

Studies on 4f-metal(III) complexes of N-thiophene-2-carboxamidosalicylaldimine

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Abstract. N-(thiophene-2-carboxamido) salicylaldimine (H_2TCS) reacts with lanthanide chlorides in the presence of KOH to give complexes of the type $K(Ln(TCS)_2)$ [$Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III)$ and $Dy(III)$]. A tentative structure for these complexes has been suggested on the basis of molar conductance, TGA and DTA, magnetic susceptibility, electronic, infrared and 1H and ^{13}C NMR data. The nephelauxetic ratio (β), covalency (δ) and bonding parameter ($b^{1/2}$) have been calculated from the electronic spectrum of the Nd(III) complex. A coordination number of six around the metal ion has been suggested.

Keywords. Lanthanide chlorides; N-thiophene-2-carboxamidosalicylaldimine complexes; tridentate ligand; hexa-coordinated lanthanide complexes.

1. Introduction

N-(thiophene-2-carboxamido) salicylaldimine has been found to behave as a neutral bidentate, mononegative tridentate and dinegative tridentate ligand in 3d-metal complexes (Singh *et al* 1985; Singh and Singh 1988). Bonding and stereochemistry of the complexes have been discussed. In view of the interesting ligational behaviour of H_2TCS and absence of reports on its lanthanide complexes, we wished to study the complexing behaviour of the aldimine towards lanthanides. In the present communication, the results of our investigations on the synthesis and structural studies of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III) and Dy(III) complexes of H_2TCS are reported.

2. Experimental

2.1 Materials

Hydrated metal chlorides (Indian Rare Earths, Kerala) and 2-thenoylhydrazine (Aldrich, Germany) were used as obtained. H_2TCS was prepared as described in the

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literature (Thyssen and Beilstein 1934), m.p. 178–179°C (Lit. 176°C). Found: C, 58.52; H, 4.04; N, 11.42%. $C_{12}H_{10}O_2N_2S$ requires: C, 58.52; H, 4.09; N, 11.37%.

2.2 Preparation of the complexes

Complexes of the type $K[Ln(TCS)_2]$ [$Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III)$ and $Dy(III)$] were prepared by mixing together aqueous-ethanolic solutions of H_2TCS (2 mmol), KOH (4 mmol) and metal chloride (1 mmol) and lowering the pH of the solution to ~ 7.5 by the dropwise addition of dilute HCl . The precipitated complexes were digested on a water bath for ~ 0.5 h, filtered and washed successively with water and ethanol, and then dried at room temperature over H_2SO_4 in a desiccator.

2.3 Analyses of the complexes

The metal contents were estimated volumetrically by EDTA titration (Lyle and Rahaman 1963) using Eriochrome Black-T as indicator, after destroying the organic matter with aqua regia, followed by treatment with sulphuric acid. Hydrazine was determined volumetrically by titrating against KIO_3 after hydrolysing the complexes in dilute HCl . Carbon, hydrogen and nitrogen were determined by microanalyses.

2.4 Physical measurements

Molar conductances were measured on a WTW conductivity-meter in DMF at $10^{-3} M$ dilution. The magnetic susceptibilities of the complexes were determined at room temperature by the Faraday method using $Hg[Co(NCS)_4]$ as the calibrant and experimental magnetic susceptibilities were corrected for diamagnetism (Figgis and Lewis 1960). TGA and DTA analyses were carried out on -200 mesh powder on a

Table 1. Analytical data and general behaviour of lanthanide(III) complexes of H_2TCS .

Complex	Colour	m.p. (°C)	Found (Calcd.) %					μ_{eff} (B.M.)	Molar conductance ($ohm^{-1} cm^2 mol^{-1}$)
			C	H	N	M	N_2H_4		
$K[La(TCS)_2]$	Bright yellow	143	43.13 (43.50)	2.51 (2.43)	8.51 (8.45)	20.6 (20.8)	9.70 (9.67)	dia.	75
$K[Pr(TCS)_2]$	Bright yellow	148	42.94 (43.37)	2.35 (2.42)	8.23 (8.43)	20.8 (21.0)	9.42 (9.64)	3.34	65
$K[Nd(TCS)_2]$	Deep yellow	137	42.87 (43.09)	2.46 (2.41)	8.22 (8.37)	21.5 (21.4)	9.24 (9.58)	3.40	79
$K[Sm(TCS)_2]$	Deep yellow	157	42.91 (42.76)	2.29 (2.39)	8.14 (8.31)	22.0 (22.1)	9.23 (9.50)	2.86	80
$K[Eu(TCS)_2]$	Yellow	149	42.38 (42.66)	2.40 (2.38)	8.32 (8.29)	22.1 (22.3)	9.51 (9.48)	3.29	72
$K[Gd(TCS)_2]$	Yellow	168	42.58 (42.33)	2.31 (2.36)	8.04 (8.22)	22.7 (22.9)	9.23 (9.41)	7.59	78
$K[Dy(TCS)_2]$	Yellow	141	41.85 (42.01)	2.43 (2.35)	8.13 (8.16)	23.6 (23.5)	9.14 (9.34)	10.68	65

Netzsch STA 409 in combination with the temperature programme 410 using alumina crucible. DTA and TGA were run upto 250°C against Sint Cavolin as standard material with the heating rate being 10°C per minute. Molar conductance and magnetic moment values are included in table 1.

Electronic spectra of H₂TCS and its complexes in nujol as well as in DMF solution were recorded on a Cary 14 spectrophotometer. IR spectra of the complexes (nujol) and the H₂TCS (nujol and MeCN) were recorded on a Perkin-Elmer spectrophotometer 783. The ¹H and ¹³C NMR spectra were recorded on a Jeol FX 90Q NMR spectrometer in DMSO-*d*₆ solution using TMS as the internal reference.

3. Results and discussion

The analytical data (table 1) indicate the formation of K[Ln(TCS)₂] [Ln = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III) and Dy(III)] complexes having 1:2 metal-ligand stoichiometry. There are no water molecules coordinated to the metal ions as inferred from TGA and DTA. The complexes are non-hygroscopic and are insoluble in water and nonaqueous solvents such as ethanol, methanol, acetone, chloroform and benzene but are soluble in dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The molar conductance values show that the complexes are non-electrolytes in solution (Geary 1971). The complexes show the expected magnetic behaviour.

3.1 Electronic spectra

The electronic spectral bands of Nd(III) complex with their assignments and various parameters are compiled in table 2. The electronic spectra of the complex both in solid (nujol) and in DMF solution are similar except for the broad shape of the mull spectra. This indicates that the complex maintains the same stoichiometry both as solid as well as in solution. There has been a red shift in the hypersensitive band compared to that of the aquoneodymium ion (Carnall *et al* 1968) and such a shift has been attributed by Jørgensen (1957) to the effects of the crystal field upon interelectronic repulsions among the 4f-electrons i.e. to the lowering of the interelectronic repulsion parameter (β) in the complex. The covalency (δ) and bonding parameter ($b^{1/2}$) have been calculated. The value of (β) being less than unity in

Table 2. Electronic spectral data for K[Nd(TCS)₂].

Band max. (cm ⁻¹)	Assignment	Spectral parameters
11425	⁴ I _{9/2} → ⁴ F _{3/2}	$\bar{\beta} = 0.995$ $b^{1/2} = 0.050$ $\delta\% = 0.50$
12420	→ ⁴ F _{5/2}	
13420	→ ⁴ F _{9/2}	
17095	→ ⁴ G _{5/2} ; ² G _{7/2}	
18870	—	

Spectral parameters are calculated for hypersensitive transition ⁴I_{9/2} → ⁴G_{5/2}, ²G_{7/2}.

conjunction with the positive value of (δ) and ($b^{1/2}$) supports the idea of a partial covalent bond between metal and the TCS (Tandon and Mehta 1970).

3.2 Infrared spectra

The sites of the H_2 TCS involved in bonding with metal ion in the complexes have been determined by careful comparison of the IR spectra of the complexes with that of the free ligand. The nujol mull spectrum of H_2 TCS displayed bands at 3360, 3200, 1640, 1590, 1530, 1260 and 1025 cm^{-1} which are attributed to $\nu(\text{OH})$, $\nu(\text{NH})$, amide I, $\nu(\text{C}=\text{N})$, amide II, $\nu_s(\text{C}-\text{O})_{\text{phenolic}}$ and $\nu(\text{N}-\text{N})$ modes, respectively. The respective bands are observed at 3610, 3270, 1650, 1610, 1520, 1270 and 1040 cm^{-1} in the acetonitrile solution spectrum of the hydrazone showing thereby that there is intermolecular hydrogen bonding in the solid state.

The disappearance of $\nu(\text{NH})$ and $\nu(\text{C}=\text{O})$ from the spectra of the complexes and appearance of new peak characteristics of $\nu(\text{NCO}^-)$ (Rao 1970) in the region 1530–1545 and $1355\text{--}1360\text{ cm}^{-1}$ suggest the destruction of $\nu(\text{C}=\text{O})$ via imide \rightleftharpoons imidol tautomerism (figure 1) and simultaneous bonding of the enolate oxygen (Sinn and Harris 1969) with the metal ion.

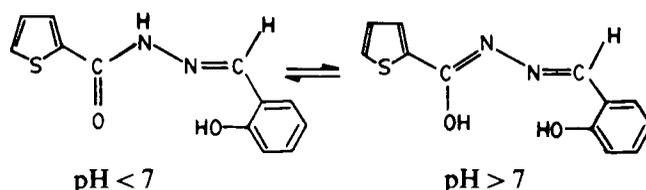


Figure 1. Structure of H_2 TCS.

The $\nu(\text{C}=\text{N})$ shifts to lower frequencies in the spectra of complexes indicating bonding through an azomethine nitrogen (Braibanti *et al* 1968). The azomethine nitrogen coordination is also supported by the shift of $\nu(\text{N}-\text{N})$ to higher frequencies in the spectra of $\text{K}[\text{Ln}(\text{TCS})_2]$. The involvement of phenoxy oxygen in bonding is inferred from the disappearance of $\nu(\text{OH})$ from the spectra of the complexes and shifts of $\nu(\text{C}-\text{O})_{\text{phenolic}}$ to higher frequencies.

Absorptions observed in the regions 360–385 and $320\text{--}345\text{ cm}^{-1}$ in the complexes may be assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ (Nakamoto and Martell 1960) modes, respectively.

3.3 ^1H and ^{13}C NMR spectra

The spectrum of H_2 TCS shows signals at δ 12.19, 11.23 and 8.56 corresponding to phenolic OH, NH and aldehydic protons (azomethine proton), respectively, while the ring protons are observed at δ 7.95 – 7.04. The spectrum of $\text{K}[\text{La}(\text{TCS})_2]$ is devoid of the signals corresponding to the phenolic OH and amide NH protons. The disappearance of amide NH is due to deprotonation through imide \rightleftharpoons imidol tautomerism and subsequent deprotonation of the imidol proton which suggest bonding through the imidolic oxygen (after deprotonation). The disappearance of $\nu(\text{OH})$ indicates bonding through the phenolic oxygen.

The ^{13}C $\{^1\text{H}\}$ NMR spectral data of H_2 TCS and its La(III) complex are given in

Table 3. ^{13}C (^1H) NMR spectral data of H_2TCS and its La(III) complex.

Complex	C=O	C ₂	CN	C ₄	C ₂	C ₃
H_2TCS	161.84	157.35	147.95	134.57	137.61	131.43
$\text{K}[\text{La}(\text{TCS})_2]$	166.75	163.08	153.91	134.25	—	131.65
Complex	C ₄	C ₃	C _{1'}	C _{3'}	C _{5'}	C _{6'}
H_2TCS	129.32	128.18	119.46	116.42	118.81	132.08
$\text{K}[\text{La}(\text{TCS})_2]$	128.61	127.69	122.22	112.63	120.27	133.65

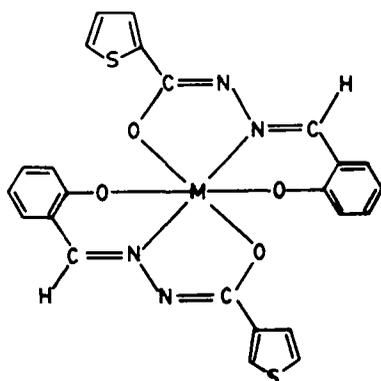
**Figure 2.** Structure of $[\text{Ln}(\text{TCS})_2] \cdot$ [$\text{Ln} = \text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}$ and Dy(III)].

table 4. In the spectrum of $\text{K}[\text{La}(\text{TCS})_2]$ the signal corresponding to the carbonyl carbon shows a significant downfield shift and suggests the bonding of the carbonyl oxygen (Paolucci *et al* 1980). Similarly the coordination of the azomethine nitrogen (Paolucci *et al* 1980) is inferred from the downfield shift of the signal due to the azomethine carbon. The signals due to the other carbons show the expected trends.

Based on analytical and physico-chemical data, the structures proposed for the complexes $\text{K}[\text{Ln}(\text{TCS})_2]$ are shown in figure 2.

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