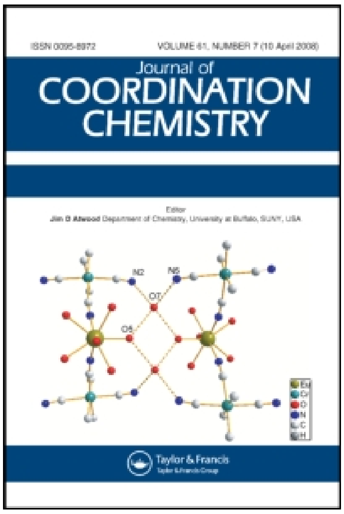

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Paramagnetic NMR shift, spectroscopic and molecular modeling studies of lanthanide(III)-morin complexes

Anees A. Ansari[a]
[a] National Physical Laboratory, New Delhi, India

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Paramagnetic NMR shift, spectroscopic and molecular modeling studies of lanthanide(III)-morin complexes

ANEES A. ANSARI*

National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi, 110012, India

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Studies on nine-coordinate lanthanide complexes of morin are described. The complexes were characterized by elemental analysis, molar conductance, UV–Vis spectra, IR spectra, thermal analysis and NMR spectra. Molecular modeling studies were also carried out. The complexes are non-electrolytes in DMSO. TGA showed anhydrous nature of the complexes. The electronic spectra of the complexes were recorded in methanol. ^{1}H NMR spectra of lanthanum, praseodymium, neodymium, samarium and dysprosium complexes have been studied in DMSO-d_6. The complexes do not dissociate in DMSO and retain their coordination. ^{1}H NMR spectra of paramagnetic and diamagnetic complexes exhibit downfield as well as upfield shifts of morin resonances that shows change in geometry during coordination.

Keywords: Morin; Molecular mechanics; Density functional theory; Paramagnetic shift

1. Introduction

Flavonoids are naturally occurring compounds widely distributed in vegetables, fruits and beverages such as tea and red wine [1–3]. Flavonoid compounds have a wide variety of applications in biomedical sciences [4–7] and display a remarkable array of biological and pharmacological activities such as antioxidant, anti-inflammatory, anti-microbial, anti-cancer and cardiovascular protection [8–12]. Flavonoids have ability to act as free radical scavengers [13–18]. Furthermore, flavonoids are effective metal ion chelators [16, 17], considered as another mechanism of the antioxidant activity of flavonoids [17–27]. Rare earth elements have physiological activities but also decreased toxicity after coordination with ligands [24–27]. In an earlier report, interaction of DNA with Ln(III) complexes was investigated, which is beneficial to understanding the mechanism of some anti-tumor and anti-viral agents to design new DNA targeted drugs [26, 27].

We have begun to investigate coordination chemistry of sterically hindered polyphenolic ligands, aiming to synthesize high coordination complexes in an oxygen-rich ligand environment. In a previous report [28], we investigated Ln(quercetin)$_3 \cdot n$H$_2$O complexes and their spectral studies, which have nine-coordinate complexes with tridentate ligand. In continuation of our studies, here we report

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*Email: aneesaansari@gmail.com

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complexes of trivalent lanthanides with morin. Liufang *et al.* have reported morin (figure 1) complexes with transition metal ions in non-aqueous solutions [19, 21]. Morin forms stable complexes with transition metal ions in 2 : 1 molar ratio with two binding sites for coordination.

2. Experimental

2.1. *Materials*

Lanthanide oxides (99.9%, Lieco Chemicals, USA) were converted to the corresponding chlorides. Morin dihydrate (99.9%, Sigma-Aldrich, USA), methanol, xylenol orange (SD Fine Chemicals) and EDTA (BDH) were used as received in this study.

2.2. *Synthesis*

2.2.1. Preparation of Ln(morin)$_3$ complexes. Hydrated lanthanide chloride (0.100 gm) was dissolved in 50 cm^3 methanol and the solution was stirred on a hot plate. This hot solution was added dropwise to the hot and stirred morin (0.225 gm) solution (50 cm^3). These two solutions were in 1 : 3 molar ratios, mixed thoroughly and constantly stirred for about 6 h on a hot plate at 100°C. Reducing the volume of the resulting solution at room temperature for slow evaporation for 2–3 days, pale yellow crystalline product was obtained, which was washed with chloroform and dried in vacuo over P_4O_{10}.

2.2.2. Methods or physical measurements. Microanalysis (Carbon and Hydrogen) was carried out with a (**FI-SONS** EA-1108) elemental analyzer. The metal contents of the complexes were estimated by complexometric titration. Molar conductances of 10^{-3} M DMSO solutions were measured by an Orion conductivity meter. The thermograms were recorded on a du Pont TA 2000 TGA machine under nitrogen at a heating rate of 10°C min^{-1}. Melting points (mp) were measured with a Gallenkamp MBF-595 apparatus. A Shimadzu UV-2501 PC spectrophotometer was used to obtain electronic spectra in the region 200–900 nm in methanol. FTIR spectra in the 4000–400 cm^{-1} region were recorded from KBr pellets on a Shimadzu-250 spectrophotometer. ^{1}H NMR chemical shifts were measured in DMSO–d_6 solvent on

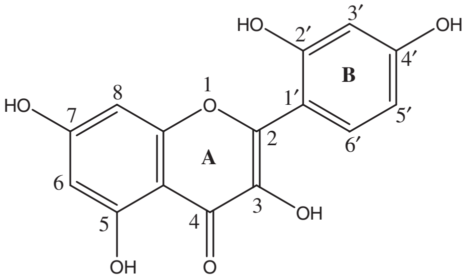

Figure 1. Structure of morin.

a Bruker 300 MHz spectrophotometer. Molecular modeling calculations were carried out through exchange-correlation STO-3G program in Hyperchem (Version 7.5).

3. Results and discussion

Physical properties of the complexes are presented in table 1. In these complexes we assume that morin is tridentate and formed a mononuclear complex where one cation is bound to three morin molecules. This assumption is in accord with elemental analysis, molar conductance, TGA/DTA, UV–Vis, IR, ^{1}H NMR and molecular modeling studies of the complexes. These spectroscopic results are in favor of complexes with general formula [Ln(morin)$_3$] (where Ln = La, Pr, Nd, Sm, Gd, Tb, Dy and Ho). These complexes are crystalline solids having no melting point up to 360°C but decomposing over the temperature range 275–280°C. Syntheses of the complexes were carried out in air and no precaution was taken to exclude moisture. These complexes are soluble in polar organic solvents, sparingly soluble in water, chloroform and acetonitrile and insoluble in non-polar organic solvents. All metal complexes show low molar conductance of the complexes in methanol and DMSO solutions (10^{-3} M solution), corresponding to non-electrolytes [29]. All lanthanide-morin complexes are anhydrous with no trace of lattice or coordinated water (TGA results).

3.1. *Electronic absorption spectra*

Electronic absorption spectra of morin and the eight lanthanide metal complexes were recorded in methanol solution within the spectral range 200–900 nm on a Shimadzu spectrophotometer. Owing to the strong absorption of morin in visible region, the solution spectra of metal complexes did not exhibit transitions of lanthanides (Pr, Nd, Dy and Ho). The absorption spectra of morin in methanol solution revealed two absorption bands in the UV–Vis region. Band I, observed at 403 nm, represents the quinolic ring A and band II at 236 nm corresponds to biphenolic ring B [30, 31]. The broad band observed at higher wavelength is related to the n-π^* and π–π^* transitions within the heterocyclic aromatic ring (quinonolic) of morin [30]. This also indicates that the chromophore groups are present in the quinolic ring [32]. The solution

Table 1. Physical properties of lanthanide-morin complexes.

			% Metal calculated (observed)		
Complex	Color	MP (°C)	C	H	M
La(morin)$_3$	Pale green	>300	51.84 (50.98)	2.61 (2.58)	13.32 (14.18)
Pr(morin)$_3$	Pale green	>300	51.74 (52.25)	2.60 (2.83)	13.49 (13.12)
Nd(morin)$_3$	Pale green	>300	51.57 (52.00)	2.59 (2.69)	13.76 (14.00)
Sm(morin)$_3$	Pale green	>300	51.27 (51.81)	2.58 (2.51)	14.26 (15.13)
Gd(morin)$_3$	Pale green	>300	50.94 (51.25)	2.56 (2.86)	14.82 (14.98)
Tb(morin)$_3$	Pale green	>300	50.86 (49.88)	2.56 (2.26)	14.95 (15.23)
Dy(morin)$_3$	Pale green	Decomp 285°C > 300	50.69 (48.68)	2.55 (2.48)	15.24 (15.56)
Ho(morin)$_3$	Pale green	>300	50.57 (51.26)	2.54 (2.68)	15.43 (15.67)

spectra of morin lanthanide complexes revealed three absorption bands in methanol. Bands of complexes shifted to higher wavelength in comparison to the free morin suggest coordination of ligand to the metal ion, as shown in table 2. Such bathochromic shifts of bands can be explained by extension of the conjugated system on complexation. Band I is slightly shifted to higher wavelength (ca 6–33 nm) while band II shifts significantly compared to free morin, suggesting that the quinonolic ring is involved in coordination to the metal ion through two sites, one site occupied by ring oxygen (C–O–C) and another by phenolic (7-OH) oxygen. It clearly indicates that the 1-carbonyl (C–O–C) group and 2′-hydroxychromone are involved in chelation; 7-hydroxychromone also has the greatest chelation power for complexation. Some investigators have reported that morin is associated to the metal ion in bidentate fashion through 1-carbonyl and 2′-hydroxychromone oxygens [19–21]. Markham has reported that 7-hydroxychromone in morin has a potential chelating site for coordination to the metal ion in complexes [32]. A high intensity band is observed between the spectral range 268–291 nm in the middle of these two spectral bands in the complexes, which is not observed in free morin [19, 21]. The presence of an extra band in the complex spectrum is due to association of methanol to the metal ion in the complexes [33–35]. The CH_3OH coordinates to the metal in complexes without displacing morin and increases the coordination number. Molar conductance of the complexes in DMSO is lower and suggests non-electrolyte nature of the complexes in DMSO solution [21, 29]. Methanol is weak donor than DMSO [36].

3.2. *Vibrational spectra*

The characteristic absorption frequencies of morin and the complexes with their tentative assignments are summarized in table 3. The absorption frequencies of metal complexes exhibited red shifts, showing the coordination between the ligand and metal ion. The appearance of ν(M–O) modes in the spectral range 500–450 cm^{-1} in the complex spectrum is absent in free morin [37–39]. A diffuse band at 3400–3200 cm^{-1} is present in the spectrum of free morin and metal complexes showing ν(O–H). In the complexes, ν(O–H) is at lower wavenumber and changed in broadness [35, 37, 39]. Bending vibrations of ν(O–H) are less affected in spectra for complexes probably due to the presence of non-bonded hydroxyl groups. In free morin spectrum, the bands centered at 1653 cm^{-1} and 1200–1173 cm^{-1} are characteristic absorptions for ν(C=O) and ν(C–O–C), respectively. These frequencies in the complexes are red shifted [19, 21]. The small shift of ν(C=O) suggests that carbonyl (4-oxo group) is not involved in coordination. These results also support literature reports [19, 21] where morin exhibits the coordination to lanthanide ions through ν(C–O–C) site. The skeletal ring vibrational frequencies are also affected, appearing at higher wavelength in comparison to morin (table 3). This red shift of the bands is due to increase in conjugation when complexes are formed.

Table 2. UV–Visible spectral data of lanthanide-morin complexes in methanol.

Ligand/Complex	Morin	La	Pr	Nd	Sm	Gd	Tb	Dy	Ho
Band I	403[a]	413	415	394	436	416	416	415	409
Band II	236	268	289	278	276	287	291	279	279
Band III	....	222	228	235	229	231	237	236	235

[a] Reference [19].

Table 3. IR absorption frequencies of lanthanide(III)-morin complexes.

Functional groups	Morin	La	Pr	Nd	Sm	Gd	Tb	Dy	Ho
ν(O–H)	3479–3295	3245	3391	3400	3368	3400b	3369	3368	3368b
ν(C–H)	2885	2906	Merged	2921	2921	2924s	2921	2930	2921asy
	2624								2850sy
ν(C=O)	1653	1606	1654	1653	1654	1628b	1653 splitted	1662 splitted	1654 splitted
ν(C=C)	1607	1509	1629	1607	1628	1508b	1603s	1606	1603s
	1572, 1508		1508	1575	1606		1543	1507s	1511sb
			1458	1508	1516		1511		
δ(O–H)	1450	1430	1376	1449	Merged	1458s	1438s	1458s	1458sh
C–O–H									
ν(C–O)	1352	1380	1241	1352	1365	1383s	1360	1376s	1365
C–O–C	1327			1307	1313	1308s	1325	1309	1314sb
C–C–O	1309								
ν(C–C)	1246	1236	1172	1245	1233	1172s	1194	1255	1236s
$\mathrm{C{-}\underset{\underset{O}{\Vert}}{C}{-}C}$	1203			1203			1173s	1225s	
	1173								
ρ(O–H) in plane deformation	1089	1175	1082	1172	1168	1078w	1099	1172sh	1172sb
(C–H) in plane deformation	1006	1010	1009	1088	1098	1007w	1009w	1082	1099sw
					1078				
(C–C) in plane deformation	975	974	968	974	1011	979w	975sw	1010sw	1009s
			872		969	831w		968w	
(O–H) out of plane deformation	828	832	828	828	874	884	884w	875w	973s
				808				832w	832w
(C–H) out of plane deformation	750	696	795	760	834	794s	806w	794sw	689w
			634		792	745w	689	731w	649
(C–C) out of plane deformation	638	642	582	562	685	634	649w	634w	566w
	568	575	562		636	562		565w	
M–O	....	488	451	468	463	454	473	455	462

3.3. *Thermal analysis*

Thermal analysis of the morin complexes under nitrogen with heating at 10°C min^{-1} was carried out from ambient to 600°C. The thermal data are given in table 4. The thermograms of all complexes were similar, showing two stepwise decompositions. No weight loss was observed in the thermograms until 300°C, indicating that the complexes are devoid of lattice and coordinated water. These anhydrous complexes begin to decompose after 300°C. Melting point results confirm this remarkable thermal stability. The thermograms show first inflexion point between the temperature range 298–323°C with the observed weight loss between the range 32.69–25.68%, which is equivalent to first unit of morin (calculated weight loss for one unit of morin is between the range 28.87–28.16%). A corresponding DTG plot shows a big exothermic peak at this temperature. After removal of the first unit of morin, second and third come out continuously without any break in the DTG curve, in the temperature range 431–462°C. The observed weight loss at this temperature between 55.92–51.83% represents elimination of two morins (calculated weight loss for two molecule of morin is 57.74–56.33%).

3.4. *NMR spectra*

The chemical and paramagnetic shifts of morin and metal complexes are summarized in table 5. The chemical shift data of the morin have been reported earlier [19], but are shown here for comparison with the lanthanide complexes. The hetero-aromatic ring proton resonances of morin with diamagnetic lanthanum were shifted to lower field relative to the free morin resonances, whereas the hydroxyl group proton resonances of morin with diamagnetic La^{3+} were remarkably shifted upfield relative to the free morin resonances, probably due to shielding of the aromatic ring. The shifts of morin

Table 4. Thermal analysis data of lanthanide(III)-morin complexes.

		% Weight loss		
Complexes	Temperature (°C)	Calcd	Obs.	Constituents eliminated
La	298	28.87	29.00	1 molecule of morin
	431	57.74	55.64	2 molecules of morin
Pr	323	28.81	33.24	1 molecule of morin
	462	57.62	52.78	2 molecules of morin
Nd	305	28.72	30.59	1 molecule of morin
	467	57.44	51.83	2 molecules of morin
Sm	310	28.55	25.68	1 molecule of morin
	444	57.11	55.92	2 molecules of morin
Gd	318	28.37	26.50	1 molecule of morin
	437	56.74	56.36	2 molecules of morin
Dy	305	28.23	30.85	1 molecule of morin
	453	56.46	51.69	2 molecules of morin
Ho	305	28.16	32.69	1 molecule of morin
	445	56.33	52.20	2 molecules of morin

resonances to lower field as well as upfield is strong evidence that the hetero-aromatic ring remains coordinated to lanthanum even in DMSO. Those protons, which are shifted to lower field, are subjected to no perturbing influence other than the deshielding expected from the electron-withdrawing inductive effect of coordination. For the diamagnetic complex, the relative chemical shifts in the NMR spectra (with respect to the free ligand) are not as prominent as for the paramagnetic complexes but still show that the ligands are bound to the Ln(III) (table 5).

^{1}H NMR spectra of paramagnetic lanthanide-morin complexes (Supplementary Material) have downfield as well as upfield shifts. Differences in relative signal broadening reflects different metal proton distances with broader peaks associated with the proton nuclei of the morin closer to the lanthanide ion. In the praseodymium and neodymium complexes, the aromatic ring and hydroxyl group proton resonances appeared as singlet and broad resonances, while in samarium and dysprosium complexes these proton resonances were narrow. Small paramagnetic (isotropic) shifts were observed for these sharp signals. Generally, Pr^{3+} and Nd^{3+} are known for induced upfield shifts, however, downfield shifts are also reported [40–43]. H-3′ resonance represents a large downfield shift and broad signal because it is close to the coordinated 2′-OH. A very large downfield shift is observed for the 7-OH group proton resonance in paramagnetic as well as diamagnetic analogues, perhaps due to coordination. Therefore, this hydroxyl group has affinity to the metal ion without deprotonation, increasing the coordination number of the metal. Since the coordination environment of the metal ion is blocked by three bulky morin molecules, no water enters into the coordination cavity. These results agree with the TGA and IR results, which represent the anhydrous nature of solid complexes and exhibit the absence of water molecules in the coordination sphere.

The paramagnetic shift (dipolar or isotropic shift) is produced by an interaction between nuclear magnetic moment and magnetic field, which is produced by the unpaired f-electrons of the lanthanides [44–48]. This interaction may occur in a through-space dipole-dipole manner, or by delocalization of f-electron density towards the resonating nucleus through bonds. In lanthanides the radial extension

Table 5. The 300 MHz ^{1}H NMR spectral data of lanthanide(III)-morin complexes in DMSO-d_6.

	Chemical shifts (Paramagnetic shifts)									
Compounds	5-OH	3-OH	7-OH	4′-OH	2′-OH	H-6′	H-5′	H-8	H-3′	H-6
Morin (JICS)[a]	12.61	12.48	10.73	10.12	9.79					
(TMC)[b]	12.62	9.78	10.55	....	....	7.07	6.28	6.20	6.15	6.05
La	12.50	8.76	10.63	9.67	....	7.96d	6.84d	7.17s	6.34s	6.09s
Pr	12.45	9.38	11.07	10.06	....	8.04d	6.90d	7.35s	6.44s	6.08s
	(–0.05)	(0.62)	(0.44)	(0.39)		(0.08)	(0.06)	(0.18)	(0.10)	(–0.01)
Nd	12.61	8.83	10.86	9.82	....	8.05d	6.94d	7.22s	6.45s	6.17s
	(0.11)	(0.07)	(0.23)	(0.15)		(0.09)	(0.10)	(0.05)	(0.11)	(0.08)
Sm	12.60	8.80	10.76	9.81	....	8.05d	6.94d	7.24s	6.41s	6.18s
	(0.10)	(0.04)	(0.13)	(0.14)		(0.09)	(0.10)	(0.07)	(0.07)	(0.09)
Dy	12.61	8.87	10.86	9.82	....	8.05d	6.94d	7.22s	6.45s	6.17s
	(0.11)	(0.11)	(0.23)	(0.15)		(0.09)	(0.10)	(0.05)	(0.11)	(0.08)

Chemical shift and paramagnetic shifts are expressed in ppm (δ); *s*: singlet; *d*: doublet.
The negative sign indicates an up field shift and positive shifts are downfield to TMS.
[a,b] Reference [19].

Table 6. Optimized geometrical parameters of morin obtained by density functional theory with STO-3G functional set.

C(1)–C(2)	1.3373	C(4)–C(2)–O(3)	113.27
C(2)–O(3)	1.3950	C(2)–C(4)–O(5)	117.48
O(3)–H(23)	0.9935	C(6)–C(4)–O(5)	128.33
C(2)–C(4)	1.5077	C(6)–C(7)–O(8)	116.587
C(4)–O(5)	1.2289	C(9)–C(7)–O(8)	122.403
C(4)–C(6)	1.4914	O(11)–C(10)–C(9)	116.851
C(6)–C(13)	1.3933	O(11)–C(10)–C(12)	122.82
C(6)–C(7)	1.4155	C(16)–O(17)–C(18)	119.236
C(7)–O(8)	1.3861	H(28)–O(17)–C(16)	104.313
O(8)–H(24)	0.9884	C(15)–C(16)–O(17)	120.669
C(7)–C(9)	1.3821	C(13)–O(14)–C(1)	119.349
C(9)–H(25)	1.0791	H(26)–O(11)–C(10)	105.931
C(9)–C(10)	1.4044	H(24)–O(8)–C(7)	105.229
C(10)–O(11)	1.3894	O(3)–C(2)–C(1)	124.411
C(11)–H(26)	0.9895	C(2)–O(3)–H(23)	101.98
C(10)–C(12)	1.3811	C(18)–C(19)–O(20)	117.078
C(12)–H(27)	1.0797	H(30)–O(20)–C(19)	105.483
C(12)–C(13)	1.4020	O(20)–C(19)–C(21)	123.329
C(13)–O(14)	1.3777		
O(14)–C(1)	1.3975		
C(1)–C(15)	1.4975		
C(15)–C(16)	1.4138		
C(16)–O(17)	1.3918		
O(17)–H(28)	0.9887		
C(16)–C(18)	1.3872		
C(18)–H(29)	1.0795		
C(18)–C(19)	1.3904		
C(19)–O(20)	1.3906		
O(20)–H(30)	0.9885		
C(19)–C(21)	1.3919		
C(21)–H(31)	1.0817		
C(21)–C(22)	1.3825		
C(22)–H(32)	1.0817		
C(22)–C(15)	1.3941		

of 4f-orbital is exceedingly small and the electrons in these orbitals are shielded from the ligand by s and p electrons. Consequently, contact interactions (through-bonds) are greatly diminished and the induced chemical shifts arise predominantly from the dipolar mechanism (through-space), which can provide information relating to the geometric configuration of the ligand with a metal ion in solution [43, 47, 48]. This can be verified if the intermolecular ratios of the shifts, Rij, of the molecules i to another nucleus j in the same molecule remains the same for all the lanthanides [44, 48]. The ratio of the chemical shifts of the protons 5-OH and 7-OH are 0.89, 0.86, 0.85 and 0.86; of the H-6′ and H-5′ are 0.86, 0.86, 0.86 and 0.86; of the H-5′ and H-3′ are 0.93, 0.93, 0.92 and 0.93; of the H-8 and H-6 are 0.83, 0.85, 0.85 and 0.85 for the complexes of praseodymium, neodymium, samarium and dysprosium, respectively. The ratios are similar in magnitude for a given set of protons and therefore, the shifts owe their origin to dipolar interaction [44]. The intermolecular shift ratio for morin protons are Pr/Nd 0.98(5-OH), 1.01(7-OH), 1.06(3-OH), 1.02(4′OH), 1.0(H-6′), 0.99(H-5′), 1.01(H-8), 1.0(H-3′) and 0.98(H-6). This too provides strong evidence that the shifts can be treated as purely dipolar.

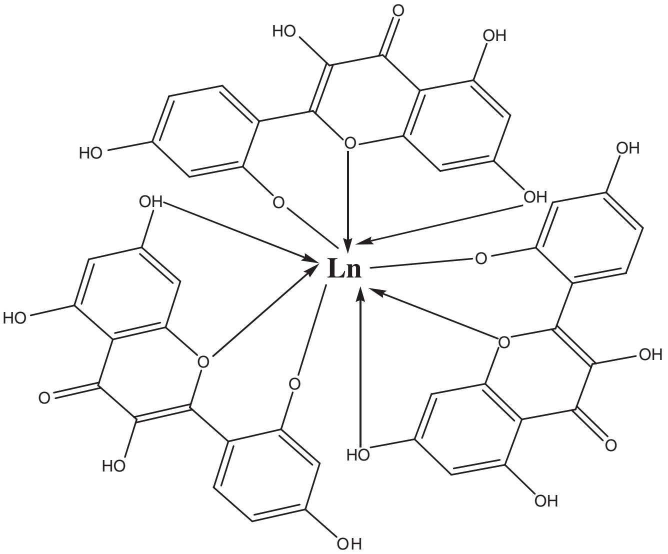

Figure 2. Proposed structure of lanthanide-*tris*(morin) complex.

3.5. *Computational details*

The goal of this experiment is to optimize the geometrical structure of lanthanide-morin complexes. Molecular modeling results make some predictions about the properties of these complexes. Optimized geometry includes bond distances, bond angle, electron density, electrostatic potential, electrophilic susceptibility and nucleophilic susceptibility etc. The principle geometrical parameters of morin obtained after minimization with the AM1 method are presented in table 6. The geometrical parameters of morin suggest that 2′-hydroxy-1-carbonyl site is more favorable for coordination to the metal ion than the 3-hydroxy-4-carbonyl site. These optimized geometrical results are in good agreement with the literature and observed NMR and IR spectral results [19–21].

4. Conclusion

The present work describes the synthesis and characterization by spectroscopic and molecular modeling studies of trivalent lanthanide complexes with 2′,3,4′,5,7-pentahydroxyflavone (morin). The IR and NMR spectral data of the complexes indicate that the ligand coordinates to metal via the ring oxygen atom (C–O–C) of the morin molecule. Spectral results presented in table 5 and figure 2 suggests that each morin has three binding sites for coordination to the metal ion. The thermoanalytical curves indicate that the Ln(morin)$_3$ complexes are anhydrous with different thermal decomposition profile than free ligand.

These results suggest nine-coordination in the solid as well as solution.

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