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Thermal and spectral properties of lanthanide(III) complexes of 3-amino-2-hydroxy-1,4-naphthoquinone

Rajeev C. Chikate ^{a,*}, Hari A. Bajaj ^b, Avinash S. Kumbhar ^a,
Vinayak C. Kolhe ^b, Subhash B. Padhye ^a

^a Department of Chemistry, University of Poona, Ganeshkhind, Pune-411 007, India

^b Department of Chemistry, Bhusawal College, Bhusawal-425 201, India

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Abstract

Octa-coordinated La(III), Ce(III), Pr(III), Nd(III), Sm(III), Gd(III) and Dy(III) complexes of 3-amino-2-hydroxy-1,4-naphthoquinone (3A2HNQ) of general formula $[M(3A2HNQ)_3(H_2O)_2]$ have been synthesized and characterized. The non-isothermal thermogravimetric profiles indicate the loss of one of the coordinated ligands along with one coordinated water molecule at a significantly higher energy of activation than that of the second step of decomposition with loss of two ligands and one water molecule. Such a difference in the energy of activation for the two steps can be correlated to the strong intermolecular hydrogen bonding interactions between quinone carbonyls and coordinated water molecules. These chelates exhibit slightly lowered magnetic moments probably due to their polymeric nature. IR and far-IR spectral data suggest that phenolic oxygen and amino nitrogen are the coordinating sites for 3A2HNQ, while coordinated water molecules are involved in the intermolecular hydrogen bonding interactions with free quinone carbonyls of 3A2HNQ molecules. The nephelauxetic ratio (β), covalency factor ($b^{1/2}$) and Sinha's parameter (δ) evaluated from electronic spectral studies of Ce(III), Sm(III), Gd(III) and Dy(III) reveal a negligible amount of covalency in metal–ligand bonding.

Keywords: Activation energy; IRS; Lanthanum compound; Ligand; TGA

* Corresponding author. Present address: M.E.S. Abasaheb Garware College, Karve Rd., Erandawana, Pune-411 004, India.

1. Introduction

Polymeric lanthanide complexes are gaining attention because of their prevalence in various applications such as glasses, ceramics, semiconducting materials [1] and shift reagents in NMR spectroscopy [2]. These features of lanthanides can be attributed to the fact that they can expand their coordination sphere to form multinuclear complexes through either ligand bridges or intermolecular hydrogen bonding associations. Quinones, which form an integral part of the electron transport chain in photosynthesis [3], as a class of ligands, are capable of coordinating two or more metal atoms, and thus can form multinuclear metal clusters [4]. Based on various physicochemical techniques, Sharma and Singh [5] have suggested that lanthanide complexes of anthraquinone are polymeric in nature involving ligand bridges, and that similar types of complexes are isolated with embelin [6], a benzoquinone derivative.

As part of our programme concerning the coordination peculiarities of hydroxy-paraquinones, we have synthesized and characterized transition metal complexes [7–11] of various naphthoquinone derivatives. A literature survey has revealed that very few rare earth chelates of hydroxy-naphthoquinone derivatives are reported; these include lanthanide complexes of lawsone (2-hydroxy-1,4-naphthoquinone) [12] and juglone (5-hydroxy-1,4-naphthoquinone) derivatives [13], and plumbagin (2-methyl-5-hydroxy-1,4-naphthoquinone) [14]. Recently, we have shown that ferrous chelate of 3A2HNQ forms a polynuclear species [11] wherein it was found that the multinuclearity is achieved through an extensive network of intermolecular hydrogen bonding interactions involving 3A2HNQ and coordinated water molecules. We therefore decided to investigate this possibility for lanthanides with 3A2HNQ. The present paper describes the preparation and thermal, spectral and magnetic properties of some lanthanide(III) chelates with 3A2HNQ (Fig. 1).

2. Experimental

The hydrated lanthanide chlorides were obtained from Indian Rare Earths Ltd., India. All the chemicals used in preparation of ligand and metal complexes were of A.R. grade. Ethanol, methanol and DMSO were purified according to standard procedures [15] before use.

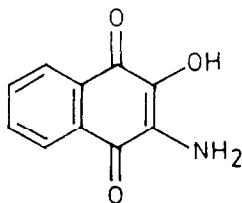


Fig. 1. 3-Amino-2-hydroxy-1,4-naphthoquinone (3A2HNQ).

2.1. Synthesis of ligands

2.1.1. Preparation of 3-nitro-2-hydroxy-1,4-naphthoquinone

2,3-Dichloro-1,4-naphthoquinone (0.06 mol) and NaNO_2 (0.2 mol) were dissolved in a mixture of 75 ml methanol and 100 ml water, stirred at 80°C for 3 h, filtered when hot and the filtrate cooled. The precipitated solid was dissolved in warm water, acidified with HCl and cooled to give light yellow crystals of 3-nitro-2-hydroxy-1,4-naphthoquinone and recrystallized from chloroform (yield 77%; m.p., $157 \pm 1^\circ\text{C}$).

2.1.2. Preparation of 3-amino-2-hydroxy-1,4-naphthoquinone

3-Nitro-2-hydroxy-1,4-naphthoquinone (0.0025 mol) was suspended in 5 ml water and 1.8 ml of 10% sodium dithionate solution was added with constant stirring. The mixture was heated to 50°C for 30 min; the precipitated solid was filtered, washed with cold water and recrystallized from ethanol to give reddish brown crystals of 3-amino-2-hydroxy-1,4-naphthoquinone (yield 80%; m.p., 234°C).

2.2. Synthesis of metal complexes

A general procedure adopted for the synthesis of lanthanide(III) chelates was as follows.

To a deaerated ethanolic solution of 3A2HNQ (0.03 mol), aqueous metal chloride (0.01 mol) solution was added under nitrogen atmosphere with constant stirring. The pH of the solution was adjusted to 6.5–7 by using 1:1 ammonia. After 1 h, a dark-coloured complex separated out which was filtered, washed with distilled water and ethanol, and finally dried under vacuum over P_2O_5 .

2.3. Physical measurements

Elemental analyses were carried out at the Micronalytical Laboratory of the University of Poona. Electronic spectra of chelates in DMSO solvent were recorded on a Hitachi 220-A spectrophotometer while IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer using a CsI window. Magnetic susceptibilities at room temperature were measured on a Faraday balance calibrated using mercury(II) tetrathiocyanatocobalt(II) ($\chi_g = 16.44 \times 10^{-4}$ cgs units) as a calibrant. Non-isothermal thermogravimetric profiles (TGA) in air were carried out on STA 409 NETZSCH Geratebau GmbH thermal analyser at a heating rate of 5°C min^{-1} .

3. Results and discussions

All the complexes are crystalline in nature, violet in colour, and insoluble in common organic solvents but soluble in DMSO, which probably indicates the presence of intermolecular associations leading to the polymeric nature. Analytical data (Table 1) suggest a $[\text{ML}_3(\text{H}_2\text{O})_2]$ stoichiometry where two water molecules are coordinated to the metal centre in each case.

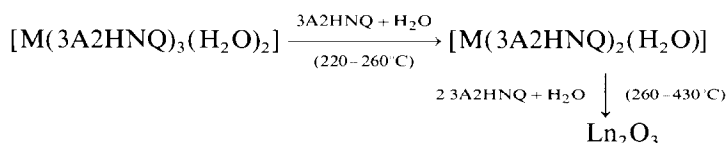
Table 1
Analytical and magnetic moments of lanthanide complexes of 3A2HNQ

Complex	Yield/%	Elemental analysis			$\mu_{\text{eff}}/\text{B.M.}$
		C/%	H/%	M/%	
[La(3A2HNQ) ₃ (H ₂ O) ₂]	55	48.67 (48.73)	2.75 (2.99)	20.75 (18.78)	D
[Ce(3A2HNQ) ₃ (H ₂ O) ₂]	61	48.89 (48.64)	3.14 (2.99)	18.75 (18.92)	2.18
[Pr(3A2HNQ) ₃ (H ₂ O) ₂]	49	48.31 (48.59)	2.97 (2.99)	19.30 (19.00)	3.29
[Nd(3A2HNQ) ₃ (H ₂ O) ₂]	53	48.04 (48.38)	3.01 (2.98)	20.19 (19.37)	3.44
[Sm(3A2HNQ) ₃ (H ₂ O) ₂]	58	47.98 (47.99)	3.19 (2.95)	20.52 (20.02)	1.38
[Gd(3A2HNQ) ₃ (H ₂ O) ₂]	56	46.90 (47.55)	2.93 (2.93)	20.94 (20.75)	7.82
[Dy(3A2HNQ) ₃ (H ₂ O) ₂]	50	48.67 (47.22)	2.75 (2.91)	21.21 (21.30)	10.50

Figures in parentheses are calculated values.

3.1. Thermal studies

The thermal characteristics of these polychelates in air (Fig. 2) indicate that they decompose in a gradual manner, in contrast to the sharp decomposition of 3A2HNQ. TGA data (Table 2) of the present complexes show that they are stable up to 200°C and undergo decomposition in two stages. During the first step (220–260°C), one of the coordinated 3A2HNQ ligands, along with one of the coordinated water molecules, is lost, while the second stage of decomposition (260–430°C) corresponds to loss of one water molecule and the remaining two 3A2HNQ ligands. The DTA curve also reveals the difference in the thermal degradation of the three bound 3A2HNQ molecules, with two exothermic peaks (one sharp at 287°C and one broad at 452°C). One endothermic peak at 395°C implies that some interchanges occur in the complex after the loss of strongly bound water molecules [16]. All the complexes are decomposed at approx. 500°C and stable oxides are formed as outlined below



The thermolytic pattern observed for these chelates probably reflects the stronger association of complex molecules through intermolecular hydrogen bonding contacts between coordinated water molecules and 3A2HNQ ligands. Such bonding can result in the formation of polymeric species which results in the decomposition

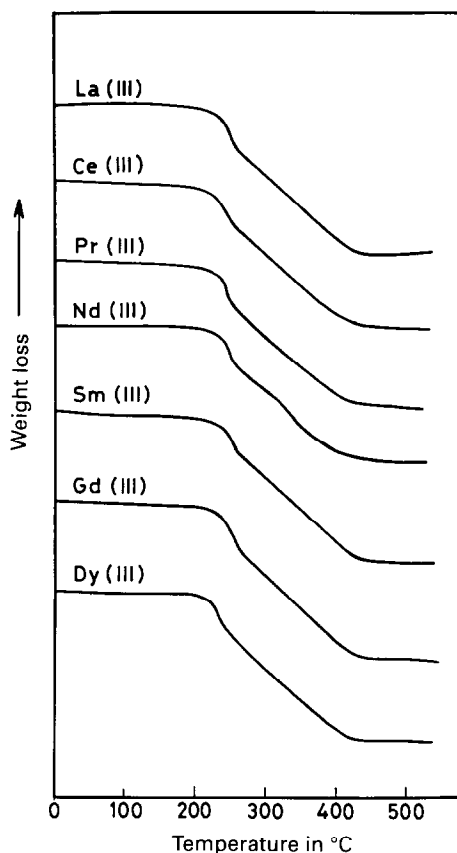


Fig. 2. Thermogravimetric profiles of rare earth chelates of 3A2HNQ.

of these chelates at higher temperatures. The kinetic parameters of the solid state thermal reaction involving decomposition and consequent weight loss have been calculated by the Coats and Redfern method [17]. The respective energies of activation for each step have been calculated using the equation

$$F(\alpha) = A e^{-E_a/RT} \quad (1)$$

where

$$F(\alpha) = -2.303 \log \left[\frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - \alpha)} \right]$$

A plot of $F(\alpha)$ versus $1/T$ for each step (Fig. 3) results in a straight line with slope equal to $-E_a/2.303R$. The thermal decomposition data listed in Table 2 suggest that the energy of activation for the first step goes on increasing from La(III) to Dy(III), suggesting that the extra stability is achieved through intermolecular hydrogen bonding. However, the reverse trend is observed for the energy of

Table 2
Thermal decomposition and energy of activation for lanthanide complexes of 3A2HNQ

Compounds	Step I ^a		Step II ^b	
	Wt. loss/%	Energy of activation ^c	Wt. loss/%	Energy of activation ^c
[La(3A2HNQ) ₃ (H ₂ O) ₂]	27.45 (27.88)	62.3	52.75 (53.33)	54.9
[Ce(3A2HNQ) ₃ (H ₂ O) ₂]	27.08 (27.83)	70.3	52.27 (53.24)	52.0
[Pr(3A2HNQ) ₃ (H ₂ O) ₂]	26.95 (27.80)	109.9	52.61 (53.18)	47.8
[Nd(3A2HNQ) ₃ (H ₂ O) ₂]	26.87 (27.68)	122.3	52.37 (52.94)	43.9
[Sm(3A2HNQ) ₃ (H ₂ O) ₂]	26.54 (27.45)	127.4	51.95 (52.51)	41.4
[Gd(3A2HNQ) ₃ (H ₂ O) ₂]	26.17 (27.20)	138.0	51.47 (52.04)	35.4
[Dy(3A2HNQ) ₃ (H ₂ O) ₂]	26.08 (27.02)	153.4	51.12 (51.68)	34.7

Figures in parentheses are calculated values. ^a This relates to the elimination of one 3A2HNQ and one H₂O. ^b Corresponds to the decomposition of one water molecule and the remaining two 3A2HNQ. ^c in kJ mol⁻¹.

activation corresponding to the second step. This probability indicates a weakening of the intermolecular associations after the first stage of decomposition.

3.2. Magnetic properties

Room temperature magnetic moments of the lanthanide complexes are presented in Table 1. The paramagnetic behaviour of the lanthanide(III) ions, except La(III), denotes the presence of unpaired electrons. Because these electrons are well shielded by the 5s², 5p⁶ octet, both in their spin and orbital moment, the magnetic moments show little deviation from the Van Vleck values [18]. The lowered magnetic moments can be attributed to antiferromagnetic exchange couplings, promoted by either ligand bridges or intermolecular hydrogen bonding interactions. Such a lowering of magnetic moment has been noted for the ferrous complex [11] of 3A2HNQ, and it was suggested that the deviation in the magnetic moment originates from the extensive network of intermolecular hydrogen bonding between coordinated water and 3A2HNQ molecules.

3.3. IR spectra

The IR spectrum of free 3A2HNQ ligand shows a strong band at around 3490 cm⁻¹ (Table 3) attributed to the stretching mode of the intermolecularly hydrogen-bonded phenolic (OH) group [19]. In polychelates, this absorption disappears and

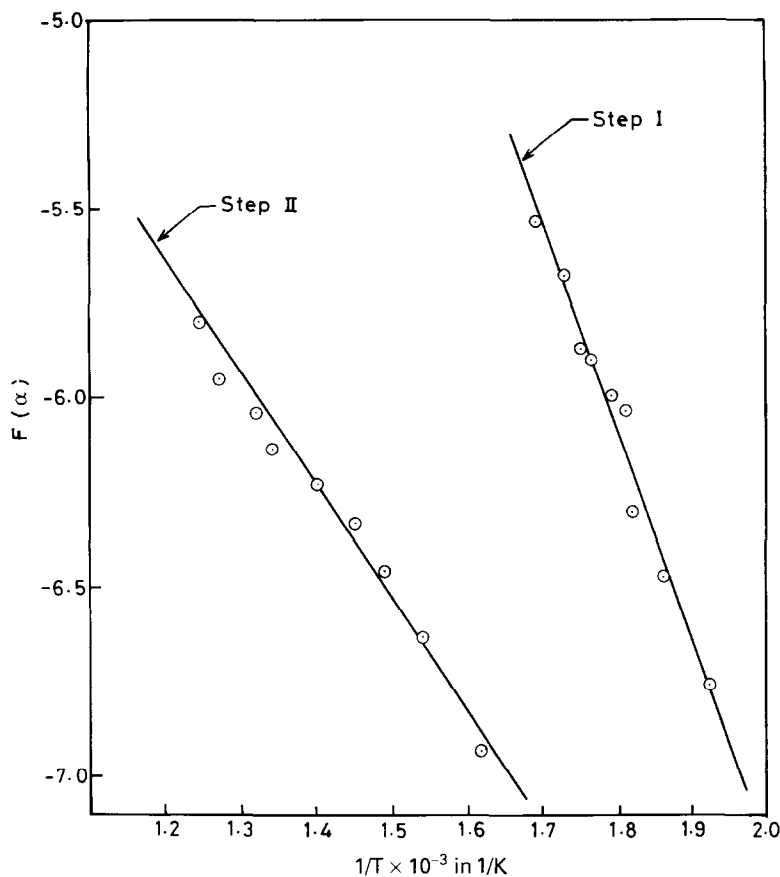


Fig. 3. Kinetic plot of $F(x)$ vs. T^{-1} for $[\text{Pr}(\text{3A2HNQ})_3(\text{H}_2\text{O})_2]$.

a new band in the range $3550\text{--}3540\text{ cm}^{-1}$ is observed presumably due to the $\nu(\text{OH})$ of water molecules [20]. Such an upward shift is mainly because of the intermolecular hydrogen bonding interaction between quinone carbonyl and coordinated water molecules. In addition, characteristic symmetric and asymmetric $\nu(\text{NH}_2)$ vibrations [21] are observed at 3380 and 3330 cm^{-1} for 3A2HNQ which, upon complexation, are broadened and shifted on the lower energy side by $60\text{--}40\text{ cm}^{-1}$, suggesting that the amino nitrogen is involved in the coordination. Thus, C(2) hydroxyl and C(3) amino groups are the donor centres in 3A2HNQ.

In the double bond region, the assignment of hydrogen bonded C_1 and free C_4 carbonyl absorptions in 3A2HNQ is rather difficult due to the overlapping of the intense $\text{C}=\text{C}$ stretching frequency of the quinone ring. On the basis of the near-IR and NMR spectra, Padhye et al. [22] have reported dimeric association in 2-hydroxy-1,4-naphthoquinone (lawsone), while Morton [23] had earlier suggested that absorption around 1610 cm^{-1} in the carbonyl region may be due to the $\text{C}=\text{C}$

Table 3
Significant peaks (cm^{-1}) in IR spectra of lanthanide complexes of 3A2HNQ

Compound	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$ free	$\nu(\text{C}=\text{O})$ chelated	$\nu(\text{C}-\text{O})$
3A2HNQ	3490	3380, 3330	1680	1640	1170
[La(3A2HNQ) ₃ (H ₂ O) ₂]	3540	3320	1650	1610	1210
[Ce(3A2HNQ) ₃ (H ₂ O) ₂]	3550	3320	1660	1620	1200
[Pr(3A2HNQ) ₃ (H ₂ O) ₂]	3545	3330	1655	1615	1200
[Nd(3A2HNQ) ₃ (H ₂ O) ₂]	3540	3340	1660	1617	1197
[Sm(3A2HNQ) ₃ (H ₂ O) ₂]	3550	3320	1665	1609	1200
[Gd(3A2HNQ) ₃ (H ₂ O) ₂]	3540	3330	1667	1605	1208
[Dy(3A2HNQ) ₃ (H ₂ O) ₂]	3550	3320	1660	1600	1210

of the quinone ring. Based on these observations, the absorptions at 1680 and 1640 cm^{-1} are due to free C(1) and hydrogen-bonded C(4) quinone carbonyls, respectively, while the quinonoidal C=C skeletal vibration is seen at 1610 cm^{-1} . The downward shift by 30 cm^{-1} upon complexation for quinone carbonyls led us to believe that intermolecular associations are present through hydrogen bonding interactions with coordinated water molecules, resulting in a polymeric nature for the present chelates. A strong $\nu(\text{C}-\text{O})$ phenolic vibration at approx. 1170 cm^{-1} for free 3A2HNQ is shifted to higher energy (Δ 40 cm^{-1}), confirming the participation of the C(2) oxygen atom in the coordination [24]. The (M–O) and (M–N) stretching modes are observed at approx. 480 and 430 cm^{-1} , respectively, for the present complexes [25].

3.4. Electronic spectra

Electronic spectra of the lanthanide complexes and the ligand have been recorded in DMSO solvent. 3A2HNQ exhibits two absorption peaks at 37 560 and 34 480 cm^{-1} which are shifted towards the higher energy side upon complexation with lanthanide ions. All the complexes are characterized by intense charge-transfer bands and most of the absorptions arising from weak f–f transitions are obscured in the visible region by broad, strong charge-transfer bands. However, Ce(III), Sm(III), Gd(III) and Dy(III) complexes exhibit two transitions in the ranges 19 500–16 000 and 24 500–23 000 cm^{-1} respectively whose assignments [26] are depicted in Table 4. The red shifts of the hypersensitive bands have been used to calculate the nephelauxetic effect ratio (β) [27], bonding parameter ($b^{1/2}$) and Sinha's parameter (δ) [28] in order to understand the bonding in the complexes. These values indicate the extent of 4f-orbital participation in complexation. As the $b^{1/2}$ value is less than unity, no appreciable overlap is present between the 4f-metal orbitals and the ligand π -orbitals. Also, the average value of Sinha's parameter (δ) and the nephelauxetic ratio (β) implies weaker covalency in metal–ligand bonding [29] for the present series of complexes.

Table 4
Electronic spectral data for lanthanide chelates of 3A2HNQ

Complex	$\lambda_{\text{max}}/\text{cm}^{-1}$	Assignments	Spectral parameters
[Ce(3A2HNQ) ₃ (H ₂ O) ₂]	19230 24390	$^2F_{5/2} \rightarrow ^2D_{3/2}$ $^2F_{5/2} \rightarrow ^2D_{5/2}$	$\beta = 0.9807$ $\delta = 1.968$ $b^{1/2} = 0.0982$
[Sm(3A2HNQ) ₃ (H ₂ O) ₂]	18181 23809	$^6H_{5/2} \rightarrow ^4I_{3/2}$ $^6H_{5/2} \rightarrow ^6P_{3/2}$	$\beta = 0.9827$ $\delta = 1.750$ $b^{1/2} = 0.0927$
[Gd(3A2HNQ) ₃ (H ₂ O) ₂]	17700 24390	$^8S_{7/2} \rightarrow ^6P_{5/2}$ $^8S_{7/2} \rightarrow ^6P_{7/2}$	$\beta = 0.9823$ $\delta = 1.80$ $b^{1/2} = 0.0939$
[Dy(3A2HNQ) ₃ (H ₂ O) ₂]	16393 23810	$^6H_{5/2} \rightarrow ^6H_{3/2}$ $^6H_{5/2} \rightarrow ^4I_{3/2}$	$\beta = 0.9836$ $\delta = 1.67$ $b^{1/2} = 0.0906$

4. Conclusions

Lanthanide complexes of 3A2NHQ are indeed polymeric in nature, as reported for anthraquinone [5] and embelin [6]. However in the present case, polymerization is occurring through intermolecular hydrogen bonding interactions between coordinated water and 3A2HNQ molecules, similar to the case observed earlier from ferrous chelate [11]. The thermal characteristics of these polychelates indicate that during the first stage of decomposition, the weakening of some of the chemical bonds takes place which results in the lowering of the activation energy for the subsequent second step of thermal degradation. The higher energies of activation for the two stages are probably due to the polymeric nature which is reflected in the lowering of the magnetic moments for these chelates. IR data suggest that the C(2) hydroxyl and C(3) amino functions are the binding sites for 3A2HNQ, while the uncoordinated quinone carbonyls are involved in intermolecular hydrogen bonding interactions with coordinated water molecules. There is negligible covalency in the metal–ligand bonding, as evidenced from the electronic absorption spectra.

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