

X-ray absorption near-edge structure study of benzil bis *o*-phenylenediamine based macro cyclic Cu-complexes

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Available online at: www.isroset.org

Received: 06/Jun/2018, Revised: 12/Jun/2018, Accepted: 21/Jun/2018, Published: 30/Jun/2018

Abstract— Schiff base condensation of benzil bis *o*-phenylenediamine with acetophenone, benzophenon, acetone, benzaldehyde and *p*-chlorobenzaldehyde and its Copper complexes were synthesised. Preparation of the free ligands was accomplished by refluxing benzil with *o*-phenylenediamine in 1:10 mole ratio in methanol. XANES spectra have been recorded at the K-edge of Cu using the dispersive beam line at 2.5GeV Indus-2 synchrotron radiation source RRCAT(Raja Ramanna Centre for Advance Technology), Indore, India. The K-absorption (E_K) and the energy of the principal absorption maximum (E_A) of copper metal and its complexes, edge width and effective nuclear charge were determined in the current study. These studies build prominent interaction between various parameters for the Cu-complexes. XANES data have been analysed using the computer software Athena and Origin. The values of the chemical shifts specify that copper is in oxidation state +2 in all of the complexes.

Keywords— Benzil bis *o*-phenylenediamine, Benzophenon, Athena.

I. INTRODUCTION

Schiff bases of *o*-phenylenediamine and its complexes have a variety of application including clinical, analytical and biological. Schiff bases derived from the salicylaldehydes are well known as polydentate ligands coordinating in neutral forms. [1,2] In the present work Schiff base condensation of benzil bis *o*-phenylenediamine with acetophenone, benzophenon, acetone, *p*-chlorobenzaldehyde and benzaldehyde and its Cu complexes were synthesised. Schiff base condensation of bis *o*-phenylenediamine with suitable aldehydes and ketones would form a macro cyclic and macro acyclic molecules which will have more number of nitrogen atoms, and this will behave as better coordinating ligands for variety of metal atoms [3]. X-ray absorption spectroscopy has been extensively used to obtain information about the molecular structure viz. the oxidation state and the effective nuclear charge of the absorbing atom in compounds and complexes.

Hence the synthesis and characterization of Characterization of benzil bis *o*-phenylenediamine based macro cyclic Cu-complexes was undertaken [4]. Paper has been written into four distinct sections, Introduction, Methodology, Results and discussion and Conclusions. Introduction section contains a brief review of literature survey related to the present work, motivation and scope of the work. The section on methodology contains sample preparation and measurements techniques. Results and discussion section deal with the results, analysis and discussion. Conclusion part narrates the major conclusions drawn from the results.

II. METHODOLOGY

Preparation of benzil bis *o*-phenylenediamine

Benzil (10.5 g, 50 mmol) was dissolved in 100 ml of methanol and *o*-phenylenediamine (54.05g, 500mmol) was added to it. The resulting solution was refluxed for 3 h and then it was left in the air. After 20 h the precipitated white microcrystalline compound was filtered off and washed with 100 mL of water. The compound was dried in air.

Synthesis of macro cyclic complexes:

Synthesis of $[\text{Cu}(\text{C}_{66}\text{H}_{56}\text{N}_8)]\text{Cl}_2$ or (Cu-AP)

Acetophenone (1.2 g, 10mmol) was added to a solution of CuCl_2 (0.55g, 5mmol) in 15 mL of methanol. To this solution, benzil bis *o*-phenylenediamine (3.9g, 10mmol) was added. The solution was stirred for 1h and 30 minutes at room temperature. Finally the precipitates were dried in air.

Synthesis of $[\text{Cu}(\text{C}_{64}\text{H}_{52}\text{N}_8)]\text{Cl}_2$ or (Cu-BZ)

To a solution of CuCl_2 (0.11g, 1mmol) in 3mL of methanol, benzaldehyde (318.39 mg, 3mmol) was added. To this solution benzil bis *o*-phenylenediamine (1.1g, 3mmol) was added. The reaction was refluxed for 2 h and left for precipitation.

Synthesis of $[\text{Cu}(\text{C}_{64}\text{H}_{50}\text{N}_8)]\text{Cl}_2$ or (Cu-P)

To a vigorously stirred solution of CuCl_2 (0.16g, 1.5mmol) in 4.5 mL of methanol, *p*-chlorobenzaldehyde (0.4g, 3mmol) was added. To this solution, benzil bis *o*-phenylenediamine (1.1g, 3mmol) was added. The reaction mixture was stirred for 2 h and left for precipitation.

Synthesis of $[\text{Cu}(\text{C}_{76}\text{H}_{52}\text{N}_8)]\text{Cl}_2$ or (Cu-BP)

To a solution of CuCl_2 (0.85g, 5mmol) in 15mL of methanol, benzophenon (1.8 g, 10 mmol) was added. To this solution benzil bis *o*-phenylenediamine (3.9 g, 10 mmol) was added. The reaction was refluxed for 2 h and left for precipitation.

Synthesis of $[\text{Cu}(\text{C}_{56}\text{H}_{52}\text{N}_8)]\text{Cl}_2$ or (Cu-AC)

To a solution of CuCl_2 (0.17g, 1mmol) in 3mL of methanol, acetone (116 mg, 2 mmol) was added. To this solution benzil bis *o*-phenylenediamine (0.78g, 2mmol) was added. The reaction was refluxed for 2 h and left for precipitation.

The X-ray absorption spectra at the K-edge of copper of these complexes have been recorded at BL-8 Dispersive EXAFS beamline at the 2.5-GeV INDUS-2 Synchrotron Source, Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India .On this beamline, the X-ray intensities I_0 and I_t are obtained as the CCD outputs without and with the sample, respectively. Using the relation, $I_t = I_0 e^{-\mu x}$, where μ is the absorption coefficient and x is the thickness of the absorber, the absorption $\mu(E)$ corresponding to the photon energy (E) are obtained. The experimental data have been analyzed using the available computer software packages Origin professional and Athena.

III. RESULTS AND DISCUSSION

The shapes of the copper K-absorption discontinuity and the associated near edge structure (XANES) for all the complexes are shown in Figure 1. The curves in this figure represent the normalized K absorption spectra. The energies of the copper K-edge (E_K) and the principal absorption maximum (E_A) along with the values of the edge-width ($E_A - E_K$), effective nuclear charge Z_{eff} and the chemical shift E_K are given in Table 1. The first peak in the derivative spectra in figure 2 gives the position of the K absorption edge (E_K). The position where the derivative is zero, gives the position of principal absorption maxima (E_A). The results of the energy of the K absorption edges (E_K) and the energies of principal absorption maximum A (E_A) of copper in metal and its five complexes are presented in Table 1. The chemical shifts (in eV) of the K absorption edge of copper in the complexes are also given in this table. For all the complexes, the distances (in eV) of the principal absorption maximum A with respect to the respective K absorption edge has also been computed and is accumulated in the same table. It can be promptly seen from table that copper K-edge is found to be shifted towards the high-energy side in all the five complexes, as compared with the copper metal K absorption edge.

3.1 Chemical Shift

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

$$E_K = E_{K(\text{complex})} - E_{K(\text{metal})}$$

For computing the chemical shift, the value of E_K (Cu metal) has been taken as 8980.1 eV [7]. In Table 1, all the five complexes have the values of chemical shifts between 7 to 13.6 eV. Hence, on the basis of values of the chemical shifts, all the complexes are found to have copper in oxidation state +2. The order for the five complexes is as follows:

$$\text{CuP} > \text{CuAP} > \text{CuBZ} > \text{CuAC} > \text{CuBP}$$

As is well known, an ionic bonding increases the chemical shift, whereas a covalent bonding suppresses it. Hence, the above order may also be taken as illustrative of the relative ionic character of the bonding in these complexes.

3.2 Effective nuclear charge Z_{eff}

In the present work, Z_{eff} has been obtained from the measured chemical shift by using the semi-experimental method by employing the procedure suggested by Nigam and Gupta [5]. A graph was plotted between the theoretical shift in the binding energy and the oxidation number for copper. The effective nuclear charge Z_{eff} on the copper atom in the complexes studied was then determined from this plot

corresponding to the measured values of the edge shifts. The effective nuclear charge on the copper in the complexes under present study varies between 0.79 – 1.27 electrons/atom.

3.3 Principal absorption maximum

In Table 1, we have also included the data for the principal absorption maximum E_A in the complexes and in the metal. It has been observed that for copper metal, the value of E_A is 8997.1 eV and for all the complexes it is shifted towards the higher energy side. For the complexes mentioned in Table 1, the energy range of chemical shift in these complexes is between 7.0 to 13.6 eV, whereas the range for shift of principal absorption maximum is between 8.6 to 16.4 eV. Hence, on the basis of the shift of the principal absorption maximum, in addition, it can be inferred that copper is in +2 oxidation state in these complexes.

3.4 Edge-width:

In Table 1, the values of the edge-width ($E_A - E_K$) have been reported in CuAC, CuAP, CuBP, CuBZ, CuP complexes, the edge-widths values are 9.4, 16.4, 8.6, 11.8 and 12.6 eV, respectively. The experimental data of edge-width of Cu complexes (Table 1) show that the edge-width decreases as follows:

$$\text{CuBP} > \text{CuP} > \text{CuBZ} > \text{CuAC} > \text{CuAP}$$

In general, edge-width of the K absorption edge increases with the increase of covalent character of the bonds provided other factors such as molecular symmetry, etc. remain the same [6].

IV. CONCLUSION

X-ray absorption spectra of mixed ligand copper complexes at the K-edge of copper have been recorded at the recently developed EXAFS beamline setup at the Indus-2 synchrotron source at RRCAT, Indore. The energy of K-edge (E_K), and principal absorption maxima (E_A) have been reported. From these, the shift of the K-edge (chemical shift), shift of the principal absorption maximum and edge-width has been obtained. The order of the chemical shift may also be taken

as characteristic of the relative ionic character of the bonding in these complexes. The chemical shift has been used to determine the effective nuclear charge on the absorbing atom. The values of the chemical shifts indicate that copper is in oxidation state +2 in all of the complexes.

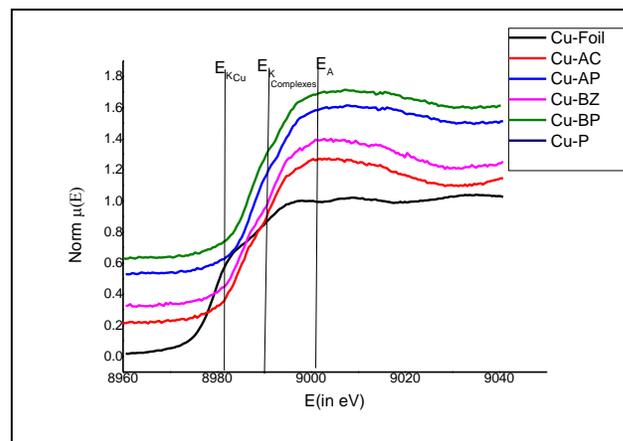


Figure 1: Normalized XAFS spectrum of Cu-complexes

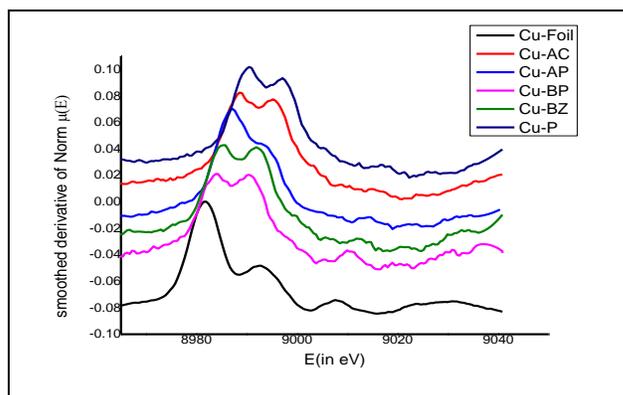


Figure 2: Derivative of normalized XAFS spectrum

Table 1

Complexes	E_k (eV)	E_A (eV)	Chemical shift $\Delta E_k = (E_{\text{complex}} - E_{\text{metal}})$ (eV)	ENC	Shift of the principal absorption maximum (eV)	Edge-width ($E_A - E_k$) (eV)
Cu Metal	8980.1	8997.1	-	-	-	17
CuAP	8987.1	9003.5	7.0	0.79	6.4	16.4
CuBZ	8990.9	9002.7	9.8	1.01	5.6	11.8
CuAC	8990.9	9000.3	10.8	1.08	3.2	9.4
CuBP	8991.4	8999.2	11.3	1.11	2.9	8.6
CuP	8993.7	9006.3	13.6	1.27	9.2	12.6

ACKNOWLEDGMENT

I would like to express my sincere gratefulness to Dr Pratima Sharma for providing their valuable guidance, Dr. S N Jha, RRCAT, Indore, India for his continuous support, criticism, inspiration and invaluable assistance throughout the course of this study. Special thanks to Dr. S. Ninama for helping and providing guidance for XAFS parameters calculation.

REFERENCES

- [1] N. Raman, Y.P. Raja, A. Kulandaisamy, "Synthesis and characterisation of Cu(II), Ni(II), Mn(II), Zn(II) and VO(II) Schiff base complexes derived from o-phenylenediamine and acetoacetanilide", Indian Academy of Sciences, Vol. 113, No 3, pp. 183-189, 2001.
- [2] A.A. Ahmed, S.A. BenGuzzi.,A.A. EL-Hadi, "Synthesis and Characterization of Divalent Transition Metals Complexes of Schiff Bases Derived From O-phenylenediamine and Benzoylacetone and Related Species", Journal of Science and Its Applications, Vol. 1, No. 1, pp. 79-90, 2007.
- [3] A.J.M. Xavier, M. Thakur, J.M. Marie, "Synthesis and spectral characterisation of hydrazine based 14-membered octaaza macrocyclic Ni(II) complexes", Journal of Chemical and Pharmaceutical Research, Vol. 4, No. 2, pp.986-990, 2012.
- [4] D. C. Koningsberger and R. Prins, "X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES", John Wiley & Sons, New York, 1988.
- [5] Nigam A K and Gupta M K J. Phys. F: Metal Physics 4 1084, 1974.
- [6] A. Kumar, A. N. Nigam, B. D. Shrivastava. X-raySpectrom.,10, 25, 1981.
- [7] J.Bhale, P.Sharma, A.Mishra, N. Parsai, "XANES Study of New Copper (II) Complexes of α -aminonitrile Derive from p-methoxybenzaldehyde with p-anisidine", International Journal of Scientific Research in Physics and Applied Sciences, Vol. 3, issue 1, 2014.