Synthesis, Spectroscopic And Powder X-Ray Diffraction Studies Of Cu(Ii) Mixed Ligands Complex Of 4-Amino, 1,2,4-Triazole And Phenylmalonic Acid

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Abstract: Novel mixed ligands complex of Cu(II) has been synthesized by slow evaporation of a mixture of methanolic solution of 4-amino-1,2,4-triazole and phenylmalonic acid with an aqueous solution of copper (II) tetraoxosulphate (VI) acid. The blue crystals of the copper (II) complex was characterized using the Energy Dispersive Analysis by X- ray (EDAX), FT-IR, UV spectral technique and Powder X-ray diffraction analysis (PXRD). The compound crystallizes in triclinic system with a space group of *P-1*. The morphology of the prepared crystal was studied by scanning electron microscope (SEM). The qualitative differences between the spectra of free ligands and the complex in the UV-Visible and Infrared regions have been used in diagnosing the different coordination mode of the metal and ligands in the complex. The present results suggested that the 4-amino 1,2,4-triazole as bidentate ligand is coordinated with metal ions through the two nitrogen atoms N1 and N2. The phenylmalonate as bidentate ligand is coordinated with metal ions through the oxygen atoms of the carboxyl group. The absorption properties of the complex studied was found to be π-π in nature with two bands that dual excitation wavelength for this complex.

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1. Introduction

The study of metal coordination polymers has received great attention as an important interface between synthetic chemistry and material science. In addition provides a solid foundation for understanding how molecules can be organized and functions can be achieved through self-assembled process (Yi *et al*., 2004; Wang *et al*., 2006). We have chosen the flexible phenylmalonate ligand, $^{-}OOC–CH_2–COO^{-}$, to develop a wide range of architectures which exhibit luminescence properties. The occurrence of two carboxylate groups in 1,3 positions allows this ligand to adopt simultaneously chelating bidentate and diferent carboxylato bridging modes (syn–syn, syn–anti and anti–anti) through one or both carb-oxylate groups (Rodríguez-Martín *et al*., 2003; Wang *et al*., 2004). In this work the coordination ability and versatility of 4-amino-1,2,4-triazole and phenylmalonic acid as mixed ligands with the copper(II) ion is focused on the self-assembly through coordinate covalent bonds or hydrogen bonding and π-π interactions. The prepared complex containing these two different ligands was found to be quite stable.

2. Materials And Methods

2.1 Materials and measurements

All chemicals were obtained from commercial sources and were used without further purifications (K_2CO_3, $CuSO_4.5H_2O$) from Sigma-Aldrich. 4-amino-1, 2, 4-triazole and phenylmalonic acid were obtained from Acros, methanol, ethanol, dimethylformamide and dimethylsulfoxide from Avocado Research Chemicals Ltd. The infrared spectrum in the range of 4000-450 cm^{-1} was recorded as potassium bromide disc on Perkin Elmer spectrum BX FT-IR 100 version 1.02.00 (Waltham) spectrophotometer. UV-Visible spectrum was measured in DMSO using Perkin Elmer Spectrum BX UV-visible spectrophotometer. Elemental analysis (C, H, N, M) was performed by the micro analytical unit on Evo Analytical SEM series (Quanta 200 FEG). Melting point was determined using Thomas-Hoover melting point apparatus fitted with digital thermometer. XPert-Pro super X-ray diffractometer was used to determine the crystal structure of the copper (II) complex.

2.2 General procedure for synthesis

This compound was prepared using a method cited in the literature (Lou *et al*., 2011). A methanol solution (5 ml) of 4-amino-1,2,4-triazole (2.5 mmol,

0.210 g) was added to a warm aqueous solution (10 ml) of $CuSO_4.5H_2O$ (1 mmol, 0.250 g). Then, potassium malonate (generated in situ by reacting 1 mmol (0.180 g) of phenylmalonic acid and 1 mmol (0.138 g) of K_2CO_3 dissolved in water, 6 ml) was added to the previously resulting solution a blue solution was obtained under continuous stirring for four hours. The resulting blue solution was filtered and the filtrate was allowed to slowly evaporate at room temperature. The complex separated as blue crystals after one week. These crystals were used for X-ray diffraction studies. Yield: 65.18 %. Anal. Calcd for $C_{20}O_{15}N_4H_{34}Cu_2$: C, 34.45; H, 4.88; N, 8.03; Cu, 18.8. Found: C, 34.67, H, 4.86, N, 8.09; Cu, 18.15.

3. Results And Discussions

The complex is crystalline and stable in air at room temperature. The complex is insoluble in water and most common organic solvents such as methanol, ethanol and acetonitrile but completely soluble in strong coordinating solvents such as dimethylsulfoxide and this suggests a polymeric nature of this complex. The SEM micrograph in Fig.1 shows the morphology of the complex indicating the incorporation of the ligands and the Cu(II) ions into square block crystals. The elemental ratio in the complex was detected with energy dispersive spectrum and this corresponds to peaks shown in Fig. 1. The experimentally found values conform closely with the calculated values. Hence, the elemental analysis data (Table 1) for Cu, C, N, O and H corresponds to the expected molecular formula of $Cu_2C_{20}N_4O_{15}H_{34}$ with a 2:2:1 metal ligands stoichiometry. These analytical data are in good agreement with the proposed stoichiometry for Cu(II) complexes with tetrahedral geometry. Table 1 gives the physical properties of the complex.

Table1. The physical properties and elemental analysis of the copper (II) complex

Compound	Color	M.P. (^oC)	Yield %	% C Found (calcd)	% H Found (calcd)	% N Found (calcd)	% O Found (calcd)	% M Found (calcd)
$[Cu_2(C_9H_8O_4)_2(C_2H_4N_4)(H_2O)_2]\cdot 5H_2O$	Blue	>170	65.18	34.45 (34.67)	4.88 (4.86)	8. 03 (8.09)	34.42 (34.23)	18.80 (18.15)

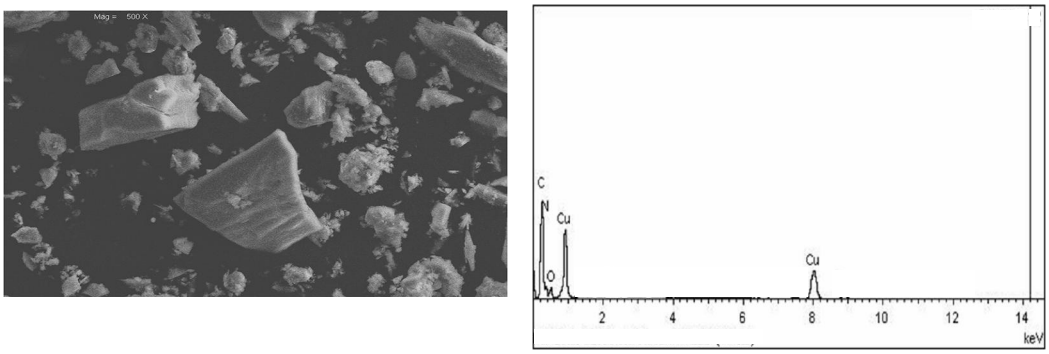

FIGURE 1: SEM-EDX spectrum for characterizing the chemical composition of the complex

3.1. Electronic spectral studies

The UV/Vis spectrum of the compound in DMSO is as presented in Fig. 2. There were two absorption bands in the UV region 273 and 248 nm of the 4-amino-1,2,4-triazole and phenylmalonic acid rings, respectively assigned to n-π*and π − π* transitions of the ligands. These transitions were also observed in the spectrum of the complex, but they were shifted toward lower frequencies, confirming the coordination of the ligands to the metal ions. The electronic absorption spectrum of the copper complex exhibited bands at 194 and 212 nm, which could be attributed to π-π* transition of aromatic rings within the complex. The bands are not closely spaced. The absorption bands observed in the spectrum is due to the arrangements of the conjugated systems of the ligands with the metal(II) ions and the splitting of energy levels caused by these ligands. Similar spectral results were obtained for self-assembled copper(II) complex with a tetrahedral structure in the literature (Zheng *et al.,*2006).

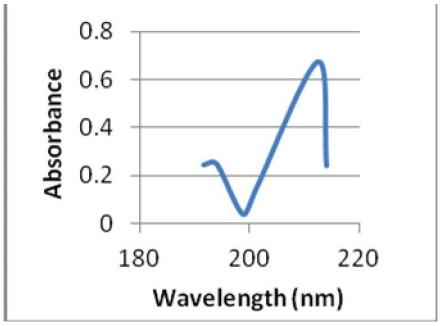

FIGURE 2: Ultraviolet-visible spectrum of Cu(II) complex

3.2. Infrared spectra studies

The characteristic infrared bands of the ligands were assigned at 3350 cm^{-1} ν (NH_2), 1701 cm^{-1} ν (COO^-), 1672 cm^{-1} ν(C=O phenyl), and 1356 cm^{-1} (C=Ntriazole) vibrations. Infrared spectrum of the complex was compared with that of the free ligands to show changes during complexation. The IR spectrum of the Cu(II) complex is presented in Fig.3. The absorption band in the region 1577 cm^{-1} is associated with the stretching vibration mode of ν(COO^-) group. This downward shift compared to that of the ligand (1701 cm^{-1}) is an indication of coordination of the carboxylate oxygen atoms in a bidentate mode. The characteristic infrared bands of the Cu(II) complex are: 626, 2854-2953, 1577 and 722 cm^{-1} assigned to õ(Cu – N), ν(CH_2) aromatic, ν(C ═ N) and ν(Cu–O), respectively. The band at 626 cm^{-1} has been assigned to (Cu – N) vibration. The various assignments are in agreement with similar compounds reported in the literature (Nakamato 1997; Kani and Aksu, 2010).

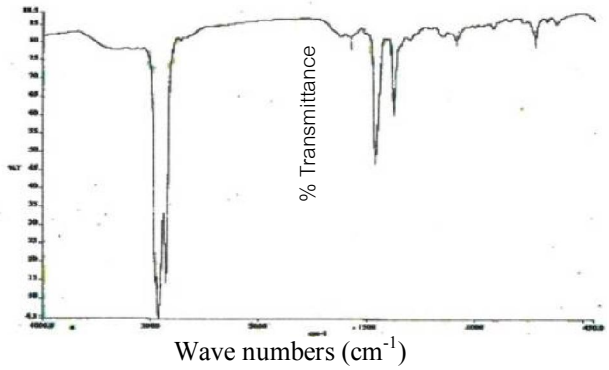

FIGURE 3: Infrared spectrum of Cu(II) complex

3.3. X-ray crystal structure of Cu(II) complex

Crystals suitable for x-ray diffraction studies were obtained. The observed X-ray powder diffraction data for this complex are listed in Table 3 and its diffractogram in Fig. 4 shows a homogeneous phase with high crystalline nature. The complex crystallized in the triclinic crystal system with a space group of *P-1*. The other relevant crystallographic data of the compound are presented in Table 4. The copper atom is four coordinated and has tetrahedral geometry. The structure consists of two different copper atoms occupying special positions and has different tetrahedral environments. Two water molecules, four oxygen atoms of two malonate ligand and two nitrogen atoms of the one triazole ligand were involved in coordination giving a proposed tetrahedral structure.

Table 3: **Peak List**

Pos.[°2Th.]	Height[cts]	FWHM[°2Th]	d-spacing[Å]	Rel.Int.[%]
6.8917	1067.53	0.0630	12.82648	100.00
7.3888	630.26	0.0630	11.96454	59.04
7.8243	108.34	0.0945	11.29957	10.15
10.6692	229.63	0.0630	8.29214	21.51
11.8718	83.76	0.1574	7.45476	7.85
12.7292	78.19	0.1260	6.95447	7.32
13.7144	67.90	0.2519	6.45703	6.36
14.7467	200.91	0.0787	6.00726	18.82
15.2591	278.91	0.1417	5.80666	26.13
15.5360	200.35	0.1102	5.70380	18.77
16.4010	70.29	0.1889	5.40487	6.58
17.6275	50.63	0.3779	5.03147	4.74
18.3128	55.41	0.1889	4.84470	5.19
19.0121	88.76	0.1260	4.66806	8.31
21.2688	143.61	0.1102	4.17757	13.45
21.8731	82.16	0.2519	4.06351	7.70

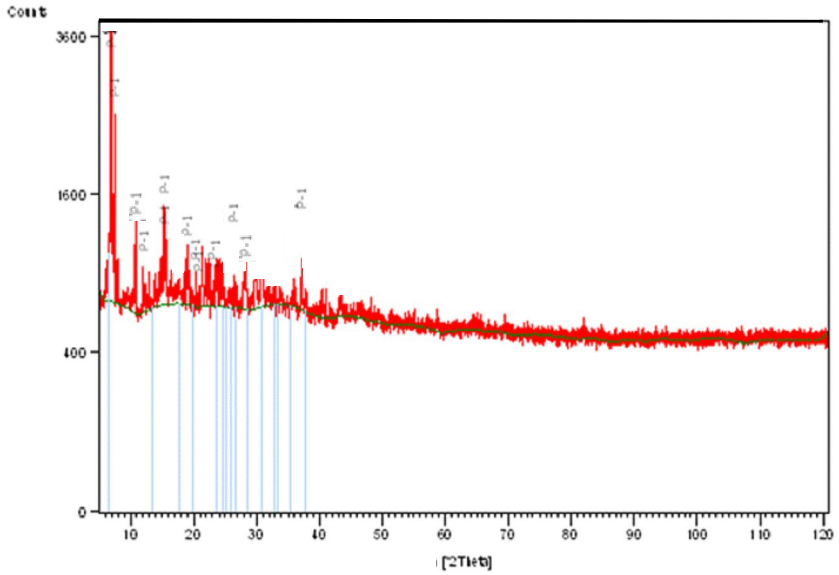

FIGURE 4: Powder X-ray diffractogram of Cu(II) complex

Table 4: Crystallographic data and structure refinement for the Cu(II) complex

Empirical formula	$C_{20}O_{15}N_4H_{34}Cu_2$
Formula weight	697.50
Temperature (K)	293
Wavelength (A°)	1.54060
Crystal system	*P-1*
Space group	Triclinic
Z	4
Theta range for data collection	6-120
Completeness to theta(27.48)	99.30 %
Absorption correction	None
Strain value	-0.0341
Particle size(nm)	26.78

4. Conclusion

A new metal organic framework has been synthesized using copper (II) ions with mixed ligands of 4-amino-1,2,4-triazole and phenylmalonate ligands as building units. The structure of this metal complex was characterized on the basis of solubility test in wide spectrum of solvents, melting point and various analytical techniques such as Fourier transform infra-red spectroscopy (FTIR), UV-Visible spectroscopy, Powder X-ray diffraction methods, SEM and EDAX. The compound show maximum absorption (212 nm) in the ultraviolet region, which suggests high energy content as well as the high thermal stability of this complex. These results show that the synthesized complex may be excellent materials for photoluminescent devices.

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