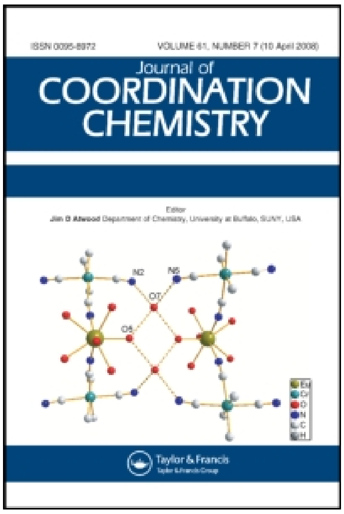

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Dependence of the mutual ligand arrangement in guanidinate complexes of lanthanoids on the ligand solid angles

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Dependence of the mutual ligand arrangement in guanidinate complexes of lanthanoids on the ligand solid angles§

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Mutual ligand arrangement in binuclear lanthanoid complexes of the type $[Gu_2Ln(\mu\text{-}H)]_2$, $[Gu_2Ln(\mu\text{-}Cl)]_2$, and $Gu_2Ln(\mu\text{-}Cl)_2Li(THF)_2$, where Gu is a substituted guanidinato ligand, is quantitatively analyzed based on the ligand solid angle approach. In complexes of Nd, Sm, and Gd the Gu ligands shield up to 87% of the metal and the bidentate ligands on opposite metal centers are in the eclipsed arrangement; in complexes of lanthanoids with smaller ionic radii Y, Yb, and Lu the Gu ligands shield over 88.3% of the metal surface and their staggered conformation is observed. The ligand solid angle approach is illustrated and its application to describing multidentate ligands is demonstrated.

Keywords: Non-bonding interaction; Ligand solid angles; Guanidinate complexes of lanthanides

1. Ligand solid angles

The overall structure of coordination compounds, as well as other kinds of compounds, is determined by all interatomic interactions; chemical bonding between atoms determines the connectivity of the molecule while non-bonding interactions such as repulsion between the outer electron shells of the ligands define the overall shape of the complex. The basis for this approach is the relative independence of the valent and non-valent interactions. Herein we analyze the composition and conformation of several Ln complexes from the point of view of steric interactions between the ligands in the metal coordination sphere.

Recently, we have improved the ligand solid angle method [1] in order to facilitate characterization of steric interactions in organometallic complexes [2, 3]. Currently, this is the best method available for description of the steric behavior of polydentate ligands. The use of geometrical considerations has proven to be fruitful in studying the structure-property parallels for some organometallic compounds [4]. In this approach,

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§Dedicated to Professor Georgy A. Domrachev on the occasion of his 70th birthday

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each ligand is characterized by a $G_M(L)$ value which is the percentage of the metal M coordination sphere shielded by ligand L. In order to compare different ligands in different systems for each ligand a value $G_{2.28}(L)$ is computed; for this calculation the ligand is positioned at 2.28 Å from the metal and the ligand's G-parameter is calculated. For bidentate ligands the distance of 2.28 Å is measured between the metal and the center of the line connecting the coordinated atoms. Frequently, different ligands shield the same region of the metal; the overlap areas of the ligand's solid angles are characterized with the value $G\gamma$ also expressed in percent. Since in most complexes the value $G\gamma$ exceeds zero, the total shielding percentage of the central metal G_M(Complex) is smaller than the sum of all the $G_M(L)$ values: $G_M(\text{Complex}) = \sum_i G_M(L_i) - G\gamma$. By means of example we consider *bis*(1,3-dicyclohexyl-2-*bis*(trimethylsilyl)guanidinato-*bis*(trimethylsilyl)amido-ytterbium(III) (**1**) [5], figure 1. In this complex the Yb is shielded by two Gu^{Cy} ligands with G–parameters $G_{Yb}(Gu^{Cy})$ equal to 33.3% and 33.2%, and by a $N(SiMe_3)_2$ ligand to an extent of $G_{Yb}(N(SiMe_3)_2) = 24.4\%$; the total shielding of the Yb center is expressed as $G_{Yb}(\mathbf{1}) = 90.8\%$, and the $G\gamma(\mathbf{1})$ is 0.1%. The "normalized" values for the ligands are $G_{2.28}(Gu^{Cy}) = 30.6\%$ and $G_{2.28}(N(SiMe_3)_2) = 25.1\%$, indicating that the bidentate ligand is considerably bulkier. The solid angles are illustrated in figure 2.

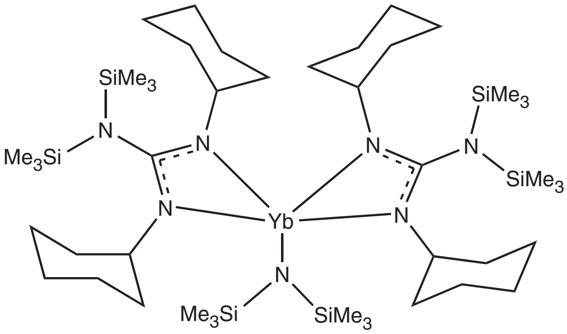

Figure 1. The Yb complex **1** used to illustrate the ligand solid angle approach.

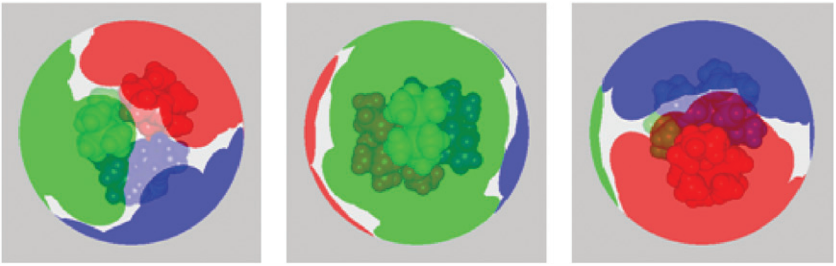

Figure 2. The solid angles of the ligands in **1** are represented by the coloured areas on the sphere of an arbitrary radius of 12 Å. Three different orientations are shown in order to help appreciate the complexity of the ligand contours. The $N(SiMe_3)_2$ ligand and its shadow are green while the 1,3-dicyclohexyl-2-*bis*(trimethylsilyl)guanidinato (Gu^{Cy}) ligands and their respective shadows are red and blue. The rightmost diagram illustrates small overlap between the projections of the red and blue ligands.

In the following discussion we will be concerned with substituted guanidinate ligands $Gu^{iPr} = (Me_3Si)_2NC(N^iPr)_2$. First we would like the compare their steric parameters with a very similar $Gu^{Cy} = (Me_3Si)_2NC(NCy)_2$ (Cy is cyclohexyl) ligands which at first sight looks much more sterically demanding or bulky. In order to meaningfully compare these two ligands we analyzed all complexes with such ligands reported to the Cambridge Structural Database (CSD) [6]. The average values and standard deviations are based on 31 $G_{2.28}$ values for Al, Ti, Zn, Zr, Nd, and Yb in the case of Gu^{iPr}, and on 23 $G_{2.28}$-parameters for Ca, Zn, Sr, Zr, Nb, Hf, Yb, and La in the case of Gu^{Cy}. The $G_{2.28}$-parameters for Gu^{iPr} and Gu^{Cy} based on such data mining are 28.6(6) and 29.9(6)%, respectively. These values indicate that Gu^{iPr} is somewhat smaller than, but comparable to, Gu^{Cy}, but the difference in size is not statistically significant. It is important to indicate that the complexes reported to the CSD were studied by different groups, at different temperatures, and the quality of the datasets varied. The standard deviation of the $G_{2.28}$ parameters is a characteristic of the ligand's flexibility, the smaller the deviation, the 'harder' and less conformationally adaptable the ligand. In the case of Gu^{iPr} and Gu^{Cy} the standard deviations for the $G_{2.28}$ parameters have the same magnitude, indicating that the ligands have comparable flexibility. The latter is insignificant as revealed by the small value of the standard deviation.

2. Geometries of Ln complexes

Here we demonstrate the application of our solid angle approach to the analysis of molecular and crystal structures of *bis*(guanidinate) lanthanide hydride complexes $[Gu^{iPr}{}_2Ln(\mu\text{-}H)]_2$, $Gu^{iPr} = (Me_3Si)_2NC(N^iPr)_2$ [7, 8] and to the products of the reaction between $LnCl_3$ (Ln = Y, Nd, Sm, Yb, Lu) with lithium guanidate [8–12]. Both our and the crystallographic data literature suggest that the principal difference among the $[Gu^{iPr}{}_2Ln(\mu\text{-}H)]_2$ complexes is the mutual orientation of the bidentate ligands on the opposite metal centers. In the complexes of the early lanthanides (Nd, Sm, Gd) the dihedral angles between the C–Ln1–C and C–Ln2–C planes (the C atoms belong to different ligands on the same metal center and are positioned between the coordinating N atoms) comprises 7.5(2)–7.7(3)° (table 1, figure 3); thus the mutual ligand orientation is eclipsed (figure 4a). In complexes of the late lanthanides (Y, Yb, Lu) the corresponding angles measure 86.0(3)–87.5(2)° resulting in staggered orientation of the ligands (figure 4b). In the absence of additional factors the reduction of ionic radii

Table 1. Geometric and steric parameters for hydride complexes.

$[Gu^{iPr}{}_2Ln((\mu\text{-}H)]_2$	Conformation	Ionic radii [13] (Å)	Distances Ln···Ln (Å)	Average distances Ln–N (Å)	$G(Gu^{iPr})$ (%)	G(complex) (%)	$G\gamma$ (%)
Complexes							
Nd^{3+}	Eclipsed	0.983	3.8892(2)	2.45(2)	29.4(2)	85.6(5)	0.14(11)
Sm^{3+}	Eclipsed	0.958	3.8102(2)	2.43(2)	29.8(3)	86.3(2)	0.20(15)
Gd^{3+}	Eclipsed	0.938	3.8069(2)	2.41(3)	29.8(3)	87.0(8)	0.21(13)
Y^{3+}	Staggered	0.900	3.6825(5)	2.36(3)	30.9(2)	88.3(14)	0.7(10)
Yb^{3+}	Staggered	0.868	3.5972(4)	2.317(15)	31.9(2)	89.3(10)	1.8(4)
Lu^{3+}	Staggered	0.861	3.5768(2)	2.31(4)	31.5(2)	89.6(2)	1.0(10)

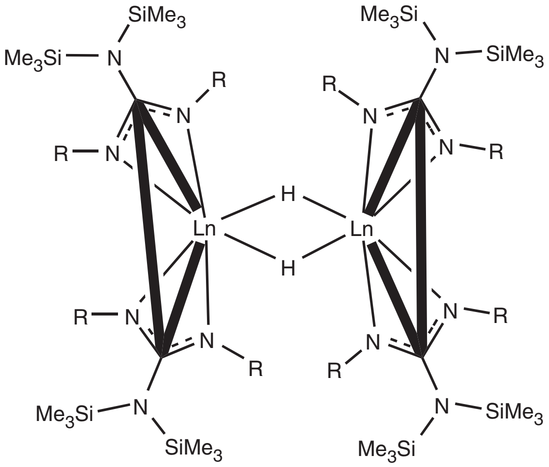

Figure 3. The angle between the highlighted C–Ln–C planes determines the staggered (90°) or eclipsed (0°) mutual ligand arrangement in Ln complexes. The *R* substituents are *iso*-propyl groups.

in the series Nd–Lu results in shorter Ln$\cdots$Ln separations and Ln–N distances and consequently to an increase of non-valent interactions in the coordination spheres of the Ln atoms, bringing about an alteration of the mutual ligand orientations.

It is instructive to consider the ligand *G* values in the structurally characterized complexes, table 1. As the ionic radii of the atoms decrease from Nd to Lu, the Ln–Gu$^{i\mathrm{Pr}}$ distance shortens and the Gu$^{i\mathrm{Pr}}$ ligands approach the metal center closer, progressively shielding a larger area of the metal, as indicated by the G(Gu$^{i\mathrm{Pr}}$) values within the series. The total metal shielding G_{Ln}(complex) concomitantly grows indicating steric saturation in the coordination sphere of the metal centers. An increase in the Gγ parameters is another indication of the degree of crowdedness about the Ln atoms. The Gγ are relatively small; this is typical for ligands of the same size that do not have many conformational degrees of freedom and cannot mesh well. Consequently, in these complexes the possibilities of relieving the steric stress are limited to an elongation of the Ln–N bonds, an asymmetric mode of coordination, and a change in the mutual orientation of the ligands on the adjacent metal centers. These three effects are observed in the discussed complexes to various degrees. In complexes of Y, Yb, and Lu with the more favorable staggered conformation the Gγ values are larger than those in the eclipsed complexes, a manifestation of ligand reorganization into a more compact arrangement.

It was tempting to test the predictive power of our method with a different ligand such as Gu$^{\mathrm{Cy}}$. The $\mathrm{G}_{2.28}$(Gu$^{\mathrm{Cy}}$) exceeds that of Gu$^{i\mathrm{Pr}}$ by 1.3% (*vide supra*), hence it is reasonable to propose the staggered mutual orientation of the ligands Gu$^{\mathrm{Cy}}$ in similar dimeric complexes of Y, Yb, and Lu, as well as other metals with comparable metal radii. Indeed, our preliminary data indicate the correctness of this hypothesis and the full details will be published in a forthcoming article. The currently available data does not allow us to determine the exact ionic radii of the metal corresponding to the transition between the staggered and eclipsed conformations.

We have also used the solid angle approach in analysis of the products of the reactions between lithium guanidinate and $\mathrm{LnCl_3}$. Structural data reveal that

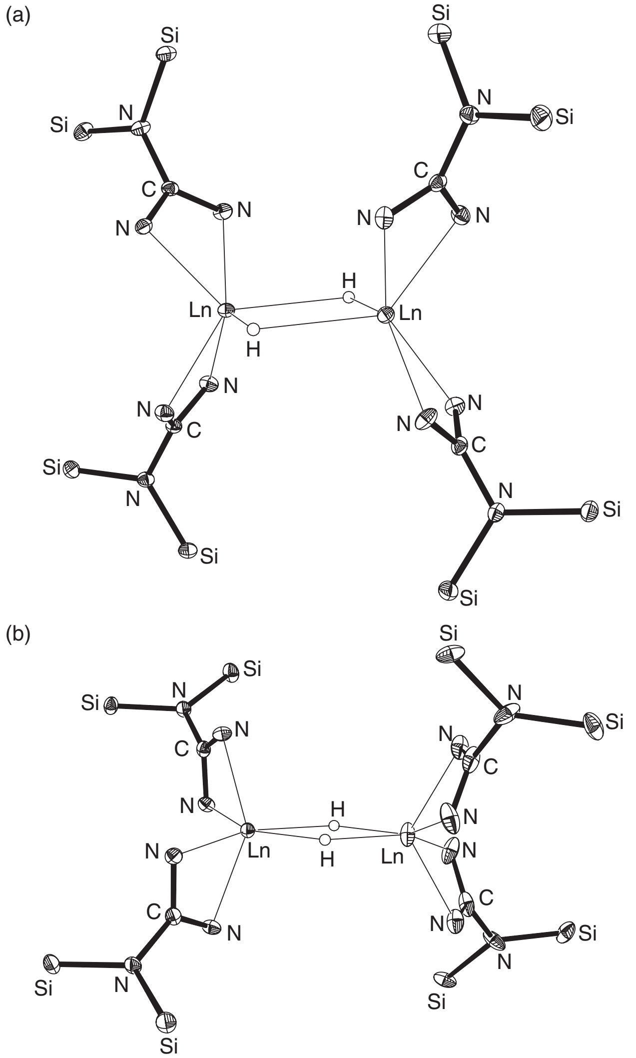

Figure 4. Molecular structure of the $[Gu^{iPr}{}_2Ln(\mu\text{-}H)]_2$ complexes (30% probability thermal ellipsoids): (a) the eclipsed conformation (Ln=Nd, Sm, Gd [7]); (b) the staggered conformation (Ln=Y, Yb, Lu [7, 8]). The Me-groups at Si atoms and ^{i}Pr-groups at N atoms are omitted for clarity.

such reactions involving Nd and Sm lead to the formation of dimeric $[Gu^{iPr}{}_2Ln(\mu\text{-}Cl)]_2$ complexes, while reactions with Yb and Lu yield ate-complexes $Gu^{iPr}{}_2Ln(\mu\text{-}Cl)_2Li(THF)_2$. Reaction involving Y may lead to either product depending on the solvent, figure 5.

For the structurally characterized dimeric complexes $[Gu^{iPr}{}_2Ln(\mu\text{-}Cl)]_2$ [8–12] with Nd and Sm, the eclipsed orientation of the ligands is observed, since the ligand $G_{Ln}(Gu^{iPr})$ values are essentially identical to those in the hydride complexes (table 2). While the $Ln \cdots Ln$ separation increased (compared to those in the hydride complexes) due to the presence of larger bridging Cl atoms, the total shielding of the Ln atoms has

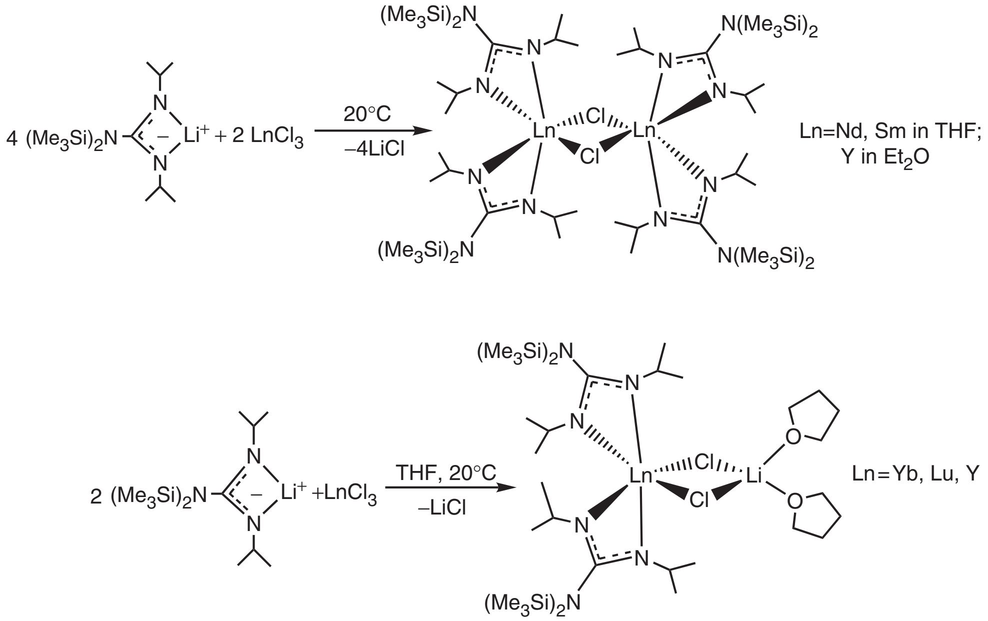

Figure 5. The binuclear Ln complexes formed with Gu^{iPr} in THF and Et_2O[10].

Table 2. Geometric and steric parameters for chloride complexes.

$[Gu^{iPr}{}_2Ln(\mu\text{-}Cl)]_2$	Conformation angle	Ionic radii [13] (Å)	Distances Ln···Ln (Å)	Average distances Ln–N (Å)	$G(Gu^{iPr})$ (%)	G(complex) (%)	$G\gamma$ (%)
Complexes							
Nd^{3+}	Eclipsed	0.983	4.438(4)	2.44(3)	29.2(3)	86.4(3)	0.3(2)
Sm^{3+}	Eclipsed	0.958	4.396(3)	2.41(3)	29.8(4)	86.3(2)	0.2(2)
Y^{3+}	Eclipsed	0.900	4.278(3)	2.36(3)	30.3(3)	89.4(5)	0.5(2)

also increased yielding complexes with slightly better protected metal centers. The Y complexes allow us to gain insight into the structural aspects of the reactions. Namely, the total shielding of Y in $[Gu^{iPr}{}_2Y(\mu\text{-}Cl)]_2$ characterized by parameter $G_Y([Gu^{iPr}{}_2Y(\mu\text{-}Cl)]_2) = 89.4(5)\%$ which is larger than that in the ate-complex, $G_Y(Gu^{iPr}{}_2Y(\mu\text{-}Cl)_2Li(THF)_2) = 87.4(2)\%$. Consequently, due to steric reasons the formation of the ate-complex is more favorable for metals with smaller radii, such as Yb and Lu, and indeed the dimeric complexes are not observed. In this regard the important question is why the dimers form in the case of hydrides where the Ln···Ln separation is shorter, but are not produced in the case of bridging chlorides in which the Ln···Ln separation will be approximately 0.5 Å longer. The difference in the products of similar reactions may be difficult to account for based on purely steric considerations as electronic factors are likely to play a key role.

The complexes discussed herein are binuclear rather than monomeric. In the solid state they exist in either a dimeric form (such as $[Gu^{iPr}{}_2Ln(\mu\text{-}H)]_2$, and $[Gu^{iPr}{}_2Ln(\mu\text{-}Cl)]_2$) or in a bimetallic form $(Gu^{iPr}{}_2Ln(\mu\text{-}Cl)_2Li(THF)_2)$. This observation poses a

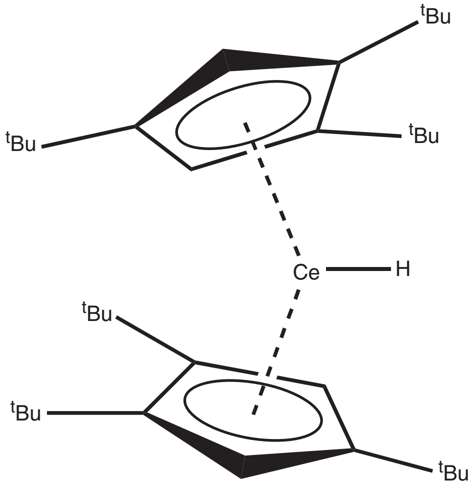

Figure 6. Monomeric Ce complex **2** in which the central metal is shielded to an extent of $G_{Ce}(\mathbf{2}) = 85.9(2)\%$.

question regarding the driving force of monomer unit association into binuclear complexes in solution. Assuming that ligand solid angles in solution are similar to those observed in the solid state, one can reason that insufficient shielding of the metal center by ligands of the monomeric unit (or the lack of steric saturation of the metal's coordination environment) leads to the component association if reagents of appropriate size and donor ability can access the metal center. The steric parameters determine the likelihood of such agglomeration.

In order to illustrate this qualitative reasoning with quantitative data we will consider the shielding of the metal in the monomeric fragments $Gu^{iPr}{}_2Nd(\mu\text{-}Cl)$ [9] and $Gu^{iPr}{}_2Lu(\mu\text{-}H)$ [8] from the respective dinuclear complexes. The G parameters for Nd and Lu are ~67.1(2) and 69.2(2)%. These values are substantially smaller than the G values in the binuclear complexes where the metal coordination spheres are saturated to 86.3(2) and 89.6(2)%, respectively. Thus, insufficient shielding of the metal in the monomeric moieties leads to formation of binuclear complexes such as $[Gu^{iPr}{}_2Ln(\mu\text{-}Cl)]_2$ or $Gu^{iPr}{}_2Ln(\mu\text{-}Cl)_2Li(THF)_2$. An indirect confirmation is the existence of the monomeric *bis*(η^5-l,2,4-*tris*(*tert*-butyl)-cyclopentadienyl)-hydridocerium (**2**) [14], figure 6, in which the central metal is shielded to an extent of 85.9(2)% and no dimerization is observed in the solid state. In the crystal structures of $[Gu^{iPr}{}_2Ln(\mu\text{-}H)]_2$, $[Gu^{iPr}{}_2Ln(\mu\text{-}Cl)]_2$, and $Gu^{iPr}{}_2Ln(\mu\text{-}Cl)_2Li(THF)_2$) there are no interactions between metals and ligands belonging to different dimers. Consequently, we estimate that the shielding of a relatively ionic lanthanoid metal center at approximately 85% is sufficient to prevent further association of donors.

We have demonstrated that the ligand solid angle approach can be successfully used to describe steric behavior of multidentate ligands in lanthanoid complexes with guanidinate ligands. Small changes (~1–2%) in the shielding ability of ligands can yield substantial alterations in the mutual arrangement of the ligands in the metal coordination sphere. The degree of steric saturation of the metal coordination sphere can be used to foresee whether incorporation of additional electron donors into the metal coordination sphere is likely.

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