



Structure versatility of cobalt complexes of 2-[α -(acetyloxime)ethylidenehydrazino]-4,6-dimethylquinoline; Synthesis, spectral, magnetic and theoretical studies



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Abstract

Reactions of the hydrazone ligand; 2-[α -(acetyloxime)ethylidenehydrazino]-4,6-dimethylquinoline (AEHDQ) with various cobalt(II) salts (acetate, nitrate, sulfate and chloride) yielded dimer, mono and binuclear complexes. The successfully prepared complexes (1-4) have been characterized by using different techniques including elemental analyses, infra-red, electronic and mass spectra, magnetic susceptibility and molar conductivity measurements. The results illustrated that AEHDQ behaves as bidentate (NO) and tridentate (NNO) chelating agent. UV/Vis spectra in binary solvent mixtures of Co complexes have been investigated. Co complexes (1-3) under study are preferring water than solvation. The hyperchem program was used to determine geometrical and structural optimizations of cobalt complexes at a *PM3* level.

Keywords: Hydrazones, cobalt complexes, molecular modeling, spectral study, quinoline.

1. Introduction

In recent years, much consideration has been paid to synthesis and characterization of hydrazones and their metal complexes.^{1,2} This interest is caused by their simple and easy synthetic methods, formation of stable complexes with different metal ions and their potential biological and pharmacological applications. These biological applications involve antimicrobial, antioxidant, anti-inflammatory, antiviral, antimalarial, and antitumor activities.³⁻⁵⁰

Quinolines and quinolines-based compounds are a prominent class of heterocyclics present in a wide range of physiologically active natural and synthesized substances. They have pharmacological properties and can be used in a variety of analytical and medicinal applications.⁵¹⁻⁶⁶

Because it is a significant component of vitamin B-12 and a range of medicines, cobalt is a vital element in life.⁶⁷ Cobalt carboxylates are also employed in the field of homogeneous oxidation catalysis to produce a variety of chemical molecules.^{68,69} Moreover, cobalt is present in a variety of proteins and enzyme active sites.^{70,71} Cobalt(II) complexes are successfully employed as potential catalysts in oxygenation process of organic molecules.⁷² On the other hand, a diversity of useful biological applications including antioxidant⁷³,

antibacterial⁷⁴ and anticancer⁷⁵ activities are given by cobalt(II) complexes.

Recently, a quinoline-based ligand; 2-[α -(acetyloxime)ethylidenehydrazino]-4,6-dimethylquinoline (AEHDQ) as well as its copper complexes were synthesized and fully characterized.⁷⁶ The flexibility of AEHDQ ligand as well as the nature of anions used allowed to obtain different complexes with diverse coordinating modes.⁷⁶

The present work is an extension to our preceding work including quinoline-based ligands^{52,57-60,63}, and our interest to investigate the effect on anions on complex-formation.⁷⁶⁻⁷⁹ Thus, the coordination behavior of 2-[α -(acetyloxime)ethylidenehydrazino]-4,6-dimethylquinoline (AEHDQ) towards different cobalt(II) salts; acetate, nitrate, chloride and sulfate was investigated in the present work. The successfully prepared complexes have been characterized by means of elemental analyses, infrared, mass, electronic spectra, molar conductance and magnetic moment measurements. UV/Vis spectra in binary solvent mixtures of cobalt complexes have been studied. All complexes under study are preferring water than solvation. The hyperchem program was used to determine geometrical and structural optimizations of Co-complexes at a *PM3* level.

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2. Experimental

2.1. Materials

Cobalt(II) salts (acetate, nitrate, chloride and sulfate), ethyl acetoacetate, *p*-toluidine, POCl₃, hydrazine hydrate, biacetylmonoxime, Na₂EDTA and murexide were BDH or Aldrich.

2.2. Preparation of the hydrazone ligand (AEHDQ)

AEHDQ was synthesized according to our preceding work.⁷⁶

2.3. Preparation of the cobalt-AEHDQ complexes

The cobalt(II) salts (acetate, nitrate, chloride or sulfate), were dissolved in methanol and then added drop by drop to the stirred AEHDQ methanolic solution in molar ratio (1:1). The mixture was then heated under reflux on a water bath for ~5–7 h, giving colored complexes. After cooling, the precipitated complexes were filtered off, then washed by methanol and lastly by diethyl ether.

2.4. Measurements

Microanalyses (% Carbon, % Hydrogen and % Nitrogen) were performed on Perkin-Elmer 2400 CHN elemental analyzer at the Microanalytical Center, Cairo University, Giza, Egypt. % Cobalt was determined complexometrically by EDTA after decomposition of the complexes with conc. HNO₃. The decomposition temperatures of Co-AEHDQ complexes were recorded on Rumo-3600 melting point apparatus. As potassium bromide disks, the IR spectra of AEHDQ and Co-AEHDQ complexes were recorded in the range (4000–400 cm⁻¹) on a BRUKER Vector 22 spectrometer (Germany). On a Jasco V-550 UV / VIS spectrophotometer, the UV-Visible spectra of AEHDQ and its Co-AEHDQ complexes were recorded as solutions (in dimethylformamide) and/or Nujol mull. Molar conductance measurements of Co-AEHDQ complexes were performed on the Corning conductivity meter NY 14831 model 441. The magnetic susceptibility measurements of Co-AEHDQ complexes were carried out at room temperature by means of a Johnson Matthey magnetic susceptibility balance (Alfa product) and Pascal's constants⁸⁰ were utilized to correct the calculated magnetic moments. Mass spectra for Co-AEHDQ complexes were recorded at 70 eV on a gas chromatographic GCMSqp 1000-ex Shimadzu mass spectrometer.

2.5 Molecular orbital calculations

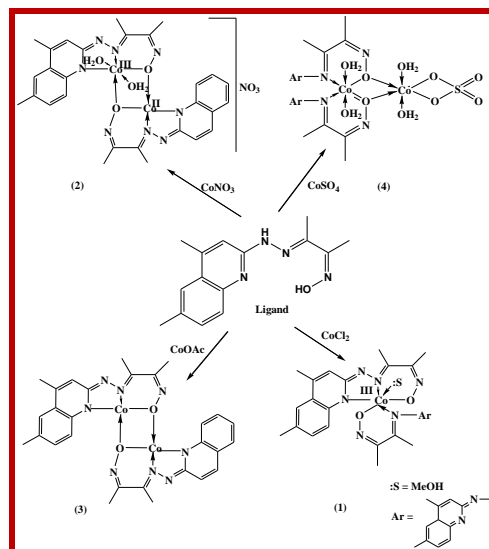
The molecular orbital calculations of Co-AEHDQ complexes were carried out by using Hyperchem 7.52 program, PM3 level.⁸¹

3. Results and discussion

3.1. General

AEHDQ ligand reacts with various cobalt(II) salts; CoX₂ in methanol (X⁻ = Cl⁻, AcO⁻, NO₃⁻ & ½ SO₄²⁻) to give four stable and non-hygroscopic

different cobaloximes (Scheme 1). All complexes are characterized by higher decomposition temperatures (>280 °C) revealing their strong bonds and high thermal stability. The prepared complexes are fully characterized by different analytical and spectral methods as illustrated below;



Scheme 1. Proposed of Co-complexes.

3.1.1. IR spectra

The IR spectra of AEHDQ ligand and its complexes are depicted in Figs. 1-3 and the main IR spectral data are tabulated in Table 2. The Co-AEHDQ complexes displayed a broad band in the range 3424 - 3390 cm⁻¹, which may be ascribed to ν(OH) of the methanol and /or water molecules linked to complexes.^{82,83} The band assigned to azomethine group in free AEHDQ ligand (at 1610 cm⁻¹) was shifted by 4-9 cm⁻¹ upon complex-formation.⁸⁴ In addition, the bands located in the range 1576- 1444 cm⁻¹ attributed to the vibrations of quinoline ring of the free AEHDQ ligand were remarkably altered on complexation. The participation of anions as well as their nature of bonding was explained as follows; in complex **2**, the new band observed at 1383 cm⁻¹ may be related to the ionic NO₃⁻ group.⁸⁵ This agrees very well with the molar conductance data (see Table 2). However, the appearance of new bands in the range 1172 - 1076 cm⁻¹ in complex **4** may be due to ν₃(S-O) of the bidentate SO₄²⁻ group. Furthermore, the chelating nature of the SO₄²⁻ group was supported by addition of BaCl₂ solution where no white precipitate is observed. All these observations were supported by the molar conductance data (Table 2). At last, the new bands detected in the regions 545-496 and 436-400 cm⁻¹ may be related to ν(cobalt-oxygen) and ν(cobalt-nitrogen), respectively.⁸⁶⁻⁸⁸

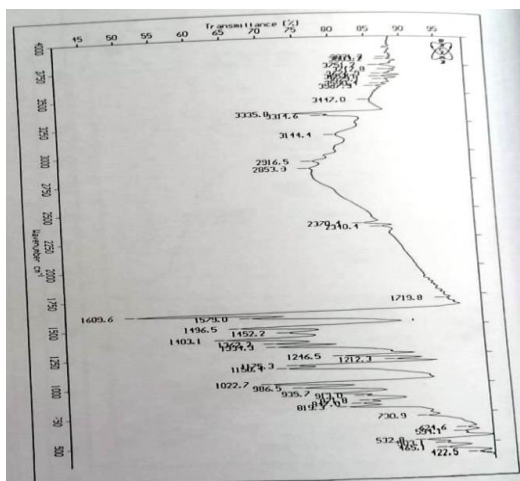


Fig. 1. IR spectrum of the ligand.

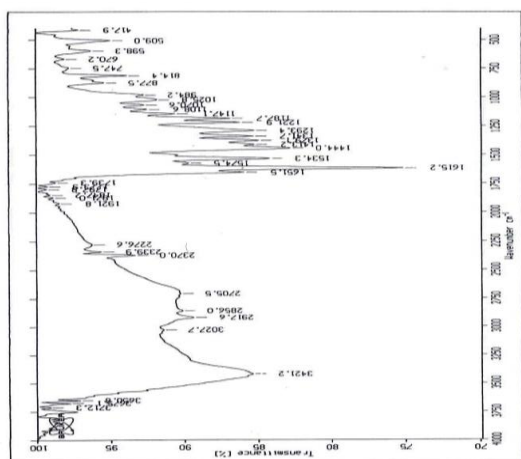


Fig. 2 IR spectrum of $[\text{Co}^{\text{III}}(\text{AEHDQ})_2(\text{MeOH})]$ (1).

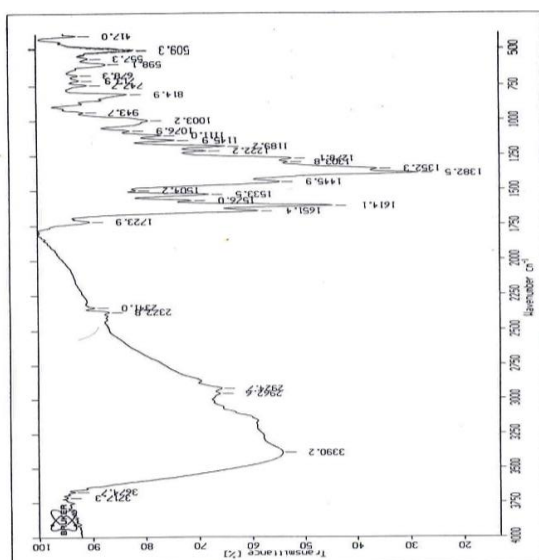


Fig. 3 IR spectrum of $[\text{Co}_2^{\text{II,III}}(\text{AEHDQ})_2(\text{H}_2\text{O})_2] \cdot \text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (2).

3.1.2. Conductance measurements

The molar conductance measurements of the prepared Co-AEHDQ complexes were performed at room temperature and the obtained results are tabulated in Table 2. The molar conductance values of complexes **1**, **3** and **4** are low within the range (3- 13) $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, revealing the non-electrolytic characters of these complexes.⁸⁷ In contrast, the molar conductance value of complex **2** is $65 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$, within the expected range for 1:1 electrolytes, indicating ionic nature of the complex.⁸⁷

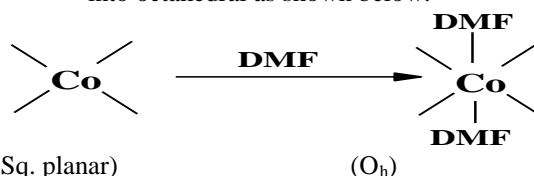
3.1.3. Electronic spectra and magnetic studies

The electronic spectral data and the magnetic susceptibilities of the Co-AEHDQ complexes (Table 2) can be utilized efficiently to predict their stereochemistry.^{90,91}

As shown from Scheme 1, a full oxidation occurs in case of the Cl^- anion (complex **1**), whereas a partial oxidation occurs in case of the NO_3^- anion (complex **2**). On the other hand, a dimeric square planar Co^{II} -complex (**3**) was obtained in case of the AcO^- anion, as evidenced from its magnetic moment ($\mu_{\text{eff}} = 1.26 \mu_{\text{B}}$) as well as an O_h binuclear Co^{II} -complex (**4**) in case of the SO_4^{2-} anion ($\mu_{\text{eff}} = 3.85 \mu_{\text{B}}$).

In spite of this discrepancy, the electronic spectra of the Co-AEHDQ are more similar and exhibited only one d-d transition in the range 540 – 548 nm, in addition to a charge transfer (CT) in the range 320 – 360 nm (Table 2). This similarity could be elucidated in the light of the following considerations:

- (i) In dimethylformamide solutions, the square planar geometry may be changed into octahedral as shown below:



- (ii) In dimethylformamide solutions, the oximic bridges may be ruptured and the dimeric or binuclear complexes exist in solutions as solvated O_h monomeric species.⁹²
- (iii) Similarity of the electronic spectra of cobalt(II) and cobalt(III) complexes.

Thus the structures of most cobalt II and III complexes are well defined based on their magnetic properties rather than their electronic spectra e.g. T_d and square planar arrangements around cobalt(II) ions can be differentiated by using magnetic susceptibility measurements as T_d -complexes have 3 unpaired electrons and square planar complexes only one. Also, O_h cobalt(III)-complexes are diamagnetic.

Table 1 Analytical and physical data of the Co-AEHDQ complexes.

No.	Complex (M. F.)	F.Wt	Color	Elemental Analysis; % Found/(Calc.)			
				C	H	N	M
1	[Co ^{III} (AEHDQ) ₂ (MeOH)] (CoC ₃₁ H ₃₇ N ₈ O ₃)	(627.9)	Chocolate brown	59.20 (59.25)	5.00 (5.89)	----- (17.84)	----- (9.38)
2	[Co ^{III} (AEHDQ) ₂ (H ₂ O) ₂]NO ₃ . ½H ₂ O (Co ₂ C ₃₀ H ₃₇ N ₉ O _{7.5})	(760.8)	Reddish- Brown	47.11 (47.32)	4.76 (4.86)	16.52 (16.56)	----- (15.48)
3	[Co ^{II} (AEHDQ)] ₂ (Co ₂ C ₃₀ H ₃₂ N ₈ O ₂)	(653.8)	Dark violet	55.03 (55.06)	5.30 (4.89)	----- (17.13)	17.81 (18.02)
4	[Co ^{II} (AEHDQ) ₂ (SO ₄)(H ₂ O) ₄].3 ½H ₂ O (Co ₂ C ₃₀ H ₄₉ N ₈ O _{13.5} S)	(886.8)	Buff	40.70 (40.60)	4.20 (5.53)	----- (12.63)	12.55 (13.28)

Table 2 Selected IR absorption bands (cm⁻¹), Electronic spectra, magnetic moments and molar conductivity data of the Co-AEHDQ complexes.

No.	IR spectral bands cm ⁻¹				UV-Vis data λ _{max} (nm)		μ _{eff} (μ _{comp.}) μ _B	Λ Ohm ⁻¹ cm ² mol ⁻¹
	v(OH))	v(C = N) free / coord.	v(C = N) (quinoline)	Other bands	DMF	Nujol mull		
AEHDQ ³ 5	3336	1610	1579, 1497, 1452, 1403	2917; OH...N	234, 309, 355	-	-	-
1	3421	1615	1575, 1534, 1444		548, 349	539, 361	Diamagnet ic	11
2	3390	1614	1576, 1534, 1446	(1383); v(NO ₃ ⁻)	541, 360	532, 334	1.92	65
3	3424	1619	1547, 1500		545, 320, 267	545, 321, 214	1.26 (1.78)	3.0
4	3390	1616	1539, 1473	(1172, 1106, 1076); v ₃ (S - O)	540, 350, 288	525, 370, 284	3.85 (5.44)	13

Consequently, the diamagnetism of complex **1**, gives a strong evidence of its O_h geometry and its oxidation. In contrast, complex **4** displayed a lower μ_{eff} value of 3.85 μ_B / each Co^{II} ion which is suggestive of 3 unpaired electrons and propose a strong antiferromagnetic interaction between the adjacent Co^{II}-cations in an O_h field.

Arguments confirming the mixed-valence binuclear Co^{II}/Co^{III} structure (**2**), start with the remark that a marked decrease in the μ_{eff} value (1.92 μ_B) was observed which corresponds to one unpaired electron, suggesting a square planar geometry around Co^{II}-ion. In contrast, the visible spectra exhibited one band at 541 nm (Table 2) which is consistent with v₂ transition for Co^{III} (d⁶ - system) in low spin O_h field; ¹A_{1g} → ¹T_{2g}

As cobalt(III) is diamagnetic, the magnetic moment of Co^{II}/Co^{III} complex (**2**) is due to the Co^{II}-cation only. The subsequent remarks must be considered:

- Low spin O_h Co^{II}-complexes and high spin O_h Co^{III}-complexes are very scarce.⁹⁰
- For most cobaloximes,⁹³⁻⁹⁵ it was verified that Co^{II} is simply oxidized to

Co^{III} (full oxidation) under aerobic conditions i.e. in presence of air. This occurs as spin pairing is expected to take advantage of the large CFSE of d⁶ configuration in the low spin state; t_{2g}⁶.

(iii) Similarly, such mixed states were described and reported for cobalt complexes^{96,97} and ruthenium complexes^{98,99} (Ru^{II,III}).

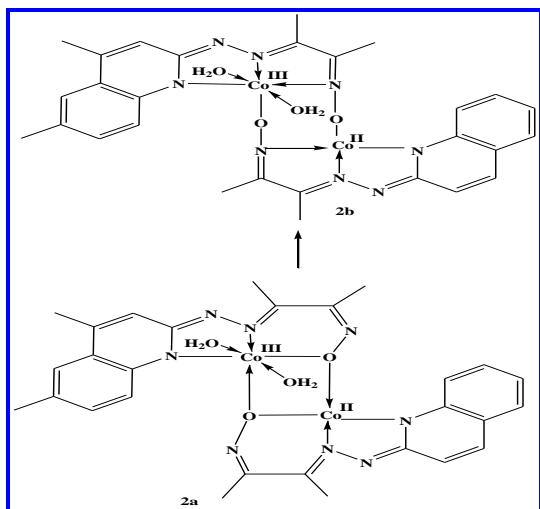
(iv) The literature cited values¹⁰⁰ of μ_{eff} for Co^{II}-complexes (d⁷) have the ranges;

O _h (high spin)	T _d	Square planar
5.2 – 4.8	4.8 – 4.4	2.8 – 2.1

Therefore, the observed lower μ_{eff} = 1.92 μ_B would refer a not purely square planar geometry.¹⁰¹ The oxime groups have three potential coordination modes, that is only N-, only O- and both N- and O-binding sites. Also, the deprotonation of the oxime groups simplify the coordinating and/or the bridging ability of the O- donors.¹⁰²⁻¹⁰⁴ Taking this into account in addition to the fact that Co^{III} displays a high

particular affinity for N- donors,¹⁰⁵⁻¹⁰⁷ one could conclude the following:

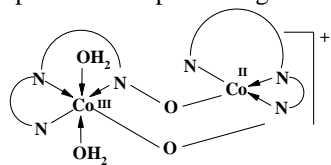
- (i) The mixed valence $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ complex (**2**) has two acceptable structures as shown below:



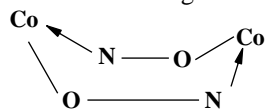
Proposed structures of $[\text{Co}_2^{\text{II,III}}(\text{AEHDQ})_2(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (**2**).

In **2b**, the $\text{Co}_2\text{N}_2\text{O}_2$ ring affords either chair or twisted boat conformations.¹⁰⁵⁻¹⁰⁷ Also, another arrangement is possible; open book shaped arrangement¹⁰³ as shown below:

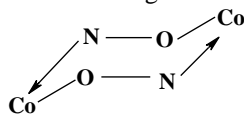
$\text{Co}_2\text{N}_2\text{O}_2$ core;
open book shaped arrangement



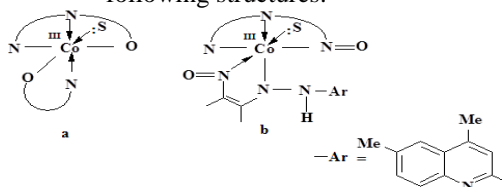
$\text{Co}_2\text{N}_2\text{O}_2$ core;
twist boat arrangement



$\text{Co}_2\text{N}_2\text{O}_2$ core;
chair arrangement

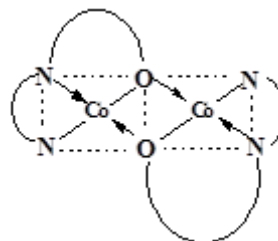


- (ii) Similarly, the Co^{III} -complex (**1**) has the following structures:



Proposed structures of $[\text{Co}^{\text{III}}(\text{AEHDQ})_2(\text{MeOH})]$ (**1**).

- (iii) In contrast, the dimeric complexes **3** have only one preferable structure as shown below:



$(\text{Co}^{2+}; d^7; \mu_{\text{eff}} = 1.26 \mu_{\text{B}}, \text{Square planar})$

The strong antiferromagnetic coupling for **3** can be illustrated in the light of the following: (i) The oximato group has good superexchange interactions. (ii) The Co-O-Co bridge angles are much greater than 97.5° .¹⁰⁵⁻¹⁰⁷ (iii) The intramolecular $\text{Co} \dots \text{Co}$ separations are short. (iv) The highest planarity of the basal ONNO plane.

Therefore, the dimers **3** must lack the $\text{Co}_2\text{N}_2\text{O}_2$ ring (see **2b**).

3.1.4. Mass Spectrometry

As representative complexes, mass spectra of complexes **2** and **3** are depicted in Figs. 4 & 5. The obtained results including the molecular ion peaks (F.W.) as well as the base peaks are shown below. The results are consistent with the proposed formula weights of the complexes based on analytical and spectral methods.

Complex	Molecular ion peak	(% abundance)	Cacl. F.W.	Base peak
2	757.3	(0.23%)	760.8	149
3	653.5	(1.75%)	653.8	157

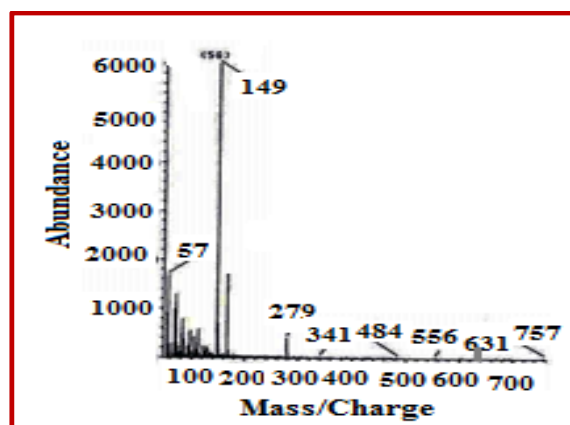


Fig. 4. Mass spectrum of $[\text{Co}_2^{\text{II,III}}(\text{AEHDQ})_2(\text{H}_2\text{O})_2]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ (**2**).

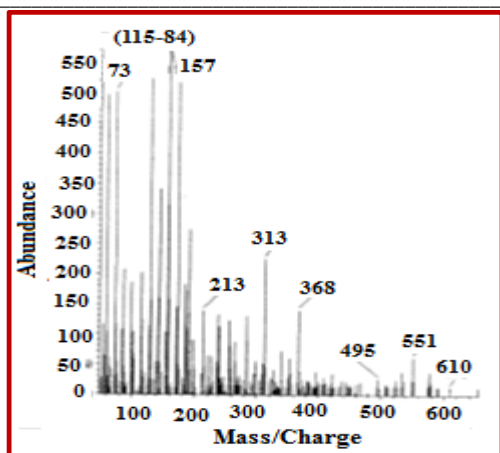
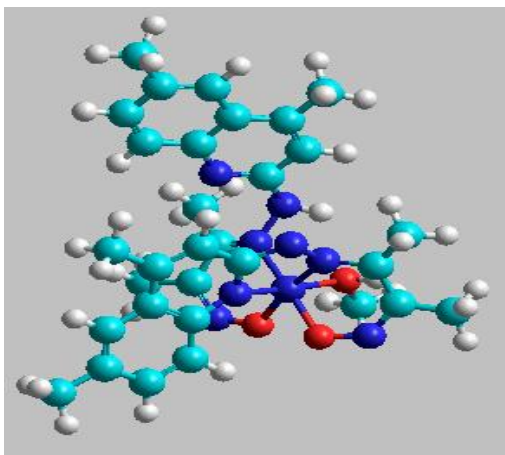


Fig. 5. Mass spectrum of $[\text{Co}^{\text{II}}(\text{AEHDQ})_2]$ (3).

3.1.5. Molecular modeling studies

The *Hyperchem 7.52* program was used to (Fig. 6 & 7 and Tables 3 & 4) give optimized structures of AEHDQ Co(II)- complexes. The heat of formation of the complexes (-212.99 to -611.13 kcal/mol) are more negative than their AEHDQ hydrazone (65.63036 kcal/mol), this means that stability of AEHDQ ligand is less than that of its AEHDQ Co(II)-complexes.^{12,30,31} Dipole moment (μ) of AEHDQ (3.335 D) is less than that of its complexes (3.647-15.63 D), which refers that the AEHDQ complexes have higher reactivity than AEHDQ.^{76,88} E_{HOMO} and E_{LUMO} have (-7.663 to -8.747 & -1.189 to -1.551 eV) negative values, which signifies the stability of compounds. The global softness (S) (0.136-0.157 eV^{-1}), softness (σ) (0.271- 0.313 eV) and global hardness (η) (3.191-3.690 eV) values refer to the reactivity and molecular stability.^{30,31,88} The electronegativity (χ) refers to capacity of the compounds, which is in the range 4.472-5.057 eV^{-1} . The electrophilicity index (ω) refers electrophilicity behavior, which is in the range 3.114-3.526 eV.^{30,31,76}

1



2

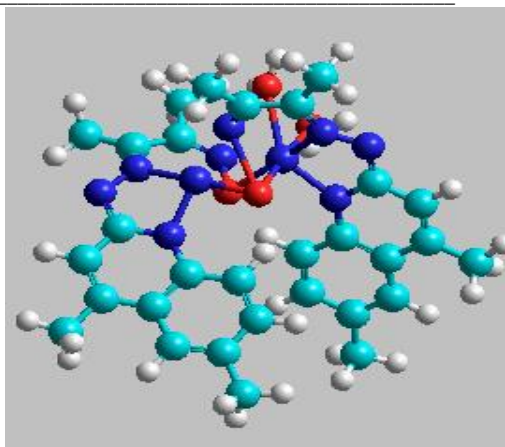
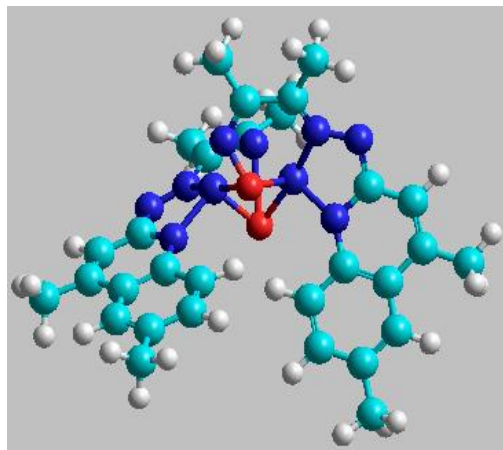


Fig. 6 optimized structures of Co(II)-complexes (1 & 2).

3



4

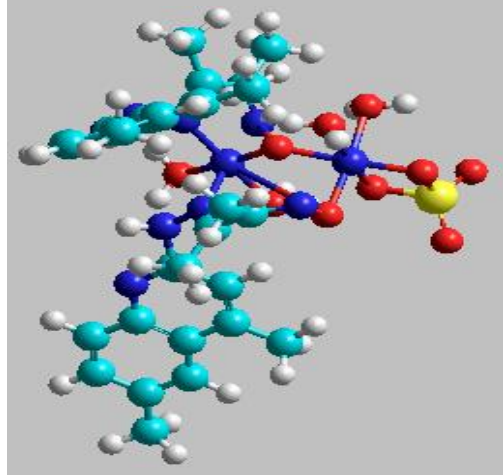


Fig. 7 optimized structures of Co(II)-complexes (3 & 4).

Table 3. Structural parameters of the free AEHDQ ligand and its metal complexes.

No.	Heat of Formation, kcal/mol	Dipole moment	HOMO Energy, [eV]	LUMO Energy, [eV]	ΔE	ω	X	S	σ	η
1	-212.99	6.949	-8.0656	-1.189	6.877	3.114	4.627	0.145	0.291	3.438
2	-611.13	4.494	-7.663	-1.281	6.382	3.134	4.472	0.157	0.313	3.191
3	-482.29	3.647	-7.947	-1.551	6.396	3.526	4.749	0.156	0.313	3.198
4	-952.51	15.63	-8.747	-1.367	7.380	3.465	5.057	0.136	0.271	3.690

Table 4. The selected bond lengths of optimized structures of Co(II)-AEHDQ complexes.

Bond	Complex			
	(1)	(2)	(3)	(4)
N19-O20	1.289	2.341	1.526	1.329
N19-C16	1.329	1.336	1.333	1.312
N14-C15	1.339	1.365	1.362	1.330
N7(Q)-C8	1.340	1.388	1.394	1.343
N7(Q)-M	----	1.929	1.899	----
O20-M	1.909	1.869	1.872	3.674
N19-M	----	----	----	----
N14-M	1.937	1.849	1.891	1.985

3.2.6. Spectrophotometric studies of Co-AEHDQ chelates

In the current research, UV/Vis spectra of binary solvent mixtures are included. Metallic complexes are frequently solvatochromic, meaning their colours vary as the solvent changes. Because of the large range of applications available, solvent mixtures are an important study topic.^{108,109} The most striking feature of these mixed solvents is the gradual change in properties that occurs as their mixture is changed.

As seen in Table 8, the distinct pattern of preferential solvation for the cobalt complexes observed in the aqueous-DMF binary solvent mixture (Tables 6-8 & Fig. 8) indicates negative deviation.

Excess function (X) defines the type and degree of deviation from the straight line.

$$\Delta X = X_A^L - X_A$$

It may be considered as quantitative criteria of preferential solvation. The negative value indicates the preference of component B (DMF) over A as observed for all complexes, while the positive value of ΔX indicates the preference of component A (water) over the component B. The $\sum \Delta X$ values at all fractions might be employed to quantify the extent of this preference, *vide infra*.

On the other hand, all complexes had X_B^{iso} lower than 0.5 (0.22-0.37), indicating that component A (water) is preferred over solvation. The

foregoing conclusion can be extracted, for the studied cobalt chelates, from the data in Table 5. These data show that; $K_{A/B}$ is lower than 1 (0.28-0.47) for all complexes.

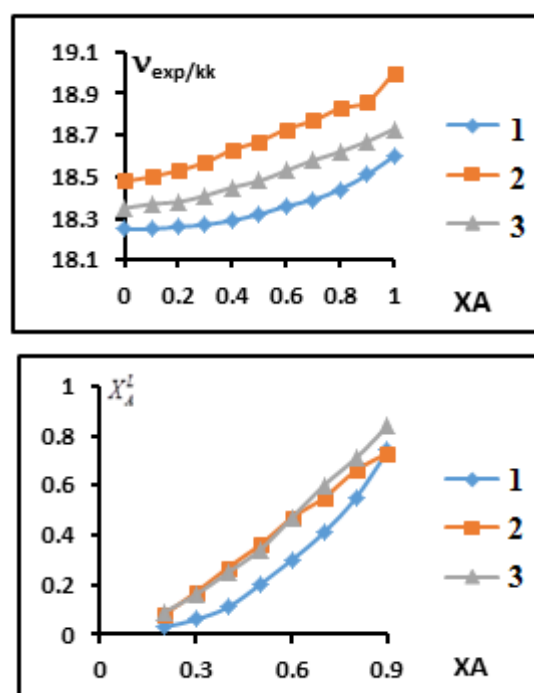


Fig. 8 Frequencies ($v_{exp/kk}$) of absorption bands of Co(II)-AEHDQ complexes (1-3) vs. X_{H_2O} & local molar fractions (X_A^L) for the preferential solvation of these complexes vs. bulk molar fractions X_{H_2O} of binary (H_2O -DMF) solvent at 25 °C.

As a conclusion, in the mixed aqueous system the results can be explained in terms of the micro-heterogeneity of the binary mixture.¹¹⁰ Other researchers have reported the breaking of the hydrogen-bonded network in water and the creation of hydrogen bonds in aqueous aprotic solvent.¹¹¹⁻¹¹³ Furthermore, in this type of solvent mixture, mesoionic compounds and Reichardt's pyridine betaine showed similar preferred solvation characteristics.¹¹⁴ Similar phenomenon was observed in a theoretical investigation of

preferential solvation in a variety of two-component systems.¹¹⁵⁻¹¹⁷ Eventually, the preferential solvation of the current cobalt chelates in aqueous-DMF

mixed solvents is determined by solute-solvent and solvent-solvent interactions.

Table 5 Frequencies ($\nu_{\text{exp/kk}}$) of the absorption bands of Co-AEHDQ complexes at various bulk molar fractions of solvent (X_A) at 25 °C.

No.	Complex / $X_{\text{H}_2\text{O}}$	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
1	[Co ^{III} (HL)L(MeOH)]	18.25	18.25	18.26	18.27	18.29	18.32	18.36	18.39	18.44	18.51	18.60
2	[Co ^{II,III} L ₂ (H ₂ O) ₂]NO ₃ ·½H ₂ O	18.48	18.50	18.53	18.57	18.63	18.67	18.73	18.77	18.83	18.86	19.00
3	[Co ^{II} L] ₂	18.35	18.37	18.38	18.41	18.45	18.48	18.53	18.58	18.62	18.67	18.73

Table 6 Local molar fractions (X_A^L) for the preferential solvation of AEHDQ complexes at various bulk molar fractions of binary (H₂O- DMF) solvent (X_A) at 25 °C.

No. / $X_{\text{H}_2\text{O}}$	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
1	0.01	0.03	0.06	0.11	0.20	0.30	0.41	0.55	0.74
2	0.03	0.08	0.17	0.27	0.36	0.47	0.55	0.66	0.73
3	0.05	0.09	0.16	0.25	0.34	0.47	0.60	0.71	0.84

Table 7 Preferential solvation parameters of the AEHDQ complexes in binary of water (A)-DMF (B) solvent mixtures at 25 °C.

No./ $X_{\text{H}_2\text{O}}$	$\Delta \nu$	ΔX	X_A^{iso}	X_B^{iso}	$K_{A/B}$	dev. type
1	733.12	-2.10	0.78	0.22	0.28	-ve
2	975	-1.17	0.63	0.37	0.40	-ve
3	418.46	-1.00	0.63	0.37	0.47	-ve

Dimer, mono and binuclear cobalt complexes of 2-[α -(acetyloxime)ethylidenehydrazino]-4,6-dimethylquinoline (AEHDQ) were synthesized and characterized by using different techniques including elemental analyses, infra-red, electronic and mass spectra, magnetic susceptibility and molar conductivity measurements. AEHDQ behaves as tridentate (NNO) and bidentate (NO) chelating agent. Binary solvent mixtures of cobalt complexes have been investigated, using spectrophotometric method. Cobalt chelates are preferring water than solvation. The geometrical and optimized structures of cobalt complexes were performed at a PM3 level, using Hyperchem program.

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