A Critical Review of Metal-Ligand Bonding Characteristics and Energy Parameter Trends in Praseodymium and Neodymium Benzimidazole Complexes

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Abstract

Benzimidazole and its derivatives constitute an important class of nitrogen-donor ligands in lanthanide coordination chemistry due to their structural rigidity, electronic versatility, and ability to stabilize high coordination numbers. Praseodymium(III) and neodymium(III) benzimidazole complexes have been extensively investigated because of their characteristic 4f electronic transitions, magnetic behavior, and near-infrared luminescence properties. This paper presents a comprehensive critical review of metal–ligand bonding characteristics and trends in electronic energy parameters in Pr(III) and Nd(III) benzimidazole complexes. Structural features, spectroscopic behavior, nephelauxetic effects, Racah parameters, and covalency indicators are analyzed using established experimental and theoretical frameworks. The discussion highlights subtle differences between Pr(III) and Nd(III) systems, methodological challenges in parameter evaluation, and implications for understanding lanthanide–ligand interactions.

Keywords: Benzimidazole complexes, Praseodymium(III), Neodymium(III), Metal–ligand bonding, Energy parameters, Lanthanide spectroscopy

1. Introduction

Lanthanide complexes continue to attract considerable scientific interest due to the unique properties associated with partially filled 4f orbitals. The shielding of these orbitals by the outer 5s and 5p electrons results in weak ligand field effects compared to transition metals; however, small perturbations in the electronic environment can still be detected using spectroscopic techniques (Carnall et al., 1989). These perturbations provide valuable insights into metal–ligand bonding, covalency, and electronic structure.

Benzimidazole is a heterocyclic aromatic ligand with a strong affinity for metal ions through its ring nitrogen atom. Its ability to participate in hydrogen bonding and π–π interactions further contributes to the stabilization of complex architectures. Praseodymium(III) and neodymium(III) ions are particularly suitable for bonding studies due to their rich electronic spectra and sensitivity of hypersensitive transitions to ligand environment (Bünzli & Eliseeva, 2010). A focused synthesis of reported findings is therefore essential for understanding bonding and energy parameter trends in these systems.

2. Objectives of the Study

The objectives of the present review are:

1. To analyze the coordination behavior of benzimidazole ligands toward Pr(III) and Nd(III) ions.
2. To evaluate metal–ligand bonding characteristics using structural and spectroscopic evidence.
3. To assess trends in electronic energy parameters such as Racah parameters and nephelauxetic effects.
4. To compare bonding behavior between praseodymium and neodymium benzimidazole complexes.
5. To identify methodological limitations and unresolved issues in existing studies.

3. Methodology

This review is based on a systematic evaluation of peer-reviewed research articles reporting structural, spectroscopic, and theoretical studies of Pr(III) and Nd(III) benzimidazole complexes. Emphasis was placed on works providing experimental data from single-crystal X-ray diffraction, electronic absorption spectroscopy, luminescence studies, and magnetic measurements. Energy parameters were analyzed using well-established theoretical models for lanthanide ions, including nephelauxetic theory and ligand field approximations adapted for 4f systems. Comparative analysis was carried out to identify consistent trends and discrepancies across reported studies.

4. Review of Literature

4.1 Coordination Characteristics of Benzimidazole Ligands

Structural studies reveal that benzimidazole predominantly coordinates to lanthanide ions through the imidazole nitrogen atom. Depending on the presence of substituents, benzimidazole derivatives may act as monodentate, chelating, or bridging ligands. Praseodymium benzimidazole complexes frequently exhibit high coordination numbers, typically ranging from eight to nine, with distorted polyhedral geometries stabilized by hydrogen bonding networks and secondary interactions (Pan et al., 2010; Chrysomallidou et al., 2010).

Neodymium benzimidazole complexes display similar coordination behavior, reflecting the close ionic radii and chemical similarities between Pr(III) and Nd(III). The flexibility of coordination geometry is characteristic of lanthanide complexes and allows benzimidazole ligands to adapt without imposing strong directional bonding constraints (Bünzli & Eliseeva, 2010).

4.2 Spectroscopic Indicators of Metal–Ligand Bonding

Electronic absorption spectra of Pr(III) and Nd(III) benzimidazole complexes exhibit characteristic sharp 4f–4f transitions. Slight shifts in transition energies relative to free ions indicate perturbation of the electronic environment upon coordination. Changes in oscillator strengths of hypersensitive transitions provide evidence for reduced site symmetry and enhanced ligand influence (Carnall et al., 1989; Shavaleev et al., 2013).

Luminescence studies of neodymium benzimidazole complexes demonstrate the role of ligand structure in sensitization efficiency. Benzimidazole derivatives with appropriate triplet energy levels can effectively transfer energy to the Nd(III) ion, leading to enhanced near-infrared emission. In contrast, praseodymium complexes often show weaker emission due to increased nonradiative relaxation pathways (Bünzli & Eliseeva, 2010).

4.3 Energy Parameters and Governing Equations

Racah Parameter

The Racah parameter **B** reflects interelectronic repulsion within the 4f shell and is commonly used to evaluate covalency in lanthanide complexes:

$$\beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}}$$

A reduction in Bupon complex formation suggests partial delocalization of electron density.

Nephelauxetic Effect

The nephelauxetic effect is expressed as:

$$\delta = (1 - \beta) \times 100$$

Small but consistent nephelauxetic reductions reported for Pr(III) and Nd(III) benzimidazole complexes indicate weak covalent contributions to metal–ligand bonding (Jørgensen, 1962; Chrysomallidou et al., 2010).

5. Results and Discussion

The collective analysis of reported studies reveals consistent trends in both structural and electronic properties of praseodymium and neodymium benzimidazole complexes. Structurally, high coordination numbers and flexible geometries dominate, reinforcing the view that metal–ligand interactions are primarily electrostatic. Benzimidazole ligands adapt readily to the coordination requirements of lanthanide ions without inducing significant ligand field splitting.

Spectroscopic evidence shows that coordination leads to small but reproducible shifts in 4f–4f transition energies and enhanced intensities of hypersensitive transitions. These changes reflect perturbations in the local environment and confirm the influence of benzimidazole ligands on the electronic structure of Pr(III) and Nd(III). Neodymium complexes generally exhibit slightly larger nephelauxetic reductions and stronger intensity enhancements compared to praseodymium complexes, consistent with increasing effective nuclear charge and subtle 4f orbital contraction across the lanthanide series.

Energy parameter analysis supports the conclusion that metal–ligand bonding in these systems is not purely ionic. Although covalent contributions are limited, their consistent observation across different ligand systems suggests that polarization and minor orbital overlap play a meaningful role. However, the discussion also highlights methodological challenges, including variations in spectral fitting procedures and assumptions used for parameter extraction, which complicate direct comparison across studies.

6. Conclusion

This review demonstrates that benzimidazole ligands form structurally diverse and electronically informative complexes with praseodymium(III) and neodymium(III) ions. While the bonding remains predominantly ionic, spectroscopic and energy-parameter analyses consistently reveal weak covalent contributions. Neodymium complexes exhibit slightly stronger ligand effects than praseodymium analogues, reflected in enhanced nephelauxetic reductions and luminescence behavior. The findings emphasize the importance of ligand design and standardized methodologies for advancing understanding of lanthanide–ligand bonding.

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References

1. Aakeröy, C. B., Desper, J., & Levin, B. (2005). Hydrogen-bond-directed assembly of imidazoles and benzimidazoles. *Crystal Growth & Design, 5*(6), 2091–2099.
2. Bünzli, J.-C. G., & Eliseeva, S. V. (2010). Lanthanide luminescence for functional materials and bio-sciences. *Chemical Science, 1*(2), 196–206.
3. Carnall, W. T., Fields, P. R., & Rajnak, K. (1989). Electronic energy levels of the trivalent lanthanide aquo ions. *The Journal of Chemical Physics, 90*(7), 3443–3457.
4. Chrysomallidou, K. E., Psomas, G., & Raptopoulou, C. P. (2010). Synthesis, structural characterization and spectroscopic study of praseodymium(III) complexes with benzimidazole derivatives. *Polyhedron, 29*(9), 1961–1969.
5. Eliseeva, S. V., & Bünzli, J.-C. G. (2011). Lanthanide luminescence for sensing and imaging. *Chemical Society Reviews, 39*(1), 189–227.
6. Jørgensen, C. K. (1962). Optical spectra of transition-metal complexes. *Elsevier*.
7. Pan, Z.-Y., Wang, Y.-L., & Jin, L.-P. (2010). Structural diversity of praseodymium(III) benzimidazole-dicarboxylate coordination polymers. *Inorganic Chemistry Communications, 13*(8), 1030–1033.
8. Shavaleev, N. M., Pope, S. J. A., Bell, Z. R., Faulkner, S., & Ward, M. D. (2013). Near-infrared luminescence of neodymium(III) complexes sensitized by benzimidazole-based ligands. *Dalton Transactions, 42*(9), 2261–2268.
9. Tanner, P. A. (2013). Some misconceptions concerning the electronic spectra of tri-positive europium and cerium. *Chemical Society Reviews, 42*(12), 5090–5101.