

# Study Notes on Lanthanide Chemistry



## Lanthanide Chemistry

### Introduction

There are two series of elements in the f block, each consisting of 14 elements, but it has been observed that a little diverse chemistry has been reported for such many elements. For the 4f elements (the lanthanides), this lack of diversity is normally ascribed to the buried nature of the 4f electrons. The chemical properties of the lanthanides are like those of other electropositive metals. The applications of the lanthanoids derive mainly from the optical spectra of their ions.

### Physical properties and Applications

Lanthanides are soft white metals, and their densities are comparable with 3d series metals. These are relatively poor conductors of heat and electricity as compared to metals. The light lanthanide metals are highly reactive towards oxygen and are normally stored in sealed glass ampoules. The metals undergo reaction with steam and dilute acids but remain passivated by an oxide coating. Most of the metals adopt hcp type structures although cubic close-packed forms are also known for most of the elements, particularly under high pressure.

### General trends

The lanthanides are electropositive metals that commonly occur in their compounds as Ln (III); other oxidation states are stable only when an empty, half-filled, or full f subshell is produced.

### Electronic Absorption Spectra

The spectra of the lanthanoid ions are normally characterized by the following properties:

- Numerous absorptions due to the large number of microstates.
- Weak absorptions due to lack of orbital mixing. Molar absorption coefficients ( $\epsilon$ ) are typically 1-10  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  compared with d metals (close to 100  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ).
- Sharp absorptions due to the weak interaction of the f orbitals with the ligand vibrations.
- Spectra that are to a large degree independent of the ligand type and coordination number.

### Emission spectra and Fluorescence

Lanthanoid ions show strong emission spectra with applications in phosphors and lasers. The most important applications of the lanthanides are generally derived from their emission spectra which is produced after excitation of the f electrons. These emission spectra show many features of the absorption spectra in that they consist of sharply defined frequencies characteristic of the lanthanoid cation and mainly independent of the ligand.

All the lanthanide ions except  $\text{La}^{3+}$  ( $f^0$ ) and  $\text{Lu}^{3+}$  ( $f^{14}$ ) show luminescence, with  $\text{Eu}^{3+}$  ( $f^6$ ) and  $\text{Tb}^{3+}$  ( $f^8$ ) being particularly strong. In part, the strong luminescence is produced due to the large number of excited states that exist, which increases the probability of intersystem crossing (the formation of excited states of different multiplicity from the ground state). The strength of the emission is also observed from the excited electron interacting only weakly with its environment and so having a long nonradiative lifetime (milliseconds to nanoseconds). That is, an electronically excited lanthanoid species rarely loses energy by transfer into vibrational modes because f orbitals overlap only weakly with the ligand orbitals whereas this mechanism provides a pathway for such relaxation in many d-metal systems where there is stronger d-orbital-to-ligand-orbital overlap.

### Magnetic properties

The magnetic moments of lanthanide compounds arise from both spin and orbital contributions. The magnetic moment  $\mu$  of many d-metal ions can be calculated by using the spin-only approximation because the strong ligand field quenches the orbital contribution. For the lanthanides, where the spin-orbital coupling is strong, the orbital angular momentum contributes to the magnetic moment, and the ions behave like almost free atoms. Therefore, the magnetic moment must be expressed in terms of the total angular momentum quantum number J:

$$\mu = g_j \{J(J+1)\}^{1/2} \mu_B$$

Where the Lande g-factor is

$$g_j = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}$$

and  $\mu_B$  is the Bohr magneton.

### Coordination compounds

High coordination numbers with ligands adopting geometries that minimize interligand repulsions are the norm for the lanthanides. The variation in structure adopted is consistent with the view that the spatially buried f electrons have no significant stereochemical influence, and consequently ligands adopt positions that minimize interligand repulsions. In addition, polydentate ligands must satisfy their own stereochemical constraints, much as for the s-block ions and  $Al^{3+}$  complexes. The coordination numbers for  $[Ln(OH_2)_n]^{3+}$  in aqueous solution are thought to be 9 for the early lanthanoids and 8 for the later, smaller members of the series, but these ions are highly labile, and the measurements are subject to considerable uncertainty. Similarly, a striking variation is observed for the coordination numbers and structures of lanthanoid salts and complexes.

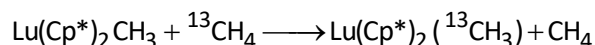
The partially fluorinated  $\beta$ -diketonate ligand  $[C_3F_7COCHCOC(CH_3)_3]^-$ , nicknamed fod, produces complexes with  $Ln^{3+}$  that are volatile and soluble in organic solvents. In terms of their volatility, these complexes can be used as precursors for the synthesis of lanthanoid-containing materials by vapor deposition, such as the high temperature superconductors.

### Organometallic compounds

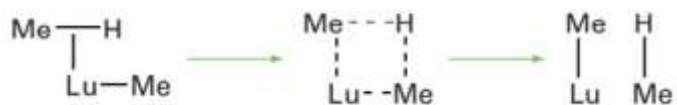
The organometallic compounds of the lanthanides are dominated by good donor ligands, with complexes of acceptor ligands being rare; the bonding in complexes is best treated based on ionic interactions, there are similarities between the organometallic compounds of the lanthanoids and those of the early d metals.

Although the organometallic chemistry of the lanthanoids is less rich as compared to d metals, there are some striking examples of unusual reactions. For instance, a lanthanide organometallic compound can be used for the activation of the C-H bond in methane.

This discovery was based on the observation that CH<sub>3</sub> exchanges <sup>13</sup>C with the CH<sub>3</sub> group attached to Lu:



This reaction can be carried out in deuterated cyclohexane with no evidence for activation of the cyclohexane C–D bond, presumably because cyclohexane is too bulky to gain access to the Lu atom. A mechanism involving a four-centre  $\sigma$ -bond metathesis-type intermediate has been proposed.



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