Synthesis and Characterization of 2,2́-(Terephthaloyl) bis (azanediyl) bis (3-mercapto propanoic acid) and its Complexes with some Metal Ions

Asia Hameed Abed
Email : asiahameed2010@yahoo.com
Department of Chemistry , College of Science , University of Al-Mustansiryah

(NJC)

(Received on 13 /6 /2013) **(Accepted for publication 15 /12 /2013)**

Abstract

The ligand 2,2́-(Terephthaloyl) bis (azanediyl) bis (3-mercapto propanoic acid) (TAMPA) was synthesized from the reaction of terephthaloyl chloride with cysteine, it has been characterized and its structure was elucidated depending upon elemental analysis (CHNS) and spectral data (IR , UV-Vis) . Series of metal complexes of the deprotenated ligand with ions such as Mn(II) , Co(II) , Ni(II) , Cu(II) and Zn(II) have been synthesized and characterized by (FT-IR) , (UV-Vis) spectroscopy , flame atomic absorption technique, magnetic susceptibility and conductivity measurements. The following general formula were suggested $[M_2(TAMPA)(H_2O)_4]$.

Keywords : Complexes, Cysteine, terephthaloyl chloride

الخلاصة

حضر الليكاند من تفاعل تيرفثالويل كلورايد مع السستاين ,ثم شخص وتم اقتراح تركيبه الكيميائي باعتماد التحليل الدقيق للعناصر , التحاليل الطيفية (طيف الاشعة تحت الحمراء وطيف الاشعة فوق البنفسجية والمرئية) , حضرت سلسلة من المعقدات الفلزية لليكاند مع الايونات الفلزية مثل Mn (II) , Co (II) , Ni (II) , Cu (II) , Zn(II), تم تشخيصها باستخدام طيف الاشعة تحت الحمراء وطيف الاشعة فوق البنفسجية والمرئية , تقنية الامتصاص الذري اللهبي للعناصر اضافة الى قياسات الحساسية المغناطيسية والتوصيلية المولارية , وقد تم اقتراح التراكيب العامة التالية استنادا الى نتائج هذه التحاليل $[M_2(TAMPA)(H_2O)_4]$.

الكلمات المفتاحية : المعقدات, السستاين, تيرفثالويل كلورايد

Introduction

The Phthaloyl chloride isomers ,terephthaloyl chloride and isophthaloyl chloride are high production volume chemicals used in polymers to import flame resistance , chemical resistance and temperature stability and as water scavengers [1] . The adsorption and reaction of terephthaloyl chloride on Ag(III) was examined using X-Ray photoelectron spectroscopy and density functional theory [2] . The electronic structure of Hg (II) , Ni (II) , Cr (II) and Mo (V) complexes with cysteine were investigated by sulfur K-edge X-ray absorption near-edge structure spectroscopy and density functional theory [3] . Vanadium (III) cysteine complexes have been reported to be antitumoral agents [4] . Some metal ions such as Co (II) , Cu (II) and Zn (II) build with Cys_2macrochelate over sulfur group . It is shown that this additional interaction with amino group and sulfur group can influence the character of some amino acid complexes in biological systems [5] . A series of new ruthenium (II) complexes with different number of aldehyde groups have been synthesized and characterized for the simple and selective sensing of homocysteine and cysteine [6] . A new system for the oligomerization of amino acids was reported using nanoparticles as nanosizedsupports . They use L-Cysteine which is water – soluble and would readily bind to the surface of gold nanoparticles [7] . The Ni (II) complex of tripeptide LLL-asparagine-cysteine-cysteine , LLL-Ni^{II}-NCC , undergoes metal – facilitated chiral inversion to DLD-Ni^{II}-NCC , which increases the observed superoxide scavenging activity[8] .

In this paper we report the synthesis and characterization of 2,2́-(Terephthaloyl) bis (azanediyl) bis (3-mercapto propanoic acid) and its Complexes with different transition metal ions .

Experimental

Physical Measurements

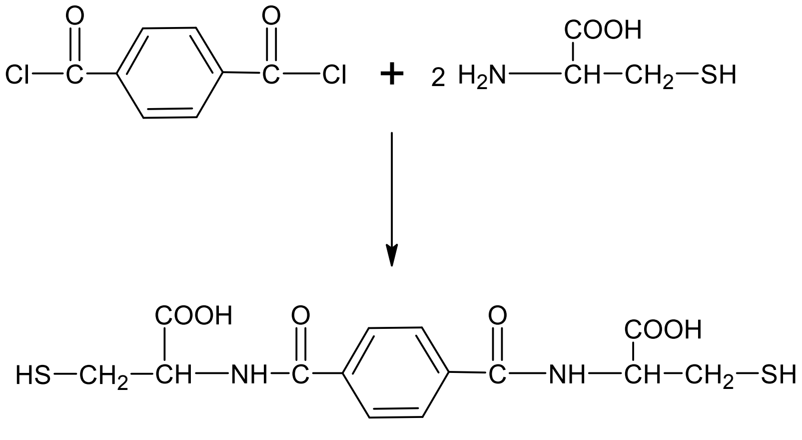
Melting points were recorded on Gallenkamp melting point apparatus and were uncorrected .Elemental analysis of the ligand was carried out on Euro EA 3000 . FT-IR spectra were recorded by using (FT-IR 8300 Shimadzu) in the range (400-4000) cm^{-1} as KBrdiscs . UV-Vis spectra for the compounds were measured in the region (200-900) nm for 10^{-3}M solution in DMSO by using VARIAN 100 concuv-vis spectrophotometer at room temperature . Metal contents of complexes were determined by Atomic absorption technique by using shimadzu (AA680 G) atomic absorption spectrophotometer . Conductivity measurmentsin (DMSO) were carried out using corning conductivity meter 220 . Magnatic susceptibility measurements were obtained at room temperature in the solid state applying Faraday's method by using Bruker BM6 instrument .

Materials

All reagents were obtained from commercial sources and used without further purification .

Synthesis of Ligand

Cysteine (2.42g , 0.02 mol) in 10 % sodium hydroxide (20 ml) was cooled at 0-5 C^o and the cold solution was added dropwise to a solution of terephthaloyl chloride (2.03g , 0.01 mol) in chloroform (30 ml) . The reaction mixture was continued under stirring for an additional 1h .Then the solution was acidified to pH 1-2 by using 10% hydrochloric acid . The product was collected by filtration and recrystallized from ethanol .The white solid was then dried to afford a yield 63% ,m.p. 190°C.



(TAMPA)

Synthesis of Metal Complexes

General procedure

Ethanolic solutions of each of the following metal ions salts containing (0.396 g , 0.476 g , 0.475 g , 0.341 g and 0.272 g) (2 mmol) of ($MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$) respectively were added to a solution of (TAMPA) (0.372g , 1 mmol) in ethanol containing sodium hydroxide (0.16 g , 4 mmol) . The mixture was heated under reflux for one hour , during this time a precipitate was formed . The product in each case was filtered , washed with hot ethanol and then dried under vacuum . Colour , yield , melting points and metal analysis for the complexes are given in Table (1) .

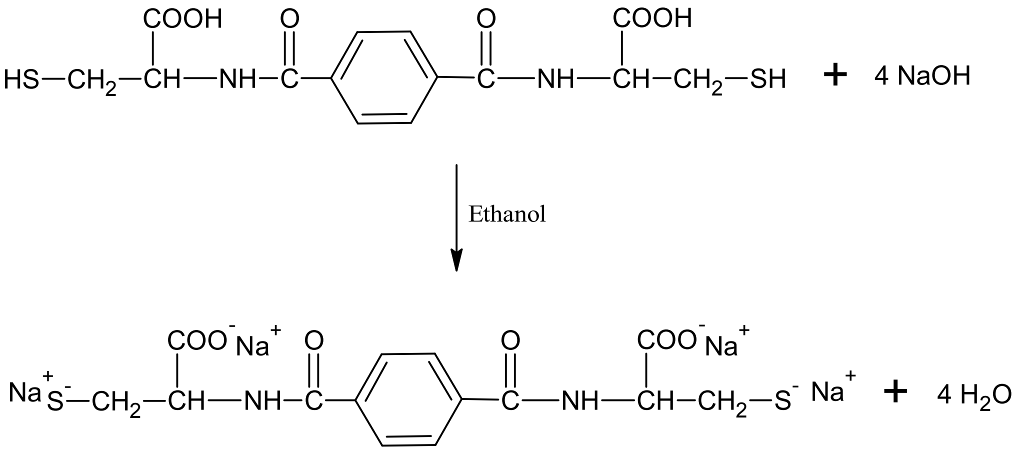
Table (1) : Physical data and metal analysis of (TAMPA) and its complexes with different metal ions .

Compound	Colour	Melting point C^o	Yield %	Metal analysis	
				Found %	Calc. %
TAMPA	White	190 dec.	63	-------	-----
$[Mn_2(TAMPA)(H_2O)_4]$	Light Brown	330 dec.	68	18.23	19.97
$[Co_2(TAMPA)(H_2O)_4]$	Pink	320 dec.	75	21.98	21.12
$[Ni_2(TAMPA)(H_2O)_4]$	Green	195 dec.	62	21.34	21.05
$[Cu_2(TAMPA)(H_2O)_4]$	Blue	180 dec.	70	22.85	22.39
$[Zn_2(TAMPA)(H_2O)_4]$	White	340 dec.	78	23.33	22.91

Results and Discussion

The ligand (TAMPA) was synthesized from the reaction of terephthaloyl chloride and L-Cysteine in mole ratios of (1:2) respectively . The ligand was characterized by elemental analysis C, 45.16 , H, 4.30 , N, 7.52 , S, 17.20 found C, 45.58 , H, 4.68 , N, 7.03 , S, 16.92 as well as IR and UV spectroscopy .

The synthesis of metal complexes involved the deprotonation of the ligand by alkaline solution (as shown below).



FTIR Spectra

In order to study the binding mode of the ligand (TAMPA) to the metal ion in complexes , the IR spectra of free ligand was compared with the spectra of the complexes (Table 2) . The IR spectrum of the free ligand was confirmed from the disappearance of the two bands at 3450 cm^{-1} and 3200 cm^{-1} of υ (NH_2) asym, sym vibrations of cysteine and appearance of characteristic peak related to υ (N-H amide) at 3306 cm^{-1} that gave us a strong evidence about the reaction of cysteine with terephthaloyl chloride as well as the ligand has absorption band at 2549 cm^{-1} which is assigned to the υ

(S-H) vibration . The band at 3406cm^{-1} is assigned to υ (O-H) vibration . The spectrum also shows band in the region 1687 cm^{-1} which is assigned to the υ (COO) asym. The absorptions bands at 1641 cm^{-1} and 1425 cm^{-1} could be explained as υ (C=O) amide and υ (COO) sym stretching respectively [9,10] .

In all complexes the ligand behaves as a bidentateand coordinate with the metal ions through the sulfur and carboxylic group , absorption assigned for υ (COO) sym was observed at range (1321-1388) cm^{-1}shifted to lower position and also the bands related to υ (COO) asym observed around (1631-1660) cm^{-1} shifted to lower positions which indicate the coordination of carboxylic group to the central metal ion [11] . In the far infrared region , all complexes exhibited bands around (443-482) cm^{-1} and (407-411) cm^{-1} which could be assigned to the vibration of υ (M-O) and υ (M-S) , respectively [12] . A broad band was observed around (3338-3402) cm^{-1} in the spectra of all complexes assigned to a υ (O-H) and suggested the presence of a water molecules in coordination sphere of the complexes .

Table (2) Important stretching vibrations (cm^{-1}) of (TAMPA) and its metal complexes

Compound	υ(N-H)	υ(O-H) υ(S-H)	υ(O-H) of water	υ(C-H) aromatic υ(C-H) aliphatic	υ(OCO) asym	υ(C=O) amide	υ(OCO) sym	Δυ (COO-)	υ(C=C) aromatic	υ(M-O) υ(M-S)
TAMPA	3306	3406 2549	—	3064 2962	1687	1641	1425	262	1535 1514	—
$[Mn_2(TAMPA)(H_2O)_4]$	3259	— —	3402	3093 2955	1631	1545	1386	245	1504	482 410
$[Co_2(TAMPA)(H_2O)_4]$	3342	— —	3398	3030 2945	1640	1581	1381	259	1500	457 407
$[Ni_2(TAMPA)(H_2O)_4]$	3305	— —	3338	3060 2900	1655	1577	1375	280	1500	459 411
$[Cu_2(TAMPA)(H_2O)_4]$	3298	— —	3398	3070 2902	1644	1573	1321	323	1504	451 410
$[Zn_2(TAMPA)(H_2O)_4]$	3383	— —	3433	3050 2902	1660	1575	1388	272	1588	443 408

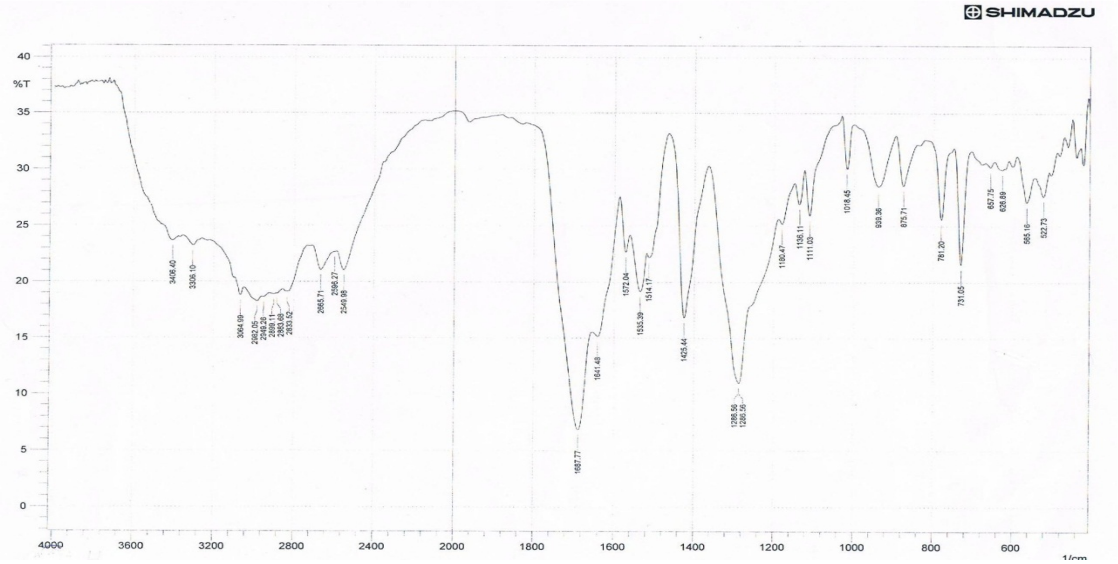


Figure 1 : FT-IR spectrum of (TAMPA)

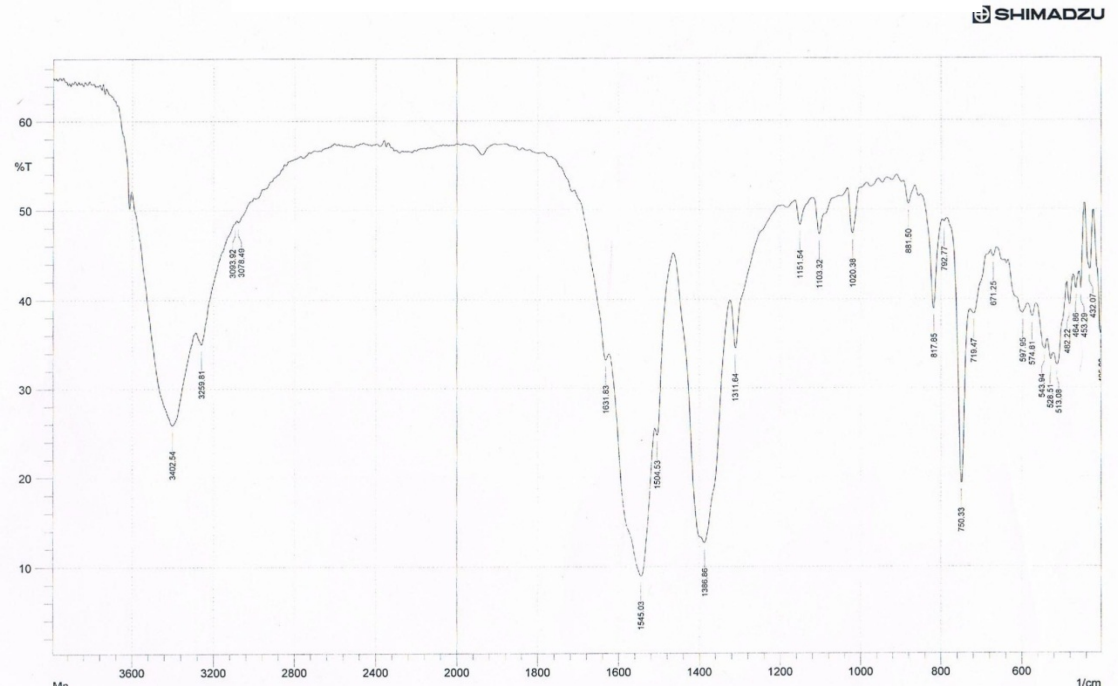


Figure 2 : FT-IR spectrum of $[Mn_2(TAMPA)(H_2O)_4]$

Electronic Spectra

UV-Vis spectrum of the ligand (TAMPA) Fig. (3)exhibited an intense absorption peak at (239 nm)(41841cm^{-1}) related to the π-π* transition and at (349nm) (28653 cm^{-1}) related to n-π* transition .

The UV-Vis spectra of all prepared complexes showed hypochromic shift of ligand band . Bands with very low extinction coefficients appeared in the visible region ,these bands were attributed to ligand field (d-d) transitions [13-15] .

The electronic spectra of the ligand and its complexes were recorded in DMSO solution , and the electronic spectral data , Magnetic moment data and molar conductivity of (TAMPA) complexes are described in (Table 3) .

The electronic spectrum of Mn(II) complex showed the (C.T) transition (259nm) (38610cm^{-1}) plus a band at (883nm) (11325cm^{-1}) which could be attributed to $^6A_1 \rightarrow ^4T_1(G)$. The position of these bands together with magnetic moment value (5.89 B.M) suggests a tetrahedral geometry around the Manganese (II) ion .

Table (3) : Electronic spectral data , Magnetic moment and metal conductivity of (TAMPA) and its metal complexes .

Compound	λmax nm (υcm^{-1})	Assigment	Molar Cond. μ S. cm^{-1}	μeff. (B.M)
TAMPA	239(41841) 349(28653)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	—	—
$[Mn_2(TAMPA)(H_2O)_4]$	259(38610) 883(11325)	C.T $^6A_1 \rightarrow ^4T_1(G)$	11.5	5.89
$[Co_2(TAMPA)(H_2O)_4]$	242(41322) 679(14727) 884(11312)	C.T $^4A_2 \rightarrow ^4T_1(P)$ $^4A_2 \rightarrow ^4T_1(F)$	10.9	4.74
$[Ni_2(TAMPA)(H_2O)_4]$	273(36630) 417(23980) 887(11273)	C.T $^1A_1g \rightarrow ^1B_1g$ $^1A_1g \rightarrow ^1A_2g$	6.5	Dia Mag.
$[Cu_2(TAMPA)(H_2O)_4]$	287(34843) 899(11123)	C.T $^2T_2 \rightarrow ^2E$	8.6	2.12
$[Zn_2(TAMPA)(H_2O)_4]$	262(38167)	C.T	12.2	Dia Mag.

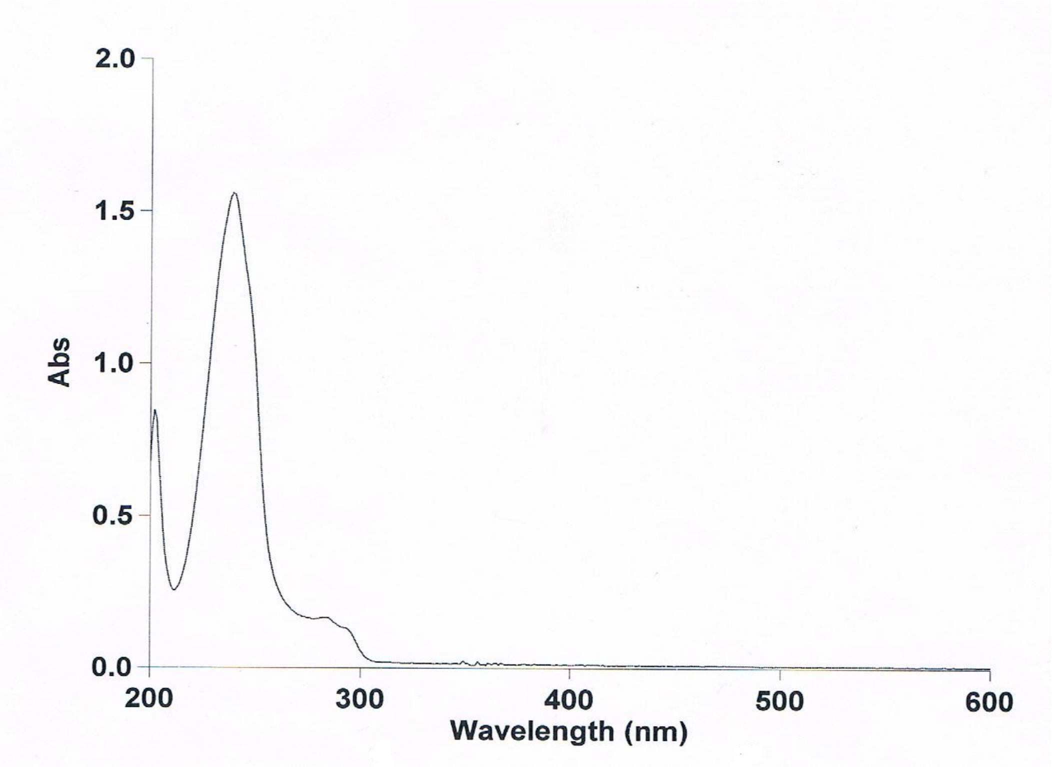


Figure 3 : Electronic spectrum of (TAMPA)

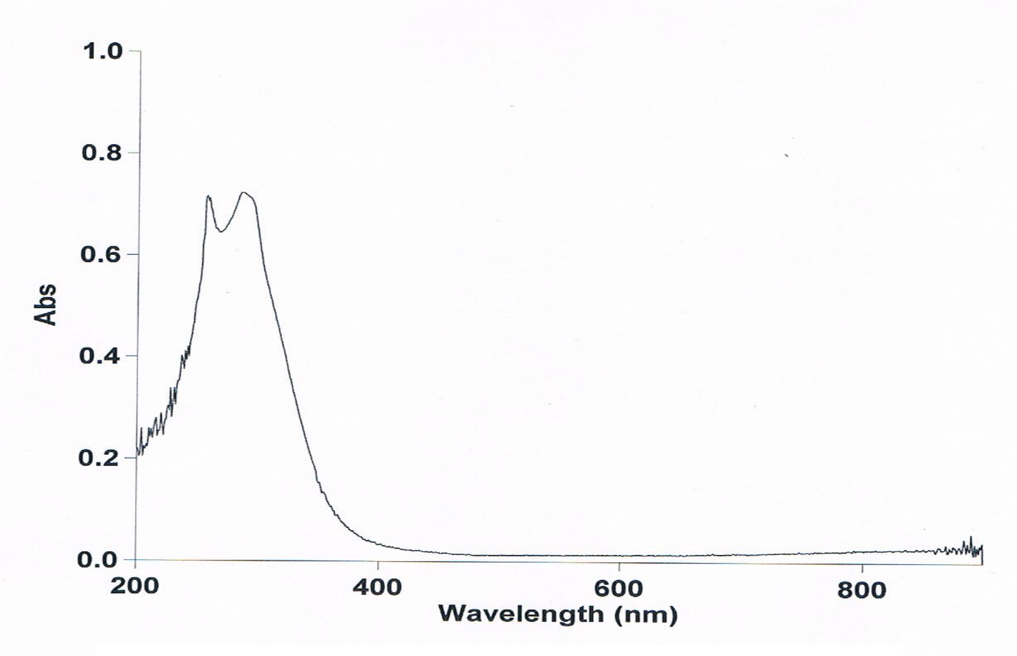


Figure 4 : Electronic spectrum of $[Cu_2(TAMPA)(H_2O)_4]$

The electronic spectrum of Co (II) complex displayed three peaks at (242nm) (41322cm^{-1}) , (679nm) (14727cm^{-1}) and (884 nm) (11312cm^{-1}) . These bands may be assigned to C.T ,$^4A_2 \rightarrow ^4T_1(P)$ and $^4A_2 \rightarrow ^4T_1(F)$ transitions respectively . The position of these bands suggests a tetrahedral environment around the cobalt (II) .

The spectrum of Ni(II) complex displayed absorption bands at (273 nm) (36630cm^{-1}) , (417nm) (23980cm^{-1}) and (887nm) (11273cm^{-1}) . These bands could be attributed to the spin allowed transitions C.T ,$^1A_1g \rightarrow ^1B_1g$and $^1A_1g \rightarrow ^1A_2g$respectively . The position of these bands together with magnetic moment value (0.00)confirms a square planar geometry of Nickel (II) complex .

The electronic spectrum of Cu (II) complex shows bands at (287 nm) (34843 cm^{-1}) and a broad band in the range (869 nm , 11507 cm^{-1} – 899 nm , 11123 cm^{-1}) , these bands corresponded to the C.T and $^2T_2 \rightarrow ^2E$transitions .

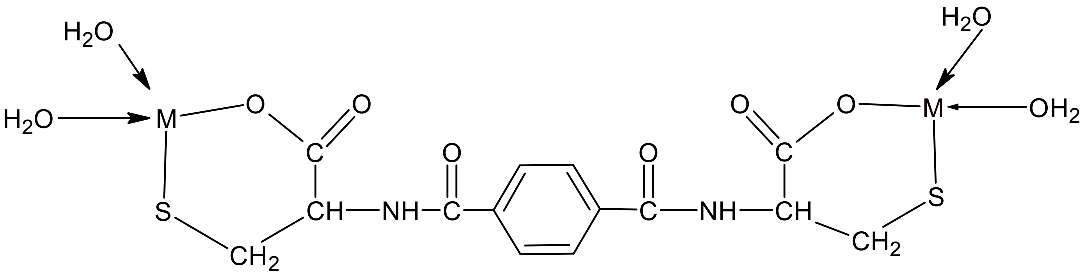
The positions of these bands confirm the Tetrahedral Cu (II) complex .Magnatic moment at room temperature of the solid complex (2.12 BM) showed a higher orbital contribution .

The electronic spectra of Zn (II) complex exhibited band related to the charge transfer transition which appeared at (262 nm) (38167 cm^{-1}) .

No ligand field transitions are observed because of filled d-orbital . Since the d^{10} configuration affords no crystal field stabilization , the stereochemistry depend on size and polarizing power of the M^{II}cation and the steric requirement of the ligand [14] .

General suggested stereo chemistry structure of complexes :

According to the results from the elemental and spectral analysis the general structure of the above mentioned complexes can be illustrated as follow :



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

References

1. William R. B. , Barry W. W., John J. K., Raymond L. S., and Robert W. F., ***Environ . Sci. Technol.,*** 2006, **40(20)** , 6330-6335 .
2. Martin S., Wolfgang H., Christoph H. S., Hans-Peter S., Moritz S., and J. Michael G., ***J. Phys. Chem. C,*** 2011, **115(30)** , 14869-14875 .
3. Bonnie O. L., Farideh J. and Robert K. S., ***J. Phys. Chem. B***, 2008, **112(15)** , 4770-4778 .
4. Papaioannou A. and Manos M. Solid , ***J. Inorganic Biochem***, 2004 , **98**, 959-968.
5. Study of stabilities of L-Cysteine and L-Menthionine with Divalent Metal Ions . A comparison of Thermodynamic Data .Journal , 2011 5th international conference on Bioinformatics and Biomedical Engineering . year 2011 , p 1-4 .
6. Mei-J., Chong-Qing Z., Mei-Juan N., Guo-Nan C., Xi chen. ***J. Inorganic Biochem***, 2011 , **105(3)**, 420-425 .
7. Kensuke N., Hideaki I., Yoshihiro T., and Yoshiki C., ***Langmuir*** , 2003, **19(13)** , 5541-5549 .
8. Amanda M. G., Mary E. K., Jennifer S. L., and Timothy A. J., ***Inorg. Chem.,*** 2012 , **51(18)** , 10055-10063 .
9. Silverstien R., Webster F., Kiemle D., Spectrophotometric Identification of Organic Compounds 7th Ed , 2005 , John wiley and sons , New York .
10. R. J. Dyer " Application of Absorption Spectroscopy of Organic Compounds " Prentice Hall , Inc., 1965 , Englewood Cliffs , N. J. London .
11. K. Nakamoto and J. Kieft, 1967, ***J. Inorg. Nucl. Chem***., **29** , 2561.
12. K – Nakamoto" Infrared Spectra of Inorganic and Coordination Compound " 6th Ed., 1997 John wiley and sons , New York .
13. Lever A., Inorganic Electronic Spectroscopy , 2nd Ed. 1986 Elsevier , New York .
14. Figgis , B., Introduction to Ligand Field 1st Ed, 1966 , John wiley and sons , New York .
15. Sutton , D., Electronic Spectra of Transition Metal Complex 1st Ed ,1969 McGraw-Hill publ. Co. Ltd., New York .