

Synthesis, XRD, EXAFS and XANES Study of Cu(II) Complexes of Aniline Dithiocarbamate

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In present investigation, seven copper(II) complexes were synthesized using various aniline dithiocarbamate. The synthesized Cu(II) complexes were studied for different structural and chemical parameters using XRD, EXAFS and XANES. The output obtained from X-ray studies was synthesized using Athena and Origin 6.0 software. The results of the investigation were used in determining the structures of the synthesized complexes. The particle size of the synthesized complexes ranged between 46.7 and 125.3 nm. The lattice constant of Cu(II) complexes was found 3.61-3.62 Å.

Keywords: Aniline dithiocarbamate, Cu(II) complex, EXAFS, Ligands, XRD, XANES.

INTRODUCTION

Copper is a soft, malleable and ductile metal with very high thermal and electrical conductivity [1]. Copper is used as a conductor of heat and electricity, as a building material and as a constituent of various metal alloys, such as sterling silver used in jewellery, cupronickel used to make marine hardware and coins and constantan used in strain gauges and thermocouples for temperature measurement [2,3]. Copper compounds, whether organic complexes or organo-metallics, promote or catalyse numerous chemical and biological processes. Copper forms coordination complexes with ligands [4]. In aqueous solution, copper(II) exists as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$. This complex exhibits the fastest water exchange rate (speed of water ligands attaching and detaching) for any transition metal aquo complex. Compounds that contain a carbon-copper bond are known as organocopper compounds [4]. They are very reactive towards oxygen to form copper(I) oxide and have many uses in chemistry. Copper(I) forms a variety of weak complexes with alkenes and carbon monoxide, especially in the presence of amine ligands [5,6].

Dithiocarbamates were discovered as a class of chemical compounds in the history of organosulfur chemistry. These are a versatile class of monoanionic 1,1-dithio ligands and as they

are easily prepared, a wide range of chemistry has been developed. Complexes of dithiocarbamate ligands like dithiocarbamate themselves have practical applications in agriculture and in the synthesis of adducts, nanoparticles and nanocomposites [7,8]. Recently gold(III) dithiocarbamate complexes have been prepared and used for treatment of human cancer by suppress tumor growth *via* direct inhibition of the proteasome activity [9]. Transition metal complexes with mixed ligands, S and N as donor atoms have found great interest among other coordination complexes [10-12]. Considering these facts, present study was conducted to synthesize copper(II) complexes with aniline dithiocarbamate ligands and their properties were studied using XRD, EXAFS and XANES techniques.

EXPERIMENTAL

Preparation of ligands: In present investigation chloro aniline dithiocarbamate, nitro aniline dithiocarbamate, fluoro aniline dithiocarbamate and toluidine dithiocarbamate ligands were synthesized and used as complexing agent for Cu(II). The ligands were prepared by adding 0.01 M of anilines to 0.016 M solution of NaOH in 15 mL distilled water with continuous stirring [13,14]. The mixture was refluxed for 2 h and further it was cooled in ice. The ligands were precipitated by drop

wise addition of carbon disulphide. The formed ligands were extracted by ether, filtered, washed with acetone and dried in vacuum.

Synthesis of Cu(II) complexes: Copper(II) complexes with dithiocarbamates were prepared by mixing 1:2 molar quantities of metal salt and ligand. The copper salt (CuSO_4) was dissolved in distilled water and dithiocarbamate was dissolved in ethanol [13,14]. The two solutions were mixed with continuous stirring. The complex produced in the form of precipitate was filtered off, washed with acetone and water in equal quantities (1:1). The product was dried in vacuum. The fine powder of the formed complexes was used for further analytical studies.

XRD studies: XRD measurements were obtained by using Bruker D8 Advance X-ray diffractometer. Monochromatic X-rays, in an exceedingly narrow, well-collimated beam were used. The X-rays were created employing a sealed tube and the wavelength of X-rays was $1.54 \text{ \AA}$ [15]. The results of all the copper(II) complexes were interpreted using Origin 6.0 software.

EXAFS and XANES studies: The XANES study was carried out using synchrotron radiation beam line (BL-08) of the Indus-2 [15]. All the samples have been studied in powder form. The EXAFS studies of copper complexes were carried out and from the position of maxima and minima, bond lengths have been estimated using various methods *viz.*, Levy's, Lytle's, LSS (Levy, Sayers and Stern) and Fourier Transform (FT) [16]. The XANES results of Cu(II) complexes *viz.* chemical shift, shift of absorption maximum and edge structure have been provided. The analysis EXAFS and XANES results were carried out using Athena and Origin 6.0 software.

RESULTS AND DISCUSSION

XRD of Cu(II) complexes: The X-ray diffraction data of copper(II) complexes are given in Fig. 1. The X-ray pattern have been indexed by using computer software and applying interactive trial and error method keeping in mind the characteristic of the various symmetry system, till a good fit was obtained between the observed and the calculated in 2θ values.

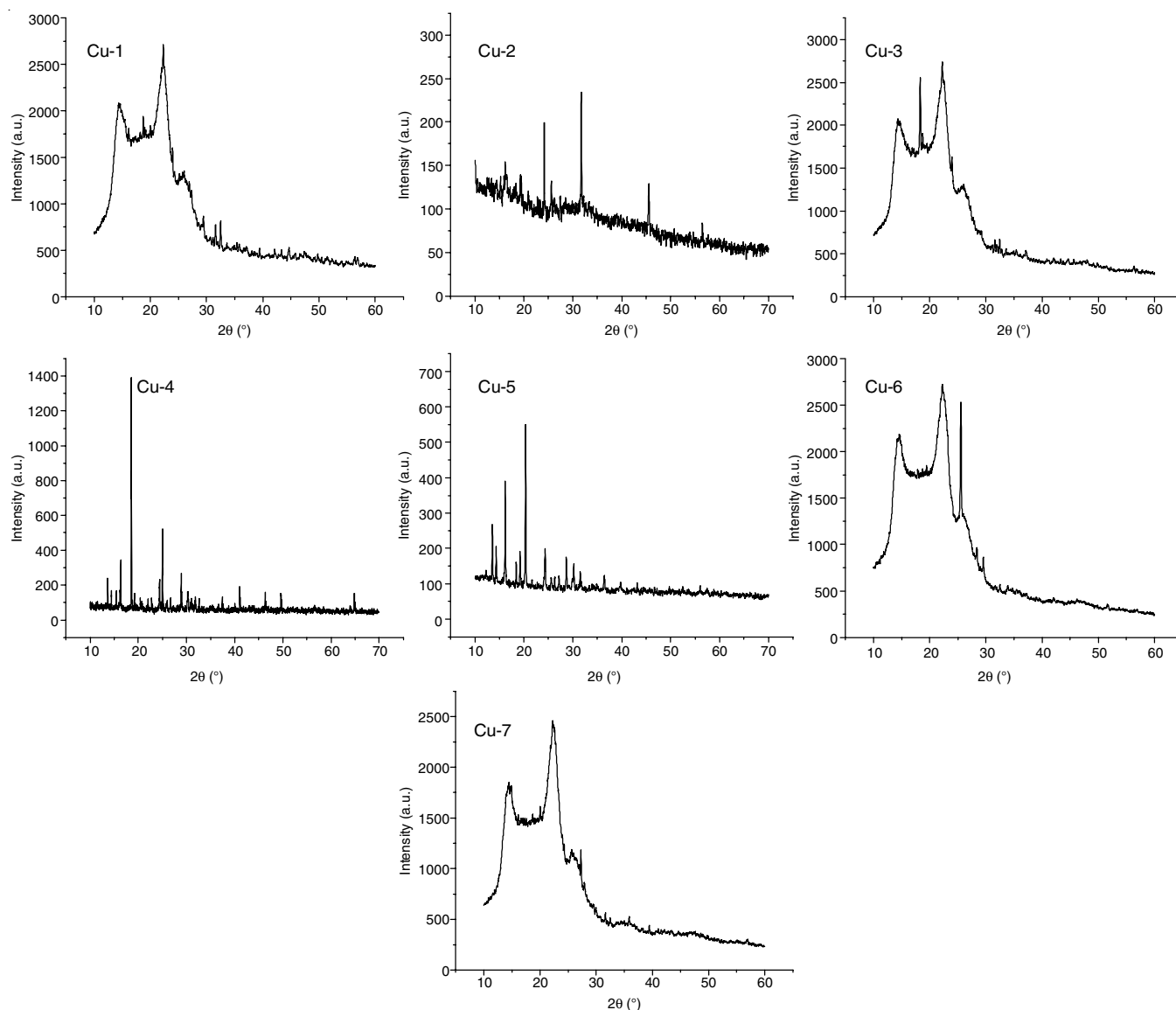


Fig. 1. XRD spectra of synthesized copper(II) complexes

The unit cell parameters were calculated from the indexed data [13]. The observed values are good fit for tetrahedral to give lattice constant that have been found to be the tetrahedral type (Table-1). The experimental value of density of the ligand and complex determined has been found to be in good agreement within the limits of the experimental error. In XRD analysis, total 20, 16 and 12 diffractograms and XRD spectra record for copper complexes are shown in Fig. 1. Comparison values revealed that there was good agreement between values of 2θ and d -values. The powder X-ray diffraction data showed identical features with very poor crystallinity. The patterns were qualitative and dispersive in intensity for copper metal complexes. The results of several researchers [15-17] are in good agreement with the present findings.

Suggested structures of Cu(II) complexes: Based upon the XRD investigation of the synthesized Cu(II) metal complexes. The structures of the complexes have been suggested and presented in Fig. 2.

EXAFS and XANES investigation of Cu(II) complexes: The chemical shift ΔE_k ranged 8.3-9.5 for Cu(II) complexes synthesized with aniline/toluidine dithiocarbamate ligands (Table-2). Similarly, the edge width ranged between 10.3 and 12.7 eV for different complexes under study whereas the edge width for Cu(II) metal was found 14.5 eV (Fig. 3). Similar findings were recorded by several researchers [15-17].

The wave factor (k) data for various complexes at various n has been shown in Table-3. The wave factor (k) ranged 1.55-5.0 Å at initial stage. It was found 4.55-4.7 Å at second level of n . The EXAFS maxima and minima at the k -absorption edge of Cu(II) has been reported for four different levels of Q and presented in Table-4. The EXAFS maxima and minima at the k -absorption edge ranged 18.61-21.43 and 39.48-49.06 eV, respectively for $Q = 2.04$ (Fig. 4-6). The EXAFS investigation was used for determining the bond length of Cu(II) complexes. The obtained data was processed in Athena and Origin 6.0 software. The bond length was determined by four different methods *viz.* LSS, FT, Lytle and Levy and shown in Table-5. The bond length of various Cu(II) complexes synthesized using aniline/toluidine dithiocarbamate ligands calculate by LSS, FT, Lytle and Levy methods were ranged 1.38-2.81, 1.01-2.97, 1.61-2.02 and 1.26-3.75 Å, respectively. All the methods employed for determining the bond length showed the similar trend for all seven complexes studied.

The binding energies for 1s electron of Cu atom in different oxidation stage (+1 to +6) and shift in binding energy has been presented in Table-6. The data revealed that the shift in binding energy ranged 8.59-130.72 eV for +1 to +6 oxidation stage of Cu atom (Fig. 6). Similar findings were also recorded by researchers previously [15-17].

TABLE-1
PARTICLE SIZE AND LATTICE CONSTANT F SYNTHESIZED COPPER(II) COMPLEXES

Complex name	m.f.	Particle size (nm)	Lattice constant (Å)
[Cu(<i>o</i> -chloroaniline dithiocarbamate) ₂] (Cu-1)	Cu(C ₇ H ₄ S ₂ NCl) ₂	46.7	3.62
[Cu(<i>o</i> -toluidine dithiocarbamate) ₂] (Cu-2)	Cu(C ₈ H ₇ NS ₂) ₂	69.4	3.62
[Cu(<i>o</i> -nitroaniline dithiocarbamate) ₂] (Cu-3)	Cu(C ₇ H ₄ N ₂ S ₂ O ₂) ₂	65.4	3.62
[Cu(4-fluoroaniline dithiocarbamate) ₂] (Cu-4)	Cu(C ₇ H ₄ S ₂ NF) ₂	69.4	3.61
[Cu(<i>p</i> -chloroaniline dithiocarbamate) ₂] (Cu-5)	Cu(C ₇ H ₄ S ₂ NCl) ₂	125.3	3.62
[Cu(<i>p</i> -nitroaniline dithiocarbamate) ₂] (Cu-6)	Cu(C ₇ H ₄ N ₂ S ₂ O ₂) ₂	73.7	3.61
[Cu(<i>p</i> -toluidine dithiocarbamate) ₂] (Cu-7)	Cu(C ₈ H ₇ NS ₂) ₂	48.9	3.61

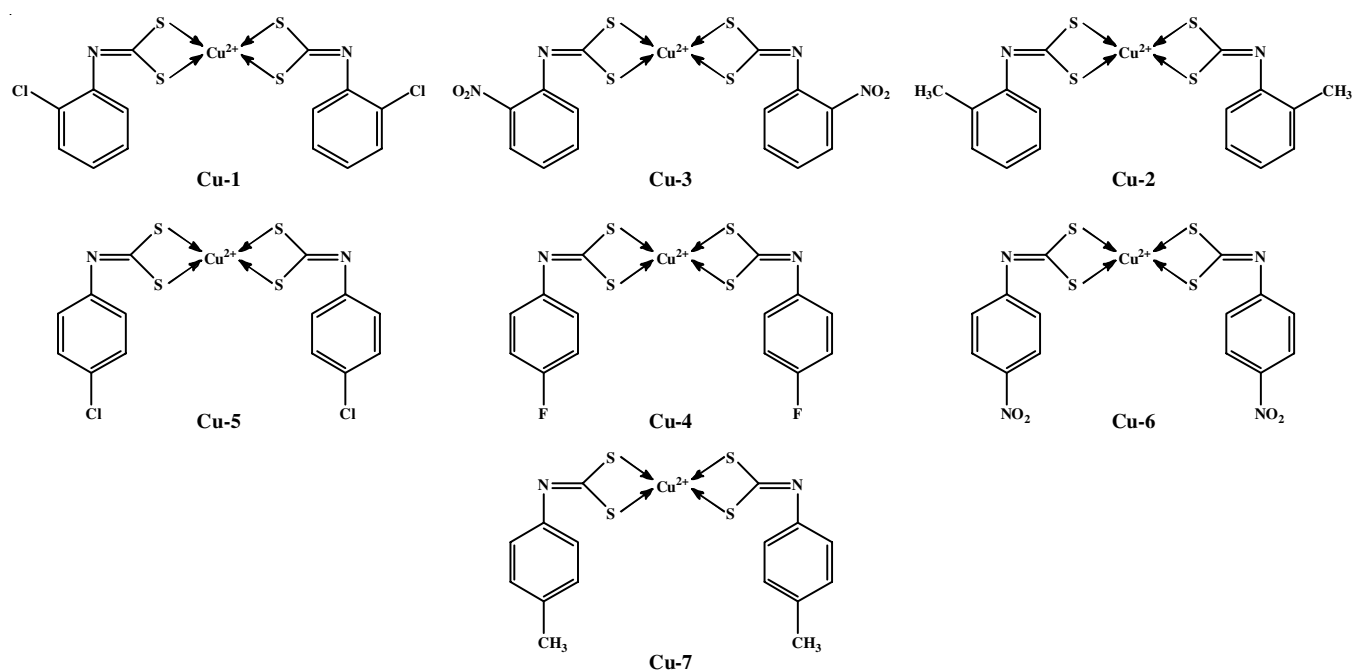
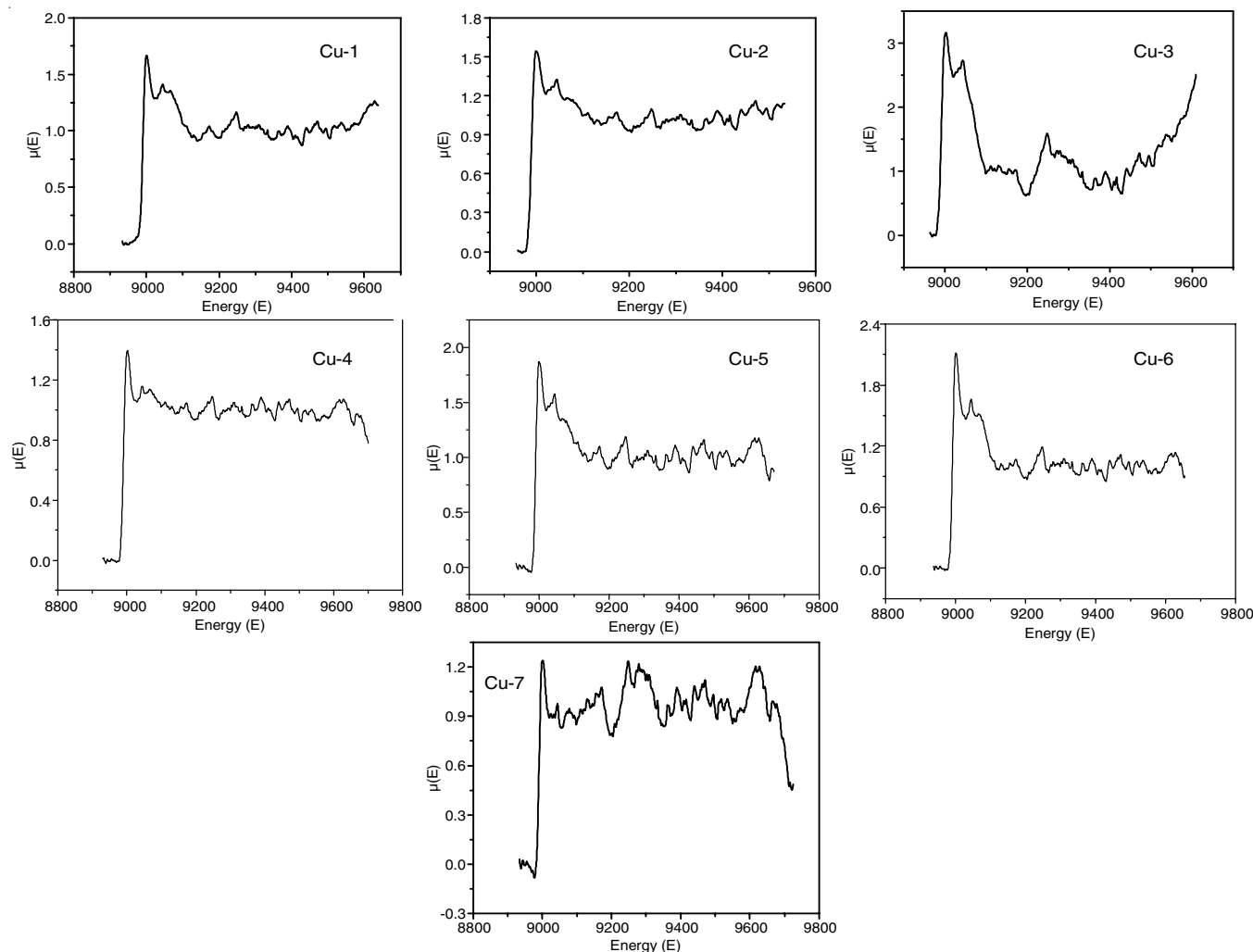


Fig. 2. Suggested structures of synthesized copper complexes

TABLE-2
 XANES DATA FOR K-ABSORPTION EDGE OF COPPER MIXED LIGAND COMPLEXES

Complex	E_{k1} (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	8980.5	8995.0	—	—	—	14.5
Cu-1	8990.0	9001.5	9.5	0.67	6.5	11.5
Cu-2	8988.8	8999.2	8.3	0.70	4.2	10.4
Cu-3	8989.6	9002.3	9.1	0.75	7.3	12.7
Cu-4	8989.5	9001.6	9.0	0.80	6.6	12.1
Cu-5	8988.6	8998.9	8.1	0.82	3.9	10.3
Cu-6	8989.5	9001.1	9.0	0.84	6.1	11.6
Cu-7	8989.0	8999.5	8.5	0.86	4.5	10.5

Fig. 3. Normalized $\mu(E)$ versus E spectra of Cu(II) complexes
 TABLE-3
 WAVE VECTOR k ($\text{\AA}^{-1}$) FOR EXAFS MAXIMA AND MINIMA AT THE K-ABSORPTION
 EDGE OF COPPER(II) COMPLEXES AND THEIR CORRESPONDING VALUES OF n

n	k ($\text{\AA}^{-1}$)						
	Cu-1	Cu-2	Cu-3	Cu-4	Cu-5	Cu-6	Cu-7
0	5.0	3.8	3.75	2.85	1.95	1.55	2.4
1	6.3	4.25	4.1	4	2.95	3.1	3.4
2	6.9	4.8	4.55	5.55	3.75	4.7	4.7
3	7.5	6.25	5.35	6.2	4.25	6.4	5.7
4	8.2	6.9	5.65	6.85	4.8	6.85	6.85
5	8.5	7.5	6.45	7.3	6.25	7.3	7.45
6	9.15	8.2	6.95	8.15	6.9	8.15	8.2
7	9.65	8.5	7.5	8.45	7.5	9.75	9.6
8	10.25	9.15	8.2	9.1	8.2	11.2	10.2
9	10.7	9.75	8.5	9.7	8.5	—	10.7
10	11.25	10.25	9.15	10.2	9.15	—	11.2
11	—	10.7	9.75	10.7	9.65	—	12.1

TABLE-4
ENERGY E (eV) FOR EXAFS MAXIMA AND MINIMA AT THE K-ABSORPTION EDGE OF
COPPER(II) COMPLEXES THEIR CORRESPONDING VALUES OF ENERGY LEVEL Q

Structure	Q	Cu-1	Cu-2	Cu-3	Cu-4	Cu-5	Cu-6	Cu-7
A	2.04	20.86	18.61	21.43	21.43	18.61	20.86	21.43
α	—	41.17	39.48	40.04	49.06	39.48	49.06	49.06
B	6.04	63.73	63.16	62.6	64.29	63.16	63.73	63.73
β	—	159.04	158.48	118.4	159.04	158.48	158.48	74.44
C	12.00	192.32	192.32	149.4	191.76	192.32	192.32	97.57
γ	—	216.01	223.9	168.07	215.4	215.4	223.9	117.87
D	20.00	266.77	266.77	189.5	266.7	266.7	266.7	191.76
δ	—	285.94	285.94	215.44	285.9	285.9	285.9	223.9

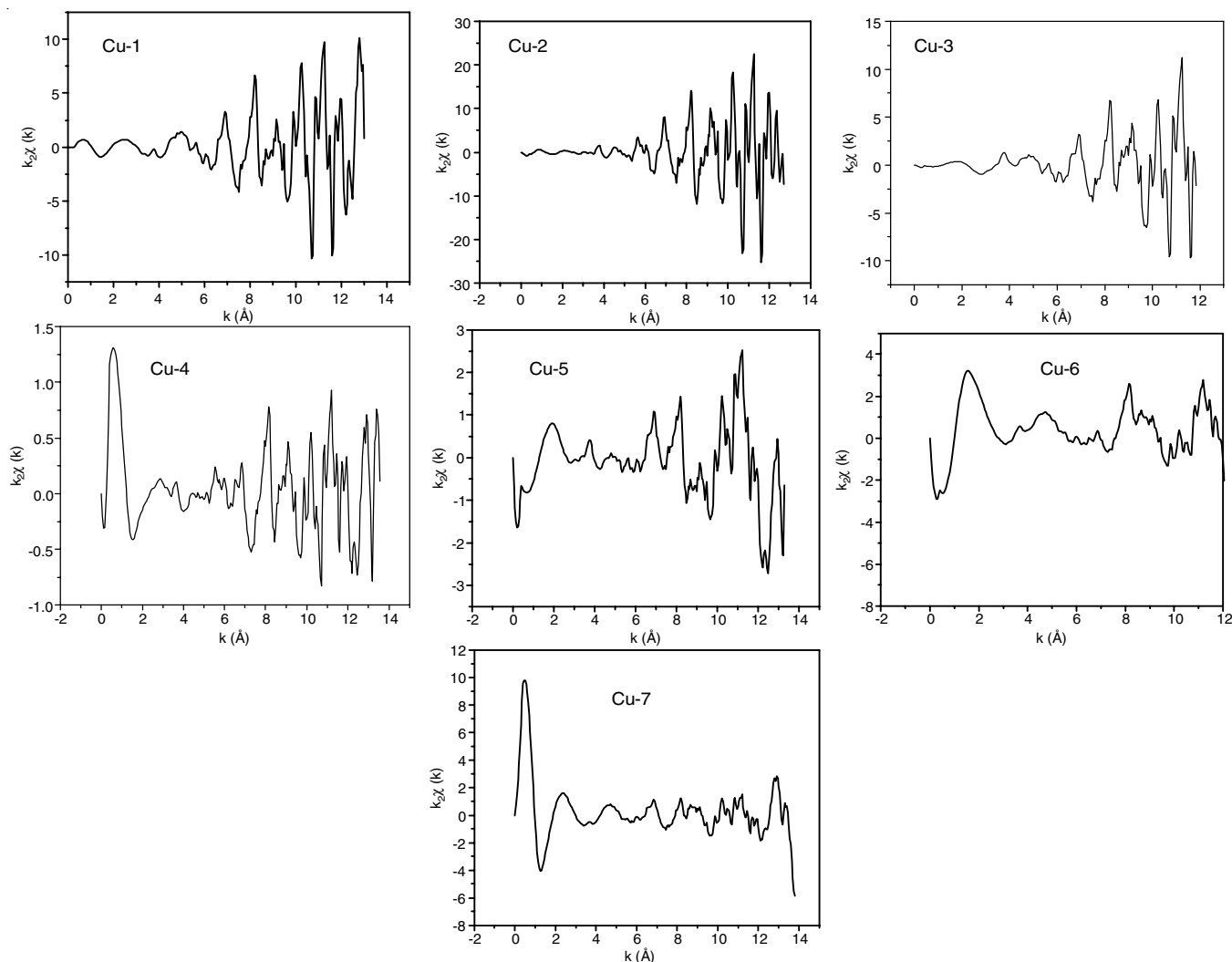


Fig. 4. $k^2\chi(k)$ versus k spectra of Cu(II) complexes

TABLE-5
VALUES OF FIRST SHELL BOND LENGTHS (Å)
CALCULATED FROM LSS AND FOURIER TRANSFORM
METHODS FOR COPPER(II) COMPLEXES

Name of complex	Phase uncorrected first shell radial distance R (Å)			
	LSS method	Fourier transform method	Lytle method	Levy method
Cu-1	2.65	2.76	1.62	1.26
Cu-2	2.38	2.94	1.61	1.26
Cu-3	2.81	2.97	1.97	1.64
Cu-4	2.27	2.88	1.62	1.26
Cu-5	2.19	1.99	1.61	1.26
Cu-6	1.38	1.01	1.62	1.26
Cu-7	1.76	1.85	2.02	3.75

TABLE-6
BINDING ENERGIES OF 1s ELECTRONS OF COPPER
ATOM IN DIFFERENT OXIDATION STATES

Oxidation state	Electronic configuration	B.E. of 1s electrons (au)	Shift in B.E. (au)	Shift in B.E. (eV)
0	$3d^{10} 4s^1$	328.79173	—	—
+1	$3d^{10} 4s^0$	329.10745	0.3157	8.59
+2	$3d^9 4s^0$	329.76836	0.9766	26.57
+3	$3d^8 4s^0$	330.55359	1.7618	47.94
+4	$3d^7 4s^0$	331.45117	2.6594	72.37
+5	$3d^6 4s^0$	332.48020	3.6884	100.37
+6	$3d^5 4s^0$	333.59556	4.8038	130.72

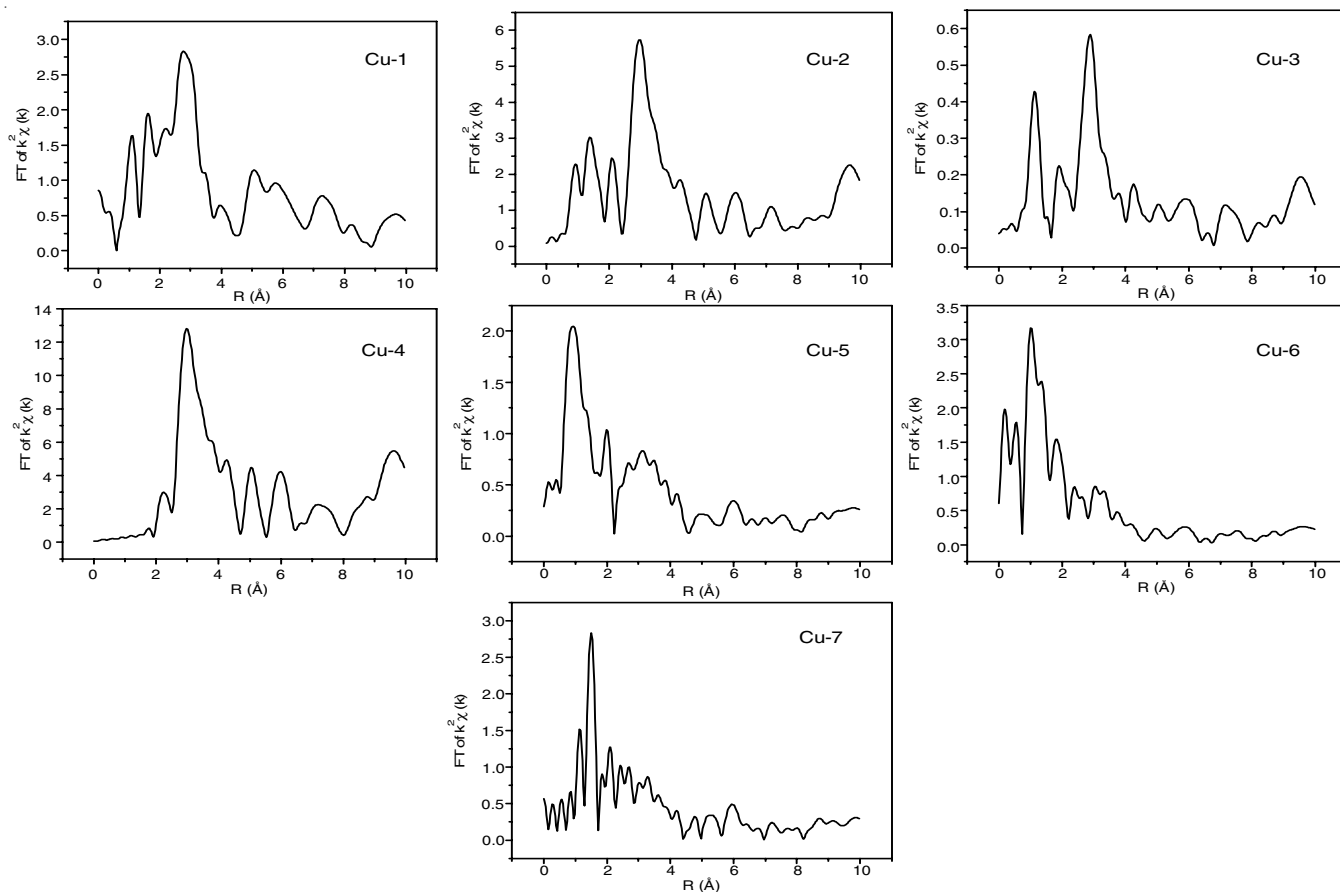
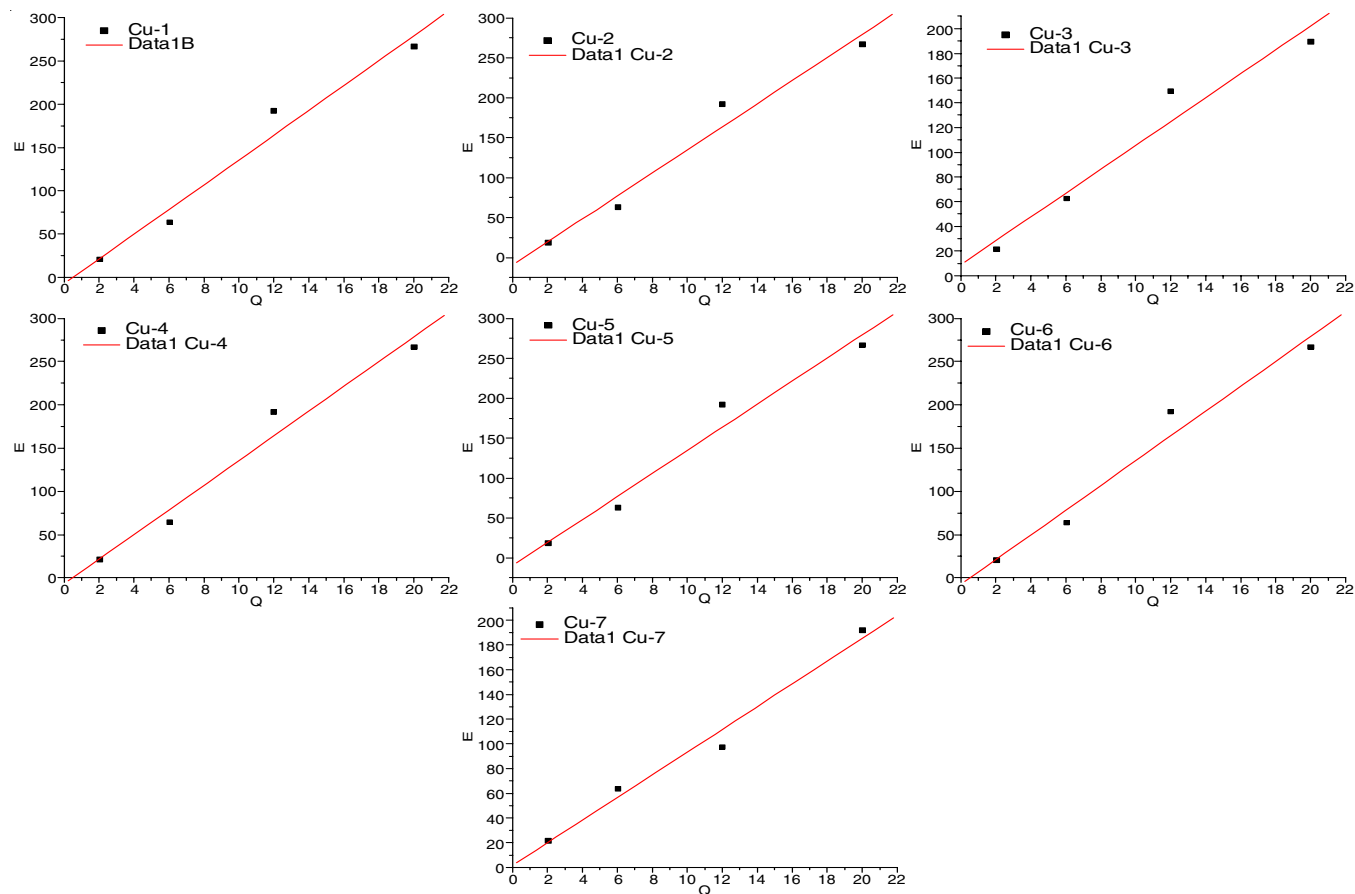
Fig. 5. Magnitude of Fourier transform of the $\chi(k)$ versus k spectra of Cu(II) complexes

Fig. 6. E vs. Q plot of Cu(II) complexes

Conclusion

The seven copper [Cu(II)] complexes synthesized using various dithiocarbamate ligands. The XRD, EXAFS and XANES investigation of copper [Cu(II)] complexes revealed that the particle size of synthesized complexes ranged between 46.7 and 125.3 nm. The lattice constant of Cu(II) complexes was found 3.61-3.62 Å. The synthesized metal complexes behaved as symmetric bidendate ligand during complexation and carry no charge and were found thermally stable.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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