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Research Article

DEVELOPMENT OF COBALT SCHIFF BASE PRECURSORS FOR NANOCRYSTALLINECOBALT OXIDE THIN FILM BY THERMAL CVD METHOD

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ABSTRACT
A novel precursor sources fornanocrystalline metal oxide thin filmswere synthesized by Thermal CVD using the following Schiff base complexes, bis(salicylaldehydato) cobalt(II) $[Co(sal)_2.(H_2O)_2]$**(1)**, bis(salicylaldiminoato) cobalt(II) $[Co(salim)_2.(H_2O)_2]$**(2),** tris(N-methyl-salicylaldimine)cobalt(III) $[Co(salmen)_3]$**(3)**, tris(N-ethyl-salicylaldimine) cobalt(III) $[Co(saletn)_3]$**(4)**, tris(N-n-propyl-salicylaldimine) cobalt(III) $[Co(salprn)_3]$**(5)**,tris(N-n-butyl-salicylaldimine) cobalt(III) $[Co(salbut)_3]$**(6)**, and tris(N-n-pentyl-salicylaldimine)cobalt(III) $[Co(salptn)_3]$**(7).** The as prepared Schiff base complexes prepared by template methodwere characterized by FTIR, UV-Vis and mass, NMR spectroscopy followed by CHNand TG/DTA analyses. Further, a single crystal analysis was done for the compound (7). Among these complexes,**(3), (4), (5), (6)** and **(7)** were found to be volatile and used in Thermal CVD for the development of nanocrystalline Cobalt Oxide thin films. The presence of Cobalt Oxide in these films was confirmed by XRD and SEM/EDAX analyses.

Keywords: Volatile Cobalt Schiff base complexes; Crystal and molecular structure.

1. INTRODUCTION

Transition metal complexes containing oxygen and nitrogen as donor Schiff base ligands have been investigated because oftheir structural, spectral and chemical properties depend upon the nature of the ligand[1], steric and electronic properties which can be modified bythe appropriate amine precursor. They are good chelating agents and find extensive applications[2-7]. Schiff base complexes containing O and N donor atoms co-ordinate with metals through phenolic oxygen and imine nitrogen linked to aldehyde[8]. The synthesis and characterization of transition metal complexes including ordinary complexes, chelates and mixed ligand complexes are beinginvestigated extensively for their catalytic properties, bioinorganic relevance as well as wide range of photochemical properties in many reactions[9-15]. Preparation of good and reproducible thin films by chemical vapour deposition mainly depends on the volatility of the co-ordination complexes. Therefore, development of stable, non-toxic and volatile solids for chemical vapor deposition of cobalt has attracted intensive research[16-22]. Cobalt Oxide occurs in two forms as CoO and Co_3O_4, both having cubic lattice structure and non-stoichiometric. Co_3O_4 has spinels of Co^{2+} and Co^{3+} ions simultaneously present at different lattice sites in the crystal[23] and the third oxide phase of cobalt is Co_2O_3. Cobalt Oxides are of great interest due to their scientific and technological importance in understanding defect chemistry, electrochemicaltransport properties of semiconducting oxides, strong electron-electron correlation in solids, high catalytic activators in oxidation reactions at low cost, antiferromagnetism, electrochromism[24-28]. Cobalt Oxide films can be used as magnetic detectors, membranes for oxidation of hydrocarbons, counter electrodes, humidity or oxygen or optical sensors, solar-sensitive absorbers and protective layers[29-32].

Nagaraja and co-workers[16] have developed volatile Schiff base complexes of Ni^{2+}, Ti^{4+}, and Cu^{2+} complexes. They have also demonstrated that the thin film coatings by Metallo organic Chemical Vapor Deposition (MOCVD) method. In the present study we have prepared Schiff base complexes of Co(III) as to test and develop volatile precursors for Thermal CVD. During the evolution of these volatile cobalt precursors (CoN_3O_3) the co-ordination of N in –C=N- was found to play a vital role in the volatility of the cobalt complexes instead of O in –C=O[33].

2. EXPERIMENTAL

2.1. Materials

Cobaltacetatetetrahydrate [Merck, 97%], liquor ammonia [Fischer Scientific, about 25% of NH_3], methyl amine [Merck, ≥40%], ethyl amine [LobaChemie, 70%], n-propylamine[Aldrich, 98%], n-butylamine [LobaChemie, 98%], n-pentylamine [Himedia, 96%] were used as such in the synthesis of cobalt complexes. Methanol, acetone and ethanol were used as solvents after distillation.

2.2. Synthesis of complexes (1)-(7)

To the aqueous solution of cobalt (II) acetatetetrahydrate (7.11g, 0.028mol)anethanolicsolution of salicylaldehyde(6.2ml, 0.050mol) was added and a yellow colouredprecipitate was obtained as the product **(1)**. To the aqueous solution of cobalt (II) acetate tetrahydrate (7.11g) an ethanolic solution of salicylaldehyde (6.2ml) and 6 moles of excess ammonia were added under constant stirring and a greenish yellow product **(2)** was obtained. To the aqueous solution of cobalt (II) acetate (7.11g) an ethanolic solution of salicylaldehyde(6.2ml) and 6 moles of respective amine [methyl, ethyl, n-propyl, n-butyl, n-pentyl] **(3) – (7)** was added(Figure 1) with constant stirring to get a green color solution which wasrefluxed for 3-4 hours at 323K and left for a week in an ambient temperature. Olive green crystalline precipitate was obtained giving **(3)-(7)** compounds which were recrystallisedusing ethanol and dried in a vacuum desiccator containing fused calcium chloride. The analytical, compositional data of complexes **(1) – (7)** are represented in Table 1.

2.3. Compositional Analysis

The empirical formulae of the cobalt complexes were confirmed by C, H, N (VarioEL III CHNS). The FT-IR spectra for the complexes were recorded in KBr medium to infer the various stretching frequencies using Perkin Elmer FTIR spectrometer in the range of 4000-400 cm^{-1}.The electronic absorption spectra of the cobalt complexes were recorded on Elico using ethanol as a solvent.The mass spectra of the Co(III) complex homologues were recorded by EI-MS model YOKUDELNA_ES+_2000 at an accelerating voltage of 32V at ambient temperature.^1H and ^{13}C NMR was recorded in BRUKER FTNMR 50HZ. The single crystal XRD data for compound **(7)** were collected on a Bruker Apex – II CCD diffractor with omega and phi scan mode using Mo-Kα (λ=0.71073 Å) at T=296.3 K. Non-isothermal TG runs for the cobalt complexes were recorded at a linear heating rate of 0.17K/s using a Perkin Elmer, Pyris Diamond TG/DTA thermoanalyser. High purity nitrogen (purity >99.99%; 6 dm^3/h), dried by passing through molecular sieves (Linde 4A), was used as a carrier gas.SEM for the Cobalt Oxide thin films was analysed by FEI Quanta FEG 200 instrument.The X-ray diffraction pattern of the Cobalt Oxide thin films was carried out by using Philip X'pert with Cu Kα radiation.

2.4. Preparation of Thin film

The thin film of cobalt oxide was prepared by using the thermal method of metallo-organic chemical vapour deposition where alumina served as a deposition chamber. Prior to each deposition, the substrates (1.0 mm thick silicon crystal wafer cut into 2.0 x 2.0 cm plates) were sonicated for 30 min on an ultrasound sonicator and the reaction chamber was cleaned by acetone. This process was done to ensure that the deposition surfaces were free from contamination and defects.

For the deposition of cobalt oxide thin film, the cleaned surface substrates and fine powder of the precursor were kept in a quartz boat which was kept in a working chamber. This chamber was maintained at 500°C in a digitally controlled furnace. On getting to the hot zone, the precursor kept in the quartz boat sublimed before it thermally decomposed resulting in the coating on the substrates. The whole process was left for 2 hours at the deposition temperature of 500°C. After cooling, the coated films were characterized by SEM/EDAX and XRD to analyze the phase transition of cobalt oxide.

3. RESULTS AND DISCUSSION

3.1. Characterization of the complexes

3.1.1. Fourier Transform Infra Red Spectroscopy

The infrared spectral studies (Figure 2) show various stretching frequencies and prominent functional groups present in the complexes**(1)-(7)**. The bands at 1597-1621 cm^{-1} correspond to υ(C=N) indicating the involvement of both the nitrogen atoms of the amine groups in the coordination.The bands at 1321-1324 cm^{-1}occurring for υ(phenolic C-O) after complexation indicate the shift due to coordination of phenolic carbon – oxygenin the ligand to the metal atom. The band observed in the region 463-469 cm^{-1} was assigned (Table 2) to υ(Co-N). The bands in the range 524-571 cm^{-1} are due to Co-O stretching.

3.1.2. UltraViolet-VisibleSpectroscopy:

The electronicspectraof the synthesized mixed ligand cobalt (III) complexes (3) - (7) are consistent with the octahedral structures assigned showing the absorption bands in the range of622 – 624 nm, 427 – 434 nm, 332 – 337 nm which are attributed to $^1A_{1g} \rightarrow {}^1T_{2g}$, $^1A_{1g}\rightarrow{}^1T_{1g}$ and LMCT transitions respectively. These transitions are comparable to six coordinated cobalt(III) complexes.When co-ordinated with the metal the wavelength was shifted to higher wavelengths, suggesting the co-ordination of the azomethine nitrogen[34–36]. The diamagnetic nature of the complexes as indicated by Vibrating Sampling Magnetometerstudies, also suggests the formation of an inner octahedral stereochemistry in cobalt (III) complexes[37].

3.1.3. ESI-Mass Spectroscopy:

The ESI spectra of the metal complexes were used to confirm their stoichiometric composition. The mass spectra of Co(III) complexes showed a molecular ion peak $[M^+]$ at m/z for **(3)** = 574, **(4)** = 588, **(5)** = 602, **(6)** = 616 and **(7)** = 630 which are equivalent to their molecular masses. With the loss of one ligand moiety the m/z values for these compounds were found to be **(3)** = 327, **(4)** = 355, **(5)** = 383, **(6)** = 411 and **(7)** = 439.The molecular ion peak fragmentations with the loss of another ligand moiety gave peaks at m/z for **(3)** = 268, **(4)** = 296, **(5)** = 325, **(6)** = 352, and **(7)** = 380. These peaks supported the structure of the complexes and confirmed the stoichiometry of the metal chelates as ML_3 type.

3.1.4. ^{1}H and ^{13}C Spectroscopy:

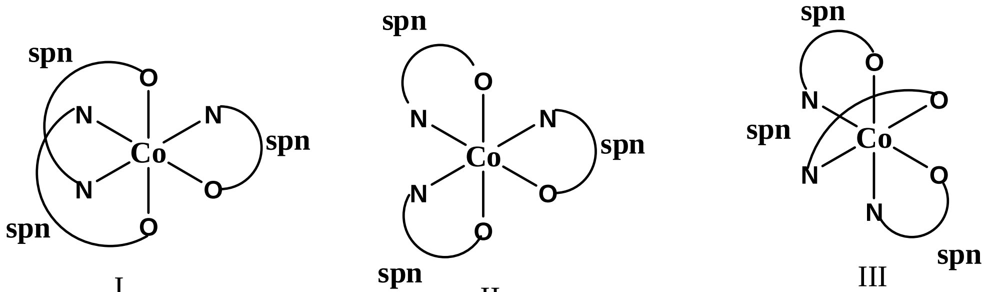
The chemical shifts of the different types of protons in the 1H and 13C NMR spectra of (3) to (7) complexes are listed in the table.

The 1H NMR spectra showed the presence of singlet at 7.85 - 8 ppm which is attributed to azomethine proton (CH=N). These signals were observed at this range which was shifted downfield upon co-ordination to the metal center. The multiplet signals at 7.26 ppm are assigned to aromatic protons. The multiplets observed at 3 – 7.7 ppm are due to the methyl and ethyl groups associated with the azomethine groups[38].

In 13C NMR spectrum, the azomethine carbon is shown at 162-168 ppm. Aromatic carbons at 113-134 ppm, methyl and ethyl carbons are observed at 11 – 59 ppm[39].

3.1.5. Structural description of Compound (7)

The ORTEP diagram (Figure3) of the complex **(7)** and the summary of the crystal data are given in Table 4. The selected bond lengths and angles are listed in Table 5. The single crystal data of the complex **(7)** reveal that it crystallizes in the monoclinic space group $P2_1/C$, with two crystallographically-independent molecules in the unit cell**(CCDC No - 998804)**; reference will be made only to one molecule as there are no significant differences between these two molecules[40]. The unique metal center (Co) is surrounded by three Schiff base ligands forming a distorted octahedron. HL acts as a bidentate ligand with one phenolato – O and one imine – N as the donor sites. The basal plane of the cobalt (III) is formed by the three imine nitrogen and three phenolato oxygen atoms which are in the axialpositions from the three Schiff base ligands giving CoN_3O_3. The bond lengths of C(41) – N(4)[1.288Å], C(54) – N(5)[1.284 Å] andC(64) – N(7)[1.275 Å] confirm the presence of double bonds and are comparable to those in other Schiff base [9] complexes. The co-ordination of nitrogen to the cobalt metal caused the reduction of bond lengths of Co(4) – O(3)[1.875 Å]of the pentyl-substituted complex from 1.921Å of the parent compound $Co(sal)_2$[41]. There is not much reduction in the bond lengths of Co(1) – O(2) [1.9 Å] and Co(4) – N(7) [1.9 Å]. The co-ordination of nitrogen which is replacing the oxygen attached to the carbon of the complex increases the covalent nature and volatility of the volatile homologues. Though the bond angle Co(4) – N(7) – C(61) is 119.7°, the rotational motion of the alkyl groups shield the cobalt atom (I) from the approach of the molecule[42]. The molecular structures of both the isomers i.e., meridional and facial are represented below [43].



I II

Meridional Isomers

III

Facial Isomers

spn = salpentylamine

3.1.6. Non-Isothermal Thermogravimetry (TG) study

A wide spectrum of precursors ranging from organo-metallic, metallo-organic and nitrogen rich single source precursors were synthesized and screened using non-isothermal TG-DTA for low melting with relative volatilities of various Co(II) and Co(III) Schiff bases complexes that could function as precursor for CVD of Cobalt Oxide besides identifying mass loss steps and their inception temperatures. It is required to know the initial Co content of the complex and that of the final residue for an assessment of overall loss of Co bearing vapour species.

The thermogram (Figure4) for (1) indicates the loss of two water molecules after the first step at 112 °C,69%residue after the second step of weight lossat about 342°C and the subsequent decomposition of the complex gives about 42% at 485°C, making it unsuitable for CVD applications. This shows that Co was retained in the residue and not transferred into the vapour phase as evidenced by the black end-residue. As observed earlier, the polarity of the metal-oxygen bond responsible for the ionic nature of the complex could be reduced by substituting nitrogen for oxygen in the carbonyl group (-C=O). Thermogram (2) shows the residue of 28% at 582°C after a single step weight loss. In this the interesting inferenceis the enhanced thermal stability and volatility as well as the expulsion of two water molecules caused by the coordination of azomethine nitrogen (-CH=NH) with Co instead of carbonyl oxygen. At this juncture it was decided to substitute H of =NH as shown in Figure1 by alkyl chains thereby tuning the volatilizationbehaviour depending upon the length of the straight chain alkyl groups. In thermograms of **(3)-(7)** the five homologues exhibited a two step weight loss in which first step commences at200°-240°C with the loss of one ligand molecule and the next step from 240°-550°Cwith no fragmentation or decomposition in which it gets vaporized and above this temperature metal oxide is formed. The weight loss percentages of the complexes **(3) – (7)** are represented in the (Table 6).

3.2. Characterization of Thin Films

The complexes **(1)**and **(2)** were not used forThermal CVDas they do not volatilize and are not soluble completely. So they cannot be good precursors for Thermal CVD.The TG/DTA studies revealed the complete volatility of these Schiff base complexes **(3) – (7)**. The coating of Cobalt Oxide was carried out by Thermal CVD using the presently established volatile Co(III) Schiff base complexes (3 – 7) as precursors.

The complex was heated and when the vapourscame in contact with the hot silica plate (2×2 cm) at an optimum temperature of 550°C in a temperature controlled furnace, the Cobalt Oxide thin films were obtained. The films were black in colour with good adherence. The deposition took 2 h and 0.5 g of precursor complex was used.

3.2.1. Scanning Electron Microscope and EDAX of Cobalt Oxide coated thin films

The surface morphologyof the thin filmswas determined by the rate of precursor transport, decomposition reaction, surface diffusion and lattice incorporation during the deposition process. The surface morphology (Figure5) of the deposited films reveals a progressive grain growth with increasing temperature. The SEM images of Cobalt Oxide thin films exhibit uniform dense microstructure grown at 500 °C over silica substrate. These SEM pictures of thin films with different magnifications indicate that the film grown on the substrate shows more particle formation on the surface.

Energy Dispersion X-Ray (EDX) analysis was carried out on the deposited Cobalt Oxide films indicating the peaks corresponding to cobalt and oxygen. Very interestingly no sizeable carbon contamination could be detected supporting the purity of the films by Thermal CVD.

3.2.2. X-Ray Diffraction

The XRD (Figure 6) spectrum was recorded in the range of 2θ=10-80° for the thinfilms deposited on silica substrate at 500 °C for 2 h. Thefilms are found to be crystalline and the peaks correspond to Co_3O_4. The films were in crystalline state with the preferential orientation of (311), (400), (511), and (440) peaks.

Estimation of the average grain size in Co_3O_4 film was carried out using the Full Width at Half maximum (FWHM) values of the (311) peaks and other respective samples in the figure by using Scherrer Formula.

$$L = \frac{0.94\lambda}{\beta Cos\theta}$$

Here λ is the wavelength (λ=1.5405 Å), β is the angular line-width at half maximum intensity and θ is the Bragg's angle. The calculations showed that the average grainsize of the Cobalt Oxide structures was 5.7nm.

The XRD data when compared with JCPDS (File No: 78-1969) revealed the presence of Face centered cubic plane orientation. Based on the XRD data the lattice constantwas found to be 8.072 Å.

CONCLUSION

Cobalt complexes (1-7) with Schiff bases have been synthesized and characterized by TG/DTA, SEM and XRD techniques. Single crystal analysis was done for compound **(7) (CCDC No - 998804)** which was found to be monoclinic with $P2_1/C$. The cobalt(III) complexes **(3) – (7)** were found to be volatile and they can be used as good precursors for Thermal CVD owing to the high covalency of imine (-CH=NH) based complexes and thesearomatic based ligand coordination complexes **(3)-(7)** can act as volatile vapour sources of cobalt. The preparation of the nanocrystalline Co_3O_4 thin films by Thermal CVD process using Schiff base complex precursors has been demonstrated in the present investigation.

Table 1: Analytical data and melting points of (1) - (7) complexes

Complex	Molecular Formulae	Color	M.P (°C)	Experimental(calculated) %				
				C	H	N	O	Co
(1)	$C_{14}H_{14}CoO_6$	Yellow	>250	49.86(49.82)	4.18(4.15)	-	28.46(28.47)	17.47(17.49)
(2)	$C_{14}H_{12}CoN_2O_2$	Greenish Yellow	>250	56.20(56.18)	4.04(4.01)	9.36(9.36)	10.69(10.70)	19.69(19.73)
(3)	$C_{32}H_{41}CoN_3O_3$	Olive Green	227	66.88(66.93)	7.19(7.19)	7.31(7.31)	8.35(8.35)	10.25(10.26)
(4)	$C_{33}H_{43}CoN_3O_3$	Olive Green	203	67.33(67.37)	7.36(7.36)	7.13(7.14)	8.15(8.15)	10.01(10.01)
(5)	$C_{34}H_{45}CoN_3O_3$	Olive Green	195	67.75(67.80)	7.52(7.05)	6.97(6.97)	7.96(7.96)	9.77(9.78)
(6)	$C_{35}H_{47}CoN_3O_3$	Olive Green	165	68.16(68.21)	7.68(7.68)	6.81(6.81)	7.78(7.78)	9.55(9.55)
(7)	$C_{36}H_{49}CoN_3O_3$	Olive Green	101	68.55(68.59)	7.83(7.83)	6.66(6.66)	7.61(7.61)	9.34(9.34)

Table 2: FT-IR frequencies of complexes (1) - (7)

Assignment	Wave number (cm^{-1})						
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
υ(OH) group	3430	-	-	-	-	-	-
υ(C=O)	1323	1323	1321	1324	1325	1323	1323
υ(C=N)	-	1650	1629	1625	1629	1621	1623
υ(Co-O) group	529	524	528	539	528	535	540
υ(Co-N) group	-	469	469	498	468	463	468

Table 3: ^{1}H and ^{13}C Spectroscopy of (3) - (7)

Compound	1H NMR	13C NMR
$C_{32}H_{41}CoN_3O_3$	S,8 ppm, (-CH=N) m, 7.29 ppm (Ar C) m, 3 – 7.7 ppm (-CH3)	164-168 ppm (-CH=N) 113-134 ppm (Ar C) 47.1 – 47.7 ppm -CH3)
$C_{33}H_{43}CoN_3O_3$	S,7.95 ppm, (-CH=N) m, 7.26 ppm (Ar C) m, 3.1 – 7.7 ppm -CH2-CH3)	164-168 ppm (-CH=N) 113-134 ppm (Ar C) 16 – 56 ppm -CH2-CH3)
$C_{34}H_{45}CoN_3O_3$	S,7.86 ppm, (-CH=N) m, 7.26 ppm (Ar C) m, 3.6 – 7.7 ppm (-CH2-CH2-CH3)	164-168 ppm (-CH=N) 113-134 ppm (Ar C) 11 – 61 ppm (-CH2-CH2-CH3)
$C_{35}H_{47}CoN_3O_3$	S,7.85 ppm, (-CH=N) m, 7.25 ppm (Ar C) m, 3 – 7.7 ppm (-CH2-CH2-CH2-CH3)	164-168 ppm (-CH=N) 113-134 ppm (Ar C) 13 – 59 ppm (-CH2-CH2-CH2-CH3)
$C_{36}H_{49}CoN_3O_3$	S,7.85 ppm, (-CH=N) m, 7.26 ppm (Ar C) m, 3 – 7.7 ppm ((-CH2-CH2-CH2-CH2-CH3)	162-168 ppm (-CH=N) 113-134 ppm (Ar C) 13 – 59 ppm (-CH2-CH2-CH2-CH2-CH3)

Table 4: Crystal data and Structure refinement for Tris(N-n-pentyl-salicylaldimine) cobalt(III) (7)

Empirical Formula	$2(C_{36}H_{48}CoN_3O_3)$
Formulae weight	1180.16
Temperature	293 K
Crystal System, Space group	Monoclinic, P 2_1/C
a(Å)	19.120(2)
b(Å)	14.6665(16)
c(Å)	25.121(3)
α(°)	90.00
β(°)	102.963
γ(°)	90.00
V(Å^3)	6864.99
Z, D_{calc} (mg/m^3)	Z: 4, 1.142
Absorption coefficient (mm^{-1})	0.994
F(000)	2320
θ Range for data collection (°)	1.62-25.00
Limiting indices	$-22 \leq h \leq 20, -14 \leq K \leq 17, -15 \leq l \leq 29$
Reflections collected / Independent reflections (R_{int})	52238 / 12085
Data/restraints/parameters	12085/0/781
Goodness-of-fit on F^2	0.851
R-Factor	6.08
Final R indices [I > 2σ(I)]	R_1=0.0608, wR_2=0.1180
R Indices (all data)	R_1=0.1610, wR_2=0.1469

Table 5: Selected bond lengths [Å] and bond angles (°) for Tris(N-n-pentyl-salicylaldimine) cobalt(III) (7)

Co(4) – N(5)	1.949	O(3) – Co(4) – N(7)	94.49
Co(4) – N(4)	1.953	C(64) – N(7) – Co(4)	122.86
Co(4) – N(7)	1.943	C(1E) – O(3) – Co(4)	126.80
Co(4) – O(3)	1.875	Co(4) – N(7) – C(61)	119.77
Co(4) – O (6)	1.871	N(4) – Co(4) – N(7)	177.32
Co(4) – O(48)	1.900	O(3) – Co(4) – O(6)	171.90
C(41) – N(4)	1.288	N(5) – Co(4) – O(48)	172.52
C(54) – N(5)	1.284	N(4) – Co(4) – N(5)	95.05
C(64) – N(7)	1.275	N(5) – Co(4) – O(3)	91.96
C(1E) – O(3)	1.299	O(3) – Co(4) – N(7)	94.49
C(41) – O(48)	1.307	N(7) – Co(4) – O(48)	85.16
C(56) – O(6)	1.296	O(48) – Co(4) – O(6)	86.47
C(1E) – C(65)	1.415	O(6) – Co(4) – N(4)	86.86
C(61) – C(62)	1.546		

Table 6: Weight loss % and melting points of (3) - (7)

complex	Weight (mg)		DTA M.P (°C)	Final		Nature/ End Residue
	Initial	Final		Residue %	T °C	
(3)	0.377	0.007	260	Nil residue	336	Volatile
(4)	1.529	0.006	228	Nil residue	542	volatile
(5)	2.931	0.2	225	5.9	595	Volatile
(6)	0.56	0.000	199	Nil residue	304	Volatile
(7)	4.160	0.000	202	Nil residue	530	Volatile

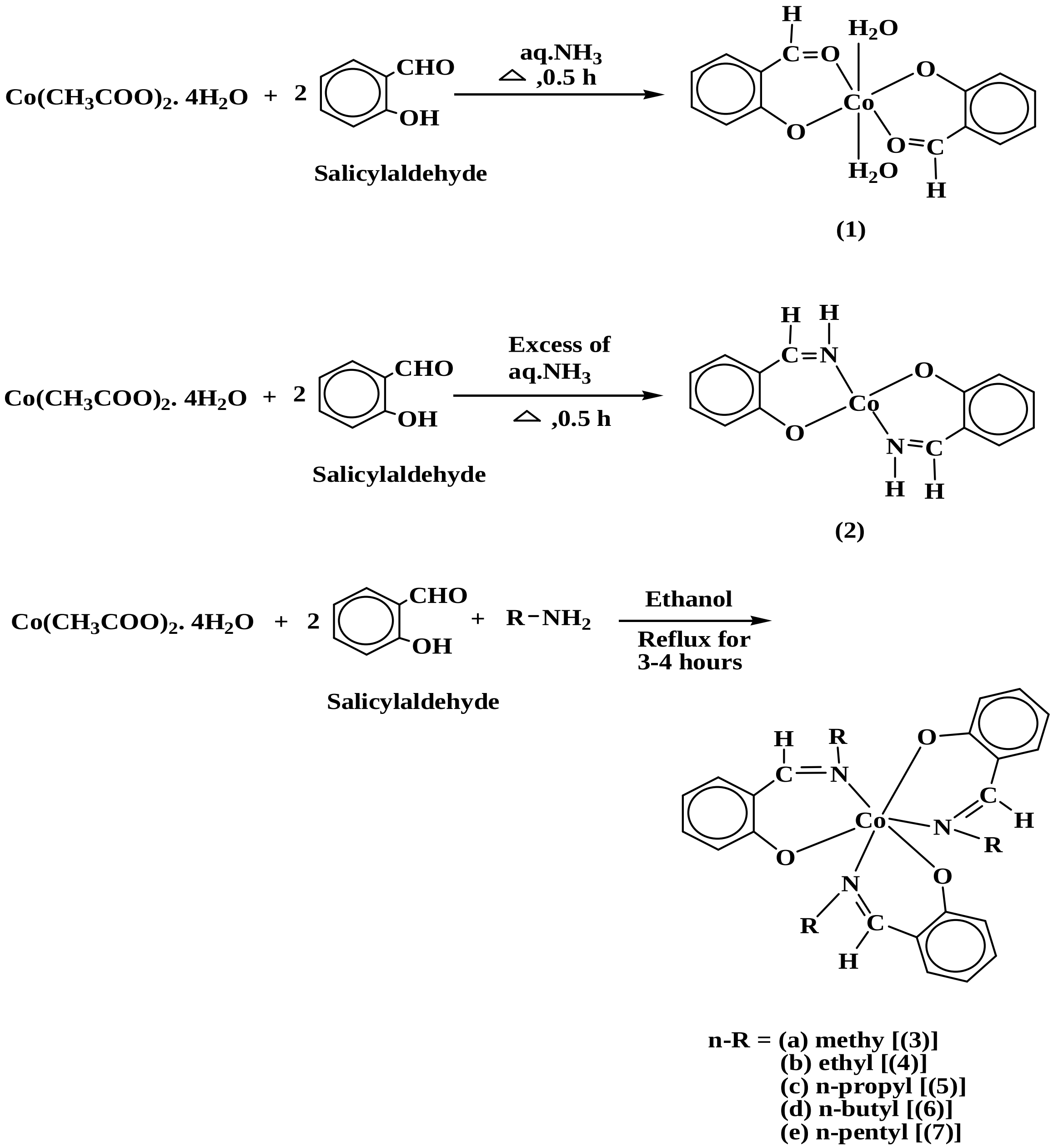


Fig. 1: Reaction Schemes of complexes (1)-(7)

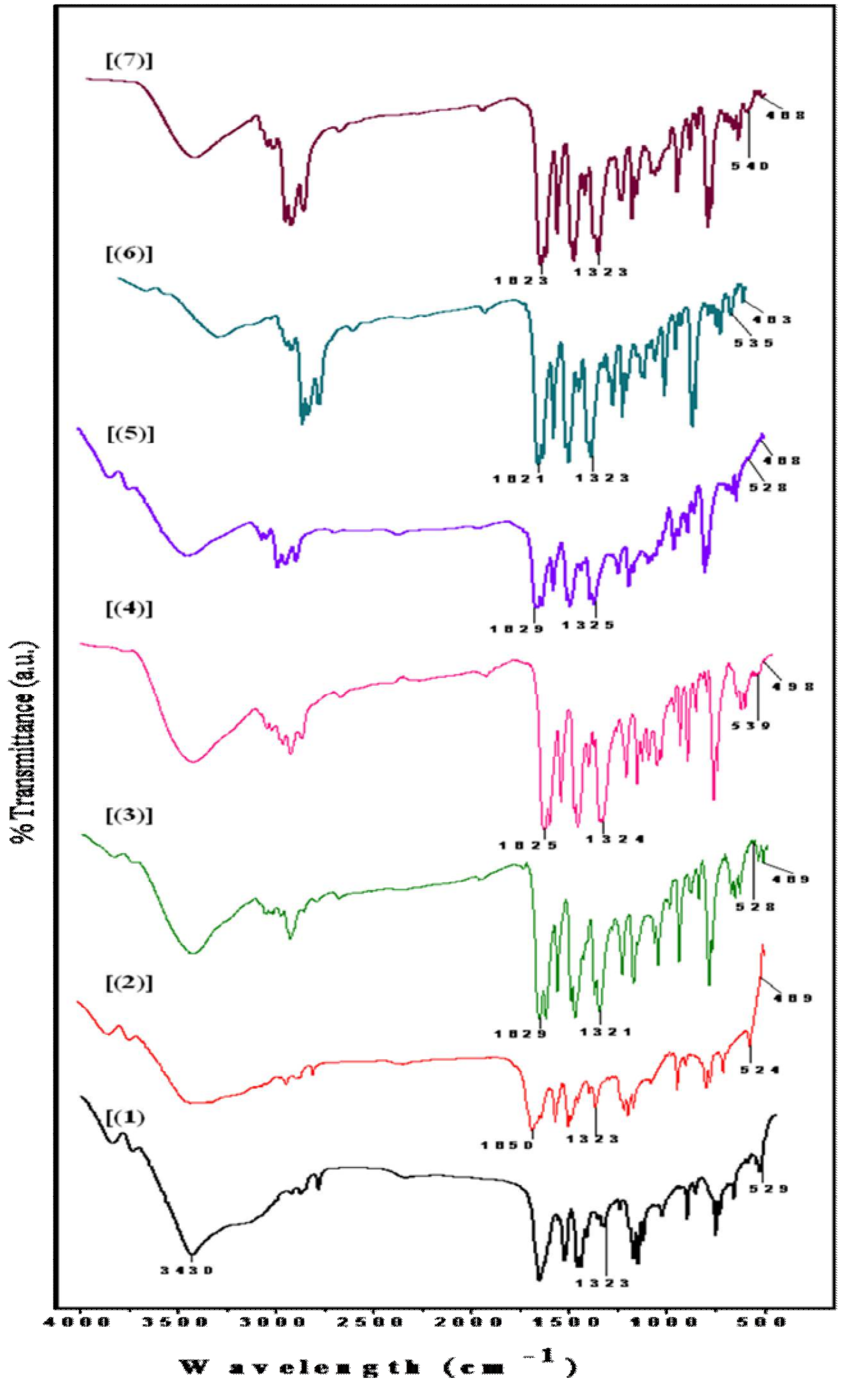


Fig. 2: FT-IR Spectra of (1) - (7) complexes

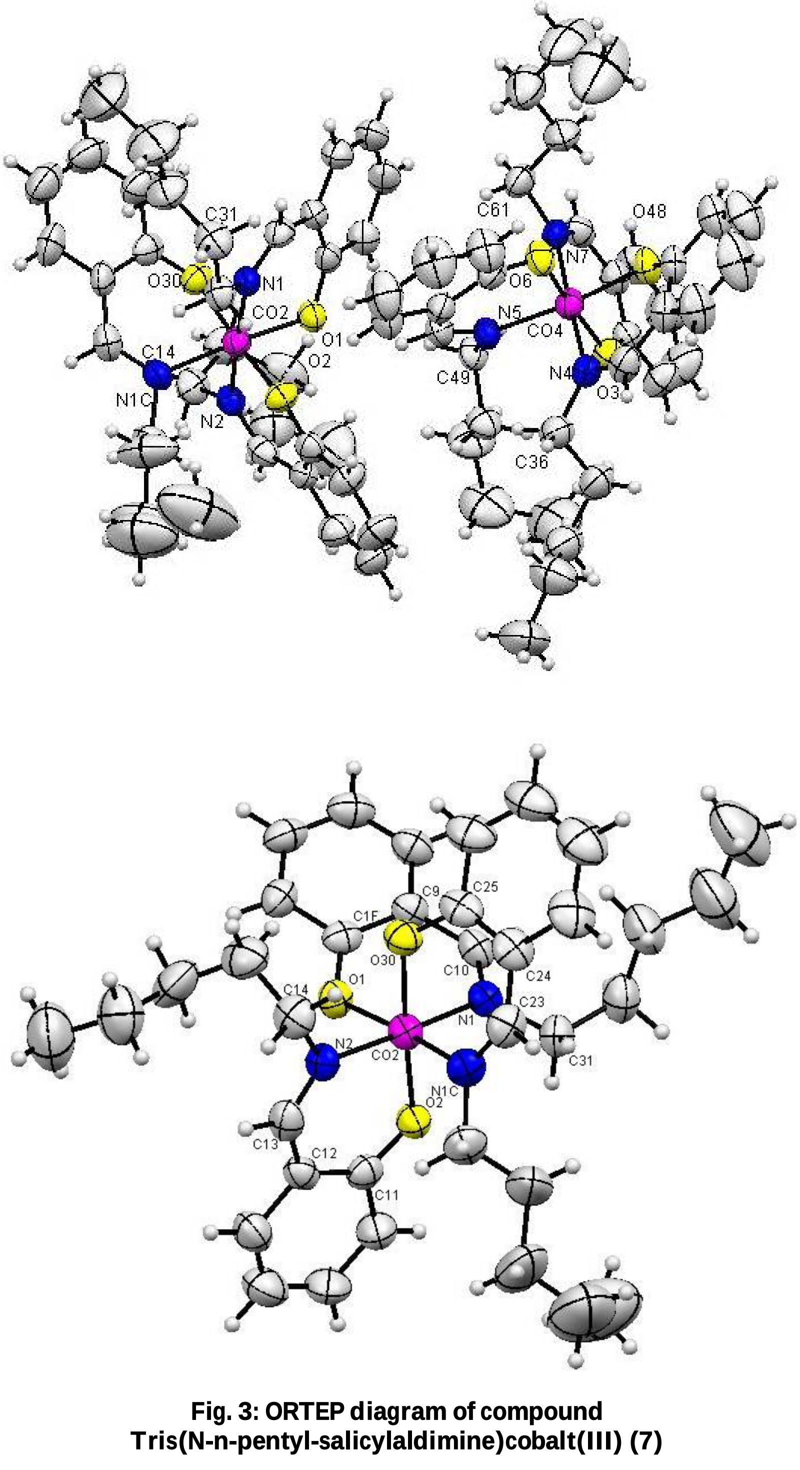


Fig. 3: ORTEP diagram of compound Tris(N-n-pentyl-salicylaldimine)cobalt(III) (7)

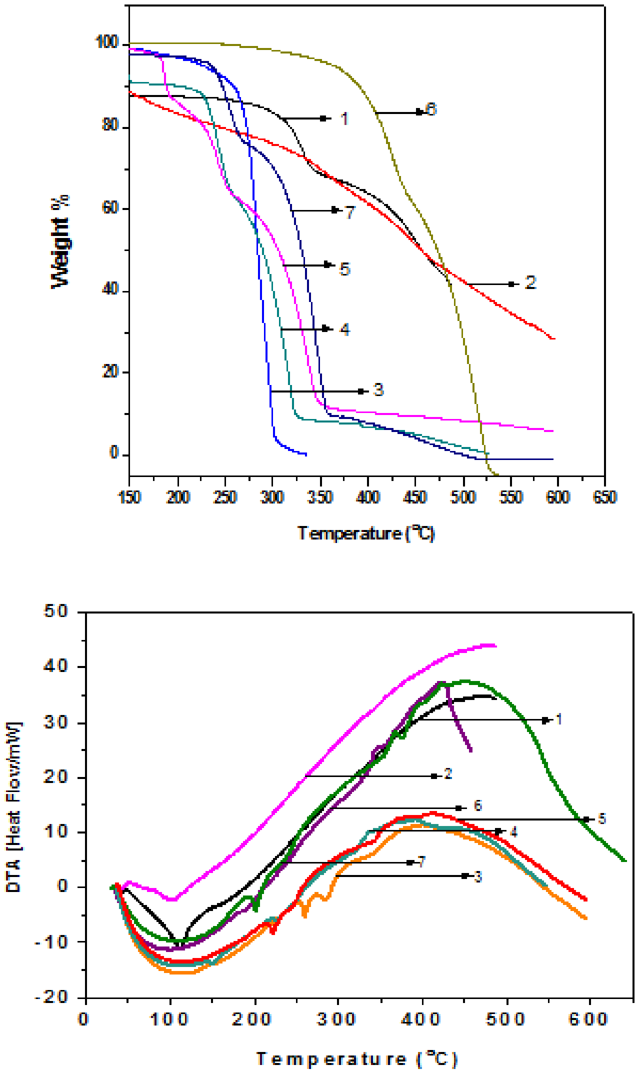
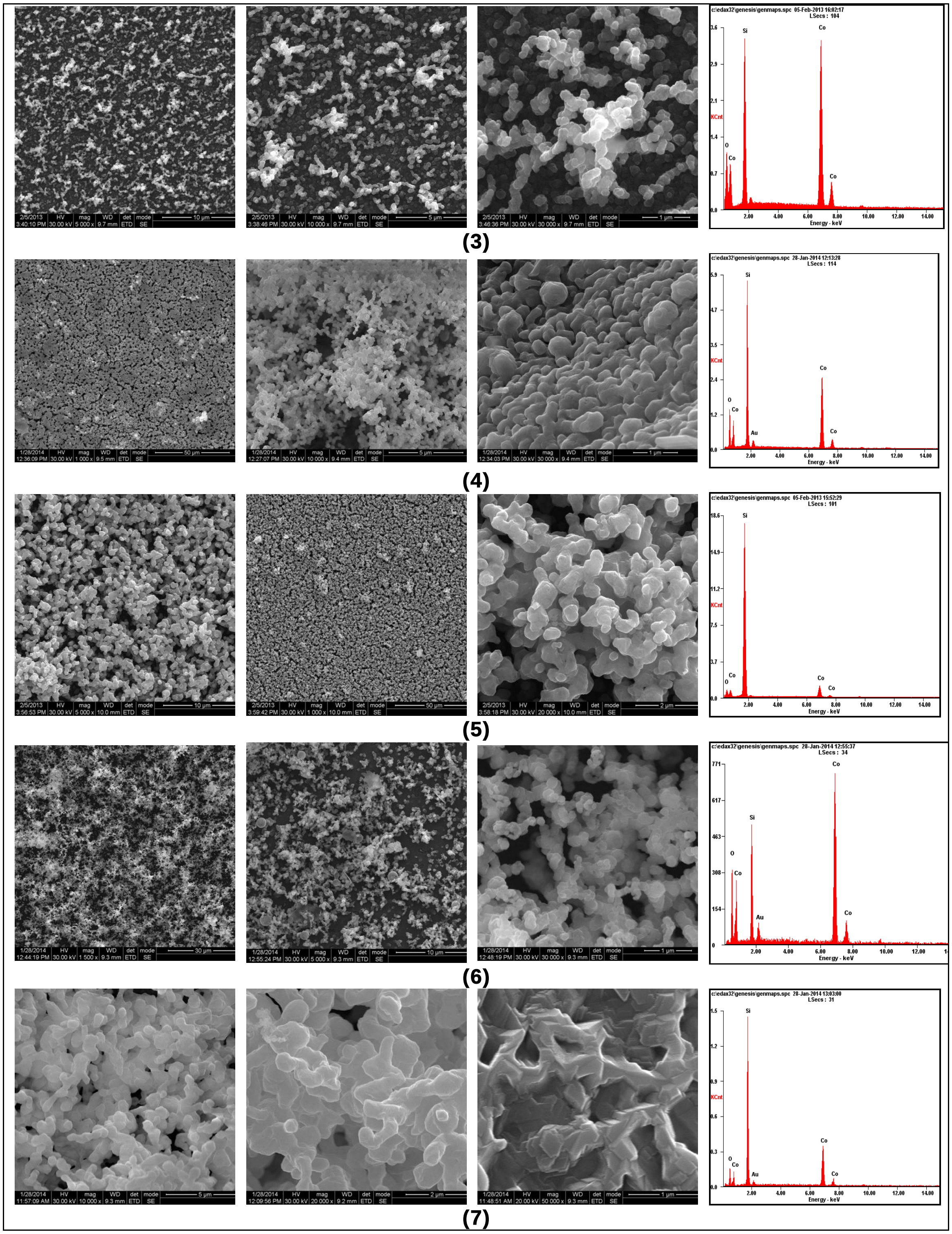


Fig. 4: TG/DTA of (1) - (7) complexes



(3)

(4)

(5)

(6)

(7)

Fig. 5: SEM images of thin film coatings of (3) - (7) on silica substrate

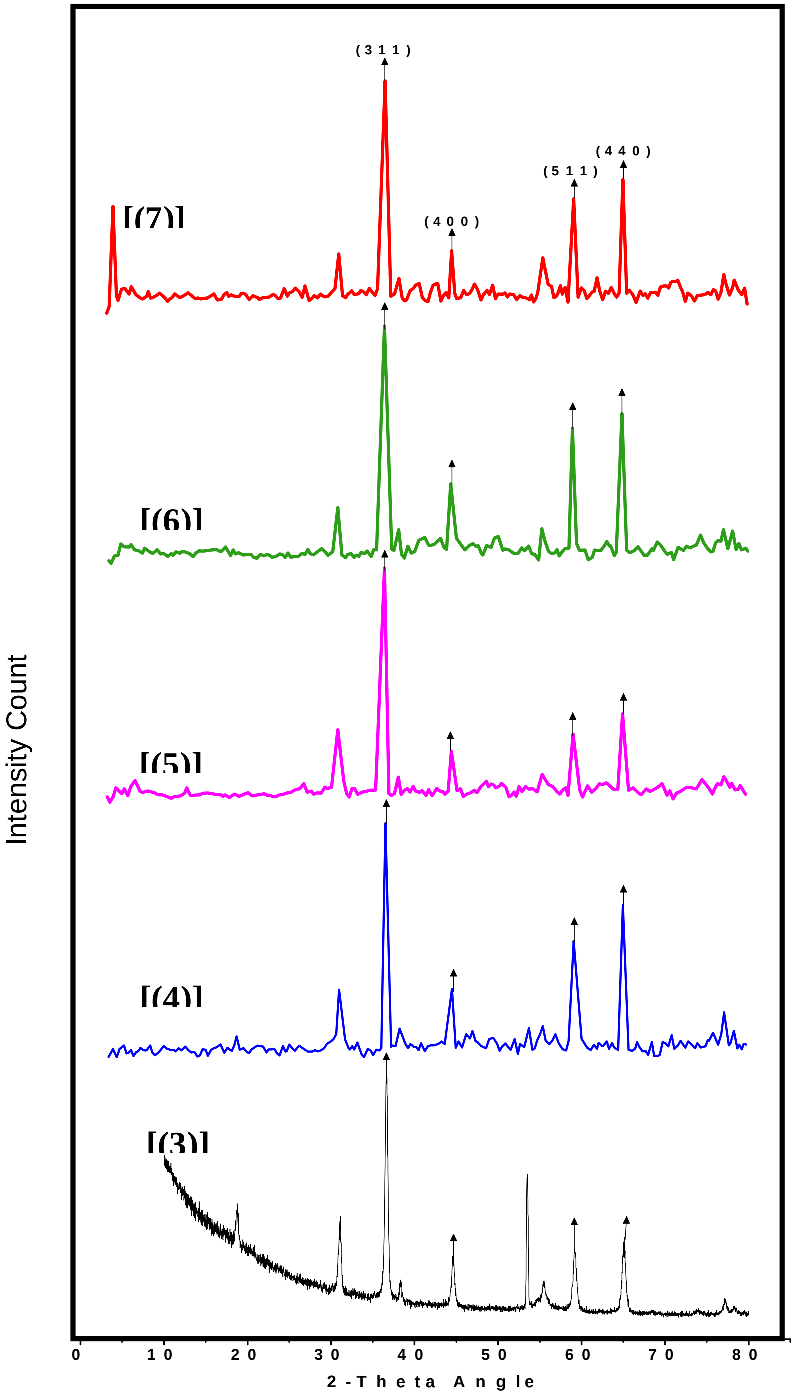


Fig. 6: Powder XRD patterns of Co_3O_4 deposited on silica substrate for (3) - (7) complexes

REFERENCES

1. Nejo AA, Kolawole GA and Nejo AO. Synthesis, characterization, antibacterial, and thermal studies of unsymmetrical Schiff-base complexes of cobalt(II). J Coord Chem. 2010;63(24):4398-4410.
2. Soliman AA and Mohamed GG. Structural and thermal study of the ternary complexes of copper with salycilidene-2-aminothiophenol and

some aminoacids. Thermo chim Acta. 2004;421(1-2): 151-159.

3. Sousa C, Freire C and Castro BD. Synthesis and Characterization of Benzo-15-Crown-5 Ethers with Appended N2O Schiff Bases. Molecules. 2003;8(12):894-900.
4. Kou HZ, Ni ZH, Zhou BC and Wang RJ. A cyano-bridged molecule-based magnet containing manganese(III) Schiff base and octacyanotungstate (V) building blocks. Inorg Chem Commun. 2004;7(10):1150.
5. Hughes MH. The Inorganic Chemistry of Biological Processes, 1984;2nd Edn
6. Tarafder MH, Saravanan N, Crouse KA and Ali AM. Coordination chemistry and biological activity of nickel(II) and copper(II) ion complexes with nitrogen-sulphur donor ligands derived from S-benzyldithiocarbazate (SBDTC). Transit Met Chem. 2001;26(6):613-618.
7. Sharma A, Mehta T and Shah MK. Synthesis and spectral studies of transition metal complexes supported by NO- bidentate Schiff-Base ligand. Der Chemica Sinica. 2013;4(1):141-146.
8. You Z L and Zhu H L. Syntheses, Crystal Structures, and Antibacterial activities of Four Schiff Base Complexes of Copper and Zinc Z. Anorg Allg Chem. 2004;630(15):2754-2760.
9. Durak D, Delikanl A, Demetgul C, Kani I and Serin S. Crystal structure of an unsymmetrical Schiff base, immobilization of its cobalt and manganese complexes on a silica support, and catalytic studies Transit Met Chem. 2013;38(2):199-206.
10. Tumer M, Koksal H, Sener MK and Serin S. Antimicrobial activity studies of the binuclear metal complexes derived from tridentate Schiff base ligands. Transit Met Chem. 1999;24(4):414-420.
11. Samsel EG, Srinivasan K and Kochi JK. Mechanism of the chromium-catalysed epoxidation of olefins, role of oxochromium (V) cations. J Am Chem Soc. 1985;107(25):7606-7617.
12. O'Reilly RK, Gibson VC, White A J and Williams DJ. Design of highly active iron-based catalysts for atom transfer radical polymerization: tridentate salicylaldiminato ligands affording near ideal Nernstian behavior. J Am Chem Soc. 2003;125(28):8450-8451.
13. Zhou X, Shearer JM and Rokita SE. A Ni(salen)-biotin conjugate for rapid isolation of accessible DNA. J Am Chem Soc. 2000;122(37):9046-9047.
14. Zhang W, Loebach JL, Wilson SR and Jacobsen EN. Enantioselective epoxidation of unfunctionalized olefins catalyzed by salen manganese complexes. J Am Chem Soc. 1990;112(7):2801-2803.
15. Shahrokhian S, Kamalzadeh Z, Bezaatpour A and Boghaei DM. Differential pulse voltammetric determination of N-acetylcysteine by the electrocatalytic oxidation at the surface of carbon nanotube-paste electrode modified with cobalt salophen complexes. Sens Actuators, B - Chem. 2008;133(2):599-606.
16. Arokiasamy S, Mallika C, Sreedharan OM, Raghunathan VS and Nagaraja KS. Precursor development, characterisation and evaluation of sublimation enthalpies of novel volatile complexes of nickel. Inorg Chim Acta. 2009;362(6):1977-1983.
17. Premkumar PA, Dasgupta A, Kuppusami P, Parameswaran P, Mallika C, Nagaraja KS and Raghunathan VS. Synthesis and Characterization of Ni and Ni/CrN Nano composite Coatings by Plasma Assisted Metal-Organic CVD. Chem Vap Deposition. 2006;12(1):39-45.
18. Hunde E T and Watkins JJ. Reactive deposition of cobalt and nickel films from their metallocenes in supercritical carbon dioxide solution. Chem Mater. 2004;16(3):498-503.
19. Bakovets VV, Mitkin VN and Gelfond NV. Mechanism of Ni Film CVD with a Ni(Ktfaa)$_2$ Precursor on a Silicon Substrate. Chem Vap Deposition. 2005;11(8-9):368-374.
20. Bakovets VV, Mitkin VN and Gelfond NV. Mechanism of Ni Film CVDwith a Ni(ktfaa)2 Precursor on a Copper Substrate. Chem Vap Deposition. 2005;11(2):112-117.
21. Martin JD, Abboud KA and Dahmen KH. Variations on nickel complexes of the vic-dioximes: An understanding of factors affecting volatility toward improved precursors for metal-organic chemical vapor deposition of nickel. Chem Mater. 1998;10(9):2525-2532.
22. Hyungsoo C, Sungho P and Tae Hyung K. Novel nickel precursors for chemical vapor deposition. Chem Mater. 2003;15(20):3735-3738.
23. Mordi CU, Eleruja M A, Taleatu BA, Egharevba GO, Adedeji AV, Akinwunmi

OO, Olofinjana B, Jeynes C and Ajayi EOB. Metal Organic Chemical Vapour Deposited Thin Films of Cobalt Oxide Prepared via Cobalt Acetylacetonate. J Mater Sci Technol. 2009;25(1):85-89.

24. Yoo HI and Lee JH. Correlation of the cationic 'charge of transport' with the nonstoichiometry and the oxygen exponents in $C_{1-\delta}O$. J Phys Chem Solids. 1996;57(1):65-73.
25. Mott SN. Metal Insulator Transition, 1990;Edn.
26. Wollenstein J, Burgmair M, Plescher G, Sulima T, Hildenbrand J and Bottner H. Cobalt oxide based gas sensors on silicon substrate for operation at low temperatures. Sens Actuators B. 2003;93(1):442.
27. Rivera E F, Atakan B and Höinghaus K K. CVD deposition of cobalt oxide (Co_3O_4) from $Co(acac)_2$.J. Phys. IV. 2001;11(PR3):629-635.
28. Granquist CG. Handbook of Inorganic Electrochromic Materials 1995 ;Edn.
29. Ando M, Kobayashi T, Iijima S and Haruta M. Opticalrecognition of CO and H_2 by use of gas-sensitive Au-Co_3O_4 composite films. J Mater Chem. 1997;7(9):1779-1783.
30. Barrera E, González I and Viveros T. Anew cobalt oxide electro deposit bath for solar absorbers.Sol. Energy Mater. Sol Cells. 1998;51(1):69-82.
31. Mane AU, Shalini K and Shivashankar SA. Cobalt oxide thin films prepared by metalorganic chemical vapor deposition from cobalt acetylacetonate. J Phys. IV 2001;11(PR3):637-643.
32. Patil PS, Kadam LD and Lokhande CD. Preparation and characterization of spray pyrolysed cobalt oxide thin films. Thin Solid Films. 1996;272(1):29-32.
33. Arockiasamy S, Johnson MG, Mallika C, Sreedharan OM and Nagaraja KS. Spectral characterisation of five volatile bis(N-R-salicylaldimine)nickel(II) (where nR = methyl to pentyl) complexes and single crystal study on methyl analogue. Mater Chem Phys. 2009;114(1):456-461.
34. Khan S, Bhar K, Roy S, Ramachandran K and Ghosh B. Syntheses, structures and molecular properties of two mononuclear cobalt(III) halide complexes containing a tetradentate N-donor schiff base. Indian J Chem Sect A. 2011;50(9-10):1429.
35. Saha D, Maity T, Bera R and Koner S. Cobalt (III) Schiff base complex: Synthesis, X-ray structure and aerobic epoxidation of olefins. Polyhedron. 2013;56:230-236.
36. Mrinalini L and Manihar Singh AK. Mixed Ligand Cobalt (III) Complexes with 1-Amidino-O-Methylurea and Amino Acids. Res J Chem Sci. 2012;2(1):45-49.
37. Dey K, Chakraborty K, Battacharya PK, Bandyopadhyay D, Nag SK and Bhowmick R. Synthesis and charaterisation of cobalt complexes of salicylaldehyde 4-methoxybenzoyl hydrazone (H-2 smbhon). Indian J Chem A. 1999;38(11):1139-1144.
38. Iranmanesh H, Behzad M, Bruno G, Rudbarim H A, Mohammad A, Taheri Oand Nazari H. Cobalt(III) Schiff base complexes derived from mesostilbenediamine: Synthesis, characterization, crystal structure, electrochemistry and antibacterial studies. Inorganica Chimica Acta. 2013;395:81–88.
39. McClure M R and Holcombe J. Synthesis and NMR Characterization of Cobalt(III) Complexes with Triethylenetetramine, 2,2-Bipyridine, and 1,10-Phenanthroline. J Coord Chem. 2004;57(11):907–915.
40. Volpe M, Hartnett H, Leeland JW, Wills K, Ogunshun M, Duncombe BJ, Wilson C, Blake AJ, McMaster J and Love JB. Binuclear cobalt complexes of Schiff-base calixpyrroles and their roles in the catalytic reduction of dioxygen. Inorg Chem. 2009;48(12):5195-5207.
41. Qiu XY. Bis(2-formylphenolato)cobalt(II). Acta Crystallogr E. 2006;62(M):1190-1191.
42. Arokiasamy S, Johnson MG, Mallika C, Sreedharan OM and Nagaraja KS. Spectral characterisation of five volatile bis(N-R-salicylaldimine)nickel(II) (where n-R = methyl to pentyl) complexes and single crystal study on methyl analogue. Mater Chem Phys. 2009;114(1):456-461.
43. Alam MM, Rahman SMM, Rahman MM and Islam SM. Simultaneous Preparation of meridional isomer of cobalt-amino acid complexes and their characterization. J Sci Res. 2010;2(1):91-98.