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Structural and thermal properties of some neodymium (III) complexes

Udai P. Singh *, Rajeev Kumar

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India

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Abstract

Some neodymium (III) complexes (**1**–**5**) having tp [hydrotris (pyrazol-1-yl) borate], bipy (2,2′-bipyridine) and phen (1,10-phenanthroline) as nitrogen donor ligands have been synthesized. These complexes have been characterized by elemental analysis, IR, thermal, magnetic measurements and X-ray crystallographically. The X-ray studies demonstrated that complexes **1**, **2** and **3** crystallize in triclinic space group $P\bar{1}$ with cell dimensions $a = 11.745(3)$, $b = 12.566(3)$, $c = 17.654(5)$ Å for **1**; $a = 11.561(5)$, $b = 12.020(5)$, $c = 12.286(5)$ Å for **2**; $a = 8.474(3)$, $b = 8.832(3)$, $c = 15.788(5)$ Å for **3**. Complexes **4** and **5** crystallize in the monoclinic space group $P2(1)/c$ with cell dimensions $a = 18.396(12)$, $b = 10.764(6)$, $c = 13.112(9)$ Å for **4**; $a = 12.587(4)$, $b = 10.629(3)$, $c = 22.696$ (8) Å for complex **5**. In all these complexes except **1**, the coordination number around neodymium center is eight whereas in complex **1**, each neodymium is seven coordinated. The IR studies suggested that the benzoate groups in complexes **1** and **2** are coordinated as bidentate bridging whereas in complex **5**, the coordination of benzoate groups occur in both bridging as well as in bidentate chelating manner. Thermogravimetric analysis showed that in complexes **3** and **4**, the loss of coordinated methanol molecule occurs at 135 °C and of coordinated water molecule occurs at 165 °C. This is followed by the complete decomposition and the formation of thermally stable neodymium oxide (Nd_2O_3).

Keywords: Neodymium (III); Carboxylate ligands; Bipyridine; Phenanthroline; X-ray studies

1. Introduction

Lanthanide compounds have interesting photophysical properties because of their long-lived and line-like emission bands in near-UV, visible and near-IR region. Due to their emission at 879, 1064 and 1337 nm, the neodymium (III) complexes became popular and play important role in developing various novel organic Nd(III) devices [1–3]. In general, the direct excitation of Nd(III) is difficult because of the weak (Laporte-forbidden) nature of their f–f transitions [4] but this can be overcome by coordinating the neodymium (III) ion with suitable organic ligands. Several neodymium compounds having organic chromophores are available in literature [5–9] but only few of them are having the luminescence properties.

The synthesis and structural studies of neodymium complexes with efficient photo luminescent properties continues to be an active area of research. Several classes of ligands have been utilized for the preparation of Nd(III) complexes [10–17], but the majority of them belongs to the group of carboxylic acid derivatives [18–26]. The neodymium complexes with carboxylate ligands are very fascinating because of variations in coordination modes of carboxylate anions which resulted the formation of different type of compounds as monomer [18–20], dimmer [21–23] and some times polymer [24–26]. The neodymium formate complexes [27–29] have also been reported for use in studies of the second harmonic generation of laser radiation Nd^{3+}: YAG laser ($\lambda_{2\omega} = 532$ nm). Different complexes available in literature suggested that some neodymium (III) complexes have luminescence properties in the NIR region, however neodymium (III) complexes with NIR-luminescence properties are very scare in literature. The less examples of suitable neodymium (III) complexes with NIR-luminescence properties and fascinating coordination mode of the benzoate ligands have prompted us to prepare the neodymium complexes having benzoate group as well as NIR luminescence

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* Corresponding author. Tel.: +91 1332 285329; fax: +91 1332 273560.
E-mail address: udaipfcy@iitr.ernet.in (U.P. Singh).

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properties. As it has been reported in literature that small variations in ligand structure can lead to remarkable changes in different spectroscopic properties, the different type of supporting ligands, viz., Ktp, bipy, phen have been employed in present study. The literature also revealed that the lanthanide complexes of 2,2′-bipyridine and 1,10-phenanthroline play important role in studies with DNA [30,31] but majority of the complexes reported for bipy and phen are with lanthanide nitrate. In view of potential applications of neodymium complexes and the fascinating properties of carboxylate ligands, the present paper reports the synthesis, structural as well as thermal studies of some neodymium (III) complexes.

2. Experimental

All solvents were purified with suitable drying agents using the literature methods [32]. The benzoic and fluorobenzoic acid were commercially available from s.d.fine-chem Limited, Mumbai and their sodium salts were prepared by reacting with the appropriate amount of sodium hydroxide in water. 2,2′-Bipyridine was purchased from s.d.fine-chem Limited, Mumbai whereas 1,10-phenanthroline was purchased from Central Drug House, Delhi. Neodymium chloride of the highest grade was purchased from Indian Rare Earths Ltd., India and the potassium salt of the ligand hydrotris(pyrazol-1-yl)borate [K(tp)] was prepared by published procedure [33].

2.1. Synthesis

*2.1.1. Synthesis of [(tp)Nd(μ-OBz)$_4$Nd(tp)] (**1**)*

A mixture of sodium benzoate (0.144 g, 1.0 mmol) and [K(tp)] (0.125 g, 0.5 mmol) in 15.0 ml methanol was added to the methanolic solution of $NdCl_3 \cdot 6H_2O$ (0.188 g, 0.5 mmol). The suspension was stirred at room temperature for 4 h. After removal of solvent under vacuum, the residue was extracted with dichloromethane (three times) and the combined solution was filtered to eliminate the salt. The filtrate was dried under vacuum to afford a powder solid in 78–80% yield. Recrystallization of the resultant solid from dichloromethane at 4 °C gave crystals suitable for X-ray measurements. The elemental analysis was performed on a completely dried sample for several hours. Anal. Calcd (%) for $C_{46}H_{40}N_{12}O_8B_2Nd_2$: C, 46.08; H, 3.36; N, 14.01. Found C, 46.24; H, 3.05; N, 14.14. IR (KBr, cm^{-1}): 2458 (νB—H), 1605 (ν_{as}COO), 1508 (ν_sCOO). Magnetic moment μ_{eff} (290 K): 3.55 B.M.

*2.1.2. Synthesis of [(tp)(pz)Nd(μ-p-F-OBz)$_4$Nd(pz)(tp)]·2CH$_2$Cl$_2$ (**2**)*

A mixture of sodium fluorobenzoate (0.162 g, 1.0 mmol), [K(tp)] (0.125 g, 0.5 mmol) and pyrazole (0.034 g, 0.5 mmol) in 15.0 ml methanol was added to the methanolic solution of $NdCl_3 \cdot 6H_2O$ (0.188 g, 0.5 mmol). The suspension was stirred at room temperature for 5 h. After 5 h. stirring, the solvent was removed under vacuum, the residue was extracted with dichloromethane (three times) and the solution was filtered on Celite. The filtrate was dried under vacuum and light purple powder was obtained in 83–85% yield. Recrystallization of compound from dichloromethane at 4 °C gave crystals suitable for X-ray measurements. The elemental analysis was performed on a dried sample for several hours. Anal. Calcd (%) for $C_{52}H_{44}N_{16}O_8F_4B_2Nd_2$: C, 44.36; H, 3.12; N, 15.92. Found C, 43.88; H, 3.25; N, 15.41. IR (KBr, cm^{-1}): 2458 (νB—H), 1603 (ν_{as}COO), 1506 (ν_sCOO). Magnetic moment μ_{eff} (290 K): 3.65 B.M.

*2.1.3. Synthesis of [Nd(bipy)$_2$Cl$_3$·CH$_3$OH] (**3**)*

To the methanolic solution of $NdCl_3 \cdot 6H_2O$ (0.188 g, 0.5 mmol), 2,2′-bipyridine (0.156 g, 1.0 mmol) solution (in methanol, 10.0 ml) was added dropwise and the resulting solution was stirred for 8 h. After stirring, the reaction mixture was filtered on Celite and the solvent was evaporated under vacuum. The resultant solid in 84–86% yield was recrystallized from acetonitrile–methanol mixture at 4 °C. The elemental analysis was performed on a several hours vacuum dried sample. Anal. Calcd (%) for $C_{21}H_{20}N_4OCl_3Nd$: C, 42.35; H, 3.36; N, 9.41. Found C, 41.84; H, 3.09; N, 9.08. IR (KBr, cm^{-1}): 1595 (ν C=C), 1569 (ν C=N). Magnetic moment μ_{eff} (290 K): 3.50 B.M.

*2.1.4. Synthesis of [Nd(phen)$_2$Cl$_3$·OH$_2$]·CH$_3$OH (**4**)*

This compound was prepared in 85–86% yield by the method as outlined for **3**. This compound was recrystallized from methanol at room temperature. Anal. Calcd (%) for $C_{24}H_{18}N_4OCl_3Nd$: C, 45.78; H, 2.86; N, 8.90. Found C, 44.86; H, 2.65; N, 8.45. IR (KBr, cm^{-1}): 1626 (ν C=C), 1581 (ν C=N), 722 and 851 (out of plane hydrogen deformation vibrations of phenanthroline). Magnetic moment μ_{eff} (290 K): 3.57 B.M.

*2.1.5. Synthesis of [Nd(OBz)$_3$(phen)]$_2$·2CH$_3$OH (**5**)*

The methanolic solution of $NdCl_3 \cdot 6H_2O$ (0.188 g, 0.5 mmol) was added to a mixture of sodium benzoate (0.216 g, 1.5 mmol) and 1,10-phenanthroline (0.099 g, 0.5 mmol) in 15.0 ml methanol. The reaction mixture was stirred for 8 h and filtered on Celite. The filtrate was dried under vacuum and the light purple powdered compound was obtained in 77–79% yield. The elemental analysis was performed on vacuum dried sample for several hours. Anal. Calcd (%) for $C_{66}H_{46}N_4O_{12}Nd_2$: C, 57.62; H, 3.34; N, 4.07. Found C, 57.25; H, 3.08; N, 4.18. IR (KBr, cm^{-1}) 1609 (ν C=C), 1567 (ν C=N), 1530 (ν_{as}COO), 1418 (ν_sCOO), 724 and 848 (out of plane hydrogen deformation vibrations of phenanthroline). Magnetic moment μ_{eff} (290 K): 3.61 B.M.

2.2. Physical measurements

Elemental analysis (C, H, N) were determined on Vario EL elementar analyser. Infrared spectra (in KBr) were obtained on a Thermo Nikolet Nexus spectrometer. The