

On the Stability and Bonding in Bis(η -arene)lanthanide Complexes

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Cocondensation of atoms of the lanthanide elements with 1,3,5-tri-*t*-butylbenzene gives the thermally stable bis(η -arene)lanthanide(0) sandwich compounds for the lanthanides Nd, Tb, Dy, Ho, Er, and Lu, thermally unstable complexes for La, Pr and Sm, and unisolable materials for Ce, Eu, Tm, and Yb; a simple bonding model is proposed to account for the stability trends, and for the magnetism of the stable complexes.

Recently we reported the synthesis of the first authentic example of a zero oxidation state lanthanide complex, the bis(η -arene) sandwich compound $[\text{Gd}(\eta\text{-Bu}^t_3\text{C}_6\text{H}_3)_2]$, and its yttrium analogue.¹ In this paper we describe the reactions of the remaining lanthanide metal atoms with 1,3,5-tri-*t*-butylbenzene, which give new stable bis(η -arene)metal(0) complexes for some of the series, and discuss the magnetism and stability of these compounds in terms of a simple bonding model.

Cocondensation of the lanthanide metal atoms, generated by electron beam evaporation, with an excess of 1,3,5-tri-*t*-butylbenzene at 77 K (as previously described²) gave highly coloured matrices in each case. Room temperature extraction of the products from the reactor with hexane, removal of excess 1,3,5-tri-*t*-butylbenzene by sublimation, and low temperature recrystallisation of the residue from pentane gave the thermally stable crystalline complexes $[\text{Ln}(\eta\text{-Bu}^t_3\text{C}_6\text{H}_3)_2]$ (Ln = Nd, Tb, Dy, Ho, Er, and Lu) in yields of ca. 20–40%.

These compounds are all highly air sensitive, very soluble in hydrocarbon solvents, and sublime with partial decomposition (*ca.* 100°C/10⁻⁴ mbar). They have been characterised by microanalysis, fast atom bombardment mass spectrometry (f.a.b.-m.s., Nujol matrix), and visible spectroscopy.

The lutetium complex displays a weak e.s.r. spectrum at room temperature, exhibiting coupling to ¹⁷⁵Lu (100% *I* = 7/2): *g*_{||} = 2.164, octet, *A* = 9.5 mT; *g*_⊥ = 2.005. This is in contrast to the previously reported yttrium analogue, which is e.s.r. silent at room temperature by virtue of its proposed rapidly relaxing ²E ground state;¹ presumably, in the lutetium case a somewhat slower relaxation allows the observation of a weak e.s.r. signal.

The structure of the holmium complex has been further confirmed by single crystal X-ray diffraction, but will not be reported in any detail here³ since it is virtually identical to that of the previously reported gadolinium counterpart,¹ the C-C bond distances being within one or two standard deviations of those of the latter. The one salient difference lies in the average metal-ring carbon distance, that for the holmium compound [2.580(3) Å] being 0.05 Å shorter than that of the gadolinium analogue [2.630(4) Å]; this effect is presumably a reflection of the smaller radius of the holmium atom, arising from the lanthanide contraction.

Of the remaining lanthanides, [Pr(η-Bu₃C₆H₃)₂] is thermally unstable much above room temperature, and thus purification by removal of the excess tri-*t*-butylbenzene from the cocondensation experiment by sublimation led to extensive decomposition; the complex has therefore been characterised by f.a.b.-m.s. and visible spectroscopy only. What we presume to be [La(η-Bu₃C₆H₃)₂] and [Sm(η-Bu₃C₆H₃)₂] decompose rapidly to the free metal in solution above 0°C and -30°C, respectively, and are only slightly more stable in the solid state, hence they have been characterised solely by the intense band in the visible spectrum assignable to a ligand to metal charge transfer transition, typical of all these compounds.

In the case of Ce, Eu, Tm, and Yb the complexes are unisolable at any convenient temperature, and only colloidal metal and free ligand resulted from the cocondensation of atoms of these elements with 1,3,5-tri-*t*-butylbenzene.

Table 1 summarises all of the above results.

In considering the bonding in these compounds, we take [Y(η-Bu₃C₆H₃)₂] to be the prototype molecule. In an eighteen electron bis(η-arene) transition metal sandwich

complex the HOMOs are the largely metal based a_{1g} and e_{2g} orbitals. The e_{2g} electrons are more stable and more delocalised onto the arene rings than the a_{1g} electrons,⁴ and therefore we expect the fifteen electron yttrium complex to have a ³E_{2g} configuration. This ground state (²E) is in accordance with the e.s.r. observations and the effective magnetic moment of 1.74 Bohr magnetons (B.M.) (*vide infra*). Application of the same bonding model to the lanthanide complexes leads to the notion that three electrons are required to contribute to the e_{2g} orbitals in order to form a stable complex.

By analogy with the yttrium compound it is reasonable to propose that, to a first approximation, a d^{1s²} configuration is required in either the ground or an easily accessible excited state of the lanthanide atom. Figure 1 shows the promotion energies for the f^{*n*s²} → f^{*n*-1}d^{1s²} transitions in the lanthanides. This suggests that Sm, Eu, Tm, and Yb will be the least likely to form stable bis(η-arene) complexes because the promotion energies are the highest, associated with the stabilities of the f⁶, f⁷, f¹³, and f¹⁴ configurations, respectively. The results in Table 1 show that, experimentally, this is indeed the case; the instability of the complexes for these elements may thus be attributed to an insufficient gain in metal-arene bond energy to offset the promotion energy.

Table 1 also shows an area of instability at the beginning of the lanthanide series which is not explicable by the above argument since the ground state of both lanthanum and cerium is d^{1s²} and the promotion energy of praseodymium is small. Here we propose that the instability of these complexes can be attributed to the greater covalent radii of the metals at the beginning of the series and that the tri-*t*-butylbenzene ligand is not sufficiently bulky to kinetically stabilise the metal centre.

The magnetic properties of these complexes should provide a testing ground for this model of their electronic structure. However, it is not easy to predict what coupling scheme should apply in such unusual compounds. Our initial assumption is that the orbital angular momentum of the three e₂ electrons is quenched, as is indicated by the spin-only moment found for the yttrium compound. Otherwise we distinguish three limiting cases for interaction between the three e₂ electrons and the f electrons.

(1) The e₂ electrons precess independently with the magnetic field, *i.e.*

$$\text{spin coupling} < kT$$

$$\mu = [3 + g_J^2 J(J + 1)]^{\frac{1}{2}} \quad (1)$$

where *g*_J is derived by the normal rules for the f^{*n*} configuration.

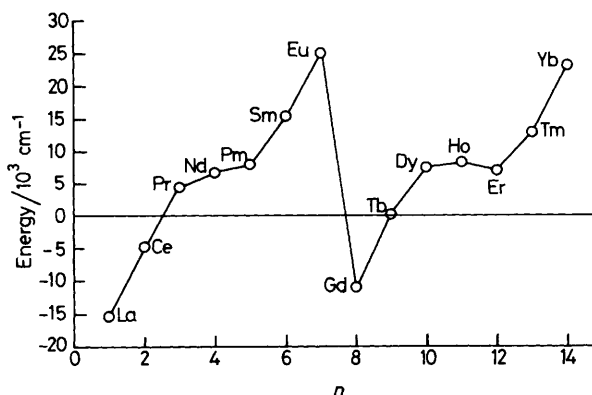


Figure 1. Promotion energies for the f^{*n*s²} → f^{*n*-1}d^{1s²} transition in the lanthanides.⁵

Table 1. Bis(η-Bu₃C₆H₃)lanthanide complexes.

Lanthanide	Atom ground state	Colour	λ _{max./nm}	Stability
Y	d ^{1s²}	Purple	529	Stable
La	d ^{1s²}	Green	637	Decomp. > 0°C
Ce	f ¹ d ^{1s²}	—	—	Unisolable
Pr	f ³ s ²	Purple	541	Decomp. > 40°C
Nd	f ⁴ s ²	Blue	544	Stable
Sm	f ⁶ s ²	Green	691	Decomp. > -30°C
Eu	f ⁷ s ²	—	—	Unisolable
Gd	f ⁷ d ^{1s²}	Purple	542	Stable
Tb	f ⁹ s ²	Purple	540	Stable
Dy	f ¹⁰ s ²	Purple	556	Stable
Ho	f ¹¹ s ²	Deep pink	507	Stable
Er	f ¹² s ²	Red	499	Stable
Tm	f ¹³ s ²	—	—	Unisolable
Yb	f ¹⁴ s ²	—	—	Unisolable
Lu	f ¹⁴ d ^{1s²}	Red-green	495	Stable

(2) That the e_2 electron spin aligns with the spins of the f electrons, the total spin couples with the orbital angular momentum, and the total angular momentum precesses with the field. This assumes

$$\text{spin coupling} \gg \text{L.S coupling}$$

This model leads to values for the total spin of $S^* = (S + \frac{1}{2})$, orbital angular momentum of $L^* = L$, and total angular momentum of $J^* = (J \pm \frac{1}{2})$ [S , L , and J are the values for the f^n configuration].

$$g = 1 + \frac{\mu = g [J^* (J^* + 1)]^{\frac{1}{2}}}{2J^* (J^* + 1)} \quad (2)$$

(3) The e_2 electron spin couples with the total angular momentum of the f electrons, *i.e.*

$$kT < \text{spin coupling} < \text{spin-orbit coupling}$$

$$\mu = g_K [K(K + 1)]^{\frac{1}{2}}, K = J \pm \frac{1}{2}, g_K = g_J \mp \frac{(g_J - 2)}{(2J + 1)} \quad (3)$$

Calculations indicate that K takes the lower value of $J - \frac{1}{2}$ for a less than half filled shell and the higher value $J + \frac{1}{2}$ for a half or greater than half filled shell. This leads to cases 2 and 3 giving identical predictions for the magnetic moments for all molecules under consideration.

The values predicted by these various coupling schemes are given in Table 2 together with the values for the free atoms, those for the Ln^{3+} ions, and the experimental values found for the bis-arene complexes. Overall the divergence of the experimental results from the free atom values is large, indicating significant perturbation of the atomic f shell on binding of the lanthanide atom to the arene rings. This fits with our promotion model. The experimental values tend to lie between the two values predicted by equations 2 and 3 and equation 1 except in the case of Ho where the experimental magnetic moment is less than expected on either scheme. For Er two values for μ were found depending on the temperature. In the low temperature region (< 125 K) μ lies near the value for the two coupled schemes, but at temperatures > 200 K is very close to that for the uncoupled scheme where kT is assumed to be significantly greater than the spin coupling. A similar situation occurs for Nd, although the discrepancy

Table 2. Predicted and experimental magnetic moments.

Metal	Atomic configuration	Atom	Ln^{3+}	$\mu/\text{B.M.}$		
				Case 1	Cases 2 & 3	Expt.
Y	d^1s^2		0	1.73	1.73	1.74
Nd	f^4s^2	2.68	3.62	4.01	2.68	1.57 ^a
Gd	$f^7d^1s^2$	6.51	7.94	8.12	8.94	8.75
Tb	f^9s^2	10.64	9.7	9.87	10.74	10.69
Dy	$f^{10}s^2$	10.61	10.64	10.79	11.67	11.20
Ho	$f^{11}s^2$	9.58	10.61	10.75	11.63	10.10
Er	$f^{12}s^2$	7.56	9.58	9.74	10.61	11.00 ^b
Lu	$f^{14}d^1s^2$		0	1.73	1.73	1.69

^a The value given is that at < 20 K. At temperatures > 200 K a value of 5.3 is found for μ . ^b The value given is that at < 125 K. At temperatures > 200 K a value of 9.7 is found for μ .

between experimental and predicted values for μ is somewhat greater.

In conclusion, the success of these somewhat naive schemes in explaining the magnetic properties of these unusual compounds supports the bonding scheme proposed whereby three of the valence electrons of the lanthanide are involved in bonding to the arene rings and the rest remain in the f shell.

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