

**New six coordinate cobalt(III) complexes of
[1,2-diaminoethane -N,N'-bis (2-butyldine -3-onedioxime)]**

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The ligand [1,2-diaminoethane -N,N'-bis (2-butyldine -3-onedioxime)][H₂L]. was reacted with Co(NO₃)₂.6H₂O and KBr in ethanol with reflux in (1:1) metal : ligand ratio to give a new complex of the general formula [Co^{III}(HL)Br₂]. A series of new complexes with some heterocyclic nitrogen and aliphatic amine ligands of the general formula [Co^{III}(HL)(X)Br]Br (where: X=pyridine, 4-picoline, and 3-picoline, piperidine, octylamine, n-propylamine and Br) were prepared. All compounds have been characterised by spectroscopic methods [IR, U.V-Vis, atomic absorption, (¹H NMR, and EI-mass spectroscopy for the ligand)], microanalysis and with conductivity measurements. From the obtained data, a distorted octahedral molecular structure about Co(III) ion has been proposed.

1. L. A. Chugaev, Zh. Russ. *Physicochem. Soc.* **41**, 184, 1909.

1,2-diaminoethane- N,N'-bis (2-butyldine -3-onedioxime) [H₂L]

(1:1)

:

[Co(HL)Br₂]

:

[Co(HL)Br.X] Br

:

X= (pyridine, 4-picoline, 3-picoline, piperidine, octylamine, and n-propylamine).

-

)

(EI

¹H NMR)

CHN

Introduction

It is well known that heterocyclic compounds play a significant role in many biological systems, especially six-membered ring systems being a component of several vitamins and drugs [1]. The chemistry of metal oximate complexes has been investigated intensively *e.g.*, preparation of nickel^(II) dimethylglyoximate, and recognition of the chelate five-membered ring character of this complex by Chugaev [2]. Transition metal complexes with *vic*-dioxime have attracted attention of many researchers because of their similarity to vitamin B₁₂ [3,4]. Numerous chemical studies have been made on the cobalt(II)-cobalt(III)-*bis*(dimethylglyoxime) system which has been called a model system for the B₁₂ moiety, [5,6] *vic*-Dioximes have great importance since they are used as chelating agents due to their stability of complexes with transition metal [7,8]. Recently Co(III) oxime based compounds showed the possibility of using in detergent industry, and 3,8-dimethyl-5,6-benzo-4,7-diazadeca-3,4-diene-2,9-diene dioxime Co(III) complex is the candidate to be used as a cationic surfactant [9]. The present paper describes the synthesis and characterisation of a new series of Co(III) *vic*-dioxime cationic complexes with (pyridine, 4-picoline, 3-picoline, piperidine, octylamine, *n*-propylamine, and Br).

Experimental

Reagents were purchased from Fluka and Rediel-Dehenge Chemical Co. IR spectra were recorded as (KBr) discs using a Shimadzu 8400 S FTIR spectrophotometer in the range (4000-400) cm⁻¹. Electronic spectra of the prepared compounds were measured in the region (200-900) nm for 10⁻³ M solution in (DMF) at 25 °C using a Shimadzu 160 spectrophotometer, with 1.000±0.001 cm matched quartz cell. Mass spectrum for the ligand was obtained by Electron-Impact (EI) on a Shimadzu GCMSQPA 1000 spectrometer. Nuclear Magnetic Resonance spectrum ¹H NMR for (H₂L) ligand was recorded in DMSO-d₆ using a Jeol EX 270 MHz instrument with a tetramethylsilane (TMS) as an internal standard. Elemental microanalyses were performed on a (C.H.N.) analyser from Heraeus (Vario EL), at the University of Free Berlin/Germany. While metal contents of the complexes were determined by atomic absorption (A.A) technique using a Shimadzu A.A 680G atomic absorption spectrophotometer. The bromide contents for complexes were determined using potentiometric titration method, on 686-Titro Processor Dosimat-Metrahm-Swiss. Electrical conductivity measurements of the complexes were recorded at 25 °C for 10⁻³ M solutions of the samples in (DMF) using a PW 9526 digital conductivity meter.

Synthesis of the ligand [1,2-diaminoethane-*N,N'*-bis(2-butyldiene-3-oxedioxime)][H₂L]^[10].

Synthesis of [Co(HL)Br₂]

To an ethanolic solution of Co(NO₃)₂.6H₂O (0.58g, 2mmole) in (10 ml) ethanol, KBr (0.24g, 2 mmole) was added. KNO₃ was separated by filtration. The solution was concentrated under reduced pressure and taken as CoBr₂. The ligand [H₂L] (0.9g, 4mmol) was added to the above solution, and the mixture was warmed to 40 °C and stirred for (30min), then cooled. Air was passed for 3 hrs, a yellow solid was formed which was collected by filtration, and dried under vacuum for (24 hrs.) to give [Co(HL)Br₂]. Yield 0.6g, (61%), m.p. (199-200 °C).

Synthesis of [Co(HL)(py)Br]Br

To an ethanolic solution of Co(NO₃)₂.6H₂O (0.58g, 2mmole) in (10mL) ethanol, KBr (0.24g, 2 mmole) was added. KNO₃ was separated as precipitate, and then filtered off. The solution was concentrated under reduced vacuum and taken as CoBr₂. The above solution was warmed and stirred for 15 min. The ligand [H₂L] (0.9g, 4mmol) was added to the solution. The mixture was warmed and allowed to stir for (30min), and then cooled. A solution of (0.31g, 4mmol) of pyridine in (10mL) was added. The reaction was allowed to reflux for 2 hrs, and then air was passed for 4 hrs. The pale brown precipitate crystals which

formed upon standing were collected, washed with (10 mL) diethylether, and dried to give 0.4g (64%) of the titled compound, m.p (220-224 °C) dec.

Synthesis of [Co(HL)(pip.)Br]Br

A similar procedure to that described for [Co(HL)py.Br]Br was employed but with piperidine (0.34g, 4mmole) in place of pyridine. The quantities of the other reagents were adjusted accordingly and an identical work-up procedure gave brown precipitate, which was washed with (10mL) diethyl ether to yield 0.35g (59%), m.p(226 -228 °C) dec.

Synthesis of [Co(HL)(oct.)Br]Br

A similar procedure to that described for [Co(HL)py.Br]Br was used but with octylamine (0.5g, 4mmole) in place of pyridine. The quantities of the other reagents were adjusted accordingly and an identical work-up procedure gave a yellow precipitate 0.48g (75%) of the title compound, m.p (180 -183°C).

Synthesis of [Co(HL)(n-pro.)Br]Br

The method used to prepare [Co(HL)(n-pro.)Br]Br was analogous to the procedure given for the complex [Co(HL)(oct.)Br]Br but with n-propylamine (0.236g, 4mmole) instead of octylamine. The quantities of the other reagents were adjusted accordingly and an identical work-up procedure gave an orange precipitate 0.42g (74%),m.p(220 °C).

Synthesis of [Co(HL)(4-pic.)Br]Br

A similar procedure to that described for [Co(HL)py.Br]Br was used but with (0.37g, 4mmole) of 4-picoline in place of pyridine. The quantities of the other reagents were adjusted accordingly and an identical work-up procedure gave a pale brown precipitate, yield 0.39g (65%), m.p (210 °C)dec.

Synthesis of [Co(HL)(3-pic.)Br]Br

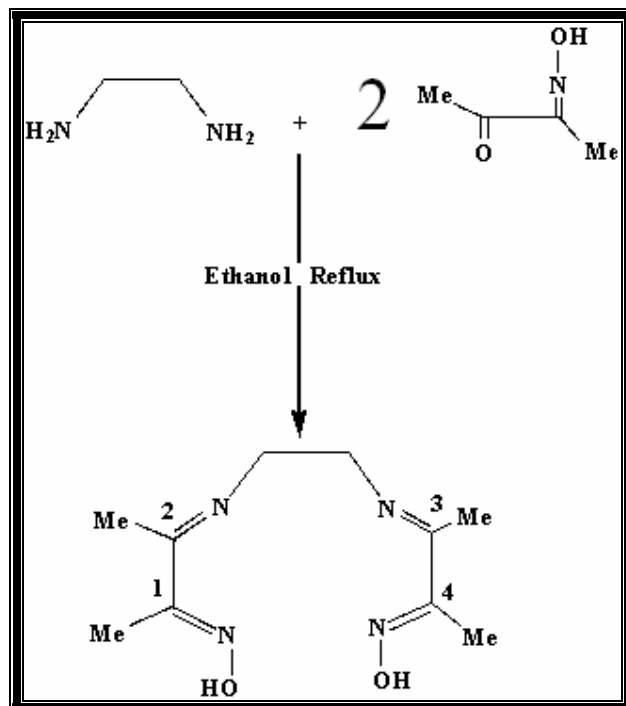
The method used to prepare [Co(HL)(3-pic.)Br]Br. was analogous to the procedure given for the complex of 4-picoline but with 3-picoline (0.37g, 4mmole) instead of 4-picoline. The quantities of the other reagents were adjusted accordingly and an identical work-up procedure gave a mustard precipitate 0.4g (67%), m.p (200 °C) dec.

Results and discussion

Synthesis of the ligand

The [H₂L] pro- ligand was prepared according to published method^[10] as shown in **Scheme(1)**. The (**I.R**) spectrum for (H₂L) displayed two bands at (1609) and (1473cm⁻¹) due to the $\nu(\text{C}=\text{N})$ stretching for the imine and oxime groups respectively, **Table(2)**. The band at (3145cm⁻¹) is attributed to the $\nu(\text{O}-\text{H})$ stretching of the oxime group. The strong

bands at (1001) and (918cm⁻¹) are attributed to $\nu(\text{N}-\text{O})$ stretching^[11]. The (**U.V-Vis**): spectrum exhibits a high intense absorption peak at (293nm) (34130cm⁻¹) ($\epsilon_{\text{max}}=1978 \text{ molar}^{-1}.\text{cm}^{-1}$) which assigned to overlap of (**n**→**π***) and (**π**→**π***) transitions^[12] **Table (3)**. The EI(+) mass spectrum of the ligand **Fig.(4)**, shows the parent ion peak at (m/z =226) which corresponds to [M]⁺, and the fragments at,(209), (192), (166), (151), (125), (112), (96),and (68), are assigned to [M-(OH)]⁺, [M-{(OH)₂}]⁺, [M -{(OH)₂-CN}]⁺, [M-{(OH)₂-CN-CH₃}]⁺, [M-{(OH)₂-CN-CH₃-CN}]⁺, [M-{(OH)₂-CN-CH₃-CN-CH₃-CN-CH}]⁺, [M-{(OH)₂-CN-CH₃-CN-CH-NH₂}]⁺, [M-{(OH)₂-CN-CH₃-CN-CH-NH₂-CNH₂}]⁺, respectively. The ¹H NMR spectrum of [H₂L], in DMSO-d⁶, Fig.(5) showed (OH) protons of the oxime appear as a broad signal at (11.46)ppm. This resonance was disappeared upon addition of D₂O to the solution^[13]. The CH₂ protons are equivalent and appear as a singlet at (3.70) ppm. As can be seen from the spectrum the two sharp singlets at (2.02) and (1.89) ppm are due to the methyl groups on carbons (C-1,4) and carbons (C-2,3) respectively. However each peak is equivalent to six protons^[14, 15].



Scheme (1) The synthesis route for the ligand

Synthesis of the complexes

The synthesis of the new six coordinate complexes of the type $[\text{Co}(\text{HL})\text{X}]\text{Br}$ ($\text{X} =$ pyridine, 4-picoline, 3-picoline, piperidine, octylamine, and n-propylamine) was carried out in EtOH solvent. These complexes are stable in EtOH solution. The analytical and physical data **Table(1)** and spectral data **Table (2)** and **Table (3)** are compatible with the suggested structure **Fig.(1)**. The (I.R) spectral data of the complexes are presented in **Table(2)**. In general the (I.R) spectra of the complexes show two bands within $(1670-1630)$ and $(1585-1562)\text{cm}^{-1}$ range which assigned to the $\nu(\text{C}=\text{N})$ for the imine and oxime groups respectively, indicating the coordination of nitrogen atoms of the imine and oxime groups.^[16] The strong $\nu(\text{N}-\text{O})$ stretching bands at (1001) and $(918)\text{cm}^{-1}$ for the free ligand

are shifted markedly to higher frequencies by *ca.* $(90)\text{cm}^{-1}$. This is presumably due to the complexation with the metal ions. For these complexes the two (N-O) bands are unequal^[17]. The weak and broad bands appeared within the region $(2580 - 2405)\text{cm}^{-1}$ and $(1765 - 1736)\text{cm}^{-1}$ are due to the $\nu(\text{O}\dots\text{H}-\text{O})$ stretching and $\delta(\text{O}\dots\text{H}-\text{O})$ bending for the hydrogen bond respectively, in which the ligand loses a proton and a hydrogen bonding will be formed. However, these bands are absent in the spectrum of the free ligand^[10]. The bands at $(514-509)\text{cm}^{-1}$ were assigned to $\nu(\text{M}-\text{N})$ stretching, indicating that the imine and oxime nitrogens were involved in coordination with metal ion^[18]. The molar conductance of the complexes in (DMF) lie within the $(60-75\ \Omega^{-1}\cdot\text{cm}^2\cdot\text{mole}^{-1})$ range **Table (3)**, indicating their electrolytic nature with 1:1

ratio (bar $[\text{Co}(\text{HL})\text{Br}_2]$ complex in which the molar conductance in DMF is $25 \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$, indicating its non-electrolytic nature)^[19]. The electronic spectral data of the complexes are summarised in **Table (3)**. The (U.V-Vis.) spectra of the complexes

displayed a peak at (500-585)nm is due to (d-d) spin allowed transition type (${}^3\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$), suggesting distorted octahedral

structure about $\text{Co}^{(\text{III})}$ ion^[20]. The (${}^3\text{T}_{2g} \leftarrow {}^1\text{A}_{1g}$) band is masked by the intense charge transfer bands. The bands at the range (293-305)nm assigned to the intra-ligand ($\pi \rightarrow \pi^*$) transitions of the coordinated ligand. The bands occurring at the range (362-383)nm are assigned to charge transfer^[21].

Table (1) Analytical and physical data of the ligand and complexes

Compound	Colour	M.P °C	Yield %	Found , (Calc.) %				
				C	H	N	Co	Br
[H ₂ L] (C ₁₀ H ₁₈ N ₄ O ₂)	White	164	56	(53.09) 52.50	(7.96) 7.32	(24.77) 24.34	-	-
[Co(C ₁₀ H ₁₇ N ₄ O ₂) Br ₂]	Yellow	199	61	(27.04) 26.50	(3.83) 3.54	(12.62) 12.14	(13.27) 12.72	(36.01) 35.42
[Co(C ₁₀ H ₁₇ N ₄ O ₂) py.Br]Br	Brown	220	64	(40.65) 40.10	(4.97) 4.60	(15.81) 15.30	(13.30) 13.00	(18.04) 17.64
[Co(C ₁₀ H ₁₇ N ₄ O ₂) pipe.Br]Br	Brown	226	59	(40.19) 39.80	(6.03) 5.75	(15.63) 15.07	(13.15) 12.71	(17.84) 17.56
[Co(C ₁₀ H ₁₇ N ₄ O ₂) oct.Br]Br	Yellow	180 dec	75	(43.56) 43.20	(7.26) 6.81	(14.12) 13.72	(11.88) 11.32	(16.11) 15.50
[Co(C ₁₀ H ₁₇ N ₄ O ₂) npro.Br]Br	Orange	220	74	(36.63) 36.32	(6.11) 5.82	(16.44) 16.24	(13.83) 13.20	(18.76) 18.24
[Co(C ₁₀ H ₁₇ N ₄ O ₂) 4pic.Br]Br	Pale brown	210 dec	65	(42.03) 41.65	(5.47) 5.15	(15.32) 15.00	(12.89) 12.50	(17.49) 17.21
[Co(C ₁₀ H ₁₇ N ₄ O ₂) 3pic.Br]Br	Mustard	200 dec	67	(42.03) 41.37	(5.47) 5.00	(15.32) 15.10	(12.89) 12.31	(17.49) 17.00

Table (2) The I.R. spectral data of the complexes and its complexes^a

compound	$\nu(\text{C-H})$ aliph $\nu(\text{C-H})$ aroma	$\nu(\text{C=N})$ imine $\nu(\text{C=N})$ oxime	$\nu(\text{N-O})$	$\nu(\text{O..H-O})$	$\delta(\text{O..H-O})$	$\nu(\text{M-N})$	Additional peaks
[H ₂ L]	2850(br) 3016(br)	1609 (s) 1473 (s)	918 (sh) 1001 (sh)	-	-	-	1415(CH ₂)(s)
[Co(HL) Br ₂]	2920 (br) 3018 (br)	1670(sh) 1562(sh)	979 (sh) 1091(sh)	2500(w)	1650(w)	512(sh)	1430 (CH ₃)(br)
[Co(HL) py.Br]Br	2925 (w) 3053 (w)	1660 (sh) 1563 (sh)	977 (sh) 1078 (sh)	2600(w)	1753(w)	509 (sh)	1450 (CH ₃)(sh) 1615 $\nu(\text{C=C})$ ring
[Co(HL) pip.Br]Br	2952 (br) 3091 (br)	1655 (br) 1562 (sh)	979 (sh) 1024 (br)	2630(w)	1699(w)	510 (sh)	1445 (CH ₃)(sh)
[Co(HL) oct.Br]Br	2920 (br) 3045 (br)	1670 (w) 1585 (sh)	1047 (w) 1091 (sh)	2519 (w)	1750 (w)	513 (sh)	1425 (CH ₃)(br) 1209 $\nu(\text{C-N})$ (w)
Co(HL) n pro.Br]Br	2970 (sh) 3058 (br)	1670 (sh) 1575 (sh)	977 (w) 1006 (w)	2565 (w)	1755 (w)	513 (sh)	1384 (CH ₃)(sh)
Co(HL) 4 pic.Br]Br	2956 (br) 3018 (br)	1630 (sh) 1570 (sh)	973 (sh) 1037 (w)	2661 (w)	1720 (w)	514 (w)	1446 $\nu(\text{C=C})$ ring
[Co(HL) 3-pic.Br]	2925 (br) 3095 (br)	1660 (w) 1565 (sh)	983 (w) 1004 (w)	2588 (w)	1730 (w)	510 (sh)	1384 (CH ₂) (s)

^a S: strong, m: medium, w: weak, br: broad, w.br: weak and broad

**Table (3) Electronic spectral data, and conductance measurements
for the ligand [H₂L] and it's complexes**

Compound	λ nm	ϵ_{\max} Molar Cm ⁻¹	Assignment	Λ_m ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{Mole}^{-1}$) in DMF
[H ₂ L]	293	1978	(n → π^*) (π → π^*)	-
[Co(C ₁₀ H ₁₇ N ₄ O ₂) Br ₂]	383	1472	charge transfer	25
[Co(C ₁₀ H ₁₇ N ₄ O ₂)(py)Br]	376	1293		60
	575	134		
[Co(C ₁₀ H ₁₇ N ₄ O ₂)(pi)Br]	313	2482		65
	376	1222		
	570	74		
[Co(C ₁₀ H ₁₇ N ₄ O ₂)(oct)Br]	301	2201		70
	362	952		
	580	46		
[Co(C ₁₀ H ₁₇ N ₄ O ₂)(n-pro)Br]	379	1334		75
	500	81		
[Co(C ₁₀ H ₁₇ N ₄ O ₂)(4-pic)Br]	300	1763		72
	358	750		
	520	113		
[Co(C ₁₀ H ₁₇ N ₄ O ₂)(3-pic)Br]	383	1472		78
	535	51		

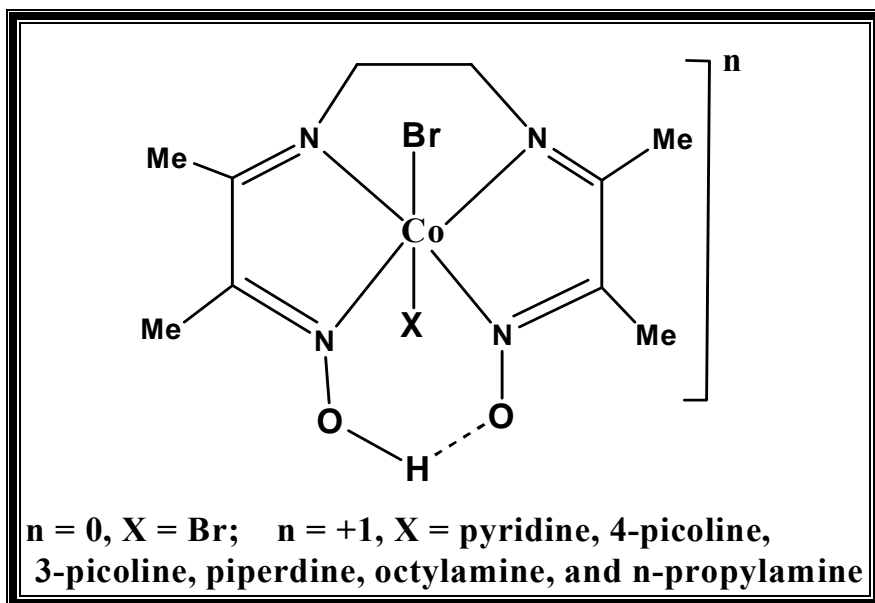


Figure (1) The suggested structure for the prepared complexes

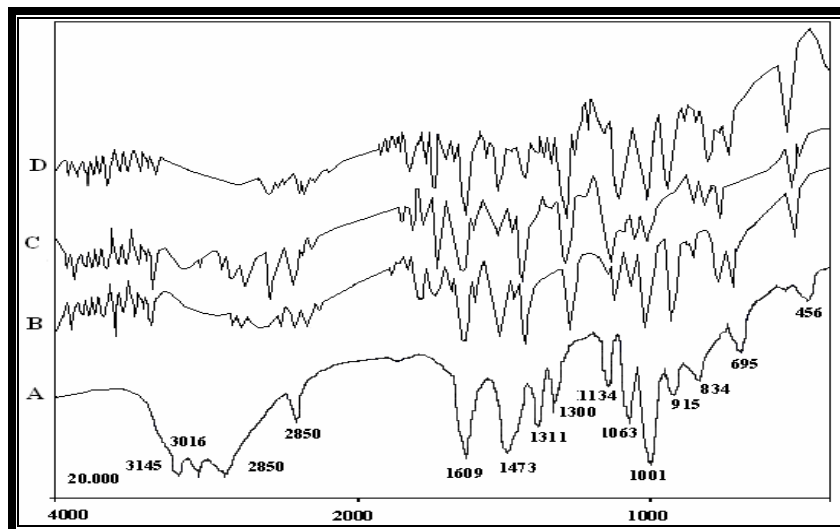


Figure (2) The IR spectra of
 (A) The ligand $[H_2L]$.
 (B) The complex $[Co(HL)(py).Br]Br$
 (C) The complex $[Co(HL)(pypi).Br]Br$
 (D) The complex $[Co(HL)(n-pro).Br]Br$

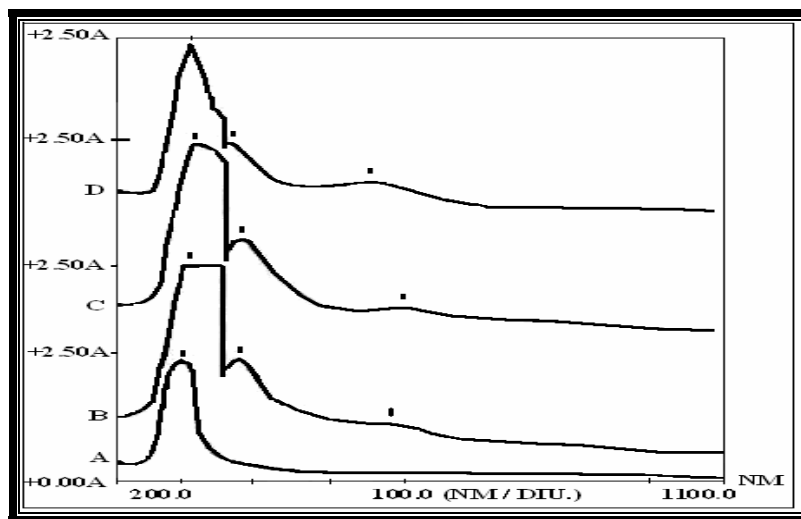
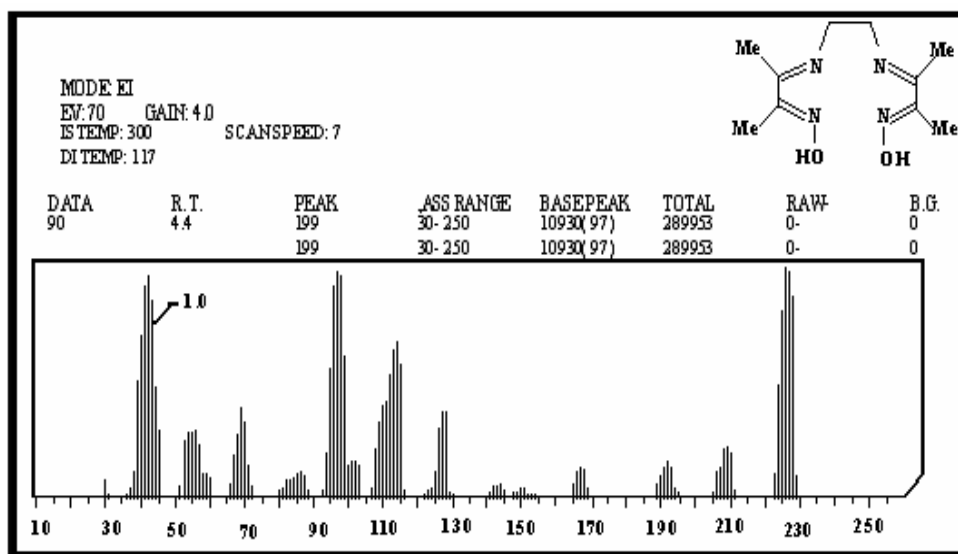
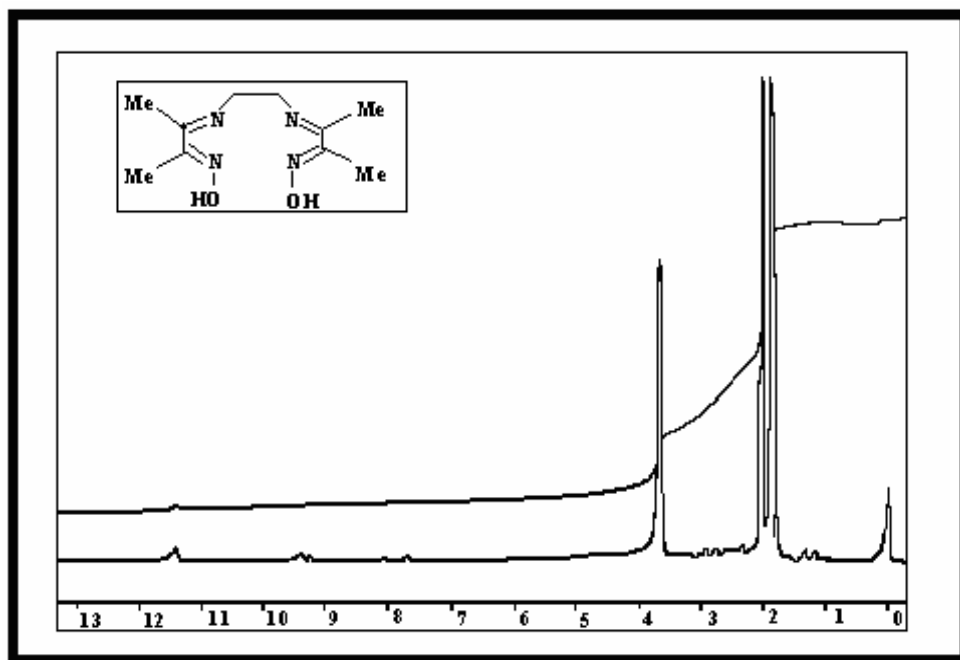


Figure (3) The U.V-Vis spectra of
 (A) The ligand $[H_2L]$
 (B) The complex $[Co(HL)(py).Br] Br$
 (C) The complex $[Co(HL)(pypi).Br]Br$
 (D) The complex $[Co(HL)(4-pic).Br]Br$

Figure (4) EI (+) Mass spectrum of [H₂L]Figure (5) ¹H NMR spectrum of [H₂L] in DMSO-d⁶

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