

CHAPTER - VI

Cobalt complexes of O,N,O chelators : Synthesis, spectral and electrochemical studies

Cobalt(II) (3) and Cobalt(III) (4) complexes of ONO donor tridentate chelates, 2-methoxyazophenols (1), and cobalt(III) complexes of type $[\text{Co}(\text{ONO})_2]$ (where H_2ONO = o-arylazocarboxylic acids) (2) have been synthesised. The complexes (3, 4, 5) have been characterised by elemental analysis, IR, UV-Vis, molecular weight measurements and ^1H NMR (for (1), (2), (4) and (5)) data. The redox activity of the complexes have been critically examined by cyclic voltammetric and coulometric measurements.

1. Introduction :

The involvement of transition metals and their complexes in important chemical, biochemical, analytical, industrial processes etc. have drawn attention to study their reactions and structures. Amongst the early transition metals, the co-ordination chemistry of cobalt has been dominated by nitrogen donor ligands². The complexes of N,O donor systems continue to attract the attention of many researchers in cobalt chemistry¹⁻³. Azophenols and Schiff bases are best known N,O donor ligands. The azo compounds are widely used as ligands for their considerable use in analytical and biological chemistry and in textile industry as dyeing agents⁴. The *ortho*-substituted azophenols with additional donor groups at the phenyl ring comparatively less studied in the chemistry of cobalt. In this chapter we describe, synthesis spectral characterisation and some redox studies of cobalt complexes of *o*-methoxyazophenols (1) and *o*-arylazophenolato carboxylic acids(2).

2. Results and Discussions :

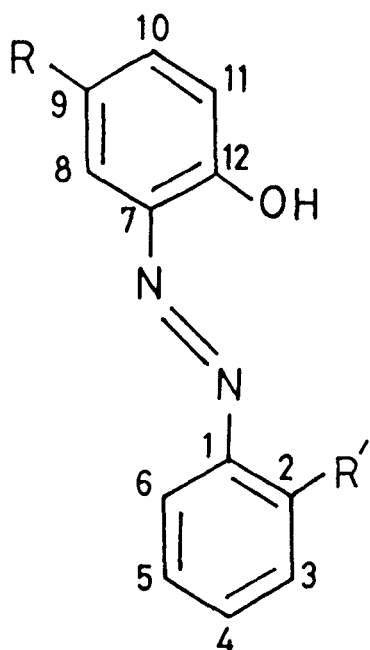
A. *Ligands and Complexes :*

Two series of ligands are used; o-methoxyazophenols (1) and o-arylazophenolato carboxylic acids(2). The ligands are tridentate (O,N,O) chelators.

The ligands(1) are monobasic and (2) are dibasic tridentate (O,N,O) donors. The cobalt(II) complexes (3) of (1) are obtained by refluxing the ligands (1) and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in MeOH under dinitrogen atmosphere for 2 hr. The brown red cobaltous complexes (3), purified by recrystallisation from CHCl_3 -MeOH. The pink red cobalt(III) complexes (4) of the ligands (1) are obtained by three different methods⁵ and the dark green cobalt(III) complexes (5) are obtained similarly from the corresponding ligands (2). The complexes are listed in Table VI.1.

B. *Physical Characteristics :*

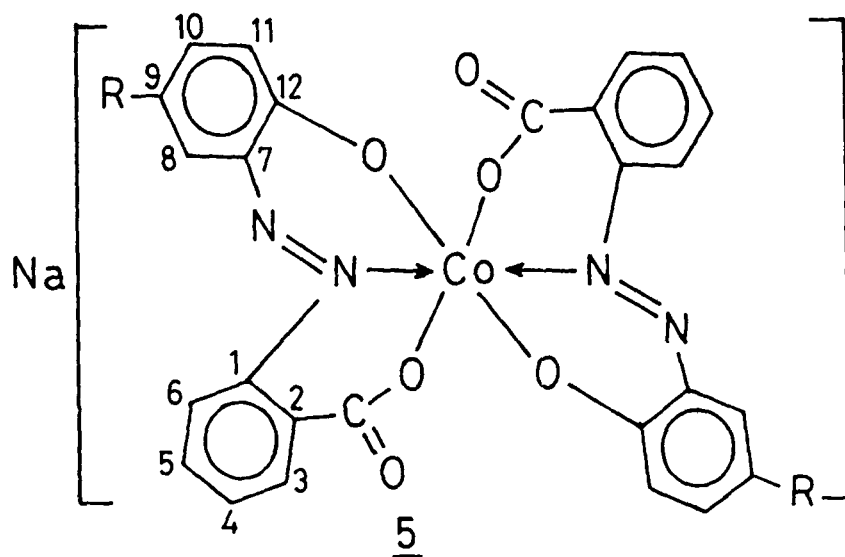
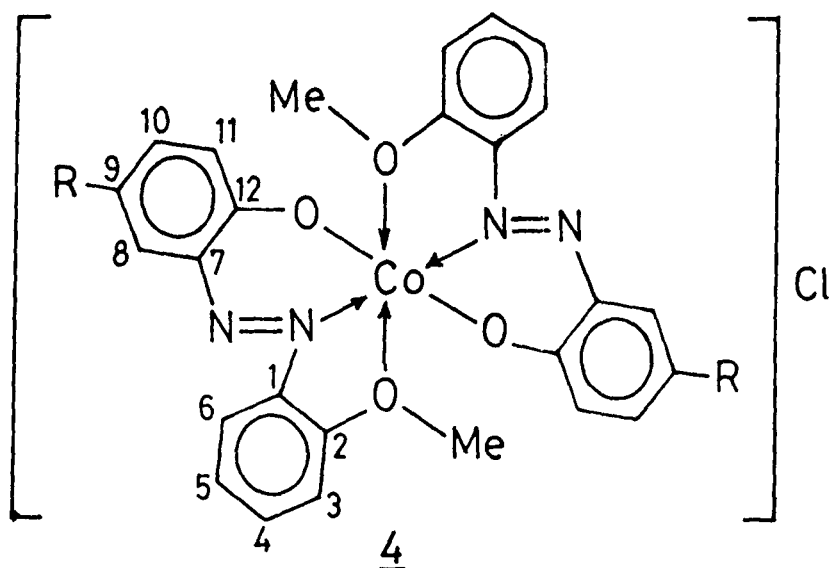
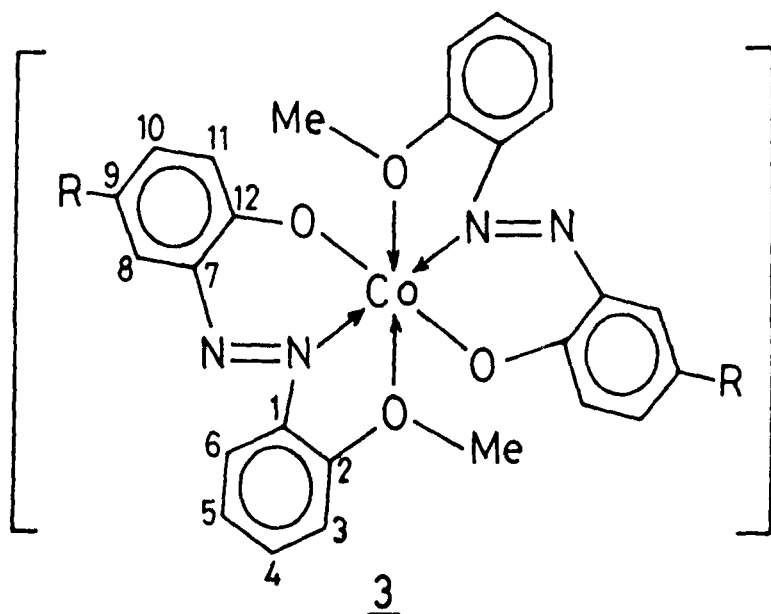
The cobalt(II) complexes (3) are fairly soluble in chloroform, acetonitrile and the solution colour is brown red. The cobalt (III) complexes (4) are soluble in common organic solvents like MeOH, CHCl_3 , acetonitrile giving pink-violet solution and the complexes (5) afford green solutions in solvents like methanol,

Table - VI.1

	R
<u>a</u>	Me
<u>b</u>	Cl
<u>c</u>	NO ₂
<u>d</u>	t-Bu
<u>e</u>	8,9-Benzo

	R'
<u>1</u>	OMe
<u>2</u>	COOH

Structures

Table-VI.1

R	Me	Cl	NO ₂	t Bu	8,9-Benzo
	<u>a</u>	<u>b</u>	<u>c</u>	<u>d</u>	<u>e</u>

Table - VI.2

Elemental analyses, molar conductances and magnetic moment data of complexes(3), (4) and (5)

	Elemental analysis				Found(calcd) %		χ	Λ_M° Ohm ⁻¹ cm ² mol ⁻¹	μ_{corr} B.M.
	C	H	N	Co	N	Co			
Co(La) ₂ (3a)	62.02 (62.11)	4.69 (4.81)	10.44 (10.35)	11.12 (10.91)			10.49	4.78	
Co(Lb) ₂ (3b)	53.5 (53.61)	3.51 (3.44)	9.74 (9.62)	10.31 (10.14)			12.82	4.62	
Co(Lc) ₂ (3c)	51.61 (51.74)	3.44 (3.32)	13.84 (13.93)	9.90 (9.78)			15.34	4.70	
Co(Ld) ₂ (3d)	65.41 (65.23)	5.92 (6.08)	9.11 (8.96)	9.59 (9.44)			14.18	4.84	
Co(Le) ₂ (3e)	66.42 (66.56)	4.36 (4.24)	9.01 (9.14)	9.48 (9.62)			8.54	4.64	
[Co(La) ₂]Cl (4a)	58.13 (58.28)	4.62 (4.51)	9.83 (9.71)	10.31 (10.23)			128.26	dia	
[Co(Lb) ₂]Cl (4b)	50.60 (50.53)	3.36 (3.24)	8.91 (9.07)	9.42 (9.55)			138.48	dia	
[Co(Lc) ₂]Cl (4c)	48.93 (48.86)	3.04 (3.13)	13.23 (13.16)	9.09 (9.24)			122.62	dia	

Table - VI.2 (Contd.)

Elemental analyses, molar conductances and magnetic moment data of complexes(3), (4) and (5)

	Elemental analysis			Found(calcd) %		Λ_M^a Ohm ⁻¹ cm ² mol ⁻¹	μ_{corr} B.M.
	C	H	N	Co	Cl		
[Co(Ld) ₂]Cl (4d)	61.86 (61.77)	5.84 (5.75)	8.33 (8.48)	8.81 (8.93)	5.46 (5.37)	130.59	dia
[Co(Le) ₂]Cl (4e)	63.11 (62.91)	3.84 (4.01)	8.52 (8.64)	8.94 (9.10)	5.39 (5.47)	140.46	dia
Na[Co(L'a) ₂]H ₂ O (5a)	55.12 (55.26)	3.71 (3.62)	9.09 (9.21)	9.56 (9.70)		110.8	dia
Na[Co(L'b) ₂]H ₂ O (5b)	47.92 (48.07)	2.59 (2.47)	8.74 (8.63)	9.21 (9.09)		124.5	dia
Na[Co(L'c) ₂]H ₂ O (5c)	59.09 (58.96)	4.80 (4.91)	8.18 (8.09)	8.34 (8.53)		108.4	dia
Na[Co(L'd) ₂]H ₂ O (5d)	46.39 (46.57)	2.44 (2.39)	12.38 (12.54)	8.74 (8.81)		135.4	dia
Na[Co(L'e) ₂]H ₂ O (5e)	59.89 (60.00)	3.16 (3.24)	8.11 (8.24)	8.80 (8.68)		128.5	dia

*In acetonitrile

ethanol, acetonitrile but sparingly soluble in chloroform, methylene chloride. The complexes (3) are non electrolytes and the complexes (4) and (5) are 1:1 electrolytes. The molar conductances (Λ_M) in acetonitrile are listed in table VI.2. The room temperature magnetic moments 4.7-4.9 B.M. for complexes (3) suggesting octahedral geometry and the cobalt (III) complexes (4 and 5) are diamagnetic. The molecular weight measurements by vapour pressure osmotic method supports the molecular formula of the complexes and the results are given in Table VI.2.

c. Spectral Characterisation :

(i) UV-VIS Spectra :

The electronic spectral data of the complexes (3) and (4) have been recorded in chloroform and of the complexes (5) in methanol solution. The reddish solution of the cobaltous complexes (3) exhibit metal centred⁶ transition with absorption maxima ~500nm having considerably high intensity and a weak band ~365nm. The band can be assigned to $4T_{1g}(F) \rightarrow 4T_{1g}(P)$ transition and supports octahedral environment of cobalt(II). The remaining two transitions ~345nm and ~250nm can be assigned to $n \rightarrow \Pi^*$ and $\Pi \rightarrow \Pi^*$ transitions centred primarily on the azo group⁷. This

Table VI.3
UV-VIS spectral data

λ max (ϵ) nm ($\text{mol}^{-1} \text{cm}^{-1}$)

(3a) ^a	495 (20,792)	365 (25,915)	348 (29,713)	250 (33,307)
(3b) ^a	500 (18,880)	365 (24,030)	345 (30,675)	245 (30,420)
(3c) ^a	505 (19,800)	365 (28,432)	350 (35,480)	245 (29,872)
(3d) ^a	490 (20,400)	360 (22,432)	340 (27,320)	250 (30,040)
(3e) ^a	500 (38,584)	395 (14,089)	306 (17,870)	250 (31,172)
(4a) ^a	645 (875)	500 (1,875)	375 (5,375)	340 (18,302) 250 (17,192);
(4b) ^a	645 (895)	502 (1,912)	370 (5,402)	341 (18,275) 252 (17,102);
(4c) ^a	640 (892)	500 (1,892)	372 (5,401)	338 (18,271) 248 (17,203);
(4d) ^a	638 (896)	503 (1,908)	375 (5,392)	340 (18,271) 250 (17,212);
(4e) ^a	650 (891)	500 (1,905)	375 (5,385)	340 (18,308) 250 (17,192);
(5a) ^b	620 (2,892)	375 (9,572)	305 (19,795)	290 (18,120)
(5b) ^b	625 (2,030)	380 (8,630)	310 (20,580)	295 (17,650)
(5c) ^b	625 (3,045)	385 (10,435)	305 (22,830)	285 (26,340)
(5d) ^b	620 (2,430)	370 (11,640)	300 (22,830)	285 (25,550)
(5e) ^b	620 (5,539)	410 (16,500)	315 (20,265)	285 (23,832)

^aIn CHCl_3 ; ^bIn MeOH

suggests tetragonally distorted octahedral stereochemistry for the complexes (3) which is supported by magnetic data. The stability constant data accounts also the distorted octahedral geometry⁸. The cobaltic complexes (4) exhibit weak absorption ~650nm and relatively moderate intense bands ~500nm and ~375nm refer to $1A_{1g} \rightarrow 1T_{1g}$ and $1T_{2g}$ transitions respectively along with the ligand centred transitions ~340nm and ~250nm. These informations suggest octahedral geometry of cobalt(III) complexes (4). The transitions in green complexes (5) in the visible region ~620nm and 375-410nm may be ascribed from spin singlet ground state ($1A_{1g}$) to $1T_{1g}$ and $1T_{2g}$ states⁹. Other transitions can be assigned to $n \rightarrow \Pi^*$ and $\Pi \rightarrow \Pi^*$ transitions centred primarily on the azo group⁷ corresponding to ~310nm and ~290nm respectively. Representative figure of the spectra are given in Fig VI.A. and data are collected in Table VI.3.

(ii) *IR spectra* :

The azophenol ligands (1) exhibit a medium intense vibrational band $\sim 3200\text{cm}^{-1}$ assignable to $\nu(\text{O-H})$ of the hydrogen bonded phenolic group¹⁰ which is absent in the complexes (3 and 4). The disappearance of $\nu(\text{O-H})$ is indicative of co-ordination of oxygen

to the metal centre¹¹. The $\nu(\text{C-H})$ (phenolic) at $1495\text{-}1520\text{cm}^{-1}$ shifts to higher frequency by $30\text{-}40\text{cm}^{-1}$ on co-ordination with metal ion¹². The ligands (2) show broad IR bands in the region $3300\text{-}2800\text{cm}^{-1}$ due to $\nu(\text{O-H})$ modes of carboxylic acid and phenolic -OH group^{13(a)}. The complexes (5) also exhibit broad IR bands in the region $3600\text{-}3200\text{cm}^{-1}$ due to $\nu(\text{O-H})$ modes of lattice water^{13(b)} and are completely removed on thermal study to $110\text{-}130^\circ\text{C}$. The presence of moderate band around 1700cm^{-1} in ligand is the indication of $-\text{CO}_2\text{H}$ group¹⁴ which is absent in the complexes (5) suggesting the co-ordination of the carboxylato group. The appearance of IR bands around $1540\text{-}1570$ and $1350\text{-}1370\text{cm}^{-1}$ correspond to $\nu_{\text{asym}}(\text{COO})$ and $\nu_{\text{sym}}(\text{COO})$ respectively indicates monodentate co-ordination ($\Delta\nu = 200\text{cm}^{-1}$) of carboxylato group¹⁵. The $\nu(\text{N=N})$ mode of the free ligands at $1455\text{-}1470\text{cm}^{-1}$ is blue shifted by $10\text{-}30\text{cm}^{-1}$ in the three series of the complexes indicating the co-ordinating of azo nitrogen¹⁶. In addition to these, all other bands appeared in the ligands are slightly blue shifted in the complexes and two new bands observed in far IR region around $520\text{-}545\text{cm}^{-1}$ and $345\text{-}360\text{cm}^{-1}$ are assignable¹⁷ to $\nu(\text{Co-O})$ and $\nu(\text{Co-N})$ respectively. Selected IR data are collected in **Table VI.4**.

Table - VI.4
Some selective Infrared spectral data
 (in cm^{-1})

Complex	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\nu(\text{Co}-\text{O})$	$\nu(\text{Co}-\text{N})$
<u>3a</u>	1,380	1,525	-	-	520	345
<u>3b</u>	1,380	1,525	-	-	525	355
<u>3c</u>	1,385	1,530	-	-	530	360
<u>3d</u>	1,375	1,520	-	-	520	345
<u>3e</u>	1,380	1,525	-	-	525	350
<u>4a</u>	1,370	1,555	-	-	540	355
<u>4b</u>	1,370	1,550	-	-	540	360
<u>4c</u>	1,375	1,555	-	-	545	355
<u>4d</u>	1,365	1,550	-	-	545	360
<u>4e</u>	1,370	1,555	-	-	540	355
<u>5a</u>	1,370	-	1,540	1,350	545	350
<u>5b</u>	1,370	-	1,550	1,365	550	355
<u>5c</u>	1,375	-	1,545	1,355	550	355
<u>5d</u>	1,360	-	1,570	1,370	545	355
<u>5e</u>	1,365	-	1,550	1,350	550	365

(c) *¹H NMR Spectra :*

The ¹H NMR Spectra of the ligand (1) and diamagnetic cobalt(III) complexes (4) have been recorded in CDCl₃. The ¹H NMR Spectra of green carboxylate cobalt(III) complexes (5) are recorded in DMSO-d₆. The phenolic -OH in (1) resonates in 12.88-15.12ppm and the signal shifting is correlated with the electronic and inductive effect of the *para* substituted group¹⁸. The disappearance of -OH signal in complexes (4) suggest the co-ordination of phenolic group. All aromatic proton signals of (1), (4) and (5) have been completely assigned on the basis of spin-spin structure and changes therein on substitution. For methyl and *t*-butyl substitution(1a, 1d; 2a, 2d; 4a, 4d and 5a, 5d), the signals suffer a shift to a higher field due to electron releasing *via* inductive effect¹⁹. The reverse effect is seen in 1b, 1c; 2b, 2c; 4b, 4c and 5b, 5c. The electron withdrawing character of -NO₂ shifts the signals to considerably downfield region¹⁹. The -OCH₃ group in complexes (4) is downfield shifted by 0.2ppm suggesting the co-ordination to the metal centre fulfilling the octahedral geometry. Representative figure of the spectra are given in **Fig. VI.8** and data are collected in **Table VI.5.1** for the complexes (4) and in **Table VI.5.2** for the complexes (5). The signal

Table VI.5.1
¹H NMR data of ligands (1) and complexes (4) in CDCl₃

Compound	δ(ppm), (J, Hz)									
	3-H ^a	4-H ^b	5-H ^b	6-H ^a	8-H ^c	10-H ^b	11-H ^b	Me	OMe	OH
(1a)	7.04 (8.0)	7.44 (8.0)	7.44 (8.0)	7.84 (8.0)	7.76	7.14 (8.4)	6.96 (8.4)	2.32	3.86	13.38
(1b)	7.05 (8.0)	7.44 (8.0)	7.44 (8.0)	7.86 (8.0)	7.89	7.19 (8.0)	6.99 (8.0)	-	3.88	13.84
(1c)	7.08 (8.0)	7.47 (8.0)	7.47 (8.0)	7.90 (8.0)	8.05	7.36 (8.0)	7.04 (8.0)	-	3.94	15.12
(1d)	7.04 (8.0)	7.44 (8.0)	7.44 (8.0)	7.82 (8.0)	7.64	7.06 (8.0)	6.84 (8.0)	1.12 ^d	3.74	12.88
(4a)	7.20 (8.0)	7.51 (8.0)	7.51 (8.0)	8.04 (8.0)	7.84	7.24 (8.0)	7.04 (8.0)	2.42	4.06	-
(4b)	7.22 (8.0)	7.50 (8.0)	7.50 (8.0)	8.08 (8.0)	7.96	7.32 (8.0)	7.11 (8.0)	-	4.08	-
(4c)	7.25 (8.0)	7.54 (8.0)	7.54 (8.0)	8.11 (8.0)	8.18	7.44 (8.0)	7.18 (8.0)	-	4.10	-
(4d)	7.20 (8.0)	7.52 (8.0)	7.52 (8.0)	8.02 (8.0)	7.78	7.18 (8.0)	7.02 (8.0)	1.20 ^d	4.08	-

^aDoublet, ^bTriplet, ^cSinglet, ^dt-Butyl group.

Table VI.5.2

¹H NMR Spectral Data^{a,b}

Complex	δ (ppm), J(Hz)						
	3-H ^c	4-H ^d	5-H ^d	8-H ^e	10-H ^e	6-H ^c	11-H ^c
<u>5a</u> ^f	8.05 (8.4)	7.45 (9.0)	7.18 (9.0)	7.35	5.85 (8.0)	7.05 (8.4)	6.65 (8.0)
<u>5b</u>	8.08 (9.0)	7.48 (8.0)	7.28 (8.0)	7.65	6.81 (8.0)	7.15 (9.0)	6.00 (8.0)
<u>5c</u>	8.11 (8.4)	7.50 (8.0)	7.36 (8.0)	7.84	7.08 (8.0)	7.21 (8.4)	6.74 (8.0)
<u>5d</u> ^g	8.04 (9.0)	7.43 (8.0)	7.16 (8.0)	7.25	5.92 (8.0)	7.05 (9.0)	6.77 (8.0)

^a Atom numbering scheme as shown in structure (Table VI.1).

^b Solvent : DMSO-d₆

^c Doublet

^d Triplet

^e Singlet

^f 9-Me resonates at 2.18 ppm.

^g t-Bu resonates at 1.27 ppm.

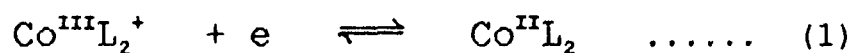
movement in the ^1H NMR spectra of complexes (5) is in accord with the inductive and resonance effect of the substituted group R. A signal in aromatic region is certainly due to 8-H and suffers a shift to higher field in (5a) and (5d). Similarly 10-H and 11-H are shifted to up field due to inductive effect of R. 3-H and 6-H protons are influenced a little by the substituent R. The signal movements are shown schematically in Fig VI.C and VI.D. The aromatic region in (5e) is complicated by signals from naphthyl group and hence is not assigned.

D. Redox Activity:

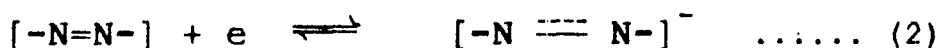
The cobaltous complexes (3) are electroactive at the platinum working electrode and display one redox process on the positive side of the SCE and more than one such process on the negative side. The cyclic voltammetric data are collected in Table VI.6. They display a reversible cobalt(III)/cobalt(II) couple around $\sim 0.40\text{v}$ at scan rate 50 mv sec^{-1} in acetonitrile (Fig. VI.E). In stirred solution electrolysis freely occurred when the potential is kept fixed on the positive side of the anodic peak at 0.6v gives Coulomb count corresponding to the transfer of $1\text{e}/\text{cobalt}$ atom. The formal electrode potential, E_{H298}^0 (average of anodic and cathodic peak potentials) movement is in accord with the

electronic effect of the substituent in the ligand frame²⁰. The electron withdrawing substituent (3b, 3c, 3e) shifts Co(III)/Co(II) couple to more anodic direction while the reverse effect is seen in case of (3a) and (3d) complexes. The plot of Hammett σ of the substituents²¹ against E_{M298}^0 is linear (viz. **Fig VI.F**).

The cyclic voltammetric response is thus due to reversible couple (eq. 1)



One distinct quasireversible couple was displayed by the complexes (3) in the range -0.7 to -1.1v (**Fig.VI.E**) and few of them exhibit peak below -1.2v while the range of measurements is limited to ± 1.5 v. The reduced species does not appear to be stable and on scan reversal some times multiple anodic responses of unclear origin are observed. The quasireversible reduction is due to electron transfer at the azo group (eq. 2) and the second reduction peak is beyond our detection limit. Cobalt (III) azophenolato carboxylates (5) exhibit ill-defined responses in the negative scan and has not been followed critically. The ligand reduction potential



$E_{L\ 298}^{\circ}$ is also plotted against Hammett σ and linearity confirms the potential movement (Fig VI.F). A decrease of the σ -donor capacity of co-ordinated ligands increases both the cobalt(III) and cobalt(II), and the first bound ligand reduction potentials. The two potentials correlate linearity (Fig VI.F). A decrease in σ -donor capacity leads to an increase in the effective charge on metal centre, and this in turn stabilises the metal $d\pi$ and ligand π^* orbitals²⁰.

Table VI.6

Cyclic voltammetric data

Compound	$E_{M\ 298}^{\circ}$ (V)	(ΔE_p , mv)	$E_{L\ 298}^{\circ}$ (V)	(ΔE_p , mv)
(3a)	0.36	(80)	-1.02	(140)
(3b)	0.40	(90)	-0.94	(160)
(3c)	0.46	(100)	-0.88	(140)
(3d)	0.32	(80)	-1.04	(120)

I. Thermal Analysis :

Thermal analysis one carried out on y for the complexes (5) under nitrogen and they lose weight at 110°-130°C corresponding to one

mole of lattice water per mole of the complex which has been confirmed by IR and also by molecular weight.

r. Epilogue :

All the spectral data suggest that the Co(II) complexes (3) are tetragonally distorted octahedral while the complexes (4) and (5) are octahedral. The complexes (4) and (5) are ionic as 1:1 electrolyte and the cobaltous complexes (3) are electroactive. From ¹H NMR it is also confirmed that the bis complexes (5) of the tridentate chelating ligands of the type (ONO) are stable through the meridional binding.

3. Experimental :

a. Materials :

β -Naphthol, ammonium chloride, *o*-anisidine *p*-cresol and anthranilic acid were obtained from S.D.'s Lab Chem Industry. 4-chloro-phenol, 4-nitrophenol and 4-tertbutylphenol were E. Merck reagents. Cobalt(II) acetate tetrahydrate, cobaltous chloride hexahydrate and Lithium chloride were BDH reagents. Hexamine cobalt(III) chloride prepared by air oxidation of ammoniacal cobaltous chloride hexahydrate solution in presence

of ammonium chloride are recrystallised before use. Electrochemically pure acetonitrile and tetraethylammonium perchlorate (TEAP) were prepared by reported procedure.

B. Physical Measurements :

The elemental analyses, IR, electronic spectroscopy, thermal study, conductance measurement, magnetic moment, molecular weight measurement, ^1H NMR and redox activity were carried out as in Chapter I cobalt was estimated by complexometric (EDTA) titration^{22(a)} and chloride gravimetrically^{22(b)}.

c. Preparation :

1. Ligands :

Two types of ligands were synthesised : *o*-methoxyazophenols (HL)(1) and *o*-arylazophenolcarboxylic acids ($\text{H}_2\text{L}'$)(2). They were synthesised by general procedure²³. Representative cases are described below.

1.a. 2-(methoxy)-2'-hydroxy-5'-methylazobenzene(1a) :

Aqueous solution of sodium nitrite (1g; 14.5 mmol) was added to ice cold solution (0° - 5°C) of *o*-anisidine (0.5g; 4.06 mmol) in hydrochloric acid solution (1:1, V/V). The diazonium solutions so

obtained was added in dropwise with continuous stirring to cold solution of *p*-cresol (0.5g;4.62 mmol) in 2M sodium hydroxide solution. The precipitate, obtained in acidified solution was filtered, washed with water and dried over P_4O_{10} . It was recrystallised from ethanol-water(1:1). The yield was 75%.

The other compounds of type (1) were synthesized similarly by using appropriate precursor. Yields varried in the range 70-80%.

1.b. The ligands of type (2) were also prepared similarly, A representative melthod for (2a) is given below.

2-((2'-hydroxy-5'-methyl)-phenylazo) phenylcarboxylic acid (2a)

Aqueous solution of sodium nitrite (1g;14.5 mmol) was added to ice cold solution (0°- 5°C) of anthranilic acid (0.6g; 4.38 mmol) in hydrochloric acid solution (1:1, V/V). Thus produced diazonium solution was added in dropwise with continuous stirring to cold solution of *p*-cresol (0.5g;4.62 mmol) in 2M sodium hydroxide solution. The precipitate, obtained in acidified solution was filtered, washed with water-ethanol mixture and finally dried. Recrystallised product was obtained from ethanol-water(1:1); yield 70%.

2. Complexes :

2.a. Preparation of Cobalt(II) Complexes(3) :

All the complexes were synthesised by common procedure. A representative method for (3a) is described below.

To a methanolic solution (10ml) of the ligand (1a) (0.5g; 2.07 mmol), the solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.25g; 1 mmol) in MeOH (10ml) was added in dropwise in a 3-necked (100ml) round bottom flask under dinitrogen atmosphere and reflux for 2 hr. The deposited brown precipitate was filtered after cooling and washed with cold MeOH, and dried in vacuo. It was then recrystallised from CHCl_3 -MeOH (1:1, V/V) mixture; yield 55%.

The yield of other complexes (3b - 3e) were varied in the range 50-60%.

2.b. Preparation of Cobalt(III) Complexes :

Complexes of The type (4)

All these complexes were synthesised following three different procedures of which two methods of Barrows and Bailar⁵.

1) Cobalt(III) Hydroxide Method :

Hydrous cobalt(III) hydroxide was prepared by adding an excess of Na_2O_2 cautiously to an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

(0.4g; 1.03 mmol + 30% excess), centrifuging and washing the gelatinous precipitate until the washing (H_2O) was neutral. This product was slurried under dinitrogen with methanolic solution of (1a) (0.5g; 2.07 mmol) and refluxed over steambath for 2 hr. Undissolved cobalt(III) hydroxide was filtered from the pink red solution and the product was obtained by adding excess LiCl solution in MeOH and recrystallised from $CHCl_3$ -MeOH (1:1, V/V) mixture. The purification was carried out by column chromatography.

11) Hexaammine Cobalt(III) Chloride Method :

Aqueous solution (10ml) of hexaammine cobalt(III) chloride (0.28g; 1.05 mmol) was added into the methanolic solution (15ml) of (1a) (0.5g; 2.07 mmol) followed by sodium hydroxide (0.085g; 2.13 mmol). The mixture was warmed on steam bath, ammonia was evolved and colour of the mixture gradually changed from brown to brown-red to pink-red. The mixture was filtered and the volume was reduced to half by evaporation. The concentrated solution was extracted with chloroform and recrystalline products were obtained from methanol-chloroform mixture as above . Yield 70-75%.

iii) Oxidation Method: (3a changed into 4a)

To a solution of (3a) (0.5g; 0.92 mmol) in chloroform-methanol mixture Cl_2 -saturated methanol solution was added in dropwise with continuous stirring till the solution colour changed from brown to red-pink. The large excess of Cl_2 -solution should be avoided. The mixture was stirred for 1 hr. and evaporated in air. The solid mass was washed with water and recrystallised from chloroform-methanol mixture (1:1, V/V) as above. Yield 60%.

2.c. Complexes of Type (5)

The synthesis was carried out by two different procedures⁵.

1) Cobalt(III) Hydroxide Method:

Hydrous cobalt(III) hydroxide was prepared by adding an excess amount of sodium peroxide to an aqueous solution of $\text{Co}(\text{NO}_2)_2 \cdot 6\text{H}_2\text{O}$ (0.4g; 1.03 mmol + 33% excess). The product, centrifuged and washed, was stirred under dinitrogen with methanolic solution of (2a) (0.52g; 2.03 mmol) and sodium hydroxide (0.09g; 2.25 mmol), and refluxed over steam bath for 2 hr. Undissolved cobalt(III) hydroxide was filtered from the deep green solution and the solution was evaporated in air slowly. The precipitated dark coloured compound was filtered and washed with 50% (V/V) water-methanol (10ml) and dried over P_4O_{10} . The residue

was dissolved in CH_2Cl_2 (5ml) and the solution was chromatographed on silica gel column (45 X 1 cm) prepared in benzene. The desired green compound was eluted by $\text{CH}_3\text{CN}-\text{C}_6\text{H}_6$ (1:3 V/V). Evaporation of the solvent in air afforded the pure crystalline product in 70% yield.

ii) Hexaammine Cobalt(III) Chloride Method :

Aqueous solution (10ml) of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ (0.27g; 1.01 mmol) was added into the methanolic solution (10ml) of (2a) (0.25g; 2.03 mmol) and sodium hydroxide (0.09g; 2.03 mmol). The mixture was warmed on steam bath for 1 hr. As reaction proceeded, ammonia was evolved and the mixture became dark green. The solution was filtered and evaporated in air. The residue so left was purified by column chromatography, as above described.

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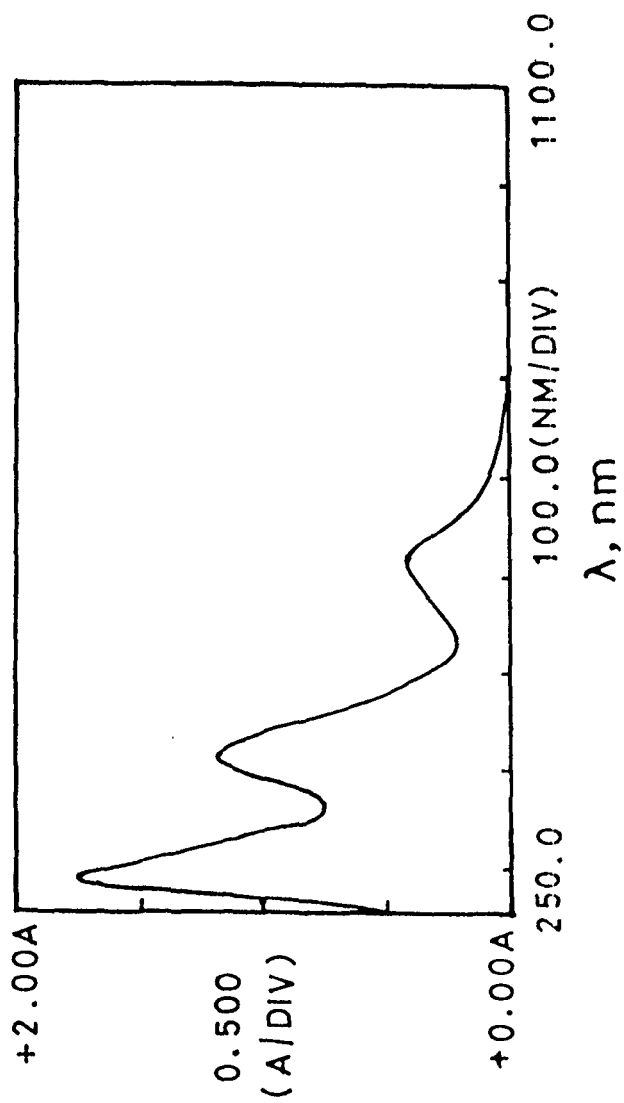


Fig.VI.A.UV-Vis spectra of 5d in MeOH.
Conc. 7.4×10^{-5} (M).

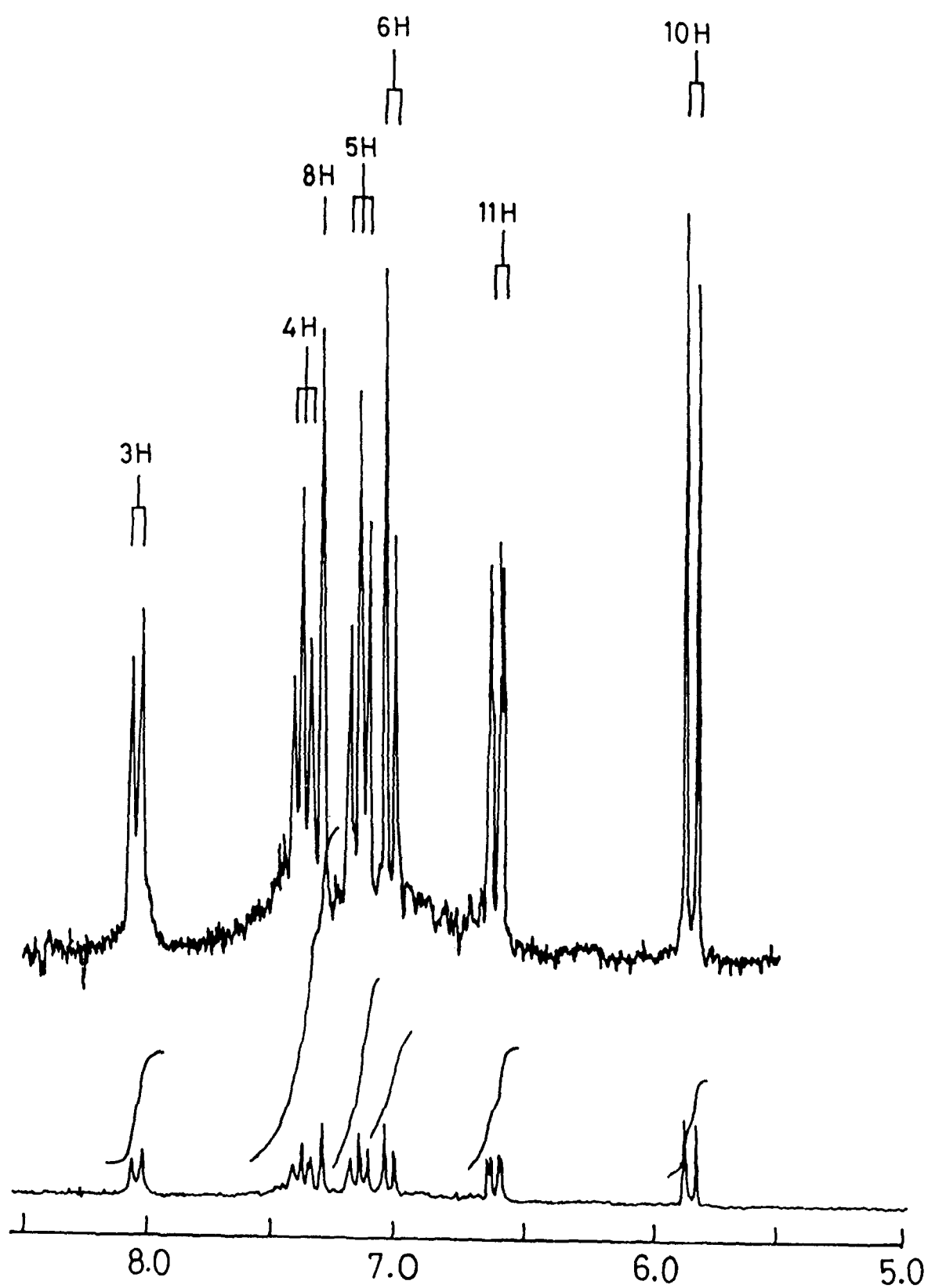


Fig.VI.B. ^1H NMR spectra of **5a** at 200 MHz in DMSO-d_6 .

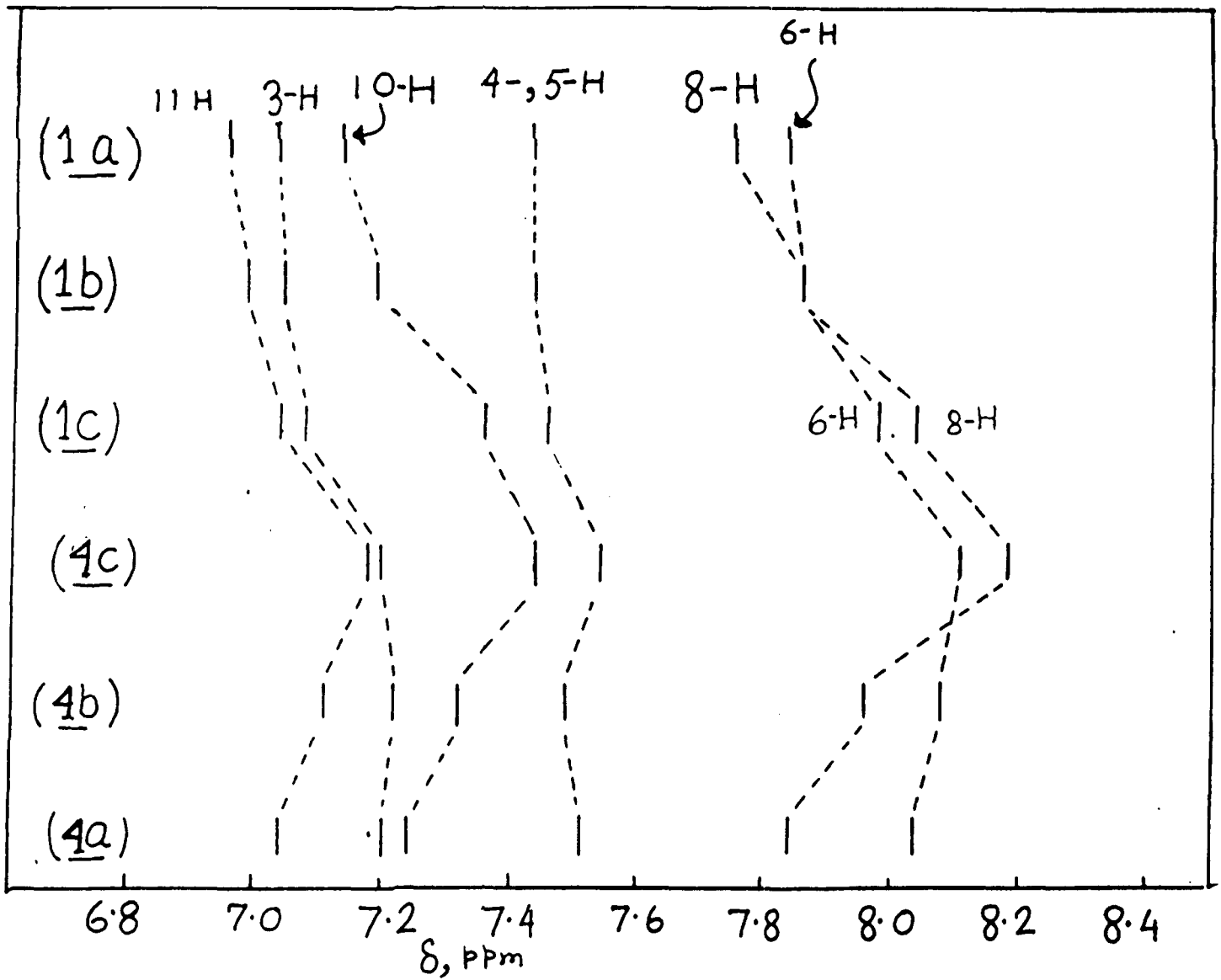


Fig.VI.C. Schematic ^1H NMR spectra of 1 and 4.

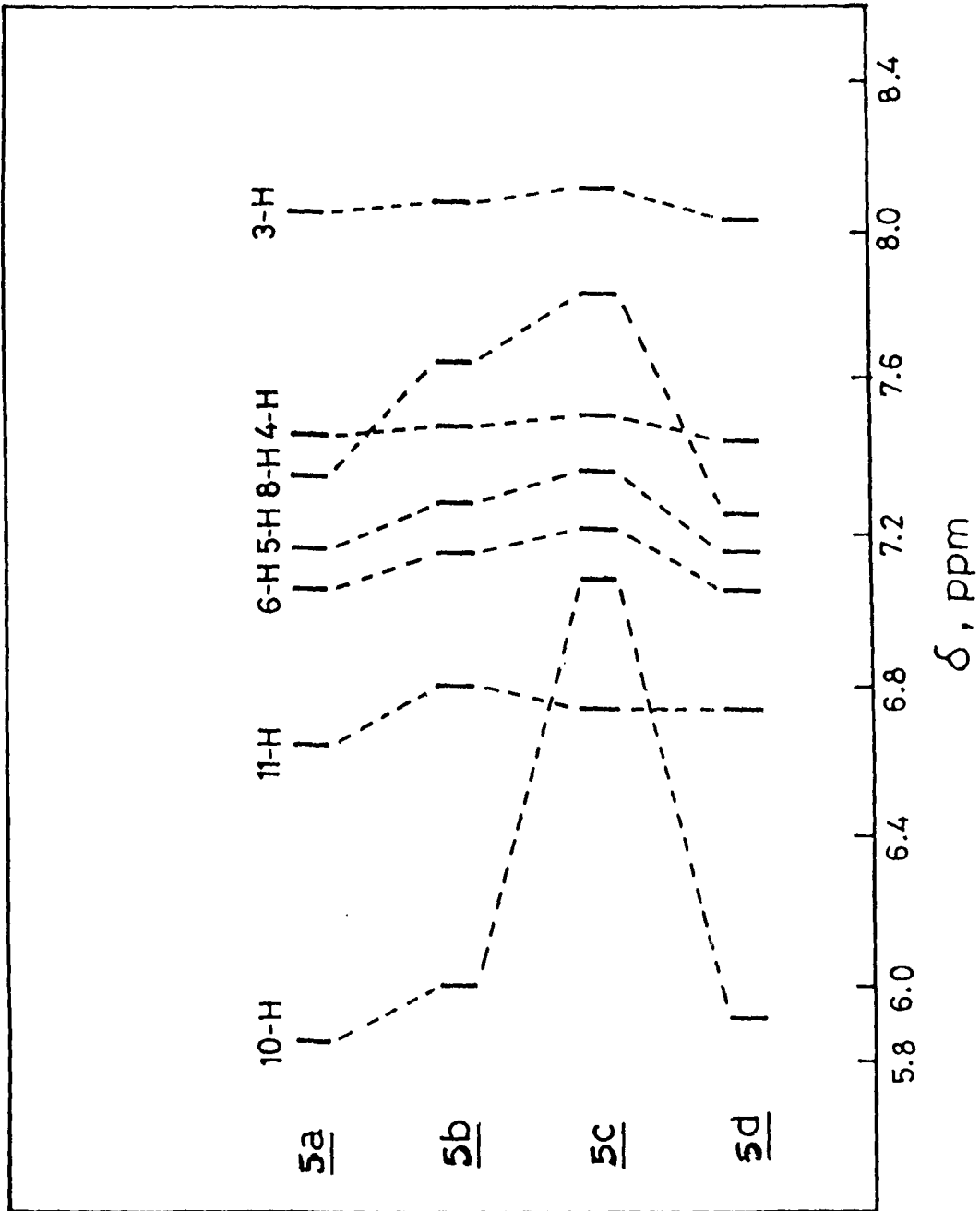
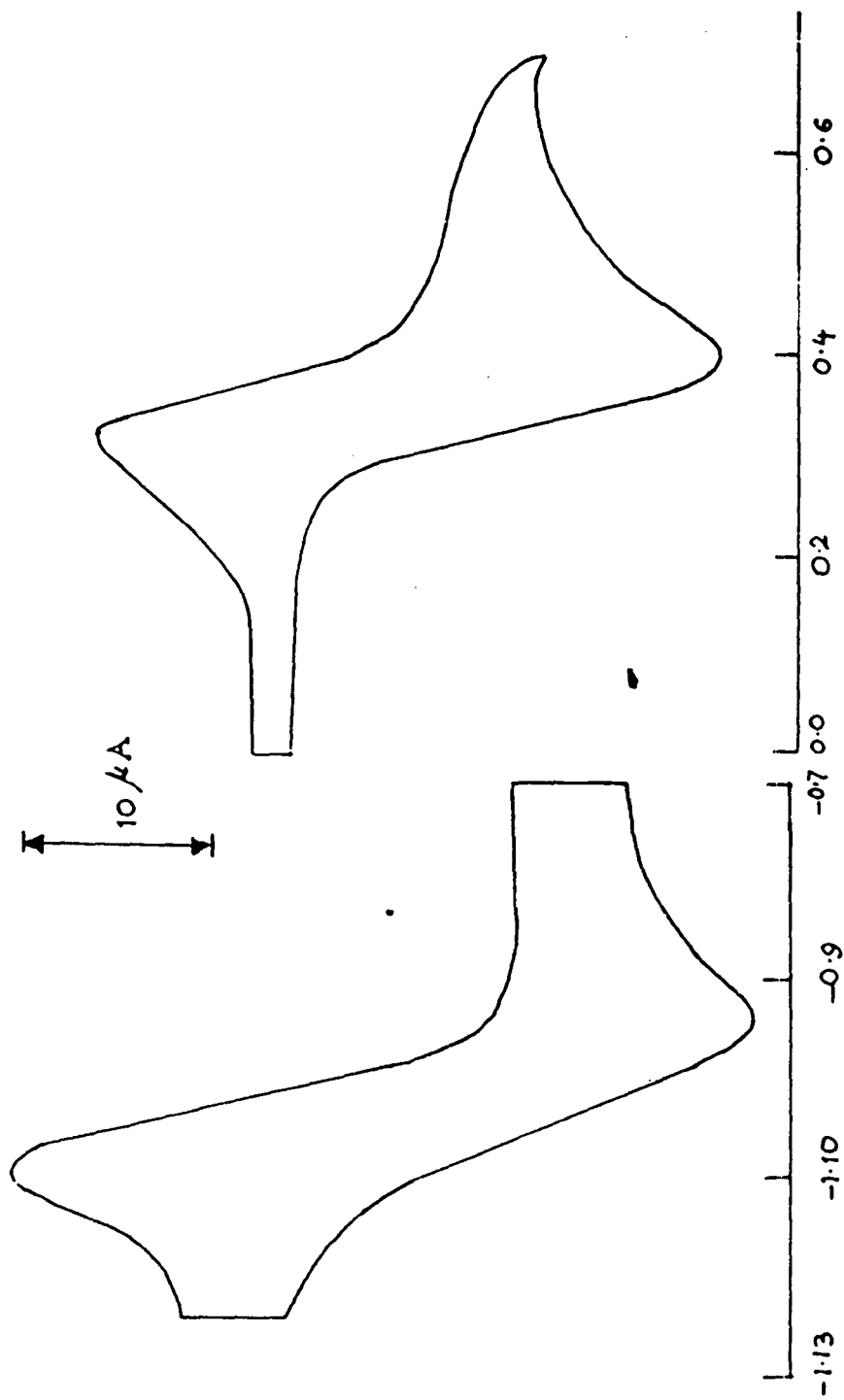


Fig.VI.D.Schematic ^1H NMR spectra of 5a - 5d.



$E(V)$ Vs SCE

Fig.VI.E. Cyclic voltammograms of 3a in acetonitrile [3a] = 2.089×10^{-3} (M), supporting electrolyte tetraethylammonium perchlorate (TEAP); reference electrode: saturated calomel electrode (SCE); working electrode: Pt-disk.

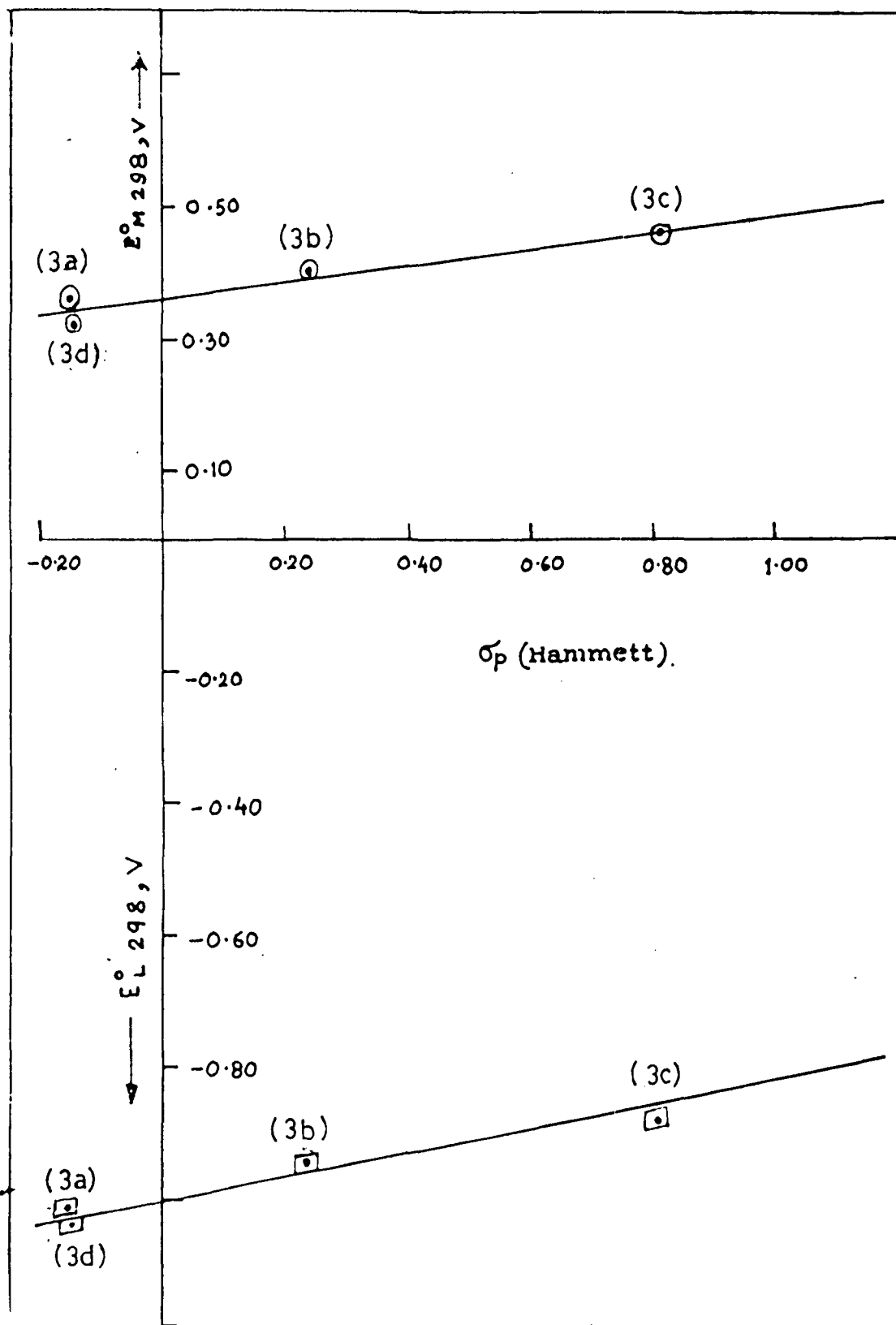


Fig.VI.F. Plot of Hammett σ vs. E_{M298}^o or E_{L298}^o (V).

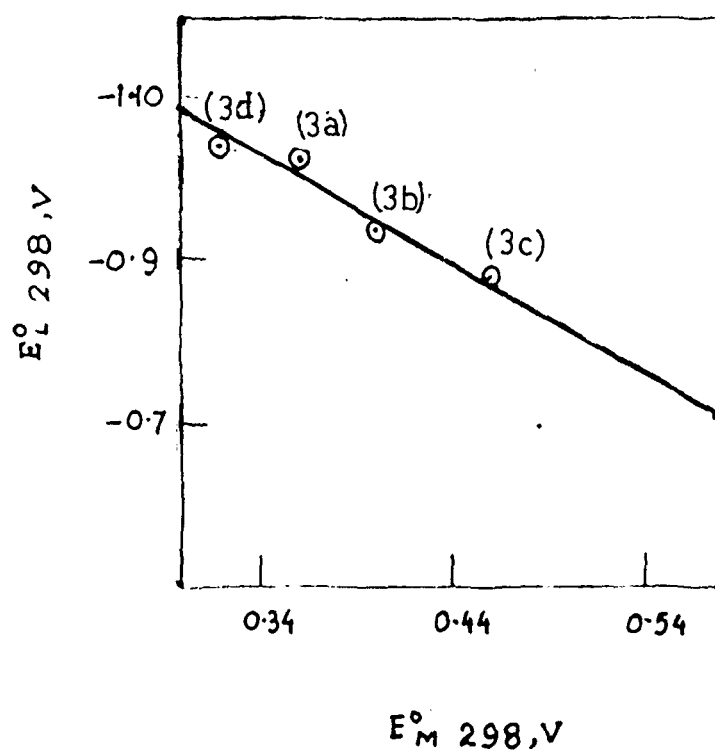


Fig.VI.G. Plot of E_M^0 (298, V) vs E_L^0 (298, V) of 3.