Journal of the Serbian Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. *76* (2) 249–261 (2011) UDC 546.654.3+542.913:543.57:66.095.13/.14
JSCS–4116 *Original scientific paper*

Synthesis and spectroscopic characterization of some lanthanide(III) nitrate complexes of ethyl 2-[2-(1-acetyl-2-oxopropyl)azo]-4,5-dimethyl-3-thiophenecarboxyate

CHEMPAKAM JANARDHANAN ATHIRA, YESODHARAN SINDHU, MATHUNNI SUSAMMA SUJAMOL and KOCHUKITTAN MOHANAN*

Department of Chemistry, University of Kerala, Kariavattom Campus,
Trivandrum-695 581, Kerala, India

(Received 14 April, revised 10 September 2010)

Abstract: Ethyl 2-[2-(1-acetyl-2-oxopropyl)azo]-4,5-dimethyl-3-thiophenecarboxyate was synthesized by coupling diazotized ethyl 2-amino-4,5-dimethylthiophene-3-carboxylate with acetylacetone. Based on various spectral studies and elemental analysis, an intramolecularly hydrogen-bonded azo-enol structural form was assigned for the ligand. This ligand is versatile in forming a series of lanthanide(III) complexes, *viz*., lanthanum(III), cerium(III), praseodymium(III), neodymium(III), samarium(III) and gadolinium(III), which were characterized through various spectral studies, elemental analysis, magnetic susceptibility measurements, molar conductance and thermal analysis. The spectral data revealed that the ligand acted as a neutral tridentate, coordinating to the metal ion through one of the azo nitrogen atoms, the ester carbonyl and the enolic oxygen of the acetylacetone moiety, without deprotonation. Molar conductance values adequately supported their non-electrolytic nature. The ligand and lanthanum(III) complex were subjected to X-ray diffraction studies. In addition, the lanthanum(III) complex underwent a facile transesterification reaction on refluxing with methanol for a long period. The thermal behaviour of the lanthanum(III) complex was also examined.

Keywords: azo derivative; lanthanum(III) complex; molar conductance; XRD; transesterification; thermal analysis.

INTRODUCTION

The ever increasing interest in the coordination chemistry of azo derivatives is attributable to their use as complexing agents, dyeing materials, antidepressants and antitubercular agents, models for biological systems and chromogenic reagents.[1–5] Recent years have witnessed a tremendous upsurge of in-

---

* Corresponding author. E-mail: drkmohanan@rediffmail.com
doi: 10.2298/JSC100414025A

terest in the synthesis and characterization of metal chelates containing heterocyclic azo dyes as ligands. Azo dyes derived from 2-aminothiophene derivatives have many advantages, including a colour deepening effect as an intrinsic property of the thiophene ring, a small molecular structure leading to better dyeability and the heterocyclic structure of thiophene ring resulting in good sublimation fastness of dyed fibres.[6] The colour of these azo derivatives depends on the diazo and the coupling components. The diazo components of 2-aminothiophene derivatives tend to show a bathochromic shift and high tinctorial strength, when compared to analogous dyes derived from a cyclic aromatic system.[7] Due to the presence of the –N=N– group and a β-diketone moiety in a single compound, their effectiveness of complex formation surpasses those of the parent compounds. Metal complexes of lanthanide(III) ions containing azo derivatives have been extensively investigated.[1,8–11] However, due to the instability of aminothiophene, lanthanide(III) complexes of azo dyes formed from 2 or 3-aminothiophene have hitherto only received sporadic attention. Nevertheless, the stability of 2-aminothiophene was increased by suitable substitution at the remaining positions by a versatile synthetic method developed by Gewald.[12] Apart from providing stability to 2-aminothiophene, the introduction of a ethoxycarbonyl group at 3-position of the thiophene ring, provided further scope for reactivity and a new coordination site. In view of this, and as part of our continuing interest on structural and thermal aspects of heterocyclic azo derivatives and their lanthanide(III) complexes, herein the synthesis, spectral and thermal studies are reported of a new series of lanthanide(III) complexes of an azo derivative of aminothiophene, *viz.*, ethyl 2-[2-(1-acetyl-2-oxopropyl)azo]-4,5-dimethyl-3-thiophenecarboxyate (HAAT). Moreover, the structural aspect of the ligand, the bioisosteric relationship of thiophene to benzene, gives added significance to this investigation.

EXPERIMENTAL

Materials

All employed chemicals were of AnalaR grade purchased from Aldrich, Fischer and Sisco chemicals and used without further purification. Lanthanide(III) nitrates were prepared by dissolving the corresponding oxide in 50 % nitric acid, followed by crystallization.

Preparation of the ligand

The thiophene intermediate was synthesized by a reported method.[12] This thiophene intermediate was diazotized at 0–5 °C using $NaNO_2$ and concentrated H_2SO_4. Urea was added to this diazonium salt solution to remove excess nitrous acid. The resulting diazonium salt solution was immediately coupled with acetylacetone in methanol. The pH of the reaction mixture was adjusted to 8–9 by adding the required amount of sodium acetate solution (10 %) while keeping the temperature below 5 °C. The obtained product was filtered off, washed with small amount of water and finally with diethyl ether and dried (m.p. 92 °C; yield: 80 %).

Preparation of the metal complexes

A solution of lanthanide(III) nitrate (0.5 mmol) in methanol was added to a warm methanolic solution (50 cm^3) of the ligand (1 mmol). After 3 h stirring, the pH of the solution was adjusted to 6.5–7.0 and the resulting solution was then refluxed on a water-bath for about 12 h. The solution was then concentrated and kept overnight. The powdery material thus separated was filtered, washed successively with small amounts of MeOH and finally with diethyl ether and dried in vacuum over P_4O_{10} (m.p. <180 °C; yield: 55–60 %).

Physical measurements

Carbon, hydrogen and nitrogen analysis were performed using a Heraeus Carlo Erba 1108-CHN analyzer. The complexes were analyzed for their metal content by the oxalate–oxide method.[13] Molar conductance measurements were performed using 10^{-3} M solution of the metal complexes in DMSO, DMF and nitrobenzene at room temperature using a Systronics direct reading conductivity meter, type 304. Infrared spectral studies were realised using KBr discs on a Shimadzu FT-IR 8000 spectrophotometer in the range 4000–400 cm^{-1} and far infrared spectra were recorded on a Polytec FIR 30 spectrometer in the range 400–200 cm^{-1} using CsI discs. The electronic spectra were recorded on a Hitachi 320 UV–Visible spectrophotometer. Magnetic susceptibility values of the complexes were measured at room temperature with a Magway MSB Mk 1 susceptibility balance. The ^{1}H-NMR spectra were recorded in DMSO-d_6 on a JEOL GSX 400NB 400 MHz FTNMR spectrometer. The X-ray diffraction study was conducted using a Siemens D 5005 model spectrometer. Thermal analysis was performed using a Mettler Toledo Thermogravimetric analyzer in dynamic air at a heating rate of 10 °C min^{-1}.

Transesterification

Transesterification of the lanthanum(III) complex was performed by a reported method.[14] About 0.1 g of lanthanum(III) complex was suspended in hot methanol (100 cm^3) and refluxed for 48 h on a water-bath. The resulting solution was then evaporated to dryness and the solid product obtained was washed repeatedly with diethyl ether and dried over P_4O_{10} in vacuum.

RESULTS AND DISCUSSION

The ligand and the metal complexes were air-stable and possessed good keeping qualities. Analytical data of the ligand and its complexes are in good agreement with their formulation, as given in the Table I. The formulation of these complexes was made based on elemental analysis, molar conductance, magnetic susceptibility measurements and various spectral data. The molar conductance values of the complexes (Table II) support their non-electrolytic nature.[15] The complexes exhibited 1:2 metal-ligand stoichiometry, in which the ligand is coordinated to the metal ion without deprotonation in a tridentate mode. The purity of the ligand and its complexes were confirmed by the TLC technique.

The principal advantage of the diazo component is that the yield is very high, the reaction time is short, and the procedure involves only one facile step. However, one disadvantage of the ester functionality is that its conjugation with amino group reduces the basicity of the nitrogen atom and thus efficient diazotization can only be achieved using nitrosylsulphuric acid obtained from $NaNO_2$

and H_2SO_4.[16] The ligand formed well defined complexes with lanthanum(III), cerium(III), praseodymium(III), neodymium(III), samarium(III) and gadolinium(III) nitrates. The formation of the metal complexes can be represented by the following general equation:

$$M(NO_3)_3 + HAAT \rightarrow [M(HAAT)_2(NO_3)_3]$$

where M = La(III), Ce(III), Pr(III), Sm(III), Nd(III) or Gd(III) and HAAT = ethyl 2-[2-(1-acetyl-2-oxopropyl)azo]-4,5-dimethyl-3-thiophenecarboxyate.

TABLE I. Analytical and magnetic moment data of the ligand and its metal complexes

Compound	Yield %	Found (Calcd.), % C	H	N	S	M	μ / μ_B
HAAT	80	54.18 (54.12)	5.85 (5.83)	9.02 (9.03)	10.33 (10.31)	–	–
$[La(HAAT)_2(NO_3)_3]$	64	35.56 (35.54)	3.84 (3.85)	10.37 (10.35)	6.78 (6.79)	14.69 (14.67)	Diamagnetic
$[Ce(HAAT)_2(NO_3)_3]$	70	35.52 (35.50)	3.83 (3.82)	10.35 (10.33)	6.77 (6.78)	14.79 (14.78)	2.55
$[Pr(HAAT)_2(NO_3)_3]$	67	35.49 (35.46)	3.82 (3.81)	10.34 (10.33)	6.76 (6.75)	14.86 (14.84)	3.57
$[Nd(HAAT)_2(NO_3)_3]$	65	35.34 (35.33)	3.81 (3.80)	10.30 (10.31)	6.74 (6.72)	(15.22) (15.20)	3.65
$[Sm(HAAT)_2(NO_3)_3]$	67	35.14 (35.15)	3.79 (3.78)	10.24 (10.22)	6.70 (6.68)	15.71 (15.70)	1.52
$[Gd(HAAT)_2(NO_3)_3]$	71	34.89 (34.87)	3.76 (3.73)	10.17 (10.18)	6.65 (6.67)	16.31 (16.30)	7.86

TABLE II. Molar conductance data (S cm^2 mol^{-1}) of the metal complexes

Complex	Solvent DMSO	DMF	Nitrobenzene
$[La(HAAT)_2(NO_3)_3]$	8.6	14.4	5.6
$[Ce(HAAT)_2(NO_3)_3]$	8.9	13.3	4.6
$[Pr(HAAT)_2(NO_3)_3]$	7.5	13.5	4.3
$[Nd(HAAT)_2(NO_3)_3]$	8.8	14.6	4.8
$[Sm(HAAT)_2(NO_3)_3]$	8.5	13.9	5.6
$[Gd(HAAT)_2(NO_3)_3]$	7.9	13.6	4.5

Structure of the ligand

Generally, compounds obtained by the coupling reaction of a 1,3-diketone with an aryl diazonium ion are capable of exhibiting azo-hydrazo tautomerism (Fig. 1). There are reports that the ultraviolet absorption spectrum of monophenyl azo compounds differ from those of monophenyl hydrazones. The former azo compounds exhibit a strong absorption band at a wavelength of 270–280 nm, while the latter hydrazones give a strong band above 320 nm. The ultra-violet spectrum of the ligand HAAT exhibited a strong band at 280 nm characteristic of the azo form.[17] The IR spectrum of HAAT adequately supported the conclusions made based on UV–Vis spectral data.

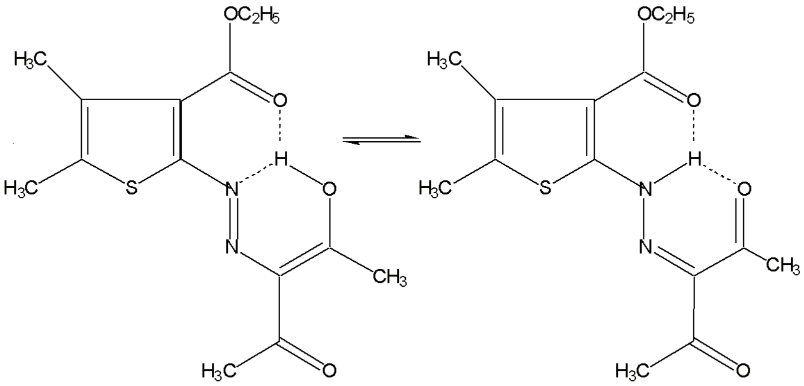

Fig. 1. Tautomeric structure of the ligand.

The IR spectrum of the free ligand (Fig. 2) exhibited a broad medium intensity band in the region 3300–3000 cm^{-1} and centred at 3100 cm^{-1}, which is assignable to the O–H stretching vibration of internally hydrogen bonded enolic group.[18] The medium intensity band observed at 1493 cm^{-1} can be assigned to ν(–N=N–), confirming the formation of the azo derivative.[19] The band observed at 1274 cm^{-1} is attributed to C–O stretching (enolic) vibration.[20] Thus, the IR spectrum strongly supports the existence of the free ligand in an intramolecularly hydrogen bonded azo-enol form. The free acetyl carbonyl band of the acetylacetone moiety was observed at 1690 cm^{-1}.[21] Apart from these vibrations, the infrared spectrum of the ligand also exhibited a strong band at 1678 cm^{-1} due to the ester carbonyl group.[22] The ester carbonyl group was also involved in weak hydrogen bonding with the OH group, forming a sort of bifunctional hydrogen bonding in the free ligand. Nevertheless, in competition with the azo nitrogen for the enolic OH, the ester carbonyl of the thiophene moiety can only manage a partial share. This elucidated the reason for the ester carbonyl frequency appearing relatively higher than that in the free amine (1660 cm^{-1}). In addition to the above frequencies, vibrations characteristic of substituted thiophene ring were observed at 1524, 1396 and 1352 cm^{-1}.[23]

In agreement with the UV and IR spectral data, the ^{1}H-NMR spectrum of the ligand (Fig. 3) clearly evinces its existence in the azo-enol form (Fig. 1). The ^{1}H-NMR spectrum of the ligand recorded in DMSO-d_6 exhibited two methyl proton signals of equal intensity, each around 2.46 and 2.33 ppm of the two acetyl groups on the acetylacetone moiety, which indicates that one of these groups undergoes a shift in the chemical environment because of hydrogen bonding with the azo group. The low intensity signal resonating at 15.42 ppm can be confidently assigned to the intramolecularly hydrogen bonded enolic proton of the ligand.[24] Signals for methyl and methylene protons of the ester function were observed at δ 1.45 and 4.49 ppm, respectively. The signal appearing 2.27 ppm could be attributed to the two methyl groups at 4th and 5th position on the thiophene moiety.

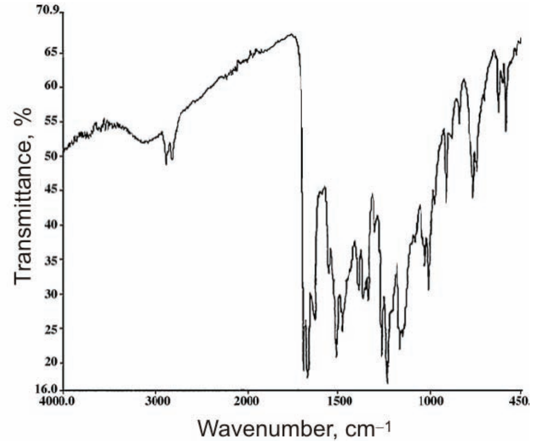

Fig. 2. IR spectrum of the ligand.

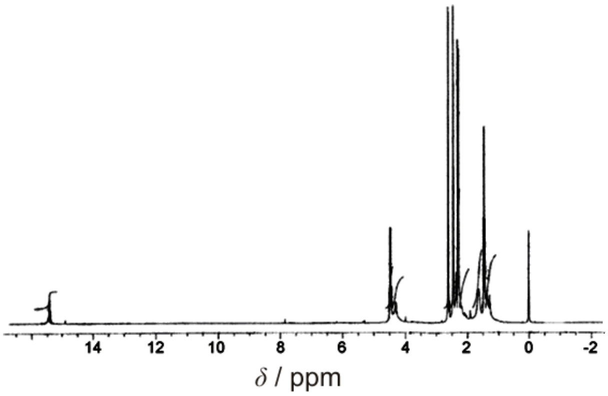

Fig. 3. ^{1}H-NMR spectrum of the ligand.

Structure of metal complexes

The electronic spectra of all the complexes recorded in DMSO are only marginally red shifted from that of the ligand, indicating that the complexes are isostructural and the ligand exhibits the same structural form in the synthesized complexes.

IR spectra. The infrared spectrum of the ligand was compared with those of the metal complexes in order to ascertain the coordination sites that may be involved in chelation (Table III). In the spectra of the metal complexes (Fig. 4), the band apparently due to the internally hydrogen bonded OH group was shifted to higher frequency and became less broad showing a peak centred at ≈3120 cm^{-1}, indicating that the OH group is coordinated to the metal ion without deprotonation. As the interaction of the lanthanide ion with the enolic oxygen does not increase the acidity sufficiently for the ionization of the proton, the enolic oxygen coordinates to the metal ion without deprotonation.[25] This is further supported by the positive shift of the ν(C–O) plane bending band by about 20 cm^{-1} in the metal complexes. The band due to ν(N=N) shifted appreciably to a lower wave number by 25–30 cm^{-1}, indicating the involvement of the azo nitrogen in the bonding with the metal ion.[26] The free acetyl carbonyl band at 1690 cm^{-1} of the acetylacetone moiety was only marginally shifted during complexation, suggesting its non-participation in the coordination.[27] The ester carbonyl stretching frequency of the ligand was lowered by ≈40 cm^{-1} in the lanthanide(III) complexes, indicating the involvement of the ester carbonyl group in the chelation.[28]

TABLE III. Infrared data of the ligand and its metal complexes (cm^{-1})

Compound	ν(O–H)	ν(C=O) of ester carbonyl	ν(N=N)	ν(C–O)	ν(C=O) of free acetyl carbonyl	ν(Ln–N)	ν(Ln–O)
HAAT	3100	1677	1493	1274	1690	–	–
$[La(HAAT)_2(NO_3)_3]$	3118	1637	1463	1294	1691	365	435
$[Ce(HAAT)_2(NO_3)_3]$	3120	1638	1465	1295	1693	367	437
$[Pr(HAAT)_2(NO_3)_3]$	3121	1636	1468	1294	1691	370	438
$[Nd(HAAT)_2(NO_3)_3]$	3119	1637	1467	1296	1689	366	436
$[Sm(HAAT)_2(NO_3)_3]$	3122	1636	1464	1293	1690	368	439
$[Gd(HAAT)_2(NO_3)_3]$	3120	1639	1466	1294	1692	367	440

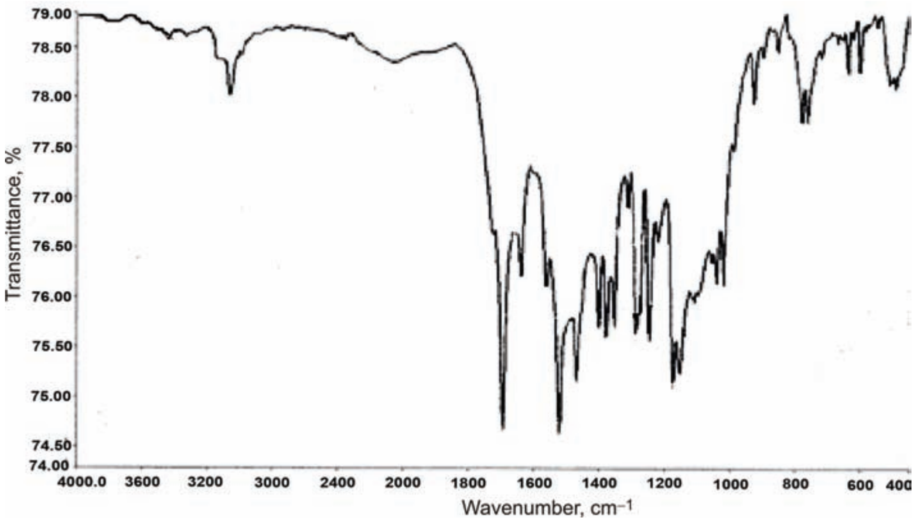

Fig. 4. IR spectrum of the lanthanum(III) complex.

The characteristic vibrations of the substituted thiophene ring remained almost unaffected in the metal chelates. This excludes the possibility of bonding by the ring sulphur atom to the metal ion. The absence of a ν(M–S) band in the far infrared spectra of the metal complexes also gives additional evidence for the non-participation of ring sulphur in coordination with the metal ion. In the spectra of the nitrato complexes, there are two additional bands observed at ≈1457 and ≈1257 cm^{-1}, which were absent in the spectrum of the free ligand. These bands are assigned to the ν_5 and ν_1 modes of the nitrate ions, respectively. Since the magnitude of the separation between ν_5 and ν_1 is >200 cm^{-1}, it is concluded that the nitrate is coordinated in a bidentate fashion.[29] Crystallographically, it has been observed that nitrate is invariably bidentate towards lanthanide ions.[30] "Short bite" ligands, such as nitrate (bidentate), minimize ligand–ligand repulsion and hence are suited to lanthanides, which show a pronounced tendency to attain relatively high coordination numbers. The far infrared spectra of the metal complexes exhibited non-ligand bands in the regions 435–440 and 365–370 cm^{-1}, assignable to ν(M–O) and ν(M–N) vibrations, respectively.[28]

^{1}H-NMR spectrum. The ^{1}H-NMR spectrum of the lanthanum(III) complex recorded in DMSO-d_6 further substantiates the mode of coordination suggested by the electronic and IR spectral studies. The ^{1}H-NMR spectrum of the complex (Fig. 5) also exhibited a signal for OH proton at 15.12 ppm, indicating that the OH group is coordinated to the metal ion without deprotonation. The signals due to other protons are found in the expected regions and shifted by about 0.1–0.2 ppm in the spectra of the metal complexes. Thus, from the above spectral data, it is clear that the ligand is coordinated to the metal ion without deprotonation in a tridentate fashion.

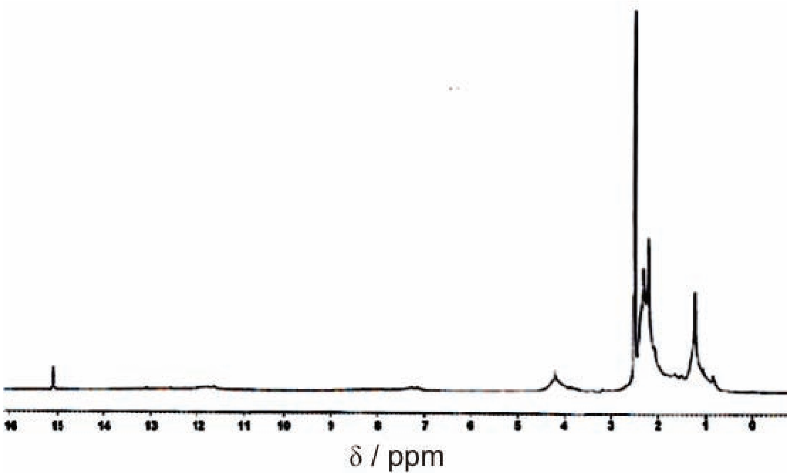

Fig. 5. ^{1}H-NMR spectrum of the lanthanum(III) complex.

Magnetic moment. Unlike the d-electrons of the transition metal ions, the f-electrons of the lanthanide ions are almost unaffected by the chemical environment and the energy levels are the same as in the free ion, due to very effective shielding by the overlying $5s^2$ and $5p^6$ shells. The magnetic moment values of the complexes showed that the lanthanum(III) complex is diamagnetic, while all others are paramagnetic, showing close agreement with the calculated values except for the samarium(III), indicating an insignificant participation of the 4f electrons in the bonding. The relatively high value obtained in the case of the samarium(III) complex may be due to the small J–J separation, which leads to thermal population of the higher energy levels and show susceptibilities due to the first-order Zeeman effect.[31]

Electronic spectra. The lanthanum(III) complex has no significant absorption in the visible region, owing to the absence of 4f orbital electrons. The visible spectral bands of the lanthanide complexes were hypersensitive to stereochemistry. An enhancement of the intensity of certain hypersensitive bands of the praseodymium(III), neodymium(III) and samarium(III) complexes compared to the respective aquated ions was observed. These variations can be attributed to the action of an inhomogeneous electromagnetic field and by changes in the symmetry of the field on the lanthanide ion.[32] The sharp bands due to f–f transitions originating within the $4f^n$ configuration of the lanthanide ions are only slightly affected by the immediate surroundings of the metal ion, and this is commonly attributed to the shielded nature of the 4f orbitals by the overlying $5s^2$ and $5p^6$ orbitals. However, a shift to a lower frequency can be considered as being due to complex formation.

X-Ray diffraction. The diffractogram of the ligand recorded 16 reflections for the 2θ range from 11 to 52° with maxima at $2\theta = 25.6069°$, which corresponds to interplanar distance $d = 3.4758$ Å. The X-ray diffraction data are given in Table IV. The X-ray diffraction pattern of the ligand indicates high crystallinity. The obtained $\sin^2\theta$ values were compared with the calculated values. The observed values of the ligand fit well with an orthorhombic crystal system,[33] with lattice parameters, $a = 6.50469$ Å, $b = 7.61705$ Å, $c = 11.53506$ Å and a unit cell volume of 571.52241 Å^3. It was observed that the crystallinity of the ligand was lost on complexation.

Transesterification

Transesterification is a process in which an ester fragment is transformed into another through interchange of the alkoxy moiety. It is more advantageous than ester synthesis from carboxylic acids and alcohols. As transesterification is an equilibrium process, the ease with which a target ester is formed is dependent on the combination of alcohol and ester reactants. It was observed that methanol has the strongest replacing power, as the formation of methyl acetate is thermodynamically favoured. Several reports indicate that metal chelates of carboxylic esters undergo facile transesterification on refluxing with an alcohol. However, such studies on heterocyclic azo complexes are rare. In the present investigation, the lanthanum(III) complex was subjected to transesterification reaction in methanol medium according to a reported method.[14]

TABLE IV. XRD Pattern of the ligand

Peak No.	*d* / Å	Relative intensity, %	Observed 2θ	Calculated 2θ	Observed $\sin^2\theta$	Calculated $\sin^2\theta$	*hkl*
1	7.54009	89.62	11.72689	11.55753	0.010426	0.010138	221
2	5.68113	35.02	15.58498	15.62098	0.018365	0.018468	101
3	5.49650	23.09	16.11191	15.34367	0.019619	0.017822	002
4	5.03394	5.37	17.60367	17.91051	0.023391	0.024231	110
5	4.11494	9.20	21.57783	20.55591	0.035005	0.031835	102
6	3.87358	28.57	22.93997	23.10314	0.039504	0.0401	003
7	3.77288	10.54	23.56093	23.66699	0.041641	0.042053	112
8	3.47587	100.00	25.60694	25.92541	0.049061	0.050318	013
9	3.32804	11.59	26.76509	26.90272	0.053517	0.054112	120
10	3.16880	10.07	28.1371	28.198721	0.05903	0.059343	121
11	3.02580	7.39	29.49633	29.38550	0.064742	0.064331	113
12	2.76088	2.91	32.40085	31.54210	0.077763	0.073872	202
13	2.66705	2.31	33.57384	33.71405	0.083331	0.084091	212
14	2.44176	2.69	36.77723	36.27854	0.099418	0.096925	220
15	2.34487	3.61	38.355	38.06944	0.107804	0.106368	213
16	2.06282	4.08	43.85236	43.45189	0.139302	0.137024	223

The crystallinity, appearance and the solubility behaviour of the product obtained after transesterification was distinctly different from those of the ethyl derivative. Apart from these, the ester carbonyl stretching frequency observed for the methyl derivative at 1627 cm^{-1} is a direct indication of the occurrence of transesterification. Substitution of ethyl group by methyl group was further confirmed by the ^{1}H-NMR spectrum of the product.

Although several mechanisms have been proposed to explain transesterification reactions, it appears that increased nucleophilicity of the acyl carbon atom induced by the azo group is of great importance. It was also reported[14] that an alkoxycarbonyl group attached to the carbon atom can be readily transesterified. As difficulties are encountered in the preparation of metal chelates of esters, the general method of synthesis by transesterification has gained acceptance.

Thermogravimetric analysis

Thermogravimetric analysis was performed on the lanthanum(III) complex with the aim of understanding the thermal behaviour of the complex. The TG profile (Fig. 6) showed no weight loss up to 170 °C, which indicates the absence of either crystallization or coordinated water molecules in the complex. The lanthanum(III) complex underwent a two-stage decomposition, as denoted by the two DTG peaks at 351 and 617 °C. The first stage of decomposition started at 180 °C and was completed at 440 °C, with a mass loss of 26.89 % (Calcd. 28.21 %), corresponding to the loss of the azo group and the acetylacetone moiety. The second stage of decomposition occurred in the temperature range 480–680 °C, with a mass loss of 65.54 % (Calcd. 63.60 %) due to the oxidative decomposition of the complex to La_2O_3. The mass loss agrees fairly well with that found in independent pyrolysis experiments.

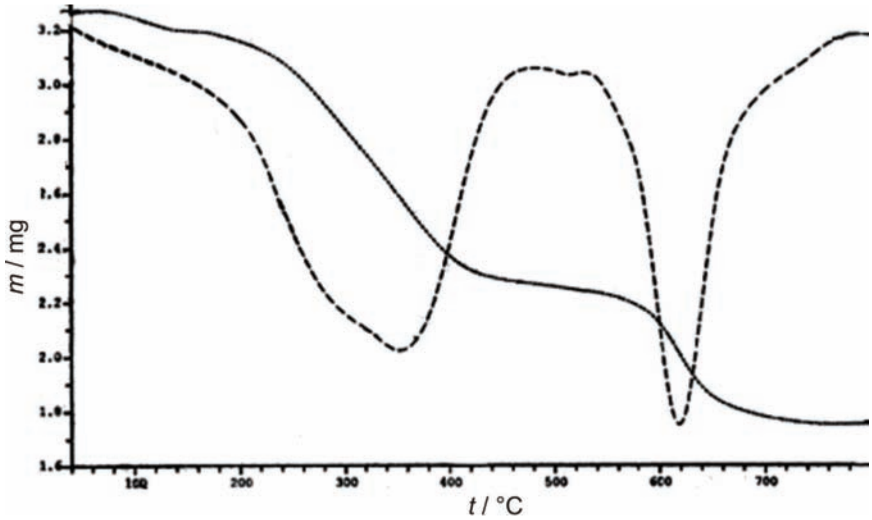

Fig. 6. TG and DTG curve of lanthanum(III) complex.

Based on the analytical, physico–chemical and spectral results, the structure of the metal complex shown in Fig. 7 was assigned.

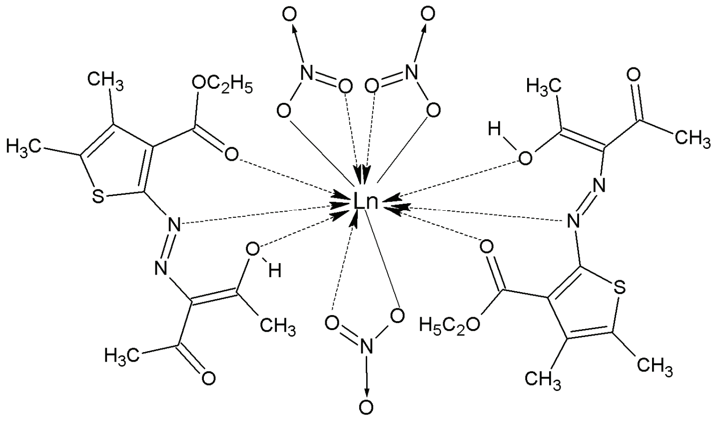

Fig. 7. Proposed structure of the lanthanide(III) complex.

CONCLUSIONS

A heterocyclic ligand obtained by the coupling of diazotized ethyl 2-amino-4,5-dimethylthiophene-3-carboxylate with acetylacetone, *viz*., ethyl 2-[2-(1-acetyl-2-oxopropyl)azo]-4,5-dimethyl-3-thiophenecarboxyate, acted as a neutral tridentate ligand. The ligand formed a series of lanthanide(III) complexes with a 1:2 metal–ligand stoichiometry. Spectral studies revealed that the ligand possessed an azo–enol structure and this structural form of the ligand persisted in the metal complexes. The infrared spectral data adequately supported the bidentate coordination of nitrate ions. Based on the spectral evidence, it could be concluded that the ligand behaved as neutral tridentate, coordinating to the metal ion through one of the azo nitrogen atoms, the ester carbonyl and the enolic oxygen of the acetylacetone moiety without deprotonation. A coordination number of twelve is proposed for the studied lanthanide(III) complexes. Thermal analyses indicated a greater stability of the lanthanum(III) complex compared to the ligand.

Acknowledgements. We express our sincere gratitude to Professor and Head, Department of Chemistry, University of Kerala, Kariavattom Campus, Trivandrum-695 581, Kerala, India, for providing the necessary facilities for carrying out this work. We are also glad to acknowledge the instrumental facilities provided by the Sophisticated Analytical Instrumental Facility, Cochin; IIT Bombay and the National Institute for Interdisciplinary Science and Technology, Trivandrum, India.

ИЗВОД

СИНТЕЗА И СПЕКТРОСКОПСКА КАРАКТЕРИЗАЦИЈА КОМПЛЕКСА ЛАНТАНОИД(III) НИТРАТА СА ЕТИЛ-2-[2-(1-АЦЕТИЛ-2-ОКСОПРОПИЛ)АЗО]-4,5-ДИМЕТИЛ-3-ТИОФЕНКАРБОКСИЛАТОМ КАО ЛИГАНДОМ

CHEMPAKAM JANARDHANAN ATHIRA, YESODHARAN SINDHU,
MATHUNNI SUSAMMA SUJAMOL и KOCHUKITTAN MOHANAN

Department of Chemistry, University of Kerala, Kariavattom Campus, Trivandrum-695 581, Kerala, India

У реакцији између диазотованог етил-2-амино-4,5-диметилтиофен-3-карбоксилата и ацетилацетона синтетизован је нови лиганд етил-2-[2-(1-ацетил-2-оксопропил)азо]-4,5-диметил-3-тиофенкарбоксилат. На бази спектроскопских испитивања и резултата елементарне микроанализе нађено је да синтетисани лиганд има интрамолекулским водоничним везама повезану азо-енолну структурну форму. Овај лиганд се показао врло погодним за грађење серије различитих комплекса лантаноида(III), као што су лантан(III), цер(III), празеодим(III), неодим(III), самаријум(III) и гадолинијум(III) комплекси који су у овом раду окарактерисани помоћу различитих спектроскопских метода, елементалне микроанализе, мерења магнетне и моларне проводљивости и термалне анализе. На основу спектроскопских изучавања закључено је да је неутрална форма лиганда тридентатно координована преко азо атома азота, карбонилног кисеониковог атома естарске групе и протонованог енолног атома кисеоника из ацетилацетонског остатка овог лиганда. Вредности за моларну проводљивост ових комплекса указују на њихову неутралну форму. Лиганд и одговарајући комплекси лантана(III) су испитивани методом дифракције X-зрака. Нађено је да комплекси лантана(III) подлежу реакцији трансестерификације приликом рефлуктовања у метанолу у току дужег временског периода. Испитивана је термална стабилност изолованих комплекса лантана(III).

(Примљено 14. априла, ревидирано 10. септембра 2010)

REFERENCES

1. A. E. Basheir, L. S. Shanker, S. A. Mohamed, M. M. Mahmoud, *Can. J. Chem.* **66** (1988) 2362
2. S. Zeynel, E. Nermin, Y. Ebru, U. Guven, *Color Technol*. **124** (2007) 27
3. A. A. Salem, Y. M. Issa, E. E. El-Shreafy, *J. Therm. Anal.* **48** (1997) 851
4. A. T. Mubarak, *Spectrochim. Acta A* **61** (2005) 1163
5. A. M. Khedr, M. Gaber, *Spectrosc. Lett.* **38 (**2005) 431
6. S. A. Alaa, H. A. Tarek, *Dyes Pigm.* **70** (2006) 8
7. M. S. Yen, I. J. Wang, *Dyes Pigm.* **62** (2004) 173
8. M. M. Moustafa, *Synth. React. Inorg. Met-Org. Chem.* **27** (1997) 1417
9. B. A. El-Shetary, S. L. Stefan, F. I. Zidan, El-Maraghy, *Monatsh. Chem.* **118** (1987) 1101
10. S. A. Abdel-Latif, *Synth. React. Inorg. Met-Org. Chem.* **31** (2001) 1355
11. K. Mohanan, C. J. Athira, Y. Sindhu, M. S. Sujamol, *J. Rare Earths* **27** (2009) 705
12. K. Gewald, E. Schinke, H. Böllcher, *Chem. Ber*. **99** (1966) 94
13. I. M. Kolthoff, P. J. Elving, *Treatise on Analytical Chemistry*, *Part II*, Vol. 8, Interscience, New York, 1963, p. 330
14. F. Jursik, B. Hajek, *Inorg. Chim. Acta* **13** (1975) 169
15. W. J. Geary, *Coord. Chem. Rev*. **7** (1971**)** 81
16. H. R. Maradiya, V. S. Patel, *Chem. Heterocycl. Compd*. **38** (2002) 1324
17. H. C. Yao, *J. Org. Chem*. **29** (1964**)** 2959
18. M. B. Ummathur, *J. Iran. Chem. Soc.* **4 (**2007) 244
19. H. B. Hassib, S. A. Abdel-Latif, *Spectrochim. Acta A* **59** (2003) 2425
20. K. Krishnankutty, P. Sayudevi, M. B. Ummathur, *J. Indian Chem. Soc.* **84** (2007) 337
21. E. V. Shchegol'kov, O. G. Khudina, L. V. Anikina, Y. V. Burgart, V. I. Saloutin, *Pharm. Chem. J.* **40** (2006) 373
22. G. Hallas, A. D. Towns, *Dyes Pigm.* **32** (1996**)** 135
23. C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, 1963
24. E. Abdel-Latif, F.A. Amer, *Monatsh. Chem***.** **139** (2008) 561
25. G. F. De Sa, E. Giesbrecht, L. C. Thompson, *J. Inorg. Nucl. Chem.* **37** (1975*)* 109
26. R. Sherif, K. Mohanan, *Asian J. Chem*. **13** (2001) 177
27. M. Thankamony, K. Mohanan, *Indian J. Chem. A* **46** (2007) 247
28. K. Mohanan, S. N. Devi, *Russ. J. Coord. Chem*. **32** (2006) 600
29. S. Kavita, B. V. Agarwala, *Synth. React. Inorg. Met-Org. Chem.* **26** (1996) 473
30. J. I. Bullock, H. A.T. Riahi, *Inorg. Chim. Acta* **38** *(*1980*)* 141
31. T. J. Marks, *Prog. Inorg. Chem*. **24** (1978) 51
32. D. G. Karraker, *Inorg. Chem*. **6** (1967) 1863
33. R. W. M. D'Eye, E. Wait, *X-ray Powder Photography in Inorganic Chemistry*, Butterworths, London, 1960.