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COMPOSITION, SPECTROSCOPIC CHARACTERIZATION AND K-ABSORPTION STUDIES OF CO(II) SCHIFF BASE COMPLEXES

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ABSTRACT
The newly synthesized complexes of [CoL1] and [CoL2] were prepared by treating with [1-(((3-nitrophenyl)imino)methyl)naphthalene-2-ol] (L1) and [1-(((4-bromophenyl)imino)methyl)naphthalene-2-ol](L2) ligands with Co(OAc)2.H2O, respectively. The complexes were investigated Fourier Transform Infrared Spectroscopy (FTIR), 1H NMR, 13C NMR, single crystal X-ray diffraction (XRD) and X-ray Absorption Fine Structure (XAFS). XRD analysis shows that complexes are crystalline in nature and having particle size and lattice parameter in the range of few micro meter and EXAFS technique extract the local structure of complexes and nearest neighboring atom distance commonly known as 'bond length' were calculated using Fourier transform method. The bond lengths determined from these methods were also compared with the bond length obtained from several other known technique.

KEYWORDS: Transition metal, Schiff base, Complexes, Ligand, X-ray

INTRODUCTION

Schiff bases and their complexes are derived from the condensation of aromatic and amines and become stable complexes with different transition metal ions [1]. Schiff bases have been extensively investigated, due to their incredible chemical properties and applications in various areas. They are also play a vital role in coordination chemistry [2]. It can be multifarious as monodentate, bidentate, tridentate, tetradentate and polydentate ligands. In bidentate (NN, ON and SN) Schiff bases, have the major donor atoms. Bidentate ligand having two bonding points for the metal ion occurs through its both negatively charged O atoms. The Schiff base ligand acts as bidentate ligand and coordinates to the metal center via N and O atoms [3].

Researchers are taken interested in transition metal complexes, due to their enormous properties like antifungal, antibacterial, antitumor, anti-inflammatory, antiviral, and antipyretic properties [4]. Also, they might be used for enzyme immobilization. Transition metals have different types of coordination geometries such as octahedral, square-planar, square-pyramidal, trigonal-bipyramidal, tetrahedral, planar, or linear geometries. The most interesting thing in transition metal complexes is that the preparation of metal complexes is highly modular and usually can be done in simple few steps, while organic compounds synthesis can be extensive and involve multiple protecting group manipulations. In the presence of N, O in Schiff base which is used extensively in coordination chemistry, because of their flexible modes of add-on to metal centers via monodentate, bidentate, chelate or bridging. It was seen that the biological activity of Schiff bases either increase or decrease upon chelation with metal ions [5]. Co(II) complexes of Schiff base derived from 2-hydroxy-1-naphthaldehyde show potent antibacterial activity and antifungal activities. Apart from these biological applications, cobalt complexes of Schiff bases are extensively used as catalysts in both homogeneous and heterogeneous systems.

In this paper, we synthesis and characterization (FTIR, 1H NMR, 13C NMR, XRD, and XAFS) of Co(II) complexes using 2-hydroxy-1-naphthaldehyde and aniline derivatives. Co(II) complexes formed form bidentate Schiff base ligands, [1-(((3-nitrophenyl)imino)methyl)- naphthalene-2-ol] and [1-(((4-bromophenyl)imino)methyl)- naphthalene-2-ol]. Transition metal complexes have been wide range of application in biologically, medicinal, industry and many more [6].

Experimental technique

Materials

All chemical for synthesis and analysis were purchased from Merck Company and were used without further purification.

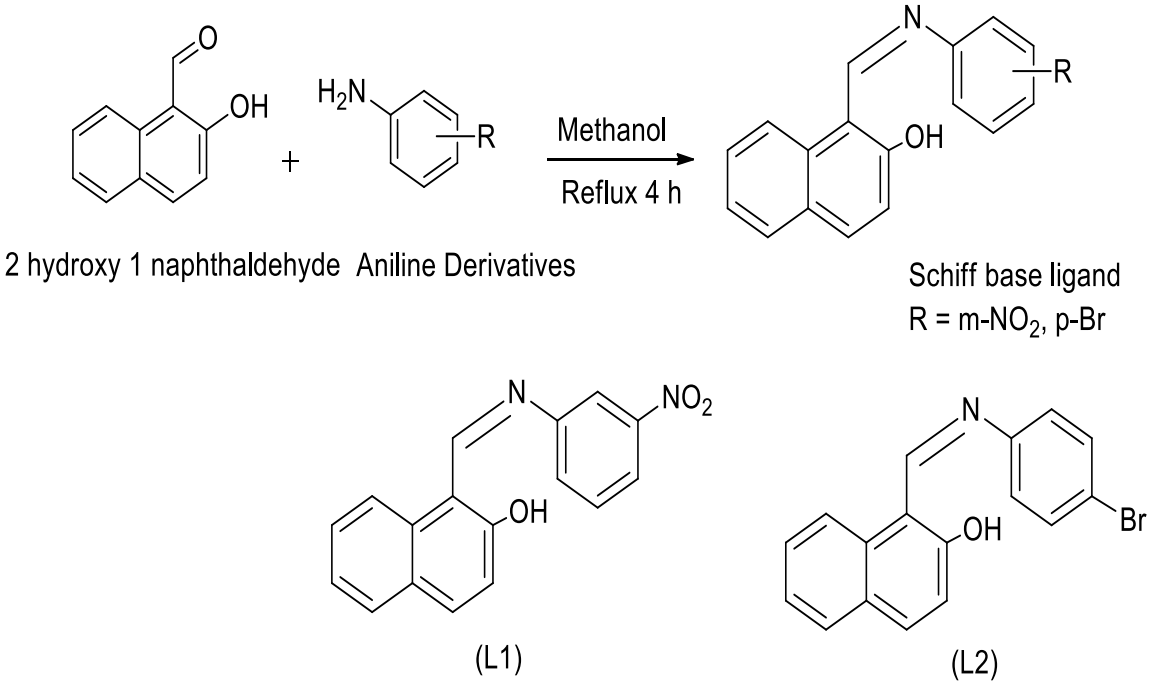
Preparation of Schiff base ligand [1-(((3-nitrophenyl)imino)methyl)naphthalene-2-ol](L1)

2-hydroxy-1-naphthaldehyde (30 mmol) and 3-nitro-aniline (30 mmol) were dissolve in 150 mL of methanol solution in 500 mL of round bottom flask. The well mixture solution was refluxed for 4h. After refluxing the solvent was evaporated and orange colour precipated was collected and dried in air. Anal. Calc. for C17H12N2O3 : C, 69.86; H, 4.13; N, 9.60 %. Found: C, 69.84; H, 4.18, N, 9.64 %. IR (KBr pellet, cm-1): 3416 (O-H phenolic), 3010, 2891 (C-H aromatic), 1632 (C=N), 1540 (NO2), 1514 (C=C). 1H NMR (400, DMSO, δ (ppm)): 5.17 (br-s, 1H, OH), 6.93 (d, 1H, Ar-H), 7.21 (d, 1H, Ar-H), 7.42 (m, 1H, Ar-H), 7.53 (m, 1H, Ar-H), 7.69 (m, 1H, Ar-H), 7.83 (s, 1H, Ar-H), 7.94 (d, 1H, Ar-H), 8.02 (d, 1H,

Ar-H), 8.12 (d, 1H, Ar-H), 8.20 (d, 1H, Ar-H), 8.61 (s, 1H, CH). 13C NMR (100 MHz, DMSO): 105.7, 116.9, 117.4, 119.4, 121.4, 123.8, 125.4, 127.5, 128.2, 128.9, 130.8, 132.7, 133.3, 146.2, 152.1, 154.4, 168.4.

Synthesis of Schiff base ligand [1-(((4-bromophenyl)imino)methyl)naphthalene-2-ol](L2)

2-hydroxy-1-naphthaldehyde (30 mmol) and 4-bromo-aniline (30 mmol) were dissolve in 150 mL of methanol solution in 500 mL of round bottom flask. The well mixture solution was refluxed for 4h. After refluxing the solvent was evaporated and yellow colour precipated was collected and dried in air. Anal. Calc. for C17H12BrNO: C, 62.60; H, 3.71; N, 4.29 %. Found: C, 62.58; H, 3.73, N, 4.34 %. IR (KBr pellet, cm-1): 3418 (OH phenolic), 3012, 2888 (C-H aromatic), 1636 (C=N), 1512 (C=C), 632 (Br). 1H NMR (400 MHz, DMSO, δ (ppm)): 5.19 (br-s, 1H, OH), 6.96 (d, 1H, Ar-H), 7.26 (d, 2H, Ar-H), 7.45 (m, 1H, Ar-H), 7.56 (m, 1H, Ar-H), 7.82 (d, 2H, Ar-1H), 8.02 (d, 1H, Ar-H), 8.10 (d, 1H, Ar-H), 8.21 (d, 1H, Ar-H), 8.62 (s, 1H, CH). 13C NMR (100 MHz, DMSO): 105.6, 117.0, 120.1, 120.8, 122.2, 124.0, 126.9, 128.3, 129.2, 132.8, 133.4, 133.9, 150.7, 152.5, 168.6.



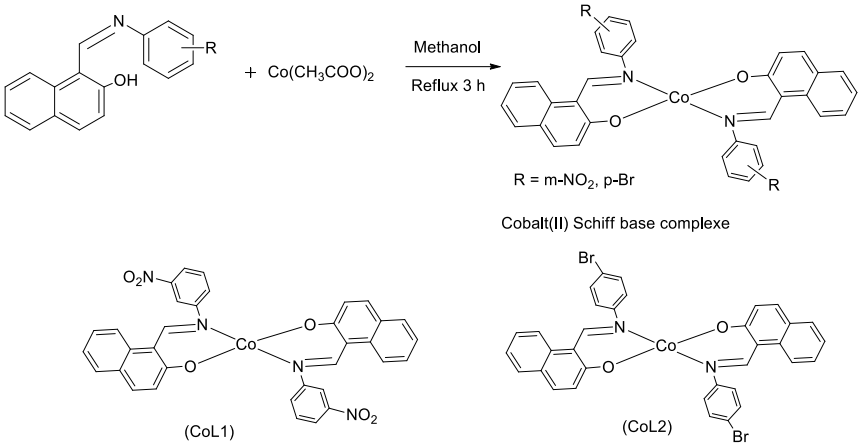
Scheme 1 Synthesis of Schiff base ligand L1 and L2

Synthesis of Co(II) metal complex (CoL1)

To a prepared Schiff base ligand (L1) (5mmol) and Co(OAc)2.H2O (2.5 mmol) were dissolved in 180 mL of methanol solution in 500 mL of round bottom flask and the mixture was refluxed for 3h. After refluxing the solvent was evaporated and gray colour precipated was collected and dried in air. The suitable crystals were dissolved in1:1 mixture of methanol and chloroform for recrystallization. Anal. Calc. for C34H22CoN4O6 : C, 63.66; H, 3.46; N, 8.73 %. Found: C, 63.64; H, 4.18, N, 9.64 %. IR (KBr pellet, cm-1): 3014, 2895 (C-H aromatic), 1606 (C=N), 1542 (NO2), 1518 (C=C).

Synthesis of Co(II) metal complex (CoL2)

To a prepared Schiff base ligand (L2) (5mmol) and Co(OAc)2.H2O (2.5 mmol) were dissolved in 180 mL of methanol solution in 500 mL of round bottom flask and the mixture was refluxed for 3h. After refluxing the solvent was evaporated and orange colour precipated was collected and dried in air. The suitable crystals were dissolved in1:1 mixture of methanol and chloroform for recrystallization. Anal. Calc. for C34H24Br2CoN2O2 : C, 57.55; H, 3.13; N, 3.95 %. Found: C, 57.57; H, 3.16, N, 3.93 %. IR (KBr pellet, cm-1): 3012, 2892 (C-H aromatic), 1610 (C=N), 634 (Br), 1520 (C=C).



Scheme 2 Synthesis of Cobalt(II) Schiff base complexes CoL1 and CoL2

Physical measurements

X-ray Diffraction pattern of prepared sample were carried out with Cu Kα radiation using a BRUKER D8 Advanced with a rotating anode scanning over the angular range 10°-80° at room temperature generating X-ray by 40 kV and 100 mA power settings monochromatic X-rays of wavelength λ=1.5406Å Kα1 line from a Co target were made to fall on the prepared samples. XAFS data was collected using synchrotron radiation. This setup available at RRCAT Indore and is called beam line. This beam line BL-8 has energy 2.5 GeV Indus-2 synchrotron radiation sources. BL-8 is in dispersive mode which is called dispersive EXAFS (DEXAFS) BL-8 beam line. FTIR Spectra were recorded on PerkinElmer FT-IR Spectrometer in the range 4000 to 400 cm−1. The 1HNMR and 13C NMR spectra of the synthesized compounds were recorded at 400 MHz and 100 MHz, respectively using Bruker AVANCE 400 MHz NMR spectrometer in DMSO-d6 solvent.

RESULTS AND DISCUSSION

NMR

In addition, 1H NMR and 13C NMR was also used to characterization of L1 (Fig. 1, 2). They proved the success of synthesis of L1. In the 1H NMR spectra splitting pattern are indicated as s: singlet, d: doublet, t: triplet, m: multiplet and br: broad peak. We get a brought peak of OH at 5.172 ppm and rest of all peaks related to aromatic ring except at 8.61 ppm which is related to CH=N.

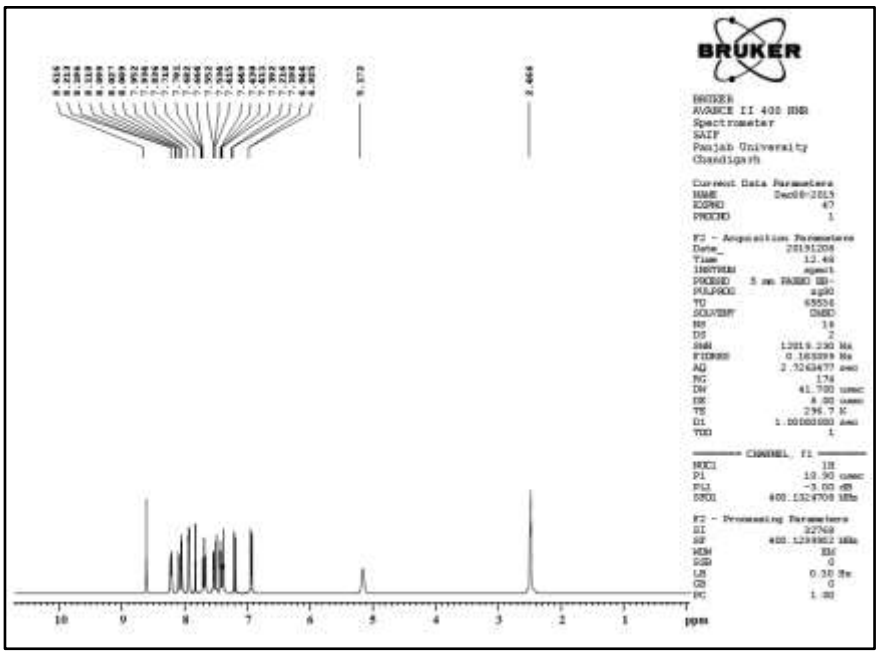


Fig. 1 1H NMR spectrum of L1

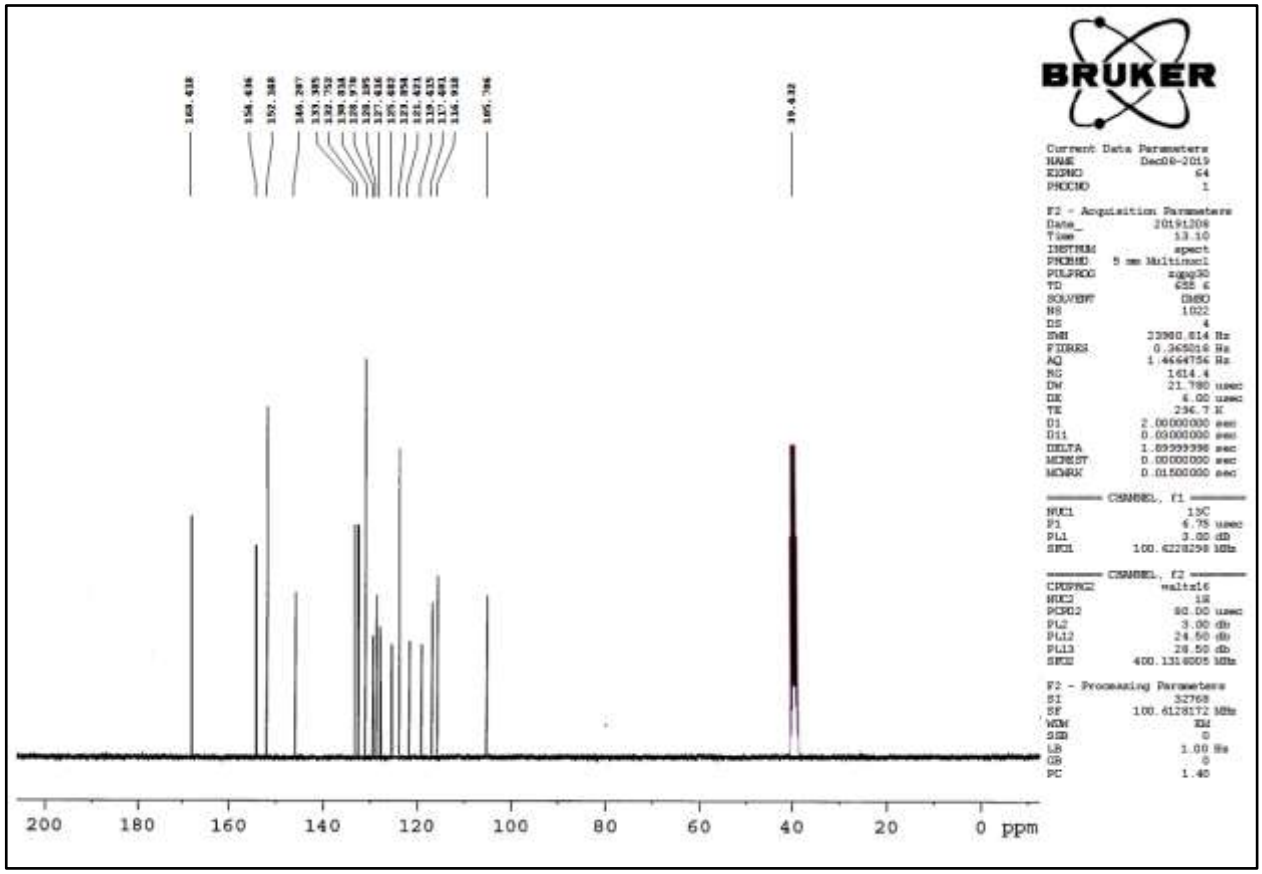


Fig. 2 13C NMR spectrum of L1

FTIR

The ligands (L1 and L2) and its metal complexes (CoL1 and CoL2) infrared spectral bands are given in experimental data. The ornament of both ligands is presence of electron pair donor sites. In the IR spectra of the ligands L1 & L2 a broad band observed at 3416 and 3418 cm-1 respectively, because of phenolic OH group (Fig. 3). Formation after the metal complexes, absorption due to the OH group disappeared indicating deprotonation and formation of the C–O bond [7]. Similarly, a sharp band at 1632 & 1636 cm-1 are assigned to the (C=N) modes respectively for ligands L1 & L2. Confirmation of the nitrogen bonding of the azomethine (C=N) group to the central metal atom stems from the shift of the ν(C=N) frequency to lower frequency by 25–35 cm-1 (1606–1610 cm-1) in both of its metal complexes. This is further confirmed by the emergence of the new band at 430 and 490 cm-1 due to ν (M-O) in the metal complexes.

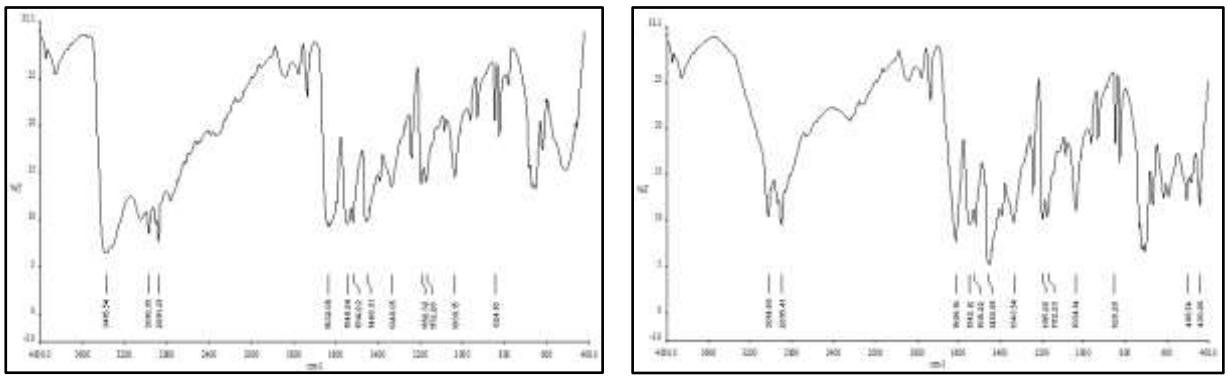


Fig. 3 FT-IR Structure of ligand L1 and Complex CoL1

X-ray diffraction

X-ray diffraction (XRD), is an essential instrumental technique that is use to detect crystalline or amorphous nature of materials. It might be concluded that, the both complexes of Co(II) have distorted monoclinic structure and the complexes of Co(II) have square planer structure. The XRD pattern of the complexes CoL1 show 12 reflection and CoL2 show 10 reflection (Fig. 4) between 2h ranging from 20° to 80° with maxima at 2θ = 33.86° and 32.91° corresponding to d value 2.644 Å and 2.719 Å respectively. The Braggs equation nλ=2dsinθ has been used for obtaining the d (inter planer distance) values. The observed inter-planar d-spacing values have been compared with the calculated ones and it was found to be in good agreement. The compounds studied show a excellent quality and all the peaks has been identified for h, k, l values using methods reported in the literature. The average nano-crystallite size was find using Scherer's equation: D = Kλ/ (β cosθ), where D is the diameter of the particle, K is a geometric factor taken as 0.9, λ is the X-ray wavelength, θ is the

diffraction angle, and β is the full width at half maximum (FWHM) of the main diffraction peak [8-11]. The average particle sizes of the samples were found to be about 109.27 and 82.51 nm. Based on XRD investigation, it has been found that the cobalt macrocyclic complexes are crystalline in nature having monoclinic crystal systems. All the peaks match with the software JCPDF. Required parameters are show in table 1.

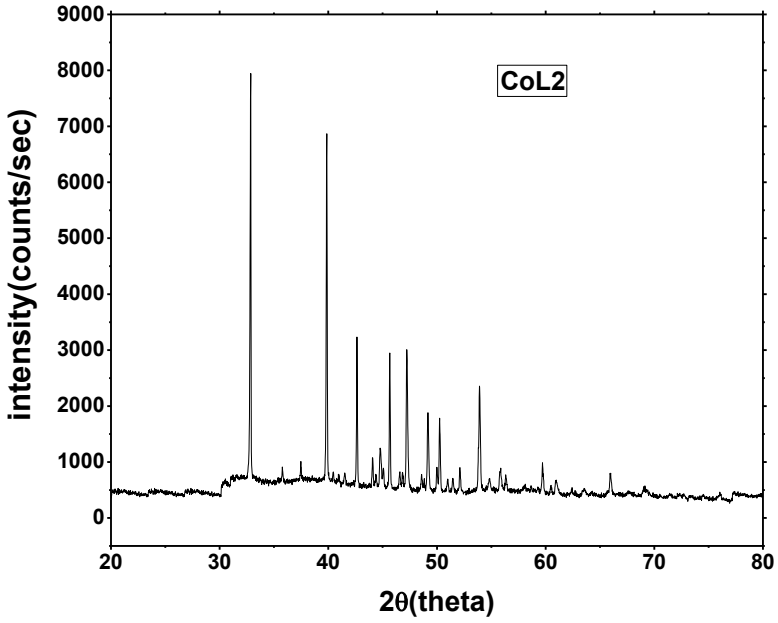


Fig. 3 XRD pattern of CoL1 and CoL2

Table 1 X-ray diffraction data of CoL1 and CoL2

	CoL1	**CoL2**
Formula Weight	C34H22CoN4O6	C34H24Br2CoN2O2
Molecular Weight	642	710
Crystal Structure	Monoclinic	Monoclinic
Space Group	P21/n	P21/n
Particle Size (nm)	109.27	82.51
d spacing of highest peak	2.644	2.719
a(Å)	5.54	5.575
b(Å)	20.2305	20.478
c(Å)	10.870	10.8216
α(deg)	90	90
β(deg)	96.157	97.014
γ(deg)	90	90
V(Å3)	1224.78	1281.5 0

X-ray absorption fine structure

XAFS is a fundamentally quantum mechanical fact which is based on the X-ray photoelectric effect. Usually, it is split into two energy regions. The first, region is X-ray absorption near edge structure (XANES), occurs in the region from the edge to approximately 40 eV above the edge, while the second, region is the extended X-ray absorption fine structure (EXAFS), extends from 40 eV to 1000 eV above the edge. Single scattering is responsible for the higher energy portions of EXAFS spectra within only some tenths of nm (5-6 Å) from the absorber, and gives information about to the local structure surrounding the absorber. On the other hand, multiple-scattering is responsible for XANES spectra, being centered close to the absorption jump, are dominated by events extending a few nm from the absorber. Both part (XANES and EXAFS), XAS provides information to determine the chemical state and local atomic structure for a selected atomic species [12-14].

The values of edge energy are 7718.953 and 7718.56 eV for complexes CoL1 and CoL2 respectively. And the chemical shift has been found to be 9.03 and 8.64 for complexes CoL1 and CoL2 respectively and also determine the value of edge width show in table 2. The EXAFS data fitted to the experimental data in k space and R-space to determine the structural parameters like coordination number (N), Debye–Waller factor (σ2), bond length using different (Levy's, Lytle's, LSS. FT) methods and R-factor describes quality of the fit are show in Table 3. Analysis revealed that for both complexes there are six O/N atoms at ~ 2.00 Å and one C atom ~ 3.00 Å around Co(II) center. All parameter are in good agreement with standard values. Also study about Fourier Transformation of EXAFS Spectrum which is also show (Figure. 4, 5 and 6). This Fourier Transformation of EXAFS spectrum is relation between the different parts of F.T. of EXAFS spectrum associated with Cobalt metal K-edge.

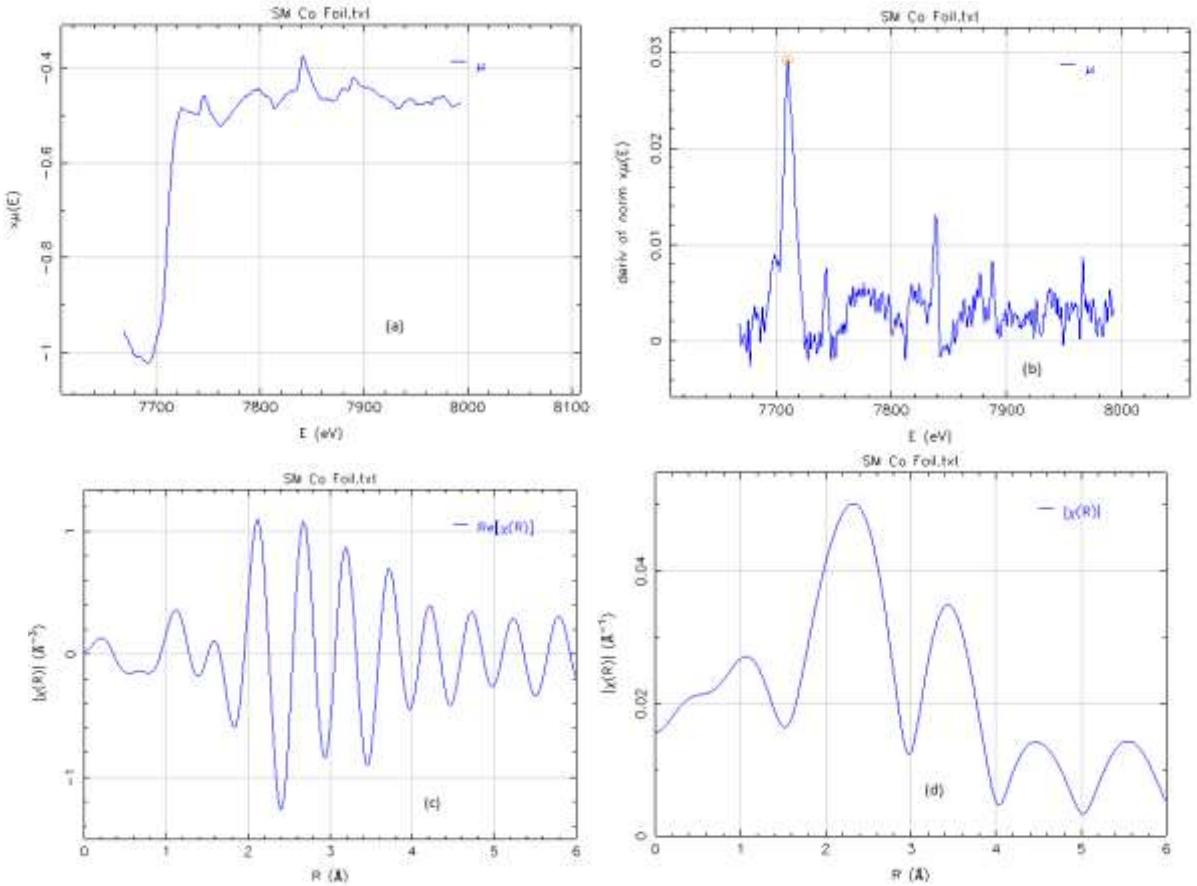


Fig. 4 EXAFS Spectra of metal foil (a) Raw absorption data (b) edge position in the corresponding derivative spectra (c) Real part of the Fourier transform (d) Magnitude of the Fourier transform.

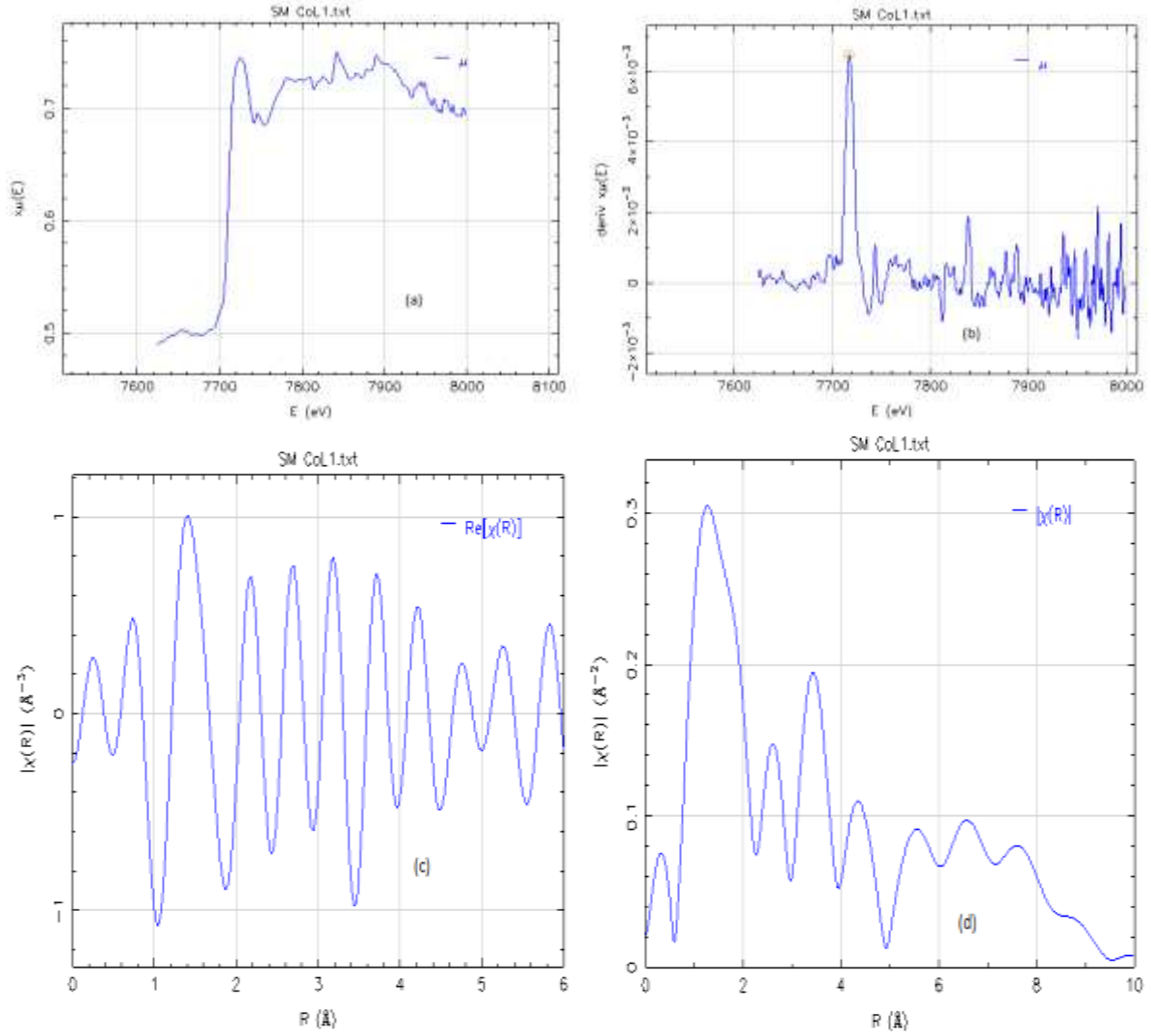
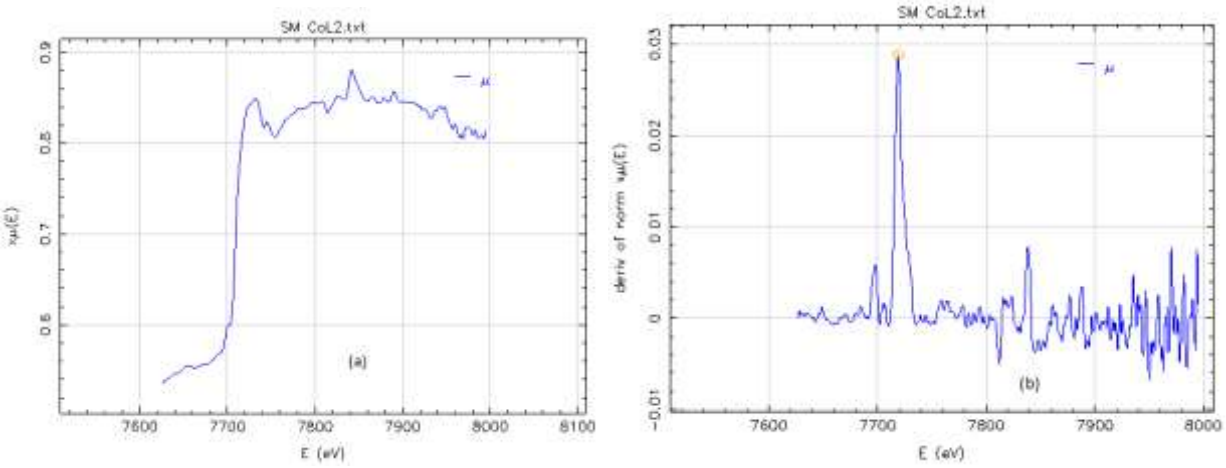


Fig. 5 EXAFS Spectra of CoL1 (a) Raw absorption data (b) edge position in the corresponding derivative spectra (c) Real part of the Fourier transform (d) Magnitude of the Fourier transform.



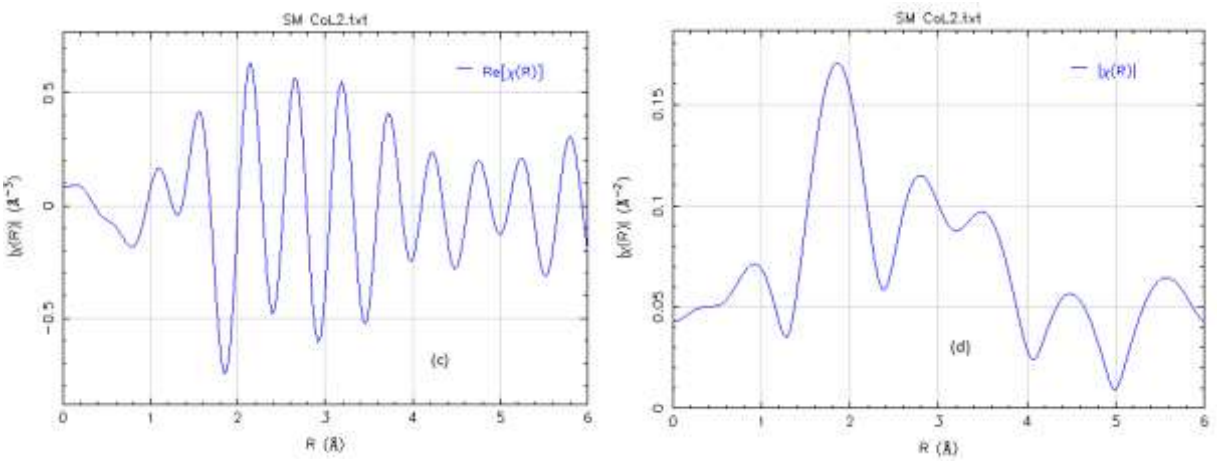


Fig. 6 EXAFS Spectra of CoL2 (a) Raw absorption data (b) edge position in the corresponding derivative spectra (c) Real part of the Fourier transform (d) Magnitude of the Fourier transform.

Table 2 XANES data for the K-absorption edge of CoL1 and CoL2 complexes

Complex	EK (eV)	EA(eV)	Chemical shift ΔEK(eV)	ENC	Shift in principal absorption maxima (eV)	Edge width (eV)
Co metal	7709.92	7726.01	-	-	-	16.09
CoL1	7718.953	7733.43	9.033	0.95	7.42	14.47
CoL2	7718.56	7733.12	8.64	0.97	7.11	14.56

Table 3 Structural parameters obtained from EXAFS of both Complexes. N=coordination number, σ^2 =Debye Waller factor, R-factor, Bond length

Complexes	Atom	N	σ 2(Å)	R-factor	Bond length			
					Phase corrected Method		Phase uncorrected Method	
					Lvey's R1	Lytle's RS	LSS R1-α1	FT R
CoL1	O/N C	4 2	0.0035 0.0034	0.001	2.23 3.1	1.73 2.17	1.42 1.86	1.3 2.6
CoL2	O/N C	4 2	0.0038 0.0036	0.002	2.5 3.4	1.82 2.3	1.54 1.84	1.85 2.8

CONCLUSION

We have to conclude that the synthesis and characterization of a new macrocyclic Schiff base complex containing bidentate O, N Schiff base ligand. The complex shows tetrahedral N2O2 coordination sphere around the Cobalt (II) with two N, O coordination. The XRD analysis shows that both Cobalt (II) complexes possess crystalline nature with monoclinic crystal lattice. An extra ordinary techniques, such as X-ray absorption spectroscopy, which are able to provide structural information even for poorly crystalline or amorphous samples are invaluable tools in coordination chemistry. In XANES, the splitting of edges and the values of the chemical shifts suggest that cobalt is in +2 oxidation state in the complexes. It has been observed that the values of bond length determined from Levy's, Lytle's, and Lytle, Sayers and Stern's (L.S.S.) method are in good agreement with Fourier transform method. The all results indicate that the studied complexes should be appropriate for application in medical field.

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