1	1	374.3	4.47	24.7
C ₄₀ H ₃₅ (pentabenzylcyclopentadienyl)	η^5	1	1	710.9	5.54	35.2

while in particular the values $R[\text{Sm}(+3)-\text{C}]$ vary in the range 2.28–3.20 Å.

It should be noted that all compounds of Sm(+3) and almost all (except one) compounds of Nd(+3) with CN = 15 belong to group I (Table 1). In particular, Nd atoms possess an abnormally large value of $V_{\text{VDP}} = 20.1 \text{ \AA}^3$ in tris(η^5 -pentamethylcyclopentadienyl)neodymium. Ln atoms also have large V_{VDP} in compounds of group VII [Ln = La (JIZNUB,

$V_{\text{VDP}} = 18.2 \text{ \AA}^3$); Ln = Pr (JIZNOV, $V_{\text{VDP}} = 20.0 \text{ \AA}^3$); Ln = Nd (JIZDUR, $V_{\text{VDP}} = 19.5 \text{ \AA}^3$)] and in complexes of group III: bis(η^5 -methylcyclopentadienyl)-(2,6-bis(2,4,6-trimethylphenyl)phenyl)ytterbium (GOCJUD, $V_{\text{VDP}} = 16.8 \text{ \AA}^3$); bis(η^5 -pentamethylcyclopentadienyl)-(dimethylphenylphosphino(trimethylsilyl)methyl)ytterbium (ZISFEM, $V_{\text{VDP}} = 16.9 \text{ \AA}^3$). In all the compounds the organic ligands are rather voluminous and cannot efficiently screen Ln atoms due to steric

Table 5

VDP characteristics for rare-earth atoms and interatomic distances.

There were no Pm and Ho complexes in the samples. Only valent Ln—C interactions and agostic Ln···H contacts were considered.

Atom	Oxidation No.	No. of compounds	No. of atoms	CN	N_f	V_{VDP} (Å ³)	R_{sd} (Å)	G_3	D_A (Å)	Distances Ln—C (Å)		Distances Ln···H (Å)	
										$\langle R \rangle$	$R_{\text{min}}-R_{\text{max}}$	$\langle R \rangle$	$R_{\text{min}}-R_{\text{max}}$
Sc	+3	3	3	11	23 (2)	13.0 (7)	1.46 (3)	0.083 (1)	0.06 (3)	2.49 (7)	2.25–2.63	2.4 (1)	2.22–2.48
Y	+3	14	18	9–15	24 (2)	14.7 (8)	1.52 (3)	0.083 (1)	0.09 (5)	2.65 (9)	2.36–3.16	2.53 (7)	2.41–2.78
La	+3	7	8	7–17	25 (5)	17.5 (1.5)	1.61 (5)	0.082 (1)	0.07 (4)	2.84 (10)	2.54–3.30	2.8 (1)	2.54–2.97
Ce	+3	10	12	8–16	26 (3)	17.7 (1.1)	1.62 (3)	0.083 (1)	0.07 (5)	2.80 (8)	2.51–3.09	2.7 (2)	2.36–3.01
	+4	1	1	16	17	16.0	1.56	0.083	0.04	2.70 (2)	2.67–2.75	–	–
Pr	+3	2	3	15, 17	28 (3)	16.9 (1)	1.59 (1)	0.082 (1)	0.05 (2)	2.81 (9)	2.59–3.13	2.76 (4)	2.71–2.78
Nd	+3	17	21	10–16	26 (2)	17.1 (1.2)	1.60 (4)	0.083 (2)	0.06 (5)	2.79 (8)	2.51–3.17	2.7 (2)	2.47–3.24
Sm	+2	11	14	10–13	26 (3)	17.9 (1.2)	1.62 (4)	0.084 (2)	0.07 (4)	2.75 (9)	2.50–3.18	2.8 (3)	2.44–3.32
	+3	25	32	10–17	24 (3)	16.5 (1.3)	1.58 (4)	0.084 (1)	0.07 (5)	2.73 (9)	2.28–3.20	2.7 (2)	2.35–3.35
Eu	+2	3	5	10–15	25 (3)	18.3 (1.0)	1.64 (3)	0.082 (1)	0.08 (3)	2.84 (11)	2.72–3.33	2.9 (2)	2.63–3.33
Gd	0	1	1	12	28	17.6	1.62	0.085	0.0	2.63 (2)	2.53–2.85	3.35	3.35–3.35
	+3	3	3	12, 15	26 (3)	17.0 (1.3)	1.59 (4)	0.084 (4)	0.02 (3)	2.74 (6)	2.59–2.66	–	–
Tb	+3	4	5	12–15	27 (2)	16.0 (8)	1.56 (3)	0.083 (2)	0.04 (4)	2.72 (10)	2.52–2.96	2.43	2.43–2.43
Dy	+3	1	1	15	27	17.7	1.62	0.087	0.04	2.71 (5)	2.65–2.78	–	–
Er	+3	3	5	12–16	22 (6)	14.7 (6)	1.52 (2)	0.083 (1)	0.06 (4)	2.64 (6)	2.43–2.82	2.5 (1)	2.46–2.62
Tm	+3	1	2	15	23	15.2 (1)	1.54 (1)	0.083 (1)	0.10 (7)	2.67 (6)	2.58–2.83	2.5 (1)	2.48–2.58
Yb	+2	11	14	4–16	23 (4)	17.5 (5)	1.61 (1)	0.085 (2)	0.09 (7)	2.68 (6)	2.51–2.87	2.9 (4)	2.56–3.45
	+3	6	7	11–15	25 (4)	15.6 (1.3)	1.55 (4)	0.084 (1)	0.06 (3)	2.64 (12)	2.36–3.19	2.6 (3)	2.37–2.92
Lu	+3	8	11	11–13	23 (3)	15.0 (6)	1.50 (2)	0.085 (2)	0.09 (4)	2.54 (10)	2.36–2.82	2.6 (2)	2.35–2.75

Table 6

VDP characteristics for Nd and Sm atoms at various CNs.

Only valent Ln—C interactions were considered.

Atom	Oxidation state	CN of atoms	No. of compounds	No. of atoms	N_f	V_{VDP} (Å ³)	R_{sd} (Å)	G_3	D_A (Å)	Distances Ln—C (Å)		
										$\langle R \rangle$	$R_{\text{min}}-R_{\text{max}}$	
Nd	+3	10	1	1	24	16.1	1.57	0.082	0.08	2.74 (6)	2.67–2.82	
		11	2	2	25 (1)	16.2 (2)	1.57 (1)	0.083 (1)	0.09 (7)	2.76 (4)	2.51–3.17	
		12	4	4	24 (3)	16.8 (9)	1.59 (3)	0.083 (1)	0.07 (4)	2.75 (8)	2.58–2.88	
		14	1	1	23	16.9	1.59	0.081	0.01	2.78 (6)	2.69–2.89	
		15	8	9	28 (1)	17.8 (1.4)	1.62 (4)	0.083 (2)	0.06 (6)	2.80 (6)	2.60–2.99	
Sm	+2	16	3	4	29 (1)	16.7 (4)	1.59 (1)	0.081 (1)	0.03 (1)	2.81 (7)	2.60–3.02	
		10	1	1	25	18.4	1.64	0.082	0.06	2.79 (1)	2.78–2.82	
		12	4	4	26 (3)	18.3 (2.1)	1.63 (6)	0.083 (2)	0.05 (3)	2.80 (12)	2.54–3.18	
		13	7	9	27 (3)	17.6 (8)	1.61 (2)	0.085 (1)	0.08 (4)	2.72 (6)	2.51–2.96	
		+3	10	2	3	24 (4)	15.7 (1.3)	1.55 (4)	0.082 (1)	0.14 (2)	2.73 (8)	2.53–2.86
			11	3	5	23 (2)	15.3 (1.0)	1.54 (3)	0.083 (1)	0.11 (4)	2.67 (11)	2.28–2.85
	12		6	8	24 (2)	16.4 (1.0)	1.58 (3)	0.084 (1)	0.08 (5)	2.70 (7)	2.49–2.87	
	13		4	5	25 (2)	16.8 (5)	1.59 (2)	0.084 (2)	0.07 (5)	2.72 (7)	2.48–3.04	
	15		6	6	25 (2)	18.3 (8)	1.64 (2)	0.084 (2)	0.03 (3)	2.78 (5)	2.68–2.91	
	16		4	4	24 (6)	15.7 (2)	1.55 (7)	0.082 (1)	0.02 (1)	2.71 (4)	2.62–2.83	
			17	1	1	23	16.1	1.57	0.083	0.13	2.81 (16)	2.66–3.20

factors, which apparently explain the growth of their atomic domains. This conclusion is also confirmed by the large values of the Ln—C distances. In particular, Table 6 shows that $\langle R[\text{Sm}(+3)-\text{C}] \rangle$ values are practically constant at $\text{CN}(\text{Sm}) = 10-16$, except compounds with $\text{CN}(\text{Sm}) = 15$. At the same time, analysis of interatomic distances does not always allow the correct estimation of atomic size. For instance, the $\langle R(\text{Sm}-\text{C}) \rangle$ value at $\text{CN}(\text{Sm}) = 17$ is also large, which can be explained by the presence of two lengthened Sm—C contacts with $R = 3.2$ Å in the crystal structure of tris(η^5 -cyclopentadienyl)samarium (CYPESM02), but the size of the Sm atomic domains is ordinary. Lu atoms in bis(*N,N,N',N'*-tetramethylethylenediamine)lithium-trimethyl-(η^5 -pentamethylcyclopentadienyl)lutetium (CUTGUT) also have large V_{VDP}

values, 18.1 Å³, but in this case the sizes of CH₃ ligands are conversely insufficient to effectively screen the domain of the central atom. The VDP characteristics of the Ln atoms in the above-mentioned seven compounds of La, Pr, Nd, Yb and Lu are not taken into account in Table 5, because their deviations from the corresponding averaged values are statistically significant.

It should be noted that in one of the compounds, bis(η^6 -1,3,5-tri-*tert*-butylbenzene)gadolinium (FOGJEO), the Gd atom formally has zero oxidation state (Brennan *et al.*, 1987), but all its VDP characteristics ($V_{\text{VDP}} = 17.6$ Å³; $R_{\text{sd}} = 1.62$ Å; $G_3 = 0.085$; $D_A = 0.00$ Å) are typical for the oxidation state +3. In particular, this value of V_{VDP} is rather less than V_{VDP} for Gd atoms in the metallic phase under normal conditions (33.1 Å).

These facts indicate that the real electronic state of the Gd atom in this complex is practically the same as that which is typical for oxidation state +3 and disagrees with the formal oxidation state.

The values of V_{VDP} , R_{sd} and $R(\text{Ln}-\text{C})$ decrease from La to Lu in the lanthanide series with a +3 oxidation state (Fig. 3) which is caused by the effect of the lanthanide contracting. In accordance with atomic size, Ln(+3) atoms are in an intermediate state between metal and ionic states (Fig. 3) which reflects the ionic covalent nature of the Ln–C bonds. A slightly larger value for dysprosium R_{sd} in comparison with adjacent Tb and Er can apparently be explained by the fact that the single complex considered with Dy atoms, tris(η^5 -1,3-dimethylsilylcyclopentadienyl)dysprosium (HITTEJ), belongs to group I (Table 1). As mentioned above, it is the large sizes of the domains of the complexing atoms which are typical for the complexes of this group. Obviously, more precise estimation of the typical sizes of dysprosium atomic domains requires additional experimental data.

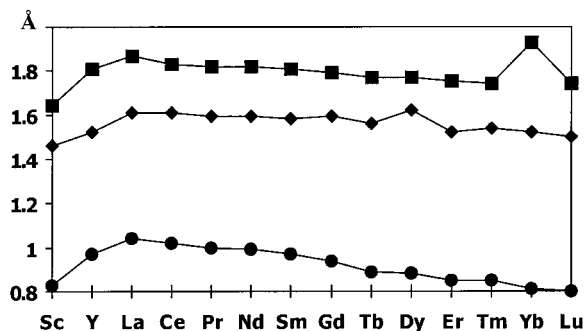


Figure 3
Variation of R_{sd} (\blacklozenge), ionic (\bullet) and metallic (\blacksquare) radii for rare-earth atoms. R_{sd} values and ionic radii are given for Ln(+3). Only the atoms listed in Table 5 are shown.

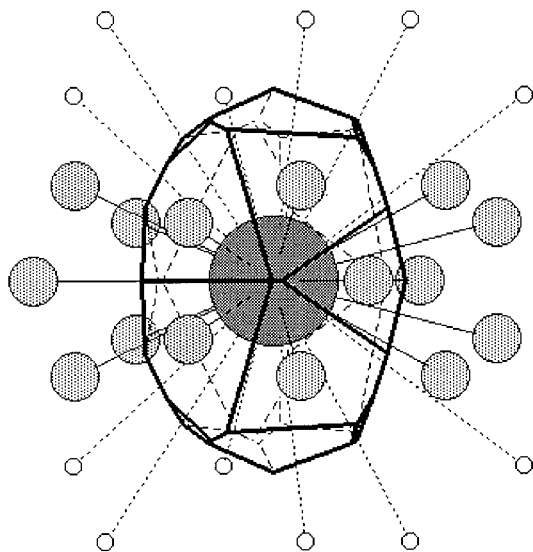


Figure 4
VDP of Nd atom in tris(η^5 -pentamethylcyclopentadienyl)neodymium (GIODUF). $G_3 = 0.084$. The central Nd atom and C atoms of the cyclopentadienyl rings are shaded. Non-valent Nd...H contacts are given by dotted lines.

At the same time, the VDP second moment of inertia (G_3) is practically independent of the nature of the Ln atoms and is rather large in comparison to the G_3 value for a sphere. This fact indicates that the shape of the VDPs of rare-earth atoms significantly deviates from spherical (Table 5, Fig. 4) and Ln–C bonds are essentially of a covalent nature. The data obtained show that there are no stereoactive lone electronic pairs near Ln atoms ($D_A < 0.10$, Table 5). However, the coordination spheres of the atoms are slightly asymmetrical (Fig. 5), which is substantially caused by their active participation in non-valent interactions and is confirmed by the rather large average numbers of faces of their VDPs (N_f) compared with CNs (Tables 5 and 6).

4.2. Agostic contacts

The contacts with $X = \text{H}$ and C make up the main part of 1988 non-valent Ln–X contacts in the sample (91.8 and 7.3%, respectively). It should be noted that almost all contacts Ln...C (131 of 145) are ‘indirect’ and therefore correspond to no interatomic interactions. At the same time a number of ‘direct’ contacts with $X = \text{H}$ (370 of 1824) were observed, which can conform to agostic interactions Ln...H–C. Such interactions are due to the unsaturated valent capabilities of Ln atoms (Schumann *et al.*, 1995) which have often been described in the literature. Ordinarily, an agostic interaction is determined by the geometrical analysis of crystal structure through the presence of sufficiently short Ln...H distances taking into account the lengthening R–C bonds in the groups R–C–H...Ln. The use of VDPs enables one to supplement and define these criteria more exactly. In terms of the VDP method of crystal-chemical analysis the existence of Ln...H–C contacts indicates the significant role of H atoms in forming atomic domains of Ln atoms, which is expressed in the following conditions:

(i) The H atoms should not only have rather short contacts with the Ln atom, but also with its ‘direct’ neighbours. For instance, in (μ_2 - η^2 , η^2 -1,4-diphenylbutadiyn)tetrakis(η^5 -penta-

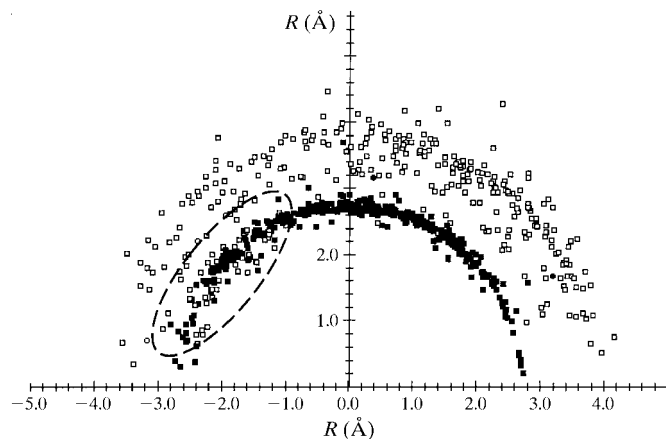


Figure 5
 (R, φ) distribution for 768 interatomic distances $R[\text{Sm}(+3)-X]$ depending on the φ angle formed by a Sm(+3)–X bond and D_A vector whose direction coincides with the positive direction of the abscissa axis: \blacksquare $X = \text{C}$; \square $X = \text{H}$. An ellipse marks the area where H atoms involved in agostic contacts Sm–H are predominantly allocated.

Table 7
Characteristics of Ln···H contacts in some compounds.

Compound	Atom	$R(\text{Ln}\cdots\text{H})$ (Å)	$\Omega(\text{Ln}\cdots\text{H})$ (%)
FEYHAS	H(1)	3.00	8.9
HAZYUC	H(38)†	2.84	4.5
JAYMIF	H(16)	2.71	5.8
	H(20)	2.97	5.6
	H(21)	2.82	7.3
	H(35)†	2.82	4.9
	H(36)	2.76	7.6
	H(38)	2.61	10.1
WAXCED	H(33)	3.45	2.1
	H(34)	3.15	7.1

† 'Minor' faces of VDP correspond to these contacts.

methylcyclopentadienyl)disamarium (FEYHAS, Fig. 6a), in spite of the relatively large Sm···H(1) distance (Table 7), the H atom of a phenyl ring is a 'direct' neighbour of the Sm atom and therefore there is an agostic interaction Sm···H(1). At the same time, in tris(η^5 -cyclopentadienyl)methyldiphenylphosphinomethylsamarium (HAZYUC, Fig. 6b) the distance Sm—

H(38) is typical for agostic contacts, but the H atom is an 'indirect' neighbour of the central atom (Table 7) and, apparently, there are no appreciable Sm···H interactions. Another instance is (η^5 -pentamethylcyclopentadienyl)bis(bis(trimethylsilyl)methyl)cerium (JAYMIF, Fig. 6c). Taking into account the relatively short Ce···H distances, Heeres *et al.* (1989) concluded that there are agostic contacts between the Ce atom and the H atoms H(16), H(20), H(21), H(35), H(36) and H(38). However, in accordance with the criterion considered, the Ce···H(35) contact is not agostic, but the authors' conclusions are justified for other atoms (Table 7).

(ii) The solid angles of VDP faces corresponding to the contacts Ln···H—C should be sufficiently non-zero [$\Omega > 3\sigma(\Omega) \simeq 5\%$ of the total solid angle 4π sr]. The data of Table 7 show that in the compounds considered above the solid angles of VDP faces corresponding to agostic contacts Ln···H are sufficiently large (>5%), while if there are no such interactions the solid angles are smaller. For instance, in tetrakis(η^5 -pentamethylcyclopentadienyl)-(μ_2 - σ^2 , η^4 -1,8-diphenylocta-3,4,5-triene-3,6-diyl)disamarium (WAXCED, Fig. 6d) the H

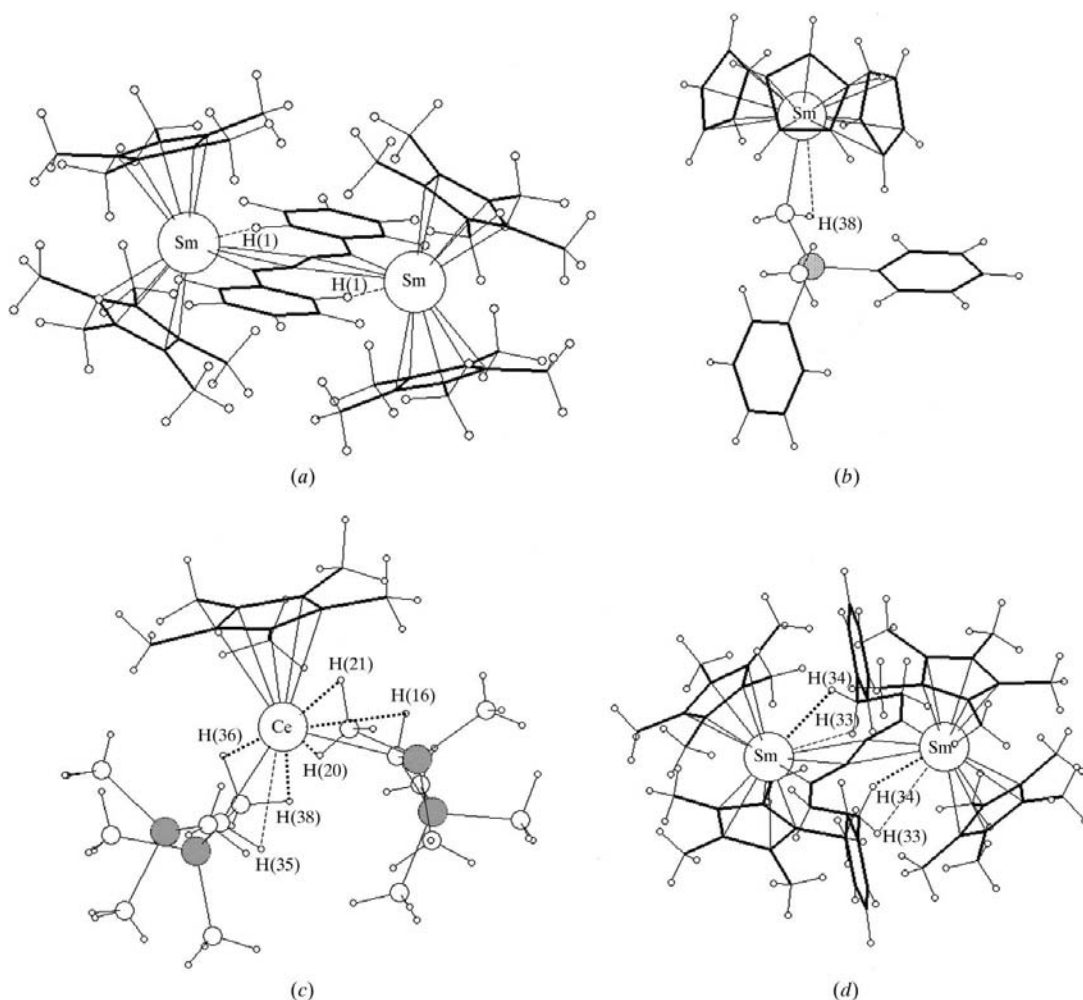


Figure 6
Ln···H contacts in (a) (μ_2 - η^2 , η^2 -1,4-diphenylbutadiyn)tetrakis(η^5 -pentamethylcyclopentadienyl)disamarium (FEYHAS); (b) tris(η^5 -cyclopentadienyl)-methyldiphenylphosphinomethylsamarium (HAZYUC); (c) (η^5 -pentamethylcyclopentadienyl)bis(bis(trimethylsilyl)methyl)cerium (JAYMIF); (d) tetrakis(η^5 -pentamethylcyclopentadienyl)-(μ_2 - σ^2 , η^4 -1,8-diphenylocta-3,4,5-triene-3,6-diyl)disamarium (WAXCED). Possible Ln···H agostic interactions are marked by bold dotted lines; non-agostic Ln···H contacts given in Table 5 are marked by thin dashed lines. Si and P atoms are shaded. All H atoms in the crystal structure of FEYHAS and the H(38) atom in the crystal structure of HAZYUC were allocated with the program *HSite*.

Table 8

VDP characteristics for Ln atoms in the compounds listed in Table 7 depending on the method of calculation.

Columns with 'without H' in parentheses: VDP characteristics for Ln atoms obtained without the consideration of H atoms.

Compound	$V_{\text{VDP}} (\text{\AA}^3)$	$V_{\text{VDP}} (\text{\AA}^3)$	$R_{\text{sd}} (\text{\AA})$	$R_{\text{sd}} (\text{\AA})$	G_3	G_3 (without H)	$D_A (\text{\AA})$	$D_A (\text{\AA})$ (without H)
FEYHAS	16.7	18.9	1.59	1.65	0.082	0.087	0.03	0.12
HAZYUC	15.9	16.3	1.56	1.57	0.081	0.082	0.01	0.02
JAYMIF	16.3	20.9	1.57	1.71	0.083	0.087	0.14	0.14
WAXCED	17.1	18.4	1.60	1.64	0.083	0.086	0.06	0.15

atoms H(33) and H(34) are 'direct' neighbours of the Sm atom, although, taking into account Ω values, one can conclude that only the Sm \cdots H(34) contact is an agostic interaction (Table 7).

(iii) The values of the VDP parameters calculated with or without considering H atoms (Table 8) indicate that H atoms strongly influence all the main characteristics of the atomic domains of Ln atoms in compounds with Ln \cdots H interactions. Table 8 shows that in the compounds FEYHAS, JAYMIF and WAXCED the values of V_{VDP} and R_{sd} for Ln atoms significantly increase if their VDPs are constructed without H atoms, except the compound HAZYUC, where agostic interactions are absent according to the aforesaid criteria.

The Ln \cdots H contacts in 74 out of 135 compounds fit these criteria; in 48 compounds the H atoms involved in agostic interactions are bonded with sp^3 -hybridized C atoms (alkyl substitutes of cyclopentadienyl rings, methyl groups of trimethylsilyl radicals and bridging alkyl groups) and with sp^2 -hybridized C atoms (cyclopentadienyl rings, alkenes or arenes) in 26 complexes. In the compounds containing trimethylsilyl groups the S—CH₃ bonds with methyl groups involved in agostic interactions are lengthened by 0.01–0.04 Å.

The large amount of agostic contacts can probably be explained by the low screening degree of the Ln atoms. Analyzing widely ranging (47–100%) $\Omega_{L\Sigma}$ values can lead to the following conclusions:

- (i) All complexes with $\Omega_{L\Sigma} < 80\%$ have agostic interactions.
- (ii) All complexes with $\Omega_{L\Sigma} > 90\%$ have no agostic interactions.

(iii) Without additional analysis one cannot make an unambiguous conclusion about the presence or absence of agostic contacts in the complexes with $\Omega_{L\Sigma} = 80$ –90%. For instance, in the structure of (η^8 -cyclooctatetraenyl)-(η^5 -1,3-ditert-butylcyclopentadienyl)terbium, $\Omega_{L\Sigma} = 86.4\%$ and agostic contacts are absent according to the aforesaid criteria, but in the compound (μ_2 - η^5 , η^5 -cyclopentadienyl)-bis(η^5 -cyclopentadienyl)praseodymium, $\Omega_{L\Sigma} = 88.5\%$ and there are agostic contacts Pr \cdots H(14) with $R[\text{Pr}—\text{H}(14)] = 2.8 \text{ \AA}$, $\Omega[\text{Pr}—\text{H}(14)] = 7.5\%$.

As a whole, in the lanthanide series the average value of $R(\text{Ln}\cdots\text{H})$ decreases [the total average $\langle R(\text{Ln}\cdots\text{H}) \rangle = 2.7(2) \text{ \AA}$ for 203 Ln \cdots H contacts fitting the above conditions (i)–(iii)], although short agostic contacts are observed for the atoms at the beginning of the series (Table 5). It is of interest that most of the agostic contacts are allocated to the same

coordination hemisphere (Fig. 5), which indicates a slight asymmetry of the electron clouds of the Ln atoms and the non-uniformity of the spatial distribution of valent Ln—C contacts. According to Blatov & Serezhkin (1997), a linear correlation between solid angles of VDPs faces corresponding to 'direct' contacts and $R(\text{Ln}\cdots\text{H})$ distances (Fig.

7) indicates the existence of interactions between Ln and H atoms. Note that a wide range of Ln \cdots H distances (up to 1 Å at Ln = Sm; Table 5) is apparently caused by the different chemical nature of such interactions. It should be noted that the question, whether the Ln \cdots H contact is a specific intermolecular interaction, *i.e.* whether the electron density of the Ln and H atoms is redistributed upon formation of the contact, is debatable in most cases. In some cases one can even make a conclusion regarding the geometrical analysis of a crystal structure that there are Ln \cdots C(H)—R interactions including C—R σ -bonds rather than Ln \cdots H—C contacts (Heeres *et al.*, 1988; Klooster *et al.*, 1999). In our opinion, it would be appropriate to give an alternative interpretation of the causes of their appearance, taking into account first the chemical inertness of H atoms in C—H bonds involved in the Ln \cdots H interactions (especially of those connected with valent-saturated C atoms that is typical for more than half of the sample) and second the small energy of agostic interactions, even when they are unambiguously determined by analysis of their ¹H NMR spectra (Stern *et al.*, 1990).

As was already mentioned, the size of the atomic domain of a complexing atom is constant for the sample considered, which was recently revealed by the analysis of other series of coordination compounds (Blatov, Shevchenko & Serezhkin, 1999; Blatov, Pogilyakova & Serezhkin, 1999). It has been

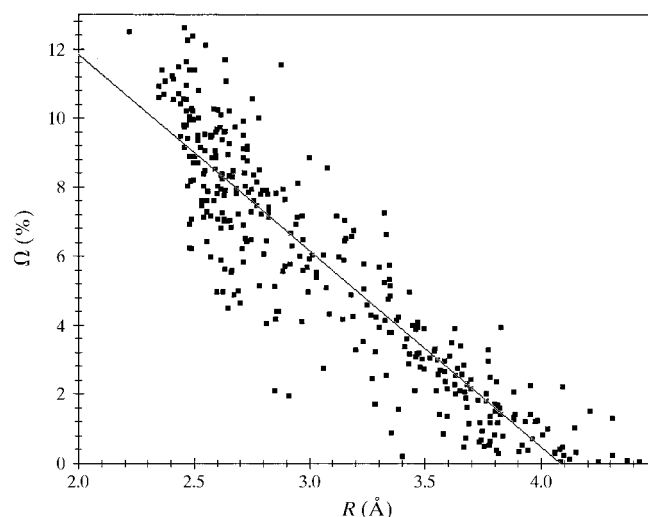


Figure 7
 $\Omega(R)$ dependence for 362 'direct' Ln \cdots H contacts. The coefficient of linear correlation is equal to -0.91 .

shown above that one of the causes of deviations from this regularity is the presence of non-screened fragments of atomic domain surface. Probably the conformation of organic ligand, where H atoms are allocated near Ln atoms formally corresponding to the criteria (i)–(iii), is caused by the condition $V_{\text{VDP}}(\text{Ln}) = \text{const}$. In our opinion, the effect of constant size of an atomic domain fits the condition of minimizing crystal internal energy during crystallization and is a result of the formation of equipotential surfaces separating atomic domains.

5. Conclusions

The data obtained show that the use of atomic and molecular VDPs is productive for studying rare-earth π -complexes. In the future we plan to specify the above regularities of the formation of Ln coordination spheres depending on the nature of the X atoms involved in Ln–X interactions.

The authors are indebted to the Russian Foundation of Basic Research for covering the License fee for the use of the Cambridge Structural Database.

References

- Bader, R. F. W. (1990). *Atoms in Molecules – a Quantum Theory*. Oxford University Press.
- Blatov, V. A., Pogilydyakova, L. V. & Serezhkin, V. N. (1999). *Acta Cryst.* **B55**, 139–146.
- Blatov, V. A. & Serezhkin, V. N. (1997). *Acta Cryst.* **A53**, 144–160.
- Blatov, V. A., Shevchenko, A. P. & Serezhkin, V. N. (1995). *Acta Cryst.* **A51**, 909–916.
- Blatov, V. A., Shevchenko, A. P. & Serezhkin, V. N. (1999). *Russ. J. Coord. Chem.* **25**, 453–465.
- Brennan, J. G., Cloke, F. G. N., Samen, A. A. & Zalkin, A. J. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1668–1669.
- Cambridge Structural Database (2000). Version 5.19. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
- Christensen, S. W. & Thomas, N. W. (1999). *Acta Cryst.* **A55**, 811–820.
- Deacon, G. B. & Shen, Q. (1996). *J. Organomet. Chem.* **511**, 1–17.
- Heeres, H. J., Meetsma, A., Teuben, J. H. & Rogers, R. D. (1989). *Organometallics*, **8**, 2637–2646.
- Heeres, H. J., Renkema, J., Booiij, M., Meetsma, A. & Teuben, J. H. (1988). *Organometallics*, **7**, 2495–2502.
- Hitchcock, P. B., Howard, J. A. K., Lappert, M. F. & Prashar, S. (1992). *J. Organomet. Chem.* **437**, 177–189.
- Klooster, W. T., Brammer, L., Schaverien, C. J. & Budzelaar, P. H. M. (1999). *J. Am. Chem. Soc.* **121**, 1381–1382.
- Peresyapkina, E. V. & Blatov, V. A. (2000). *Acta Cryst.* **B56**, 1035–1045.
- Schumann, H., Meese-Marktscheffel, J. A. & Esser, L. (1995). *Chem. Rev.* **95**, 865–986.
- Serezhkin, V. N., Mikhailov, Yu. N. & Buslaev, Yu. A. (1997). *Russ. J. Inorg. Chem.* **42**, 1871.
- Stern, D., Sabat, M. & Marks, T. J. (1990). *J. Am. Chem. Soc.* **112**, 9558–9575.
- Thomas, N. W. (1996). *Acta Cryst.* **B52**, 939–953.
- Tolman, C. A. (1970). *J. Am. Chem. Soc.* **92**, 2956–2965.
- Wilkinson, G. & Birmingham, J. M. (1954). *J. Am. Chem. Soc.* **76**, 6210–6217.
- Xi-Geng, Z., Zu-En, H., Rui-Fang, C., Sheng-Nan, Y. & Xiao-Ying, H. (1997). *J. Struct. Chem.* **16**, 384–388.
- Zacharov, L. N., Safyanov, Yu. N. & Domrachev, H. A. (1990). *Probl. Cryst. Chem.* pp. 111–148 (in Russian).