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Synthesis, Characterization and Thermal Properties of Two Novel Lanthanide 2,2'-Biquinoline-4,4'-Dicarboxylate Complexes

(Sintesis, Pencirian dan Sifat Terma Dua Kompleks Lantanida 2,2'-bikuinolin-4,4'-dikarboksilat)

S. ZATI-HANANI, R. ADNAN*, A.F.A. LATIP & C.S. SIPAUT

ABSTRACT

*Two new lanthanide coordination complexes with 2,2'-biquinoline-4,4'-dicarboxylic acid (H_2bqda) and 1,10-phenanthroline (phen), $[La_2(Hbqda)_2(bqda)_2(phen)]_n$ [**1**] and $[Gd(bqda)_{1.5}(phen)]_n$ [**2**] were successfully synthesized and characterized. The complexes were obtained through hydrothermal method at 170°C for 3 days. The metal to acid to 1,10-phenanthroline ratio, 1:1:2 had been chosen to synthesize **1** and **2**. The percentage yield for **1** and **2** was 68% and 75%, respectively calculated based on the starting lanthanide salt used. The yellow coloured complexes were found to be stable at room temperature and insoluble in organic solvents. The complexes obtained were characterized by elemental analysis (CHN), infrared spectroscopy (FTIR) and thermogravimetric (TGA) analysis. The FTIR spectra of these complexes confirm the complexation had taken place by the existence of COO^- symmetric and asymmetric stretching peaks at 1385 and 1542-1532 cm^{-1}, respectively.*

Keywords: 1,10-phenanthroline; 2,2'-biquinoline-4,4'-dicarboxylic acid; hydrothermal method; lanthanide

ABSTRAK

*Dua kompleks koordinatan baru lantanida dengan asid 2,2'-bikuinolin-4,4'-dikarboksilik (H_2bqda) dan 1,10-fenantrolina (phen), $[La_2(Hbqda)_2(bqda)_2(phen)]_n$ [**1**] dan $[Gd(bqda)_{1.5}(phen)]_n$ [**2**] telah berjaya disintesis dan dicirikan. Kompleks ini telah diperoleh melalui kaedah hidroterma pada suhu 170°C selama 3 hari. Nisbah logam kepada asid kepada 1,10-fenantrolin, 1:1:2, telah dipilih untuk mensintesiskan **1** dan **2**. Peratus hasil bagi **1** dan **2** masing-masing adalah 68% dan 75% dikira berdasarkan garam lantanida yang digunakan. Kompleks berwarna kuning ini didapati stabil pada suhu bilik dan tidak larut dalam pelarut organik. Kompleks yang diperoleh telah dicirikan menggunakan analisis unsur (CHN), spektroskopi inframerah (FTIR) dan analisis termogravimetri (TGA). Spektra FTIR bagi kompleks membuktikan pengkompleksan telah berlaku dengan kewujudan puncak simetrik dan asimetrik COO^- masing-masing pada 1385 dan 1542-1532 cm^{-1}.*

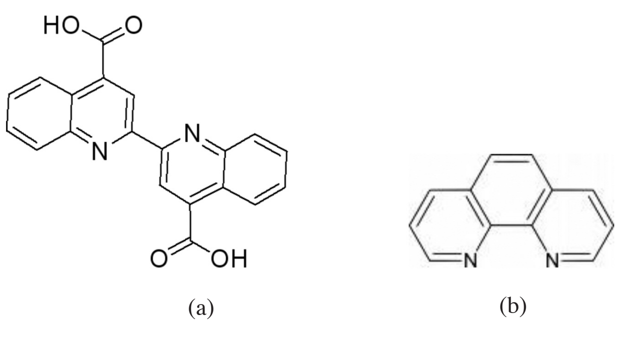
Kata kunci: asid 2,2'-bikuinolin-4,4'-dikarboksilik; kaedah hidroterma; lantanida; 1,10-fenantrolina

INTRODUCTION

The control and design of polymeric coordination complexes is an interesting theme of modern chemistry due to their potential applications as catalyst (Liu et al. 2005; Sun et al. 2004; Wan et al. 2002), molecular recognition (Qin et al. 2006; Sun et al. 2004; Wan et al. 2002), ion exchange (Liu et al. 2005), nonlinear optical devices (Qin et al. 2006) and gas storage (Kongshaug & Fjellvåg 2003). The polymeric coordination complexes must be thermally stable to be used in applications mentioned above (Janiak 2003; Rowsell & Yaghi 2004). Thus, the selection of appropriate organic ligands is crucial to the design and synthesis of the thermally stable coordination polymers.

The 2,2'-biquinoline-4,4'-dicarboxylic acid (H_2bqda, Figure 1(a)) is a good candidate to construct polymeric complexes as it has four coordination sites which is available to coordinate with metal (Chen et al. 2007; Xiel 2009). Furthermore, the two quinoline rings which are linked by a single bond could be adjusted freely depending on the nature of the metals and may lead to various structures and properties (Ye et al. 2006; Zhang et al. 2008b).

On the other hand, 1,10-phenanthroline (phen, Figure 1(b)) had been used as terminal ligand to give higher dimension of coordination complexes through hydrogen bonding and other inter and intramolecular interactions.



(a) (b)

FIGURE 1. Structures of (a) 2,2'-biquinoline-4,4'-dicarboxylic acid and (b) 1,10-phenanthroline

Lanthanide was selected to be used in this study because of the possible useful applications that may arise from the special electronic, magnetic, photochemical and catalytic properties shown by these metals (Robson 2000). Besides, lanthanide ions offer higher coordination modes than transition metals and this leads to remarkable structures which are highly unlikely to be encountered when using transition metal ions (Hill et al. 2005). Here in, we report the hydrothermal synthesis and thermal properties of two novel lanthanide 2,2'-biquinoline 4,4'-dicarboxylate with 1,10-phenanthroline, complexes $[La_2(Hbqda)_2(bqda)_2(phen)]_n$ and $[Gd(bqda)_{1.5}(phen)]_n$.

Materials and Methods

All reagents used in this work were purchased from commercial sources and were used as received. The IR spectra were obtained from Perkin-Elmer System 2000 FTIR spectrometer using KBr pellet. Elemental microanalyses were carried out on a Perkin-Elmer 2400 CHN analyzer. Thermogravimetric analyses (TGA) were performed on Perkin-Elmer TGA 7 thermogravimetric analyzer.

SYNTHESIS OF COMPLEXES (1) AND (2)

A mixture of lanthanum nitrate hexahydrate $[La(NO_3)_3.6H_2O]$ (0.1 mmol), H_2bqda (0.1 mmol) and 1,10-phenanthroline (0.2 mmol) together with deionized water (25 mL) was stirred for 30 min. After that, the mixture was transferred into a Teflon tube and heated to 170°C for 72 h. Upon cooling to room temperature at a rate of 5°C h^{-1}, small crystals of **1** were obtained. The crystals obtained were washed with ethanol and distilled water. The yield was 68% based on lanthanum salt used. Similar steps were repeated using gadolinium nitrate hexahydrate $(Gd(NO_3)_3.6H_2O)$ and small crystals of **2** were obtained. The yield was 75%.

Results and Discussion

PHYSICAL APPEARANCES

Complexes **1** and **2** were found to adopt the yellow colour of the acid. The complexes were also observed to be stable under ambient temperature and insoluble in organic solvents. The solubility test was done by adding a few milligrams of crystals **1** and **2** into a few mL of organic solvents in a test tube. The test tube was then heated to the boiling point of the solvent for 30 min and any change was recorded.

INFRARED CHARACTERIZATION

Table 1 shows tentative assignments of the IR peaks for $[La_2(Hbqda)_2(bqda)_2(phen)]_n$ [**1**] and $[Gd(bqda)_{1.5}(phen)]_n$ [**2**] together with the acid and 1,10-phenanthroline.

The presence of water molecules causes the appearance of strong and broad O-H stretching bands in the region of 3473-3417 cm^{-1} in the IR spectra of **1** and **2** (Cho et al. 2003; Zhai et al. 2006). This is due to the complexes absorbing water from moisture. The strong and sharp absorption bands at 1543, 1534 and 1532 cm^{-1} in IR spectra of **1** and **2** is indicative of the asymmetric stretching COO^- vibration while peak at 1385 cm^{-1} region is due to its symmetric stretching (Fang et al. 2004; Si et al. 2003; Xu et al. 2003; Zhang et al. 2006). The presence of these two absorption bands confirmed that complexation had taken place as previously, these two bands were not observed in the IR spectrum of the starting material. Furthermore, the new peak attributed to M-O bending which appeared at 471 cm^{-1} in **1** and **2** further confirmed **bqda** had coordinated with lanthanide ions through oxygen atom of carboxylate group (Nakamoto 2009).

The presence of strong and sharp band near 1697 cm^{-1} in the IR spectrum of **1** indicates incomplete deprotonation. Furthermore, the absorption bands at 911 cm^{-1} which represent the C-O-H bending for COOH and the absorption band at 3084-2605 cm^{-1} which corresponds to the O-H stretching for carboxylic acid can still be observed in the IR spectrum of **1.** These confirmed the incomplete deprotonation of H_2bqda in **1** (Qin et al. 2005; Yong et al. 2004).

On the other hand, the absence of absorption bands in the region at about 3084-2605 cm^{-1} and 1697 cm^{-1} in IR spectrum of **2** confirmed the complete deprotonation of the ligand in the complex (Du et al. 2008; Zhang et al. 2006). Further confirmation comes from the absence of C-O-H bending peak for COOH group at 908 cm^{-1} (Ye et al. 2005; Zhang et al. 2008b).

The presence of two absorption peaks that attributed to the aromatic C=C and C=N stretching of 1,10-phenanthroline around 1619 cm^{-1} and 1419 cm^{-1} in **1** and **2** confirmed the complexation between 1,10-phenanthroline and lanthanide ion took place through its nitrogen atom (Ren et al. 2006; Rogan et al. 2000). This fact is further supported by the appearance of C-H in-plane bending peak of 1,10-phenanthroline at 1149 cm^{-1} in **1** and 1107 cm^{-1} in **2** (Rogan et al. 2000). In fact, the C-H out-of-plane bending peak of 1,10-phenanthroline which could be observed at 731 cm^{-1} in **1** and **2** is also an evidence of the coordination between 1,10-phenanthroline and lanthanide ions had took place (Rogan et al. 2000).

PREDICTION OF COORDINATION MODE OF LANTHANIDE AND H_2BQDA BASED ON CARBON-OXYGEN STRETCHING FREQUENCIES OF 1 AND 2

In order to predict the coordination mode of lanthanide and H_2bqda in **1** and **2**, we compared the difference of the value between the asymmetric and symmetric stretching of COO^- frequencies ($\Delta v = \nu_{sym}COO^- - \nu_{asym}COO^-$) of **1** and **2** with potassium 2,2'-biquinoline-4,4'-dicarboxylate. Table 2 shows the difference value between the asymmetric and symmetric stretching of COO^- frequencies of **1**, **2** and dipotassium 2,2'-biquinoline-4,4'-dicarboxylate.

TABLE 1. Tentative assignments of the IR peaks for $[La_2(Hbqda)_2(bqda)_2(phen)]_n$ [**1**] and $[Gd(bqda)_{1.5}(phen)]_n$ [**2**] together with the acid and 1,10-phenanthroline

Assignment	H_2bqda	1,10-phenanthroline	**1**	**2**
$v(\text{O-H})_{\text{water}}$	3417 (b)	3473, 3421 (b)	3422 (b)	3418 (b)
$v(\text{O-H})_{\text{carboxylic acid}}$	3080–2331 (m,b)	-	3084–2605 (m,b)	-
$v(\text{C=O})_{\text{carboxylic acid}}$	1698 (s,sh)	-	1697 (m)	-
$v[(\text{C=C})+(\text{C=N})]_{\text{aromatic}}$	1585 (m), 1505 (m), 1451 (m)	1619 (m,sh), 1588 (m,sh), 1506 (m,sh), 1494 (m,sh), 1419 (s,sh)	1609 (m), 1584 (m), 1505 (m), 1449 (m), 1415 (m)	1616 (s,sh), 1587 (s,sh), 1505 (m), 1450 (m), 1420(m)
$v_{\text{asym}}(\text{COO}^-)$	-	-	1543 (s,sh), 1532 (s,sh)	1534 (m)
$\delta(C{-}O{-}H)_{\text{carboxylic acid}}$	1428 (m)	-	1429 (m)	-
$v_{\text{sym}}(\text{COO}^-)$	-	-	1385 (s,sh)	1385 (s)
$v(\text{C-O})_{\text{carboxylic acid}}$	1286 (s,sh)	1283 (m)	-	
$\delta_{\text{ip}}(\text{C–H})_{\text{aromatic}}$	1203 (m), 1158 (m), 1083 (m)	1138 (m), 1093 (m)	1204 (m), 1158 (m), 1149 (m), 1084 (m)	1208 (m), 1147 (m), 1107 (m), 1078 (m)
$\delta_{\text{oop}}(\text{O–H})$	911 (m, b)	-	905 (m, b)	-
$\delta_{\text{oop}}(\text{C–H})_{\text{aromatic}}$	744 (m) 775 (m),	848 (s), 841 (s), 733 (s)	850 (m), 774 (m), 750 (m), 731 (m)	850 (m), 775 (m), 752 (m), 732 (m)
$\delta(\text{M–O})$	-	-	471 (w)	471 (w)

Abreviations: s, strong; m, medium; w, weak; b, broad; sh, sharp; ip, in-plane; oop, out-of-plane; asym, asymmetric; sym, symmetric.

TABLE 2. Difference value between the asymmetric and symmetric stretching of COO^- frequencies **1**, **2** and potassium 2,2'-biquinoline-4,4'-dicarboxylate

Complexes	Asymmetric COO^-, $v_{asym}COO^-$ (cm^{-1})	Symmetric COO^-, $v_{sym}COO^-$ (cm^{-1})	Difference of peak value, Δv (cm^{-1})	Prediction of coordination mode (Nakamoto 2009)
1	1543	1385	158	Bidentate chelating
	1532		147	
2	1542	1385	149	Bidentate chelating
K_2bqda	1543	1372	171	-

The 2,2'-biquinoline-4,4'-dicarboxylic acid may coordinate with lanthanide through monodentate, bidentate chelating and bridging as shown in Figure 2. According to Nakamoto (2009) and Deacon & Phillips (1980), the monodentate coordination will shift the asymmetric stretching of COO^- to higher wavenumber while shifting the symmetric stretching to the lower wavenumber from its potassium salt due to the redistribution of electron density. Thus, Δv will be larger than that of the potassium salts. On the other hand, bidentate chelating or bridging coordination would not alter the bond orders thus bidentate coordination will give lower Δv value than the potassium salts. According to the authors too, the increase in v_{asym} COO^- relative to potassium salt is an indicative of bridging where as the decrease in v_{asym} COO^- is indicative of a chelating coordination mode.

Based on the findings, we could suggest 2,2'-biquinoline-4,4'-dicarboxylate ion bind to the lanthanide via bidentate chelating mode as the Δv for **1** (154 cm^{-1}, 148 cm^{-1}) and **2** (158 cm^{-1}) are lower than potassium 2,2'-biquinoline-4,4'-dicarboxylate (171 cm^{-1}).

ELEMENTAL ANALYSIS (CHN)

The results of elemental analysis performed on **1** and **2** are tabulated in Table 3.

From the CHN analysis calculation, we could suggest that **1** has an empirical formula of $La_2C_{92}H_{50}N_{10}O_{16}$ or

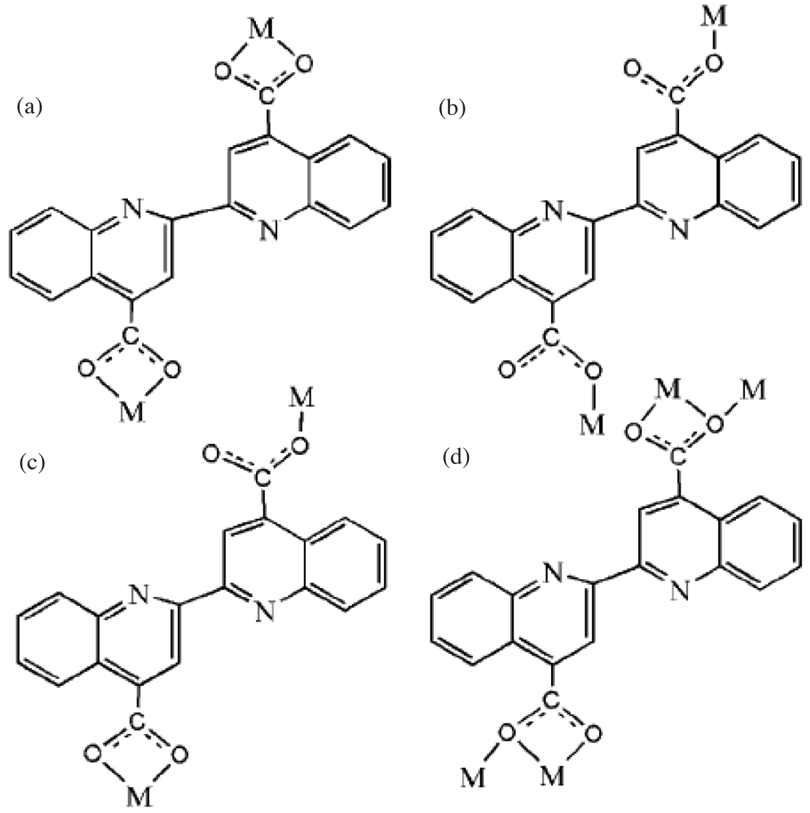


FIGURE 2. Coordination modes of 2,2'-biquinoline-4,4'-dicarboxylate ion: (a) bis-bidentate chelating (b) bis-monodentate (c) monodentate-bidentate chelating (d) bis-chelating-bridging tridentate (Dai et al. 2008)

TABLE 3. The differences between found and calculated percentage composition of the C, H and N of **1** and **2**

Complex	Empirical formula	Mass (g mol^{-1})	%C		%H		%N	
			Calc.	Found	Calc.	Found	Calc.	Found
1	$La_2C_{92}H_{50}N_{10}O_{16}$	1829.34	60.39	60.48	2.76	2.54	7.66	7.74
2	$GdC_{42}H_{23}N_5O_8$	850.95	59.28	59.05	2.72	2.37	8.23	8.20

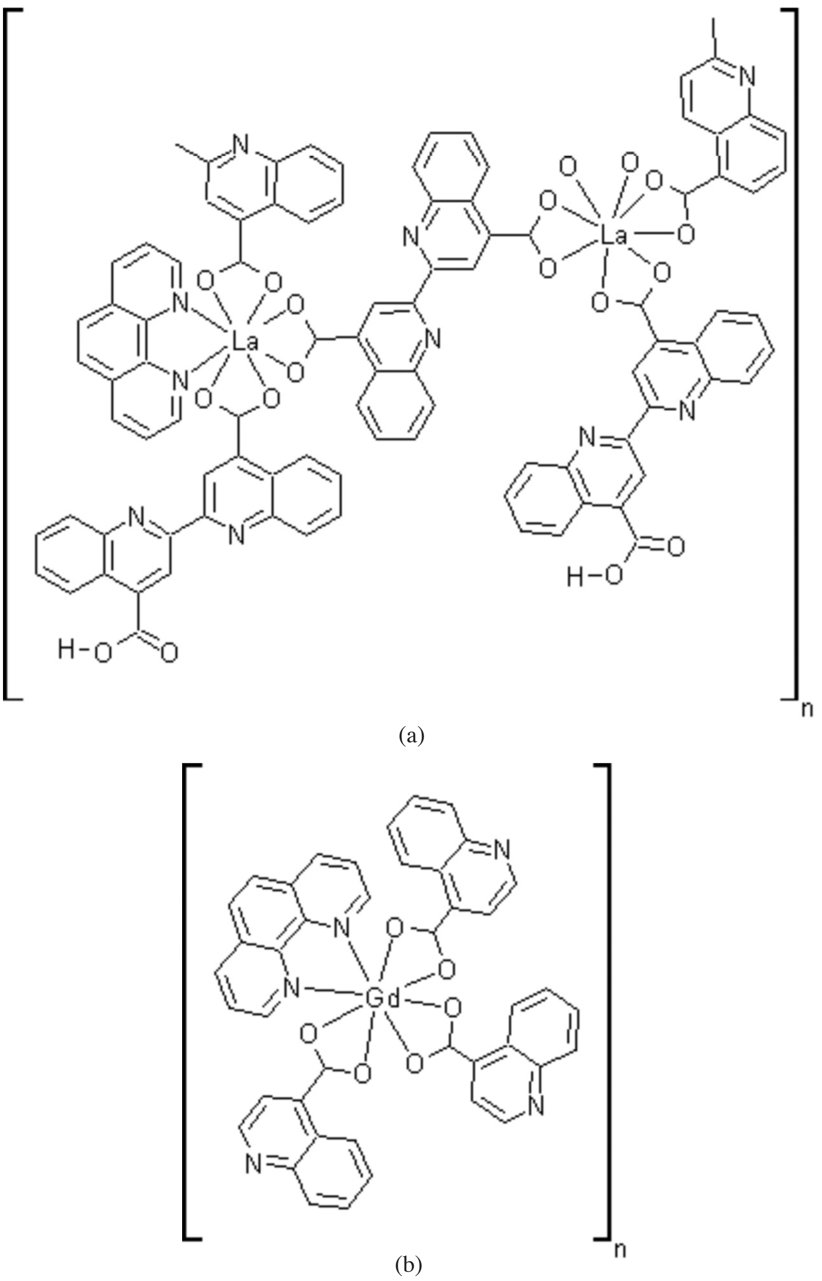
molecular formula of $[La_2(Hbqda)_2(bqda)_2(phen)]_n$ while **2** has an empirical formula of $GdC_{42}H_{23}N_5O_8$ or molecular formula of $[Gd(bqda)_{1.5}(phen)]_n$. This empirical formula of **1** and **2** is in good agreement with the FTIR results, which show that **1** had unprotonated ligand while **2** had fully protonated ligand, respectively. On the basis of above evidence and literature (Wan et al. 2003; Zhang et al. 2008a), the possible structure for **1** and **2** have been suggested as shown in Figure 3.

THERMAL PROPERTIES

Thermogravimetric analyses were performed under nitrogen atmosphere at the heating rate of 20°C min^{-1} on the complexes obtained to examine their thermal stability of the complexes. Figure 4 shows the thermograms of **1** and **2**.

The TG-DTG curves of **1** (Figure 4(a)) show the first weight loss of 1.24% from 45 to 60°C which corresponds to the removal of moisture absorbed by **1**. This phenomenon can also be seen in TG-DTG curves of **2** (Figure 4 (b)). Upon increasing the temperature, **1** decomposed in four more steps at the temperature range between 292 and 610°C. This can be assigned to the loss of biquinoline carboxylic acid and 1,10-phenanthroline in stages. The total weight loss of the biquinoline carboxylic acid and 1,10-phenanthroline are 69.60% (calcd. 69.47%). The remaining weight of 29.16% at above 610°C can be attributed to the formation of lanthanum oxide and amorphous carbon.

For **2**, the TG-DTG curves (Figure 4(b)) shows rapid decomposition between 429 to 610°C which indicates the removal of biquinoline dicarboxylate acid and



(a)

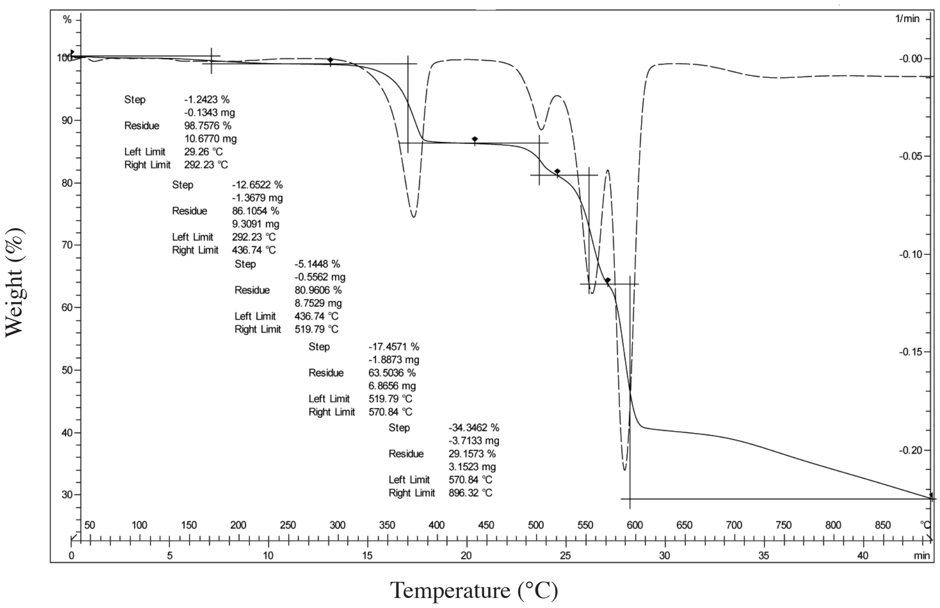
(b)

FIGURE 3. The suggested structures of (a) $[La_2(Hbqda)_2(bqda)_2(phen)]_n$ [**1**] and (b) $[Gd(bqda)_{1.5}(phen)]_n$ [**2**]

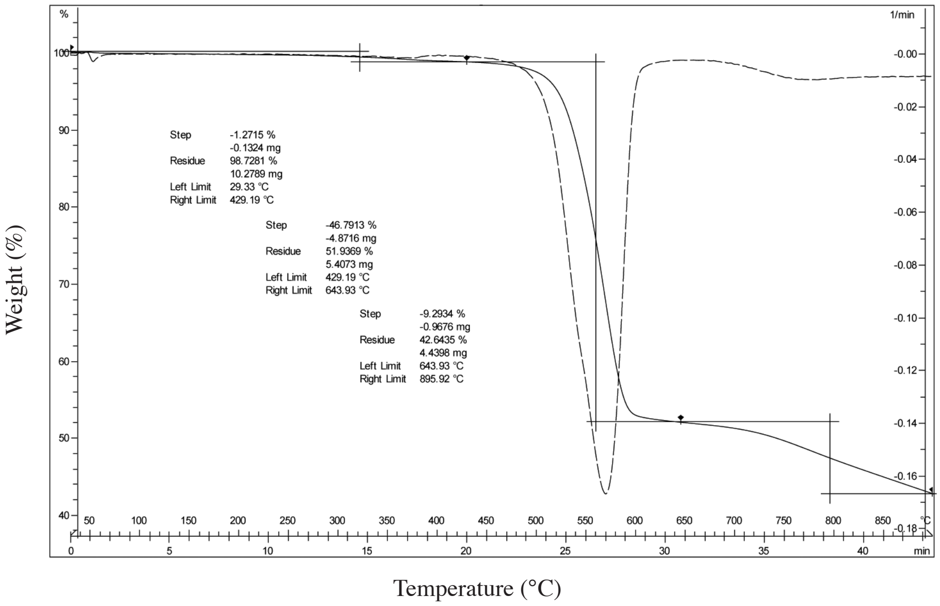
phenanthroline. The total mass reduction of the ligand is 55.08% (calcd. 56.1)0%). The remaining weight of 42.64% can be attributed to the formation of gadolinium oxide and amorphous carbon. Complexes **1** and **2** exhibit higher thermal stability compared to $[Cd(bqdc)(phen)_2]_n$ and $[Co(bqdc)(phen)(H_2O)_2]_n$,(bqdc=2,2'-biquinoline-4,4'-dicarboxylic acid) which decomposed at 520 and 396°C, respectively (Dai et al. 2008). This result showed that higher coordination number by lanthanide than transition metal could contribute to higher thermal stability and rigidity of the complex **1** and **2** (Liu et al. 2002; Pan et al. 2001). In addition, the π- π interactions within phenantroline and biquinoline dicarboxylate moiety also contribute to the stability of the complexes (Hu et al. 2007; Wu et al. 2006).

CONCLUSION

By using 2,2'-biquinoline-4,4'-dicarboxylic acid as ligand and 1,10-phenanthroline as secondary ligand, lanthanide complexes, Ln=La(**1**) and Gd(**2**) were hydrothermally synthesized and characterized. TGA studies performed on **1** and **2** indicate both complexes were thermally stable. In the future, the photoluminescence properties and structures of the series will be investigated.



(a)



(a)

FIGURE 4. Thermograms of (a) $[La_2(Hbqda)_2(bqda)_2(phen)]_n$ [**1**] and (b) $[Gd(bqda)_{1.5}(phen)]_n$ [**2**]

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Pusat Pengajian Sains Kimia
Universiti Sains Malaysia
11800 Pulau Pinang
Malaysia

*Corresponding author; email: r_adnan@usm.my

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