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Aging effect on bonding properties of fluorescent neodymium materials

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Abstract

The neodymium complexes with nitrogen and oxygen donor pyrazoline ligands were synthesized by the conventional method. To observe the effect of the change in environment, the mixed ligand complexes along with pure neodymium-pyrazoline complexes were synthesized. Shelf-life of these newly synthesized materials was studied by the absorbance spectral peaks, whereby the aging effect was clearly seen in all these neodymium complexes. Considering the effect of time and shelf-life, the neodymium-pyrazoline complexes show comparatively lower stability than the mixed ligand complexes of neodymium. The detailed characteristics of these newly synthesized materials are presented in this manuscript.

Keywords: Neodymium; Pyrazoline; Mixed ligand complexes; Aging

1. Introduction

The lanthanide complexes seem to seek the attention in its designing and synthesis due to its potential properties in different fields. Lanthanides are well known to have optical properties [1–6] used in the field of optoelectronic technology [7], optical communication system and amplifiers [8], backlights [9], mechanoluminescence, bioscience and bio imaging [2,10–21], solar energy conservation and technology [22–26] etc. The rare earth complexes are well known to have the luminescence property with different ligands [27,28] as well as in doped materials [29]. The luminescence property is somehow related to the less known redox behavior of the inner transition elements [30]. After the synthesis and structural determination, the stability of the rare earth complexes is of considerable interest. The thermodynamic stability [31], mechanical resistance, stability towards the chemicals and the thermal resistance [32–37] are well explained in the literature. Comparatively less attention has been devoted to the stability of the complexes with respect to time. Zheng et al. discussed the time dependent dielectric properties of neodymium-ceramics with the help of XRD pattern [38]. By perceiving the importance of rare earth complexes in diverse field, we have taken here an example of

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neodymium to study the most important fluorescence behavior. The stability of the complexes, the bonding and structural properties, were taken as an important phenomenon to consider these fluorescent active neodymium complexes at commercial level. Stability with respect to time and high quantum yield, make these materials of high commercial value.

2. Material and methods

All the solvents (benzene, methanol, ethanol etc.) were rigorously dried and purified by standard methods before use [39]. The chemicals used are of analytical grade. Neodymium chloride hexahydrate (HPLC), sodium diethyldithiocarbamate (S.D. Fine), o-hydroxyacetophenone (CDH) and benzaldehydes (E. Merk) were used as received. Pyrazolines and potassium ethyl xanthate were prepared by the reported methods [40,41].

2.1. Synthesis of metal-pyrazoline complexes by 1:1 M ratio of metal chloride and pyrazoline ligand

Freshly cut pieces of sodium metal were taken with excess of isopropanol and refluxed for about 30 min until a clear solution of sodium isopropoxide was obtained. The benzene solution of 3(2-hydroxyphenyl)-5-(4-substituted phenyl) pyrazoline was added in the above prepared sodium isopropoxide and the reaction mixture was further refluxed for 2 h, whereby a yellow colored solution was obtained. The content was cooled to room temperature after that, methanolic solution of metal chloride was added with constant stirring. The stirring continued for about 2 h, till the color of the reaction mixture underwent a change from greenish yellow to greenish brown. The reaction mixture was filtered to remove precipitated NaCl. The solvent was removed under reduced pressure from the filtrate whereby dirty greenish brown solid was obtained. Complex 1–4 were prepared by this procedure [Reaction Scheme 1].

2.2. Synthesis of mixed ligand complexes of metal chloride with pyrazoline and diethyldithiocarbamate/ethylxanthate in 1:1:1 M ratio

The mixed ligand complexes of neodymium with diethyldithiocarbamate and ethylxanthate were prepared by two steps. In first step, a methanolic solution of neodymium chloride was added in benzene solution of pyrazoline and refluxed for about 6 h. The color of solution underwent change, after that, the content was cooled at room temperature. In second step, the methanolic solution of sodium diethyldithiocarbamate/potassium ethylxanthate was added in the above content and stirred for about 8–9 h at room temperature. The reaction mixture was filtered to remove the precipitated NaCl or KCl. The solvent was reduced from the filtrate in vacuum, which yielded some insoluble colored material, which was finally separated by filtration. The solid thus obtained was washed with water. The complex 5–12 were prepared by this method [Reaction Scheme 2].

3. Characterization measurements

For the determination of molecular weights, the molecular ion peak was detected by DART mass spectra on a JMS-T100LC Accu TOF mass spectrometer. The accelerating voltage was 10 kV and spectra were recorded at room temperature. Elemental analysis (C, H, N and S) were carried out on an Elementar Vario EL III C, H, N, S analyzer. Chlorine was estimated by Volhard's method [42]. Oxygen was analyzed by EuroVector elemental analyzer. Neodymium is estimated as Nd_2O_3 by reported analytical method [43]. IR spectra were recorded on Thermo Nicolet Fourier Transform Infrared Spectrometer (Model: 6700) in the range 5000–50 cm^{-1}. Electronic spectra were recorded in dichloromethane on Varian, Cary 5000 UV–visible spectrophotometer within the range 1000–230 nm. Scanning electron microscopy (SEM) studies have been carried out on JEOL

$$NdCl_3.6H_2O + [C_{15}H_{12}N_2OX]Na \longrightarrow [Nd(C_{15}H_{12}N_2OX)Cl_2.nH_2O] + NaCl$$

Reaction Scheme 1. Synthesis of Neodymium-Pyrazoline complex.

$$[NdCl_2(C_{15}H_{12}N_2OX).nH_2O] + Na[C_5H_{10}NS_2].3H_2O \longrightarrow [Nd(C_5H_{10}NS_2)(C_{15}H_{12}N_2OX)Cl.nH_2O] + NaCl$$

$$[NdCl_2(C_{15}H_{12}N_2OX).nH_2O] + K[C_2H_5OCS_2] \longrightarrow [Nd(C_2H_5OCS_2)(C_{15}H_{12}N_2OX)Cl.nH_2O] + KCl$$

Reaction Scheme 2. Synthesis of Neodymium-pyrazoline-diethyldithiocarbamate and Neodymium-pyrazoline-ethylxanthate complex.