SYNTHESIS, XRD AND XANES SPECTRAL INVESTIGATION OF BIOLOGICALLY ACTIVE COBALT (II) SCHIFF BASE COMPLEXES

Mona Gupta[*]
Pradeep Sharma[**]
Ashutosh Mishra[***]

Abstract

Keywords:

Schiff base ;
Metal complexes;
XRD;
XANES;
p-methoxy benzaldehyde;
α-aminonitrile.

Few Cobalt (II) complexes of the ligands of Schiff base have been synthesized. These ligands has been prepared by Strecker's method at room temperature which included the reaction of p-methoxy benzaldehyde with p-toludine and p-anisidine respectively.The data obtained has been analysed by XRD and XANES.XRD data analysed by the program Origin 6.0 Professional and XANES by Athena. From the experimental measurements, various important parameters have been estimated (lattice parameter, particle size, chemical shift, edge width, ENC, Percentage covalency). Particle size found to be in the range of nanometers and chemical shift in eV respectively. The XRD analysis revealed the crystalline nature of the complexes and XANES signalized the variation in ionic nature of the prepared sample.

Author correspondence:

Mona Gupta,
Doctorate Program, School Of Physics
Devi Ahilya University, Indore (M.P), Indi

1. Introduction

Nitrile, α-aminonitrile compounds and their derivatives are subjective to special attention due to their application. They act as potential ligands for a large number of metal ions. In recent decades, a number of nitrile-related enzymes are analyzed for application in synthetic fields. Significant progress has been made to understand the structure and methods of regulating hydrates containing nitrile. Their derivatives are biologically active and used as herbicides of large pharmacological agents and moreover, they are also used in the biological synthesis of chemical compounds by its microbial metabolism in certain organisms[1]. The ligands involved in the reaction called Schiff bases play an important role in coordination chemistry as they easily form stable complexes with most transition metal ions. Complexes with more than one metal center realize synthetic models of ferromagnetic interaction between metal centers that can demonstrate oxidation-reduction processes in biological systems in addition to their catalytic and biological activities [2]. Besides that, some aminonitriles were used to prepare racemic compounds[3]. Scanning of literature has revealed that there is no work has been done on the XRD and XANES of transition metal complexes of the L. Keeping this in view, the present paper describes the results of the synthesis

and the X-ray characterization- of new metal complexes of some transition metal ions Co(II) of L [(p-methyl anilino) –p- methoxy phenyl acetonitrile] and [(p-methoxy anilino) –p- methoxy phenyl acetonitrile] .

* Doctorate Program, School Of Physics, Devi Ahilya University, Indore (M.P), India
**Dept. Of Physics, Govt. Holkar Science College, Indore (M.P), India
*** School of Physics, Devi Ahilya University, Indore (M.P), India

----
----

2. Research Method

MATERIALS: -All reagents used were analytical grade purity. Metal salt; $Co(NO_3)_2$ 99% (Merck), p-methoxy benzaldehyde 99% (Merck), glacial acetic acid 99% (Merck), concentrated H_2SO_4 99% (Merck), ethanol absolute 99% (Fluka) were used as received from the suppliers. p-toluidine and p-anisidine sulfonic acid were supplied by R K Synthesis ltd. All chemicals were prepared by Strecker's method [4]. Purity as well as the progress of the reaction was checked by TLC on silica gel plate. TLC plates were visualized with UV light and/or in an iodine chamber.

PREPARATION OF LIGAND (L)

The p-methoxy benzaldehyde 0.05 moles was dissolved in 50 ml of glacial acetic acid, toluidine sulfonic acid was added in small portions to bring the pH to 2, followed by the additions of 0.05 moles of the amine. The pH was adjusted to 3-4 by adding concentrated H_2SO_4 drop wise. KSCN 0.05 mole was added to the mixture which was kept stirring. Prior to reaction work-up, the end of the reaction was checked by the disappearance of the starting material (the amine) and development of a higher spot on T.L.C. The reaction mixture was poured on ice and made slightly alkaline with ammonia. The solid product was filtered, washed several times with water and dried.

PREPARATION OF COMPLEX OF LIGAND L

A solution of a salt of the metal (II) in absolute ethanol was added to an ethanolic solution of the ligand with a continuous stirring. The molar ratio of the reactants was 2:2. Precipitation of the complex took place immediately. The product was filtered off, washed several times with ethanol and dried under vacuum[5].

(A) (B)

Fig.1. Structure of metal complexes (A*) [bis{(p-methyle anilino)-p-methoxy phenyl acetonitrile}cobalt(II)] nitrate
and   (B) [bis{(p-methyle anilino)-p-methoxy phenyl acetonitrile}cobalt(II)] nitrate*

X-RAY DIFFRACTION

The sample is irradiated with a beam of monochromatic x-rays over a variable incident angle range. The X-rays were produced using a sealed tube and the wavelength of X-ray as 0.15 nm (Cu K-alpha) having voltage 40kV and current 100mA.The X-rays has been detected using a fast counting detector based on silicon strip technology (Bruker Lynx Eye detector). Interaction with atoms in the sample results diffracted x-rays when the Bragg equation is satisfied[6]. The XRD patterns were recorded on Bruker D8 Advanced X-ray diffractometer. XRD is a resourceful, non-destructive technique that gives the perfect information about the chemical composition and crystallographic structure of materials[7]. The samples were characterized at room temperature by X-ray diffraction using Co Kα radiation. The pattern has been indexed using Joint Committee for Powder Diffraction (JCPDF) software.

X-RAY ABSORPTION NEAR EDGE STRUCTURES (XANES)

The X-ray absorption spectra at the K-edge of Cobalt and it's mixed ligand Cobalt (II) complexes have been recorded at the Dispersive Extended X-ray Absorption Fine Structure (DEXAFS) beam line, by Applied Spectroscopy Division, BARC. This beam line BL-8 has been recently commissioned at the 2.5 GeV Indus-2 synchrotron radiation source. To select a band of energy from the white synchrotron beam, a bent crystal (Si 111) polychromator is used in this beamline, which is horizontally dispersed and focused on the sample. A position sensitive CCD detector is used to record the transmitted beam intensity from the sample, thus the whole XAFS spectrum around an absorption edge takes place in a single shot. The experimental data have been analysed using the available computer software packages Athena, Hephaestus and Origin 6.0.

3. Results and Analysis

All the samples are characterized at room temperature by X-ray diffraction using Co Kα radiation. The diffraction pattern of the complexes is recorded between 2θ ranging from 10° to 80°. The particle size of the samples is estimated using the Scherrer's formula[8].
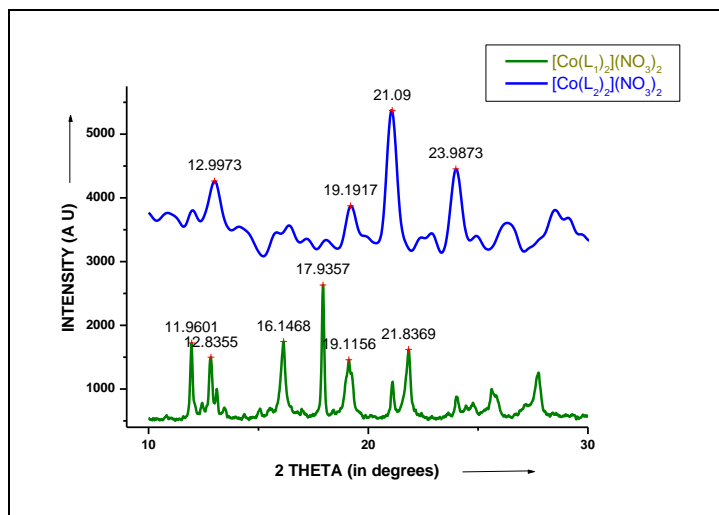

Figure 2: *X-Ray diffraction pattern of metal (II) complexes of L.*

L_1 (Ligand):- $(C_{16}H_{16}N_2O)$ [(p-methyl anilino)-p-methoxy phenyl acetonitrile]

L2 (Ligand):-$(C_{16}H_{16}N_2O_2)$[(p-methoxy anilino)-p-methoxy phenyl acetonitrile]

The particle size is given by Scherrer's equation

$$t = \frac{0.9\lambda}{B\cos\theta} \quad \text{................................... (4.1)}$$

Where t is the crystal thickness (in nm), B is half width (in radians), θ is the Bragg angle and λ is the wavelength. The particle size corresponding to each diffraction maxima is determined from the measurement of the half width of the diffraction peak (FWHM).

Lattice parameter for simple cubic crystal structure is determined by

$$a^2 = \frac{h^2 + k^2 + l^2}{4\sin 2\theta} \quad \text{........................(4.2)}$$

The value of Lattice parameter and the particle size are shown in 'table 1' for both the complexes.

Table-1
Calculated Lattice Parameter and particle size of metal (II) Complexes of series I

S.No.	Complexes	Lattice Parameter a(nm)	Particle Size t (nm)
1.	$[Co(L_1)_2](NO_3)_2$	.03	0.5
2.	$[Co(L_2)_2](NO_3)_2$	0.04	0.7

The The range of particle size (a) for the series is 0.03 to 0.04 (nm)

$$a_{[Co(L1)2\ ](NO3)2]} < a_{[Co(L1)2\ ](NO3)2]}$$

The range of thickness (t) for the series is 0.53   to   0.72 (nm)

$$t_{[Co(L1)2\ ](NO3)2)]} < t_{[Co(L1)2\ ](NO3)2]}$$

Figure 3
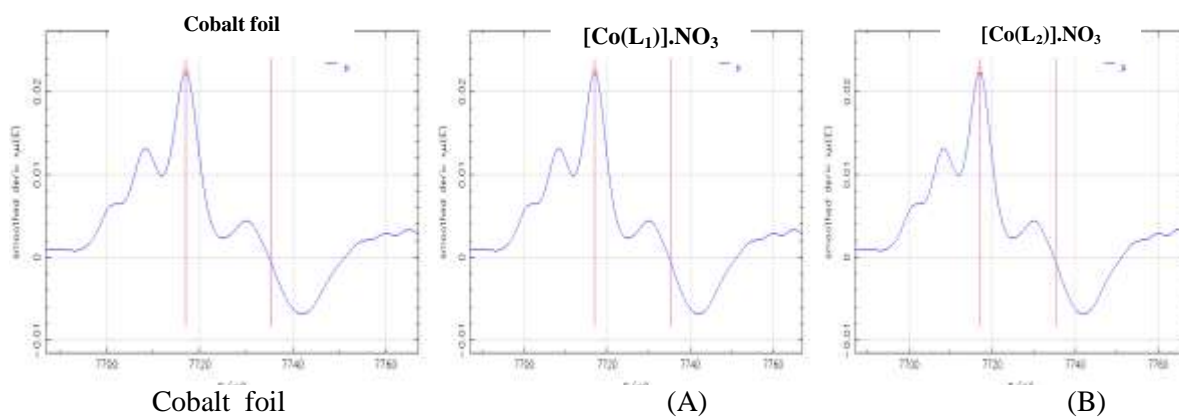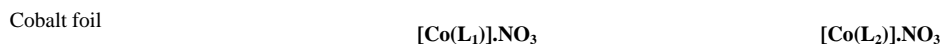*Derivatives of the Cobalt foil & its Complexes*

Cobalt foil   (A)   (B)

Figure 4
Normalised graphs of the Cobalt Foil & its Complexes

Cobalt foil $[Co(L_1)].NO_3$ $[Co(L_2)].NO_3$

(a) Cobalt foil   (b)L_1(Ligand) Complex   (c) L_2
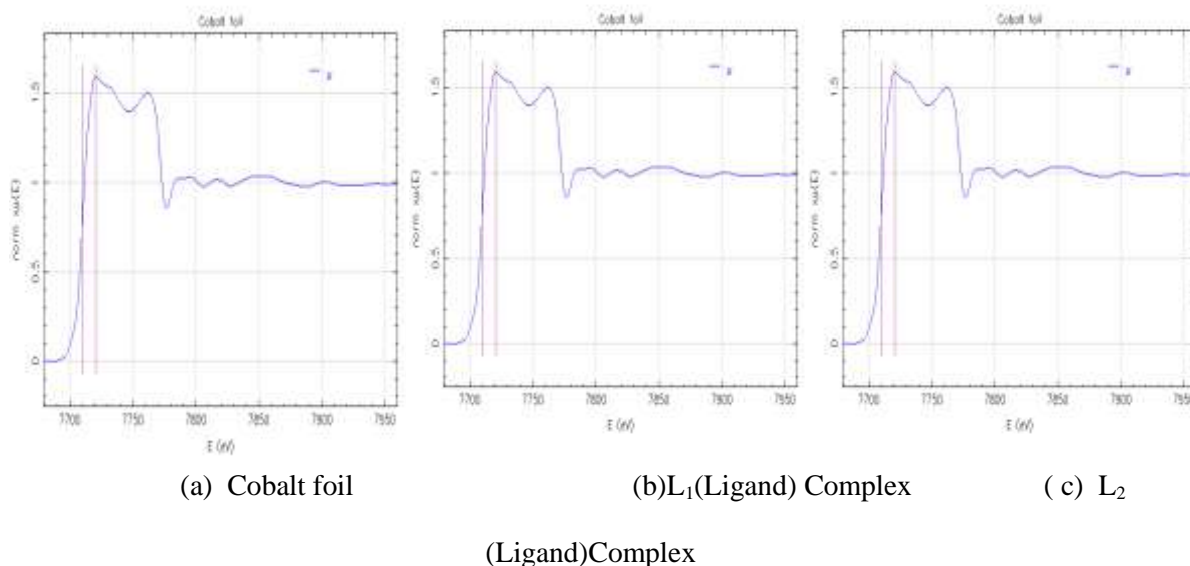
(Ligand)Complex

Table 2
XANES parameter of the Cobalt & its complexes

samples	Abbreviation	Ek (eV)	EA (eV)	chemical shift (eV)	shift of principal absorption maxima (eV)	edge width (eV)	ENC	% covalancy
Co Foil		7709.85	7720.71	0.0	10.9	10.9	0.0	40.2
Co 11	$[Co(L_1)_2](NO_3)_2$	7717.1	7735.22	7.3	25.4	18.1	0.5	67.1
Co12	$[Co(L_2)_2](NO_3)_2$	7719.86	7730.42	10.0	20.6	10.6	0.7	39.1

The range of Chemical shift and Shift of principal absorption maxima is 7.8 to 8.4eV and 20.7 to 22.4 eV respectively. For the complexes, the range of the shift of the principal absorption maximum is between 20.7 to 22.4 eV. Edge widths decreased with respect to pure metal foil almost 6-3 eV. i.e (B) complex is less ionic than the (A) .The chemical shift has been used to determine the effective nuclear charge of the absorbing atom. For all the complexes, the range of effective nuclear charge is between 0.58-0.54 electron/atom. The chemical shift has also been used to determine the percentage covalency on the absorbing atom. For both the complexes, the range of percentage covalency is between 43 - 50 % approx.   The shift of the principal absorption maximum has been obtained. The shift of the Principal absorption maximum is inversely proportional to the ionic character for these complexes.The edge-width has also been obtained for the complexes. It is clear that the edge-width is inversely proportional to ionic character for these series of complexes[9]. For both the complexes, the range of edge-width is between 12.4 – 14.6 eV. i.e B is less ionic than A.which is also verified by shift in principal absorption maxima values. The values of the chemical shifts lies under 10 eV which suggests that Cobalt is in oxidation state +2[11].

4. Conclusion

The XRD pattern is indicative of their crystalline in nature which is confirmed by the main peaks positioned Obtained for synthesised complexes. XRD analysis informs about the particle size in **(nm) &** lattice parameter in **(nm) for** [*Co (II)*] complexes. The range of particle size (a) for the samples: 0.03 to 0.04 (nm) & the range of thickness (t) is 0.5 to 0.7 (nm) approx respectively.

$$a_{[Co(L1)2](NO3)2]} < a_{[Co(L2)2](NO3)2]}$$
$$t_{[Co(L1)2](NO3)2)]} < t_{[Co(L2)2](NO3)2)]}$$

The main conclusion is that the behaviour of the same metal salt is different with the different ligand $(C_{16}H_{16}N_2)$ [(p-methyl anilino) -p-methoxy phenyl acetonitrile] & $(C_{16}H_{16}N_2O)$ [(p-methoxy anilino) -p-methoxy phenyl acetonitrile] from aldehyde group. After complex formation each sample has different lattice parameter as well as their thickness. The lattice parameter is least in Cobalt complex with ligand L_2 while it is highest for the Cobalt with L_1 Similarly for the thickness . The X-ray analysis reveals that the sample is cubic in structure as seen from the presence of extra peaks in XRD pattern. All the peaks match with the software JCPDF.

The order of chemical shift in each of complexes may also be taken as representative of the relative ionic character of the bonding[10] in these complexes i.e later complex is less ionic than first one .The values of the chemical shifts lie in between 7.8 to 8.4eV which suggests that Cobalt is in oxidation state +2 .

References

[1]   Wong, C.H. and Whitesides, G.M., "*Enzymes in Synthetic Organic Chemistry,"* Elsevier, 1994.
[2]   Kobayashi, M. and Shimizu, S., "Nitrile hydrolases," *Currs Opin Chem Bio.*, vol. 4, no. 1, pp. 95–102, Feb
          2000.
[3]   Kouznetsov, V.V., and Galvis, C.E.P., "Strecker reaction and α-amino nitriles: Recent advances in their
          chemistry, synthesis, and biological properties," *Tetrahedron*, vol. 74, no. 8, pp. 773–810, Feb 2018.
[4]   Harusawa, S., Hamada, Y., and Shioiri, T. "Diethyl phosphorocyanidated (DEPC). A novel reagent for the
          classical Strecker's α-amino nitrile synthesis," *Tetrahedron Lett.*, vol. 20, no. 48, pp. 4663–4666, Jan 1979.
[5]   Majeed, R. A., "Synthesis and Characterization of New Metal Complexes of α - Aminonitriles Derived from P-Methoxybenzaldehyde with Aromatic Amines," *Pure & Appl Sci vol., 22 (2) 2009*.
[6]   Das, J., Moholkar, V.S., and Chakma, S. "Structural, magnetic and optical properties of sonochemically
          synthesized Zr-ferrite nanoparticles," *Powder Technol.*, vol. 328, pp. 1–6, Apr 2018.
[7]   Lee, A.Y. D., Park, Y., and Jeong, M.S. "Correlational study of halogen tuning effect in hybrid perovskite
          single crystals with Raman scattering, X-ray diffraction, and absorption spectroscopy," *J. Alloys Compd.*, vol.
          738, pp. 239–245, Mar 2018.

[8]   Oueslati, H., Rabeh, M. B., and Kanzari, M. "Effect of thermal annealing on the structural and optical properties

of Cu_2FeSnS_4 thin films grown by vacuum evaporation method," *Appl. Phys. A*, vol. 124, no. 2, p. 201, Feb.

2018.

[9]   Yamamoto, T., and Yukumoto, A. "Discrepancy in the quantitative oxidation-state analysis of Eu species in sulfide phosphors by K-, L1- and L3- edge XANES spectrometry: choice of absorption edge and measurement mode - Journal of Analytical Atomic Spectrometry, Mar 2018.

[10]   Magnuson, M., Tengdelius, L., Greczynski, G., Hultman, L., and Högberg, H. "Chemical Bonding in Epitaxial

ZrB2 Studied by X-ray Spectroscopy," *Thin Solid Films*, vol. 649, pp. 89–96, Mar 2018.

[11]   Gupta, M., Sharma, P., and Mishra, A. " XRD and XANES characterisation of schiff base Cu(II) complex of

alpha amino   nitrile", "Optics,Photonics and Synchrotron Radiation", April 28- May 2, RRCAT Indore, abstract no OPSR- 94, May 2018.