

Determination of some X-ray near Edge parameters of Nickel (II) Complexes of Schiff base ligands

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ABSTRACT

Three nickel (II) complexes of Schiff base ligands, L1 = (P-methoxy anilino)-P- methoxy phenyl acetonitrile, L2 = (P-methoxy anilino)- phenyl acetonitrile and L3 = (P- methoxy anilino) –P– chloro phenyl acetonitrile have been prepared by the condensation of P-methoxybenzaldehyde, benzaldehyde and P-chloro-benzaldehyde with P-anisidine respectively. The mentioned three ligands L1, L2 and L3 were used to prepare three nickel (II) complexes Ni-21 = [Ni₂(p-Methoxy ben)(p-Ani)](NO₃)₂, Ni-22 = [Ni₂(ben) (p-Ani)](NO₃)₂ and Ni-23 = [Ni₂(p-Chloro ben)(p-Ani)](NO₃)₂ respectively. X-ray k-Absorption Near Edge (XANES) spectra of these three complexes have been recorded at RRCAT (Raja Ramanna Center for Advance Technology), Indore, M.P, India by using Synchrotron radiation source. Various X-ray absorption parameters e.g., chemical shift, edge-width and shift of the principal absorption maximum have been obtained with the help of XANES spectra. Data analysis program Athena and the computer software Origin 6.0 professional have been used to process the obtained data. The results of the study have been reported in this paper.

Keywords: Schiff base, XANES, RRCAT, Athena, Origin 6.0

I. INTRODUCTION

Aminonitrile compounds are documented species for its biologically activity like pharmaceutical interest and biocatalysis in industrial synthesis. 1-3 They were also used as synthetic activating transcription for the explanation of biological reaction. It is identified as biologically inhibitors. 4-7 Aminonitrile is potentially a chelating ligand. 8-9 α -Amino nitriles were first prepared by Strecker by treating aldehydes or ketones with alkaline cyanide and salts of amines. 10 The ligands - L1 = (P-methoxy anilino)-P- methoxy phenyl acetonitrile, L2 = (P-methoxy anilino)- phenyl acetonitrile and L3 = (P- methoxy anilino) –P– chloro phenyl acetonitrile which included the reaction of P-anisidine with P-methoxybenzaldehyde, benzaldehyde and P-chloro-benzaldehyde respectively were synthesized by a modified Strecker's procedure. 11-12 XANES and EXAFS studies of some of the Cu(II) and Co (II) complexes of P-methoxybenzaldehyde, benzaldehyde, P-chloro-benzaldehyde with P-anisidine and P-toluidine have been already discussed in previous literature. 13-20 A search through literature reveals that no work has been done on the XANES of nickel(II) complexes of P-

methoxybenzaldehyde, benzaldehyde, P-chloro-benzaldehyde with P-anisidine . Keeping this in view, we have studied X-ray K absorption spectra of nickel in the nickel complexes. The results of the study have been reported in this paper.

II. METHODS AND MATERIAL

Three nickel (II) complexes of Schiff base ligands, L1 =(P-methoxy anilino)-P- methoxy phenyl acetonitrile, L2 = (P-methoxy anilino)- phenyl acetonitrile and L3 = (P- methoxy anilino) –P– chloro phenyl acetonitrile have been prepared by the condensation of P-methoxybenzaldehyde , benzaldehyde and P-chloro-benzaldehyde with P-anisidine respectively. The three complexes studied in the present investigations are Ni 21= [Ni2(p-Methoxy ben)(p-Ani)](NO3)2 , Ni 22 = [Ni2(ben) (p-Ani)](NO3)2 and Ni 23 = [Ni2(p-Chloro ben)(p-Ani)](NO3)2 respectively. All the three complexes were synthesized according modified Strecker's procedure and their purity was checked. 11-12 The X-ray absorption spectra at the K-edge of nickel (II) complexes have been recorded at the Dispersive Extended X-ray Absorption Fine Structure (DEXAFS) beamline, which has been recently set-up by Applied Spectroscopy Division, BARC at the Indus-2 synchrotron radiation source at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore.21-23 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. The crystal is bent in the shape of an ellipse in such a way that source and sample positions are at the two foci of the ellipse. The position sensitive

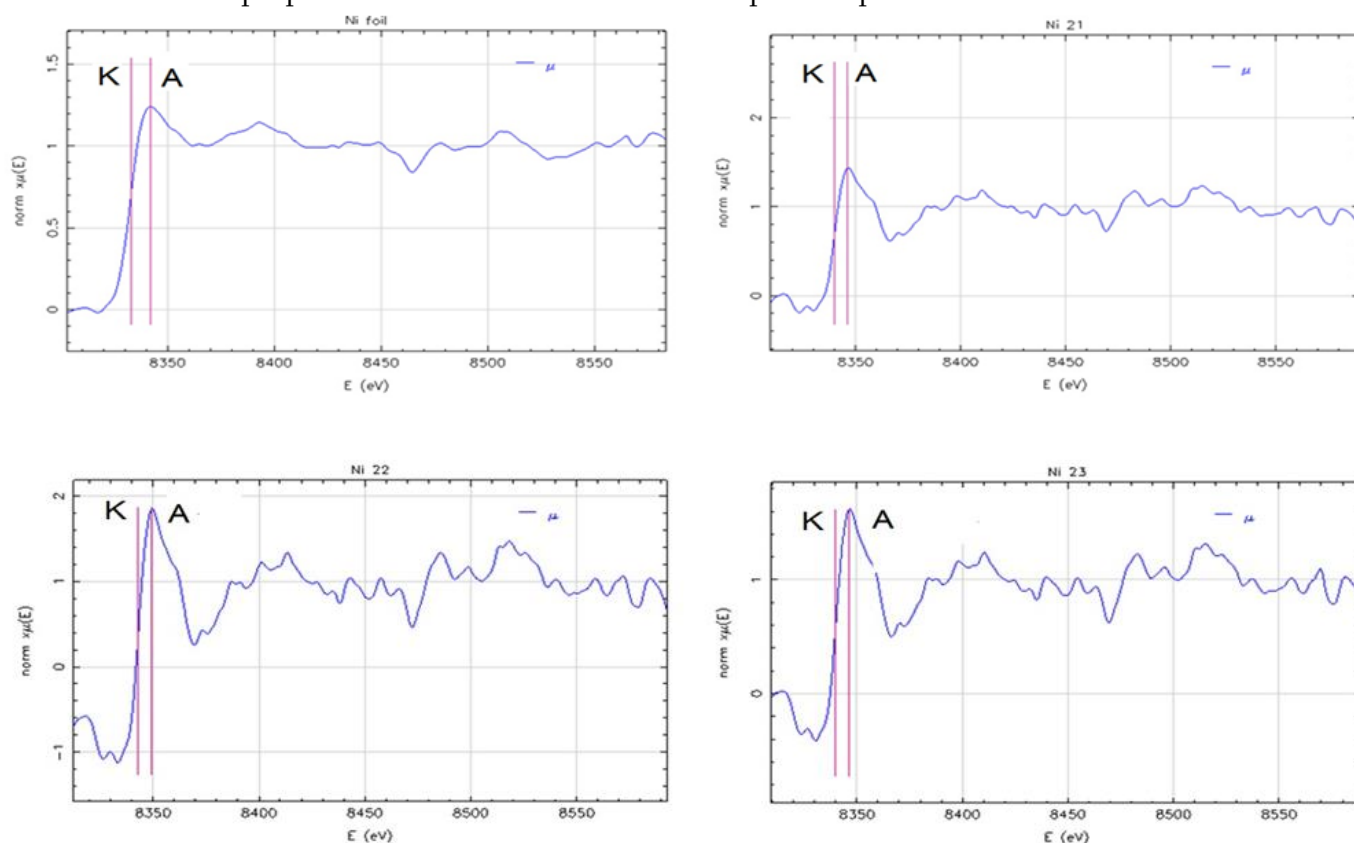


Fig.1. Metal K-edge XANES E(eV) Vs normalized $\mu(E)$ spectra for the metal complexes

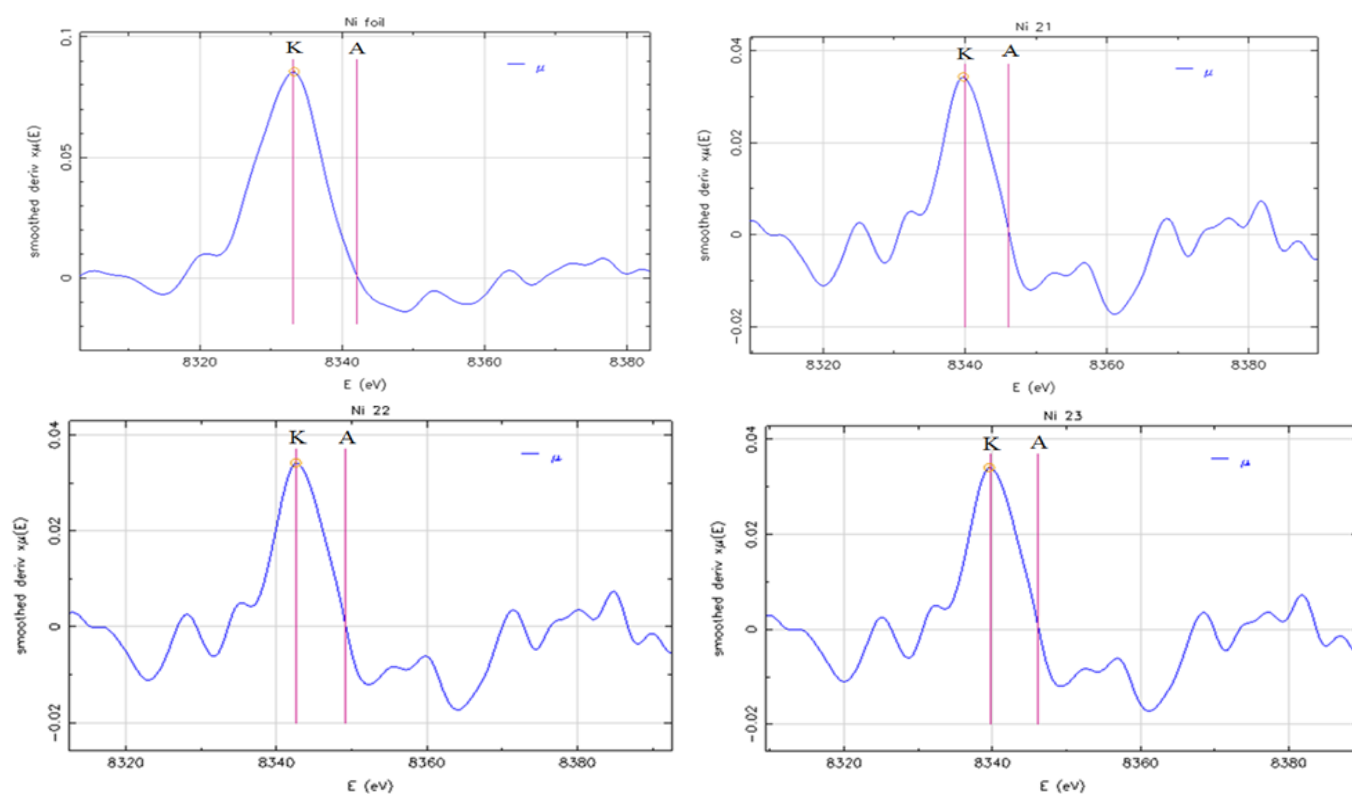


Fig.2. Derivative of the XANES region of the absorption spectrum at the K- edge of metal in the complexes indicating positions of the absorption edge K and the principal absorption maxima A.

Table 1. XANES data for the K absorption edge of metal in the complexes

Complexes		E_k value(eV)	E_A (eV)	Chemical shift (eV)	Shift of principal maxima (eV)	Edge width (eV)	ENC (eV) Electron atom	% covalency
Ni foil	Metal	8333.2	8342.2	-	-	-	-	-
Ni 21	[Ni 2(p-Methoxy ben) (p-Ani)](NO ₃) ₂	8340.0	8346.1	6.8	3.9	6.1	0.71	65.15
Ni 22	[Ni 2(ben) (p- Ani)] NO ₃) ₂	8342.7	8349.2	9.5	7.0	6.5	0.91	42.10
Ni 23	[Ni 2(p-Chloro ben) (p-Ani)] (NO ₃) ₂	8339.0	8346.0	5.8	3.8	7.0	0.63	68.38

III. RESULTS AND DISCUSSION

The normalized K absorption spectra for nickel metal and all the three complexes are shown in Fig 1. The first derivative of the spectra, indicating positions of the absorption edge K and principal absorption maximum A are shown in Fig. 2. The energies of the cobalt K-edge (E_K) and the principal absorption maximum (E_A) alongside the values of the edge-width ($E_A - E_K$), effective nuclear charge Z_{eff} and therefore the chemical shift ΔE_K are

given in Table 1. It can be readily seen from the table that nickel k-edge is found to be shifted towards the high-energy side in all the complexes, as compared with the nickel metal k- absorption edge.

3.1. Chemical Shift

The shift of the X-ray absorption edge of an element in a complex with respect to that of the pure element is written as:

$$\Delta EK = EK(\text{complex}) - EK(\text{metal})$$

For computing the chemical shift, the value of EK(Ni metal) has been taken as 8333.2 eV. For the complexes under study, the order during which the ligands contribute to the chemical shift is:

$$\text{Ni 23} < \text{Ni 21} < \text{Ni 22}$$

Thus it is clear from the data that the value of the chemical shifts in all the three complexes is more than 5 eV. Hence, on the basis of values of the chemical shifts, the complexes are found to have nickel in oxidation state +2.

3.2. Principal absorption maximum

The shift of principal absorption maximum of an element in a complex with respect to that of the pure element is written as:

$$\Delta EA = EA(\text{complex}) - EA(\text{metal})$$

The principal absorption maximum EA of copper metal has been taken as 8342.2 eV for computing the shift. It has been observed that for all the three complexes, the value of EA is shifted towards the higher energy side.

3.3. Edge-width

The edge-width is computed by (EA-EK). In Table 1, we have reported the values of the edge-width. The edge-width values are 6.1, 6.5 and 7.0 eV, respectively for Ni 21, Ni 22 and Ni 23.

3.4. Effective nuclear charge [Z_{eff}]

Various methods have been proposed for the estimation of effective nuclear charge.²⁷⁻²⁸ By employing the procedure which was suggested by Nigam and Gupta, Z_{eff} has been obtained from the measured chemical shift by using the semi-experimental method.²⁹ The effective nuclear charge on the nickel in the complexes under present study is 0.71, 0.91 and 0.63 electrons/atom respectively for Ni 21, Ni 22 and Ni 23. The order for Z_{eff} in the complexes is as follows:

$$\text{Ni 23} < \text{Ni 21} < \text{Ni 22}$$

The order is found to be same as that of order of chemical shift. The results show that chemical shift increases with ENC. A parabolic co-relation is observed between them.

3.5. Percentage covalency

Percentage covalency of studied three nickel complexes is 65.15, 42.1 and 68.38 % respectively for Ni 21, Ni 22 and Ni 23. The order for percentage covalency in the complexes is as follows:

$$\text{Ni 23} > \text{Ni 21} > \text{Ni 22}$$

Inverse relation is observed between percentage covalency and chemical shift, i.e percentage covalency decreases as chemical shift increases. A parabolic co-relation is observed between them.

Similar relation is observed between percentage covalency and effective nuclear charge i.e percentage covalency decreases as effective charge increases. A parabolic co-relation also observed between them.

IV. CONCLUSIONS

X-ray absorption spectra of schiff base nickel complexes at the K-edge of nickel are recorded at the EXAFS beamline setup at the Indus-2 synchrotron source at RRCAT, Indore. The energy of K-edge (EK), and principal absorption maxima (EA) alongside the allied parameters are reported. The shift of the K-edge (chemical shift), shift of the principal absorption maximum and edge-width has been obtained from the allied parameters. The chemical shift has been used to determine the effective nuclear charge on the absorbing atom. Reported chemical shifts suggest that nickel is in oxidation number +2 altogether of the complexes.

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V. REFERENCES

- [1]. Schoemaker, H.E., Mink, D. and Wubbits, M.G. (2003). Dispelling the Myths – Biocatalysis in industrial Synthesis, *Science*. 299(5613), 1694- 1697.
- [2]. Perrier, V.; Wallace A.C., Kaneko, K., Safar, J. and Prusiner, S.B. (2000). Mimicking dominant negative inhibition of prion replication through structure –based drug design. *Proc. Natl. Acad. Sci. USA*, 23;97(11), 6073-8.
- [3]. Kalir, A., Edery, H., Pelah, Z.D. and Porath, G. (1969). 1-Phenylalkyl amine Derivatives. II Synthesis and Pharmacological Activity. *J. Med. Chem.* 12, 473 - 477.
- [4]. Meyers, M.J., Sun, J., Carlson, K.E., Marriner, G.A., Katzenellenbogen, B.S. and Katzenellenbogen, J.A. (2001). Estrogen receptor –beta potency-selective ligands: structure –activity relationship studies of diarylpropionitriles and their acetylene and polar analogues. *J. Med. Chem.* 22(44)24, 4230-51.
- [5]. Favata, M.F., Horiuchi, K.Y., Manos, E.J., Daulerio, A.J., Stradella, D.A., Feese, E.S., Vandyk, D.E., Pitts, W.J., Earl, R.A., Hobbs, F., Copeland, R.A., Magolda R. L., Scherle, P.A. and Trzaskos, J.M. (1998). Identification of a novel inhibitor of mitogen-activated protein kinase kinase. *J. Biol. Chem.* 17(273)29, 18623-32.
- [6]. Duncia, J.V., Santella, J.B., Higley, C.A, Pitts, W.J., Wityak, J., Fietze, W.E., Pankin, F.W. and Sun, J.H. (1998). MEK inhibitors: the chemistry and biological activity of UO123, its analogs, and cyclization product. *Bio. Org. Chem. Lett.* 20(8)20, 2839-46.
- [7]. Patel, R.N., Banerjee, A., Nivaduri V.B., Goldberg, S.L., Johnston, R.M., Hanson, R.L. and McNamee, C.G. (2000). Biocatalytic Preparation of a chiral synthon for a vasopressinase inhibitor: enzymatic conversion of N²-[N-(Phenylmethoxy) Carbonyl] L-homocysteinyl]-L-lysine (1- α')-disulfide to [45-(41,71,10 a)] – octahydro-5-oxo-4-[phenylmethoxy) carbonyl] amino]-7H-Pyrido [2,1-b] [1,3] thiazepine -7-carboxylic acid methyl ester by a novel L-lysine α -aminotransferase. *Enzyme and Microbial Technology*, 27. Issue 6, 376 - 389.
- [8]. Njoroge, F.G., Vibulbhan, B., Alvarea, C.S., Bishop, W.R., Pertin, J., Doll, R.J., Girijavallabhan V. and Ganguly, A.K. (1996). Novel tricyclic aminoacetyl and sulfonamide inhibitors of Ras farnesyl protein transferase. *Bioorganic and Medicinal Chemistry Letters*. 6, Issue 2, 2977-2982.

- [9] . Van Nhien, A.N., Pillon,M., Villa, P. and Ronco,G. (2000). Stereoselective Synthesis of aminonitriles at non-anomeric positions of monosaccharides. *Tetrahedron Letters* .41,Issue 33, 6403-6406.
- [10] . a) Harusawa,S., Hamada Y. and Saiori,T. (1979). *Tetrahedron Letters*, 48, 4663-4666. b) Ogata ,Y. and Kawasaki, A. (1971). Mechanistic Aspects of the Strecker Aminonitrile Synthesis. *J.Chem. Soc. (B)*, 4, 325-329.
- [11] . Kalir,A., Ederay, H., Pelah,Z., Baldormon D. and Porath,G. (1969). 1-Phenylcycloalkylamine derivatives. II. Synthesis and pharmacological activity *J. Med.Chem.*,12, 473-477.
- [12] . Wyatt J.M and Linton, E.A. (2007). *John wiely, Inter science online Book*.
- [13] . Jaishree Bhale, Pradeep Sharma, A.Mishra, (2017). EXAFS Study of Copper (II) Complexes of Aeromatic Aldehydes. *IJSRD*, Vol. 5(2), 1039- 1042.
- [14] . Jaishree Bhale, Pradeep Sharma, A.Mishra. (2017). XAFS Study of Copper (II) Complexes of P Anisidine. *IJIRST*, Vol 3(12), 94- 101.
- [15] . Jaishree Bhale, Pradeep Sharma and A.Mishra.(2017). XANES Study of Copper (II) Complexes of Aeromatic Amines. *IJSRD*, Vol. 5(2), 736- 739.
- [16] . Jaishree Bhale, Pradeep Sharma, A.Mishra and ,S.Ninama. (2016). X-ray Spectral Study by EXAFS of Some Copper (II) Complexes using Synchrotron Radiation Source. *IJCPS*, Vol. 5(2), 17-22.
- [17] . Jaishree Bhale, Pradeep Sharma and A.Mishra (2015). XANES Study of Copper (II) Mixed Ligand Complexes of alpha-Aminonitrile. *IJMPSR*, Vol. 2(2), 203-210
- [18] . Jaishree Bhale, Pradeep Sharma, A. Mishra and Neetu Parsai. (2015). XANES Study of New Copper (II) Complexes of α -aminonitrile Derived from p- methoxybenzaldehyde with p-anisidine. *ISROSET- Int. J. Sci. Res. Physics and Applied Sciences*, Vol-3(1), 40-42.
- [19] . Jaishree Bhale, Pradeep Sharma, A. Mishra, Neetu Parsai.(2015). Determination of bond length from EXAFS spectra of some copper(II) mixed ligand complexes. *ISROSET*, Vol-3(3), 1-3.
- [20] . Jaishree Bhale, Mona Gupta, Pradeep Sharma, A. Mishra. (2020). Xanes Study Of Some Cobalt (II) Complexes Of Aldehydes. *Aayushi International Interdisciplinary Research Journal* , Special Issue No.70, 236-240.
- [21] . N. C. Das, S. N. Jha, D. Bhattacharya, A. K. Poswal, A. K. Sinha and V. K. Mishra,(2004). Design, Fabrication and Testing of Elliptical Crystal Bender for the EXAFS Beam Line at INDUS-II Synchrotron Source. *Sadhana* , vol 29(5), 545.
- [22] . D. Bhattacharya, A. K. Poswal, S. N. Jha, Sangeeta, S. C. Sabharwal (2009). X-ray absorption spectroscopy of PbMoO₄ single crystals. *Bull. Mater. Sci.*, vol 32, 1-5.
- [23] . D. Bhattacharya, A. K. Poswal, S. N. Jha, Sangeeta, S. C. Sabharwal (2009). First Results From a Dispersive EXAFS beamline developed at INDUS-2 Synchrotron Source at RRCAT, Indore, India. *Nuclear Instruments and Methods in Physics Research A*, vol 609, 286.
- [24] . Ravel B and Newville M (2005). Athena, Artemis, Hephaestus: data analysis for X-ray absorption spectroscopy using IFEFFI. *J Synchrotron Rad*, vol.12, (4), .537-541 .
- [25] . L. S. Kau, D. J. Spira-Solomon, J. E. Penner-Hahn, K. O. Hodgson, and E. I. Solomon. (1987). *J. Am. Chem. Soc.*, Vol 109, 6433-6442.
- [26] . B.K Teo.(1986). EXAFS: Basic Principles and data analysis, Springer- Verlag, Berlin.
- [27] . Gianturco and C.A.Coulson.(1968). Inner-electron binding energy and chemical binding in S. *Mol Phys*, vol.14,(3), 223- 232 .

- [28] . H.-U. Chun. (1970). Determination of atomic charges in compounds of the 3rd period elements by means of X-ray spectroscopy. Physics Letters A, vol.31(3), 118-119.
- [29] . Nigam A K and Gupta M K . (1974). X-ray K absorption edge of copper in some of its compounds J. Phys. F: Metal Physics , vol 4, 1084.