

Six-coordinate oxime-imine cobalt(III) complexes with amino acid co-ligands; synthesis and characterisation

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Abstract :

In this publication, several six coordinate Co(III)-complexes are reported. The reaction of 2,3-butanedione monoxime with ethylenediamine or o-phenylenediamine in mole ratios of 2:1 gave the tetradentate imine-oxime ligands diaminoethane-N,N'-bis(2-butyldine-3-onedioxime) H_2L^1 and o-phenylenediamine-N,N'-bis(2-butyldine-3-onedioxime), respectively. The reaction of H_2L^1 and H_2L^2 with $Co(NO_3)_2$, and the amino acid co-ligands (glycine or serine) resulted in the formation of the required complexes. Upon complex formation, the ligands behave as a neutral tetradentate species, while the amino acid co-ligand acts as a monobasic species. The mode of bonding and overall geometry of the complexes were determined through physico-chemical and spectroscopic methods. These studies revealed octahedral geometry about Co(III) complexes in which the co-ligands bound through the amine and the carboxylate groups. Molecular structure for the complexes have been optimised by CS Chem 3D Ultra Molecular Modelling and Analysis Program and supported six coordinate geometry.

Keywords: Schiff-base imine-oxime ligands; diaminoethane-N,N'-bis(2-butyldine-3-onedioxime) H_2L^1 and o-phenylenediamine-N,N'-bis(2-butyldine-3-onedioxime) H_2L^2 ; Six coordinate Co(III)-complexes; Structural study.

Introduction:

The coordination chemistry of metal complexes of α -dioxime has been investigated widely [1]. Approaches such as synthetic routes to obtain vicinal imine-oxime complexes and analytical and structural applications of these oxime species have been reviewed extensively [2]. Schiff-base oxime species based on transition metal compounds and polydentate ligands has been the subject of extensive research due to their potential applications in materials science [3, 4] and environmental chemistry and medicine [2] and biomimetic model including the preparation and molecular structure of Co(III)-complexes called cobaloxime

[5, 6]. The interesting feature of these complexes is due to their relevance to the chemistry of vitamin B₁₂. As models for coenzyme B₁₂, cobaloxime have been subjected to extensive studies including their electrochemical [7] and structural properties [8]. Furthermore, a new family of cobalt and nickel complexes with tetradentate ligands providing a diimine-dioxime coordination sphere was reported as efficient and stable electrocatalysts for hydrogen evolution from acidic nonaqueous solutions with lower over-voltages [9]. Recently, we reported the formation of phenoxo-bridged binuclear transition metal ions with the Schiff-oxime ligand -((E)-(hydroxyimino)methyl)-5-methylbenzylideneamino)ethylimino)m

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ethyl)-5- methylbenzaldehyde oxime [10]. As part of our continuing efforts to explore the use of mixed ligands based on the multidentate Schiff-base oxime ligands and amino acid co-ligands, we describe here the formation and the spectral investigations of Co(III)-complexes with the mixed ligands; the amino acids (glycine or serine) and the tetradentate imin-oxime ligands diaminoethane- N,N' -bis(2-butylidene-3-onedioxime) H_2L^1 and *o*-phenylenediamine- N,N' -bis(2-butylidene-3-onedioxime) H_2L^2 .

Materials and methods

All reagents were obtained commercially (Aldrich) and used without further purification. Solvents used in the synthesis were distilled from appropriate drying agent immediately prior to use.

2.2. Physical measurements

Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL). IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer from 4000-400 cm^{-1} . Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. Electronic spectra were measured from 200-900 nm for 10^{-3} M solutions in H_2O at 25°C using a Shimadzu 160 spectrophotometer. 1H NMR spectra were acquired in $DMSO-d_6$ solution using a Jeol 270 MHz spectrometers with tetramethylsilane (TMS) as an internal standard. Mass spectra obtained by positive Electron Impact (EI) recorded on a VG autospec micromass spectrometer. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Conductivity measurements were made with DMF solutions using a Jenway 4071 digital conductivity meter and room temperature magnetic moments were measured with a magnetic

susceptibility balance (Jonson Matthey Catalytic System Division).

1. Synthesis

The preparation of the ligands was adopted according to a method published in [11], and as follows:

Preparation of H_2L^1

A solution of ethylenediamine (0.5 g, 8 mmol) in methanol (20 mL) was added slowly to a mixture of diacetylmonoxime (1.68 g, 16.6 mmol) dissolved in methanol (20 mL). The reaction mixture was allowed to reflux for 2 h, and then stirred at room temperature for a further 1h. A white solid was collected by filtration, recrystallised from a mixture of hot methanol: H_2O , and dried under vacuum for 24 hr to give H_2L^1 as a white solid (yield 56%), m.p. = 166 °C. 1H NMR data (ppm), δ_H (270 MHz, $DMSO-d_6$): 1.9 (6H, s, 2 x CH_3), 2.0 (6H, s, 2 x CH_3), 3.7 (4H, s, $-C=NCH_2$), 11.5 (2H, s, $-C=N-OH$). The positive EI mass spectrum of H_2L^1 showed the following fragments; 226 (96%) $M+$, 209 (19 %) $[M-(OH)]^+$, 195 (15) $[M-(OH)_2]^+$, 166 (11%) $[M-\{(OH)_2-CN\}]^+$, 113 (64%) $[M-\{(OH)_2-CN-CH_3-CN-CH\}]^+$, 97 (100%) $[M-\{(OH)_2-CN-CH_3-CN-CH-NH_2\}]^+$, 69 (36%) $[M-\{(OH)_2-CN-CH_3-CN-CH-NH_2-CN-CH_2\}]^+$, 42 (93%) $[M-\{(OH)_2-CN-CH_3-CN-CH-NH_2-CN-CH_2\}]^+$.

Preparation of H_2L^2

The method used to prepare the ligand H_2L^2 was similar to that used for H_2L^1 but *o*-phenylenediamine (0.50 g, 4.6 mmol) was used in place of ethylenediamine. The quantities of other reagents used were adjusted accordingly, and the reaction mixture was allowed to reflux for 6 h to yield (64%) of the title compound. m.p. = 192 °C. NMR data (ppm), δ_H (270 MHz, $DMSO-d_6$): 2.0 (6H, s, 2 x CH_3), 2.7 (6H, s, 2 x CH_3), 8.0-7.7

(4H, m, Ar-H), 11.4 (2H, br, -C=N-OH). The positive EI mass spectrum of H_2L^2 showed the following fragments; 274 (6%) M^+ , 158 (100%) $[M-\{(CH_3-C=NOH)_2\}]^+$, 117 (67%) $[M-\{(CH_3-C=NOH)_2-(CH_3-C=N)\}]^+$, 76 (25%) $[M-\{(CH_3-C=NOH)_2-(CH_3-C=N)_2\}]^+$, 40 (46%) $[M-\{(CH_3-C=NOH)_2(CH_3-C=N)_2-C_3\}]^+$.

General synthesis of the Co(III)-complexes with H_2L^1 and H_2L^2 & amino acid co-ligand

The appropriate imin-oxine ligand (1 mmol) was added in small portions to a solution of $Co(NO_3)_2 \cdot 6H_2O$ (1 mmol) in methanol (10 mL), and followed by a solution of the appropriate amino acid, glycine or serine, (1 mmol) in methanol (15 mL), and then a saturated solution of $NaIO_4$ in water (2 mL) was added to above solution. The mixture was stirred vigorously and oxygen gas was then bubbled through the reaction mixture for 3 h, resulting in the formation of a solid mass which was washed several times with diethyl ether. Elemental analysis data, colours, and yields for the complexes are given in (Table 1).

Molecular modelling

3D molecular modelling of the proposed structure of the complexes was performed using CS Chem 3D Ultra Molecular Modelling and Analysis Program [12]. It is an interactive graphics program that allows rapid structure building, geometry optimization with minimum energy and molecular display. It is well known program and has the ability to handle transition metal complexes [13]. The correct stereochemistry was assured through the manipulation and modification of the molecular coordinates to obtain reasonable low energy molecular geometries.

Results and Discussion

4.1. Chemistry

The reaction of 2,3-butanedione monoxime with ethylenediamine or o-phenylenediamine in mole ratios of 1:2 gave the tetradentate imine-oxime ligands diaminoethane- N,N' -bis(2-butyldine-3-onedioxime) H_2L^1 and o-phenylenediamine- N,N' -bis(2-butyldine-3-onedioxime), H_2L^2 respectively in moderate yield (Scheme 1). The Schiff-base oxime ligands were characterised by elemental analysis (Table 1), IR (Table 2), UV-Vis (Table 3) spectroscopy, 1H NMR and mass spectrometry. The 1H NMR and the EI (+) mass spectra of the ligands were consistent with the proposed structural formula (see experimental section).

The di-electrolyte Co(III)-complexes were synthesised by mixing at RT 1 mmole of the appropriate ligand with 1 mmole of the cobalt nitrate in methanol followed by a solution of the appropriate amino acid, glycine or serine, (1 mmol) in methanol, and then a saturated solution of $NaIO_4$ in water was added to above solution. The mixture was stirred vigorously with bubbling air for 3 h. Bubbling air was introduced to facilitate the oxidation of Co(II) to Co(III). Complexes of the general formulae $[Co(H_2L^n)(A^-)]^{+2}$ (where $n = 1$ or 2 ; A^- = amino acid, glycine or serine) was obtained (Scheme 1). The complexes are air-stable solids, soluble in H_2O , and partially in DMSO and DMF. The complexes are sparingly soluble in EtOH and not soluble in other common organic solvents. The coordination geometries of the complexes were deduced from their spectra. The analytical data (Table 1) agree well with the suggested formulae. Conductivity measurements of the Co(III) mixed complexes lie in the 142.7-150 $cm^2\Omega^{-1}mol^{-1}$ range,

indicating their 2:1 electrolytic behavior (Table 1) [14].

IR Spectra

The important infrared bands for the ligands and their complexes together with their assignments are listed in Table 2. The IR spectra of the ligands show characteristic bands at 1609 – 1634 and 1473 -1481 cm^{-1} due to the $\nu(\text{C}=\text{N})$ imine, $\nu(\text{C}=\text{N})$ oxime functional groups, respectively. The bands at 3145, 1000 cm^{-1} and 3184, 989 cm^{-1} assigned to the $\nu(\text{O}-\text{H})$ stretching of the oxime and $\nu(\text{N}-\text{O})$ stretching group for ligands H_2L^1 and H_2L^2 , respectively [10, 11, 15]. The IR spectra of the complexes exhibited ligand bands and the amino acid co-ligand with the appropriate shifts due to complex formation (Table 2). The $\nu(\text{C}=\text{N})$ imine and $\nu(\text{C}=\text{N})$ oxime stretching bands around 1609 - 1634 and 1473-1481 cm^{-1} , respectively in the free Schiff-base oxime ligands is shifted to lower frequency and observed in the range 1604-1627 cm^{-1} and 1408-1446 for the complexes. The bands are assigned to a $\nu(\text{C}=\text{N})$ stretch of reduced bond order. This can be attributed to delocalisation of metal electron density (t_{2g}) to the π -system of the ligand [16, 17], indicating coordination of nitrogen of the $\text{C}=\text{N}$ moieties to the metal atoms [18]. The strong $\nu(\text{N}-\text{O})$ stretching bands at 1000 and 989 cm^{-1} in the free ligand are shifted to higher frequencies and appeared at 1029-1091 cm^{-1} for the complexes. The increase in the $\text{N}-\text{O}$ bond order can be attributed to the distribution of the π -electron of the oxime moiety upon complex formation [19]. It seems that the two $\text{N}-\text{O}$ bands are equivalent. Further, the IR spectra of the complexes display characteristic bands for the amino acid co-ligand. The asymmetric and symmetric bands at 1560, 1578 cm^{-1} and 1412, 1435 cm^{-1} of the carboxylate moiety for the

glycine and serine, respectively [20] is shifted to lower frequency and appeared around 1500-1512 and 1330 - 1384 cm^{-1} for the asymmetric and symmetric bands, respectively in the complexes. The bands in the range 3136-3147 cm^{-1} assigned to the coordinated NH_2 amine moiety of the amino acids indicating the coordination through the nitrogen atom. The IR spectra of the complexes show a strong bands around 740-748 cm^{-1} assigned to the $\nu(\text{IO}_4^-)$ group [15]. These bands have providing a further evidence for the formation of cationic ion for the cobalt complexes. At lower frequency the complexes exhibited bands around 410–450 and 530-582 cm^{-1} which could be assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ vibration modes, respectively [13, 16]. Due to the larger dipole moment change for $\text{M}-\text{O}$ compared to $\text{M}-\text{N}$, the $\nu(\text{M}-\text{O})$ usually appears at higher frequency than the $\nu(\text{M}-\text{N})$ band [21].

cv

The UV-Vis spectrum of H_2L^1 exhibit a high intense absorption peak at 293 nm, assigned to overlapping of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ [22]. The spectrum for H_2L^2 exhibits a high intense absorption peak at 304 nm, with a shoulder at 273 nm, assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$, respectively. The electronic spectra of the cobalt (III) complexes of H_2L^1 exhibit a high intense peaks at 227 and 236 nm for $[\text{Co}^{\text{III}}(\text{H}_2\text{L}^1)(\text{gly})](\text{IO}_4)_2$ (1) and $[\text{Co}^{\text{III}}(\text{H}_2\text{L}^1)(\text{ser})](\text{IO}_4)_2$ (2), respectively due to ligand field. The absorption bands at 291 and 295 nm for 1 and 2, respectively attributed to transition involving the metal oxime grouping [23]. The low intense peaks for 1 and 2 at 348 and 345 nm, respectively attributed to the charge transfer transitions. This may be assigned to the spin-allowed ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$ transition which is masked

by the intense charge transfer bands of the complexes and confirming an octahedral structure around Co(III) ions [23-25]. The electronic spectra of the cobalt (III) complexes of H_2L^2 show two peaks at 229 and 224 nm for $Co^{III}(H_2L^2)(gly)](IO_4)_2$ (3) and $Co^{III}(H_2L^2)(ser)](IO_4)_2$ (4) complexes, respectively. These peaks were assigned to ligand field. Bands at 298 and 295 nm for (3) and (4), respectively attributed to transition involving the metal oxime grouping. Additional low intense peaks at 348 and 350 nm for 3 and 4, respectively assigned to the spin-allowed $^1A_{1g} \rightarrow ^1T_{2g}$ transition which is masked by the intense charge transfer bands confirming an octahedral structure around Co(III) ions [23-25]. The room temperature magnetic moments of the complexes are reported in Table 3. They show magnetic moments in the range of 0–0.5 BM. The very low observed moments are allowed us to conclude safely that the complexes are diamagnetic, low-spin d^6 cobalt(III) complexes [20, 21, 26]. This assignment agrees with the electronic spectral measurements.

D molecular modelling and analysis of bonding modes

Molecular mechanics attempts to reproduce molecular geometries, energies and other features by adjusting bond length, bond angles and torsion angles to equilibrium values that are dependent on the hybridization of an atom and its bonding scheme. In order to obtain estimates of structural details of these complexes and in view

the six-coordination of all the complexes, we have optimised the molecular structure of the ligands and their Co(III)-complexes and we have included $[Co^{III}(H_2L^1)(gly)](IO_4)_2$ as a representative compound (Figure 3). The detail of bond lengths and bond angles per the 3D molecular structure is given in Tables 4. Energy minimization was repeated several times to find the global minimum [27]. The energy minimization value for octahedral and without restricting the structure for the prepared Co(III)-compounds is 159.9147, 195.8127, 160.9463, 275.0271 kcal/mol for complexes 1, 2, 3 and 4, respectively (Table 3). The molecular modelling for the modulated Co(II)-complex (Figure 3 and Table 4) shows the bond lengths bond angles around cobalt atom, indicating a distorted octahedral geometry around Co(III) ion [28], and thus the proposed structure of the Co(III)-complexes are acceptable.

Conclusion

In this paper, we have explored the synthesis and coordination chemistry of some imine-oxime Co(III)-complexes derived from the tetradentate Schiff-base oxime ligands H_2L^1 and H_2L^2 and the amino acid co-ligands. The ligands behave as a neutral species upon complexation with the involvement of the nitrogen atoms of the oxime groups in coordination for all complexes. The magnetic susceptibilities and electronic spectra of the complexes indicated that they are low-spin d^6 octahedral.

Table(1): Colours, yields, elemental analyses, and molar conductance values.

Compound $\Lambda_M(\text{cm}^2\Omega^{-1}\text{mol}^{-1})$	Colour	Yield (%)	m.p °C	Found (Calcd.) (%)			
				M	C	H	N
H_2L^1	White	56	166	-	53.3 (53.1)	8.1 (8.0)	25.0
(24.8) [Co ^{III} (H ₂ L ¹)(gly)](IO ₄) ₂	Brown 142.7	50	240*	8.3 (8.0)	19.2 (19.5)	2.6 (2.9)	9.2 (9.5)
[Co ^{III} (H ₂ L ¹)(ser)](IO ₄) ₂	Brown yellow 158.1	55	220*	7.4 (7.7)	20.7 (20.3)	3.6 (3.0)	8.9 (9.1)
H_2L^2	Brown yellow	64	192	-	61.2 (61.3)	6.9 (6.6)	20.2
(20.4) [Co ^{III} (H ₂ L ²)(gly)](IO ₄) ₂	Brown 145.6	38	270*	7.8 (7.5)	24.2 (24.4)	2.6 (2.7)	8.6 (8.9)
[Co ^{III} (H ₂ L ²)(ser)](IO ₄) ₂	Dark brown 150	65	190*	7.7 (7.2)	24.7 (25.0)	3.1 (2.8)	8.8 (8.6)

(*) Decomposed.

Table (2): IR frequencies (cm^{-1}) of the compounds.

Compound	$\nu(\text{NH}_3)$	$\nu(\text{OH})$	$\nu(\text{C=N})_{\text{imin}}$ $\nu(\text{C=N})_{\text{oxime}}$	$\nu(\text{N-O})$	$\nu(\text{COO}^-)_{\text{as, sy}}$	$\nu(\text{Co-N})$	$\nu(\text{Co-O})$	$\nu(\text{IO}_4^-)$
H_2L^1	-	3145	1609(s) 1473(s)	1001 (s)	-	-	-	-
H_2L^2	-	3184	1634 1481	989 (s)	-	-	-	-
[Co ^{III} (H ₂ L ¹)(gly)](IO ₄) ₂	3136 (br)	3385	1604(s) 1446(w)	1091 (m)	1500 (m) 1330	450(w)	582 (w)	740 (s)
[Co ^{III} (H ₂ L ¹)(gly)](IO ₄) ₂	3147 (br)	3360	1606 1408(m)	1037	1512 (w) 1384	412	551	748 (s.br)
[Co ^{III} (H ₂ L ¹)(gly)](IO ₄) ₂	3143	3380	1604 1408	1091	1492 1334	425	530	752
[Co ^{III} (H ₂ L ¹)(gly)](IO ₄) ₂	3145	3332	1627 1411	1029	1509 1346	435	582	748

br = broad , w =weak, m =medium, sh =sharp, s.br =strong broad

Table (3): Magnetic moment, u.v-vis spectral data in H₂O solutions and total minimisation energy.

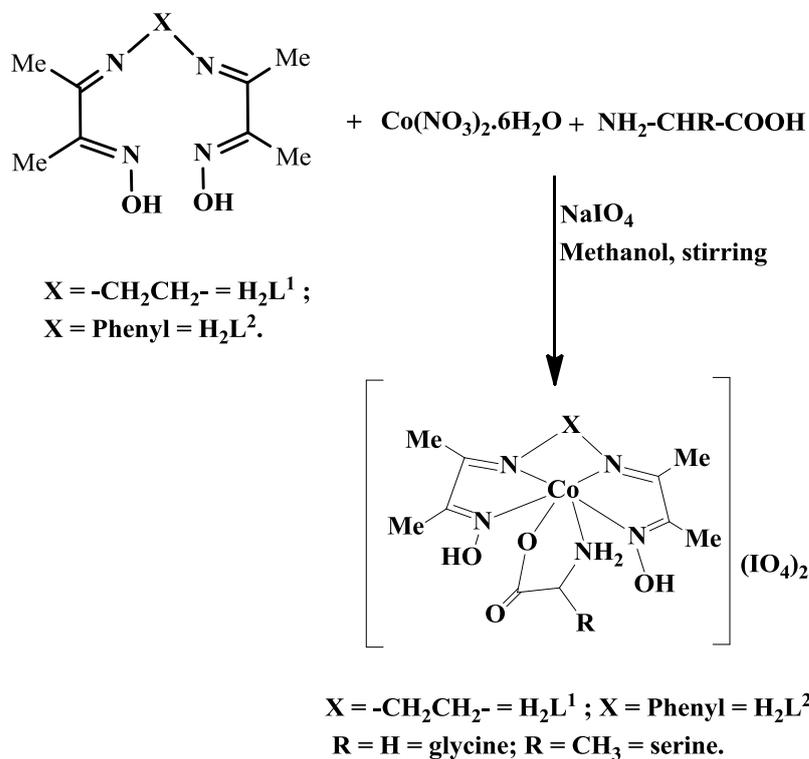
Compound	μ_{eff} (BM)	Band position (λ_{nm})	Extinction coefficient ϵ_{max} (dm ³ mol ⁻¹ cm ⁻¹)	Assignments	Total minimisation Energy; kcal/mol
H ₂ L ¹	-	293	1978	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	18.0999
[Co ^{III} (H ₂ L ¹)(gly)] (IO ₄) ₂	0.37	227 291 348	1631 693 400	$\pi \rightarrow \pi^*$ ligand field $^1A_{1g} \rightarrow ^1T_{2g}$	159.9147
[Co ^{III} (H ₂ L ¹)(ser)] (IO ₄) ₂	0	236 291 345	2014 558 375	$\pi \rightarrow \pi^*$ ligand field $^1A_{1g} \rightarrow ^1T_{2g}$	195.8127
H ₂ L ²	-	273 304	1125 2310	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	40.0806
[Co ^{III} (H ₂ L ²)(gly)] (IO ₄) ₂	0.5	229 298 348	2100 1570 734	$\pi \rightarrow \pi^*$ ligand field $^1A_{1g} \rightarrow ^1T_{2g}$	160.9463
[Co ^{III} (H ₂ L ²)(ser)] (IO ₄) ₂	0	224 295 345	2110 962 450	$\pi \rightarrow \pi^*$ ligand field $^1A_{1g} \rightarrow ^1T_{2g}$	275.0271

Table (4): Proposed bond lengths and bond angles of [Co^{III}(H₂L¹)(gly)]²⁺.

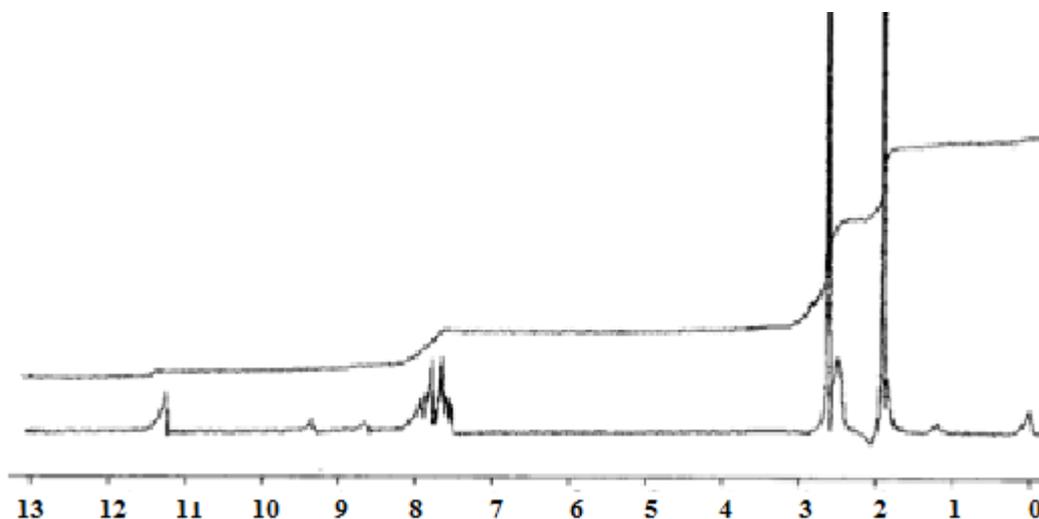
Type of bond	Bond lengths(Å)	Type of bond	Bond angles(°)
O(2)-H	0.9383	O(1)-Co(1)-N(5)	88.7212
O(3)-H	0.9410	O(1)-Co(1)-N(4)	87.6116
Co (1)- O(1)	1.8081	O(1)-Co(1)-N(1)	93.1164
Co(1)-N(5)	1.8440	O(1)-Co(1)-N(2)	88.7133
Co(1)- N(1)	1.8501	O(1)-Co(1)-N(3)	171.8279
Co(1) - N(2)	1.8485	N(5)-Co(1)-N(4)	89.1369
Co(1)- N(3)	1.8481	N(5)-Co(1)-N(1)	91.8125
Co(1)- N(4)	1.8497	N(5)-Co(1)-N(3)	174.3354
N(1)-O(2)	1.3212	N(5)-Co(1)-N(3)	91.5633
N(4)-O(3)	1.333	N(4)-Co(1)-N(1)	178.8156
		N(4)-Co(1)-N(2)	95.8009
		N(4)-Co(1)-N(3)	84.2267
		N(1)-Co(1)-N(2)	83.2855
		N(1)-Co(1)-N(3)	95.0374
		N(2)-Co(1)-N(3)	91.6940

		O(3)-N(3)-Co(1)	115.4792
		O(2)-N(71)-Co(1)	119.0420

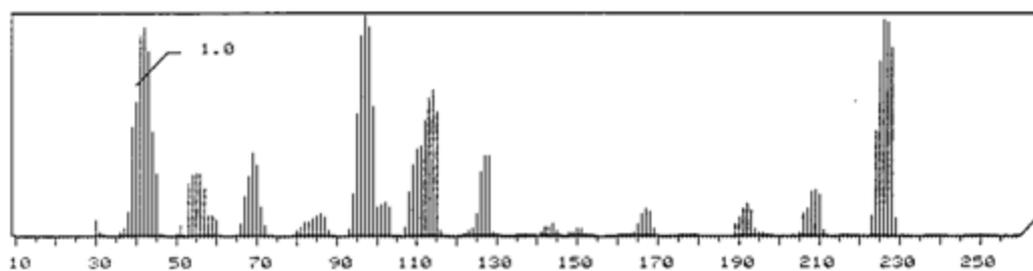
(Å) = Angstrom (°) = Degree



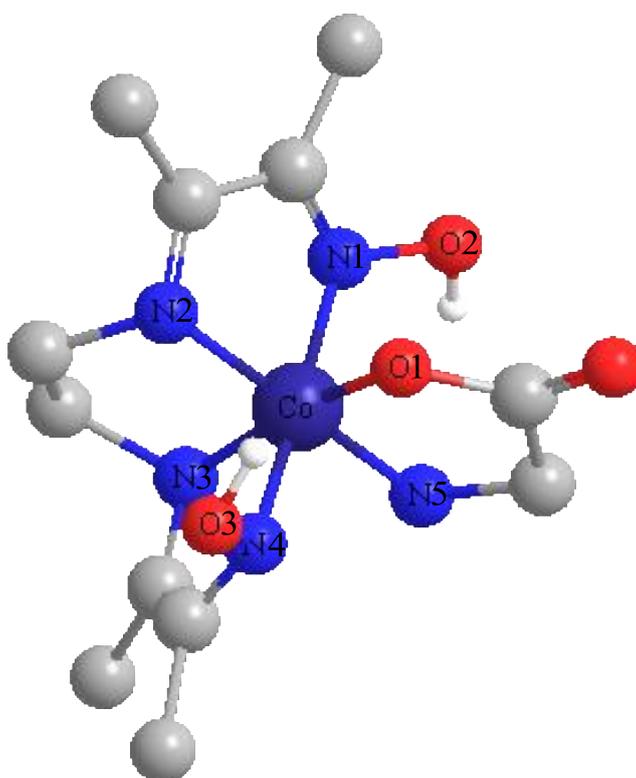
Scheme 1: Chemical structures of Schiff-base oxime ligands and the proposed Co(III) imine-oxime complexes.



Fig(1): ^1H NMR spectrum analysis of H_2L^2 .



Fig(2): EI (+) Mass spectrum analysis of H_2L^1 .



Fig(3): 3D molecular modelling of complex $[Co^{III}(H_2L^1)(gly)]^{2+}$.

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نحضير وتشخيص معقدات الكوبلت الثلاثية مع ليكاند نوع ايمين – اوكسيم وبعض الاحماض الامينية

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الخلاصة:

تم في هذا البحث تحضير ست معقدات للكوبلت الثلاثي وذلك بمفاعلة 2,3-butanedione monoxime مع ethylenediamine او o-phenylenediamine وبالنسبة المولية 2:1 لتعطي ليكاندين نوع ايمين – اوكسيم رباعية السن H_2L^1 and o-phenylenediamine-N,N'-bis(2-butylidene-3-oxobutanedione) H_2L^2 ، وعند مفاعلة الليكاندين مع نترات الكوبلت والاحماض الامينية (الكلايسين والسيرين) ينتج لدينا المعقدات الست المشار اليها. سلوك الليكاند هنا رباعي السن ومتعادل بينما الاحماض الامينية احادية القاعدية. تم تعيين الشكل الهندسي ونوع التآصر في المعقدات من خلال الدراسات الطيفية حيث اقترح الشكل الثماني السطوح للمعقدات بحيث يتناسق الحامض الاميني مع الفلز من خلال مجموعتي الامين والكاربوكسيل . وكذلك تم استنتاج الاشكال الجزيئي للمعقدات باستخدام برنامج CS Chem 3D Ultra Molecular Modelling واكدت ايضا الشكل الثماني السطوح للمعقدات.