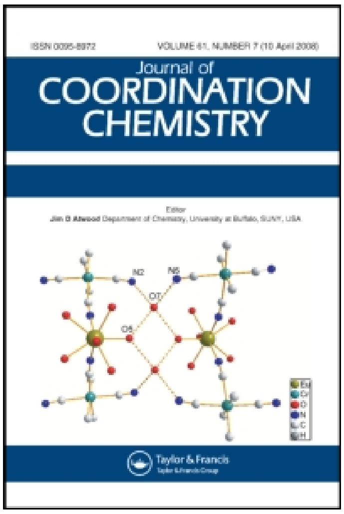

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Non-valent interactions and structural features of monomeric guanidinate complexes of rare earth metals: analyses and predictions based on the ligand solid angle

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Non-valent interactions and structural features of monomeric guanidinate complexes of rare earth metals: analyses and predictions based on the ligand solid angle

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Analysis of steric saturation of rare earth metal centers in monomeric guanidinate coordination complexes with the use of ligand solid angles indicates that the observed optimal metal shielding is 85(3)%. Non-valent ligand–ligand interactions in the metal coordination sphere affect the shielding of the metal and can facilitate or preclude formation of agostic interactions. Analysis of all structurally characterized to date guanidinate complexes of Ln is presented and general and unique features of such complexes are identified.

Keywords: Ligand solid angle; Non-valent interactions; Guanidinate complexes; X-ray data mining

1. Introduction

Recently, we improved the ligand solid angle computation approach [1] and demonstrated its application for complexes of the type $[\mathrm{Gu}^{i\mathrm{Pr}}{}_2\mathrm{Ln}(\mu_2\text{–H})]_2$ (Ln = Nd, Sm, Gd, Yb, Lu and Y; $\mathrm{Gu}^{i\mathrm{Pr}} = (\mathrm{Me_3Si})_2\mathrm{NC}(\mathrm{N}^i\mathrm{Pr})_2$) and analyzed steric aspects of reactions between $\mathrm{LnCl_3}$ (Ln = Nd, Sm, Yb, Lu and Y) and lithium guanidinate [2]. A distinctive feature of rare earth metal coordination complexes is their tendency to attain steric saturation of the metal coordination sphere [3]. Steric saturation is achieved with both intra- and intermolecular interactions which include non-valent interligand interactions. The latter play an important role in formation of organometallic and coordination compounds. This is especially noticeable in the case of compounds with highly ionic metal–ligand bonds such as lanthanoid complexes. Therefore, it is imperative to include qualitative characterization of the ligand steric requirements in the studies of organic derivatives of rare earth metals. The use of ligand solid angles is particularly suitable for quantification of the ligand–ligand interactions in the metal coordination sphere [4–8].

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Currently, there are several groups working toward "rigid" mono- and dianionic polydentate N- and/or O-coordinating ligands capable of steric saturation of the rare earth metal coordination environment whereby rendering the metal complex kinetically stable without reducing its reactivity [9–11]. We decided to revisit and re-examine relevant complexes reported by us and other authors to scrutinize the steric saturation of rare earth metal coordination spheres in order to establish common trends in the complex structures and to identify their unique features. Herein we report our analysis of the relationship between non-valent interactions in the metal coordination sphere and formation of mononuclear guanidinate complexes of lanthanoids and yttrium.

2. Discussion

Selected important geometric parameters of all monomeric guanidinate complexes of lanthanoids reported to date are tabulated in table 1. The G-values represent metal shielding as a percentage of the metal coordination sphere; interpretation of G-values is described by Guzei and Wendt [1]. Only two types of guanidinate ligands have found wide application: isopropyl ($Gu^{iPr} = (Me_3Si)_2NC(N^iPr)_2$) and cyclohexyl ($Gu^{Cy} = (Me_3Si)_2NC(NCy)_2$). We have previously compared the steric characteristics of these two ligands to show that the difference in their normalized solid angles is not statistically significant ($G_{2.28} = 28.6(6)$ and 29.9(6)% for Gu^{iPr} and Gu^{Cy}, respectively) [2]. Thus, in terms of steric saturation of the metal coordination environment these two ligands behave similarly.

Guanidinate (figure 1) is a sterically bulky, bidentate ligand shielding close to 30% of the central metal. Monomeric guanidinate complexes of lanthanoids exhibit low coordination numbers between 4 and 6. Guanidinate ligands almost always coordinate in an asymmetric fashion. Their asymmetric η^2 mode in the majority of the structurally characterized complexes does not result in appreciable localization of the N–C bonds in the NCN fragment, i.e. the electron density in this fragment remains delocalized (figure 1a). However, in **11** the asymmetric coordination is particularly prominent with Ln–N distances of 2.409(9), 2.330(9) Å, and the N–C distances within the NCN fragment (figure 1b) substantially different at 1.290(9) and 1.377(9) Å. At the same time the longer Y–N bond (2.409(9) Å) corresponds to the shorter N–C distance (1.290(9) Å) whose length compares to that of a N=C double bond (1.279–1.329Å) [12].

Another feature of the monomeric guanidinate complexes of lanthanoids is the presence of agostic interactions C–H···Ln. Such interactions are found in both solid state and solution where they can affect the reactivity of the complex; thus a careful analysis of conditions necessary for agostic interactions to take place is desirable [13]. In the following discussion we will consider Ln···C distances in lieu of agostic C–H···Ln interactions due to the fact that the hydrogen atom positions in the vicinity of heavy elements in the X-ray crystal structures are frequently not very reliable.

The most interesting part of the solid state structure of **2** (figure 2a) is the agostic interactions between Y and carbon atoms of the methyl groups as revealed by the short contacts Y(1)–C(30) (2.978(2) Å), Y(2)–C(56) (3.050(2) Å), and Y(2)–C(61) (3.044(2) Å), similar to those in $[Y(OC_6H_3Ph_2\text{-}2,6)_3]$ (2.84(1)–3.43(1) Å) [14] but substantially shorter than the other Y–C(Me) separations in **2** (3.251–4.712 Å).

Table 1. Selected geometric and steric parameters for guanidinate complexes of lanthanoids.

		Distances (Å)				
Complex	Ln–N(Gu)	Ln–C(R)	Ln–N(R)	N–C	G (%)	Ref
$\mathrm{Gu^{Cy}Y(CH_2SiMe_3)_2(THF)_2}$ (**1**)[a]	2.416(2) 2.385(2)	2.461(2) 2.474(2)		1.336(2) 1.328(2)	87.2(2)	[21]
$\mathrm{Gu^{Cy}Y\ [N(SiMe_3)_2]_2}$ (**2**)[a,c]	2.311(1) 2.343(1); {2.354(1) 2.327(1)}		2.252(2) 2.235(1); 2.226(1) 2.255(1)	1.344(2) 1.333(2) {1.336(2) 1.339(2)}	86.2(2) {87.0(2)}	[22]
$\mathrm{Gu^{Cy}La\ [N(SiMe_3)_2]_2}$ (**3**)[b]	2.486(3) 2.475(3)		2.382(3) 2.377(3)	1.333(4) 1.328(4)	83.4(2)	[23]
$\mathrm{Gu^{Cy}La(OAr)_2}$ (**4**)[b,d]	2.467(5) 2.448(8)			1.340(8) 1.322(8)	79.1(2)	[23]
$\mathrm{Gu_2{}^{Cy}YBu^t}$ (**5**)[a]	2.336(2) 2.355(2); 2.399(2) 2.317(1)	2.399(2)		1.338(3) 1.333(3); 1.334(3) 1.341(3)	82.8(2)	[24]
$\mathrm{Gu_2{}^{Cy}YCH_2SiMe_3 \cdot LiCH_2SiMe_3}$ (**6**)[a]	2.400 (1) 2.351(1); 2.367(1) 2.392(1)	2.544(2) 2.546(2)		1.334(2) 1.331(2); 1.333(2) 1.335(2)	87.3(2)	[21]
$\mathrm{Gu_2{}^{Cy}SmCH(SiMe_3)_2}$ (**7**)[b,c]	2.424(4) 2.424(4); 2.395(4) 2.426(4) {2.452(4) 2.404(4); 2.396(4) 2.438(4); 2.396(4) 2.483(4); 2.467(4) 2.375(4)}	2.472(5) {2.475(5); 2.450(5)}		1.336(7) 1.333(7); 1.341(7) 1.343(6) {1.325(7) 1.348(6); 1.344(6) 1.330(6); 1.341(6) 1.328(6); 1.333(6) 1.333(6)}	86.1(2) {87.8(2) 84.2(2)}	[25]
$\mathrm{Gu_2{}^{\mathit{i}Pr}YCH(SiMe_3)_2}$ (**8**)[b]	2.373(2) 2.305(2); 2.374(2) 2.372(2)	2.402(3)		1.333(3) 1.342(3); 1.341(3) 1.348(3)	84.8(2)	[26]
$\mathrm{Gu_2{}^{Cy}YbN(SiMe_3)_2}$ (**9**)[b]	2.329(13) 2.301(15); 2.311(13) 2.328(12)		2.343(19)	1.304(20) 1.380(21); 1.324(20) 1.306(20)	90.8(2)	[25]
$\mathrm{Gu_2{}^{\mathit{i}Pr}YNPr^i{}_2}$ (**10**)[b]	2.403(3) 2.346(3); 2.399(2) 2.348(3)		2.199(3)	1.330(4) 1.337(4); 1.324(4) 1.338(4)	86.1(2)	[27]
$\mathrm{Gu_2{}^{\mathit{i}Pr}YBu^t}$ (**11**)[b,c]	2.409(9) 2.330(9); 2.359(9) 2.328(9) {2.342(9) 2.323(9); 2.365(9) 2.347(9)}	2.332(9) {2.343(9)}		1.290(9) 1.377(9); 1.310(9) 1.344(9) {1.335(9) 1.331(9); 1.346(9) 1.311(9)}	80.5(2) {80.0(2)}	[26]
$\mathrm{Gu_2{}^{Cy}YCl(THF)}$ (**12**)[a]	2.387(5) 2.327(5); 2.377(4) 2.344(5)			1.335(8) 1.332(7); 1.314(8) 1.348(7)	86.4(2)	[24]

[a] Own data; [b] literature data; [c] data for the second (and third) independent molecules are in curly braces; [d] $\mathrm{Ar = 2,6\text{-}Me_2C_6H_3}$.

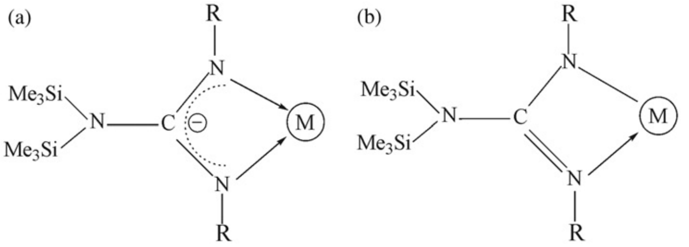


Figure 1. Schematic representation of the η^2 coordination mode of the guanidinate ligand: (a) symmetric; (b) asymmetric with single and double C–N bond character in the NCN unit.

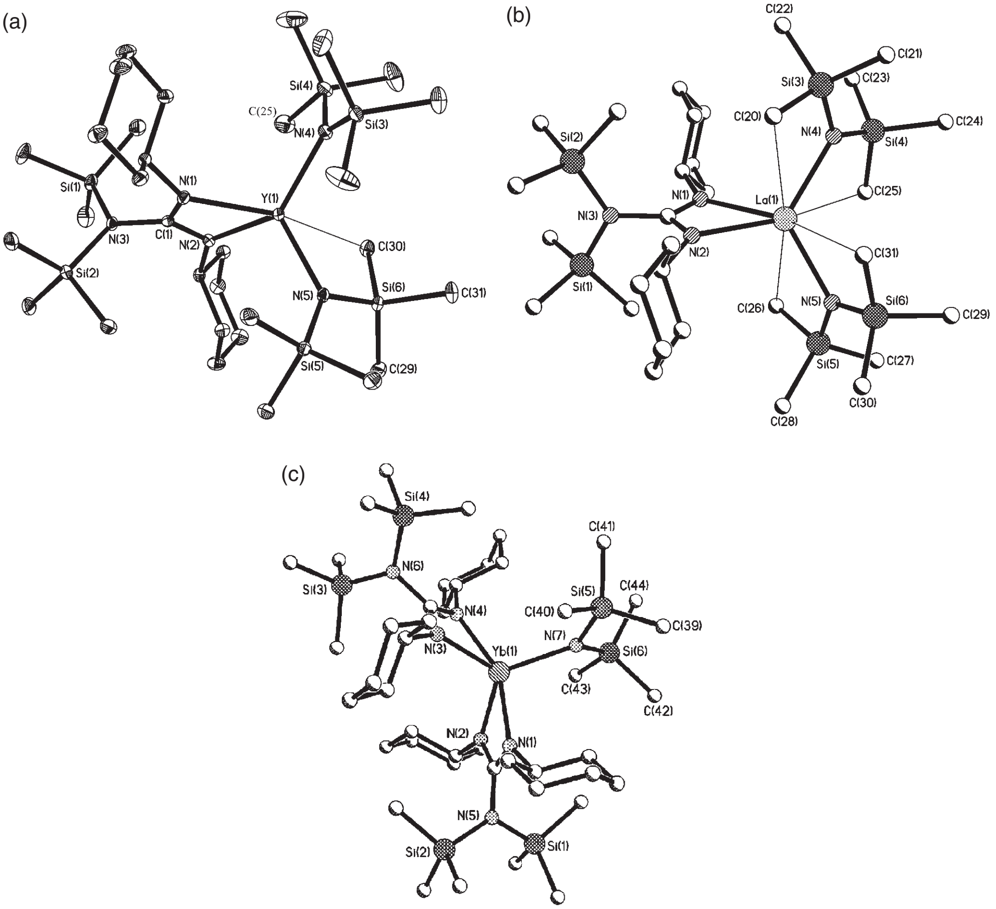


Figure 2. Thermal ellipsoid drawing of **2** (a) [22] and ball-and-stick representations of **3** (b) [23], and **9** (c) [25]. All H atoms are omitted.

The non-valent interactions in **2** between C(30), C(56), and C(61) and the central yttrium result in concomitant elongation of bonds Si(6)–C(30) 1.893(2), Si(10)–C(56) 1.892(2), and Si(12)–C(61) 1.882(2) Å relative to the other Si–C(Me) bond distances (1.853(2)–1.878(2) Å). More indicative evidence for the agostic interactions is the values of the valent angles N–Si–C(30, 56, 61) (106.1(4), 105.8(4), and 106.0(4)°, respectively), that are systematically smaller than the corresponding angles in compounds without such interactions (108.0(1)–115.50(8)°). The Y(1) ··· C(25) separation of 3.251(2) Å does not result in elongation of the Si(4)–C(25) bond (1.858(2) Å), but causes a noticeable contraction of the N(4)–Si(4)–C(25) angle to 106.77(9)°. It appears that the valent angles are more sensitive to agostic interactions than the covalent bonds involving the participating atoms. Previously, Anwander *et al.* reported similar changes in the geometry about the Si atoms in the sterically encumbered silylamides $(C_5Me_5)_2YN(SiHMe_2)_2$ and $(C_5Me_4H)_2YN(SiHMe_2)_2$ [15]. Agostic interactions in **2** are a probable reason for two distinct signals of the methyl carbon atoms of the bistrimethyl sililamide groups in the ^{13}C NMR spectrum (2.6 and 4.1 ppm).

Complex **3** (figure 2b) can be analyzed in similar terms. While no Si–C bond elongation similar to that in **2** is detected, the distortion of the valent N–Si–C angles due to agostic interactions is clearly seen. The values of the N–Si–C angles on the side of the agostic interaction fall between 106.2–107.7° and are systematically smaller than for the corresponding angles for the Me group devoid of such interactions (113.2–115.3°). The shortest distances between the La atom and the Me carbon atoms of the bistrimethylsililamido groups measure 3.235–3.470 Å. Similarly, complex **9** contains a $(Me_3Si)_2N$ group (figure 2c), however agostic interactions in this complex are not observed. This conclusion is substantiated by the "normal" span of the N–Si–C angles (109.0, 111.2°) and non-bonded distances Yb ··· C(Me) of 3.709 and 3.794 Å for the methyl groups closest to the metal. The question arises as to why agostic interactions are observed in complexes of Y(**2**) and La(**3**) but absent or exceedingly weak in Yb, complex **9**. To answer this question one should examine the degree of the steric saturation of the coordination environment about the metal atom in complexes **3**, **2**, and **9** with the use of the G-parameter [1], which depends on the radius of the central metal and increases as the metal radius decreases ($R_{ion}(Ln^{3+}) = 1.032$ Å for La (**3**), 0.900 Å for Y (**2**), and 0.868 Å for Yb (**9**) [16]). Using table 1 we establish that in the sequence **3**, **2**, **9** the value of the G-parameter increases from 83.4(2) to 86.2(2) {87.0(2)} and 90.8(2)%. Two values are provided for **2** because there are two symmetry independent complexes in its crystal structure. Thus, in **9** the non-valent (steric) ligand–ligand interactions in the metal coordination sphere preclude the formation of agostic interactions. In other words, there is insufficient room about the Yb atom to accommodate steric distortion of the Me group of the $(Me_3Si)_2N$ ligand induced by a possible agostic interaction. The $(Me_3Si)_2N$ ligand in **9** shields the central metal to a smaller degree than in **2** and **3**. A convenient quantitative assessment of this assumption is the normalized $G_{2.28}$ parameter that represents the shielding of the metal by a certain ligand repositioned without any conformational changes to 2.28 Å from the metal. The $G_{2.28}$-parameters for the $(Me_3Si)_2N$ ligand are 30.6(2), 35.1(2)% in **3**, 29.4(2), 34.2(2) {29.7(2), 30.6(2)}% in **2**, and substantially smaller in **9** (25.1(2)%), clearly illustrating that non-valent interactions between ligands may restrict ligand ... metal agostic interactions in rare earth metal complexes.

It is instructive to explain the different geometries of two complexes with similar compositions $Gu_2{}^{Cy}YBu^t$ (**5**) and $Gu_2{}^{iPr}YBu^t$ (**11**) on the basis of G-parameters. The geometrical analyses of **5** and **11** (figure 3) indicate that in **5** the Y ··· C(Bu^t) separation of 2.399(2) Å is substantially larger than the analogous distances in **11** (2.332(9), {2.343(9)} Å). Moreover, agostic interactions Y ··· C(Me) in **5** bring about a distortion of the geometry of the *tert*-butyl group. A substantial tilt of the *tert*-butyl group in **5** results in highly unusual angles C(41)–C(39)–Y(1), C(42)–C(39)–Y(1) and C(40)–C(39)–Y(1) spanning (91.7(2), 99.0(2), 135.6(2)°, as compared to the values expected for an sp^3-hybridized carbon atom. This situation is similar to those observed in **2** and **3**. The agostic interactions in **5** are confirmed by shortened intermolecular

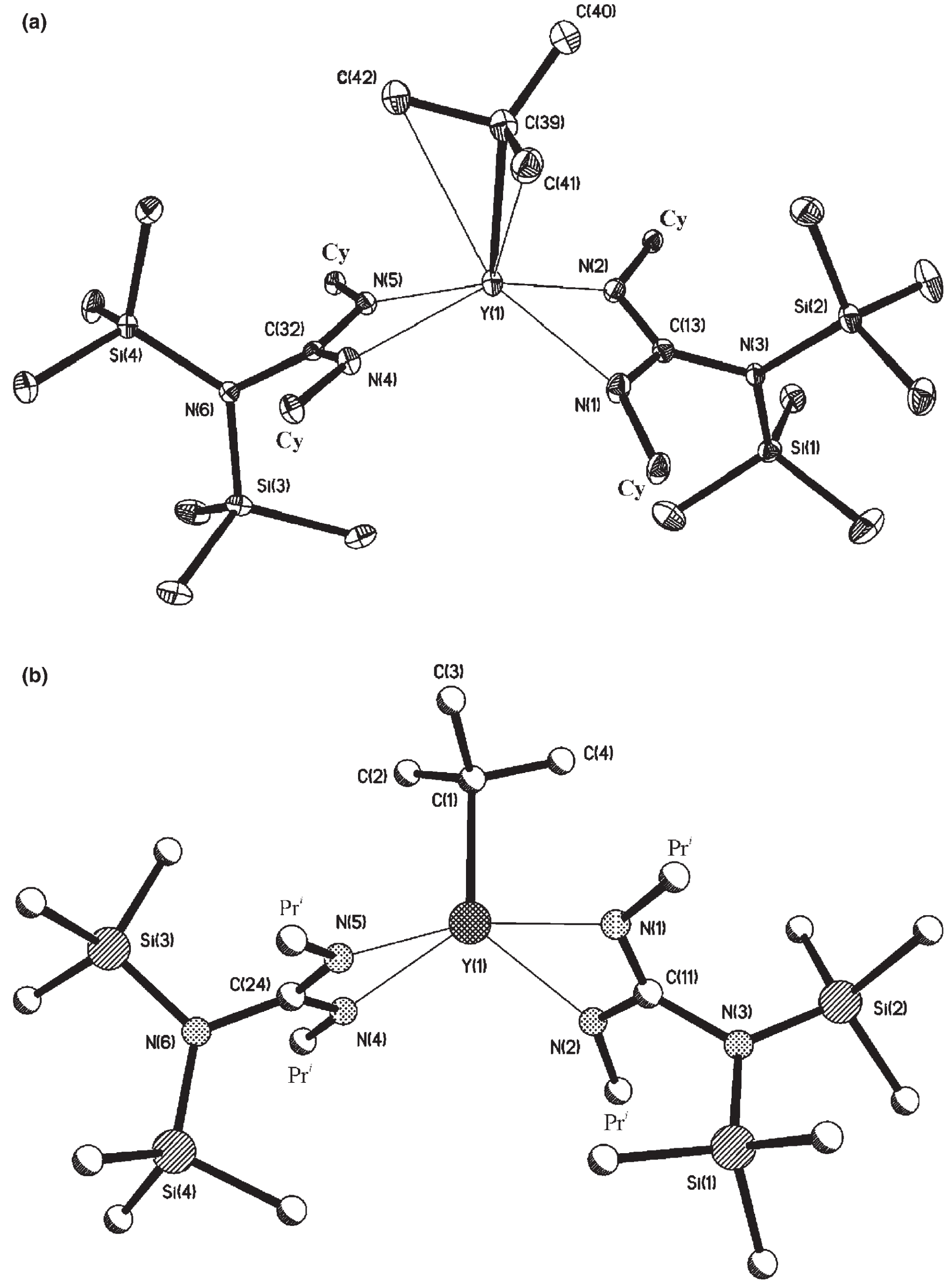


Figure 3. Graphic representation of **5** (a) [24] and **11** (b) [26]. All H atoms are omitted.

separations Y(1) ⋯ C(41, 42) of 2.877(3) and 3.038(3) Å. Interactions of this kind in **11** are absent both in solid state and in solution and the corresponding values for the discussed angles and distances in **11** fall in the usual range of 111.0–113.4° and 3.189–3.229 Å. Agostic interactions in **5** also exist in solution. According to the ^{13}C NMR spectrum, the methyl carbon atoms of the *tert*-butyl group produce a doublet at 30.6 and 30.7 ppm with the splitting constant $^{2}J_{Y,C} = 2.3$ Hz. Therefore, the molecular geometries of **5** in solid state and solution are similar.

In order to estimate the non-valent energy of rotation of the ^{t}Bu group about the Y(1)–C(39) bond in **5** we performed calculations with MOLDRAW [17–19] that computes the energy of non-valent interactions as a function of the torsion angle (figure 4). According to figure 4 the energy minimum in **5** corresponds exactly to the experimentally observed torsion angle N(5)–Y(1)–C(39)–C(42) of 22.5°. At this angle the shortest intramolecular contacts between carbon atoms of the ^{t}Bu group and Cy and $SiMe_3$ ligands (3.653–4.122 Å) exceed the sum of two carbon van der Waals radii (3.4 Å [20]). The highest maximum in figure 4(a) is observed in the 163–172° range,

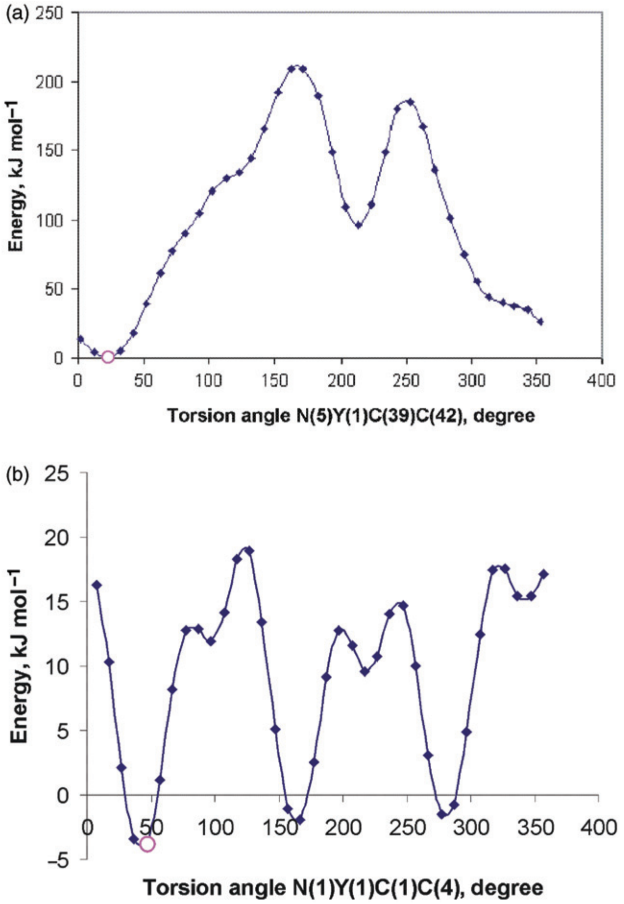


Figure 4. Energy diagram of the non-bonding interactions in **5** (a) and **11** (b) as a function of the torsion angle. The small circles denote the values of the experimentally observed torsion angles.

corresponding to a molecular conformation with a short contact of 2.7 Å between C41 of the ^{t}Bu and C8 of the cyclohexyl ring. The second maximum in figure 4(a) is found between 243–253°, where a short contact (2.8 Å) between C(42) of the ^{t}Bu group and C8 of the cyclohexyl ring is expected. In the case of **11** (figure 4b) the intramolecular contacts induced by rotation of the ^{t}Bu-group are comparable to the sum of the vdW radius of two carbon atoms. These observations are in excellent qualitative agreement with the expectations based on our analysis of the agostic interactions and molecular geometries. In the case of **11** non-valent rotational energy is 10 times smaller than that in **5** since in the latter unfavorable short intramolecular interactions are more likely.

The stabilization of the σ-bond Y–C(^{t}Bu) in **11** is achieved by strengthening (shortening) of the bond whereas in **5** the stabilization mechanism is different and involves agostic interactions. At this point it is appropriate to compare the G-parameters for **5** and **11**. In **11** the G-parameter (80.5(2) and 80.0(2)%) is noticeably smaller than that in **5** (82.8(2)%). The saturation of the metal coordination sphere to higher degree in **5** results in better shielding of the labile σ-bond Y–C(Bu^t) whereby stabilizing the complex. Similarly to **2**, **3**, and **9**, the *tert*-butyl group participating in agostic interactions in **5** shields the Y atom to a higher extent than the ^{t}Bu group in **11**, where such interactions are missing. The normalized G$_{2.28}$ values for the ^{t}Bu groups in **5** and **11** are 21.6(2) and 19.3(2)%, respectively. If one were to reposition the ^{t}Bu group in **5** from 2.399 to 2.332 Å away from the Y center (the Y $\cdots$ C distance observed in **11**), the non-valent interactions among the ligands would increase and prevent shortening of the bond. Indeed, the G parameter for **5** computed for the same ligand geometries but with the Y–C(Bu^t) distance reduced to 2.332 increases to 84.4(2)%.

Based on the data tabulated in table 1 the metal shielding in mono and bis-complexes average to 85(3) and 84(4)%. Note that the standard deviation on the G-parameter is an indicator of the ligand conformational flexibility in the complex. Since the G-parameter is the same for the mono and bis-complexes, we propose that the number 85(3)% can be the criterion of such steric saturation of lanthanoid coordination environment that prevents oligomerization of monomeric units.

Circumstantial evidence of this conclusion is supplied by analysis of lanthanoid guanidinate complexes containing ligated THF molecules. Thus, we would like to determine why in the solid state complexes **1** and **12** have ligated THF molecules whereas in **9** the metal does not bear a THF molecule but there is an uncoordinated THF in the asymmetric unit. To answer this question we compute the G-parameters for **1** and **12** disregarding the presence of THF, and obtain 60.4(2) and 74.0(2)%, respectively. The value for **1** is lower that in **12** because the Ln center in **1** bears two molecules of THF. The two values are substantially smaller than the average saturation value of 85(3)% reported above; thus the non-THF ligands in **1** and **12** do not shield the central metal sufficiently and additional available ligands (THF) are incorporated into the metal coordination sphere. In the absence of a strongly coordinating THF in the reaction mixture other metal-ligand interactions could form, such as a dimer or trimer, or even a product with an entirely different composition and ligand arrangement. In the crystal of **9** there is THF that does not coordinate to the metal. The G-parameter for complex **9** (G$_{\mathrm{Yb}}$(**9**) = 90.8(2)%) exceeds the average "expectancy" value of 85(3)% for this type of complex and thus there is insufficient room about the metal to accommodate an additional ligand.

A second example illustrating the tendency to optimally saturate the coordination sphere in monomeric guanidiante complexes of rare earth metals is an unexpected observation of **6** (figure 5). The synthetic route in scheme 1 was to prepare a complex similar to **1** that would not have THF coordinated to yttrium ($Gu^{Cy}Y(CH_2SiMe_3)_2$), but **6** was isolated instead. This complex combines two different molecules, $Gu_2^{Cy}YCH_2SiMe_3$ and $LiCH_2SiMe_3$, and the crystal $Li^+[Gu_2^{Cy}Y(CH_2SiMe_3)_2]^-$ exists in the cation–anion "ate" form. The most noteworthy feature of **6** is the geometrical equivalency of the bridging CH_2SiMe_3 groups. Distances Y(1)–C(39) (2.544(2) Å) and Y(1)–C(43) (2.546(2) Å) are identical within experimental error, and statistically significantly longer than the corresponding distances in terminal

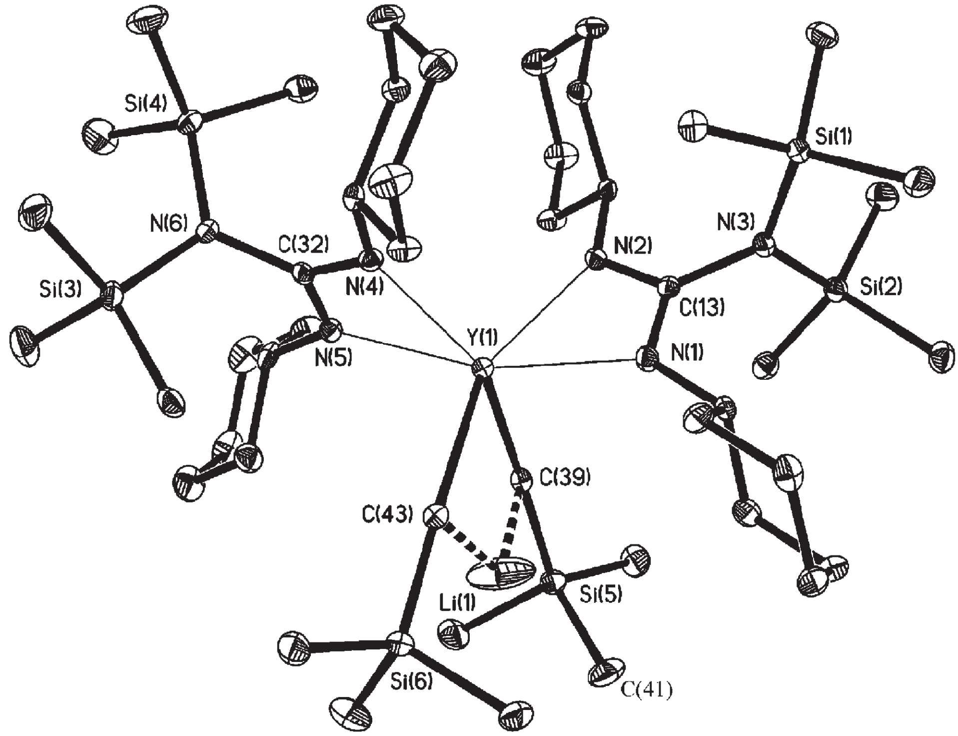
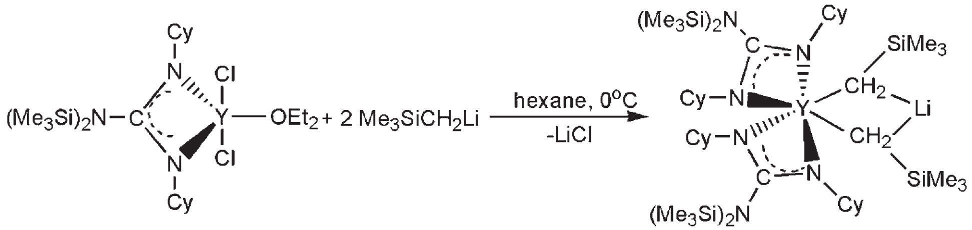


Figure 5. A molecular drawing of **6** [21] shown with 30% probability ellipsoids. All H atoms are omitted.



6 34%

Scheme 1. Synthesis of **6**.

CH_2SiMe_3 groups in **1** (2.461(2) and 2.474(2) Å). The Li(1)–C(39) and Li(1)–C(43) distances are similar at 2.104(5) and 2.084(5) Å; however, the difference between them is statistically significant. The second striking feature of **6** is the extremely low formal coordination number for Li. Since "nature abhors a vacuum" and since the coordination sphere of the Li cation should be filled, its coordination saturation may be achieved by agostic interactions with the methyl groups of the CH_2SiMe_3 ligands. The shortest Li(1) $\cdots$ C(41) measures only 2.514(5) Å and results in concomitant elongation of the Si(5)–C(41) bond length to 1.897(2) Å, a distance that is markedly longer than the analogous bond distances of 1.865(2)–1.875(3) Å in **6**. The G-parameter computed for $Gu^{Cy}Y(CH_2SiMe_3)_2$ by itself (60.4(2)%) is smaller than the expectancy value of 85(3)% for monomeric guanidinate molecules, but for the actual complex **6** the G-parameter is calculated to be 87.3(2)% in accord with the expected value. Steric unsaturation of $Gu^{Cy}Y(CH_2SiMe_3)_2$ allows further molecular modification resulting in formation of **6**.

In conclusion we compare the average value of 85(3)% computed for monomeric complexes with analogous characteristics of dimeric and dinuclear guanidinate complexes of lanthanoids [2]. G-parameters for $[Gu^{iPr}{}_2Ln(\mu_2\text{–}H)]_2$ (Ln = Nd, Sm, Gd, Yb, and Lu), $[Gu^{iPr}{}_2Ln(\mu_2\text{–}Cl)]_2$ (Ln = Nd, Sm, and Y) and $Gu^{iPr}{}_2Ln(\mu_2\text{–}Cl)_2Li(THF)_2$ (Ln = Yb, Lu, and Y) fall in the corresponding ranges 85.6(5)–89.6(2)%, 87.0(2)–89.4(4)%, and 87.4(2)–89.1(2)%, with the average values for each group being 87.7(16), 88.1(12), and 88.2(9)%. The differences among the average G-values for monomeric, dimeric, and bimetallic guanidinate complexes of rare earth metals are not statistically significant. Thus, the 85–88% range of steric saturation in the metal coordination sphere is a universal characteristic of the structural unit (e.g. monomer, dimer. etc.) in crystals of lanthanoid guanidinate complexes.

Herein we have demonstrated that solid angle-based geometrical analysis of non-valent interactions in the coordination spheres of guanidinate complexes of Ln and Y is a viable approach both to studying the individual features of the complexes and to predicting the general complex composition in the condensed phase. This methodology may help understand the formation of "unexpected" products in the course of chemical reactions.

Acknowledgments

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