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SYNTHESIS AND CHARACTERIZATION OF 2, 2' BIPYRIDYL ADDUCTS OF LANTHANUM (III) DITHIOCARBAMATES

Jiya Lal Maurya
Assistant professor
Department of Chemistry
Brahmanand College, Kanpur.

Some lanthanum (III) dithiocarbamates of the bipyridyl adducts LaL_3. (bipy) [Where L= dimethyldithiocarbamate (Me_2DTC^-), piperidine dithiocarbamate ($PipDTC^-$), morpholine dithiocarbamate ($MorphDTC^-$) (bipy = 2,2' bipyridyl)] have been synthezied and charecterized by elemental analysis and various physico-chemical technique. Molar conductance measurements show the non ionic behaviour of the complexes. Thermo-gravimetric analysis of the complexes starts to decompose on further heating to a mass of lanthanum sulfide (La_2S_3). Infrared spectra suggest mono-anionic bidentate mode of bonding of the ligands.

Keywords: Lanthanum dithiocarbamate bipyridyl, adduct, Spectroscopic studies.

Introduction

Chemistry of dithiocarbamates could be dated to start in the early twentieth century precisely, in 1930 Commercial application was used as a fungicide for the first time during World War II [1]. Dithiocarbamates are highly versatile mono-anionic chelating ligands which form stable complexes with all transition & lanthanide elements and also with the majority of main groups [2-4]. The chemistry of dithiocarbamate complexes can be seen in the presence of lone pair of electron donor sulphur atoms [5,6]. Metal complexes of dithiocarbamates have innumerable value in many fields. The various applications that can be cited are in chemical process, such as vulcanization in rubber industry [7], paraffin base oil lubricant additives [8,-10] & many more like in the areas of analytical chemistry [11], photochemistry [12] antimicrobial activity [13,14] medicine [15] and electrochemical sensors [16]. More recently nanomaterial dithiocarbamate complexes are widely applied in catalysis, electronic, optical and magnetic materials because of their unique chemical and physical properties [19]. Besides, they are also used in light emitting devices, solar cells and bio-imaging Lanthanum dithiocarbamates as precursors of lanthanum sulfide (Ln_2S_3) is applicable in a number of processes like, for the fabrication of lanthanide sulfide nanoparticles [20,21]. Mostly, dithiocarbamates reacts with lanthanide (III) ion to form neutral [Ln(Dtc)3L] complexes [L = 2,2′-bipyidine or 1,10-phenanthroline].

Synthesis of sodium dithiocarbamates

For synthesis of piperidine dithiocarbamate, a solution of piperidine 0.1 mol (10ml) in20 ml ethanol was added to a mixture of carbon disulfide, 0.1 mol (6.25ml) and sodium hydroxide 50% aqueous solution (8 ml), at approximately 4°C temerature after stirring for 2 h. The obtained precipitate was filtered, washed with ether, recrystallized from acetone and dried *in vacuo*. m.p. 160 °C.

Synthesis of 2, 2' bipyridyl adducts of lanthanum dithiocarbamates

The 2, 2' bipyridyl of adducts of lanthanum (III) dithiocarbamates were prepared according to the following reaction

$$LaCl_3.7H_2O + bipy + 3\,PipDTC \xrightarrow{Ethanol} [La(PipDTC)_3(bipy)]$$

When dimethylamine (diMeDTC), piperidine (PipDTC), diphenylamine (diPhDTC), morpholine (MorphDTC).

Preparation of lanthanum piperidine dithiocarbamate 2, 2’ bipy

A solution of 0.03 mol (5.5g) piperidine dithiocarbamate in 30ml ethanol was added to a solution of 0.01mol (3.71g) lanthanum chloride in 15ml ethanol and then 0.1 mol of 2,2’bipyridyl was added slowly. The mixture was stirred and left to stand for several hours; the complex was precipitated and filtered, washed several times with ethanol and dried *in vacuo*.

Analysis of the complexes

The complexes were analyzed for lanthanum , sulphur hydrogen carbon and nitrogen content. The lanthanum content was estimated as sulphide by direct combustion in a platinum crucible. The estimation was further confirmed by dissolving the product of direct combustion in dilute HCl. The acid extract was transfer in to flask; pH was adjusted to 5.8-6.4 by the addition of acetic acid sodium acetate buffer and was then titrated against 0.1M EDTA solution using xylenol orange indicator. The result from both methods was compared and found to be within the experimental errors.

The structure of lanthanum dithiocarbamates was elucidated on the basis of analytical method, molar conductance and IR spectral data table. On the basis of the analytical data presented in table general formula $ML_3.2,2'$ bipy **[**where L = dimethyl dithiocarbamate(Me_2DTC^-), piperidine dithiocarbamate ($PipDTC^-$), morpholine dithiocarbamate ($MorphDTC^-$), diphenyldithiocarbamate (Ph_2DTC^-) (bipy=2,2’bipyridyl)] is proposed for the synthesized complexes. The complexes are insoluble in common organic solvents but soluble in coordinating solvents like DMF, DMSO etc. Molar conductance values of the complexes are indicative of their non-ionic behavior. Magnetic susceptibility measurements show the diamagnetic nature of the complexes.

IR Spectra

The characteristic absorption frequencies of the lanthanum complexes are presented in table 2. Infrared spectra of the ligands exhibit strong bands at about 1450 and 980 cm^{-1}due to ν C-N and C-S stretching vibrations respectively. These bands undergo a positive shift of about 35 cm^{-1} in the corresponding lanthanum complexes. Thus IR data indicate bidentate behavior of dithiocarbamate moiety [240-243]. The bands at 1598, 1562 and 769 cm^{-1} are characteristic bands of 2, 2’bipy. The La-S stretching vibration is observed in the region 310-320 cm^{-1} in the lanthanum complexes.

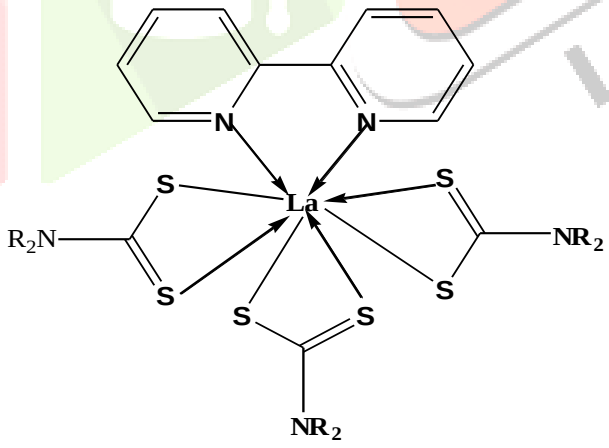
Table1. analytical data and general behavior of the lanthanum (III) dithiocarbamate bipyridyl complexes.

Complex formula	Color	C% Found (Calc.)	H% Found (Calc.)	N% Found (Calc.)	La% Found (Calc.)
$[La(diMeDTC)_3(bipy)]$	White	35.00 (34.81)	3.98 (3.97)	10.60 (10.68)	20.50 (21.22)
$[La(PipDTC)_3(bipy)]$	White	43.15 (43.35)	4.95 (4.90)	9.00 (9.03)	17.86 (17.94)
$[La(MorphDTC)_3(bipy)]$	White	38.00 (38.41)	4.10 (4.09)	8.85 (8.96)	17.50 (17.79)
$[La(diPhDTC)_3(bipy)]$	White	57.22 (57.25)	3.72 (3.70)	6.82 (6.81)	13.52 (13.53)

Table: 2 IR adsorption bands (cm^{-1}) of the lanthanum (III) dithiocarbamate bipyridyl complexes

Complex	ν (-c-n)	ν (-c=s)	ν (la-s)	ν (bipy)
$[La(dimedtc)_3(bipy)]$	1479	1005	312	1600, 1565 , 769
$[La(pipdtc)_3(bipy)]$	1475	995	320	1598, 1562 , 770
$[La(morphdtc)_3(bipy)]$	1487	985	318	1602, 1561 , 772
$[La(diph\ dtc)_3(bipy)]$	1490	990	315	1597, 1562, 768

On the basis of analytical, IR, and electronic spectral data the following structure is proposed for bipyridyl adducts of lanthanum (III) dithiocarbamates-



Tentative structure of Lanthanum (III) 2, 2' bipyridyl adducts of dithiocarbamates

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