Complexes of 2-Thioacetic Acid Benzothiazole with Some Metal Ions

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Abstract: New metal complexes of the ligand 2-thioacetic acid benzothiazole with the metal ions Ni(II), Cu(II), Zn(II), Cd(II) and Sn(II) were prepared in alcoholic medium. The prepared complexes were characterized by FTIR Spectroscopy, electronic spectroscopy, $^{1}$H NMR, $^{13}$C NMR, magnetic susceptibility and conductivity measurements. From the spectral measurements, monomer structures for the complexes were proposed. Square planar geometry was proposed for the copper complex. The other complexes were proposed to be tetrahedral.

Keywords: thioacetic acid, benzothiazole; metal complexes

INTRODUCTION

Increasing physiological importance of Oxygen donor organic compounds[1] and active role played by coordination certain metal ions to them[2] have interested use in synthesizing and studying structural aspects of metal complexes with some oxygen, sulphur and nitrogen donor ligands[3].

The aromatic benzothiazole nucleus is associated with a variety of antihistamine activity[4], pharmacological actions[5] such as fungicidal[6] and leishmanicides activities[7]. These activities are probably due to the presence of the -N = C-S group. Substituted benzothiazole have been reported to display diverse applications as photostabilizer and metal complexing agents[8,9].

The wide range of application of the ligand and its metal complexes aroused our interest to prepare a new series of some metal complexes.

MATERIALS AND METHODS

Synthesis of 2-thioacetic acid benzothiazole: A mixture of 2-mercapto benzothiazole (0.1 mole) and chloroacetic acid (0.1 mole) in presence of KOH as a basic media was refluxed for 3 h to give 2-thioacetic benzothiazole (LH), the white yellow precipitate which formed was filtered and crystallized from ethanol to give the final product.

The steps of the synthesis of 2-thioacetic benzothiazole can be shown below.

Preparation of complexes: Addition of ethanol solution of the suitable metal salt (Nickel acetate tetrahydrate, Tin chloride, Copper acetate, Cadmium acetate dihydrate and Zinc acetate dihydrate) to an ethanol solution of 2-thioacetic acid benzothiazole in 2:1 (ligand: metal) molar ratios was carried out. After reflux for half an hour, crystalline colored precipitates formed at room temperature. The rustling solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50°C. Table 1 shows the melting point of the prepared compounds.

Instrumentation: Elemental C, H, N and S analysis were carried out on a Fison EA 1108 analyzer, the FTIR spectra in the range (4000-200) cm$^{-1}$ cut were recorded as CsI disc on FTIR.8300 Shimadzu Spectrophotometer, uv-visible spectra were measured using Shimadzu Uv-vis. 160 A-Ultra-violet Spectrophotometer in the range (200-1000) nm. The magnetic susceptibility values of the prepared
Table 1: Physical data for preparation ligand and the complexes

| Compound | Melting point °C | Found(Calcd)% |
|----------|-----------------|----------------|
| L_2     | 177-179         | 48.11(47.98)   |
| Ni(L)_2 | 141-143         | 24.99(24.62)   |
| Cu(L)_2 | 180-182         | 33.67(24.22)   |
| Zn(L)_2 | 161-163         | 42.65(42.07)   |
| Cd(L)_2 | 145-147         | 38.84(38.11)   |
| Sn(L)_2 | 350-352         | 37.65(38.54)   |

Table 2: Characteristic absorption bands of 2-thioacetic acid benzothiazole and its complexes

| Compound | υ(C=O) cm⁻¹ | υ(C-O) cm⁻¹ | υ(M-O) cm⁻¹ |
|----------|-------------|-------------|-------------|
| L_2      | 1710        | 1033        | -           |
| Ni(L)_2  | 1590        | 1002        | 440         |
| Cu(L)_2  | 1670        | 985         | 412         |
| Zn(L)_2  | 1564        | 995         | 428         |
| Cd(L)_2  | 1569        | 979         | 435         |
| Sn(L)_2  | 1660        | 985         | 414         |

Table 3: Electronic spectra for 2-thioacetic acid benzothiazole and its complexes in DMSO solvent

| Compound | Color | Absorption bands (nm) | Assigned transition |
|----------|-------|-----------------------|---------------------|
| L_2      | Yellow| 282 301 328           | π → π*              |
| Ni(L)_2  | Pale green | 281 301 460     | π → π*              |
| Cu(L)_2  | Green | 296 308 610 3A_2 → 3T_1       | π → π*              |
| Zn(L)_2  | Pale Yellow | 290 301 330 2B_1g → 2A_1g | π → π*              |
| Cd(L)_2  | White | 280 290 300           | π → π*              |
| Sn(L)_2  | White | 284 302               | π → π*              |

RESULTS AND DISCUSSION

**Infra-red spectroscopy:** The ligand was prepared by the reaction of one mole of 2-mercapto benzothiazole with one mole of chloroacetic acid in presence of KOH. Table 1 shows the physical data for the ligand and the prepared complexes. The data of CHNS and metal analysis were obtained using flame atomic absorption technique. The calculated values were in a good agreement with the experimental values.

The FTIR spectrum of the ligand, shows a characteristic stretching absorption bands at 3435, 1710, 1573 and 694 cm⁻¹ assigned to hydroxyl, carbonyl, C = N of the thiazole ring and the stretching of C-S group respectively.

The reaction between this ligand with Ni (II), Cu (II), Zn (II), Cd (II) and Sn (II) gave different types of complexes. In the free ligand, the bands at 1710 and 1033 cm⁻¹ were assigned to the stretching of C = O and C-O of the hydroxyl in the carboxylate 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 (412-440) cm⁻¹.[10]

The IR data of the complexes are shown in Table 2. The Table lists the stretching frequency (υ) for some of the characteristics groups exhibited by the ligand and complexes.

**Ultraviolet-visible spectroscopy:** The ultraviolet visible electronic spectrum of the 2-thioacetic acid benzothiazole (L_2) in DMSO solvent is recorded in Table 3. Bands at the wavelengths (282, 301 and 328 nm) This transition may be attributed to π→π* electronic transition.[11]

The electronic spectra of 2-thioacetic acid benzothiazole complexes showed, as expected, different absorptions from that of the free ligand. In the complexes these bands were shifted to different wavelength than the corresponding bands in the ligand as shown in Table 3, which appears in the wavelength range between 280-381 nm.

The ligand field electronic transitions between the metal d orbital’s appear in Ni (II) and Cu (II) bands located in the visible region at 460 nm for Ni (L)_2 assigned to the transition 3A_2 → 3T_1 (p) and 610 nm for Cu (L)_2 assigned to the transitions 2B_1g → 2A_1g. The other complexes were diamagnetic as expected for d⁰ ions, so that no (d-d) transition can be expected in the visible region.

**Magnetic susceptibility and conductivity measurements:** The experimental magnetic moment...
Table 4: Magnetic Moment, Conductivity measurements in DMF solvent

| Symbol  | Name                                      | Conductivity ohm$^{-1}$ cm$^2$ mol$^{-1}$ | Magnetic moment (B.M) | Suggested structure |
|---------|-------------------------------------------|------------------------------------------|-----------------------|---------------------|
| Ni(L)$_2$ | Bis(2-thioacetic acid benzothiazol) nickel(II) | 12                                       | 3.11                  | Tetrahedral         |
| Cu(L)$_2$ | Bis(2-thioacetic acid benzothiazol)copper(II) | 19                                       | 1.44                  | Square Planner      |
| Zn(L)$_2$ | Bis(2-thioacetic acid benzothiazol) zinc(II) | 10                                       | 0.00                  | Tetrahedral         |
| Cd(L)$_2$ | Bis(2-thioacetic acid benzothiazol) cadmium(II) | 15                                       | 0.00                  | Tetrahedral         |
| Sn(L)$_2$ | Bis(2-thioacetic acid benzothiazol) tin(II) | 10                                       | 0.00                  | Tetrahedral         |
| LH | 2-thioacetic acid benzothiazol | -                                       | -                     | -                   |

A series of solutions were prepared having a constant concentration (10$^{-3}$M) of the metal ion and (L).

Table 5: $^1$H NMR spectral data(δ,ppm) of the ligand and complexes

| Symbol  | -OH         | -CH$_2$ aliphatic | Aromatic       |
|---------|-------------|-------------------|----------------|
| Ni(L)$_2$ | 4.16        |                   | 6.35-7.14      |
| Cu (L)$_2$ | 4.22        |                   | 6.45-7.87      |
| Zn(L)$_2$ | 4.24        |                   | 6.35-7.94      |
| Cd(L)$_2$ | 4.23        |                   | 6.55-7.78      |
| Sn(L)$_2$ | 4.18        |                   | 6.65-7.87      |
| LH | 12.22       | 4.19              | 7.35-8.12      |

Table 6: $^{13}$C NMR spectral data (δ,ppm) of the ligand and complexes

| Symbol  | C = O       | aliphatic | Aromatic      |
|---------|-------------|-----------|---------------|
| Ni(L)$_2$ | 159.64      | 28.34     | 121.34-115.65 |
| Cu (L)$_2$ | 158.64      | 28.46     | 121.22-114.23 |
| Zn(L)$_2$ | 158.76      | 29.43     | 121.07-114.43 |
| Cd(L)$_2$ | 159.32      | 28.53     | 121.15-115.17 |
| Sn(L)$_2$ | 158.46      | 29.47     | 121.13-114.06 |
| LH | 169.51       | 30.30      | 121.22-114.26 |

The [M/L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M/L]. The results of complexes formation in solution.

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.

On the basis of the preceding discussion, the structure of the complexes suggested as follows:

**CONCLUSION**

The ligand 2-thioacetic acid benzothiazole 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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