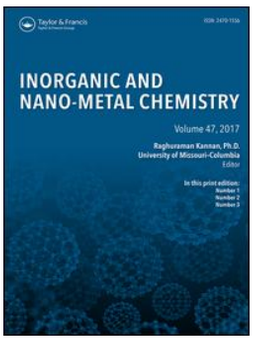

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Solid-state synthesis and characterization of copper–penicillamine complexes

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ABSTRACT

In the present study two new metal complexes of penicillamine (PenA) with molecular formula Cu $[C_{10}H_{20}O_4N_2S_2]$ and Cu$[C_{20}H_{42}O_8N_4S_4]$ were synthesized by solid-state reaction of the penicillamine ligand with copper acetate monohydrate. Analytical characterization of the complexes were based on elemental (C, H, N, and S) and UV–visible analyses. Infrared spectroscopic measurement indicate coordination of penicillamine to Cu(II) through the sulfur atom. Study based on the Powder X-ray diffraction confirmed that phase changes take place in complexes with respect to the starting material. It was also observed that both metal complexes are soluble in common solvent such as water; slightly soluble in methanol; and insoluble in acetone, dimethyl sulfoxide, dimethyl formamide, and pyridine.

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Solid-state synthesis; elemental analysis; FT-IR spectroscopy; UV–visible spectroscopy; powder X-ray diffraction

Introduction

Metal complexes play an important role in various biological systems and in different fields of chemistry. Hence, the formation stability and reactivity of these complexes have been an active field of research.[1] Metal ions are essential for biological functions, and some of the best known examples are iron(II) present in the structures of hemoglobin and myoglobin, zinc (II) in the enzyme superoxide dismutase, calcium in bone formation, sodium and potassium in homeostatic processes, and so on.[2] A large number of metal complexes have been investigated for their interesting and important properties such as catalytic activity and complexing ability toward toxic chemicals in biological system.[3–5] There are also many examples of metal ions and their complexes that are used as pharmaceutical agents in diagnosis or in the treatment of a variety of diseases.[6] Copper is an essential trace element with many physiological functions and easily cycle between Cu(I) and Cu(II) allowing the metal to play an essential role in redox chemistry in cellular life.[7] It affects the activity of many enzymes both as a cofactor and as an allosteric component e.g., Cu/Zn-superoxide dismutase (Cu/Zn-SOD), ceruloplasmin, cytochrome oxidase, tyrosinase, dopamine hydroxylase and lysine oxidase. These enzymes are essential for melanin synthesis, cellular respiration, defense against free radicals, and formation of connective tissue; and for iron metabolism. In addition, copper-dependent transcription factors play an important role in gene expression.[1] Copper(II) complexes play a significant role in the active sites of a large number of metalloproteins in biological systems and have potential application for numerous catalytic processes in living organisms that involve electron transfer reactions and/or the activation of some antitumor substances.[8] Various copper(II) N,S,O/N,N-donor chelators are good anticancer agents due to their strong binding ability with DNA base pairs[9] and play an important role in protecting biological systems against oxidative stress.[10]

Penicillamine is a structural analogue of cysteine and shows nearly similar chemical properties (Figure 1). The significance of penicillamine is enhanced in the recent years due to its widespread and different pharmacological effects.[11] Penicillamine (*d*-3, 3-dimethylcysteine) is a chelating agent, attributed with the capabilities of the mercapto group to under various complex formation process which facilitates the elimination of heavy metal ions including copper (Cu), lead (Pb), and mercury (Hg) from the organism by the formation of stable soluble complexes[12] and has been used in the treatment of Wilson's disease, rheumatoid arthritis, and other cases of metal toxicity.[13,14] Due to the presence of a mercapto group, penicillamine is an active ligand that easily forms complexes with transition metals. The most important reactions involving the participation of the mercapto group and the main biochemical aspects of these have been reviewed by Jocelyn.[15] However, the interest of penicillamine as a ligand can be extended to its several possibilities of coordination. Some of its complexes have been reported with soft metals such as mercury (II) in acidic and neutral condition[16] with Pd(II) and Pt(II),[17] Cu(I) and Cu(II),[18] Pb $(CH_3COO)_2$, and $NiSO_4$.[14] The molecule of penicillamine, together with its zwitterionic form, has three functional groups ($—NH_2$, $—S^-$, and COO^-). Penicillamine molecule usually forms bidentate complexes by coordination of N and S atoms, and the formation of monodentate (S), tridentate (N, O, and S), or tetradentate (N, O, O, and S) complexes cannot be dismissed for consideration.[17]

The present article reports a simple solid-state solvent-free method (system in which neat reagents react together, in the

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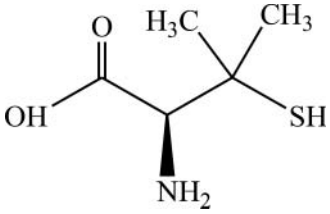

Figure 1. Structure of dl-penicillamine.

absence of a solvent) for the synthesis of copper penicillamine complexes. Sufficient amounts of pure material for broad-range testing can be easily obtained from this method, which is intermittently difficult when using the common synthetic routes. Furthermore, the solid–solid reaction typically produces quantitative yields. This novel way of synthesis leads directly to products in powder form. Hence, the materials are ready for various applications without the need of time-consuming treatments. The proposed method is based on the reaction between the copper(II) acetate and dl-penicillamine with the formation of grayish blue and light grayish blue complexes. The characterization and investigation of the complexes were done by elemental analysis, FT-IR, UV–visible, and powder X-ray diffraction. Other advantages of the method are cost effectiveness and prediction of its binding sites confirming the formation of complexes.

Experimental

Chemicals

dl-Penicillamine (≥99.9%) was purchased from Sigma-Aldrich (Germany). Copper acetate monohydrate (≥ 99.9%) and acetone were purchased from Riedel-de Ha.n (Germany). All the chemicals used in the synthesis were of analytical grade and were used without further purification.

Synthesis of Cu (II)–penicillamine complexes

Procedure for copper(II)–penicillamine complex 1:2

An accurately weighted quantity of ligand dl-penicillamine 1.491 g (0.01 mole) and copper(II) acetate monohydrate 0.998 g (0.005 mole) were taken in an agate mortar and ground gently with pestle under neat condition at ambient temperature for 2–3 h. The reaction produced a solid powder after 30 min of grinding, which is a partly intermediate complex and partly unreacted starting material. On grinding dl-penicillamine with copper acetate monohydrate under neat condition, acetic acid was released as a by-product, which was identified by its characteristic odor (Figure 2). The formation of reaction product was indicated by a change in color from blue to grayish blue and ascertained by cessation of acidic acid odor. Microcrystalline powder of grayish blue product was obtained and characterized as such and after washing with acetone.

Procedure for copper(II)–penicillamine complex 1:4

The experiment was repeated (as mention above) by taking accurately weighted quantity of ligand dl-penicillamine 2.984 g (0.02 moles) and copper(II) acetate monohydrate 0.998 g (0.005 mole). Microcrystalline powder of light grayish blue color product was obtained and characterized as such and after washing with acetone.

Elemental analysis

Elemental analysis for carbon, hydrogen, sulfur, and nitrogen was carried out by VarioMICRO CHNS analyzer (Elementar, Germany). An accurately weighed amount of sample was put in a tin foil along with appropriate amount of V_2O_5 as an oxidizing agent. The sample was loaded onto the micro analyzer, and measurements were recorded.

FT-IR spectroscopy

FT-IR spectra of the samples were obtained using IR-Prestige (Shimadzu, Japan) spectrophotometer in the range of 4000–400 cm^{-1}. The spectra were recorded by KBr disk method with the resolution of 4 cm-.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) spectra of the complexes were recorded on Bruker D8 advance, CuKα radiation. The diffraction spectra of samples were collected with a CuKα source ($\lambda = 1.540598$ nm) and using a θ-2θ geometry, with a scanning time of 0.5 s and a step of 0.03°.

UV-visible spectroscopy

UV-Visible spectra of the samples were recorded by employing 2300 UV-Visible TECHCOMP (Shimadzu, Japan) dual beam spectrophotometer at room temperature in the range of 190–900 nm with the scanning speed of 1200 nm/min.

Solubility of complexes

The solubility of the complexes were investigated in hot and cold water, *N,N*-dimethyl formamide, dimethyl sulfoxide, and other common organic solvents by shaking a small amount of complex in a test tube.

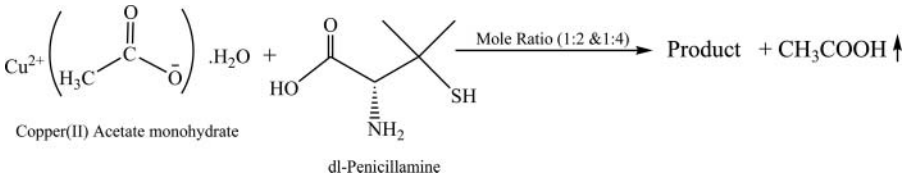

Figure 2. Reaction of copper(II) acetate monohydrate with dl-penicillamine.

Table 1. Solubility data of complexes.

Complexes	Solvents					
	Water	Methanol	DMSO	DMF	Acetone	Pyridine
Cu(II)-PenA 1:2	S	Sp	IS	IS	IS	IS
Cu(II)-PenA 1:4	S	Sp	IS	IS	IS	IS

S, soluble; IS, insoluble; Sp, sparingly soluble.

Table 3. UV-Vis data of ligand and of its complexes.

Reactant and complexes	λ_{max} (nm)		Transitions
	Visible range	UV range	
DL-penicillamine	Not observed	215 nm	π-π^*
Copper (II) acetate monohydrate	712 nm	Not observed	d-d
Cu(II)-PenA 1:2	510 nm	Not observed	d-d
Cu(II)-PenA 1:4	556 nm	Not observed	d-d

Results and discussion

Penicillamine possesses a sulfur atom, which reacts with metal ions forming stable complexes. Determination of penicillamine in the pharmaceutical drugs by complexation with a large number of metal ions such as Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Mn^{2+} has already been reported.[12] The solid-state synthesis of the Cu(II)–PenA complexes resulted in the production of grayish blue and light grayish blue colored, non-hydroscopic solid powder. They are found to be stable at room temperature and soluble in water, giving yellow color in methanol and insoluble in all other organic solvents. The solubility data of the complexes under investigation are given in Table 1.

Characterization of Cu(II)–penicillamine complexes

Elemental analysis

The percent (%) of carbon, hydrogen, and nitrogen was determined by elemental analysis and given in Table 2. Based on the analytical data and the molecular formula assigned to complexes, the elemental analysis shows that Cu(II)–PenA complexes revealed 1:2 and 1:4 mole ratios and correspond well with general formula type ML_2 and ML_4 (M=Cu, L = dl-penicillamine). The obtained values were very much similar to the calculated values and indicate that complexes are fairly pure.

UV-visible spectrum of penicillamine and Cu(II): Penicillamine complexes

The electronic spectra of copper acetate monohydrate, penicillamine, and Cu(II)–PenA complexes have been measured in distilled water (violet-colored solution). The significant bands that appear in UV-Vis spectral data of copper(II) complexes in water are listed in Table 3 and the spectra are shown in Figure 3a and b. Penicillamine has maximum absorbance at 215 nm and copper(II) acetate monohydrate has maximum absorbance at 712 nm, and Cu(II)–PenA complexes show absorbance maxima at 510 and 556 nm. There were 2 absorption bands, assigned to π-π^* and d-d transition in the electronic spectrum of reactants. The d-d transition was also observed in the spectra of complexes, but they were shifted toward lower wavelength. The difference in the maxima positions is associated with coordination environments around the metal centers with ligand field strength. These shift changes may be attributed to the ligand to metal charge transfer transition that occurs from filled ligand-based orbital to the partially occupied metal d-shell.[19] Generally, the spectra of the complexes are similar; however, the intensity of the peaks was concentration dependent and its position varied slightly as the copper:penicillamine ratio was changed as shown in Figure 3a. The similarity of the complexes' spectra could be an additional proof of their similar structure. The coordination of the ligand to the metallic ion was the evidence by the gradual decrease in the absorbance of free copper salt and the consequent appearance of peaks at 510 and 556 nm.

Furthermore, the complexes exhibited an absorption band at λ_{max} 510 and 556 nm in visible region corresponding to the d-d electronic transition of Cu metal ion, since it is a d^9 system. It has been suggested that visible spectrum of a d^9 system in an octahedral field is rare due to the Jahn-Teller effect. This effect causes liability and plasticity of copper(II) complexes and leads to various coordination arrangements and extremely fast ligand exchange reactions,[20] while d → d electronic transitions are extremely sensitive indicators of the d^9 configuration of copper(II) complexes.[21,22] In this case, the set of five d-orbitals is affected differently by the presence of ligands, breaking down into doubly degenerate e_g orbitals (dx^2-y^2 and dz^2) and a triply degenerate set of orbitals (d_{xy}, d_{xz}, and d_{yz}), which transform according to the t_{2g} irreducible symmetry point representation group. Since the dz^2 and dx^2-y^2 orbitals have much of their electron density along with metal ligand bonds, their electrons experience more repulsion by the ligand electrons than those in the d_{xy}, d_{xz}, and d_{yz} orbitals. The result is that the e_g orbitals are pushed up in energy, while the t_{2g} orbitals are pushed down. The energy difference between these sets of orbitals is defined by the Δ_o parameter, denominated by 10Dq. This amount is typically promotion of an electron from the t_{2g} to the e_g orbital, which leads to an absorption in the visible region of the spectrum.

FT-IR data of complexes

The infrared (IR) spectra of Cu(II)–PenA (1:2 and 1:4) were analyzed in comparison to the free ligand penicillamine. The assignment of most useful bands in establishing the structure identity of the ligands and its complexes are listed in Table 4 and spectra shown in Figure 4. The penicillamine molecule has a thiol (−SH), a carboxylate, and an amine group, which are

Table 2. Microanalytical data [% found (calculated)].

Complexes	Molecular formula	Mol. Wt.	Color	Nitrogen	Carbon	Hydrogen	Sulfur
Cu(II)-PenA 1:2	$CuC_{10}H_{20}O_4N_2S_2$	356.96 g/mol	Grayish blue	7.81 (7.77)	33.29 (33.36)	5.58 (5.55)	17.84 (17.81)
Cu(II)-PenA 1:4	$CuC_{20}H_{42}O_8N_4S_4$	658.48 g/mol	Light Grayish blue	8.48 (8.50)	36.52 (36.48)	6.34 (6.37)	19.52 (19.47)

PenA = dl-Penicillamine.

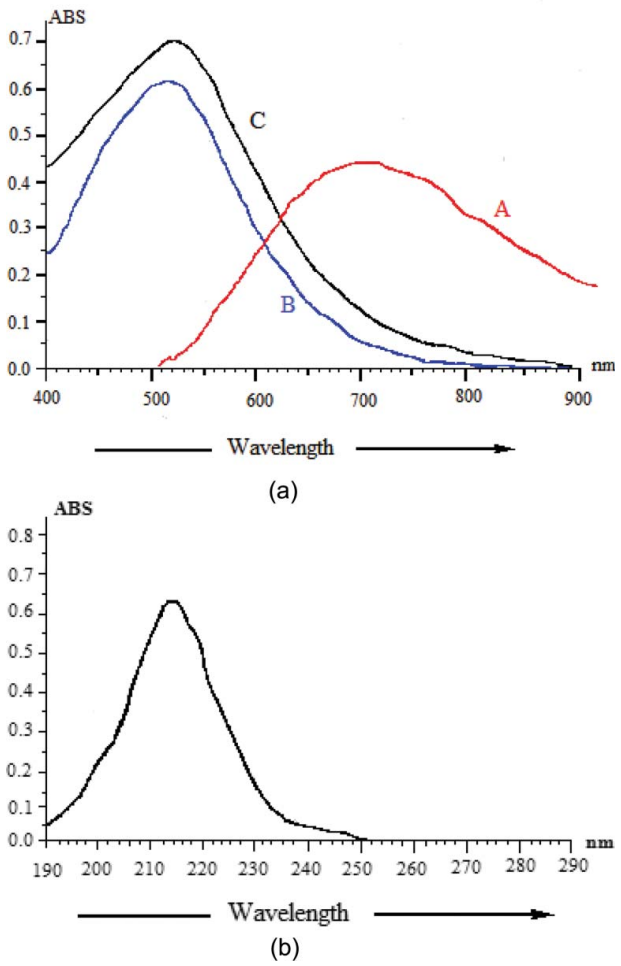

Figure 3. (a) Electronic spectra of (A) Copper(II) acetate monohydrate, (B) Cu(II)–PenA 1:2, and (C) Cu(II)–PenA 1:4 complex. (b) Electronic spectra of ligand dl-penicillamine.

potential sites for coordination to metal ions. The most important bands in the spectrum of the dl-penicillamine are assigned to νNH_3^+ at 3047–2978 cm^- and νCOO^- at 1589 cm^- correspondingly to the zwitterionic form of amino acid. Consequently, $\nu(C=O)$ at 1700 cm^- of protonated carboxylic group is absent. The band at 2596 cm^- assigned to sulfhydryl (−SH) stretch is only present in dl-penicillamine and disappears in the spectra of Cu(II)–PenA 1:2 complex indicating that the thiol group loses its hydrogen atom upon coordination to Cu(II) and decrease of sulfhydryl stretch in 1:4 complex indicates the deprotonation of the two sulfhydryl group and subsequent binding of Cu(II) to penicillamine via the sulfur atom. The downshift in the C–S stretching band from 680 to 660 cm^- for both complexes also confirms coordination via the thiolate (R–S) group.[2] The band at 1589 cm^- for Cu(II)–PenA 1:4 in the IR spectra of complex is assigned to anti-symmetrical and symmetrical NH_3^+ deformation modes, respectively. The presence of these bands in the complex spectra shows that the amine group remains protonated ($-NH_3^+$) and uncoordinated to the metal ions. The shift of νNH_3^+ toward higher frequencies in the spectra of Cu–PenA complex (1:2) typical for coordination of NH_2,[23] and the changes in the band related with νNH_3^+ confirm the coordination through nitrogen atom.[24] The presence in the spectra of Cu(II)–PenA 1:2 and 1:4 bands at frequencies higher than 1700 cm^- assigned to free carboxylic group indicates no coordination by oxygen atom.[25,26] The band shift located at the 680–690 cm^- is due to the C-S stretching vibration. The intensity enhancement of this band in complexes indicates that important electronic arrangement might occur in the S atom. This fact implies that S atom is directly involved in the ligand to copper metal.[27]

Table 4. Infrared band assignments of dl-Penicillamine and Copper(II)–penicillamine complexes mole ratios of 1:2 and 1:4.

dl-penicillamine	Cu-PenA 1:2	Cu-PenA 1:4	Assignments
3047.53	3068.75	3051.39	νNH_3^+
2978.09	2958.80	2970.38	—CH stretch
2596.19	Absent	2596.19 (minor)	—SH stretch
2351.23	2343.51	2347.37	Not assigned
1589.34	1598.99	1600.92	$-CO_2^-$ stretch —NH deformation
1521.84	1481.33	1521.84	$-NH_3^+$deformation
1390.68	1377.17	1390.68	—CO stretching
1278.81	1246.02	1280.73	—OH deformation
1199.72	1192.01	1182.36	—C—O stretch(Alkyl—O stretch)
1097.50	1112.93	1103.20	—CO stretch
883.40	885.33	887.26	—CH deformation
758.02	773.46	758.02	—CH deformation
680.87	688.94	684.87	—C—S shift

The carboxylate bands, namely (C=O) stretch, (−OH) bending, (COOH) anti-symmetric, and (−COOH) symmetric stretch, arise formerly at 1097, 1199, 1390, and 1589 cm^- and show a slight shift to 1112 and 1103 cm^-, 1192 and 1182 cm^-, 1277 cm^-, and 1598 and 1600 cm^- in the penicillamine–Cu complexes spectrum.

These findings are consistent with the bidentate coordination through N and S atoms shown by the penicillamine in Cu(II)–PenA 1:2. In this case, the penicillamine has lost two protons, while coordination in Cu(II)–PenA 1:4 is only through sulfur atoms, which behave as bridging ligand. In a similar work it was reported that the coordination of penicillamine to Cd(II) occurs only via the sulfur atom of the thiolate group and the –SH group also lost its hydrogen atom during chelation.[28] The peaks in the range of 650–1000 cm^- are attributed to the C-H bending vibration of –HC–CH– link. Furthermore, the FT-IR curve in the finger print region (below 750 cm^-) confirms that the Cu(II)–penicillamine complexes in 1:2 and 1:4 (Cu(II)–PenA) are different from the originating parent molecules, as they possess different spectroscopic signals.

Powder X-ray diffraction analysis

The occurrence of a reaction was ascertained by comparison of the PXRD patterns of the product to those of the reactants. PXRD patterns of Cu(II)–PenA complexes were compared with dl-penicillamine and copper acetate monohydrate as shown in Figure 5. The diffractograms and associated data describe the 2θ value for each peak, the relative intensity, and inter-planning spacing (d-values). The powder XRD diffraction patterns of the complexes are completely different from the starting materials. Several new peaks were observed in the complexes. Major peak in dl-penicillamine at the angle of 30–40° disappeared in Cu(II)–PenA 1:2 and

Figure 4. IR Spectra of (A) dl-penicillamine, (B) Cu(II)–PenA 1:2 complex, and (C) Cu(II)–PenA 1:4 complex.

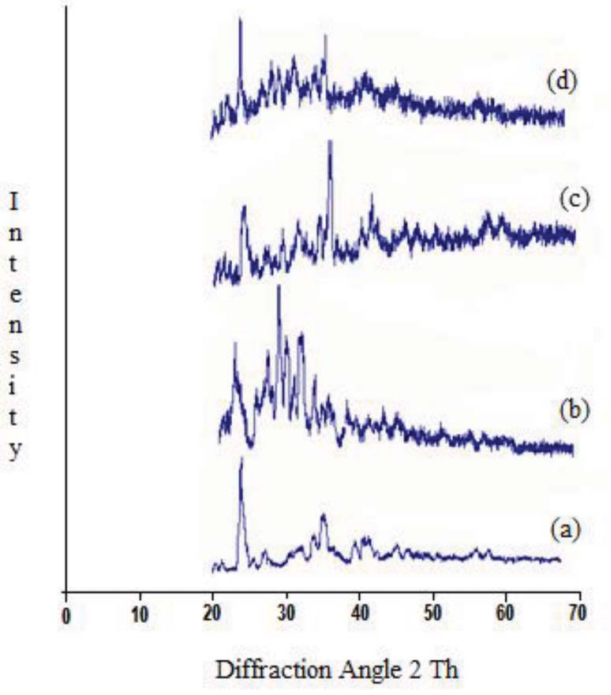

Figure 5. Comparison of powder X-ray diffraction pattern. (a) copper acetate monohydrate, (b) dl-penicillamine, (c) Cu(II)–PenA 1:2, and (d) Cu(II)–PenA 1:4 complex.

1:4 (mole ratios) complexes due to the complexation. Two new peaks were observed at the angle of 30–35° in case of Cu(II)–PenA 1:2 complexes: One with lower angle but higher intensity and other with high angle but lower intensity. Higher intensity at 2θ value of 30–35° indicates the formation of new phase with highly oriented crystalline. On the other hand, in case of Cu(II)–PenA 1:4 complex, a new peak in different intensity was observed, which is different as compared to the reactants. The difference in intensity might be due to the different alignment of the powder sample. These results suggest that the complexation of dl-penicillamine and copper acetate most probably occurred and also confirm that the products were single-phase materials.

Proposed structure of Cu(II)–PenA complexes

Copper(II) is found in many reported compounds of diverse structure with the d^9 electronic configuration, exhibiting a wide range of stereochemistries with four coordinate complexes spanning approximately tetrahedral, compressed tetrahedral, and square coplanar geometries.[29,30] Based on the spectroscopic data, elemental analysis and powder X-ray diffraction enable us to predict the possible proposed four-coordinated structure of the copper(II)–PenA complexes as shown in Figure 6. It has been found that copper(II) atoms are four-coordinated with S and NH_2 donor set for 1:2 Cu(II)–PenA complex and S donor for 1:4 Cu(II)–PenA complex.

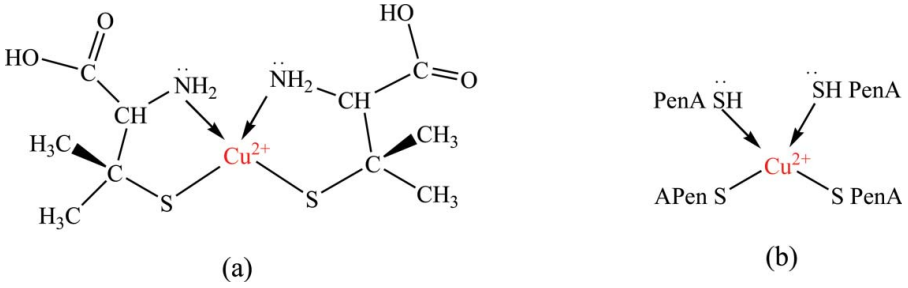

Figure 6. Proposed structure of (a) Cu(II)-PenA 1:2 complex and (b) Cu(II)-PenA 1:4 complex.

Conclusion

In conclusion, this work reported a eco-friendly and convenient method for the synthesis of Cu(II)–penicillamine complexes in mole ratio 1:2 and 1:4 using solid-state methods at room temperature. The proposed method is simple, accurate, and very rapid, and no harmful organic solvent is required for this method, which is environmentally friendly. Solvent-free solid-state reaction can be used to obtain the same product as that obtained for the solvent-based method. The developed complexes were thoroughly characterized by CHNS, UV-Vis, IR, and powder X-ray diffraction, which clearly revealed the structures of the complexes. Chemical composition of the synthesized complexes were established by CHNS analysis. The FT-IR analysis verified all the functional groups, and binding occurred almost exclusively through bridging sulfur bonds on the thiols of dl-penicillamine. UV-Visible spectral analysis verified different electronic transition in complexes. Difference between the phase changes of reactant and complexes were determined by PXRD. This solid-state technique can be a promising method for the preparation of other organometallic complexes and can be valuable in environment.

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