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Surface layer-by-layer chemical deposition reaction for thin film formation of nano-sized metal 8-hydroxyquinolate complexes $\stackrel{\circ}{\approx}$

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ABSTRACT

The feasibility of a novel and simple layer-by-layer chemical deposition method for the preparation of nano-sized metal 8-hydroxyquinolate complexes has been investigated and reported. Uniform nanocrystalline films have been synthesized via dipping a substrate alternately in metal ion solution followed by ligand solution. The stoichiometry of the as-grown anhydrous Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complex crystals were confirmed from the metal analysis and molar stoichiometric ratio of metal ion to 8-hydroxyquinoline. This was characterized as 1:2 for the Co(II), Ni(II), Cu(II) and Zn(II)–quinolate complexes. The Fe(III)–quinolate thin film was found to exhibit a 1:3 ratio. Electron impact-mass spectra (EI-MS) of all the synthesized thin film metal quinolate complexes were recorded and the results refer to the existence of the molecular ion peak at the corresponding *m*/*z* values. Confirmation of such stoichiometric 1:2 and 1:3 ratios were also evident from the (EI-MS) study. The deposited thin film swere also subjected to analysis by a scanning electron microscope (SEM) and a particle size ≥ 50 nm was detected. FT-IR and UV–Vis spectroscopy were further used to confirm the structure of the metal 8-hydroxyquinolate complexes. Thermal gravimetric analysis (TGA) was also used to follow up the possible thermal decomposition steps and to calculate the thermodynamic parameters of the nano-sized metal complexes.

1. Introduction

Recently, more research efforts have been focused on the beneficial applications of the layer-by-layer deposition technique. This methodology has emerged and been found a more economic alternative for the direct preparation of thin films [1–3]. The highly sophisticated gas-phase layer deposition method can be easily replaced by this simple and direct liquid-phase solution-based layerby-layer technique for thin film formation [4,5]. The formation of a variety of important compounds was successfully synthesized via the layer-by-layer thin film deposition approach. Polyelectrolyte thin films were prepared via alternately dipping the substrate into polycation and polyanion solutions to form polyelectrolyte multilayer films [6] as well as polymer-nanoclay multilayers [7]. The application of the layer-by-layer deposition method for the formation of various metal oxide [8–10] and metal sulfide thin films [11– 13] have been reported and their optical properties investigated.

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8-Hydroxyquinoline, 8HQ, also known as oxine, its derivatives as well as related metal complexes, are playing a uniquely important role in different disciplines of chemical research and applications. 8HQ, as a complexone or sequestering reagent, is considered second to EDTA and its analogues in binding with metal ions [14]. 8HQ was mainly applied for analytical purposes and separation techniques as an excellent reagent for the extraction of metal ions due to its extraordinary coordinating capabilities [15-20]. However, in coordination chemistry, versatile synthetic approaches for the formation of metal complexes of 8HQ and its derivatives were extensively used to open a wide range of di and tri-valent metal complexes that can be used as an arsenal for various impacts and applications in different fields. Among these applications are the utilization of 8-hydroxyquinoline as an interesting chelating agent for the formation of luminescent coordination compounds as light emitting devices. A review covering the applications of metal complexes of 8-hydroxyguinoline derivatives to obtain new supramolecular sensors, emitting devices or self-assembled aggregates was recently published [21]. Moreover, tris(8-hydroxyguinoline) aluminum (Alq3) is widely used in modern organic light emitting diodes (OLEDs) due to its excellent stability and electroluminescent properties via the high dependence on the injection behavior of the metallic contacts [22-24]. Most recent research efforts have also been focused on the synthesis of quinolate metal

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complex nanomaterials by physical vapor deposition [25,26] and adsorbent assisted physical vapor deposition [27] techniques, with positive results at the end.

The strong necessity to fabricate thin films of various metal derivatives in the form of oxides, sulfides and complexes to desired shapes and sizes by an easy and simple technique has been previously reported [28]. Therefore, we present and describe in this work a simple and rapid method for the synthesis of nanomaterials derived from quinolate complexes of Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) based on the application of a layer-by-layer technique via successive and alternative deposition of metal ions and ligand molecules from their aqueous and methanolic solutions, respectively, for the formation of a thin film loaded on a glass substrate. The structures of the thin film synthesized metal quinolate complexes were confirmed on the basis of scanning electron microscopy (SEM), electron impact-mass spectrometry (EI-MS) UV–Vis spectroscopy, Fourier Transform infrared spectroscopy (FT-IR) and thermal gravimetric analysis (TGA).

2. Experimental

2.1. Layer-by-layer thin film formation of 8HQ metal complexes

The formation of the 8HQ metal complexes was carried out by a chemical dipping method according to the following procedure. In this method, a clean glass micro-slide of the size 76.2 mm by 25.4 mm by 1 mm was used as the solid substrate. A solution of 0.1 M metal acetate or chloride was prepared in double distilled water and the 8HQ solution was also prepared (0.1 M) in methanol. The clean substrate was vertically immersed into the metal ion solution for a 30 s period to deposit the corresponding metal ion on the substrate surface. The substrate was then immersed in the ligand solution for another 30 s, where the pre-adsorbed metal ion on the glass substrate was allowed to react with the ligand. A colored and uniform thin film of the metal complex was formed after a few dipping cycles. The reaction substrate was rinsed with distilled water after each reaction cycle. This procedure was repeated several times (15-50 times) to increase the film thickness and homogeneity.

2.2. Instrumentation

A Shimadzu gas chromatography–mass spectrometer (GCMS-QP2010S) interfaced with a direct insertion probe (DIP) was used to acquire the electron impact-mass spectra (EI-MS) of the metal quinolate complexes, viz. Fe(III), Co(II), Ni(II), Cu(II) and Zn(II), by the application of 70-eV as the ionization energy. The heating temperature programming of the DIP was performed at 20 °C min⁻¹ for all the metal quinolate complexes. The maximum temperature was set to 350 °C and the run time was completed in 20.0 min. The collected mass spectrum of each metal quinolate complex was library searched to obtain the best possible match.

Scanning electron microscopes (JSM-6360LA, JEOL Ltd.), (JSM-5300, JEOL Ltd.) and an ion sputtering coating device (JEOL-JFC-1100E) were used to examine the deposited thin film of the metal quinolate complexes. SEM specimens were coated with gold to increase the conductivity. The thermal gravimetric analysis (TGA) and thermoanalytical curves were obtained using a Perkin–Elmer TGA7 Thermobalance at Moubarak City, Egypt. The operating conditions were as follows: a temperature heating range of 20– 1000 °C with a heating rate of 10 °C min⁻¹, a flow rate of 20 ml min⁻¹ in a pure nitrogen atmosphere and a sample mass in the range 5–12 mg. The FT-IR spectra of the metal quinolate complexes were measured on a Shimadzu Fourier Transform infrared spectrophotometer (FTIR-8400S) in the range 4000–200 cm⁻¹. The metal contents of the quinolate complexes were determined on a Shimadzu (AA-6650) atomic absorption spectrophotometer after acid decomposition and suitable dilution. UV–Vis spectra of the metal quinolate complexes were measured on a Perkin–Elmer UV–Vis Spectrometer Lambda EZ210.

2.3. Chemical and materials

The metal salts were all of analytical grade and were purchased from Aldrich Chemical Company, USA and BDH limited, Poole, England. The acetate salts were cobalt acetate, $Co(OAC)_2 \cdot 4H_2O$, nickel acetate, $Ni(OAC)_2 \cdot 4H_2O$, copper acetate, $Cu(OAC)_2 \cdot H_2O$ and zinc acetate, $Zn(OAC)_2 \cdot 2H_2O$. Only iron was in the chloride form, FeCl₃. 8-Hydroxyquinoline (8HQ) and methanol were obtained from BDH limited, Poole, England and were used as received. The metal ion solutions (0.1 M) were prepared from doubly distilled water by dissolving the appropriate mass of the metal salt in a 500 ml flask. A 0.1 M methanolic solution of 8HQ was also prepared and used. The glass micro-slide glass substrate, of the size 76.2 mm by 25.4 mm by 1 mm, was cleaned as previously reported [10].

3. Results and discussion

3.1. SEM of the metal 8HQ complexes

Fig. 1 shows the SEM images of an 8HQ deposited thin film on a glass substrate for simple comparison with the thin film metal 8-quinolate complexes. It is evident that the 8HQ molecules are distributed into nano-sized tubes upon direct deposition on the glass substrate and the SEM images of 8HQ are somewhat similar to the SEM image of a carbon nanotube structure [29,30]. The diameter of the 8HQ-nanotube was found to be in the range 33–43 nm, as measured from the SEM images.

The detected SEM images of the various metal complexes were found to be completely different from that of 8HQ. Fig. 2(i)–(iii) shows the SEM images of the Co(8HQ)₂ complex deposited thin film on a glass substrate after 50 times of alternate dipping in metal ion solution and 8HQ ligand counter part solution. The Co(8HQ)₂ complex was observed to start forming uniform complex particles after only a few dipping cycles, indicating that a fast complex reaction is taking place for the formation of the desired thin films. Fig. 2(i) is a 30,000-times magnified image of the Co(8HQ)₂ complex particle, showing a number of deposited molecules under one particle aggregate. Fig. 2(ii) is a 7500 times magnified image of the Co(8HQ)₂ complex and clearly refers to the existence of several particles with different contributions of nano-sized aggregates.



Fig. 1. SEM image of the 8HQ deposited thin film.



25kV X7,500 059088 1 H M

(ii) 25kV X1,500 100 059087 m (iii)

Fig. 2. SEM images of the thin film Co(8HQ)₂ complex on glass substrate based on 50-dipping cycles.

Finally, Fig. 2(iii) represents a 1500-times magnified SEM image of the Co(8HQ)₂ complex deposited thin film and refers to the high homogeneity and similarity in the Co(8HQ)₂ crystal growth based on layer-by- layer complex formation.

Fig. 3(i) and (ii) shows the SEM images of the deposited thin film of the Fe(8HQ)₃ complex after 50-dipping cycles in metal ion and 8HQ ligand solutions. Fig. 3(i) shows a homogeneous particle size distribution of the formed Fe(8HQ)₃ complex with 10,000-times magnification. Most of the Fe(8HQ)₃ complex particle sizes were identified as being under 200 nm. In a similar fashion to the thin film formation of the $Co(8HQ)_2$ complex, a fast complex formation reaction of Fe(8HQ)₃ thin film was characterized after only a few dipping cycles. Fig. 3(ii) represents a SEM image of the Fe(8HQ)₃ complex deposited thin film with a homogeneous





Fig. 3. SEM image of thin film Fe(8HQ)₃ complex on glass substrate based on 50dipping cycles.

distribution of Fe(8HQ)₃ crystal growth based on layer-by-layer complex formation. The SEM images of the other metal complexes synthesized based on layer-by-layer thin film formation are shown in Figs. 4-6 for the Ni(8HQ)₂, Cu(8HQ)₂ and Zn(8HQ)₂ complexes, respectively. The numbers of dipping cycles are 30, 15 and 15 for the three tested complexes, respectively.

It is evident from the SEM study that all the synthesized metal quinolate complex crystals were found to grow up from just a single molecule to several molecules in an aggregate distribution with particle sizes starting from a few nanometers to several hundred nanometers. In addition, various characteristic shapes of metal



Fig. 4. SEM image of the thin film $Ni(8HQ)_2$ complex on glass substrate based on 30-dipping cycles.



Fig. 5. SEM image of the thin film $Cu(8HQ)_2$ complex on glass substrate based on 15-dipping cycles.

quinolate complexes were identified and these SEM images are quite different from that of 8HQ alone. The shape difference of the metal quinolate complex crystal aggregates deposited on the thin films is mainly dependent on the reacted metal ions.

3.2. Stoichiometry based on metal analysis and EI-MS of the metal quinolate complexes

The molar stoichiometric ratios of the synthesized metal complexes, determined on the basis of the metal analysis, are listed in Table 1. The metal analysis of the characterized layer-by-layer thin film formation of the Co(II), Ni(II), Cu(II) and Zn(II) complexes proved a good similarity to the reactions with 8HQ providing a 1:2 stiochiometric ratio. It is important to report here that the two reaction species, metal ion and 8HQ, were prepared as 0.1 M and



Fig. 6. SEM image of the thin film $Zn(8HQ)_2$ complex on glass substrate based on 15-dipping cycles.

Table 1		
Some characteristic data	of thin film metal quinolate complexes.	

Structure	FW	Color	% Theoretical	% Experimental	Film (mg/ cm ²)	Dipping cycles
Co(8HQ) ₂	346.93	Orange	% Co = 16.99	% Co = 16.79	4.569	50×
Ni(8HQ) ₂	347.01	Yellowish green	% Ni = 16.91	% Ni = 16.87	4.194	30×
Cu(8HQ) ₂	351.87	Olive green	% Cu = 18.07	% Cu = 18.06	4.869	15×
Zn(8HQ) ₂	353.39	Yellowish green	% Zn = 18.50	% Zn = 18.66	4.469	15×
Fe(8HQ) ₃	488.33	Black	% Fe = 11.44	% Fe = 11.35	4.328	$50 \times$



Fig. 7. EI-MS of layer-by-layer thin films of metal quinolate complexes.

when the glass substrate was first dipped in metal ion solution followed by the ligand solution, a rapid complexation reaction took place between the metal ion and 8HQ in a 1:2 ratio, respectively. Thus, the relative concentration of the two reacting species is considered of less importance when layer-by-layer thin film metal quinolate complexes are formed. In the same manner, the Fe(III) ion was characterized by its reaction with 8HQ in a 1:3 ratio based on the metal analysis of Fe(III) in the layer-by-layer thin film Fe(8HQ)₃ complex. The same observation of concentration independence can be also assigned in this case.

Electron impact-mass spectra (EI-MS) were also acquired to confirm the molecular masses of all the metal guinolate complexes. The collected spectra of the metal complexes were library searched for the best possible fit. The EI-MS of the Cu(8HQ)₂ complex, shown in Fig. 7(i), was found to exhibit a few characteristic ion peaks. A molecular ion peak at m/z 351 (rel. int. = 75%) was detected assuming ⁶³Cu as the most abundant copper isotope. The base peak in the EI-MS of the Cu(8HQ)₂ complex, m/z 207, is related to a loss of 144 amu as the deprotonated 8HQ ligand from the molecular ion peak. Some other fragment ion peaks were characterized in the EI-MS of the Cu(8HQ)₂ complex and these are directly related to direct and possible successive losses from the ligand ion. These ion peaks were identified at m/z 145, 117, 89 and 63, with relative abundances of 35%, 20%, 23% and 40%, respectively. The library search for the acquired EI-MS of the Cu(8HQ)₂ complex was found to strongly fit with the stored mass spectra of the copper 8-hydroxyquinoline complex.

Similar EI-MS of Co(8HQ)₂, Ni(8HQ)₂ and Zn(8HQ)₂ to that of Cu(8HQ)₂ were characterized. The molecular ion peaks of these metal quinolate complexes were characterized at m/z 347 (rel. int. = 100%), 346 (rel. int. = 35%) and 352 (rel. int. = 95%) assuming ⁵⁹Co, ⁵⁸Ni, ⁶⁴Zn as the most abundant isotopes of cobalt, nickel and zinc, respectively. These metal quinolate complexes were found to exhibit a loss of 144 amu, for the deprotonated 8HQ ligand, from the molecular ion peak, similar to Cu(8HQ)₂. In addition, the same characteristic ion peaks that are derived from 8HQ at m/z 145, 117, 89 and 63 are evident in the EI-MS of these metal complexes, as represented in Fig. 7(ii)–(iv).

The EI-MS of Fe(8HQ)₃ exhibited a molecular ion peak at m/z 488 (rel. int. = 20%). Two successive losses of 144 amu were identified and characterized in the mass spectrum of Fe(8HQ)₃ due to elimination of two deprotonated 8HQ ligand molecules from the molecular ion peak. These two fragment ion peaks are recorded at m/z 344 (rel. int. = 100%) and 200 (rel. int. = 40%). Fragment ion peaks at m/z 145, 117, 89 and 63 were also characterized in the EI-MS of the Fe(8HQ)₃ complex based on fragmentation parts

Table 2

FT-IR assignments of major peaks.

8HQ [18] 3410 VoH 3090 VcH 1570 VcO 1380 Vring 1223 VcN Co(8HQ)2 ST 3057 VcH 1574 VcO 1338 Vring 1277 VcN Ni(8HQ)2 VoH 3058 VcH 1577 VcO 1340 Vring 1284 VcN Zn(8HQ)2 Soft VcH 3053 VcH VcH 1569 VcO VcH 1569 VcO VcH 1569 VcO VcH 1570 VcO VcH 1570 VcO VcH 1339 Vring VcH 1570 VcO VcH 1378 VcH VcH	Compound	Peak (cm ⁻¹)	Assignment
3090 VcH 1570 VcO 1380 Vring 1223 VcN 1223 VcN 200(8HQ)2 VoH 3057 VcH 3057 VcH 1574 VcO 1338 Vring 1277 VcN Ni(8HQ)2 VoH 3058 VcH 1577 VcO 1340 Vring 1284 VcN 2n(8HQ)2 VoH 3053 VcH 1569 VcO 1348 Vring 1278 VcN Cu(8HQ)2 VoH 1339 VcH 1570 VcO 1339 VcH 1570 VcO 1339 VcH 1570 VcO 1378 VcH 1378 Vring	8HQ [18]	3410	VOH
1570 Vc0 1380 Vring 1223 VCN Co(8HQ)2 VoH 3057 VcH 1574 VcO 1338 VcH 1337 VcN 1338 VcH 1338 VcN 1338 VcN 1338 VcN 1338 VcN 1338 VcN 1377 VcN Ni(8HQ)2 VOH 3058 VcH 1577 VcO 1340 Vring 1284 VcN 2n(8HQ)2 VoH 3053 VcH 1569 VcN 1569 VcN 1278 VcN Cu(8HQ)2 VoH 1339 VcH 1339 VcH 1339 VcH 1570 VcN 1570 VcN 1570 VcN 1570 VcN 1570 VcN 1570 VcN		3090	v_{CH}
1380 Vring 1223 VCN 200 3057 VCH 3057 VCH 1574 VCO 1338 Vring 1277 VCN Ni(8HQ)2 VGH 3058 VCH 1577 VCO 1340 Vring 1284 VCN Zn(8HQ)2 VOH 3053 VCH 1569 VCO 1348 Vring 1278 VCN Cu(8HQ)2 VOH 1339 VCH 1570 VCO 1339 VCH 1570 VCO 1339 Vring 1279 VCN Fe (8HQ)3 Sofs VCH 1570 VCO 1339 1570 VCO 1378 1378 Vring 1378		1570	V _{CO}
1223 VCN C0(8HQ)2 3057 VCH 3057 VCH 1574 VCO 1338 Vring 1277 VCN Ni(8HQ)2 VOH 3058 VCH 1577 VCO 3058 VCH 1577 VCO 1340 VCN 2001 VCN 2015 VCN 2016 VCN 2017 VCN 2018 VCN 2018 VCN 2019 VCN 2010 VCN 2010 VCN 2011 VCN 2011 VCN 2011 VCN 2011 VCN 2011 VCN		1380	v_{ring}
Co(8HQ)2 VoH 3057 VcH 1574 VcO 1338 VcG 1338 VcG 1338 VcH 1338 VcH 1330 VcH 3058 VcH 3058 VcH 1340 VcN 2004 1340 VcN 2018HQ)2 VoH 1284 VcN 2018HQ)2 VoH 1569 VcO 1348 VcH 1569 VcO 1348 VcH 1570 VcO 1378 VcH 1378 VcH 1378 VcH 1570 VcO 1378 VcH 1570 VcO 1570 VcO		1223	V _{CN}
3057 VCH 1574 VCO 1338 Vring 1338 VCH 1377 VCN Ni(8HQ)2 VOH 3057 VCH 1577 VCO 1577 VCN 1577 VCN 1577 VCN 1340 VCN 1584 VCN 27n(8HQ)2 VOH 3053 VCH 1569 VCO 1348 Vring 1278 VCN Cu(8HQ)2 VOH 3053 VCH 1570 VCO 1339 Vring 1279 VCN Fe (8HQ)3 S055 VCH 1570 VCO 1378 Vring 1271 VCN	Co(8HQ) ₂		V _{OH}
1574 Vc0 1338 Vring 1277 VcN 1277 VcN Ni(8HQ)2 VoH 3058 VcH 1577 VcO 1340 Vring 1284 VcN 2n(8HQ)2 VoH 3053 VcH 1569 VcO 1348 Vring 1278 VcN Cu(8HQ)2 VoH 3053 VcH 1569 VcO 1348 Vring 1278 VcN Cu(8HQ)2 VoH 1339 VcH 1570 VcO 1339 Vring 1279 VcN Fe (8HQ)3 So55 VcH 15700 VcO 1378 Vring 1271 VcN		3057	ν_{CH}
1338 Vring 1277 VCN 1277 VCN 3058 VCH 1577 VCO 1340 Vring 1280 VCN 2180 VCN 2180 VCN 2180 VCN 2180 VCN 2180 VCN 2181 VCN 2191 VCN 2191 VCN 2191 VCN 2191 VCN		1574	v_{co}
1277 VCN Ni(8HQ)2 VOH 3058 VCH 1577 VCO 1340 Vring 1284 VCN Zn(8HQ)2 S053 Cu(8HQ)2 VOH 3053 VCH 1569 VCO 1348 Vring 1278 VCN Cu(8HQ)2 VOH S053 VCH 1570 VCO 1339 Vring 1279 VCN Fe (8HQ)3 S55 VCH S053 VCH 1570 VCO 1378 Vring 1271 VCN		1338	v_{ring}
Ni(8HQ) ₂ VoH 3058 VoH 1577 VoC 1340 VoT 1340 VoT 1284 VoH 2004 2004 2004 2004 2004 2004 2004 2005		1277	V _{CN}
3058 VCH 1577 VCO 1340 Vring 1340 Vring 1284 VCN 2n(8HQ)2 VOH 3053 VCH 1488 Vring 1278 VOH Cu(8HQ)2 VOH 1348 Vring 1278 VOH 1570 VCN 1339 VCH 1570 VCO 1339 Vring 1279 VCN 540 VCN 1570 VCN 1570 VCN 1570 VCN 1570 VCN 1570 VCH 1570 VCH	Ni(8HQ) ₂		V _{OH}
1577 Vc0 1340 Vring 1284 VcN Zn(8HQ)2 VoH 3053 VcH 1569 VcN 1278 VcN Cu(8HQ)2 VoH 3053 VcH 1570 VcO 1339 Vring 1278 VcN Fe (8HQ)3 VoH 3053 VcH 1570 VcO 1378 VcH 1271 VcN		3058	v_{CH}
1340 Vring 1284 V _{CN} 2n(8HQ)2 VoH 3053 V _{CH} 1569 V _{CO} 1348 Vring 1278 VOH Cu(8HQ)2 VoH 3053 V _{CH} 1378 V _{CN} Fe (8HQ)3 VoH 3055 V _{CH} 1570 V _{CO} 1570 V _{CO} 1570 V _{CO} 1570 V _{CO} 1378 Vring 1271 V _{CN}		1577	v_{co}
1284 V _{CN} Zn(8HQ)2 V _{OH} 3053 V _{CH} 1569 V _{CO} 1348 V _{ring} 1278 V _{CN} Cu(8HQ)2 V _{OH} 3053 V _{CH} 1570 V _{CO} 1339 V _{ring} 1279 V _{OH} 5055 V _{CN} 1570 V _{CO} 1378 V _{ring} 1271 V _{CN}		1340	v_{ring}
Zn(8HQ)2 VoH 3053 VcH 1569 VcO 1348 Vring 1278 VCN Cu(8HQ)2 VOH 3053 VCH 3053 VCH 1570 VCN Fe (8HQ)3 VoH 3055 VCH 3055 VCH 3055 VCH 1570 VCN 1378 VCN		1284	V _{CN}
3053 V _{CH} 1569 V _{CO} 1348 V _{ring} 1278 V _{CN} Cu(8HQ) ₂ V _{OH} 3053 V _{CH} 1570 V _{CO} 1339 V _{ring} 1279 V _{CN} Fe (8HQ) ₃ V _{OH} 3055 V _{CH} 3055 V _{CH} 1570 V _{CO} 1378 V _{ring} 1271 V _{CN}	Zn(8HQ) ₂		ν_{OH}
1569 V _{CO} 1348 V _{ring} 1278 V _{CN} 20(8HQ)2 V _{OH} 3053 V _{CH} 1570 V _{CO} 1339 V _{ring} 1279 V _{OH} 3055 V _{CH} 1570 V _{CO} 1378 V _{ring} 1271 V _{CN}		3053	v_{CH}
1348 Vring 1278 VCN 2178 VCN 3053 VCH 3053 VCH 1570 VCO 1339 Vring 1279 VCN Fe (8HQ)3 VCH 1570 VCH 1570 VCH 1570 VCH 1570 VCH 1570 VCO 1378 Vring 1271 VCN		1569	v_{CO}
1278 V _{CN} Cu(8HQ)2 V _{OH} 3053 V _{CH} 1570 V _{CO} 1339 V _{ring} 1279 V _{OH} S055 V _{CH} 1379 V _{OH} 1570 V _{CH} 1570 V _{CH} 1570 V _{CH} 1570 V _{CN} 1378 V _{ring} 1271 V _{CN}		1348	v_{ring}
Сu(8HQ)2 VoH 3053 VcH 1570 VcO 1379 VcN Fe (8HQ)3 VoH 3055 VcH 3055 VcH 1570 VcO 1378 Vring 1271 VcN		1278	ν_{CN}
3053 V _{CH} 1570 V _{CO} 1339 V _{ring} 1279 V _{CN} Fe (8HQ) ₃ V _{CH} 3055 V _{CH} 1570 V _{CO} 1378 V _{ring} 1271 V _{CN}	Cu(8HQ) ₂		VOH
1570 V _{CO} 1339 V _{ring} 1279 V _{CN} Fe (8HQ) ₃ V _{CH} 3055 V _{CH} 1570 V _{CO} 1378 V _{ring} 1271 V _{CN}		3053	ν_{CH}
1339 Vring 1279 V _{CN} Fe (8HQ) ₃ V _{OH} 3055 V _{CH} 1570 V _{CO} 1378 V _{ring} 1271 V _{CN}		1570	V _{CO}
1279 V _{CN} Fe (8HQ) ₃ V _{OH} 3055 V _{CH} 1570 V _{CO} 1378 V _{ring} 1271 V _{CN}		1339	v_{ring}
Fe (8HQ) ₃ V _{OH} 3055 V _{CH} 1570 V _{CO} 1378 V _{ring} 1271 V _{CN}		1279	ν_{CN}
3055 V _{CH} 1570 V _{CO} 1378 V _{ring} 1271 V _{CN}	Fe (8HQ) ₃		ν_{OH}
1570 Vco 1378 V _{ring} 1271 V _{CN}		3055	v_{CH}
1378 V _{ring} 1271 V _{CN}		1570	VCO
1271 V _{CN}		1378	v_{ring}
		1271	ν_{CN}

of 8HQ as described above for $Cu(8HQ)_2$, $Co(8HQ)_2$, $Ni(8HQ)_2$ and $Zn(8HQ)_2$. The EI-MS of the Fe(8HQ)_3 complex is shown in Fig. 7(v).

3.3. FT-IR and UV–Vis spectrophotometric analysis of thin film metal 8HQ complexes

The FT-IR spectrum of 8HQ exhibited characteristic absorption peaks for v(C=N) and v(OH). In the FT-IR spectra of the five thin film complexes, the absorption peak v(OH) disappeared with deprotonation of the H-atom of C_{8-OH} while the v(C=N) was shifted, indicating that coordination of 8HQ to the various metal ions has taken place via the nitrogen atom of the imine group and oxygen atom of the C_{8-OH} group, consistent with the results outlined in Section 3.2. A comparison of the FT-IR spectra with



Fig. 8. FT-IR of Cu(II)-quinolate complex.



Fig. 9. UV-Vis of Cu(II)-quinolate complex in ethanol.

the molar stoichiometric ratio, metal analysis data and the EI-MS of the metal complexes revealed that 8HQ is behaving as a monobasic bidentate ligand in the process of layer-by-layer thin film formation of all the tested complexes. The metal ions are coordinated through two N,O metal-chelate rings in the case of Co(II), Ni(II), Cu(II) and Zn(II), indicating that these complexes have similar structures, and three N,O metal-chelate rings in Fe(8HQ)₃, proving the structure assigned for these thin film complexes by the stoichiometric metal analysis and the EI-MS. Fig. 8 is given as a representative FT-IR spectrum of the Cu(II)-8-hydroxyquinolate complex and the FT-IR assignments of the major peaks are given in Table 2.

The UV–Vis electronic spectra of the layer-by-layer thin film of metal quinolate complexes were also studied and proved to exhibit characteristic d–d transition bands. This band was centered at a wavelength of ~381 nm, with a shoulder band at ~433 nm, for the Co(8HQ)₂ complex. The Zn(8HQ)₂ complex showed a d–d transition band centered at a wavelength of ~371 nm with a shoulder band at ~427 nm. The d–d transition bands of the Ni(8HQ)₂ complex were centered at a wavelength of ~386 nm with a shoulder band at ~427 nm. The Cu(8HQ)₂ complex showed d-d transition bands at a wavelength of ~391 nm and two shoulder bands at ~235 and 427 nm. Finally, the Fe(8HQ)₃ complex exhibited three d–d transition bands centered at ~363, 461 and 578 nm. Fig. 9 shows a representative UV–Vis spectrum for the Cu(II)–8-hydroxy-quinolate complex.

3.4. Thermal gravimetric analysis of the metal 8HQ complexes

Thermal gravimetric analysis of the layer-by-layer synthesized thin film metal quinolate complexes was performed and the ther-

tion steps were identified and are mainly due to the direct decomposition of 8HQ from the metal complexes. The Co(8HQ)₂ and $Zn(8HQ)_2$ complexes showed three possible degradation steps, with the final stable product expected to be the metal oxide at \geq 985 K and \geq 965 K, respectively. Cu(8HQ)₂ was found to decompose via two degradation steps in the temperature ranges 586-701 K and 765-977 K, due to the possible loss of 8HQ from the complex. The final product formed from the Cu(8HQ)₂ complex is also expected to be the metal oxide species at a temperature \geq 977 K. On the other hand, Ni(8HQ)₂ and Fe(8HQ)₂ were characterized by their thermal gravimetric decomposition via four various degradation steps. These steps also refer to the direct decomposition of the bound 8HQ molecule from these two metal quinolate complexes, leaving the corresponding metal oxide at temperatures \geq 919 K and \geq 1018 K for the Ni(8HQ)₂ and Fe(8HQ)₂ complexes, respectively. The assigned temperature range of the metal oxide formations is very important if the study of the optical or electric applications of these layer-by-layer thin films of nanosized particles is targeted, as previously reported for similar oxides [8-10].

mal parameters are compiled in Table 3. Several thermal degrada-

4. Conclusion

The outlined results in this work directly refer to the suitability and applicability of the layer-by-layer chemical dipping method as a simple, efficient, low cost and rapid technique for the formation of nano-sized metal 8-hydroxyquinolinate complexes based on crystal growth and thin film formation. The reaction between the metal ion and 8HQ is very fast and a uniform thin film can be observed after only a few dipping cycles. The stoichiometry of the metal quinolate thin film is complete regardless of the concentration of these two interacting species. In addition, the assigned temperature for metal oxide formation is another dimension in this work owing to the possible extension of the presented method for such thin film oxide formation by simply annealing the metal complexes.

Several factors are considered to be of great importance upon application of the layer-by-layer thin film formation of metal complexes that must be explored in order to identify the optimum conditions and generalize the presented method for the formation of nano-sized metal complexes. These include the effect of (i) metal and ligand concentration on the stoichiometry of the metal complex and the particle size, (ii) number of dipping cycles on the particle size, (iii) immersion time on the particle size, (iv) pH of the metal and ligand solutions on the complex formation and (v) sol-

Table 3

Thermal gravimetric data of the layer-by-layer metal quinolate complexes.

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Compound	Step	Temperature range (K)	$DTG_{max}(K)$	Wt. loss (% calculated)	п	$E_{\rm a}$ (J mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	R	Ln(A)
Co(8HQ) ₂	1	394-455	433	8.40	1	69.66	-91.69	0.97753	18.80
Compound Co(8HQ) ₂ Ni(8HQ) ₂ Cu(8HQ) ₂ Zn(8HQ) ₂ Fe(8HQ) ₂	2	685–743	725	11.45	1	186.47	0.53	0.98484	30.41
	3	959–985	893	34.40	1	208.26	-35.62	0.98775	26.27
Ni(8HQ)2	1	381-437	413	10.38	1	76.29	-68.87	0.98504	21.50
	2	621–719	701	42.39	1	176.67	-3.52	0.99419	29.89
	3	719-832	739	18.36	1	103.05	-129.9	0.96222	14.73
	4	832-919	881	16.16	zero	28.76	-249.4	0.47928	0.54
Cu(8HQ) ₂ Zn(8HQ) ₂	1	586-701	636	45.65	1	107.08	-95.39	0.95730	18.74
	2	765–977	863	31.70	1	98.99	-155.8	0.97669	11.78
Co(8HQ) ₂ Ni(8HQ) ₂ Cu(8HQ) ₂ Zn(8HQ) ₂ Fe(8HQ) ₂	1	387-429	413	8.19	1	58.03	-110.3	0.95632	16.51
	2	629-731	708	23.84	zero	173.73	-11.33	0.94297	28.96
	3	765–965	843	45.21	1	139.51	-108.3	0.99169	17.48
Fe(8HQ) ₂	1	622-650	643	5.33	0.5	283.81	188.87	0.92750	52.94
	2	652-677	663	6.66	0.5	140.75	-43.46	0.94548	25.03
	3	768-868	824	22.20	1	178.75	-45.74	0.97676	24.97
	4	967-1018	983	10.65	1	274.36	19.95	0.93071	33.05

vent on the particle size and complex formation. An evaluation study of these important factors is now underway.

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