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Lanthanum(III) and praseodymium(III) derivatives with dithiocarbamates derived from α-amino acids

Anita Rai[a,*], Soumitra K. Sengupta[b], Om P. Pandey[b]

[a] Department of Chemistry, Jagatpur P.G. College, Varanasi 221005, India
[b] Chemistry Department, D.D.U. Gorakhpur University, Gorakhpur 273009, India

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Abstract

Lanthanum(III) and praseodymium(III) complexes with dithiocarbamates have been synthesized by the reactions of lanthanum(III) and praseodymium(III) chloride with barium dithiocarbamate and complexes of type $[LnCl(L)H_2O]_n$ have been obtained (where Ln = La(III) or Pr(III); L = barium salt of dithiocarbamate derived from glycine, L-leucine, L-valine, DL-alanine). The complexes have been characterized by elemental analysis, molar conductance, electronic absorption and fluorescence, infrared, far infrared, ^{1}H NMR spectral studies. The presence of coordinated water molecule is inferred from thermogravimetric analysis which indicates the loss of one water molecule at 150–170 °C.

The oscillator strength, Judd–Ofelt intensity parameter, stimulated emission cross-section, etc. have been obtained for different transitions of Pr^{3+}.

Keywords: Oscillator strength; Stimulated emission cross-section; Dithiocarbamate complexes; Bidentate; Thioureid bands

1. Introduction

Dithiocarbamate complexes have been reported to a great number of metal ions, and they have been used extensively in analytical chemistry [1,2]. They also have been used with success as fungicides, pesticides, vulcanization accelerators, floatation agents and high-pressure lubricants [3,4]. Some papers have appeared on simple dithiocarbamate derivatives of transition metals [5–8]. In all these derivatives, the dithiocarbamate group coordinates through two sulphur atoms resulting in the formation of four membered chelate rings. It has also been observed that the dithiocarbamate ligands, by virtue of their low charge and small bites (∼2.8–2.9 Å), are well suited for stabilization of higher coordination states of metals. The introduction of the dithiocarbamate group in α-amino acids gives rise to molecules with upto three ligating residues, amino (N), dithiocarbamato ($-CS_2$) and carboxylate ($-COO^-$). Complexes of Ni(II) with alkane thiols, where coordination takes place through the sulphur atoms, have been used to study the active centers existing in urease from jackbean (*Canavalia ensiformis*) [9]. However, the complexes formed between metallic cations and dithiocarbamate derivatives of α-amino acids have rarely been reported (see Ref. [10]). In this paper, we report the synthetic and structural aspects of the complexes of lanthanum(III) and praseodymium(III) with dithiocarbamates derived from α-amino acids. We have also calculated the spectroscopic parameters for Pr^{3+} in the dithiocacrbamate hosts using absorption and fluorescence spectra.

The structures of the ligands, used for the present study are shown below (I):

$Ba(S_2C - NH - CH - (R) - COO)$

R	**Abbrevation**
H	GDTC.Ba
$(CH_3)_2CH - CH_2$	LDTC.Ba
$(CH_3)_2CH$	VDTC.Ba
CH_3	ADTC.Ba

(I)

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[*] Corresponding author. Present address: C/O Prof. S.B. Rai, Physics Department, BHU, Varanasi 221005, India. Tel.: +91 542 2570711; fax: +91 542 2368468.
E-mail address: sbrai49@yahoo.co.in (A. Rai).

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Table 1
Characterization data of lanthanum(III) and praseodymium(III) complexes

Reactants (molar ratio)	Refluxing time (h)	Product yield (%)	Colour	Found (calculated%)			
				C	H	N	Ln
$LaCl_3$ + GDTC.Ba (1:1)	12	[La(GDTC)Cl(H_2O)] (70)	Cream	10.46 (10.55)	1.29 (1.48)	3.90 (4.10)	40.60 (40.67)
$PrCl_3$ + GDTC.Ba (1:1)	12	[Pr(GDTC)Cl(H_2O)] (70)	Cream	10.32 (10.49)	1.35 (1.47)	3.92 (4.08)	41.0 (41.01)
$LaCl_3$ + LDTC.Ba (1:1)	14	[La(LDTC)Cl(H_2O)] (55)	White	21.06 (21.14)	3.18 (3.30)	3.34 (3.52)	34.86 (34.93)
$PrCl_3$ + LDTC.Ba (1:1)	16	[Pr(LDTC)Cl(H_2O)] (60)	Off white	21.02 (21.04)	3.10 (3.28)	3.43 (3.51)	35.20 (35.26)
$LaCl_3$ + VDTC.Ba (1:1)	13	[La(VDTC)Cl(H_2O)] (68)	Cream	18.66 (18.79)	2.70 (2.89)	3.43 (3.65)	36.10 (36.21)
$PrCl_3$ + VDTC.Ba (1:1)	13	[Pr(VDTC)Cl(H_2O)] (65)	Cream	18.60 (19.69)	2.70 (2.88)	3.51 (3.63)	36.34 (36.54)
$LaCl_3$ + ADTC.Ba (1:1)	17	[La(ADTC)Cl(H_2O)] (50)	Light cream	13.40 (13.51)	1.89 (1.98)	3.90 (3.94)	39.00 (39.07)
$PrCl_3$ + ADTC.Ba (1:1)	17	[Pr(ADTC)Cl(H_2O)] (55)	Light cream	13.32 (13.44)	1.86 (1.97)	3.84 (3.92)	39.35 (39.41)

GDTC.Ba, barium salt of dithiocarbamate derived from glycine; LDTC.Ba, barium salt of dithiocarbamate derived from leucine; VDTC.Ba, barium salt of dithiocarbamate derived from valine; ADTC.Ba, barium salt of dithiocarbamate derived from alanine.

2. Experimental

The reagents and solvents were of analytical grade and lanthanum(III) and praseodymium(III) chloride were purchased from B.D.H. The ligands were prepared by the method similar to that described by Musil and Irgolic (see Ref. [10]) in the inert atmosphere.

2.1. Preparation of the complexes

To a solution of $LnCl_3$ (0.01 mol) in methanol (~50 cm^3) was added appropriate amount of ligand (0.01 mol). The reaction mixture was refluxed for 12 h. The precipitate was obtained. The precipitated complex was removed by filtration and washed with methanol and dried in vacuo. *Yield*: (50–70%) complex. The details of the reactions along with the analytical data of the products are given in Table 1.

The IR and NIR spectra of these complexes were recorded using Jasco-FTIR-5300 and Lambda-19-UV–vis–NIR double beam spectrophotometers. For fluorescence studies we have used 457.9 nm line from a 10 W Ar^+ laser coupled with 0.5 m Spex monochromator.

3. Results and discussion

A systematic study of the reactions of lanthanum(III) or praseodymium(III) chloride with barium dithiocarbamate of α-amino acids (molar ratio 1:1) in methanol may be represented by the following equation:

$$LnCl_3 + Ba(S_2C\text{–}NH\text{–}CH(R)\text{–}COO)$$

$$\xrightarrow{\text{Methanol}} LnCl(H_2O)(S_2C\text{–}NH\text{–}CH(R)\text{–}COO) + BaCl_2$$

$$\{Ln = La(III)\ \text{or}\ Pr(III)\}$$

Physical and analytical data of the trivalent lanthanum(III) and praseodymium(III) complexes are given in Table 1. The complexes are insoluble in all common organic solvents, but only partially soluble in dimethyl formamide and dimethylsulphoxide. The presence of coordinated water molecule is inferred from thermogravimetric analysis, which indicates the loss of one water molecule at 150–170 °C.

3.1. Magnetic moments and electronic spectra

In the electronic spectra of diamagnetic lanthanum(III) complexes, no band appears due to f–f transition, which is in accordance with the $5d^04f^0$ configuration of lanthanum(III). The magnetic moment of the praseodymium(III) complexes lie in the range of 3.52–3.60 μ_B. These values show little deviation from the Van Vleck values [11] and those of hydrated sulphate. This is probably due to very effective shielding of 4f electrons from external forces by $5s^2$ and $5p^6$ electrons.

The triply ionized praseodymium ion has the outer electronic configuration $4f^25s^2sp^6$ and to some extent follows L–S coupling scheme. The outer 5s, 5p sub shells shield the 4f electrons from the effect of coordinated ligands to a large extent if not completely. The transition in between the states arising from the same configuration are forbidden according to Laporte rule however they are made allowed due to mixing of the levels arising from $4f^25s^25p^6$ with levels from $4f^15d^15s^25p^6$ configuration. The ground state of Pr^{3+} is $^3H_4$. The electronic absorption spectra of these compounds show six bands in between 400 and 2000 nm region at 1930, 1560, 583, 481, 469 and 448 nm (see Fig. 1). These bands

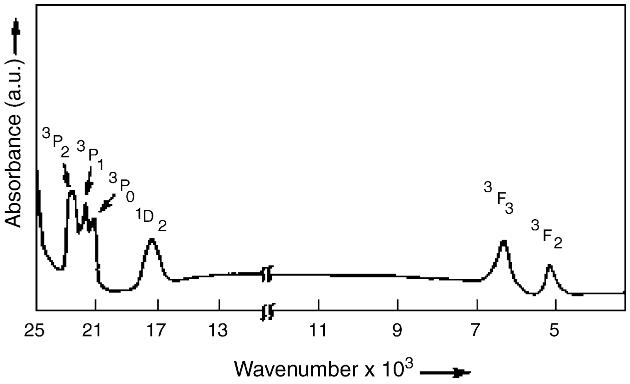

Fig. 1. Absorption spectrum of Pr(III) doped in barium thiocarbamate derived from glycine.