

Synthesis and Spectrophotometric Studies of Some Transition Metal Complexes with New Azo Dye 2-[2-(6-Methoxy benzothiazolyl)azo]-4-Nitro Phenol[‡]

KHALID J. AL-ADELY

Department of Chemistry, College of Science, University of Al-Qadisiya, Dewaniya, Iraq

Corresponding author: E-mail: khalidke-1962@yahoo.com

AJC-11705

This paper reports the preparation and identification of Ni(II), Pd(II), Pt(IV), Cu(II), Ag(I) and Au(III) metal complexes with new aryl thiazolyl azo 2-[2-(6-methoxy benzothiazolyl)azo]-4-nitro phenol (6-MBTANP = HL). The structure of the isolated chelat complexes characterized by elemental analysis, IR, electronic spectral, magnetic moment and molar conductivity. The obtained results indicated that the ligand (6-MBTANP) behaves as a tridentate chelating agent with 1:1 and 1:2 (metal:ligand) complexes. Investigation of the stereochemistry of these chelat complexes showed that, Ni(II), Cu(II) and Pt(IV) complexes are octahedral while Pd(II) and Au(III) complexes are square planer and Ag(I) complex is tetrahedral geometry. Conductance measurements suggest the 1:2 electrolytic nature of the Pt(IV) and (1:1) electrolytic nature of the Au(III) complexes but non-electrolytic nature of remaining complexes. The analytical data show the existence of coordination water in Ni(II), Pt(IV), Cu(II), Ag(I) and Au(III) complexes. Stability constants of complexes were calculated by spectrophotometrically.

Key Words: New benzothiazolyl azo ligand, Metal complexes.

INTRODUCTION

Azo dyes are characterized by the -N=N- azo group, which is important in the dye-stuffs industry^{1,2}, drugs³, cosmetics⁴, redoxmetallochromic indicators⁵ and biological activities including antibacterial^{2,6} and some pathogenic bacteria⁷. The benzothiazolyl azo compounds and its complexes are very important in the biological field because they contain atoms such as oxygen, nitrogen and sulfur, which make them able to connect with different metal ions⁸. Benzothiazolyl azo is iso-electron with α -imine and the active function is the (π -acidic) azo imine group -N=N-C=N- consequently a number of these compounds were prepared as chelating ligand^{9,10}. These compounds have an important field to determine the trace amount of elements especially transition metal ions because of high sensitivity and selectivity¹¹⁻¹³. The formation of one or two metalo cyclic ring make the chelating complexes of these compounds have high stability constant and suitable for spectrophotometric studies^{14,15}.

This work shows the preparation and spectral identification of new benzothiazolyl azo ligand (6-MBTANP) and its chelate complexes with Ni(II), Pd(II), Pt(IV), Cu(II), Ag(I) and Au(III) metal ions.

EXPERIMENTAL

All chemical and solvents were highest grade from Aldrich, BDH and Fluka and used with out further purification except of 2-amino-6-methoxy benzothiazole was prepared as described in the literature¹⁶.

The analysis of CHN and S of the ligand and its metal complexes were carried out on a CHNOS. Euro EA 300 elemental analyzer. IR spectra were recorded using KBr discs in 4000-400 cm^{-1} range on FT-IR Shimadzu spectrophotometer model 8400. The electronic spectra of the ligand and its complexes were measured in ethanol solvent using UV-VIS-1650 PC Shimadzu. The metal contents of the complexes were measured by using atomic absorption technique by Shimadzu AA-160. The molar conductance measurements were carried out in DMF (10^{-3} M) at room temperature by using conductivity meter model 31A digital. The magnetic moment measurements of the complexes were measured as powder samples using Faraday method, balance magnetic MSB-MKI was employed for this purpose. The pH measurements were carried out using a Philips pw 9421 pH meter ($\text{pH} \pm 0.001$) and the melting points were determined on an electro thermal, melting point 9300 was used to measure the melting points of the ligand

[‡]Presented at International Conference on Global Trends in Pure and Applied Chemical Sciences, 3-4 March, 2012; Udaipur, India

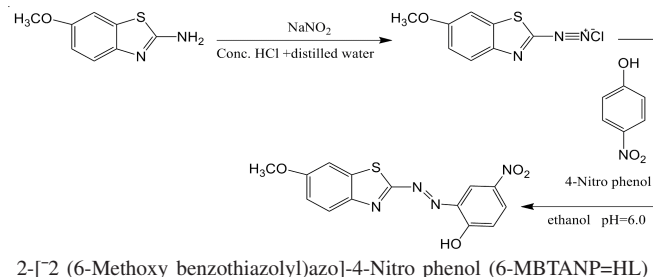
TABLE-1
ELEMENTAL ANALYSIS AND SOME PHYSICAL DATA FOR LIGAND AND THEIR METAL COMPLEXES

Compound	Optimal pH	Colour	m.p. (°C)	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (calc.)				
						C	H	N	S	M
LH = ligand	6.0	Dark red	96	74	C ₁₄ H ₁₀ N ₄ O ₃ S (330.31)	50.68 (50.91)	2.97 (3.05)	17.05 (16.96)	9.84 (9.71)	-
[NiL ₂].H ₂ O	7.5	Purple	165	71	C ₂₈ H ₂₀ N ₈ O ₃ S ₂ Ni (735.33)	45.89 (45.73)	2.68 (2.74)	15.33 (15.24)	8.87 (8.72)	8.14 (7.98)
[Pd L Cl]	6.5	Reddish brown	187	65	C ₁₄ H ₉ N ₄ O ₄ SClPd (471.00)	35.51 (35.69)	1.87 (1.92)	11.71 (11.89)	6.63 (6.80)	22.39 (22.58)
[PtL ₂]Cl ₂ .H ₂ O	8.0	Dark purple	198	78	C ₂₈ H ₂₀ N ₈ O ₃ S ₂ Cl ₂ Pt (942.62)	35.55 (35.68)	2.02 (2.14)	11.75 (11.89)	7.03 (6.80)	20.49 (20.70)
[Cu L ₂].H ₂ O	7.5	Green bluish	176	83	C ₂₈ H ₂₀ N ₈ O ₃ S ₂ Cu (740.16)	45.52 (45.44)	2.65 (2.72)	15.23 (15.14)	8.83 (8.66)	8.39 (8.58)
[Ag L (H ₂ O)]	6.5	Reddish purple	183	69	C ₁₄ H ₁₁ N ₄ O ₃ SAg (455.19)	36.73 (36.94)	2.38 (2.43)	12.44 (12.31)	7.17 (7.04)	23.84 (23.70)
[Au L Cl] Cl.H ₂ O	7.0	Red yellowish	217	72	C ₁₄ H ₁₁ N ₄ O ₃ SCl ₂ Au (615.19)	27.51 (27.33)	1.86 (1.80)	9.32 (9.11)	5.39 (5.21)	31.83 (32.02)

LH = (6-MBTANP)

and their complexes. The chloride ions was estimated by Mohr method¹⁷.

Synthesis of the azo ligand (6-MBTANP): The heterocyclic azo ligand (6-MBTANP) has been synthesized by the diazotization coupling reaction by using Gusev method¹⁷ with some modification (**Scheme-I**). 2-Amino-6-methoxy benzothiazole (1.8 g, 0.01 mol) was dissolved in 30 mL of distilled water and 8 mL of concentrated hydrochloric acid. The filtered solution was diazotized at (0-5) °C with (0.75 g, 0.01 mol) sodium nitrite in 20 mL distilled water drop wise and stirred for 30 min at 0 °C. The resulting diazonium chloride solution was added drop wise with cooling and stirring continues at (0-5) °C to a solution of 4-nitro phenol (1.39 g, 0.01 mol) dissolved in 150 mL absolute ethanol, the mixture was stirred continuously for 2 h at (0-5) °C in ice-bath and allowed to stand over night. The mixture was acidified with dilute hydrochloric acid until (pH = 6.0). The crystals was filtered and washed several times with cold distilled water until a negative chloride reaction with silver nitrate as well as washed with mixture distilled water and ethanol solution to remove the excess of unreacted substances. The isolated dark red product was recrystallized from hot ethanol twice and finally dried in oven at 60 °C for several hours and stored in a desicator over anhydrous calcium chloride. The melting point of the dark red crystals found to be 96 °C. The purity was confirmed by the elemental analysis and TLC techniques.



Scheme-I: Synthesis of the ligand (6-MBTANP)

Metal complexes of Ni(II), Pd(II), Pt(IV), Cu(II) and Ag(I) ions: All the chelates complexes were prepared by mixing ethanolic solution of ligand (0.002 mol, 0.661 g) with

0.001 mol of NiCl₂.2H₂O, PtCl₄ and CuCl₂ at molar ratio 1:2 (M:L) and 1:1 (M:L) molar ratio of PdCl₂ and AgNO₃ (0.001 mol, 0.330 g form ligand) dissolving in 30 mL buffer solution (ammonium acetate) at optimal pH for each metal ions. The reaction mixtures were stirred at (60-70) °C for (40-50) min and left overnight. The colored powders were filtered hot, washed thoroughly distilled water until the solution become colourless. The isolated solids were washed with 10 mL hot ethanol to remove the excess of ligand and metal ions unreacted and finally dried in oven at 70 °C for several hours and stored in a desiccator over anhydrous calcium chloride.

Au(III)-complex: This complex was prepared by dissolving (0.001 mol, 0.595 g) of NaAuCl₄.H₂O in 30 mL hot ethanol and mixed with a solution of ligand (0.001 mol, 0.331 g) at molar ratio 1:1 (M:L). To this mixture 10 mol of buffer solution (pH = 7.5) was added slowly with stirring continuously and the resulting mixture was heated to 70 °C for 1 h, cooled and filtered. Recrystallization from hot absolute ethanol affords a red yellowish precipitate. The product was dried in air and stored in a desiccator over anhydrous calcium chloride.

RESULTS AND DISCUSSION

The azo dye (6-MBTANP) are dark red crystals but the isolated metal complexes of this ligand vary in colour from red yellowish to green bluish depending on the nature metal ion. The ligand is soluble in strongly acidic solution giving a red cation with absorption maximum (λ_{max}) at 483 nm and in strongly alkaline solution giving violet blueish anion with an absorption maximum at 528 nm. The elemental analysis data of the ligand and its complexes as shown in Table-1 exhibit the formation of 1:1 (M:L) molar ratio of Pd(II) and Au(III) ions and 1:2 ratio with Ni(II), Pt(IV), Cu(II) and Ag(I) ions. It was found that the theoretical values are in a good agreement with found data. The ligand and its complexes are stable in air at room temperature for long time and are insoluble in water but soluble in most common organic solvents such as methanol, ethanol, acetone, DMF and DMSO. The purity of azo dye complexes were tested by TLC technique and CHNS elemental analysis.

Metal: Ligand ratio: The composition of the complexes were determined by molar ratio method at fixed concentration and optimal pH at wavelengths of maximum absorption. This method indicated that the ratio of metal ion to ligand molecules was (1:1) chelates with Pd(II), Ag(I) and Au(III) metal ions and (1:2) chelates with Ni(II), Pt(IV) and Cu(II) metal ions, these results are in agreement with the values reported for some benzothiazolylazo complexes^{18,19}.

Effect of pH and time: For evaluation of the optimal pH values for formation of chelat complexes, the effects of pH on the absorbance were studied with results shown in Figs. 1 and 2. The azo dye ligand (6-MBTANP) formed a very stable complex with metal ions Ni(II), Pd(II), Pt(IV), Cu(II), Ag(I) and Au(III) at pH (6.0-8.0). At pH > 8.0 a decrease in absorbance many be due to the hydrolysis of complexes and also when pH < 5.5 a decrease in absorbance occur due to form azolium cation result from the reaction between hydrogen ion and the ion pair of electron which found in the nitrogen atom for thiazole ring. Also the reaction is complexe in 10 mint at room temperature and remains stable for about 24 h, this show the azo dye ligand strong coordination with all metal ions. The result are shown in Figs. 3 and 4.

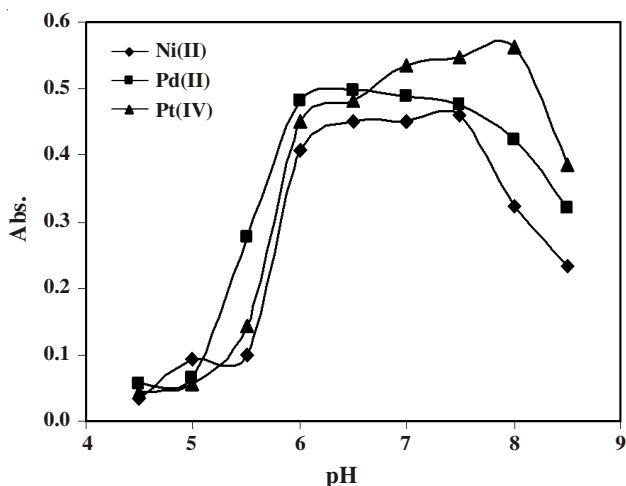


Fig. 1. Absorbance spectra of 6-MBTANP-metal chelats $(1.75-2.25) \times 10^{-5}$ M, in aqueous ethanolic solution

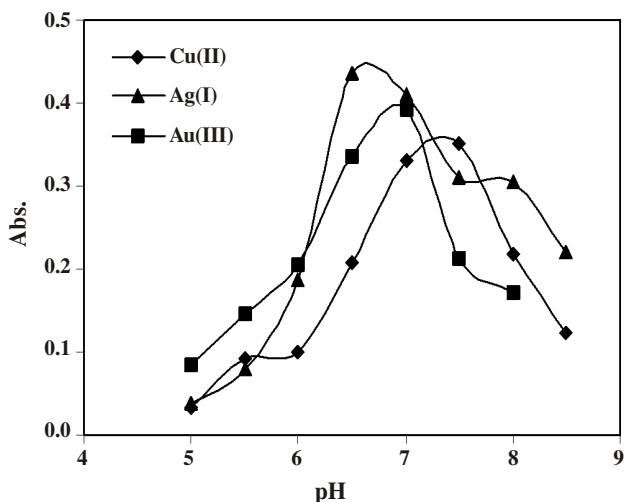


Fig. 2. Absorbance spectra of 6-MBTANP-metal chelats $(1.5-1.75) \times 10^{-5}$ M, in aqueous ethanolic solution

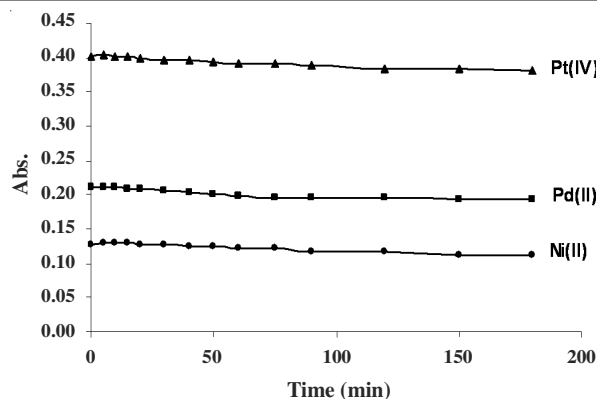


Fig. 3. Effect of time on the absorbance of metal complexes; at room temperature. M = Ni(II), Pd(II) and Pt(IV)

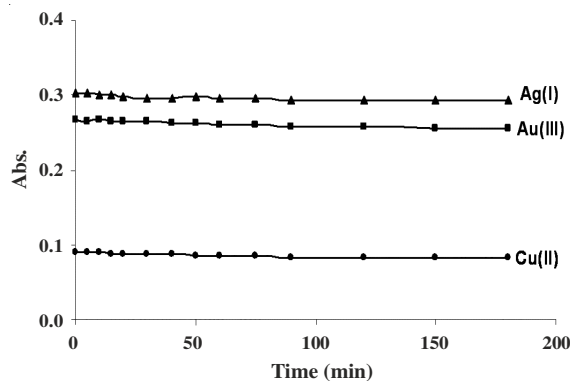


Fig. 4. Effect of time on the absorbance of metal complexes; at room temperature. M = Cu(II), Ag(I) and Au(III)

Calculation of the metal complexes stability constant:

Stability constants are obtained spectrophotometrically by measuring the absorbance of solution of ligand and metal ion mixture at fixed wavelength (λ_{max}) and pH values. The degree of formation of the complexes are obtained according to the relation ship²⁰, $\beta = (1-\alpha/4\alpha^3c^2)$ for 1:2 (M:L) metal complexes and $\beta = (1-\alpha/\alpha^2c)$ for 1:1 (M:L) metal complexes and $\alpha = A_m - A_s/A_m$ where, A_s and A_m are the absorbance of the partially and fully formed complex respectively at optimum concentration. The calculated β and $\log \beta$ values for the prepared complexes are recorded in Table-2.

Molar conductivity measurement: The molar conductance of the prepared complexes are shown in Table-2 were carried out in DMF (10^{-3} M) at room temperature. The values of conductivity indicate the complexes of Ni(II), Pd(II), Cu(II) and Ag(I) ions are non-electrolytes nature, where suggest that no anions present outside the coordination spheres^{2,21}. But the high value of molar conductivity for the Pt(IV) and Au(III) complexes indicating that there complexes are 1:2 and 1:1 electrolyte respectively²².

Infrared spectra: The infrared spectra of ligand (6-MBTANP) and their complexes have been studied and listed in Table-3.

Electronic spectra and magnetic moments: The electronic spectra of ligand and their complexes were recorded in absolute ethanol and their assignments are given in Table-4. The free ligand spectral dated display three absorption bands were detected first band located at 219 nm (45662 cm^{-1}) for $n \rightarrow \sigma^*$ of the hydroxyl group (OH), while the second was at

TABLE-2
METAL: LIGAND, STABILITY CONSTANT VALUES (β and $\log \beta$) MOLAR CONDUCTIVITY; OPTIMAL CONCENTRATION AND WAVELENGTH WITH MOLAR ABSORPTIVITY (ϵ) OF CHELATE COMPLEXES

Ligand	Metal ions	Metal: ligand	Optimal molar conc. $\times 10^{-5}$ M	Optimal wave length (λ_{\max} , nm)	Molar absorptivity (ϵ) $\times 10^4$ L mol $^{-1}$ cm $^{-1}$	β L 2 mol $^{-2}$	Log β	Molar conductivity (s mol $^{-1}$ cm 2)
6-MBTANP $\lambda_{\max} = 437$ $\epsilon = 10.55 \times 10^4$ L mol $^{-1}$ cm $^{-1}$ Conc = 1.5×10^{-5} M	Ni(II)	1:2	2.25	519	1.73	1.31×10^{10}	10.11	13.78
	Pd(II)	1:1	1.75	544	1.54	1.66×10^{10}	10.22	8.93
	Pt(IV)	1:2	2.0	550	1.43	4.84×10^{11}	11.68	86.15
	Cu(II)	1:2	1.5	638	2.31	1.08×10^{10}	10.03	12.43
	Ag(I)	1:1	1.75	528	1.77	2.17×10^{10}	10.33	10.98
Au(III)	1:1	1.5	485	1.14	3.21×10^{10}	10.50	43.86	

TABLE-3
IR SPECTRAL DATA OF THE AZO DYE LIGAND (6-MBTANP) AND THEIR COMPLEXES (KBr DISK, cm $^{-1}$)

Assignment	6-MBTANP (HL)	Ni $^{2+}$	Pd $^{2+}$	Pt $^{4+}$	Cu $^{2+}$	Ag $^{+}$	Au $^{3+}$
v(O-H)	3344 3380 (w.br.)	3439 w.br.	-	3502 w.br.	3387 w.br.	3445 w.br.	3460 w.br.
v(C-O)	1736 s.	1638 s.	1626 w.	1676 m.	1658 s.	1605 s.	1653 s.
v(C=N)	1614 s.	1602 s.	1595 m.	1591 m.	1610 s.	1560 m.	1575 s.br.
v(N=N)	1525 vs 1464 s.	1523 w.br; 1460 m.	1520 m. 1448 m.br.	1493 m. 1458 w.	1449 m. 1435 m.br.	1467 s. 1440 m.	1471 m. 1433 w.
v(C=C)	1361 Vs.	1415 s.	1400 m.br.	1335 m.	1410 m.	1345 Vs.	1402 m.br.
v(C-N=N-C)	1265 w.br.	1320 m.	1296 w.	1334 m.	1331 m.br.	1301 m.	1321 s.
v(C-S)Thi	1246 w.br.	1245 m.	1240 m.	1245 w.	1243 m.	1245 m.br.	1246 m.
v(C-N)Thia	993 m.	875 m.	862 m.br.	860 m.	885 m.	865 s.	880 m.
Thia.r.def.	771 s. 739 vs.	775 m.; 712 s.	760 s.; 725 m.	765 m.; 696 s.	771 m; 717 m.br.	760 s.; 720 vs.	783 vs.; 675 vs.
v(M-O)		537 w.	580 w.	510 w.	535 w.	520 w.	590 w.
v(M-N)		455 w.	460 w.	445 w.	465 w.	460 w.	485 w.

TABLE-4
ELECTRONIC ABSORPTION BAND (nm, cm $^{-1}$) OF LIGAND AND ITS COMPLEXES

Complexes	λ_{\max} nm	Absorption bands (cm $^{-1}$)	Transition	Geometry	Hybridization
Ligand=LH	219	45662	$n \rightarrow \sigma^*$	-	-
C $_{14}$ H $_{10}$ N $_4$ O $_4$ S	267	37453	$\pi \rightarrow \pi^*$		
	439	22883	$n \rightarrow \pi^*$		
[NiL $_2$] H $_2$ O	320	31250	$^3A_{2g} \rightarrow ^3T_{1g(p)} (v_1)$	Octahedral	sp^3d^2 (high spin)
	519	19268	$^3A_{2g} \rightarrow ^3T_{1g(f)} (v_2)$		
	936	10683	$^3A_{2g} \rightarrow ^3T_{2g} (v_3)$		
[PdLCl]	544	18382	$^1A_{1g} \rightarrow ^1B_{1g}$	Squer planer	dsp^2
[PtL $_2$] Cl $_2$.H $_2$ O	309	32362	$^1A_{1g} \rightarrow ^1T_{1g(t)} (v_1)$	Octahedral	d^2sp^3 (low spin)
	401	24938	$^1A_{1g} \rightarrow ^1T_{2g(t)} (v_2)$		
	550	18182	$^1A_{1g} \rightarrow ^1E_{g(t)} (v_3)$		
[CuL $_2$].H $_2$ O	641	15601	$^2E_g \rightarrow ^2T_{2g}$	Octahedral (distorted)	sp^3d^2
[AgL(H $_2$ O)]	528	18939	M \rightarrow L, CT	Tetrahedral	sp^3
[AuLCl] Cl.H $_2$ O	485	20619	$^1A_{1g} \rightarrow ^1B_{1g}$	Squer planer	dsp^2

267 nm (37453 cm $^{-1}$) for $\pi \rightarrow \pi^*$ of the two interact (C=C) group of aromatic and thiazole rings and the third one located at 537 nm (22883 cm $^{-1}$) for $n \rightarrow \pi^*$ of the azo group (N=N) this band showed at a red shift on coordination with a metal ion. For the spectra of metal complexes the following results were obtain.

Nickel(II)-complex: The electronic spectrum of this complex show three absorption bands at 320 nm (31250 cm $^{-1}$), 519 nm (19268 cm $^{-1}$) and 936 nm (10683 cm $^{-1}$), which are assigned to $^3A_{2g} \rightarrow ^3T_{1g(p)} (v_1)$; $^3A_{2g} \rightarrow ^3T_{1g(f)} (v_2)$ and $^3A_{2g} \rightarrow ^3T_{2g} (v_3)$ transition respectively with an octahedral spatial configuration 2 . This complex exhibit magnetic moment of 3.41 B.M., which may suggest a high spin octahedral structure (hybridization; sp^3d^2).

Palladium(II)-complex: The electron spectrum of Pd(II)-complex shows one absorption band in the visible region at the position 544 nm (18382 cm $^{-1}$), which was attributed to $^1A_{1g} \rightarrow ^1B_{1g}$ transition in a square planer. The magnetic susceptibility of this complex gave $\mu_{\text{eff}} = 0.0$ B.M. because of location of this metal (Pd) in second round (low spin) indicate a square planer geometry (hybridization dsp^2), which is the common stereo chemistry for tetra coordinate Pd(II)-complex 2 .

Platinum(IV)-complex: The electronic spectrum data exhibit three bands at 309 nm (32362 cm $^{-1}$), 401 nm (24938 cm $^{-1}$) and 550 nm (18182 cm $^{-1}$) due to presence of a $^1A_{1g} \rightarrow ^1T_{1g(t)} (v_1)$, $^1A_{1g} \rightarrow ^1T_{2g(t)} (v_2)$ $^1A_{1g} \rightarrow ^1E_{g(t)} (v_3)$ transitions respectively and an octahedral geometry was suggested $^{24-28}$.

The magnetic moment for Pt(IV)-complex found to be diamagnetic character ($\mu_{\text{eff}} = 0.0$ B.M.). Suggest a low spin octahedral because of location of the platinum in third round (hybridization is d^2sp^3).

Copper(II)-complex: The electronic absorption spectrum of this complex show a broad band at 641 nm (15601 cm^{-1}), which may assigned to ${}^2E_g \rightarrow {}^2T_2g$ transition. The value magnetic moment for the Cu(II)-complex found to be 1.74 B.M. due to presence of one electron unpaired suggest a distorted octahedral geometry (Z-out or Z-in) and hybridization^{2,24-28} sp^3d^2 .

Silver (I)-complex: The electronic spectrum of Ag(I)-complex do not show any $d-d$ transition. The band at 528 nm (18939 cm^{-1}), which could be attributed to the presence of a charge transfer ($M \rightarrow L$, CT)². The magnetic susceptibility moment for this complex found to be zero and electronic configuration d^{10} to be diamagnetic character ($\mu_{\text{eff}} = 0.0$ B.M.) and an tetrahedral geometry.

Gold(III)-complex: For the Au(III) azo dye complex, the electronic spectral data exhibit one band at 485 nm (20619 cm^{-1}) due to the presence of a ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition. The intensity suggest square planer geometry²⁴⁻²⁸. The result of magnetic susceptibility for Au(III)-complex is zero magnetic ($\mu_{\text{eff}} = 0.0$ B.M.) indicate square planer geometry because of the Au metal location in third round (d^8 -low spin) and hybridization dsp^2 . The obtained magnetic moment values show the presence of a paramagnetic phenomena for both Ni(II) and Cu(II) complexes and diamagnetic character for Pd(II), Pt(IV), Ag(I) and Au(III) complexes.

From the previous mentioned chemical analysis data, we can suggest the following geometrical structures for the prepared metal complexes for the prepared metal complexes in Figs. 5-7.

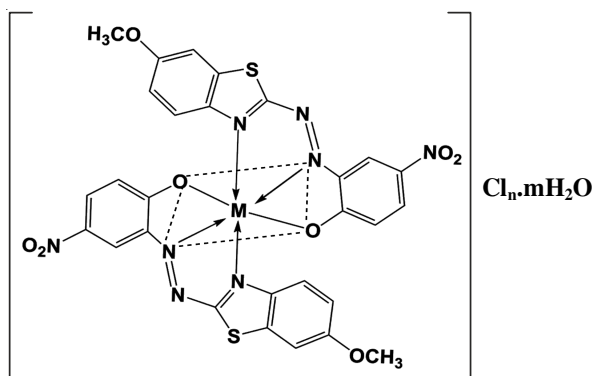


Fig. 5. Proposed chemical structure of Ni(II), Pt(IV) and Cu(II) complexes
M = Ni(II) and Cu(II); n = 0, m = 1, M = Pt(IV); n = 2, m = 1

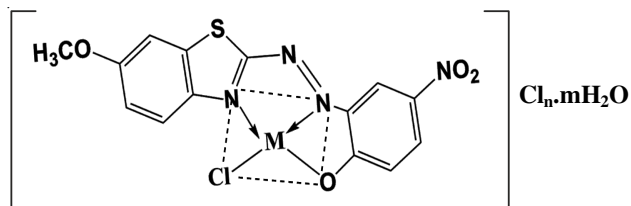


Fig. 6. Proposed chemical structure of Pd(II) and Au(III) complexes; M = Pd (II); n = 0, m = 0; M = Au (III); n = 1, m = 1

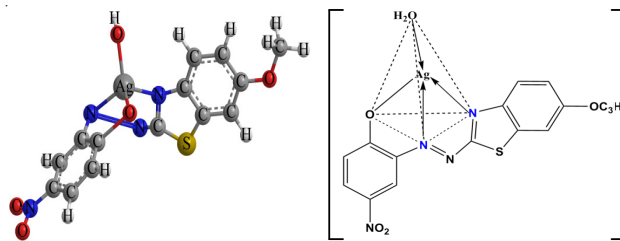


Fig. 7. Proposed chemical structure of Ag(I)-complex

Conclusion

In this paper, we report the preparation and spectrophotometric studies of new azo dyes ligand derived from thiazole and its complexes with Ni(II), Pd(II), Pt(IV), Cu(II), Ag(I) and Au(III) metal ions.

REFERENCES

- L. Ahlstrom, C.S. Eskilsson and E. Bjorklund, *Trends Anal. Chem.*, **24**, 49 (2005).
- K.J. Al-Adely, H.K. Dakhil and F.F. Karam, *J. Al-Qadisia Pure Sci.*, **16**, 50 (2011).
- G.A. Hadjiparlou, C. Chatziopoulou and G. Soloupis, *Molecules*, **8**, 472 (2003).
- D.M. Marmion, Handbook of U.S. Colourant; John Wiley & Sons, Inc., New York (1999).
- V.A. Lemos, E.S. Santos, M.S. Santos and R.T. Yamaki, *Microchim. Acta*, **158**, 189 (2007).
- I.M.A. Awad, A.A.M. Aly, A.M. Abdel-Alim, R.A. Abdel-Aal and S.H. Ahmed, *J. Inorg. Biochem.*, **33**, 77 (1998).
- B. Rittich, M. Pirochtová, J. Hrib, K. Jurtková and P. Doleal, *Coll. Czech. Chem. Commun.*, **57**, 1134 (1992).
- O.E. Woisetschlager, K. Sunkel, W. Weigand and W. Beck, *J. Organomet. Chem.*, **584**, 122 (1999).
- J. Savic and V. Vasic, *Acta Chem. Slov.*, **53**, 36 (2006).
- A.A.M. Ali, *Nat. J. Chem.*, **23**, 335 (2006).
- R. Gurkan, T. Cepken and H.I. Ulusoy, *Turk J. Chem.*, **36**, 159 (2012).
- M.S. Hosseini and H. Hashemi-Moghaddam, *Talanta*, **67**, 555 (2005).
- N. Rajesh and M.S. Hari, *Spectrochim. Acta A*, **70**, 1104 (2008).
- S. Pal, S. Das, P. Chattopadhyay, C. Sinha, K. Panreerselvam and T.H. Lu, *Polyhedron*, **19**, 1263 (2000).
- A.A.M. Ali, *Nat. J. Chem.*, **28**, 676 (2007).
- A.G. Kuhait, M.Sc. Thesis, University of Baghdad, Baghdad, Iraq (1984).
- S.I. Gusev, M.V. Zhvakin and I.A. Kozhevnikov, *Zh. Anal. Khim.*, **29**, 859 (1971).
- Khalid J. Al-Adely, Ph. D. Thesis, University of Baghdad (2000).
- H. Oyama, A. Ohasin and H. Watarai, *Anal. Sci.*, **20**, 1543 (2004).
- W.C. Vosburgh and G.R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).
- R.N. Raja and Y.P. Kulandaisary, *Indian Acad. Sci. A*, **113**, 183 (2001).
- W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
- T. Shanouchi and I. Nakagawa, *Spectrochim. Acta*, **18**, 89 (1962).
- W. Manch and W.C. Fernetins, *J. Chem. Educ.*, **38**, 192 (1961).
- B.N. Figgis and J. Modern, *Coordination Chemistry Interscience*, New York (1980).
- A. Wasey, R.K. Bansal, B.K.F. Kmil and S. Chandra, *Transition Met. Chem.*, **8**, 341 (1983).
- B.N. Figgis, *Introduction to ligand Field*, Interscience, New York (1966).
- A.B.V. Lever, *Inorganic Electronic Spectroscopy*, Amsterdam-London-New York (1986).