

**Synthesis and Characterization of the Ligand  
2-[(6-Nitro-2-benzothiazolyl)azo]-4,6-dimethylphenol (6-NBTADMP)  
and It's Complexes with Fe(II), Co(III), Ni(II), Cu(II), Zn(II), Cd(II),  
Pd(II) and Ag(I) Ions**

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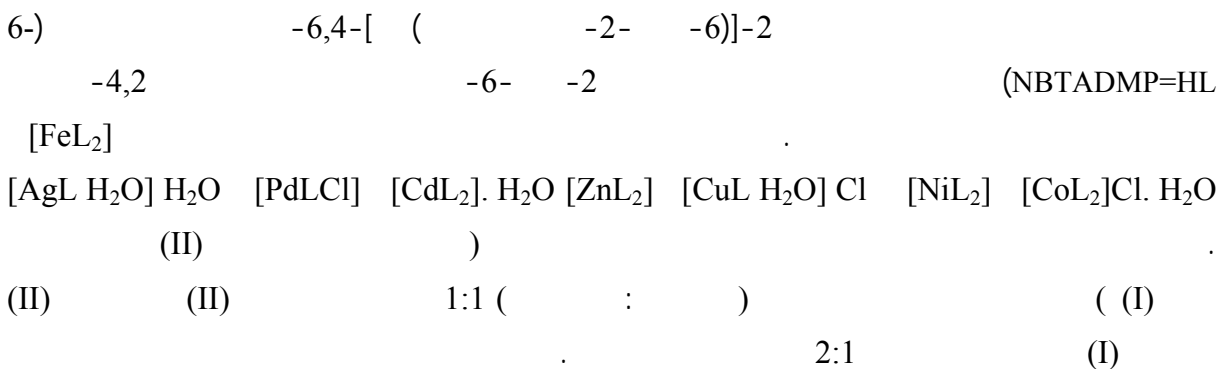
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**Abstract**

A new ligand 2-[(6-Nitro-2-benzothiazolyl)azo]-4,6-dimethylphenol (6-NBTADMP = HL) has been synthesized by coupling diazotized 2-amino-6-nitrobenzothiazole with 2,4-dimethylphenol in alkaline alcoholic solution. Metal complexes have the general formula  $[FeL_2]$ ,  $[CoL_2]Cl \cdot H_2O$ ,  $[NiL_2]$ ,  $[CuL \cdot H_2O]Cl$ ,  $[ZnL_2]$ ,  $[CdL_2] \cdot H_2O$ ,  $[PdLCl]$ , and  $[AgL \cdot H_2O] \cdot H_2O$ , were synthesized from thiazolylazo ligand and metal chloride (sulfate for Fe(II) and nitrate for Ag(I)) in 1:1 molar ratio (metal:ligand) for Cu(II), Pd(II) and Ag(I) and 1:2 for the rest metal ions. Based on elemental analysis, molar conductivity, magnetic susceptibility data, IR and UV-Vis spectra. The data show that the ligand coordinates to the metal ion via phenolate O, azo N and with thiazole N atoms. All complexes are insoluble in water but these are soluble in common organic solvents such as acetone, DMF and DMSO. According to results obtained the geometry for the complexes was suggested.

**Key words:** *Synthesis, Thiazolylazo, Ligand, Metal Complexes, Characterization.*



. DMSO      DMF

## Introduction

The thiazole and its derivatives are of biological important and they are used in the synthesis of drugs<sup>(1-3)</sup>. Heterocyclic amines have been used extensively in the preparation of azo dyes<sup>(4-6)</sup>. Dyes from 2-amino-5-nitrothiazole have been reported to have high extinction coefficient, and they are reddishblue depending upon the substitution pattern in the coupler<sup>(7,8)</sup>. Thiazolylazophenols have attracted much attention as analytical reagent owing to the high sensitivity<sup>(9-11)</sup>. This class of organic ligands that contain two nitrogen atoms coupled in conjugated system of  $\pi$ -bonds, and usually react with metal ions as tridentate ligands<sup>(12-15)</sup>.

This paper describe the synthesis of new thiazolylazo ligand and some of it's metal complexes

## Experimental

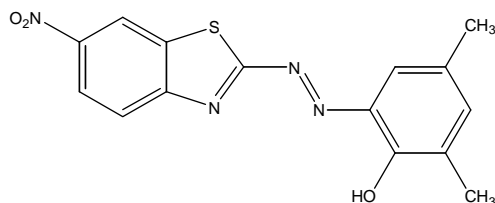
### Material and Measurements

All reagents used are chemically pure or analytical grads, except of 2-amino-6-nitrobenzo-thiazole was prepared and purified according to the literature<sup>(16)</sup>. Melting points were taken in open capillaries on a Stuart melting point apparatus and are uncorrected. C,H,N analysis data were obtained at Al-Albayt University, on a Perkin-Elmer 240 elemental analyzer. The metal contents were determined by using a Shimadzu-AA-160, Atomic absorption spectrophotometer. All conductivity measurements were performed in DMSO using conductivity Bridge 31A at 25 °C, the concentration of the solution was  $10^{-3}$  mol L<sup>-1</sup>. pH measurements were carried out using HANNA pH meter model HI 9321. Magnetic susceptibility measurement were

made by faraday method at room temperature using Balance Magnetic MSB-MK apparatus, and diamagnetic corrections for the ligand were calculated using Pascal's constants<sup>(17)</sup>. IR spectra were recorded on a Pye-Unicom SP3 - 300, spectrophotometer, in the 4000-200 cm<sup>-1</sup> using CsI disc. Electronic spectra from 200-1000 nm were determined in ethanol on a Shimadzu UV-Vis 1700 spectrophotometer

### Synthesis of Azo ligand (6-NBTADMP)

The azo ligand (6-NBTADMP) Fig.1, was synthesized as in the procedure described for thiazolylazo dyes<sup>(18)</sup>. The details are given as follows; sulfuric acid 96% 10ml was cooled and stirred, and sodium nitrite ( 0.84g, 12mmol ) was added in small portions at in such rate as to avoid the evolution of nitrous gases. The solution was stirred and slowly heated to 50°C until the salts were completely dissolved. The solution of nitrosyl sulfuric acid obtained was stirred and cooled to 5-10°C, then (1.95g, 10mmol) of 2-amino-6-nitrobenzothiazole was added, the reaction mixture was then stirred at 0-5°C for 1hr. The resulting diazonium sulfate solution was added drop-wise with continuous stirring to a solution of 2,4-dimethylphenol (1.22g ,10m mol) in alkaline ethanol 150ml. The reaction mixture was stirred for 3hrs at 0-5°C, and left in the refrigerator over night. The mixture was acidified with dilute sulfuric acid until (pH=6). The soiled product was filtered off, washed with 500ml cold water, air dried and recrystallized twice from hot ethanol then dried in the oven at 70°C for several hrs.



**Fig.1: Structure of the ligand (6-NBTADMP)**

### Synthesis of Metal Complexes

The metal complexes were prepared by dissolving (0.328g, 1mmol) from ligand in hot ethanol 50ml and added drop-wise with stirring to a stoichiometric amounts of 1 : 1 (metal : ligand) molar ratio of Cu(II) and Pd(II) chloride and Ag(I) nitrate or 1 : 2 ratio of Fe(II) ammonium sulfate and Co(II), Ni(II), Zn(II) and Cd(II) chloride salts, dissolving in 10ml hot distilled water. The resulting mixture solution was stirred under reflux for 1h. The solid product thus formed was filtered off from the ice-cooled reaction mixture, washed with 5ml hot ethanol and dried at 80°C over night.

### Results and Discussion

The reaction of azoligand (6-NBTADMP) with the metal ions mentioned above different color crystals, depending on the nature of metal ion. The complexes are air-stable, insoluble in water, but soluble in common organic solvents. Decomposition accure with conc.nitric acid, and the resultant solution was used after suitable dilution for metal analysis. The elemental analysis data of the ligand and it's complexes are given in Table (1), they are consistent with the calculated results from the empirical formula of each compound.

**Table.1: Analytical and physical data of the ligand and its complexes**

No.	Compound	Color	M.p °C	Yield%	Formula	Found (Caled) %			
						C	H	N	M
1	HL	Reddish-brown	143	62	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub> S	54.56 (54.78)	3.52 (3.65)	16.83 (17.07)	-----
2	[FeL <sub>2</sub> ]	Brown	171	67	C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Fe	50.51 (50.70)	2.97 (3.09)	15.48 (15.77)	7.64 (7.88)
3	[CoL <sub>2</sub> ]Cl. H <sub>2</sub> O	Dark green	189	70	C <sub>30</sub> H <sub>24</sub> N <sub>8</sub> O <sub>7</sub> S <sub>2</sub> ClCo	46.82 (46.96)	3.04 (3.13)	14.37 (14.61)	7.41 (7.69)
4	[NiL <sub>2</sub> ]	Green	212	63	C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Ni	50.26 (50.49)	3.01 (3.08)	15.39 (15.70)	7.89 (8.27)
5	[CuL(H <sub>2</sub> O)]Cl	Brown	166	62	C <sub>15</sub> H <sub>13</sub> N <sub>4</sub> O <sub>4</sub> SClCu	40.32 (40.54)	2.80 (2.92)	12.43 (12.61)	14.06 (14.30)
6	[PdLCl]	Brown	223d	63	C <sub>15</sub> H <sub>11</sub> N <sub>4</sub> O <sub>3</sub> SClPd	38.14 (38.37)	2.23 (2.34)	11.76 (11.94)	-----
7	[ZnL <sub>2</sub> ]	Red	159	59	C <sub>30</sub> H <sub>22</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Zn	49.78 (50.04)	2.92 (3.05)	15.32 (15.56)	8.72 (9.09)
8	[CdL <sub>2</sub> ]. H <sub>2</sub> O	Red	198	61	C <sub>30</sub> H <sub>24</sub> N <sub>8</sub> O <sub>7</sub> S <sub>2</sub> Cd	45.71 (45.89)	2.89 (3.05)	14.08 (14.27)	-----
9	[AgL(H <sub>2</sub> O)].H <sub>2</sub> O	Red	201	64	C <sub>15</sub> H <sub>15</sub> N <sub>4</sub> O <sub>5</sub> SAg	38.02 (38.21)	3.09 (3.18)	11.67 (11.88)	-----

HL=(6-NBTADMP), d = decompose

### Effect of pH and Time

The effect on the absorbance of the complex solutions of varying various pH was observed. The absorption of M<sup>+n</sup> – (6-NBTADMP) solution of all complexes approach maximum at pH 5.5-7.0. This result agree with the fact of the lower basicity of the thiazole nucleus, will lead to shift of reaction conditions for the formation of complexes towards the more acidic region<sup>(19)</sup>. Also the reaction are complete in 5min at room temperature. This shows that (6-NBTADMP) demonstrates strong coordination with all metal ions.

### Metal : Ligand Ratio

The metal : ligand ratio of the complexes were determined by the method of molar ratio at fixed pH, and maximum absorption wavelengths. The results are summarized in Table (2). The ligand was found to form 1:2 chelates with Fe(II), Co(III), Ni(II), Zn(II) and Cd(II), metal ions and 1:1 chelates with Cu(II), Pd(II) and Ag(I), metal ions. The results are in agreement with the values reported for some thiazolylazo phenol complexes<sup>(20,21)</sup>.

**Table.2: Metal: Ligand ratios and Stability constant values**

ligand	Metal ion	pH	$\lambda_{max}$ nm	Metal : Ligand	$\beta$	Log $\beta$
HL	Fe(II)	5.5	622	1 : 2	$3.217 \times 10^5$	5.507
	Co(III)	7.0	628	1 : 2	$2.512 \times 10^7$	7.400
	Ni(II)	6.0	614	1 : 2	$2.016 \times 10^6$	6.304
	Cu(II)	5.5	540	1 : 1	$6.332 \times 10^5$	5.801
	Pd(II)	6.5	423	1 : 1	$3.424 \times 10^6$	6.534
	Zn(II)	6.5	472	1 : 2	$1.219 \times 10^4$	4.086
	Cd(II)	6.0	481	1 : 2	$2.731 \times 10^4$	4.436
	Ag(I)	6.0	487	1 : 1	$4.526 \times 10^3$	3.655

### Determination of the Metal Complexes

#### Stability Constant

Stability constants are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelengths  $\lambda_{max}$  and pH values. The degree of formation of the complexes are obtained from the relationship<sup>(22)</sup>,  $\beta = (1 - \alpha)/(\alpha^2 c)$  for 1:1 metal chelates and  $\beta = (1 - \alpha)/(4\alpha^3 c^2)$  for 1:2 metal complexes and  $\alpha = A_m - A_s / A_m$ . Where  $A_m$  and  $A_s$  are the absorbance's of the fully and partially formed complex respectively at optimum concentration. The calculated (log  $\beta$ ) values of these complexes are given in Table2.

#### Infrared Spectroscopic Study

The active site of the ligand and their bonding to the metal ions was characterized by careful comparison of the main infrared absorption bands of the free ligand and it's complexes Table3. IR spectra of all metal complexes show that (6-NBTADMP) behaves as monobasic tridentate ligand, coordinating via (C=N), (N=N) and the phenolic (O-H)

groups with displacement of hydrogen atom from the latter. The absences of a broad band at 3360-3180  $\text{cm}^{-1}$  indicate the deprotonation of the phenolic oxygen and cleavage of the hydrogen bond with the involvement of the oxygen atom in bonding<sup>(23)</sup>. In the  $\nu(\text{O-H})$  water region, the spectrum of the Cu(II) complex show strong sharp band at 3455  $\text{cm}^{-1}$  attributed to the coordination of water<sup>(24)</sup>. In the spectra of the Co(III) and Cd(II) complexes show a strong and broad absorption at 3450-3160  $\text{cm}^{-1}$  which may indicates the lattice water<sup>(25)</sup>. The spectrum of Ag(I) complex exhibit, in addition to the band of coordinated water, a broad continuous absorption peak at 3370-3110  $\text{cm}^{-1}$ , this is apparently due to both coordinated and crystal water<sup>(26)</sup>. No such band are observed in the spectra of Fe(II), Ni(II), Zn(II) and Pd(II) complexes, this may indicates the absence of coordinated and / or lattice water. The appearance of strong band at 1620  $\text{cm}^{-1}$  in the ligand spectrum assigned to  $\nu(\text{C=N})$  of thiazole ring<sup>(27)</sup>. It is observed with a little change in shape and shift to lower frequencies

1600-1590  $\text{cm}^{-1}$  in prepared complexes spectra. These differences indicating coordination of thiazole-N atom<sup>(28)</sup>. The IR spectra of chelat complexes showed considerable reduction in the  $\nu$  (N=N) stretching frequency, absorption frequencies at 1540-1530  $\text{cm}^{-1}$  as compared to that of the parent free ligand 1560  $\text{cm}^{-1}$ . This shift could be attributed to the metal-azo back bonding<sup>(29)</sup>. Another band appeared at 1270  $\text{cm}^{-1}$  in the ligand spectrum, this band is due to  $\nu$ (C-S) of the thiazole ring<sup>(30)</sup>. The

existence of this band in all metal complexes means that the sulphur atom of the heterocyclic ring does not participate in coordination<sup>(28)</sup>. Some other new bands appeared in the region of 270-490  $\text{cm}^{-1}$  in the complexes spectra, which are not present in the spectrum of the ligand may be attributed to the  $\nu$ (M-O),  $\nu$ (M-N), and  $\nu$ (M-Cl) bands<sup>(31)</sup>.

Thus the above IR spectra data lead to suggest that the ligand behaves as a tridentate chelating ligand coordinating through the positions of phenolic oxygen, nitrogen of azo group and thiazole ring nitrogen.

**Table.3: Characteristic IR absorption bands of the ligand and its complexes in  $\text{cm}^{-1}$  units**

Compound	$\nu$ (O-H)	$\nu$ (C=N)	$\nu$ (N=N)	$\nu$ (C-S)	$\nu$ (M-O)	$\nu$ (M-N)	$\nu$ (M-Cl)
HL	3360-3180 br	1620 m	1560 m	1270 m	-----	-----	-----
[FeL <sub>2</sub> ]	-----	1590 m.br	1530 msh	1270 m	490 w	390 w	-----
[CoL <sub>2</sub> ]Cl.H <sub>2</sub> O	3450-3390 s.br	1600 m. br	1535 m	1270 m	480 w	380 w	270 w
[NiL <sub>2</sub> ]	-----	1595 m	1530 m	1265 m	490 w	410 w	-----
[CuL(H <sub>2</sub> O)]Cl	3450 s	1600 m	1540 m	1270 m	470 w	400 w	270 w
[PdLCl]	-----	1595 m	1540 m.sh	1270 m	480 w	410 w	260 w
[ZnL <sub>2</sub> ]	-----	1600 m. br	1535 m	1265 m	480 w	410 w	-----
[CdL <sub>2</sub> ]. H <sub>2</sub> O	3440-3180 s.br	1590 m	1540 m.sh	1265 m	470 w	400 w	-----
[Ag.L(H <sub>2</sub> O)].H <sub>2</sub> O	3370-7110	1600 m	1530 m.sh	1270 m	480 w	390 w	-----

**HL = ligand,  $\nu$  = very, w = weak, s = strong, m = medium, br = broad, shr = sharp**

### Conductivity Measurements, Electronic Spectra and Magnetic Properties

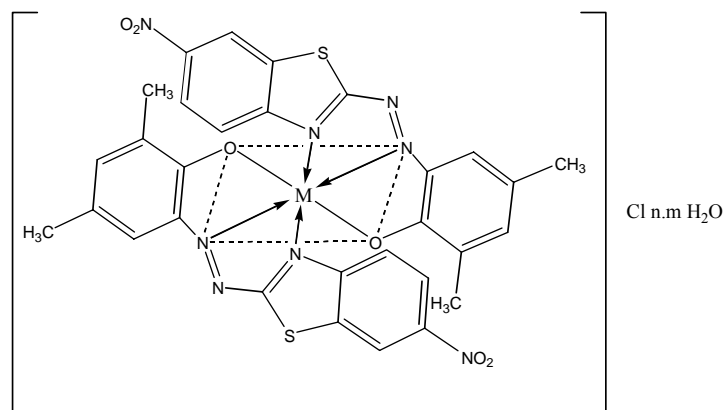
All chelate complexes except of Co(III) and Cu(II) complexes showed the conductivity measurements values rang between 8.45-7.18 S. cm<sup>2</sup> mol<sup>-1</sup>. Table 4, in DMSO (10<sup>-3</sup>M) at room temperature, the values indicating that non-ionic character<sup>(32)</sup>. But the low values of conductivity 69.44 and 76.35 S. cm<sup>2</sup> mol<sup>-1</sup> for the Co(III) and Cu(II) complexes respectively indicating that these complexes is (1:1) ionic structure.

The electronic spectrum of Fe(II) complex shows a single absorption band at 10200 cm<sup>-1</sup>, corresponding to <sup>5</sup>T<sub>2g</sub> → <sup>5</sup>E<sub>g</sub> transition. This complex exhibit magnetic moment of 5.46 B.M, which can be a normal value for high-spin octahedral geometry<sup>(33)</sup>. The UV-Vis spectrum of Co(III) complex show two absorption bands at 15923 cm<sup>-1</sup> and 21739 cm<sup>-1</sup> characteristic of octahedral stereo absorption<sup>(34)</sup>. They were assigned to the transitions of <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>1g</sub> and <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>T<sub>2g</sub> respectively. The magnetic moment of this complex has been found to be diamagnetic the low spin behavior of Co(III) complex indicates that the Co(II) ion is oxidized to the Co(III) ion during complexation. The change of the oxidation state agrees with the earlier observation of the aqueous solution of Co(II) salts which are spontaneously oxidized to Co(III) in the presence of strong ligand such as thiazolylazo compounds<sup>(21)</sup>. The spectrum of Ni(II) complex exhibit three bands at

10400 cm<sup>-1</sup>, 16286 cm<sup>-1</sup> and 22870 cm<sup>-1</sup> corresponding to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(F), and <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub>(P) transitions respectively with an octahedral spatial configuration<sup>(35)</sup>. This complex exhibit magnetic moment of 3.17 B.M, which can be a normal value for octahedral high-spin Ni(II) complexes<sup>(36)</sup>. The visible absorption spectrum of Cu(II) complex provide abroad absorption band around 18518 cm<sup>-1</sup> corresponding to <sup>2</sup>B<sub>1g</sub> → <sup>2</sup>A<sub>1g</sub> transition. It is reasonable to assign square planer structure<sup>(37)</sup>. The value of magnetic moment of this metal complex was found to be 1.86 B.M, this suggests the presence of one unpaired electron in this complex. The electronic spectrum of Pd(II) complex show absorption band in the visible region around 23130 cm<sup>-1</sup>, which was attributed to <sup>1</sup>A<sub>1g</sub> → <sup>1</sup>B<sub>1g</sub> transition in square planer environment<sup>(38)</sup>. The zero magnetic value of this complex indicate square planer geometry which is the common stereo chemistry for tetra coordinate Pd(II) complex. The UV-Vis spectra of Ag(I), Zn(II) and Cd(II) complexes with (6-NBTADMP) do not show any d→d transition bands. The magnetic susceptibility show that all complexes have diamagnetic moment for d<sup>10</sup> ions. The spectral data and magnetic moments are listed in Table 4. According to the above data the structural formula of metal complexes may be proposed in Figs. 2, 3, 4 and 5.

**Table.4: Molar conductance, Electronic spectra and Magnetic moment of Complexes**

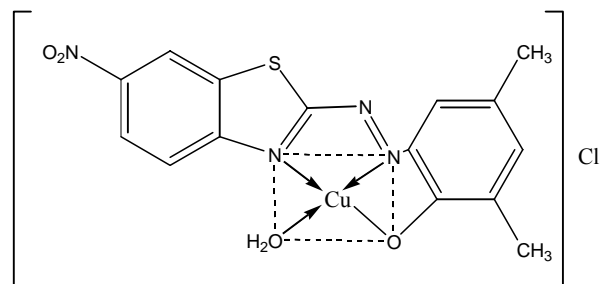
Complex	Absorption bands (cm <sup>-1</sup> )	Transition	Conductivity S.mol <sup>-1</sup> .cm <sup>2</sup>	$\mu_{\text{eff}}$ (B.M)
[FeL <sub>2</sub> ]	10200	<sup>5</sup> A <sub>2g</sub> → <sup>5</sup> E <sub>g</sub>	8.45	5.46
[CoL <sub>2</sub> ].Cl.H <sub>2</sub> O	15923 21739	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub> (F) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F)	69.35	dia
[NiL <sub>2</sub> ]	10400 16286 22870	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub> (F) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (F) <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (p)	7.52	3.17
[CuL(H <sub>2</sub> O)].Cl	18518	<sup>2</sup> B <sub>1g</sub> → <sup>2</sup> A <sub>1g</sub>	76.35	1.86
[PdLCl]	23130	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>	7.77	dia
[ZnL <sub>2</sub> ]	-----	-----	7.63	dia
[CdL <sub>2</sub> ].H <sub>2</sub> O	-----	-----	7.25	dia
[Ag.L(H <sub>2</sub> O)].H <sub>2</sub> O	-----	-----	7.18	dia



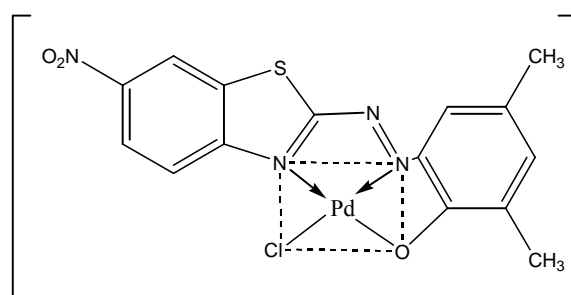
M = Fe(II), Ni(II) and Zn(II) , n = 0, m = 0  
M = Co(III), n = 1, m = 1  
M = Cd(II), n = 0, m = 1

**Fig.2: The proposed structural formula of Fe(II),Co(III), Ni(II), Zn(II) and Cd(II) complexes**

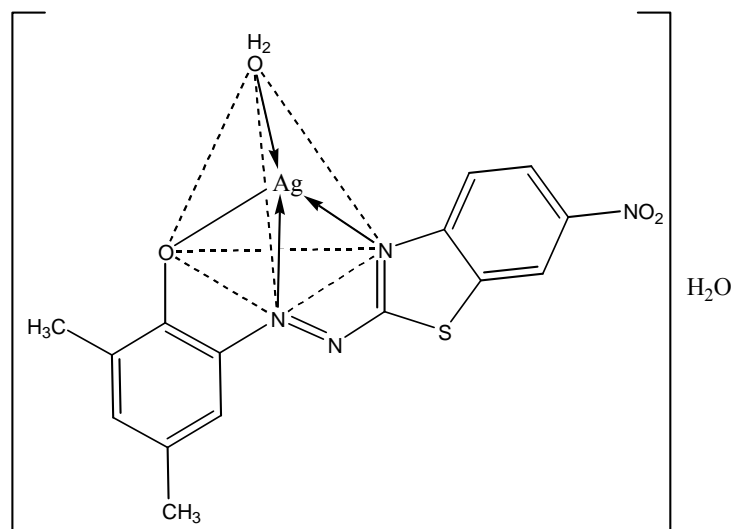




**Fig.3: The proposed structural formula of Cu(II) complex**



**Fig.4: The proposed structural formula of Pd(II) complex**



**Fig.5: The proposed structural formula of Ag(I) complex**

## References

1. A. Geronikaki, D. Hadjipavlou, C. Chatziopoulos, and G. Soloupis ; *Molecules* ., 2003, 8, 472.
2. A. Geronikaki, and D. Hadjipavlou ; *Arzneim. Forsc./ Drug Res* ., 1996, 46, 1134.
3. A. Geronikaki, and D. Hadjipavlou ; *Pharmazie* ., 1993, 48, 948.
4. K. Singh, A. Mahajan, and W. T. Robinson ; *Dyes and Pigments* ., 2006, (xx), 1.
5. S. J. Naik, and U. p. Halkar ; *ARKIVOC* ., 2005, (xiii), 141.
6. V. Patel, M. Patel, and R. Patel ; *J. Serb. Chem. Soc* ., 2002, 67 (11) , 719.
7. Nippon Kayaku Co. ltd. Jap. Patent 1986, 6128555 ; *Chem. Absr.* 1986, 105, 135408w.
8. H. Tappe, K. Roth, and A. G. Cassella ; Ger. Offen. 3, 036578 ; *Chem. Absr.* 1982, 97, 571167z.
9. L. S. D. Carvalho, A. C. S. Costa, S. L. C. Ferreira, and L. S. G. Teixeira ; *J. Braz. Chem. Soc.*, 2004, 15, 153.
10. V. A. Lemos, M. D. L. Guardia, and L. G. Ferreira ; *Talanta.*, 2002, 58, 475.
11. L. S. G. Teixeira, A. C. S. Costa, and J. C. R. Assis ; *MicroChem. Acta* ., 2001, 137, 29 .
12. A. M. Ali ; *Nat. J. of Chem* ., 2006, 23, 335 .
13. R. T. Mehdi, and A. M. Ali ; *Ibn AL-Haitham. J. for pure and appl. Sci.*, 2005, 18 (3), 50 .
14. A. M. Ali ; *Sic. J. Babylon University.*, 2004, 9 (3), 841.
15. M. S. Masoud, G. B. Mohamed, and Y. H. Abdul – Razek ; *J. Korean. Chem.. Soc.*, 2002, 46 (2), 110,
16. R.Q.Brewster, and F.B.Dains ; *J.Am. Chem. Soc.*, 1936, 58, 1364.
17. P.W. Selwood ; " *Magneto Chemistry* " ; Inter science, New York, 1956.
18. J. Prikryl, A. Lycka, V. Bertolasi, M. Holcapek, and V. Machacek ; *Eur. J. Org. Chem.*, 2003, 4413
19. H. R. Hovind ; *Analyst* ., 1975, 100, 769 .
20. H. Oyama, A. Ohasih, and H. Watarai ; *Anal. Sic.*, 2004, 20, 1543 .
21. M. Kurahashi ; *Bull. Chem. Soc. Jap.*, 1974, 47 (8), 2067 .
22. W. C. Vosburgh, and G. R. Cooper ; *J. Am. Chem. Soc.*, 1941, 63, 437 .
23. F. A. Snavely, and C. H. Yodeer ; *J. Org. Chem* ., 1968, 33, 513 .
24. A. A. El-Bindary ; *Transition Met. Chem* ., 1996, 22, 381 .
25. A. Z. El-Sonbati ; *Transition Met. Chem* ., 1991, 16, 45 .
26. A. Z. El-Sonbati, and A. A. El-Bindary ; *Polish. J. Chem* ., 2000, 74, 621 .
27. S. I. Gusev, M. V. Zhvakina, and I. A. Kozhevnikov ; *Zh. Analit. khim* ., 1971, 26, 859 .
28. L. Mangsup, S. Siripaisarnpipat, and N. Chaichit ; *Anal. Sci.*, 2003, 19, 1345 .
29. M. W. Bes, S. F. Kettle, and D. B. Powell ; *SpectroChem. Acta* ., 1974, 30 (A), 139 .

30. N. B. Colthup, L. H. Daly, and S. E. Wiberley ; "Introduction to infrared and Raman Spectroscopy", 2<sup>nd</sup> edn. Academic press. Inc. J. R. Dyer., 1975 .
31. Y. Saito, C. W. Schlapfer, M. Cordes, and K. Nakamoto ; *Applied Spectra* ., 1973, **27**, 213 .
32. W. J. Geary ; *Coord. Chem. Rev.*, 1971, **7**, 81 .
33. A. A. El-Bindary, and A. Z. El-Sonbati ; *SpectroscopyLett* ., 1999, **32 (4)** , 581 .
34. J. C. Bailer, H. Emeleus, and R. Nypholm ; "Comprehensive Inorganic Chemistry"., pergamon press, 1973.
35. A. Syamal ; *Chem. Educ* ., 1987, **4**, 33 .
36. F. A. Cotton, and G. Wilkinson ; "Advanced Inorganic Chemistry"., 3<sup>rd</sup> edn. New Delhi .1985.
37. N. K. Singh, and S. B. Singh ; *Indian. J. Chem* ., 2001, **A (40)**, 1070 .
38. B. N. Figgis, and J.; "Modern Coordination Chemistry", Interscience, New York., 1980.