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Synthesis and Characterization of polymeric metel complexes with thiol groups of thiadiazole ring
تحضير وتشخيص بوليمرات تناسقية مع مجموعة الثايول لحلقة الثايادايازول

*Ahmed S. Hamad
University of karbala
College of pharmacy

**Iman A. Yass
Universityof Tikrit
college of education for women

Abstract

This paper describes the prepration of bis thiadiazole-2-thiol derivatives by conversion hydrazide derivatives of carboxylic acid to xanthate salt through its reaction with carbon disulfide.

The bis thiadiazole derivatives were obtained through ring closur of xanthat salt by adding sulfuric acid as catalyst.

Bis Thiadiazole-2-thiol derivatives have been used as ligands to prepare polymeric coordinated complexes by direct reaction between ligand and divalent ion(Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+}) in a basic aqueos solution. On the basis of IR , UV analytical studies and literature data the probable structures have been proposed , it has been found that the divalent metal ions coordinate with polydentate ligand BTH-H_{1-3} forming octahedral polymeric complexes.

الملخص:

تضمن هذا البحث تحضير مشتقات الثايادايازول-2- ثايول الثنائية من خلال تحويل مشتقات الهايدرازايد لحوامض ثنائية الكاربوكسيل المقابلة إلى ملح الزانثات بتفاعلها مع ثنائي كبريتيد الكاربون ، ثم بالغلق الحلقي لملح الزانثات نحصل على مشتقات الثايادايازول الثنائية وباستخدام حامض الكبريتيك المركز كعامل مساعد.

استخدمت مشتقات الثايادايازول -2- ثايول الثنائية كليكاندات لتحضير معقدات تناسقية بوليمرية من خلال التفاعل المباشر بين الليكاند و آيونات الفلزات ثنائية التكافؤ (Cd^{2+} , Zn^{2+}, Cu^{2+} , Ni^{2+} , Co^{2+}) في محلول مائي قاعدي. وقد تبين من خلال التشخيص الطيفي UV , IR والأدبيات إن آيون الفلز الثنائي التكافؤ يتناسق مع الليكاند الثنائيالسن مكوناً معقدات بوليمرية تناسقية ثمانية السطوح.

Introduction:

The growing patent literature from the sixties demon state that the 1,3,4-Thiadiazole and its derivatives have received much attention. This is primarily due to large number of uses of 1,3,4-thiadiazole in the most diverse areas for example disperse dyes(1),photography and corrosion inhibitors (2-4).1,3,4-thiadiazoles have been synthesized and reported as a bactericides(5),fungicides(6), insecticides(7) ,herbicides(8,9) ,flower controlagent (10),herbicides anti-inflammatory(11),tranquiliziing agent(12),hypoglycemic activity(13) ,thiadiazole used as agood ligand to prepare different complexes , most of these complexes gives pharmacological activity(14) and antitumor activity in bioactivity measurements(15). Also thiadiazole ligand made polymericcoordinated complexes with divalent metal ion (Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+},Zn^{2+},Cu^{2+})(16-18).

Experimental

Chemicals employed were of analytical grade and used without further purification, melting points were determined by using a "Electro thermal" melting point apparatus and are un-corrected. The conductivity were measure by using Elecyro conductivity meter consort C83.

The IR spectra was used Perkin-Elmer FT-IR spectrophotometer, in the 4000-200cm^{-1} rang using (KBr and KI disk). Electronic spectra were recorded on Jusco V-530 UV-Visible spectrophotometer Shimadzu in range 200-800nm in dimethyl formamide as a solvent at room temperature.

preparation of ester(19) [1-3]

A mixture of dicarboxilic acids (0.1mol), excess of methanol and concentrated sulphuric acid (5ml) were refluxed for 6 hrs, with stirring. then the solvent was evaporated under vacuum, the product washed with sodium bicarbonate solution then with diethyl ether (40ml) ,melting points as it is in periods, yield=70%.

preparation of hydrazide derivatives(20) [4-6]

Ester derivatives [1-3] (0.1mol) were dissolved in absolute ethanol 40ml and hydrazine hydrate 98% (0.2mol) and refluxing a mixture for 3-4 hrs. cooling to room temperature. The precipitate was washed, recrystallized and dried from ethanol. Melting points, Yield% data are listed in Table(1).

Preparation of Xanthat salts derivatives(21)[7-9].

Hydrazide derivatives[4-6](0.01 mol) were dissolved in a solution of potassium hydroxide(0.02 mol)in (100 ml)of ethanol. Carbon disulfide(0.02 mole) was added gradually. The whole solution was refluxed on water bath until the evolution of hydrogen sulfide ceases (about 2-3hrs). The excess of solvent was evaporated under vacuum and the residue was poured on to ice water containing hydrochloric acid. The precipitate was separated , filtered, washed with distilled water and recrystallized from ethanol. Melting points, Yield% data are listed in Table(2).

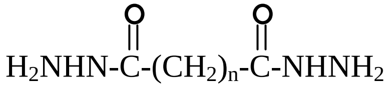
Preparation of Bis Thiadiazole-2-thiol derivatives BTH-H_{1-3} (21)[10-12].

Excess of sulfuric acid was added slowly with cooling to xanthat salts and let it under mixing until hydrogen sulfide end. After 3hours the mixture was diluted with cold water , The precipitate was separated , filtered, washed with water, ethanol and ether. Melting points, Yield% data were listed in Table(3).

Preparation of polymeric complexes of ligands Bis Thiadiazole-2-thiol derivatives BTH-H_{1-3} with Co(II), Ni(II), Cu(II), Zn(II), Cd(II)(22)[13-27].

Ligands BTH-H_{1-3} [10-12] (o.o1mol) and (0.01mol)of KOH in 50% mixture of water-ethanol(30ml) were mixed together .A yellow suspension started to form which mostly dissolved after stirring and heating for while. then the metal salt(0.01 mole)in(20ml) of water – ethanol was added dropwise. The mixture was heated with stirring for (15-25) min. , On cooling the polymeric complex was precipitated, The precipitate was separated , filtered, washed with distilled water, ethanol and ether then dried at 50^{O}c for about 3hours. Melting points, Yield% data were listed in table(4).

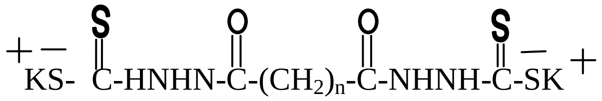
Table (1):Physical properties ofcompounds[4-6].



$H_2NHN-\overset{\overset{O}{\|}}{C}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-NHNH_2$

Comp No.	**n**	**Molecular Formula**	**M.P C^0**	**Color**	**Yield%**	**Solvent Crystalli.**
4	0	$C_2H_6O_2N_4$	146-148	White	55	Ethanol
5	2	$C_4H_{10}O_2N_4$	186-188	=	75	Ethanol
6	4	$C_6H_{14}O_2N_4$	181-183	=	70	Ethanol

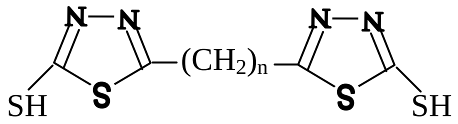
Table (2):Physical properties ofcompounds[7-9].



$\overset{+\,-}{KS}-\overset{\overset{S}{\|}}{C}-HNHN-\overset{\overset{O}{\|}}{C}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-NHNH-\overset{\overset{S}{\|}}{C}-\overset{-}{S}\overset{+}{K}$

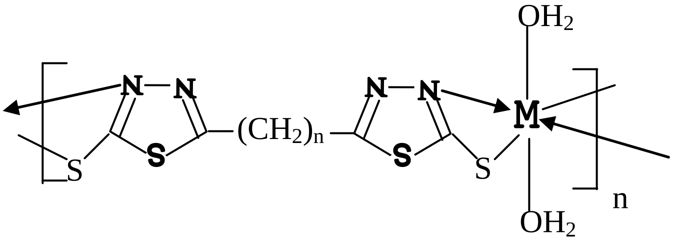
Comp No.	**n**	**Molecular Formula**	**M.P ^{0}C**	**Color**	**Yield %**	**Solvent Crystalli.**
7	0	$C_4H_4O_2N_4S_4K_2$	$188_{dec.}$	Yellow	90	Ethanol
8	2	$C_6H_8O_2N_4S_4K_2$	$224_{dec.}$	=	90	Ethanol
9	4	$C_8H_{12}O_2N_4S_4K_2$	$228_{dec.}$	=	90	Ethanol

Table (3):Physical properties ofcompounds[10-12].



Comp No.	**R**	**Molecular Formula**	**M.P ^{0}C**	**Color**	**Yield %**	**Solvent Washing**
10	0	$C_4H_6N_4S_4$	180dec.	Yellow	90	Water+Etol+Ether
11	2	$C_6H_{10}N_4S_4$	190dec.	=	90	Water+Etol+Ether
12	4	$C_8H_{14}N_4S_4$	192dec.	=	90	Water+Etol+Ether

Table (4): Physical properties ofcompounds[13-27].



Comp No.	R	Molecular Formula	M.P ^{0}C	Color	Yield%	Solvent washing
13	0	$C_4H_4N_4S_4Co$	290dec.	Green	90	Water+EtOl+ Ether
14	=	$C_4H_4N_4S_4Ni$	>350	Dark green	90	Water+EtOl+ Ether
15	=	$C_4H_4N_4S_4Cu$	300dec.	Dark brown	85	Water+EtOl+ Ether
16	=	$C_4H_4N_4S_4Zn$	280 dec.	Pink	90	Water+EtOl+ Ether
17	=	$C_4H_6N_4S_4Cd$	300 dec.	Yellow	90	Water+EtOl+ Ether
18	2	$C_6H_4N_4S_4Co$	280dec.	Grey	90	Water+EtOl+ Ether
19	=	$C_6H_8N_4S_4Ni$	250dec.	Dark Green	90	Water+EtOl+ Ether
20	=	$C_6H_8N_4S_4Cu$	160dec.	Brown	90	Water+EtOl+ Ether
21	=	$C_6H_8N_4S_4Zn$	>350	White	95	Water+EtOl+ Ether
22	=	$C_6H_8N_4S_4Cd$	250dec.	Yellow-white	90	Water+EtOl+Ether
23	4	$C_8H_{12}N_4S_4Co$	235dec.	Grey	90	Water+EtOl+Ether
24	=	$C_8H_{12}N_4S_4Ni$	270dec.	Green-Grey	90	Water+EtOl+Ether
25	=	$C_8H_{12}N_4S_4Cu$	>350	Brown	85	Water+EtOl+Ether
26	=	$C_8H_{12}N_4S_4Zn$	>350	White	90	Water+EtOl+Ether
27	=	$C_8H_{12}N_4S_4Cd$	>350	Yellow-White	90	Water+EtOl+Ether

Results and Discussion

The IR spectrum of the ligand bis thiadiazole-2-thiol(BTH-$H_{1\text{-}3}$) shows a broad band at (3090-3120)cm^{-1} and shoulder band at (2610-2630) cm^{-1} which assignes to tautomerism N-H band and S-H stretching $^{(23)}$.These bands were disappeared in the spectra of polymer PBTH-$H_{1\text{-}3}$ indicating the involvement of thiol S-H group in polymerization .The strong band at (610,620,740) cm^{-1} due to stretching of thioether group$^{(24)}$.These bands were shifted to higher frequences in crosslinking complexes. Ligands shows C=N stretching at (1650-1660) cm^{-1} which was shifted to (1560-1610)cm^{-1} on complexes indicating the involvement of N=C-S group in coordination. New bands have been observed at (317-450) cm^{-1} and(290-390) cm^{-1} in IR spectra of complexes and these bands assigned to M-N and M-S stretching vibration respectivity. The bands at (3400-3600) cm^{-1} and (1510-1560) $cm^{-1}$are attributed to OH and M-OH_2 stretching. The important IR frequencies of ligands BTH-$H_{1-3}$and there complexes are showd in tables(5,6).

Table(5):IR spectra of ligands BTH-H_{1-3}

Comp. No.	n.	IR. (KBr) / υ (cm^{-1})				UV (DMF) max λ nm
		N-H υ δ N-H	C=N	N-C=S S-H	C=S C-S	
10	0	3090 b 1525 s	1660m	1230 sh 2630 sh	1010s 740 s	274 416
11	2	3120 b 1520 s	1650 m	1150 sh 2610 sh	1020 s 610 s	274 306 356
12	4	3120 b 1525 s	1660 m	1150 sh 2620 b	1020 s 620 s	272 314 356

Table (6): IR spectra of $[BTH_{1-3}M.2H_2O]_n$

Comp. No.	M	IR. (KBr) /υ (cm^{-1})			
		C=N	C-S	OH_2 δ OH_2	M-N M-S
13	Co	1610 s	735 m	3430 b 1510 w	440 m 390 m
14	Ni	1610m	820 w	3420 b 1550 w	319 m 295 m
15	Cu	1600m	830 w	3390 b 1560 w	317 w 293 m
16	Zn	1560 s	770 m	3430 b 1490 w	450 m 290 w
17	Cd	1610 s	820 s	3400 s 1540 w	380 m 310 s
18	Co	1660 b	5oo s	3630 b 1550 w	440 m 370 m
19	Ni	1610m	820 w	3420 b 1550 w	319 m 295 m
20	Cu	1650 b	510 m	3650 m 1550 w	355 m 315 m
21	Zn	1650 m	600 m	3400 b 1550 w	348 m 295 m
22	Cd	1620 m	800 m	3600 s 1550 w	348 m 293m
23	Co	1650b	500s	3630s 1550w	343m 294m
24	Ni	1620b	510s	3650s 1550w	355m 318m
25	Cu	1600m	630s	3450b 1550w	347m 300m
26	Zn	1640m	600m	3420b 1550w	355m 310m
27	Cd	1640b	650m	3600s 1560w	335m 280m

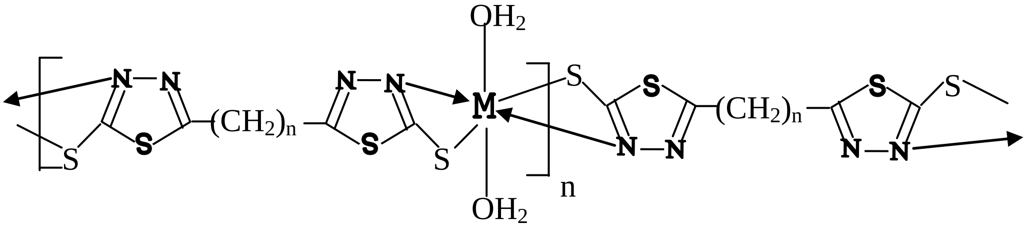
s: strong , sh:sholder , m: middle , w: weak , b: broad

The UV spectra of BTH-H_{1-3} ligands in DMF showed three absorption peaks at (274,290,416)nm ,(272,314,354)nm and(274,306,356)nm. By comparing the spectra of this ligands with the spectra of the polymeric complex its observed that some of the absorption peaks are shifted to the blue region and the others are shifted to the red region. The observed bands are tentatively assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition and these are due to the N-C-S group (25). We can conclude that the red region may be happened as a result of the coordination between the ligand and the metal ion, also the shift to the blue region is in accordance with the strong coordination between the ligand and the metal ion.The shoulder band in the spectra can be considered as a good evidence for the bidentate behavior of the BTH-H_{1-3} ligands(26). Table (7) shows the UV-Visible absorption of BTH-H_{1-3} ligands and there prepared complexes.

Table (7): UV-Visible absorption of BTH-H$_{1-3}$ ligands and there complexes.

Complex	λ1	A	λ2	A	λ3	A	λ4	A
BTH-H$_1$	**247 290 sh**	**3.1 2.9**			**416.0**	**3.1**		
Co	**270**	**2.1**	**323**	**2.5**	**463.2 sh**	**0.261**	**620 746**	**0.003 0.001**
Ni	**270270 290**	**3.0 3.0**	**368**	**0.3**	**sh429 580**	**0.7 0.1**	**620**	**0.02**
Cu	**270**	**2.5**	**310 380**	**4.0 3.8**			**710**	**0.18**
Zn	**290**	**4.0**	**310**	**4.0**	**429 sh**	**0.7**		
Cd	**272**	**1.22**	**350 sh**	**1.2**	**429 sh**	**0.5**		
BTH-H$_2$	**274**	**1.8**	**306 356**	**1.5 2.0**				
Co	**298**	**0.06**	**310 360**	**0.2 0.1**	**440 sh**	**0.1**	**660**	**0.1**
Ni	**265**	**2.4**	**330 394.3**	**1.6 0.25**	**450 sh 550 sh**	**0.05 0.35**	**670**	**0.5**
Cu	**270**	**2.8**	**308 350**	**4.0 4.0**			**706**	**0.051**
Zn	**272 291**	**1.28 1.3**	**360 sh**	**1.2**				
Cd	**274**	**2.53**	**313 sh**	**2.25 1.9**				
BTH-H$_3$	**272**	**1.5**	**314 354**	**2.5 1.6**				
Co	**270**	**2.2**	**300**	**2.45**	**400**	**0.25**	**670 600**	**0.03 0.05**
Ni	**270**	**0.521**	**314**	**0.32**	**420**	**0.05**	**625 663**	**0.06 0.007**
Cu	**270**	**1.1**	**360sh 390sh**	**0.2 0.16**			**668**	**0.14**
Zn	**273**	**1.25**	**324 350**	**1.35 1.39**				
Cd	**272**	**1.33**	**313**	**0.94**				

From modern analytical studies about coordinatig Cu(II) and Pd(II) with semi ligand is found that the coordinating amount of metal ion with ligand is 1:1(27).The formula of these complexes were identified from studies of IR and UV-Visible spectra the following structure may be suggested.



When we measure molaric electrical conductivity for poly complexes (10^{-3}M) at (25^{0}c) in dioxan as a solvent , it gives values between (0-3) $mol^{-1}.S.cm^{2}$ that means it is in range complexes which have straight behavior not electrolyte and non connecting in a solvent. .

Fig (1):IR spectrum of compound(4)

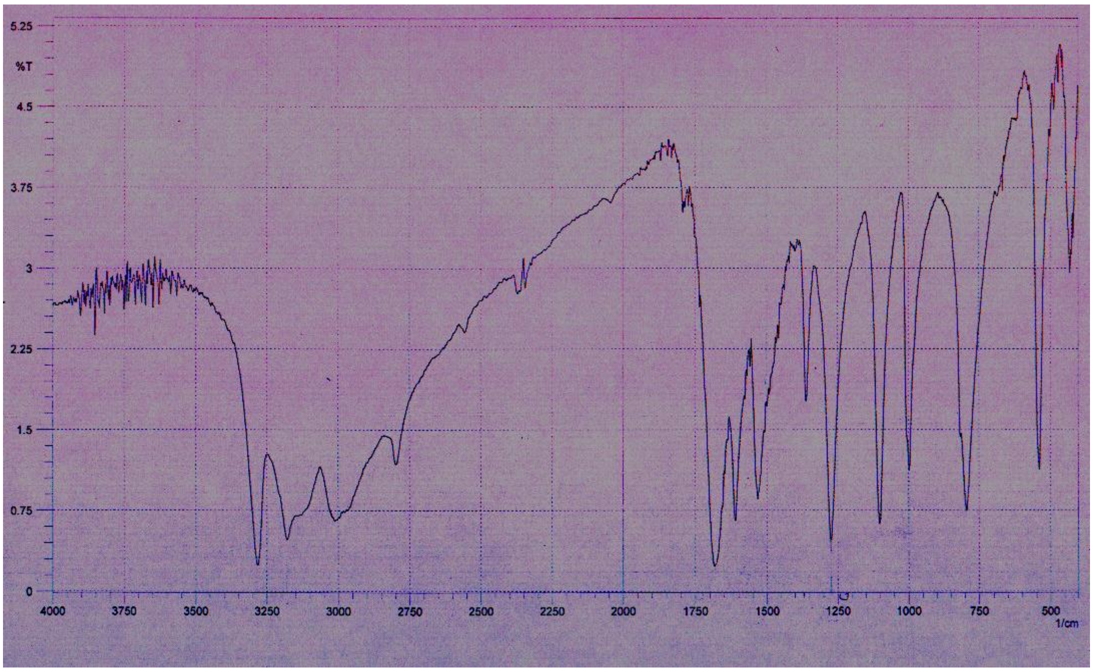


Fig (2) IR spectrum of compound (7)

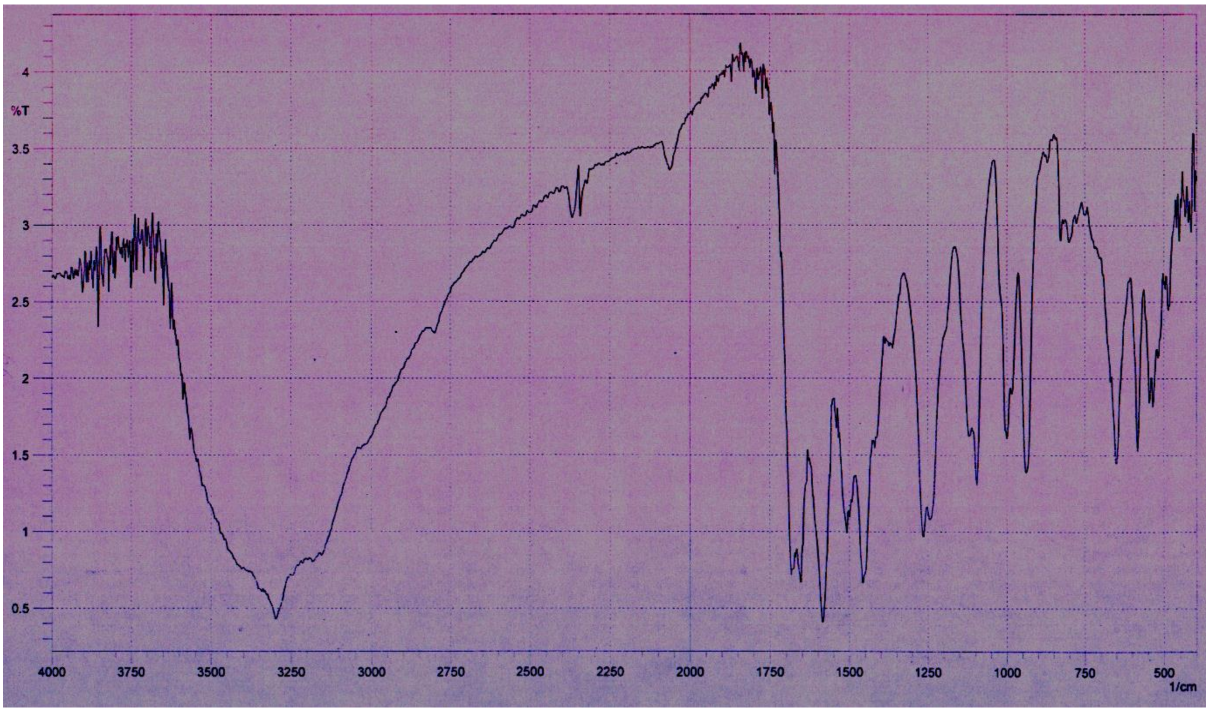


Fig (3):IR spectrum of compound(10)

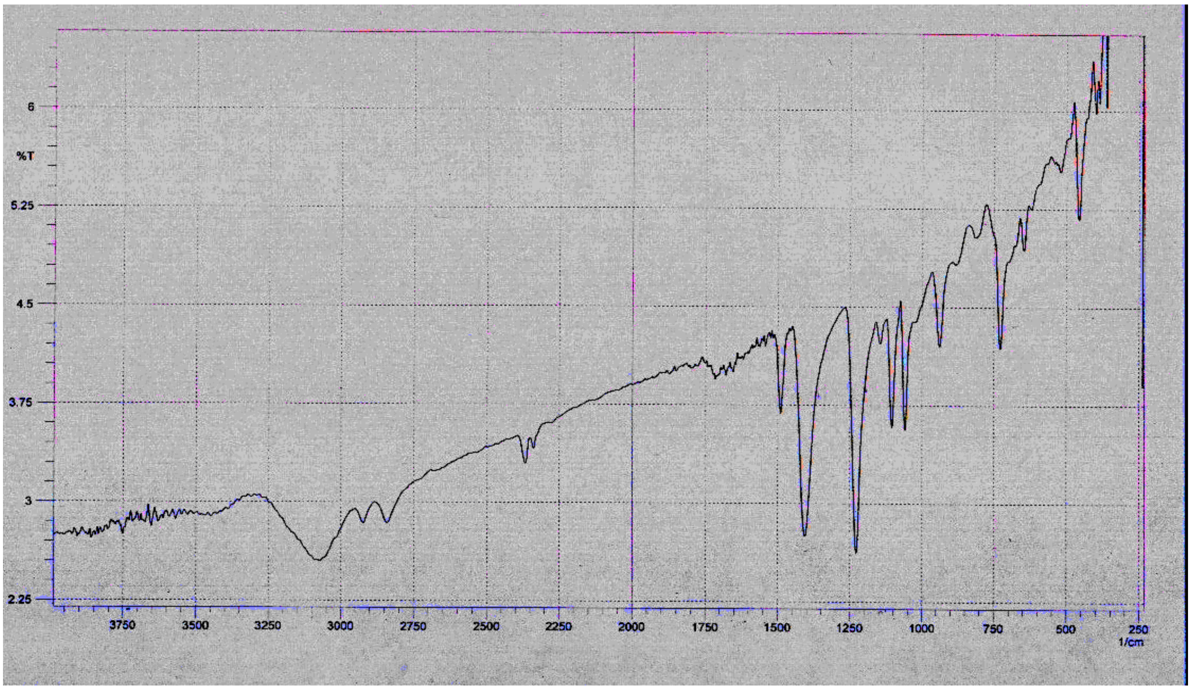


Fig (4):IR spectrum of compound(13)

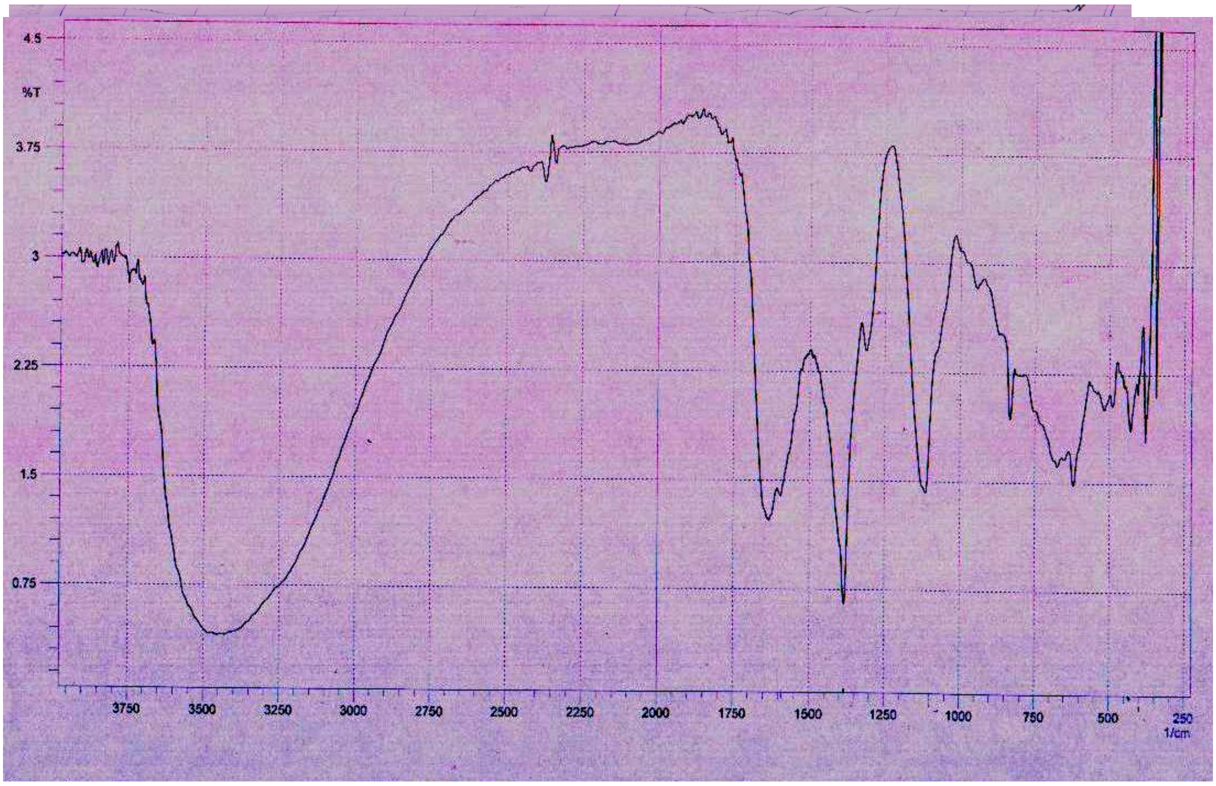


Fig (5) UV spectrum of compound (10)

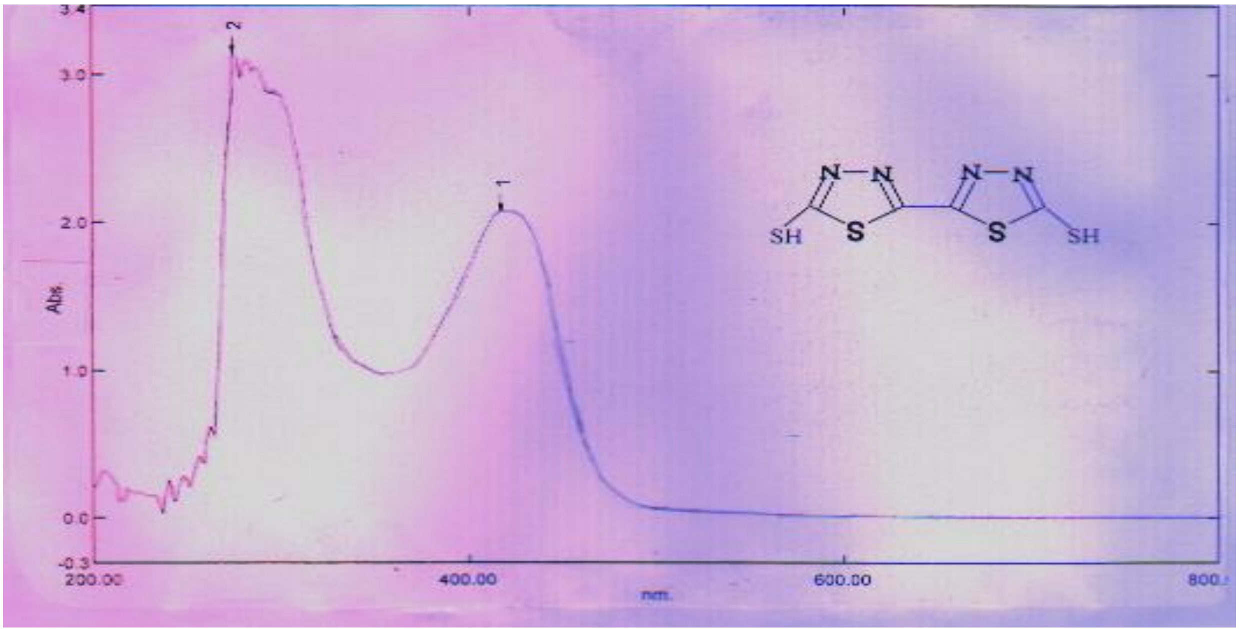


Fig (6):UV spectrum of compound(13)

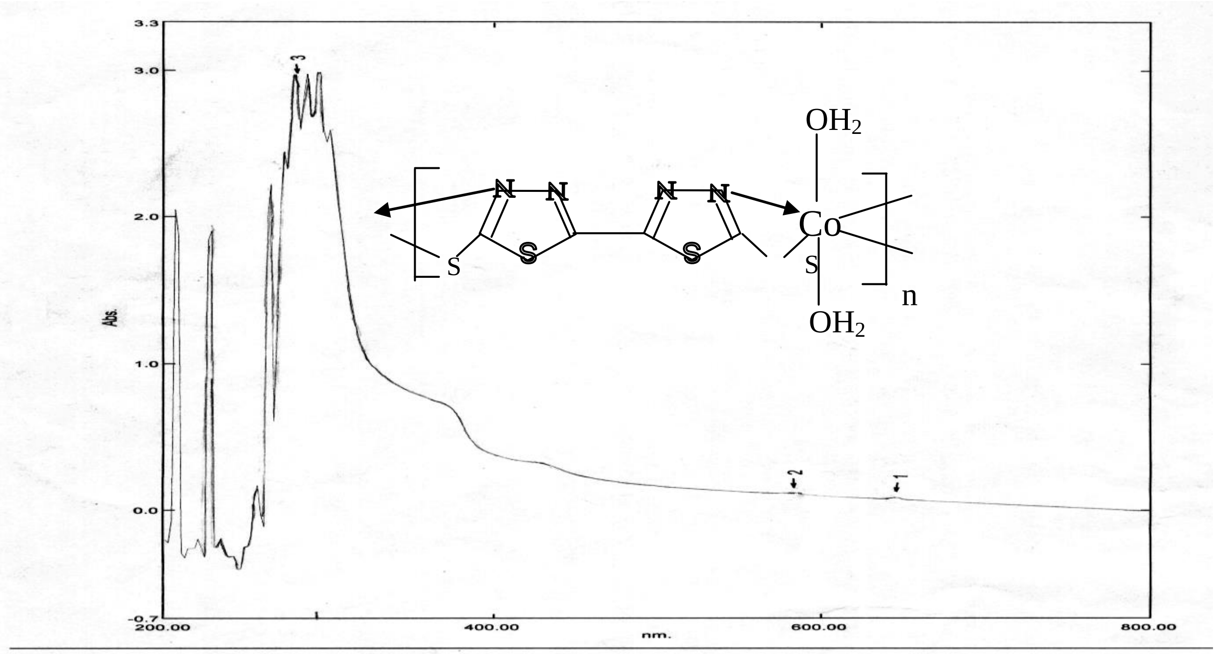


Fig (7):UV spectrum of compound(11)

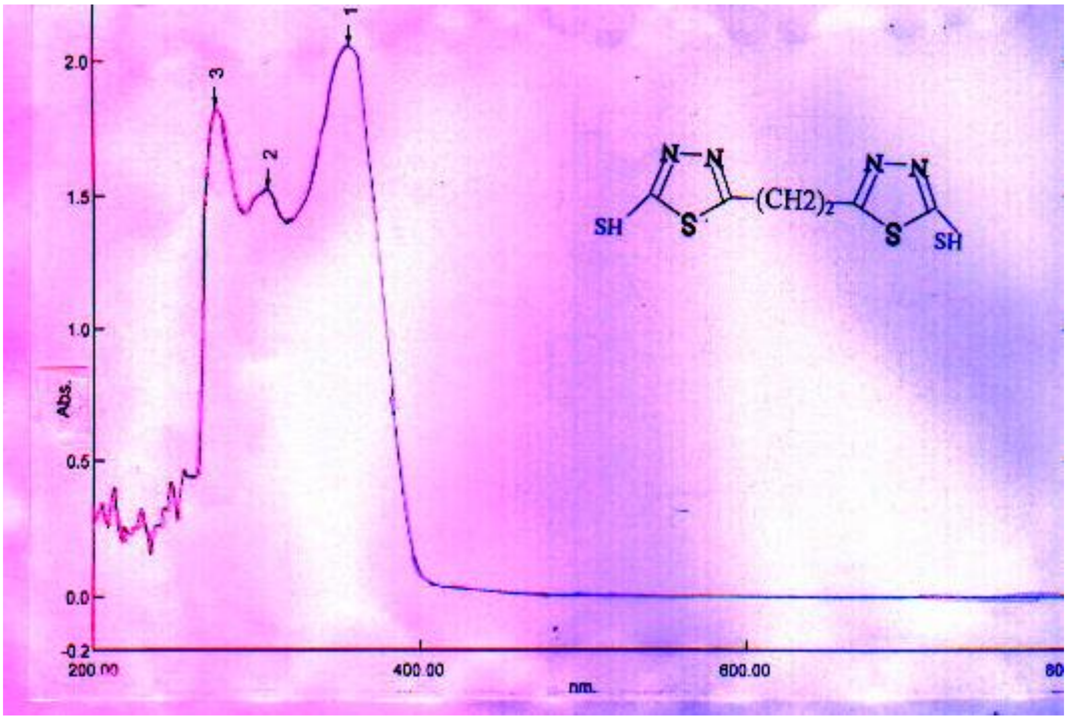


Fig (8):UV spectrum of compound(20)

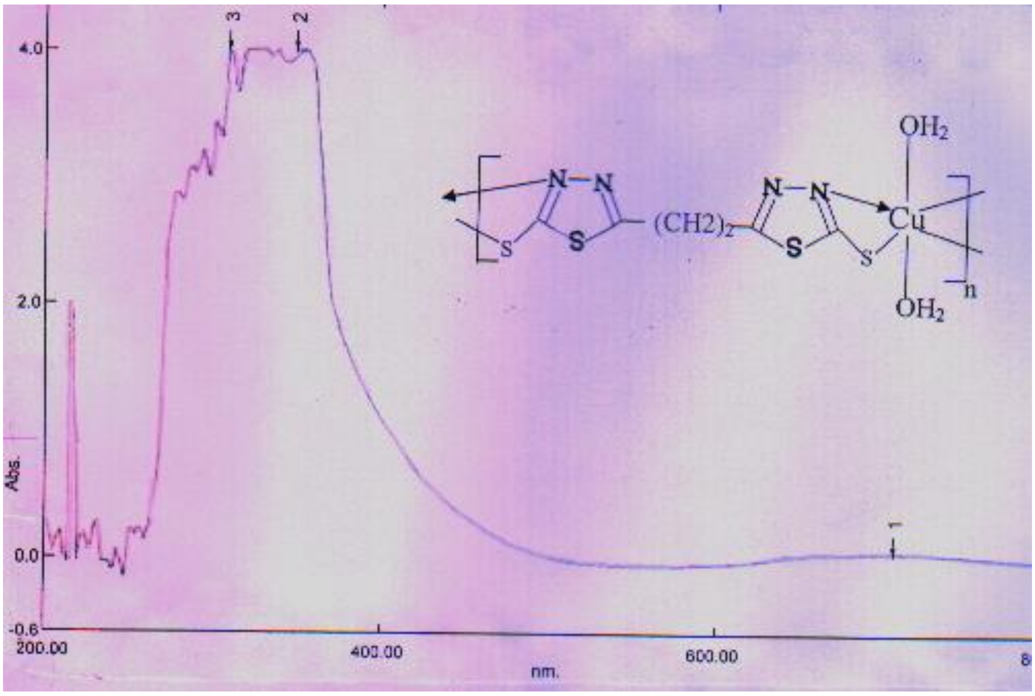
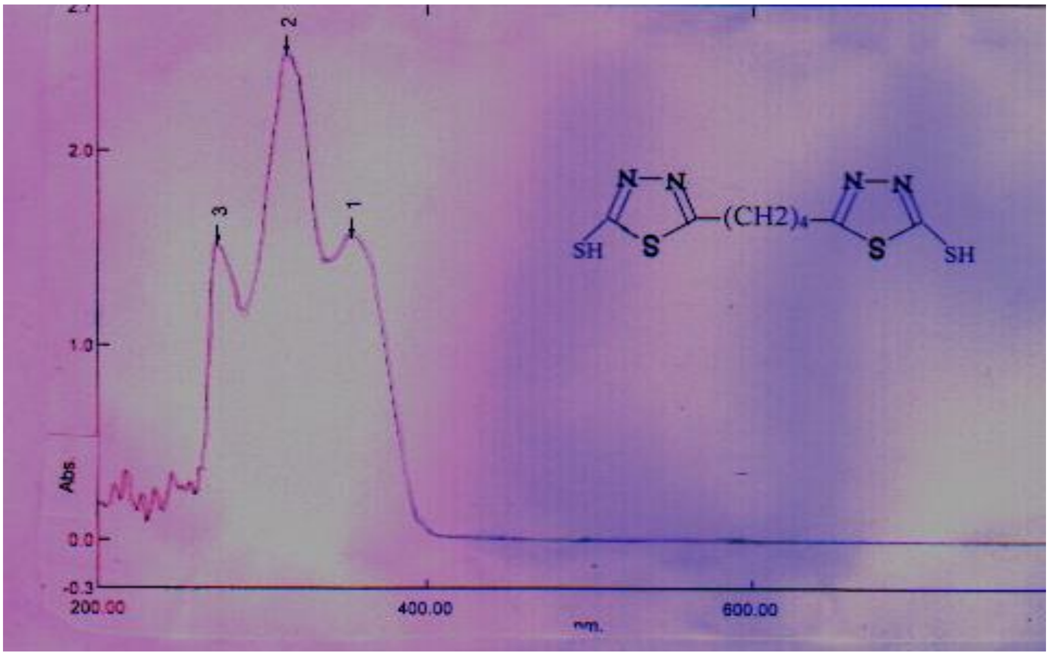


Fig (9):UV spectrum of compound(12)



References

1-H.R. Maradiya , J. Serb.Chem. Soc.,67(11),709.(2002).
2-R.C. Elderfieid , Hetrocyclic compounds,Vol.7.wiley new York(1966).
3-A. Hetzheim and K. Mockel,"Advances in Heterocyclic chemistry", A.R. katrizky and A.J. Boulton (Editors), Vol.7 ,Academic press, New York(1966).
4-F.bentiss and M. Traisnel, Corrosion Sci.,42(1),146,(2000).
5- F.H. Jumaa , Tikrit, J. for Pure Sci. ,10 (1),144,(2005).
6-I.K.Jassim,Tikrit J.of Pharmaceutical Sci.,5(2),127,(2009).
7-S.S. Tiwari, A.T. Sengupta and J. Kumar, Indian J. Pharm.,91,32.(1970).
8-S. Giri, H. Singh and L.D.S. Yadvo, Agr. Biol. Chem., 40, 17.(1976).
9-V.J. Ram and H.N. Fanday, J. Indian Chem. Soc., 51,634.(1974).
10-I. Angelini and F. Sparaco, British Patent,1,801.(1969).
11-H. Nager, R. Cindicelli and J. Menin, Bull. Soc. Chem.,153.(1966).
12-S.K.Chandhary and S.S. Parmar, J. Pharm. Sci.,67, 1507.(1978).
13-J.B. Onel, H. Rosen, P.B. Rusell, A.C. Adam and A. Blumenthal, J.Med. Pharm. Chem.,5,617.(1962).
14-F. Briganti, S.Tilli , G. Mincione , F. Mincione ,L. Menabuoni ,Supuran C.T.; J. Enzyme Inhib., 15(2), 185 . (2000).
15-R.F. Zhang , F. Li, K.Z. Li and C.L. Ma ;Polish J. Chem. ,78,753.(2004).
16-A.S. Hamed , M.Y. Mohammed ,S.A. Jabar ;Iraqi. J. Sci. , 40A(2),1.(1999).
17-A.S.Hamed , M.Y. Mohammed ,S.A. Jabar ;Iraqi. J. Sci., ,40A(3), 26.(1999).
18-S.A. Jabar, Tikrit J. of pure Sci.,6,1,16.(2000).
19- A.I. Vogel "A Text Book of Practical Organic Chemistry" 3ed Ed. Longman group Ltd. London ;710, 719,181 (1974).
20-A. Kh. Ahmed and A.O.M. Obaid, J. Edu. Sci,16,3.(2004).
21-A.I. Vogel "Quantitative Inorganic Analysis" , Howe and Brydon. Etd., London(1972).
22- S.A. Jabar, M.Sc. Thesis University of Tikrit (1997).
23- B. Silverstein and Morill "Spectrometric identification of Organic Compounds " ,4th ed. ,John ,Wiley and Sons (1980).
24-S.Giri , H. Singh and L.D.S. Yadar. Agr Biol. Chem., 42(1),4.(1976).
25-A.O. Emane ,M.Sc. Thesis University of Baghdad (1990).
26-R.A. Haines and W. Louch, J. Inorganic Chem.Acta., 71,1. (1983).
27-K.N. Rashied , M.SC. Thesis University of Tikrit (2005).