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# Synthesis and Characterization of Mn(II), Co(II), Ni(II) and Cu(II) complexes with 1,1,2,2-tetrakis-(benzothiazolethio) ethylene and mercaptobenzothiazole salt

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## الخلاصة

تم تحضير وتشخيص الليكاند الجديد 2,2,1,1-رباعي- (بنزوثايازول ثايو) اثيلين كذلك ميركبتوبنزوثايازول البوتاسيوم وتم استخدامها في تحضير عدد من معقدات $Mn^{+2}$, $Co^{+2}$ , $Ni^{+2}$ , $Cu^{+2}$ ، كذلك تم تحضير مركبات الإضافة لبعض المعقدات المحضرة أعلاه مع 10,1 – فينانثرولين. تم تشخيص المعقدات ومركبات الإضافة بواسطة الطيف الالكتروني وطيف الأشعة تحت الحمراء والطيف الذري والتوصيلية الكهربائية والقياسات المغناطيسية. بينت كل من الطيف الالكتروني والقياسات المغناطيسية للمعقدات ومركبات الإضافة بان قسم من المعقدات يمتلك بنية رباعي السطوح، اما المعقدات الأخرى وكذلك مركبات الإضافة تمتلك بنية ثماني السطوح.

## Abstract

A new ligands 1,1,2,2-tetrakis-(benzothiazolethio) ethylene ($L_1$) and mercaptobenzothiazole potassium ($L_2$) had been synthesized, investigated and used in the preparation of $Mn^{+2}$, $Co^{+2}$, $Ni^{+2}$ and $Cu^{+2}$ complexes. Also the reaction of the above complexes with 1,10-phenanthroline has been reported. The complexes and adducts were characterized using IR and UV-visible spectroscopy, atomic absorption molar conductivity and magnetic moments measurements.

Electronic spectra and magnetic measurement showed that some of the complexes have tetrahedral geometry, the other complexes and the adducts have an octahedral geometry.

* Auther for correspondance

## Introduction

In recent years there has been intensive activity in the synthesis and evaluation of the biological activities of nitrogen and sulphur containing substituted mercapto compounds and their metal complexes[1-3].

The bis (N,N′-mercaptoethyl) -1,5-diazocyclooctane ligand and its dimethyl derivatives,bis (N,N′-mercapto-2-methylpropyl)-1,5-diazocyclo-octane provide a $N_2S_2$ molecular matrix that readily accommodates square-palnar geometry in its coordination complexes[4,5].

The 1H-pyridine-2-thione or its conjugate anion pyridine-2-thionate (Pys) can coordinate as monodentate ligands through the sulphur atoms[6].The anion also can coordinate as doubly bridging ligand through both sulphur and nitrogen atoms and through sulphur alone[7,8] as a chelating ligand with a very small bite[9] and as triply bridging ligand[10] such as $RhPd_2$ complex reported by Deeming et al.[8].

Model studies by coordination chemists were first published for the repair protein using thiolatozincate and it was found that in these compounds the thiolate dissociate from zinc prior to alkylation[11] subsequent studies by Hammes and Carrano[12] and Chiou et al.[13],employing uncharged zinc thiolate complexes in non polar solvents, have rendered it more likely that the thiolate is alkylated in the zinc bounded state.

In view of these results and in continuation of our comprehensive studies on the Co(II), Ni(II), Pd(II), Pt (II) and Cu(II) metal complexes with sulphur containing ligands[14-16], we describe here the reaction of metal chloride with the 1,1,2,2-tetrakis-(benzothiazolethio) ethylene ligand and potassium salts of the mercaptobenzothiazole. Also reported the synthesis of adduct of the above complexes with 1,10-phenanthroline.

## Experimental

All chemicals were of reagent grade were used as supplied from Fluka A.G.

The metal contents of the complexes were determined by standard methods[17]. The IR spectra of the complexes in KBr, as well as in nujol mull were recorded on Bruker IR spectrophotometer Tensor 27 in the range 4000-400cm$^{-1}$ and Perkin-Elmer 580B spectrophotometer in the 4000-200 cm$^{-1}$ range. The molar conductances of $10^{-3}$ M dimethyl sulfoxide (DMSO) solution of the complexes were recorded with a conductivity meter 4070 (Jenway) at room temperature. Electronic spectra were recorded on Shimadzu U.V/vis spectrophotometer UV160 for $10^{-3}$M solution of the complexes in (DMSO) at 25°C.Magnetic measurements were carried out on the solid by the Faraday's method using Bruker BM6 instrument.

## Preparation of compounds:

### Ligand:

The ligand 1,1,2,2-tetrakis-(benzothiazolethio) ethylene was prepared according to the following method.

The reaction of 2-mercaptobenzothiazole (5.40g,0.04 mmol) and NaOH (1.60g, 0.04 mmol) in ethanol (30 ml) with 1,1,2,2-tetrachloroethylene (1.56g,0.01mol) in ethanol (10ml). The mixture was boiled under reflux for ca. 6h. After cooling to room temperature, NaCl was removed by filtration. The solution was reduced in volume to ca 15ml and on cooling to ca 5°C a yellow precipitate was obtained, the product can be recrystallized from ethanol giving white solid.

## Preparation of $K_2[M(L_2)_4]$ complexes:

An aqueous solution (10 $cm^3$) of cobalt chloride hexahydrate (2.37g, 0.01 mol) was added to a stirred solution of 2-mercaptobenzo-thiazole (6.69 g, 0.04 mol) in ethanol (10 $cm^3$) and (2.24 g,0.04 mol) KOH in ethanol (20 $cm^3$). The mixture then refluxed about two hour and, then concentrated where upon standing a dark green precipitate was formed which was filtered off, washed with water and diethyl ether and dried over $P_2O_5$ .

The preparation of the other metal complexes followed essentially the same procedure.

## Preparation of $[M_2(L_1)Cl_4]$ complexes:

(M=Mn(II),Co(II),Ni(II) and Cu(II)

The complexes were prepared according to the to the following procedure. An alcoholic solution of metal salt (0.02 mol) in ethanol (10 ml) was mixed with a solution of the ligand (0.01 mol) dissolved in acetone (20 ml). This mixture was stirred with reflux for 2-3h.to ensure completion of the reaction. The solid thus obtained were filtered off, washed with ethanol, ether and dried under vacuum for several hours.

## Preparation of $[M_2(L_1)(phen)_2]Cl_4$ adducts:

The complex ($M_2LCl_4$) (0.01 mol) in (10 ml) DMF was added to a solution of the ligand 1,10-phenanthroline (0.36g,0.02 mol) in methanol (10 ml). The mixture was stirred with gentle heat for ca 2h.,during which time a precipitate started to deposit. This was cooled to room temperature and the solid filtered off, washed with methanol then dried under vacuum for several hours.

## Results and Discussion

Treatment of tetrachloroethylene with a sufficient amount of mercaptobenzothiazole in presence of NaOH results in the formation of the corresponding 1,1,2,2-tetrakis(benzothiazolethio) ethylene ligand($L_1$).

The complexes can be prepared directly by treating the prepared ligand ($L_1$) or potassium benzothiazolethiolate ($L_2$) with either $MnCl_2.4H_2O$, $CoCl_2.6H_2O$,$NiCl_2.6H_2O$ or $CuCl_2.4H_2O$ in boiling aqueous ethanol in a (1:2) or (4:1) metal for ratio[18], as well as, the adducts of some of the prepared complexes. The isolated complexes and adducts with 1,10-phenanthroline were also prepared, their physico chemical properties are listed in Table 1. In general, the complexes were slightly soluble in halogenated solvents but rather more soluble in N,N'-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO).

The molar conductances of $10^{-3}$ of complexes in DMF solution are in the 10-20, 60-90 and 140-160 $ohm^{-1}.mol^{-1}.cm^2$ range indicating the non electrolytic and electrolytic nature of the complexes and adducts with (1:2) and (1:4) molar ratios. This is consistent with the stoichiometry assumed for the complexes and adducts $K_2[M(L_2)_4]$, $[M_2(L_1)Cl_4]$ and $[M_2(L_2)(phen)_2]Cl_4$ . The ligands does not show any υ(SH) band in the region of 2500-2600 $cm^{-1}$ in which this stretching frequency generally expected[19]. The characteristic bands in the infrared of the free ligand occur at 1650,1590-1610 and 660-650 $cm^{-1}$ due to the stretching vibrations of υ(C=C), υ(C=N) and υ(C–S) respectively[20]. In the complexes and adducts of the above ligands, it was found that the band υ(C=C) and the bands υ(C=N) and υ(C–S) show lowering in the frequencies, indicating that these bands are involved in the coordination with metal ions (Table 2). The infrared of the complexes and adducts show new bands at 410-460,360-380 and 320-340 $cm^{-1}$, assigned to υ(M–N), υ(M–S) and υ(M–Cl)[21,22] respectively.

The electronic spectra of the complexes and adducts were recorded as $10^{-3}$ M solutions in DMSO and the results are presented in (Table 2). The complexes (3-6) are consistent with a tetrahedral coordination geometry. Mn(II) complex (3) shows maximum absorption at 28974 $cm^{-1}$ and a charge transfer band at 29673 $cm^{-1}$ indicating that Mn(II) complex has a tetrahedral environment[23].The electronic spectra of Co(II) complex (4) show bands observed in the visible region 14792 and 16286 $cm^{-1}$ is generally considered to a transition from singlet level of F state ($^4A_2$) to the P state ($^4T_1$) in tetrahedral geometry[23]. In the Ni(II) complex (5), the observed bands at 11534, 15060 are due a transition from the F state ($^3T_1$) to P state ($^3T_1$) in tetrahedral geometry. In the Cu(II) complex (6) the observed band at 11933 ,16286 $cm^{-1}$ which correspond to the transition $^2B_1g \longrightarrow {}^2A_2g$ and other transition at 32051 $cm^{-1}$ which correspond to charge transfer transition.

The electronic spectra of the complexes and adducts (7-14) recorded in DMSO are listed in Table 2.The electronic spectra of Mn(II) complexes (7 and 11) shows a number of bands (16923-18710,22500-25430 and 32258 $cm^{-1}$ of medium intensities. Since Mn(II) has $d^5$ electronic configuration, the same type of energy level diagram applies weather the metal ion surrounded by tetrahedral or octahedral environment, Generally the four band observed are assigned to $^6A_1g \longrightarrow {}^4T_1g(^4G)$, $^6A_1g \longrightarrow {}^4A_1g(^4G)$, $^6A_1g \longrightarrow {}^4Eg(^4D)$ and $^6A_1g \longrightarrow {}^4T_1g(^4p)$ transitions respectively. These values suggest octahedral geometry for Mn(II) complex and adduct. The Co(II) complex and adducts (8 and 12) show there presence of three bands in the region 22843-23809,17575-17980 and 10121-11200 $cm^{-1}$ which are assigned to $^4T_1g \longrightarrow {}^4T_2g(F)$, $^4T_1g(F) \longrightarrow {}^4A_2g(F)$ and $^4T_1g(F) \longrightarrow {}^4T_1g(p)(\upsilon_3)$ transitions respectively. These transtions are correspond to an octahedral Co(II) and adducts[24].The Ni(II) complex and adducts (9 and 13) shows the presence of three bands in the region 27548-28204,16230-18300, 12500-12836 $cm^{-1}$ which are assigned to $^3A_2g \longrightarrow {}^3T_1g(p)$ $(\upsilon_3)$, $^3A_2g \longrightarrow {}^3T_2g(F)(\upsilon_2)$ and $^3A_2g \longrightarrow {}^3T_1g(F)(\upsilon_1)$ transitions respectively. This shows an octahedral geometry around Ni(II).

The electronic spectra of Cu(II) complexes (10 and 14) show the presence of the bands at 15772-15948 $cm^{-1}$ a high may be assigned to $^2B_1g \longrightarrow {}^2Eg$ or $^2B_1g \longrightarrow {}^2B_2g$ transition and a bands at 26730-27850 $cm^{-1}$ attributed to charge transfer transition of Cu(II) ion[25].

The magnetic moment values of the Mn(II) complexes (1,7 and 11) are (5.63,5.90 and 5.82 B.M) (Table 1). These values of magnetic moments reveals the presence of five unpaired electrons these by showing that the complexes are of high spin type.

The Co(II) complexes (3,8 and 12) have magnetic moments of (4.56,4.24 and 4.13 B.M) which indicates the spin free nature of the complexes. It is also shows the presence of three unpaired electrons. The high spin tetrahedral Co(II) complexes have magnetic moments ranging from (4.0-5.20) and the octahedral complexes in the range of (4.0-4.80)[22]. So that our Co(II) complexes (4) has tetrahedral geometry while the complexes (8 and 12) has an octahedral geometry.

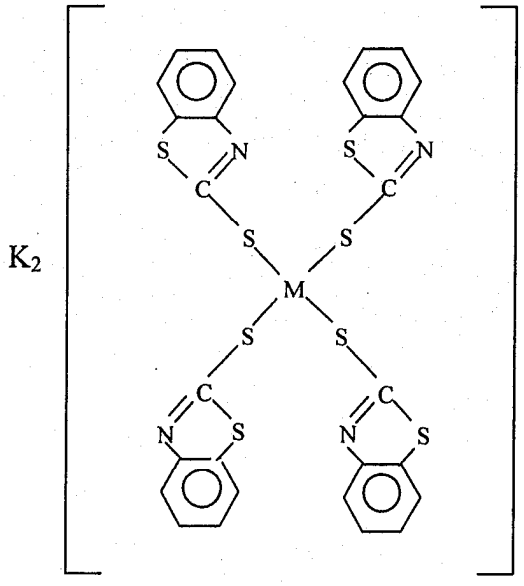
The Ni(II) complexes (5,9 and 13) have magnetic moments of (4.01,3.32 and 3.49 B.M), this suggest the presence of two unpaired electrons which reveal the high spin nature of the complexes. The tetrahedral Ni(II) complexes have magnetic moments in the range (3.2-4.0 B.M), while the octahedral Ni(II) complexes have magnetic moments in the range (2.9-3.4 B.M)[26]. The value of Ni(II) complexes (5) is a greed well with the tetrahedral geometry the high values are due to orbital contribution, while the complexes (9 and 13) have an octahedral geometry.

The magnetic moment of Cu(II) complexes (6,10 and 14) has been found to be (1.89,2.02 and 1.98 B.M). This corresponds to the presence of one unpaired electron in the complexes. These values with the electronic spectra indicate that complex (6) has tetrahedral geometry, while complexes (10 and 14) have higher values than spin only of respective metal ion indicating the spin free octahedral environment around the Cu(II) ion[24].

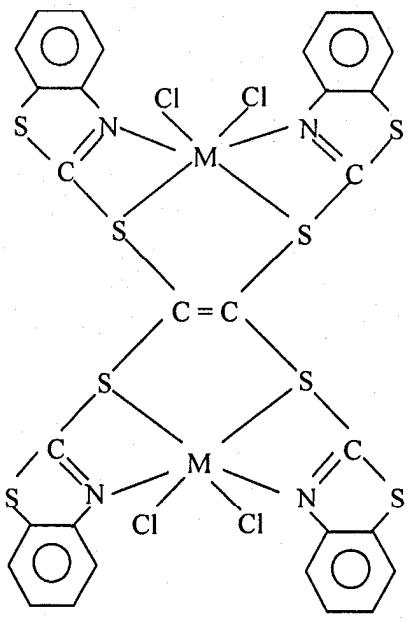
As a conclusion the ligands $L_1$ and $L_2$, used in this study, coordinate to the metal ions in monodentate and bidentate fashion from the S and S and N site of the ligand forming mononuclear and dinuclear complexes (3-14) as shown in Fig 1.

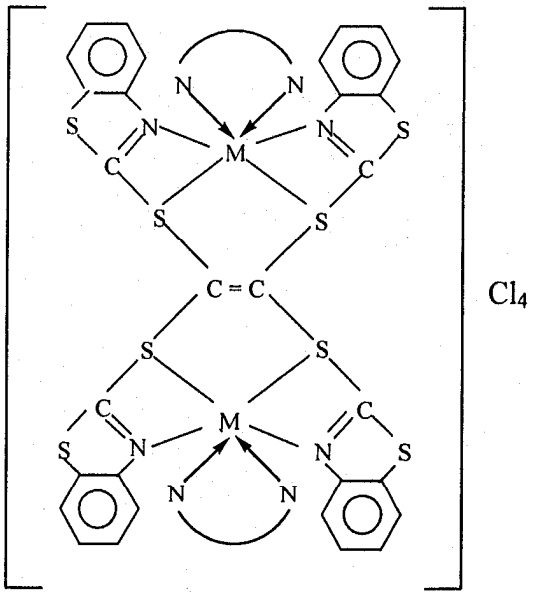
**Aknowldegment**

Dedicated to the memory of Prof.T.A-K.AL-Alaf.



(3-6)





(7-10) (11-14)

M = $Mn^{+2}$,$Co^{+2}$,$Ni^{+2}$ and $Cu^{+2}$

 = 1,10-phenanthroline

**Fig 1: Possible structure of the complexes**

**Table 1: Physical properties of the free ligand and their metal complexes**

| No. | Compounds | Colour | m.p (°C) | found (calcd.) % | | | | $\mu_{eff}$ (B.M) | $\Lambda$ $Ohm^{-1}.cm^2.mol^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | M | | |
| 1 | $C_3H_{16}N_4S_8$ ($L_1$) | white | 217 | *52.12 (52.33) | 2.31 (2.33) | 8.11 (8.14) | ---- | ---- | 10 |
| 2 | $C_7H_4NS_2K$ ($L_2$) | yellow | 270 | 40.91 (40.98) | 1.93 (1.95) | 6.81 (6.83) | ---- | ---- | 42 |
| 3 | $K_2[Mn(L_2)_4]$ | pale brown | 198-200 | | | | (6.90) | 5.63 | 79 |
| 4 | $K_2[Co(L_2)_4]$ | dark green | 160 d | | | | (7.36) | 4.56 | 85 |
| 5 | $K_2[Ni(L_2)_4]$ | dark brown | 221 d | | | | (7.33) | 4.01 | 90 |
| 6 | $K_2[Cu(L_2)_4]$ | dark yellow | 193 d | | | | (7.89) | 1.98 | 80 |
| 7 | $[Mn_2(L_1)Cl_4]$ | pale brown | 293-295 | | | | (11.70) | 5.90 | 20 |
| 8 | $[Co_2(L_1)Cl_4]$ | olive | 280-282 | | | | (12.45) | 4.24 | 30 |
| 9 | $[Ni_2(L_1)Cl_4]$ | kaki | 360 | | | | (12.39) | 3.32 | 18 |
| 10 | $[Cu_2(L_1)Cl_4]$ | green | 290 | | | | (13.27) | 2.02 | 28 |
| 11 | $[Mn_2(L_1)(phen)_2]Cl_4$ | dark green | 235 d | | | | (10.04) | 5.82 | 160 |
| 12 | $[Co_2(L_1)(phen)_2]Cl_4$ | dark green | 136 | | | | (10.69) | 4.13 | 140 |
| 13 | $[Ni_2(L_1)(phen)_2]Cl_4$ | greenish yallow | 191 | | | | (10.64) | 3.49 | 155 |
| 14 | $[Cu_2(L_1)(phen)_2]Cl_4$ | pale olive | 177 | | | | (11.41) | 1.89 | 150 |

d = decomposition temperature

* = CHN were carried out using Carlo Erba (CA1100) in Germany by Prof.Dr.T.K.AL-Alaf.

**Table 2: Electronic and infrared data of the ligands and its metal complexes and adducts**

| No. | Band position ($cm^{-1}$) | υ(C = C) | υ(C = N) | υ(C–S) | υ(M – S) | υ(M – N) | υ(M – Cl) |
|---|---|---|---|---|---|---|---|
| 1 | 31948 | $1650_s$ | $1610_s$ | $660_m$ | ---- | ---- | ---- |
| 2 | 28011 | --- | $1590_s$ | $650_m$ | ---- | ---- | ---- |
| 3 | 18974,29673 | --- | $1595_s$ | $635_m$ | $360_w$ | ---- | ---- |
| 4 | 14792,16286 | --- | $1590_s$ | $630_m$ | $370_w$ | ---- | ---- |
| 5 | 11534,15660 | --- | $1589_s$ | $640_m$ | $380_w$ | ---- | ---- |
| 6 | 11933,16286,32051 | --- | $1591_s$ | $638_m$ | $360_w$ | ---- | ---- |
| 7 | 16923,18550,23400,32258 | $1650_s$ | $1580_s$ | $630_m$ | $370_m$ | $410_m$ | $330_w$ |
| 8 | 10121,17575,22843 | $1660_s$ | $1582_s$ | $640_m$ | $360_m$ | $460_m$ | $340_w$ |
| 9 | 12500,16230,28154 | $1650_s$ | $1590_s$ | $542_m$ | $365_w$ | $450_m$ | $320_w$ |
| 10 | 15772,26730 | $1650_s$ | $1581_s$ | $635_m$ | $375_w$ | $450_m$ | $335_w$ |
| 11 | 17320,18710,22500,25430 | $1650_s$ | $1580_s$ | $645_m$ | $380_w$ | $460_m$ | ---- |
| 12 | 11200,17980,23809 | $1650_s$ | $1590_s$ | $650_s$ | $380_w$ | $420_m$ | ---- |
| 13 | 12836,18300,27548 | $1650_s$ | $1585_s$ | $630_m$ | $370_w$ | $440_m$ | ---- |
| 14 | 15948,27850 | $1650_s$ | $1580_s$ | $636_m$ | $360_w$ | $460_m$ | ---- |

s= strong, m = medium, w = weak

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