

A new set of molecular descriptors

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A new set of criteria for quantitative analysis of molecular interactions is proposed, which is based on the conceptions of atomic and molecular Voronoi–Dirichlet polyhedra. It is shown that the calculation of solid angles of ligands and complexes as a whole allows one to estimate screening effects and the probability of forming intra- and intercomplex non-valent contacts. The set proposed was used to study the influence of steric factors on the stability of complex groups as well as on the presence or absence of agostic contacts in crystal structures of 808 rare-earth π -complexes.

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1. Introduction

It is well known that the crystal structure of any molecular substance is determined by intermolecular forces, in which the valent component either is missing (van der Waals forces) or is non-dominant [specific (secondary) interactions, hydrogen bonds]. Although at present an adequate description of molecular contacts often becomes possible with computer modelling in some force field (Chaka *et al.*, 1996), in crystallochemical analysis the most reliable information about geometrical properties of molecular packing is usually used, which is obtained as the main result of the structural experiment. In this respect the atomic van der Waals radius (r_{vdw}) is the most important and the most frequently used characteristic. Apparently, there are two main crystallochemical problems to solve in which r_{vdw} values are used as a rule:

- (i) identification of intermolecular contacts;
- (ii) determination of molecular dimensional factors (molecule size, surface area, steric features *etc.*).

One can say that the r_{vdw} concept lies in the base of all sets of molecular descriptors traditionally used in crystal chemistry, since many other characteristics and criteria include it in explicit or implicit form. Thus, to analyze molecular interactions the r_{vdw} sum for contacting atoms is to be compared with interatomic distance which has been additionally corrected to allow the deformation of van der Waals spheres (Zefirov & Zorky, 1978). In the classic model of the closest molecular packing (Kitaigorodskii, 1973) a molecule is represented as an object formed by internal surfaces of overlapping van der Waals atomic spheres. The surfaces confining molecules must be tangent to each other, *i.e.* must not interpenetrate and have no gaps between each other. Tolman (1970) and Zaharov *et al.* (1990) proposed the use of the sum of solid angles of ligand atoms to estimate the existence probability for non-valent intercomplex interactions and steric limitations to forming molecular complex structural units. For this purpose a solid angle with its apex at the central atom was used, enclosing the ligand with van der Waals spheres representing the atoms. The sum of all the ligand solid

angles defines the degree of filling of the coordinating sphere of the central atom by the ligands and can be used to estimate the probability of intermolecular contact realisation.

However, the concept of van der Waals radii has a number of disadvantages, which have often been discussed in the literature. Firstly, for the description of packings with polyatomic molecules this concept loses its direct physical meaning, ceasing to determine atomic volume owing to significant anisotropy of its form (Zefirov & Zorky, 1989) as the spherical atom model becomes invalid for heterodesmic crystals. Secondly, the method of estimation of van der Waals radii has not been completely developed. Although considerable progress has been attained in this field, the method of selection of 'reference' structures and 'reference' intermolecular contacts to calculate van der Waals radii is still controversial (Zefirov & Zorky, 1989, 1995; Zefirov, 1997). As a result there are several van der Waals radii systems in which the radius values for the same atom can differ from each other by almost 1 Å (Zefirov, 1997). Atomic van der Waals spheres are easily deformable resulting in shortening or lengthening of the interatomic contacts compared with the sum of the van der Waals radii and, hence, frequent deviations from Kitaigorodskii's model (Peresyphkina & Blatov, 2000).

An alternative method of crystallochemical description of molecules and determination of intermolecular contacts using 'molecular' Voronoi–Dirichlet polyhedra (VDP) was proposed by Fischer & Koch (1979) and recently developed by Ovchinnikov *et al.* (1995) and Peresyphkina & Blatov (2000). Molecular VDP is a space domain confined by the set of intersecting planes, each of which is perpendicular to the segment joining an atom of a molecule to an atom of an adjacent molecule, and divides this segment into a ratio depending on the nature of contacting atoms. Obviously, the division factor is 0.5 for atoms of the same type (intermolecular contacts are mostly formed by H atoms). The notion of boundary surface was introduced by Ovchinnikov *et al.* (1995) as a set of atomic VDP faces corresponding to the contacts between atoms of two adjacent molecules. This method takes only standard crystal structure information and allows one to find intermolecular contacts using no additional data, including r_{vdw} values. According to Ovchinnikov *et al.* (1995) the area of a molecular VDP face is proportional to the strength of the interatomic interaction. Similarly, each boundary surface corresponds to a *molecule–molecule* contact and its area is determined by the strength of the molecular interaction. However, Ovchinnikov *et al.* (1995) specified no concrete values for the minimum area of boundary surface to be considered when searching for intercomplex contacts.

Peresyphkina & Blatov (2000) used the solid angle value (Ω) for the VDP face corresponding to the intermolecular contact as a criterion for the presence or absence of molecular interactions. Unlike face area, the Ω value expressed as a percentage of the total solid angle 4π steradian is invariant to the similarity transformation. Peresyphkina & Blatov (2000) used this property to introduce the common criteria to select contacts in any crystal structure irrespective of the contact nature and length. A solid angle value shows how much (in

percentage) valent resources an atom provides to interact with an atom of an adjacent molecule. Peresyphkina & Blatov (2000) accepted a typical value of $3\sigma(\Omega)$ caused by experimental error to be approximately equal to 1.5% as a minimum limit that corresponds to appreciable intermolecular contact. Moreover, only 'major' not 'minor' VDP faces conforming to 'direct' neighbours of the central atom correspond to atomic interactions (Blatova *et al.*, 2001). Thus, the only surrounding molecules to be considered as adjacent are those which have a common boundary surface with the central molecule, including at least one 'major' face with $\Omega \geq 1.5\%$.

Blatova *et al.* (2001) studying rare-earth (Ln) π -complexes LnC_nH_m introduced the concept of ligand solid angle,

$$\Omega_L = \sum_i \Omega(\text{Ln} - Z_i), \quad (1)$$

where only valent contacts between the central Ln atom and donor Z_i atoms of a ligand L were taken into consideration. It was shown that the value of the integral characteristic,

$$\Omega_{L\Sigma} = \sum_l (\Omega_L)_l, \quad (2)$$

where all ligands connected to the Ln atom are included in the sum, in most cases allows an accurate estimation of the steric features of molecular ligands and prediction of the chemical composition of the complex. Unlike Tolman's method, the calculation of Ω_L and $\Omega_{L\Sigma}$ values does not require atomic r_{vdw} values and takes into account atomic sizes, depending on the atomic states in a crystal structure. However, if in the complex there are voluminous umbrella-type ligands with small denticity (usually of σ^1 or σ^2 coordination types), the $\Omega_{L\Sigma}$ value calculated by (2) can be understated. For instance, in tris- $(\mu_2\text{-}\eta^2, \sigma^3\text{-}2,6\text{-diphenylphenoxy})\text{-}(2,6\text{-diphenylphenoxy})\text{dieuropium}$ [HOCFOU],¹ $\Omega_{L\Sigma}$ is only 57.4%; however, the central Eu atom is almost completely screened by monodentate but voluminous diphenylphenoxy ligands. This can be elucidated, in particular, by the fact that there are no contacts between Eu atoms and ligands of adjacent complex groups.

The objective of this study was the development of a descriptive procedure for complex compounds using molecular VDPs recently proposed by Blatova *et al.* (2001), and its approbation with all known Ln π -complexes with no limitations on their chemical composition.

2. Set of molecular descriptors

In addition to the dimensional characteristics of molecular VDPs used by Peresyphkina & Blatov (2000) [volume (V_{VDP}) and radius of spherical domain (R_{sd})] as being suitable to describe molecular particles of any nature, in this study we have calculated a number of parameters concerned with the solid angles of ligands and having a clear physical meaning in the case of molecular coordination compounds:

(i) 'valent' solid angles of a ligand (Ω_L^V) and a complex ($\Omega_{L\Sigma}^V$) to be calculated using (1) and (2), respectively. Here-

¹ Hereinafter the Reference Codes of compounds in the Cambridge Structure Database are given in brackets.

inafter, the solid angles of complexes are to be calculated relative to the concrete complexing atom; at any one time several such angles correspond to a polynuclear complex particle, according to the number of coordinating centers.

(ii) 'total' solid angles of a ligand (Ω_L^T) and a complex ($\Omega_{L\Sigma}^T$) to be calculated as

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

$$\Omega_{L\Sigma}^T = \sum_I (\Omega_L^T)_I, \quad (4)$$

where, unlike (1), the index term i enumerates *all* (including non-valent) *central atom–ligand* contacts, even if the ligand is *non-valently* bonded with the complexing atom and only screens it while the index I , as in (2), enumerates all the ligands in the complex which are *valently* bonded with the complexing atom. Note that consideration of all the ligands screening the central atom, including those directly non-bonded to it, is senseless in (4) because $\Omega_{L\Sigma}^T$ would be strictly 100% in this case.

(iii) 'agostic' solid angles of a ligand (Ω_L^{ag}) and a complex ($\Omega_{L\Sigma}^{\text{ag}}$). These values are to be calculated by formulae analogous to (3) and (4), but with merely the solid angles of atomic VDPs corresponding to agostic contacts $\text{Ln} \cdots \text{H} - \text{C}$. All such contacts must be considered, including those formed by the H atoms of ligands which are not directly bonded with the complexing atom [presence or absence of agostic contacts can be ascertained according to the criteria of Blatova *et al.* (2001)].

(iv) 'residual' solid angles of a ligand ($\delta = \Omega_L^T - \Omega_L^V$) and a complex ($\Delta = \Omega_{L\Sigma}^T - \Omega_{L\Sigma}^V$).

The parameters Ω_L^V , $\Omega_{L\Sigma}^V$, Ω_L^T , $\Omega_{L\Sigma}^T$, Ω_L^{ag} , $\Omega_{L\Sigma}^{\text{ag}}$, δ and Δ , together with dimensional characteristics (V_{VDP} and R_{sd}), constitute the proposed set of molecular descriptors based on the concept of molecular VDP and intended for solving the problems specified in §1 without using r_{vdw} values. The calculation of the aforementioned descriptors can be performed for molecular compounds of any complexity and for samples of any size by means of the programs *ADS*, part of the *TOPOS* program package (Blatov *et al.*, 2000). As an example, the molecular VDPs constructed by the program *IsoCryst* (which is also integrated into *TOPOS*) for a 1,3-bis(trimethylsilyl)cyclopentadienyl ligand (Fig. 1*a*) and for the complex bis(η^5 -[1,3-bis(trimethylsilyl)cyclopentadienyl]-ytterbium (Fig. 1*b*) in the crystal structure of [YAMNEF] are shown in Figs. 1(*c*) and 1(*d*). Each face of the molecular VDP of a ligand L corresponds to the L –Ln bond or to the non-valent contact $L \cdots A$ and makes a contribution to Ω_L^T or Ω_L^V , respectively (and to Ω_L^{ag} if $A = \text{Ln}$). The VDP of the complexing La atom in [YAMNEF] constructed by the program *Dirichlet* of the *TOPOS* package is shown in Fig. 1(*e*). Analysis of the solid angles of the VDP faces allows the calculation of $\Omega_{L\Sigma}^V$, $\Omega_{L\Sigma}^T$ and $\Omega_{L\Sigma}^{\text{ag}}$. Let us consider the application details of the proposed descriptor set using the example of 808 rare-earth π -complexes, whose crystal data were obtained from the Cambridge Structural Database (release

5.20). As in the previous study (Blatova *et al.*, 2001), only those compounds were considered for which:

- (i) all atoms were located (except, in some cases, H atoms);
- (ii) there were no statistically disordered atoms.

The positions of the non-located H atoms were determined using the program *HSite* of the *TOPOS* package (Blatova *et al.*, 2001).

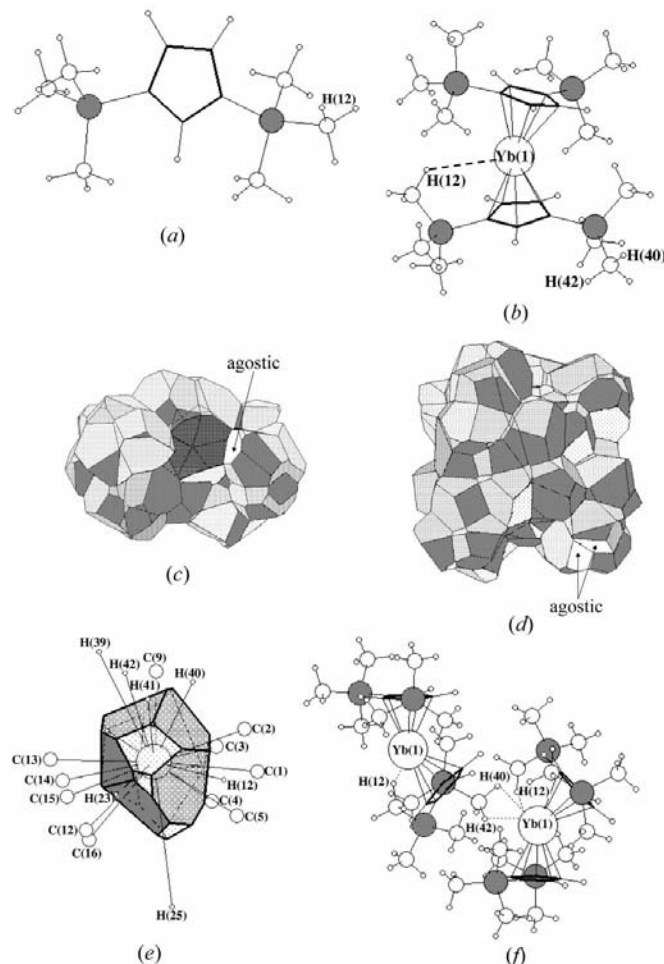


Figure 1

(*a*) Molecular structure of the 1,3-bis(trimethylsilyl)cyclopentadienyl ligand in [YAMNEF]. Si atoms are shaded. The H12 atom is labelled which participates in agostic intracomplex contacts. (*b*) Molecular structure of the complex bis(η^5 -[1,3-bis(trimethylsilyl)cyclopentadienyl]-ytterbium [YAMNEF]. Si atoms are shaded. H12, H40 and H42 atoms are labelled, the two last of which are involved in intercomplex agostic contacts. (*c*) Molecular VDP of the ligand shown in (*a*). Five dark VDP faces in the center of the ligand correspond to valent interactions of carbon atoms of cyclopentadienyl rings with the Yb atom. The VDP face corresponding to the intracomplex agostic contact $\text{Yb1} \cdots \text{H12}$ is indicated by the arrow. (*d*) Molecular VDP of the complex particle shown in (*b*). The VDP faces corresponding to intercomplex $\text{Yb1} \cdots \text{H40}$ and $\text{Yb1} \cdots \text{H42}$ agostic contacts are indicated by arrows. (*e*) VDP of the complexing Yb atom in [YAMNEF]. The most dark VDP faces correspond to valent contacts between atoms C12–C16 of the cyclopentadienyl ring with the Yb atom, grey VDP faces conform to intracomplex and intercomplex agostic contacts, and light VDP faces correspond to weak non-valent contacts $\text{Yb1} \cdots \text{H23}$, $\text{Yb1} \cdots \text{H25}$ and $\text{Yb1} \cdots \text{H41}$. The small triangular face is 'minor'; the corresponding 'non-direct' contact $\text{Yb1} \cdots \text{C9}$ is depicted by a dashed line, which does not intersect the 'minor' face. Other VDP faces are 'major'. (*f*) Molecular structure of the complex dimer in [YAMNEF]. Si atoms are shaded. Agostic contacts are depicted by dashed lines.

Table 1

Ligand characteristics.

It is indicated in parentheses the number of cases in which H atoms of the ligand form agostic contacts. The ligands given in italics are those which usually take part in agostic contacts (they form such contacts in more than half the cases). If a ligand is connected with several complexing atoms by different ways, Ω_L^T and Ω_L^V values are given for each coordination type in ascending ligand denticity and are separated by a 'plus' symbol. For instance, for the coordination type σ, η^5 two numbers are to be given: for σ^1 and η^5 coordination, respectively.

Ligand	Coordination type	No. of compounds	No. of ligands	V_L (Å ³)	R_{sd} (Å)	Ω_L^T (%)	Ω_L^V (%)
F ⁻	μ_2	8	11	16.4 (1.4)	1.58 (4)	11.6 (1.8)	11.6 (1.8)
Cl ⁻	μ_3	13	20	22.6 (1.6)	1.75 (5)	11.1 (1.6)	11.1 (1.6)
	μ_2	93	184	22.3 (2.1)	1.75 (5)	13.6 (1.8)	13.6 (1.8)
	σ^1	53	85	21.2 (1.4)	1.72 (4)	14.3 (1.8)	14.3 (1.8)
Br ⁻	μ_3	2	2	23.7 (2.8)	1.78 (7)	10.3 (2.2)	10.3 (2.2)
	μ_2	10	20	25.5 (2.2)	1.83 (5)	13.6 (9)	13.6 (9)
	σ^1	4	6	22.1 (2.1)	1.74 (6)	11.9 (1.4)	11.9 (1.4)
I ⁻	μ_2	3	3	29.0 (2.9)	1.91 (6)	11.8 (8)	11.8 (8)
	σ^1	19	29	27.3 (1.7)	1.87 (4)	10.7 (1.4)	10.7 (1.4)
[AlCl ₄] ⁻	$\mu_2-\sigma^2, \sigma^2$	6	11	131.3 (6.9)	3.15 (6)	22.6 (1.2)	22.6 (1.2)
	$\mu_2-\sigma^1, \sigma^2$	2	3	133.0 (5.1)	3.17 (5.1)	14.3 (2.3)	12.1 (1.2)
	σ^2	12	31	130.1 (9.5)	3.14 (8)	+ 25.0 (1.6)	+ 25.0 (1.6)
O ²⁻	μ_3	2	2	17.7 (4)	1.62 (1)	23.8 (1.1)	23.8 (1.1)
	μ_2	5	5	17.6 (1.0)	1.61 (3)	16.9 (3.1)	16.9 (3.1)
	σ^1	11	22	26.5 (1.9)	1.85 (5)	20.2 (2.5)	20.2 (2.5)
CO (carbonyl)	σ^2	14	20	23.7 (2.3)	1.78 (6)	13.0 (4.9)	13.0 (4.9)
	σ^1	2	2	23.0 (2.9)	1.76 (5)	17.0 (7)	16.6 (7)
OH ⁻	σ^1	2	2	23.0 (2.9)	1.76 (5)	15.4 (1.3)	14.6 (2)
	μ_3	1 (1)	1 (1)	23.6	1.78	19.0 (1.6)	9.6 (2.9)
H ₂ O	σ^1	6	10	30.2 (4.0)	1.93 (9)	11.5 (1.0)	10.9 (1.6)
	$\mu_2-\sigma^1, \eta^1$	1	1	71.8	2.58	18.5 (1)	18.5 (1)
	$\mu_2-\sigma^1, \eta^2$	3	4	72.6 (3.9)	2.59 (5)	15.9 (7)	15.9 (7)
C ₂ H ₃ O ₂ (acetato)	σ^1, η^1	2	2	75.3 (3.9)	2.62 (5)	+ 23.1 (1.5)	+ 23.1 (1.5)
	η^3	7 (6)	13 (10)	78.0 (4.2)	2.65 (5)	23.7 (4.2)	23.7 (4.2)
	σ^1	208 (4)	368 (4)	119.0 (6.1)	3.05 (5)	26.4 (4.2)	15.6 (4.9)
C ₃ H ₅ (<i>allyl</i>)	σ^1	208 (4)	368 (4)	119.0 (6.1)	3.05 (5)	16.1 (1.9)	15.0 (1.5)
	σ^2	2	2	112.9 (1.3)	3.00 (1)	11.8 (4.1)	9.35 (4.0)
	σ^2	5 (5)	9 (8)	131.7 (6.8)	3.16 (6)	23.4 (1.1)	16.9 (6)
C ₄ H ₉ O (<i>tert</i> -butoxo)	σ^1	6	11	132.0 (7.4)	3.16 (6)	21.4 (9)	21.2 (1.4)
	σ^2	17	20	151.0 (6.8)	3.30 (5)	30.1 (3.2)	27.7 (2.1)
C ₄ H ₁₀ O ₂ (<i>dimethoxyethane</i>)	σ^2	17	20	151.0 (6.8)	3.30 (5)	30.1 (3.2)	27.7 (2.1)
	η^5	177 (2)	443 (2)	100.9 (6.5)	2.89 (6)	30.5 (2.7)	29.1 (2.0)
C ₅ H ₅ (<i>cyclopentadienyl</i>)†	$\mu_2-\sigma^1, \eta^5$	1 (1)	1 (1)	99.9	2.88	16.5	5.1
	$\mu_2-\sigma^1, \eta^4$	4 (4)	7 (5)	94.3 (2.0)	2.82 (2)	+ 26.3	+ 25.5
	$\mu_2-\sigma^2, \eta^5$	3 (3)	3 (3)	96.0 (4.7)	2.84 (5)	9.7 (1.8)	8.1 (1.0)
	$\mu_2-\sigma^2, \eta^5$	3 (3)	3 (3)	96.0 (4.7)	2.84 (5)	+ 32.0 (1.5)	+ 21.8 (1.1)
C ₆ H ₆ (<i>benzene</i>)	η^6	7	7	157.3 (9.7)	3.35 (7)	17.2 (5.0)	9.5 (1.7)
	η^5	33 (3)	78 (5)	127.2 (9.5)	3.12 (7)	+ 28.6 (4.7)	+ 23.6 (4.7)
C ₆ H ₇ (<i>methylcyclopentadienyl</i>)†	η^5	33 (3)	78 (5)	127.2 (9.5)	3.12 (7)	30.1 (1.5)	29.5 (5)
	$\mu_2-\sigma^1, \eta^5$	1	1	124.7	3.10	30.3 (2.1)	29.1 (2.0)
C ₆ H ₁₈ N ₃ OP (<i>hexamethylphosphoramide</i>)	σ^1	1	1	124.7	3.10	14.3	25.7
	σ^1	7 (1)	12 (1)	273.8 (7.0)	4.03 (4)	+ 26.9	+ 4.9
C ₆ H ₁₈ N ₃ Si ₂ [<i>bis(trimethylsilyl)amido</i>]	σ^1	14 (3)	22 (19)	275.1 (19.7)	4.03 (9)	18.7 (1.4)	17.0 (1.4)
	σ^1	14 (3)	22 (19)	275.1 (19.7)	4.03 (9)	34.1 (6.5)	17.3 (9)
C ₇ H ₁₁ (<i>2,5-dimethylpentadienyl</i>)	η^5	8 (2)	19 (4)	165.3 (10.7)	3.40 (7)	34.5 (1.6)	29.2 (3.4)
	η^3	2 (2)	2 (2)	156.5 (7.2)	3.34 (5)	38.0 (5.7)	15.2 (1.3)
	η^2	1 (1)	1 (1)	158.0	3.35	30.5	11.3
C ₇ H ₁₆ Si ₂ [<i>bis(trimethylsilyl)methyl</i>]	σ^1	22 (21)	32 (30)	275.5 (7.6)	4.04 (4)	35.2 (4.3)	13.6 (1.7)
	σ^1, σ^1	2 (2)	2 (2)	270.9 (2.3)	4.01 (1)	34.2 (3.4)	14.3 (1.8)
	μ_2	5	8	140.7 (3.9)	3.23 (3)	16.1 (9)	14.9 (1.2)
C ₈ H ₅ (<i>phenylethyldien</i>)	σ^1	3	5	140.7 (6.4)	3.23 (5)	15.7 (1.0)	15.7 (1.0)
	$\mu_2-\eta^8, \eta^8$	6	7	145.8 (5.1)	3.29 (4)	43.5 (5.4)	43.5 (5.4)
C ₈ H ₈ (<i>cyclooctatetraenyl</i>)	η^8	43	59	149.3 (6.2)	3.29 (4)	48.4 (4.0)	48.3 (3.8)
	$\mu_2-\eta^3, \eta^8$	1	1	149.8	3.30	23.8	14.2
	$\mu_2-\eta^3, \eta^8$	1	1	149.8	3.30	+ 47.9	+ 47.9

Table 1 (continued)

Ligand	Coordination type	No. of compounds	No. of ligands	V_L (Å ³)	R_{sd} (Å)	Ω_L^T (%)	Ω_L^V (%)
C ₈ H ₁₁ O (methoxyethyl- cyclopentadienyl)	η^1, η^5	16	27	185.7 (8.2)	3.54 (5)	39.9 (3.5)	39.0 (3.1)
C ₈ H ₁₃ Si (trimethylsilyl cyclopentadienyl)	η^5	9	10	185.4 (6.9)	3.54 (4)	27.5 (1.1)	26.6 (1.2)
C ₉ H ₇ (indenyl)	η^5	12	36	224.9 (9.1)	3.77 (5)	32.7 (5)	31.0 (1.3)
	$\mu_2-\eta^2, \eta^5$	25	63	158.7 (5.0)	3.36 (4)	29.2 (2.0)	27.2 (1.8)
		1 (1)	1 (1)	151.0	3.30	17.2	6.0
						+ 26.6	+ 25.4
	η^4	1	1	155.0	3.33	28.0	21.4
C ₉ H ₁₃ (<i>tert</i> -butylcyclo- pentadienyl)	η^5	38 (1)	70 (1)	201.4 (9.2)	3.64 (5)	32.2 (3.5)	28.4 (2.9)
C ₁₀ H ₁₅ (pentamethyl- cyclopentadienyl)†	η^5	188 (11)	444 (18)	227.1 (9.9)	3.78 (5)	33.4 (2.9)	30.6 (1.0)
C ₁₁ H ₁₇ (ethyltetramethyl- cyclopentadienyl)	η^5	9 (3)	14 (4)	242.2 (8.0)	3.87 (94)	36.0 (6.6)	30.3 (2.7)
C ₁₁ H ₂₁ Si ₂ [bis(trimethylsilyl)- cyclopentadienyl]†	η^5	29 (4)	62 (5)	357.5 (8.8)	4.40 (4)	33.4 (2.4)	31.1 (1.9)
	$\mu_2-\eta^5$	1 (1)	1 (1)	340.5	4.33	42.2 (3.5)	24.1 (5.0)
C ₁₂ H ₁₀ N (diphenylamido)	σ^1, η^5	8	13	228.1 (5.3)	3.79 (3)	21.8 (1.6)	16.1 (7)
	σ^1	1	2	227.1 (1.8)	3.79 (1)	23.0 (2.4)	18.0 (3)
C ₁₂ H ₁₀ N ₂ (azobenzene)	$\mu_2-\eta^2, \eta^4$	1 (1)	1 (1)	228.1	3.79	21.0	21.0
						+ 30.5	+ 24.7
	$\mu_2-\eta^2, \eta^2$	2	3	230.8 (8.8)	3.81 (5)	23.9 (1.2)	22.6 (4)
	η^2	2 (2)	2 (2)	220.7 (8)	3.75 (1)	37.1 (8)	13.5 (1)
	$\mu_2-\eta^1, \eta^1$	1	1	256.4	3.94	21.4	21.4
C ₁₂ H ₁₇ O (2,6-diisopropyl- phenoxy)	$\mu_2-\sigma^1, \eta^6$	2	3	270.0 (1.7)	4.01 (1)	24.0 (8)	19.7 (1)
						+ 27.3 (2)	+ 25.7 (3)
	σ^1	4 (2)	4 (2)	277.9 (4.4)	4.05 (2)	24.7 (2.1)	18.9 (1.5)
C ₁₃ H ₂₁ [di(<i>tert</i> -butyl)cyclo- pentadienyl]	η^5	19 (6)	35 (8)	307.4 (10.2)	4.19 (5)	33.8 (3.8)	29.0 (2.2)
	η^3	1	1	306.6	4.18	32.4	14.8
C ₁₄ H ₂₁ O (2,6-di- <i>tert</i> -butyl- phenoxy)	σ^1	6 (6)	9 (9)	322.5 (19.5)	4.25 (8)	36.8 (2.8)	16.0 (1.9)
C ₁₇ H ₁₄ P (diphenylphosphino- cyclopentadienyl)	η^5	8	22	344.5 (9.5)	4.35 (4)	33.1 (2.7)	31.2 (2.0)
C ₁₈ H ₁₃ O (2,6-diphenylphenoxy)	σ^1, η^6	6	6	334.2 (3.4)	4.31 (2)	41.5 (1.2)	41.2 (1.3)
	η^6	1	1	337.8	4.32	38.3	36.0
	$\mu_2-\sigma^2, \eta^3$	1 (1)	1 (1)	320.6	4.25	25.0	14.4
						+ 33.3	+ 27.1
	$\mu_2-\sigma^2, \eta^2$	1 (1)	2 (2)	334.4 (2)	4.31 (1)	25.8 (2.2)	13.4 (6)
						+ 33.3 (8)	+ 24.0 (1)
	σ^1, η^1	5 (1)	5 (1)	330.3 (4.1)	4.29 (2)	30.9 (6)	24.3 (7)
	σ^1	11 (4)	26 (6)	334.5 (10.4)	4.31 (4)	25.0 (2.8)	18.3 (2.1)
C ₂₆ H ₄₀ Si (menthylcyclopentadienyl- tetramethylcyclopenta- dienyldimethylsilane)†	η^5, η^5	10	15	600.5 (16.8)	5.24 (5)	60.3 (3.6)	56.8 (2.6)
C ₃₆ H ₄₈ N ₄ (octaethyl- porphyrinogen)	μ_2, η^5, η^5	6	8	794.8 (25.3)	5.75 (6)	76.5 (5.1)	74.4 (4.4)
	$\mu_3-\eta^2, \eta^3, \eta^5, \eta^5$	1	1	786.7	5.72	23.8	12.6
						+ 72.5	+ 72.3
	$\mu_3-\eta^5, \eta^5$	2	2	756.1 (7.1)	5.65 (2)	71.7 (5.7)	70.5 (6.4)

† The ligands participating in rather strong intercomplex nonvalent interactions.

Table 2
Characteristics of agostic contacts in [JOOPEK].

Ligand	H atom	$R(\text{Sm} \cdots \text{H})$ (Å)	$\Omega(\text{Sm} \cdots \text{H})$ (%)
L1 ($\delta = 8.3\%$)	H21	2.81	3.6
	H22	2.95	2.1
	H26	3.65	2.5
	H28	4.08	0.1
L2 ($\delta = 8.7\%$)	H52	2.79	2.3
	H53	2.79	2.5
	H57	3.53	3.9
	H59	4.06	0.1

3. Physical meaning and use of molecular descriptors

3.1. Solid angles of ligands

The most important characteristics of molecular VDPs for all ligands occurring in more than five compounds of the sample studied are given in Table 1. As shown in Table 1, Ω_L^V values are independent of ligand size. For instance, all cyclopentadienyl derivatives have the same (within the error) solid angle ($\Omega_L^V \simeq 30\%$), while their volumes vary from $V_L = 100.9 \text{ \AA}^3$ for η^5 -cyclopentadienyl to $V_L = 357.5 \text{ \AA}^3$ for η^5 -bis(trimethylsilyl)cyclopentadienyl. At the same time Ω_L^T values increase slightly with an increase in number and volume of cyclopentadienyl substitutes. With a decrease in ligand denticity relative to the complexing atoms, Ω_L^V decreases (for instance, for dimethylcyclopentadienyl Ω_L^V decreases from 29.2 to 11.3% on changing the ligand coordination type from η^5 to η^2 , Table 1).

Ω_L^V , Ω_L^T , Ω_L^{ag} and δ characteristics can be used to judge the ligand L capability to screen the central Ln atom and to form non-valent contacts, including agostic $\text{Ln} \cdots \text{H}(L)$ contacts. Note that agostic interactions are observed in 185 out of 808 complexes. The following variants are possible:

(i) $\Omega_L^V \simeq \Omega_L^T$ ($\delta < 5\%$). In this case the ligand is involved in practically no intercomplex non-valent interactions with central atoms, therefore, agostic ligand–Ln contacts are also missing. For instance, in the crystal structure of bis{bis[1,3-bis(trimethylsilyl)-(η^5 -cyclopentadienyl)]-(μ_2 -hydroxo)-lutetium} [YANXUG], for two crystallographically independent bis(trimethylsilyl)cyclopentadienyl ligands, $\Omega_L^V = 31.8\%$, $\Omega_L^T = 33.6\%$ and $\Omega_L^{\text{ag}} = 31.7\%$, $\Omega_L^T = 31.8\%$, respectively, and these ligands participate in no agostic interactions despite the presence of trimethylsilyl substitutes which are inclined to form $\text{Ln} \cdots \text{H} - \text{C} - \text{Si}$ contacts. As can be seen from Table 1, all the 12 ligands containing H atoms which are disinclined to form agostic contacts have $\delta < 5\%$. The only exception is the trimethylsilylmethyl ligand ($\delta = 6.9\%$) which does not participate in agostic contacts. However, in all the complexes considered this ligand takes part in numerous weak non-valent $\text{Ln} \cdots \text{H}$ interactions which explains the rather large δ value. For instance, in 2,2'-bis(η^5 -indenylidene)ethylether-trimethylsilylmethylttrium [JOOPEK] both trimethylsilyl ligands $L(1,2)$ are involved in weak non-valent interactions with the Y atoms (Table 2).

(ii) $\delta > 5\%$. In this case to screen the central Ln atom the ligand often uses A atoms, which are non-donors (as a rule $A = \text{H}$) and enable the formation of $\text{Ln} \cdots A$ contacts (including

agostic) by a dative mechanism. According to the criteria of Blatova *et al.* (2001), 69 chemically different ligands in 283 cases participate in agostic contacts and δ varies from 5 to 45% for these ligands. In the case of $\delta = 5\text{--}10\%$, the central atom enables the formation of an agostic contact with only one H atom since the minimum solid angle corresponding to such a contact is 5% (Blatova *et al.*, 2001). Note that of 353 chemically different ligands, all 33 ligands which can potentially form agostic contacts (*i.e.* they contain C–H bonds) and have $\delta > 17.5\%$, *practically always* form such contacts. The only exception, bis{bis(μ_2 -isocarbonyl)-[tris(3-*tert*-butyl-5-methylpyrazolyl)borato]-(η^5 -methyl-cyclopentadienyl)-(tetrahydrofuran)molybdenum-ytterbium} [GIWVOX], will be considered below.

(iii) $\Omega_L^V = 0$, $\Omega_L^T > 5\%$. In this case the ligand takes part in intercomplex non-valent interactions. For instance, in the aforementioned [YAMNEF] the bis(trimethylsilyl)cyclopentadienyl ligand has $\Omega_L^V = 32.0\%$, $\Omega_L^T = 39.4\%$, $\Omega_L^{\text{ag}} = 5.7\%$ and forms the intracomplex agostic contact $\text{Yb1} \cdots \text{H12}$ [$R(\text{Yb1} \cdots \text{H12}) = 3.34 \text{ \AA}$, $\Omega(\text{Yb1} \cdots \text{H12}) = 5.7\%$], but relative to the neighboring Yb atom the ligand has $\Omega_L^V = 0$, $\Omega_L^T = 22.1\%$, $\Omega_L^{\text{ag}} = 17.9\%$ and gives intercomplex agostic contacts $\text{Yb1} \cdots \text{H40}$ [$R(\text{Yb1} \cdots \text{H40}) = 2.59 \text{ \AA}$, $\Omega(\text{Yb1} \cdots \text{H40}) = 9.1\%$] and $\text{Yb1} \cdots \text{H42}$ [$R(\text{Yb1} \cdots \text{H42}) = 2.59 \text{ \AA}$, $\Omega(\text{Yb1} \cdots \text{H42}) = 8.8\%$; Fig. 1(*f*)]. There are 23 out of 808 compounds which obey these conditions (Table 1). The ability to participate in intercomplex contacts is determined by the ligand nature: the cyclopentadienyl derivatives with voluminous alkyl substitutes [pentamethylcyclopentadienyl (12 cases), methylcyclopentadienyl (three cases), bis(trimethylsilyl)cyclopentadienyl (two cases)] most often take part in such contacts.

The value $\Omega_L^{\text{ag}} > 0$ directly indicates the participation of the ligand in agostic interactions, which correlates with the ligand capability to form non-valent contacts. The hydrogen atoms of alkyl groups usually take part in agostic interactions if they are allocated near the central atom [bis(trimethylsilyl)methyl and 2,6-di-*tert*-butylphenoxy ligand most often form such contacts, Table 1]. Planar cyclic π -conjugated molecules (cyclopentadienyl, cyclooctatetraene, benzene *etc.*) give no intracomplex $\text{Ln} \cdots \text{H}$ contacts; as a rule, this agrees on the whole with the conclusions of Schumann *et al.* (1995) because cyclopentadienyl and indenyl take part in intercomplex agostic contacts. The only exception is bis(μ_2 -chloro)bis[bis(η^5 -cyclopentadienyl)diytterbium] [JADGAW01]. However, in this case the presence of $\text{Yb1} \cdots \text{H2}$ contacts with $R[(\text{Yb1} \cdots \text{H2})] = 2.69 \text{ \AA}$, $\Omega(\text{Yb1} \cdots \text{H2}) = 5.4\%$, is apparently caused by incorrect localization of the H2 atom (this atom is allocated outside the cyclopentadienyl ring plane: deviation from the plane of 0.13 Å).

3.2. Solid angles of complexes

Integral characteristics $\Omega_{L\Sigma}^V$, $\Omega_{L\Sigma}^T$, $\Omega_{L\Sigma}^{\text{ag}}$ and Δ allow the prediction of the composition of complex groups and the appearance of intra- and intercomplex agostic interactions in the crystal structure. Consider the most important variants, which can be addressed in forecasting.

Table 3
Characteristics of agostic contacts in [BIJMEM].

Eu atom	H atom	$R(\text{Eu}\cdots\text{H})$ (Å)	$\Omega(\text{Eu}\cdots\text{H})$ (%)
Eu1	H29	3.11	5.4
	H30	2.92	8.1
	H14	2.74	11.0
	H20	2.84	10.8

(i) $\Omega_{L\Sigma}^T \approx \Omega_{L\Sigma}^V \approx 100\%$ ($\Delta < 5\%$). In this case the degree of screening of the central atom by ligands is rather high and no intermolecular contacts are observed. For example, in tris[η^5 -bis(1,3-trimethylsilyl)cyclopentadienyl]samarium [KEXREK] $\Omega_{L\Sigma}^T = \Omega_{L\Sigma}^V = 93.6\%$, and agostic interactions are missing in the complex, in spite of the trimethylsilyl substitutes in cyclopentadienyl being inclined to participate in agostic contacts.

(ii) $\Omega_{L\Sigma}^T \approx \Omega_{L\Sigma}^V < 90\%$ ($\Delta < 5\%$). The screening of an Ln atom is incomplete in such complexes, therefore, its coordination valence is unsaturated and such an atom will compensate by interacting with ligands of adjacent complex groups and by forming intercomplex non-valent contacts. Only 36 out of 808 compounds obey this condition. Thus, rather small values of $\Omega_{L\Sigma}^T = 70.2\%$ and $\Omega_{L\Sigma}^V = 73.1\%$ in $(\mu_2\text{-}\eta^8, \eta^8\text{-cyclooctatetraenyl})\text{bis}[(\eta^5\text{-pentamethylcyclopentadienyl})\text{europium}]$ [BIJMEM] indicate insufficient screening of the central Eu atom and its valent non-saturation (Fig. 2). As a result, Eu atoms compensate for their non-saturation by intercomplex interactions with pentamethylcyclopentadienyl hydrogen atoms (Table 3).

(iii) $\Omega_{L\Sigma}^T \approx 100\%$, $\Delta > 20\%$. In 103 out of 109 such complexes the central atoms compensate for their valent non-saturation by intracomplex agostic contacts with ligands. Thus, for example, there are agostic contacts $\text{Y1}\cdots\text{H34}$ [$R(\text{Y1}\cdots\text{H34}) = 2.50$ Å, $\Omega(\text{Y1}\cdots\text{H34}) = 8.0\%$] and $\text{Y1}\cdots\text{H35}$ [$R(\text{Y1}\cdots\text{H35}) = 2.50$ Å, $\Omega(\text{Y1}\cdots\text{H35}) = 9.4\%$] in the crystal structure of bis(2,6-di-*tert*-butylphenolato)(η^5 -pentamethylcyclopentadienyl)yttrium [KIRSUZ]. There are only six exceptions. In the aforementioned [GIWVOX] [$\Omega_{L\Sigma}^T$ (Yb) = 100%, $\Omega_{L\Sigma}^V$ (Yb) = 76.7%] and in $(\mu_2\text{-}\eta^4\text{-peroxo})\text{bis}[\text{bis}[\text{bis}(\text{trimethylsilyl})\text{amido}](\text{triphenylphosphineoxide})\text{lanthanum}]$ [LABTSA10] [$\Omega_{L\Sigma}^T$ (La) = 99.7%, $\Omega_{L\Sigma}^V$ (La) = 77.0%], the

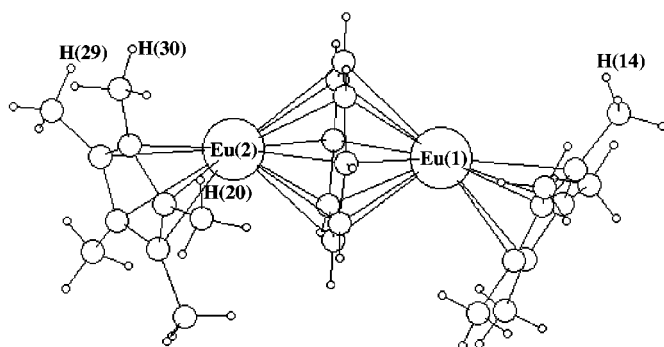


Figure 2
Molecular structure of $(\mu_2\text{-}\eta^8, \eta^8\text{-cyclooctatetraene})\text{bis}[(\eta^5\text{-pentamethylcyclopentadienyl})\text{europium}]$ [BIJMEM]. H atoms are labelled which participate in intercomplex agostic interactions.

Table 4
Characteristics of agostic contacts in [GIWVOX] and [LABTSA10].

Compound	H atom	$R(\text{Ln}\cdots\text{H})$ (Å)	$\Omega(\text{Ln}\cdots\text{H})$ (%)
[GIWVOX]	H10	2.97	4.4
	H26	2.93	4.8
	H37	2.87	4.7
[LABTSA10]	H43	3.12	4.3
	H44	3.11	4.0
	H49	3.22	4.2
	H51	3.20	3.3

interactions of Ln atoms with H atoms can be considered as weak agostic contacts [$\Omega(\text{Ln}\cdots\text{H}) \Rightarrow 5\%$, Table 4]. Note that the corresponding $\Omega(\text{Ln}\cdots\text{H})$ contacts are greater than 5% in samarium-containing complexes [GIWVIR] isostructural to [GIWVOX]. In the complexes tris(η^5 -cyclopentadienyl)-tetrahydrofuran-cerium [JAPRAT11] [$\Omega_{L\Sigma}^T$ (Ce) = 100%, $\Omega_{L\Sigma}^V$ (Ce) = 79.5%], tris(η^5 -1,3-di-*tert*-butylcyclopentadienyl)-ytterbium [BOBNAH] [$\Omega_{L\Sigma}^T$ (Yb) = 100%, $\Omega_{L\Sigma}^V$ (Yb) = 72.9%], bis(*N,N,N',N'*-tetramethylethylenediamine)-lithium trimethyl-(η^5 -pentamethylcyclopentadienyl)lutetium [CUTGUT] [$\Omega_{L\Sigma}^T$ (Lu) = 99.5%, $\Omega_{L\Sigma}^V$ (Lu) = 74.5%] and tris($\mu_2\text{-}\eta^2, \sigma^3$ -2,6-diphenylphenoxy)(2,6-diphenylphenoxy)dieuropium [HOCFOU] [$\Omega_{L\Sigma}^T$ (Eu2) = 100%, $\Omega_{L\Sigma}^V$ (Eu2) = 75.1%], the ligands are of the umbrella type, hence the H

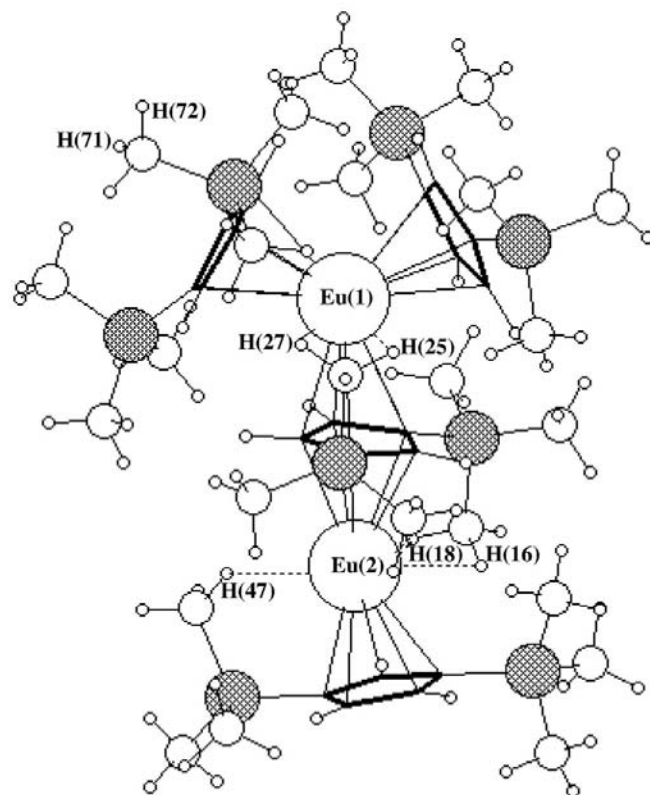


Figure 3
Molecular structure of $(\mu_2\text{-}\eta^5, \eta^5\text{-1,3-bis}(\text{trimethylsilyl})\text{cyclopentadienyl})\text{-tris}[\eta^5\text{-1,3-bis}(\text{trimethylsilyl})\text{cyclopentadienyl}]$ dieuropium [YAMNIJ]. Si atoms are shaded. H atoms are labelled, which participate in inter- and intracomplex agostic contacts. Intracomplex agostic contacts are depicted by dashed lines.

Table 5
Ligand characteristics in [YAMNIJ].

Ligand	Eu atom connected with the ligand	Coordination type	$\Omega_{L\Sigma}^V$ (%)	$\Omega_{L\Sigma}^T$ (%)	$\Omega_{L\Sigma}^{ag}$ (%)
L1	Eu2	η^2	27.6	38.9	5.9
L2	Eu1	$\mu_2\text{-}\eta^5$	20.5	39.7	16.1
	Eu2	η^5	27.6	44.7	15.7
L3	Eu1	η^5	26.9	29.0	0
	Eu2	–	0	16.5	15.2
L4	Eu1	η^5	29.3	31.3	0

atoms are allocated far from the central atom and cannot appreciably interact with it. As a result, the central atom has to compensate for its non-saturation by numerous weak ($\Omega < 5\%$) interactions with H and C atoms of the ligands.

An unambiguous conclusion cannot be made regarding the presence or absence of agostic contacts for compounds with $5 < \Delta < 20\%$. For instance, agostic contacts are found in ($\mu_2\text{-}\eta^5, \sigma^1\text{-methylcyclopentadienyl}$)pentakis($\eta^5\text{-methylcyclopentadienyl}$)dicerium [KEDBOK] {for Ce1 with $\Delta = 14.3\%$ the intracomplex Ce1 \cdots H18 interaction has $R(\text{Ce1}\cdots\text{H18}) = 3.01 \text{ \AA}$, $\Omega(\text{Ce1}\cdots\text{H18}) = 6.0\%$; even for Ce2 with $\Delta = 4.4\%$ there is the intercomplex contact Ce2 \cdots H10 with $R[(\text{Ce2}\cdots\text{H10})] = 2.73 \text{ \AA}$, $\Omega(\text{Ce2}\cdots\text{H10}) = 9.2\%$ }, but agostic contacts are absent in bis[$\eta^5\text{-1,3-bis(trimethylsilyl)cyclopentadienyl}$]tetrahydrofuran-ytterbium [TEYVIC]. In this complex there are only weak contacts between the Yb1 atom and H5 [$R(\text{Yb1}\cdots\text{H5}) = 3.94 \text{ \AA}$, $\Omega(\text{Yb1}\cdots\text{H5}) = 1.7\%$] and with H17 atoms [$R(\text{Yb1}\cdots\text{H17}) = 3.69 \text{ \AA}$, $\Omega(\text{Yb1}\cdots\text{H17}) = 3.4\%$].

(iv) $\Omega_{L\Sigma}^T, \Omega_{L\Sigma}^V < 90\%$, $\Delta > 20\%$. In this case the complexing atom participates in both intra- and intercomplex non-valent interactions. This condition was satisfied in only one case – for the Eu2 atom in [$\mu_2\text{-}\eta^5, \eta^5\text{-1,3-bis(trimethylsilyl)cyclopentadienyl}$]tris[$\eta^5\text{-1,3-bis(trimethylsilyl)cyclopentadienyl}$]diuropium [YAMNIJ] [$\Omega_{L\Sigma}^T$ (Eu1) = 100%, $\Omega_{L\Sigma}^V$ (Eu1) = 76.7%; $\Omega_{L\Sigma}^T$ (Eu2) = 83.6%, $\Omega_{L\Sigma}^V$ (Eu2) = 55.2%]. There are four crystallochemically different bis(trimethylsilyl)cyclopentadienyl ligands L1–L4 in the complex, as shown in Table 5, L1 interacts with only Eu2, L2 is bonded by valent and non-valent contacts with Eu1 and Eu2, L3 is bonded by valent and non-valent contacts with only Eu1, while L4 forms only non-valent contacts with Eu2, L4 interacts with only Eu1. Note that for Eu2 $\Omega_{L\Sigma}^{ag} = 36.8\%$ exceeds $\Delta = 28.3\%$. This is caused by the fact that Eu2 is involved in intercomplex agostic interactions with L3 [$R(\text{Eu2}\cdots\text{H71}) = 2.63 \text{ \AA}$, $\Omega(\text{Eu2}\cdots\text{H71}) = 9.6\%$; $R(\text{Eu2}\cdots\text{H72}) = 2.89 \text{ \AA}$, $\Omega(\text{Eu2}\cdots\text{H72}) = 5.6\%$, Fig. 3]. Note that according to the analysis of intermolecular contacts this complex is a dimer, not a chain as was indicated in the CSD.

The value $\Omega_{L\Sigma}^{ag} > 0$ indicates the ability of the complexing atom to form agostic bonds. For practically all types of Ln

atoms, examples of their participation in such interactions were found (excepting Ho atoms, for which there were only eight complexes in the sample). At the same time no correlations were found between the nature of the complexing atoms, typical $\Omega_{L\Sigma}^{ag}$ values and the frequency of their participation in agostic contacts. Apparently, the aforementioned features of ligand structure, not the nature of the Ln atoms, play a key role in this case.

4. Conclusions

In our opinion, the molecular descriptors proposed substantially extend the list of parameters to be used in the study of intermolecular interactions in coordination compounds and are evidence of the applicability of the method of crystallochemical analysis, based on the conceptions of atomic and molecular VDPs for the investigation of rare-earth π -complexes. Since this approach requires no *a priori* knowledge about the type and nature of interatomic interactions, allowing subdivision objectively both into valent/non-valent and intra/intermolecular contacts, it also seems to be useful in solving supramolecular chemistry problems.

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