



Complexes of 4, 6-dinitrobenzothiazole-2-amine acetate with some transition metal ions: Synthesis, characterization and magnetic properties

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ABSTRACT

Complexes of 4, 6-dinitrobenzothiazole-2-amine acetate with Cu(II), Zn(II), Cd(II) and Ni(II) metal ions were synthesized from ethanol solutions. The complexes have been characterized by ¹H NMR, FT-IR spectroscopy, magnetic susceptibility and conductivity measurement. The characterizations revealed that, the copper complex which is formed, obtained square planar geometry. However, other metal complexes were obtained tetrahedral geometry.

Key Words: 4, 6-dinitrobenzothiazole-2-amine acetate; magnetic susceptibility; transition metal ion complexes.

INTRODUCTION

Synthesis and antimicrobial activity of 2-aminobenzothiazole and its derivatives is reported [1]. Further, their other pharmacological activities such as anticancer, antiulcer, antihistaminic, anti-inflammatory activity and analgesic activities also reported [2-6]. It was envisaged that the compounds containing these moieties in their molecular frame work might show enhanced biological activity. Increasing physiological importance of oxygen donor organic compounds [7] and active role played by coordination certain metal ions to them [8] is of interest towards use in synthesizing and studying structural aspects of metal complexes with some oxygen, sulphur and nitrogen donor ligands [9]. The aromatic benzothiazole nucleus is associated with a variety of antihistamine activity [10], pharmacological actions [11] such as fungicidal [12] and leishmanicides activities [13]. The complexes of the ligand 2- amino acetate, 6-chloro benzothiazole with some transition metal ions have been studied [14]. In the present study we now report the synthesis of complexes of 4, 6-dinitrobenzothiazole-2-amine acetate and their study of magnetic properties for the wide range of applications.

EXPERIMENTAL SECTION

Synthesis of 2-aminoacetic acid benzothiazole: A mixture of 2-amino benzothiazole (0.1 mol), chloroacetic acid (0.1 mol) and KOH has been refluxed for 3 hrs. The resultant yellow precipitate is filtered and crystallized from ethanol. The steps in the synthesis of 2-aminoacetic benzothiazole are shown in figure 1.

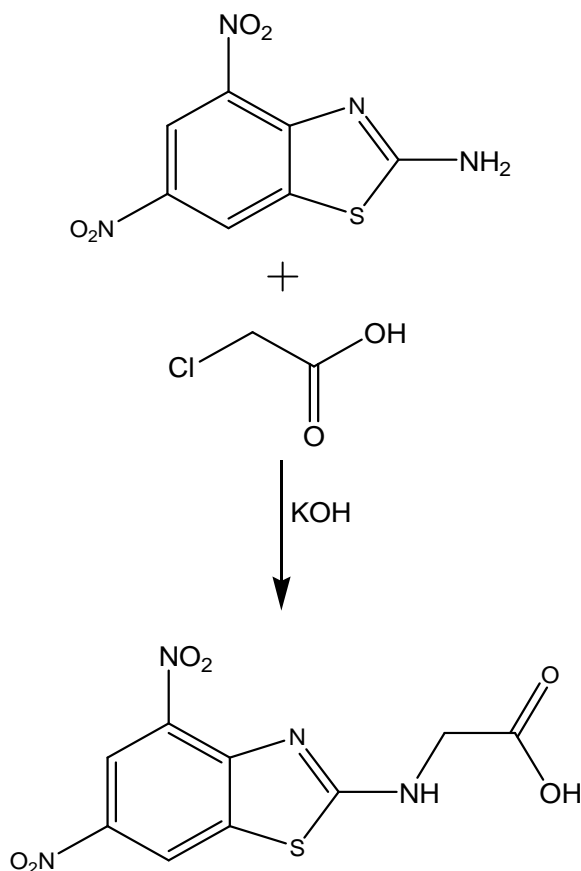


Figure: 1

Preparation of complexes:

All the metal complexes have been prepared by refluxing the ethanol solution of the suitable metal salt (Nickel acetate tetrahydrate, Copper acetate, Cadmium acetate dihydrate and Zinc acetate dihydrate) and 2-aminoacetic acid benzothiazole for one hour. The 2:1 ratio of ligand to metal is maintained throughout all the experiments. The obtained crystalline colored precipitates upon cooling the solutions at room temperature were filtered off, washed with distilled water and recrystallized from ethanol.

Instrumentation: FT-IR spectra in the range, $4000-200\text{ cm}^{-1}$, were recorded on 8300 Shimadzu Spectrophotometer, UV-visible spectra were measured by using Shimadzu 160 spectrophotometer in the range 200-1000 nm. The magnetic susceptibility values of the prepared complexes were obtained at room temperature using Magnetic Susceptibility on Bruker Magnet B.M.6, The ^1H nuclear magnetic resonance spectra were recorded on a BRUKER ADVANCED II 400 MHz spectrometer in DMSO as a solvent, relative to the internal standard Tetramethylsilane (TMS). Melting points were recorded on a Tanco Laboratory melting point apparatus.

4, 6-dinitrobenzothiazole-2-amine: Solid, mp 195°C , UV (λ_{max}) in ethanol: 258 nm, (IR) ν_{max} (KBr/cm-1): 3375.66 (NH), 3181.24 (Ar=C-H), 1538 (C=N), 1244.85 (CN), 1265.12 (C-S), (NO₃)1387.75 and 1517.84. $^1\text{H-NMR}$ (δ -ppm): 3.46 (s, 2H, NH₂), 7.77 (d, aryl H, adjacent to sulphur), 8.88 (d, aryl H, adjacent to NO₂).

4, 6-dinitrobenzothiazole-2-amine-acetic acid: Solid, mp 186°C , UV (λ_{max}) in ethanol: 264 nm, (IR) ν_{max} (KBr/cm-1): 3449.77 (NH), 3107.40 (Ar=C-H), 1495.76 (C=N), 1257.68 (C-N), 1246.69 (C-S), 1730 and 1057 cm^{-1} (stretching of C = O and C-O of the hydroxyl in the carboxyl ate). $^1\text{H-NMR}$ (δ -ppm): 3.46 (s, 1H, NH), 7.12 (s, 1H, Ar- H in between two NO₂), 8.88 (Ar-H adjacent to sulphur), 11.69 (for O-H of COOH).

Bis-(4, 6-dinitrobenzothiazole-2-amine acetate) cadmium(II) Complex : Solid, mp 192⁰C, UV (λ_{max}) in ethanol : 256 nm, (IR) ν_{max} (KBr/cm-1): NH(3449.82), 3025.78(Ar=C-H), 1496.17(C=N), 1264.09(C-N), 1276.24(C-S), 1724 and 1048 cm⁻¹ (stretching of C = O and C-O of the hydroxyl in the carboxyl ate). ¹H-NMR (δ -ppm): 4.16 (t, 2H, -NH), 6.08 (d, 2H, -CH₂), 7.15(d, 1H, Ar-H), 8.10(d,Ar-H), 8.92 (d,Ar-H).

Bis-(4, 6-dinitrobenzothiazole-2-amine acetate) copper(II) Complex : Solid, mp 123⁰C UV (λ_{max}) in ethanol: 277 nm, (IR) ν_{max} (KBr/cm-1): 3450.41 (NH), 3107(Ar=C-H), 1425.21 (C=N), 1258.54 (C-N), 1368.77 (C-NO₂), 1263 (C-S), 573.16, 917.86 (stretching and bending vibration for Cu-O), 1718 and 1030 cm⁻¹ (stretching of C = O and C-O of the hydroxyl in the carboxylate). ¹H-NMR (δ -ppm): 4.1 (t, 1H, NH), 8.12 (dd,1H,Ar-H), 5.86 (d, 2H, CH₂), 8.86 (d, 1H, Ar-H), 7.12 (d,1H, Ar-H).

Bis-(4, 6-dinitrobenzothiazole-2-amine acetate) Nickel(II) Complex : Solid, mp 133⁰C UV (λ_{max}) in ethanol: 286 nm, (IR) ν_{max} (KBr/cm-1): 3345.52 (NH), 3081.68 (Ar=C-H), 1456.61 (C=N), 1288.34 (C-N), 1343.90 (C-NO₂), 1245.09 (C-S), 525.43, 936.42 (stretching and bending vibration for Ni-O), 1720 and 1035 cm⁻¹ (stretching of C = O and C-O of the hydroxyl in the carboxylate). ¹H-NMR (δ -ppm): 4.56 (t, 1H, NH), 8.70 (dd,1H,Ar-H), 5.47 (d, 2H, CH₂), 8.68 (d, 1H, Ar-H), 7.57 (d,1H, Ar-H).

Bis-(4, 6-dinitrobenzothiazole-2-amine acetate) Zinc(II) Complex : Solid, mp 158⁰C UV (λ_{max}) in ethanol: 272 nm, (IR) ν_{max} (KBr/cm-1): 3469.25 (NH), 3147.73 (Ar=C-H), 1436.47 (C=N), 1289.63 (C-N), 1373.72 (C-NO₂), 1285.32 (C-S), 573.90, 989.43 (stretching and bending vibration for Ni-O), 1713 and 1040 cm⁻¹ (stretching of C = O and C-O of the hydroxyl in the carboxylate) ¹H-NMR (δ -ppm): 4.26 (t, 1H, NH), 8.13 (dd,1H,Ar-H), 5.89 (d, 2H, CH₂), 8.57 (d, 1H, Ar-H), 7.79 (d,1H, Ar-H).

Table: Magnetic Moment, Conductivity measurements in DMF solvent

Symbol	Name	Conductivity ohm ⁻¹ cm ² mol ⁻¹	Magnetic moment (B.M)	Suggested structure
LH	4,6-dinitrobenzothiazole-2-amine-acetic acid	-	-	-
Ni(L) ₂	Bis(4,6-dinitrobenzothiazole-2-amine acetate) nickel(II)	13	4.09	Tetrahedral
Cu (L) ₂	Bis(4,6-dinitrobenzothiazole-2-amine acetate)copper(II)	20	1.78	Square planner
Zn(L) ₂	Bis(4,6-dinitrobenzothiazole-2-amine acetate) zinc(II)	14	0.05	Tetrahedral
Cd(L) ₂	Bis(4,6-dinitrobenzothiazole-2-amine acetate) cadmium(II)	12	0.12	Tetrahedral

RESULTS AND DISCUSSION

Infra-red spectroscopy: The compound was synthesized by the reaction of one mole of 4, 6-dinitrobenzothiazole-2-amine with one mole of chloroacetic acid in presence of KOH. The above given data of FT-IR spectrum of the ligand, shows a characteristic stretching absorption bands at 3375.66 cm⁻¹ (NH), 3181.24 Cm⁻¹ (Ar=C-H), 1538 Cm⁻¹ (C=N), 1244.85 Cm⁻¹ (C-N), 1265.12 cm⁻¹ (C-S), 1387.75 and 1517.84 Cm⁻¹ (NO₃). The reaction between this ligand with Ni (II), Cu (II), Zn (II) and Cd (II) gave different types of complexes. In the free ligand, the bands at 1730 and 1057 cm⁻¹ were assigned to the stretching of C=O and C-O of the hydroxyl in the carboxyl ate group. On complexation these bands were shifted to a lower frequency region. This shift is probably due to the complexation of the metal to the ligand through oxygen of the carbonyl group, the disappearance of the hydrogen from hydroxyl group on complexation indicate the complexation is through the oxygen atom. Stretching of metal-oxygen bands of the complexes appeared in low frequency region (400-600) cm⁻¹.

UV-Visible Spectroscopy: The UV-Visible of the 4, 6-dinitrobenzothiazole-2-amine in ethanol solvent is recorded as given above the bands at the wavelengths 258 nm this transition may be attributed to $\pi \rightarrow \pi^*$ electronic transition. The electronic spectra of 4, 6-dinitrobenzothiazole-2-amine-acetic acid (LH) showed, as expected, at 264 nm. The absorptions appears for the complexes these bands were shifted to different wavelength than the corresponding bands in the ligand as shown in the above given data, which appears for the Ni(L)₂, Cu (L)₂, Zn(L)₂ and Cd(L)₂ in the wavelength range between 256-286 nm.

NMR spectroscopy: The ¹H NMR data of the 4, 6-dinitrobenzothiazole-2-amine; 4, 6-dinitrobenzothiazole-2-amine-acetic acid (LH) and its complexes were soluble in DMSO. The spectral data gave support for the interpretation of composition of the complexes, as explain above. The changes observed are the evidences of complexation had happened because the chemical shift of a compound is heavily depended on the environment of

proton. The ¹H NMR spectrum of the complexes confirmed the disappearance of OH signal at 11.69 ppm in the free ligand. The δ 7.24-8.92 ppm resonance signal protons of the aromatic ring shifted to the higher field upon complexation, while the proton of the -CH₂ aliphatic group shifted to higher field also. It is most likely that shift is due to the decrease of electron density at carbon atoms when oxygen is bonded to metal ion.

Magnetic susceptibility and conductivity measurements: The magnetic moment for each metal complex is given in Table. Magnetic measurements are widely used in studying transition metal complexes. The magnetic properties are due to the presence of unpaired electrons in the partially filled d-orbital in the outer shell of given elements. These magnetic measurements give an idea about the electronic state of the metal ion in the complex. The magnetic moment for Ni (II) in any complex is approximately 4.09 B.M., this value refers to a high spin tetrahedral structure, while the value of Cu (II) is approximately 1.78 led to suggest the square planar structure which can become in a good agreement with the data of electronic transitions. Other complexes have very less magnetic moment because it's diamagnetic. Molar conductivity measurement in DMF solvent at 30°C showed that the complexes were non-electrolyte as suggested in Table.

Study of complex formation in solution: Complexes of 4, 6-dinitrobenzothiazole-2-amine acetate with metal ions were studied in solution using ethanol as a solvent, in order to determine [M:L] ratio in the complex follow Molar ratio of 1:2. A series of solutions were prepared having a constant concentration for all complexes. The results of complexes in ethanol, suggest that the metal to ligand ratio was [1:2] for all complexes which were similar to that obtained from solid state Study. The structural arrangement is shown in figure 2.

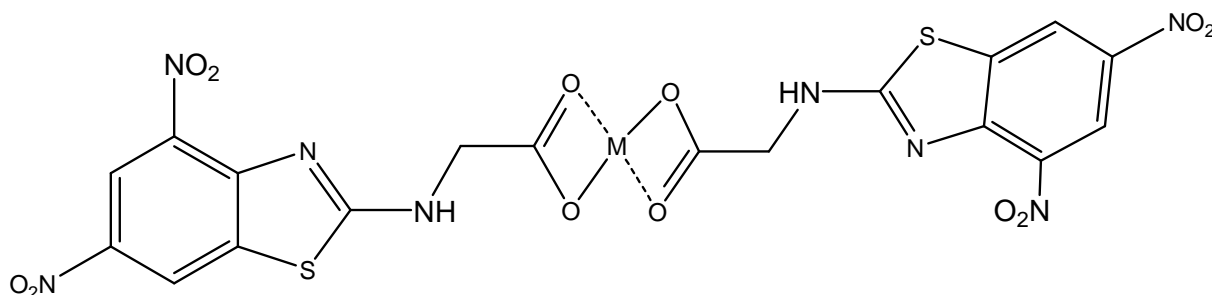


Figure: 2

CONCLUSION

The ligand 4, 6-dinitrobenzothiazole-2-amine-acetic acid were successfully synthesized by condensation method. The ligand was treated to different metal salts to afford the corresponding complexes. Square planar geometry was proposed for the copper complex. The other complexes were proposed to be tetrahedral.

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