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Synthesis and Characterization of Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2} and Hg^{+2} Complexes with 1,1,2,2-tetrakis (Sodium Thioproponate) ethylene

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Abstract

The new ligand 1,1,2,2-tetrakis(sodium thioproponate) ethylene, has been prepared from the reaction of disodium salt of 3-mercaptoproponic acid and tetrachloroethylene in (4:1) molar ratio. Diand tetranuclear complexes were obtained by direct reaction of the above ligand with Co^{+2},Ni^{+2},Cu^{+2} , Zn^{+2} and Hg^{+2} metal ion in (1:2) and (1:4) ligand to metal molar ratio. The prepared complexes were characterization by elemental analysis, spectral studies (FTIR.,UV/vis), magnetic measurements, conductivity measurements. Electronic spectra and magnetic moment values indicate the presence of tetrahedral geometric around the metal ions.

Keywords: 1,1,2,2-tetrakis(sodium thioproponate), 3-mercaptoproponic acid and tetrachloroethylene, ligand to metal molar ratio, elemental analysis, spectral studies, magnetic measurements, conductivity measurements.

Introduction

Polyfuntional ligands with P-,S-,N-or O-donor atoms are often employed in the synthesis of polynuclear complexes. Heterobimetallies have received increasing attention,as they can be employed as biometallic compounds or in homogeneous catalysis or heterogeneous catalysis a combination of two or more different metals often enhances the catalytic properties[1-4].

New metal complexes of the ligand 2-thioacetic acid-5-pyridyl-1,3,4-oxidiazole with the metal ions Co(II), Ni(II) were prepared in alcoholic medium, the prepared complexes were characterized by F-TIR, electronic spectroscopy, elemental analysis, magnetic moment, conductivity measurements[5].

Yousif etal.[6,7] prepared new metal complexes of the ligand 2-2-thioacetic acid benzothiazole with the metal ions Ni(II),Cu(II),Cd(II) and Sn(II). The prepared complexes were characterized by IR,electronic spectroscopy ^{1}HNMR, magnetic moment and conductivity measurements, from spectral measurements, monomer structures for the complexes were proposed.

The synthesis and structural characterization of a novel In(II) complex is described. The reaction between $InCl_3$ with sodium mercaptoacetic acid ($NaSCH_2COOH$) in 4-methyl pyridine (4Mepy) at 25°c affords $[InCl(SCH_2COO)_2]^{-2}[(4\text{-}MepyH)_2]^{+2}$(1). X-ray diffraction studies of (1) show it to have a distorted square pyramidal geometry, with the [SCH_2COO] ligands in a trans conformation[8].

The photostablization of poly(vinylchloride) film by 2-thioacetic acid-S-phenyl-1,3,4-oxadiazole with Sn(II), Ba(II), Ni(II), Zn(II), Cu(II) and Ca(II) complexes was investigated[9].

A new multidentate ligand 1,4-bis(sodiumthioglycolate)butane (L) was prepared from the reaction between 1,4-dichlorobutane and disodiumthioglycolate. Complexes of general formula [M(L)], [M_2(L)], [$M_2(L)Cl_2(H_2O)_2$] and [$Zn_2M(L)_2]Cl_2$ where (M= Co(II), Ni(II),Cu(II) and Zn(II) were prepared through direct reaction of the above ligand with $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ respectively in (1:1), (1:2) and (2:3) ligand to metal ratio. The prepared complexes were characterized by their metal content, IR, U.V, magnetic and conductivity measurements[10].

Metal complexes with sulfur and oxygen containing are very interesting according to the above results we are presenting have the preparation of a new ligand 1,1,2,2-tetrakis (sodiumthioproponate) ethylene and there Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) complexes.

Material and Methods

All chemical were of ragent grade, were purchased from commercial source (BDH and Fluka) were used as supplied.

Physical characterization: Elemental analysis of the isolated complexed were accomplished by microanalytical techniques on Perkin Elmer 2400 (IEES) at AL-Abait University (Jordan) Metal estimation were done on PYEUNICAM Spg Atomic Absorption spectrophotometer. Conductivity measurements for 10^{-3}M solution of the complexes in (DMSO) were carried out on Jenway 4070 conductivity meter. Infrared spectra were recorded on a FTIR Brucker Tensor 27co spectrophotometer in the 200-4000 cm^{-1} range using CsI disc. The UV/Vis spectra were recorded on a Shimadzu UV-160 spectrophotometer for 10^{-3} M solution the complexes in DMSO using 1 cm quartz cell. Magnetic suceptiblities values were corrected for diamagnetic contribution using Pascal's constants.

Preparation of the ligand: preparation of disodium thioproponate: The reaction of equimolar amount of 3-mercaptoproponic acid sodium salt (0.11 g,0.001 mol) in (20 ml) ethanol with NaOH (0.80 g,0.002 mol) in (10 ml) absolute ethanol. The mixture was boiled under reflux for 2h. the product was obtained through filtrations, the precipitate was washed with ethanol , diethyl ether, then dried under vacuum for several hours.

preparation of 1,1,2,2-trakis (sodium thiolacte) ethylene (L): A solution of disodium thioproponate (0.60g,0.004 mol) in (20 ml) of ethanol was added to a solution of tetrachloroethylene (0.17 g,0.001 mol) in (10 ml) ethanol. The mixture was boiled under reflux for 6h., NaCl was removed by filtration, the precipitate was filtered off washed several times with ethanol and diethylether then dried under vacuum for 4h.

Preparation of [M_2L] complexes: M= Co^{+2},Ni^{+2},Cu^{+2} and Zn^{+2}

A solution of a metal chloride (0.002 mol) in (10 ml) ethanol was added to a stirred solution of the ligand (L) (0.53 g,0.001 mol) in (10 ml) ethanol. The reaction mixture was refluxed for 3h., and then the mixture was left 24h. at room temperature to give the precipitate , which was filtered off in order to remove the NaCl formed, then washed several times with ethanol and diethylether, then dried under vacuum for several hours.

Preparation of [$M_2Hg_2(L)Cl_4$] complexes: A solution of metal chloride (0.002 mol) in (10 ml) ethanol, and mercuric chloride (0.54g, 0.002mol) in (10 ml) ethanol were added to a solution of the ligand (L)(0.53g,0.001mol) in (10 ml) ethanol. The mixture was refluxed for 3h. and the product were obtained as in the above procedure.

Results and Discussion

The ligand 1,1,2,2-trakis (sodium thioproponate) ethylene is prepared from the substituation reaction of disodium salt of this proponic acid with tetrachloroethylen in (4:1) molar ratio as show in scheme 1, white solid and acts as tetradentate and octadentate from oxygen sulfur and atoms with the metal ions. The complexes were prepared through direct substitution and addition reactions by the relevant thiolactate ligands as oxygen or sulfur has stronger preferences for metal ions. All complexes are thermally stable and insoluble in organic solvent, however fair solubility in DMSO and DMF. The analytical data (table 1) of the metal complexes show that all complexes are non electrolytic nature[11].

The infrared spectrum of the ligand, show a characteristic stretching absorption bands at 1588,1424 and 884 cm^{-1} assigned to carbonyl υ (COO) $_{sym}$ and υ (C-S) groups respectively. The (COO) stretching vibrations are important to predict the bonding mode of the ligand. The values of Δυ (Δυ = $υ_{asym}$(COO)- $υ_{sym}$ (COO)) can be divided into three groups[12-15]. i. in compound where Δυ (COO)> 350 cm^{-1} , the caboxylate group binde in a mono dentate fashion. ii. when Δυ (COO)< 200 cm^{-1} the carboxylate groups of thesecompounds can be considered to be bidentate. iii. in compounds where Δυ (COO)> 200 cm^{-1} and < 350 cm^{-1} an intermediate state between mono and bidentate (an isobidentate) occurs. It has also been suggested that the Δυ (COO) value in the chelating mode is less than the Δυ (COO) in a bridging mode[16].

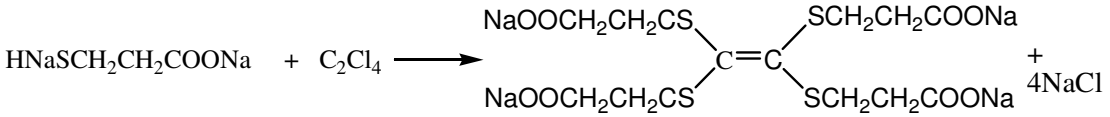
Two bands are observed at 1582-1617 and 1361-1424 cm^{-1} and the difference in ΔυCOO- (187-232) cm^{-1} (table 2) are indicative of bidentate nature of carboxylate group[17].

Further support for this argument cane from the IR of the complexes which showed a new bands at 480-510 cm^{-1} which may attributable to υ (M-O), and also bands in the region 290-320 cm^{-1} υ (Hg-Cl)[18,19].

The υ (C-S) band of the ligand was observed at lower frequency values in the complexes table 2, further support for this coordination has provided from the appearance of new bands in the 340-370 cm^{-1} ranges which tentatively attributed to υ (M-S)[20,21].

The experimental magnetic moment for each complex in listed in table 1. The magnetic measurements give an idea about the electronic state of the metal ion in the complex. The magnetic moments are (4.56 and 4.24) B.M for Co(II) complexes (1 and 5) respectively, while for Ni(II) complexes (2 and 6) are (3.20 and 3.79) B.M, for Cu(II) complexes (3 and 7) are (1.9 and 2.09) B.M, suggest the presence of one unpaired electron , Zn(II) complexes (4,8) and Hg(II) complexes are diamagnetic.

The UV-visible spectra of the ligand and their complexes in 10^{-3} M solution of DMSO were recorded, the results were listed in table 3. The band observed at 34364, 29041 cm^{-1} were due to π-π* or n-π* transition with in the ligand. The spectrum of cobalt (II) (1 and 5) complexes show a bands at (14641-15974 and 30030-30209) cm^{-1} these bands is assigned to ^4A_2g $^4T_1g(p)$ transition and charge transfer, which is consistent with proposed tetrahedral symmetry for these complexes. Further the blue and violet colors of these complexes support its proposed tetrahedral geometry[22].

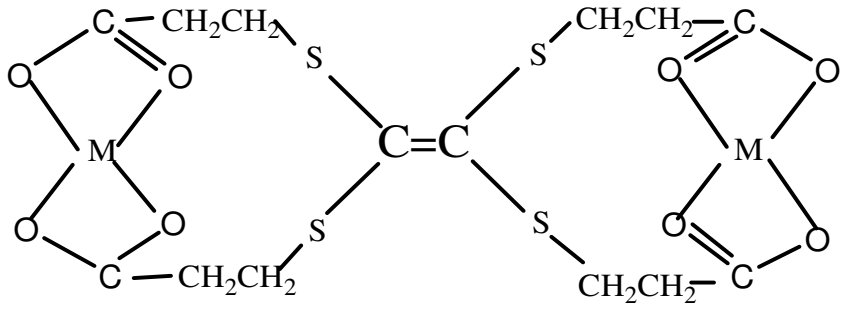


Scheme-1
Preparation of the ligand (L)

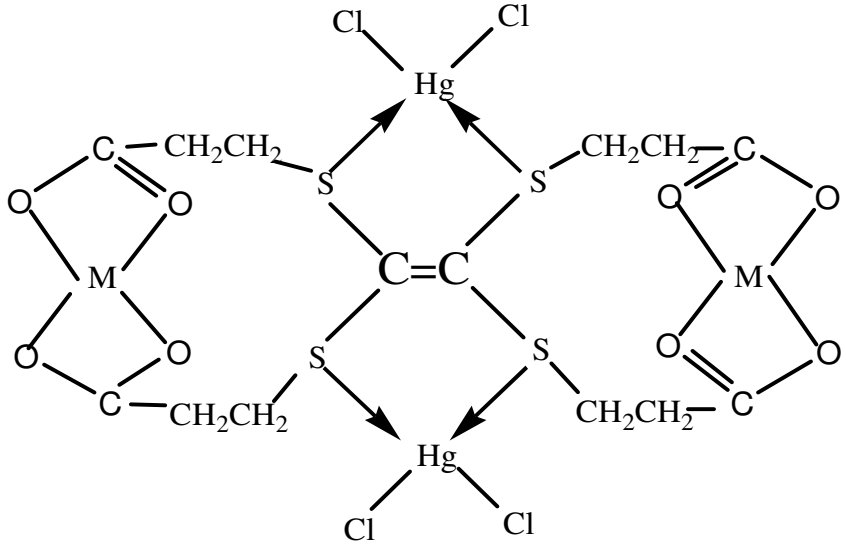
The electronic spectra of Ni(II) complexes No(2,6) the observed bands at (14124 and 12771) cm^{-1} are due to transition $^3T_1(F) \longrightarrow {}^3T_1(p)$ (υ_3) in tetrahedral symmetry[23].

In case of Cu(II) complexes (3 and 7) a band at (15220 and 12903) cm^{-1} were assigned to $^2T_2 \longrightarrow {}^2E$ transition in tetrahedral environment[24]. The magnetic susceptibility showed that all Zn(II) and Hg(II) complexes (4,5-8) were diamagnetic and the electronic spectra of these complexes do not show any d-d band.

The ligand used in this study, coordinate to the metal ions from the oxygen atoms of the carboxylate groups and the sulfur atoms of thioether groups acting as tetradentate and octadentate ligand, as show in figure 1.



(1-4)



(5-8)

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

Figure-1
Suggest structures for the complexes

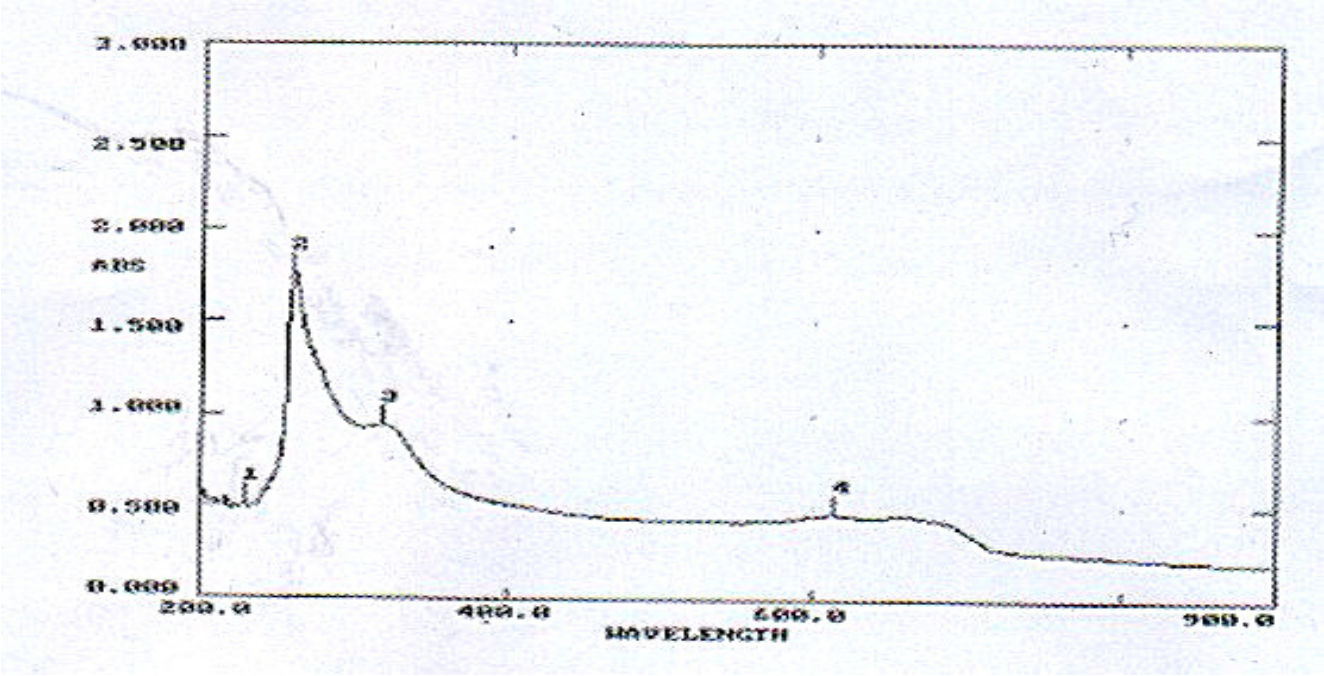


Figure-2
Electronic spectra of $[Co_2(L)]$ complex(1)

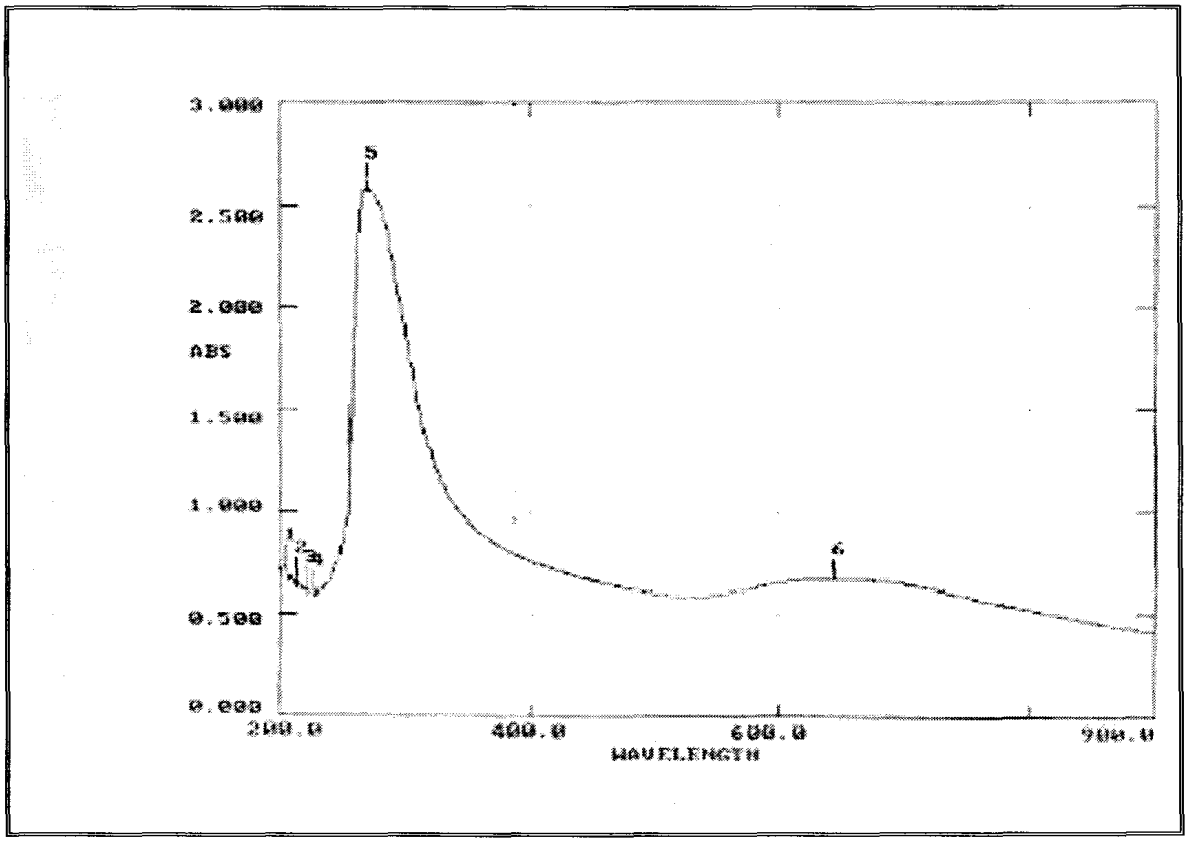


Figure-3
Electronic spectra of $[Cu_2(L)]$ complex(3)

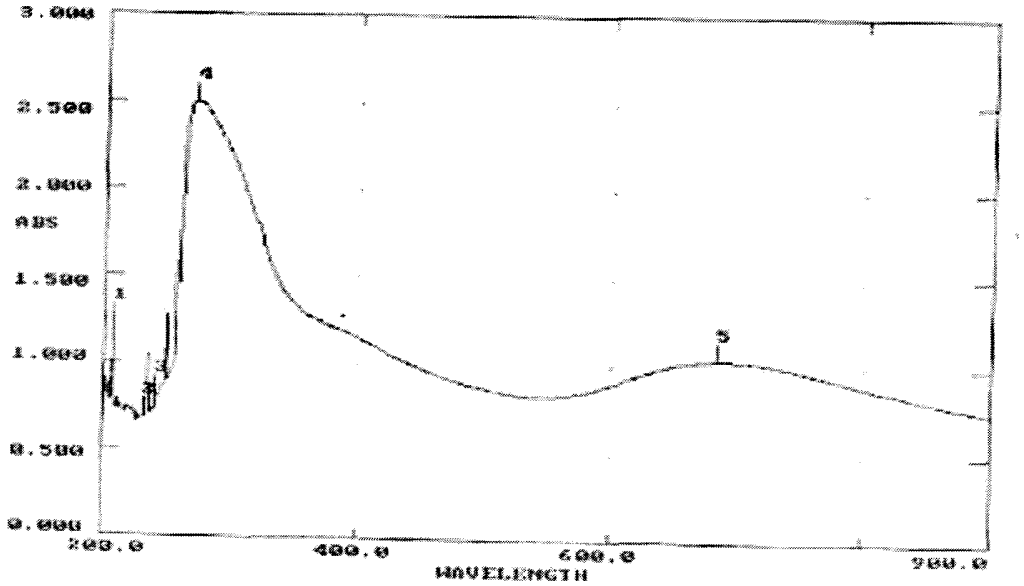


Figure-4
Electronic spectra of $[Cu_2Hg_2(L)]$ complex(7)

Table-1
Physical properties of the complexes

Seq.	compound	m.p (°c)	Color	Analysis ,found (calc.)%					Molar conductivity (Λ) $cm^2.ohm^{-1}.mol^{-1}$	μ_{eff}
				C	H	S	M	Hg		
L	$C_{14}H_{16}O_8S_4Na_4$	238-239	Bieje	31.21(31.29)	3.00(3.01)	24.01(24.06)	----	----	---	---
1	$[Co_2(L)]$	>350	Blue	30.06(30.10)	2.79(2.86)	22.89(22.94)	21.09(21.15)	----	15	4.56
2	$[Ni_2(L)]$	290	Dark brown	30.09(30.16)	2.81(2.87)	22.91(22.98)	21.00(21.10)	----	12	3.20
3	$[Cu_2(L)]$	285	Olive sreen	29.10(29.16)	2.79(2.820	22.51(22.57)	22.35(22.40)	----	20	1.90
4	$[Zn_2(L)]$	272	White	29.39(29.43)	2.75(2.80)	22.39(22.42)	22.89(22.92)	----	18	Dia
5	$[Co_2Hg_2(L)]$	180	Violet	15.20(15.26)	1.41(1.45)	11.59(11.63)	10.69(10.72)	36.39(36.43)	26	4.24
6	$[Ni_2Hg_2(L)]$	160	Green	15.19(15.27)	1.40(1.45)	11.59(11.64)	10.60(10.64)	36.40(36.47)	22	3.79
7	$[Cu_2Hg_2(L)]$	130	Dark yellow	15.10(15.13)	1.41(1.44)	11.51(11.53)	11.40(11.44)	35.99(36.14)	14	2.09
8	$[Zn_2Hg_2(L)]$	213	Yellowish	15.03(15.08)	1.40(1.43)	11.21(11.49)	11.69(11.74)	35.97(36.02)	18	Dia

d= decomposition temperature

Table-2
IR spectra and electronic spectral data of the ligand and their complexes

Compl. no.	Band maxima (λ_{max})cm^{-1}	$\upsilon_{as.}$(COO)	$\upsilon_{sy.}$(COO)	$\Delta\upsilon = (\upsilon_{as.} - \upsilon_{s.})$	υ (C-S)	υ (M-Cl)	υ (Hg-S)	υ (M-O)
L	34364,26041	1588_S	1424_S	---	884_m	---	---	---
1	14164	1583_S	1362_S	221_w	880_w	---	---	500_m
2	14124	1616_S	1409_m	305_S	881_m	---	---	520_w
3	15227	1617_m	1430_w	187_m	882_m	---	---	510_m
4	29940	1616_S	1384_S	232_m	884_w	---	---	525_w
5	14814	1616_S	1400_m	216_w	832_S	325_S	380_w	530_S
6	12771	1594_S	1361_S	233_m	835_m	310_S	370_m	496_w
7	14619	1622_m	1411_m	211_S	846_S	320_m	390_m	504_m
8	28653	1582_m	1364_S	218_m	845_m	312_S	404_S	514_m

Conclusion

The prepared complexes were characterization by elemental analysis, spectral studies (FTIR.,UV/vis), magnetic measurements, conductivity measurements. Electronic spectra and magnetic moment values indicate the presence of tetrahedral geometric around the metal ions.

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