

Synthesis, Characterization of Zn(II) and Cd(II) complexes with mixed ligands of dithiocarbamate and tertiary phosphine

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ABSTRACT

This work includes synthesis and characterization of some binuclear complexes of Zn(II) and Cd(II) with mixed ligands of dithiocarbamate derived from barbituric acid and tertiary phosphines the formed complexes have the general formula of $[M_2(BADTC)_2(Phosphine)_n]$, $M=Zn(II), Cd(II)$, $BADTC=Barbituric\ acid\ bis(dithiocarbamate)$, $Phosphine = dppm, dppe, dppp$; $n=2, PPh_3$; $n= 4$ the synthesized complexes were identified using the micro elemental analysis (CNH), melting point measurement, molar electrical conductivity and the spectral methods (FT-IR and ¹H, ¹³P-NMR). Antibacterial activity of ligand and complexes was evaluated with two types of bacteria staphylococcus aureus (gram positive) and Escherichia coli (gram negative).

Keywords: Dithiocarbamate, tertiary Phosphine, binuclear Complexes

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INTRODUCTION

Dithiocarbamate, $R_2NC(S)S^-$, are highly versatile mono-anionic chelating ligands which form stable complexes with all the transition elements. They are capable of stabilizing transition metals in a wide range of oxidation states and frequently stabilize the metal central in an unusually high apparent formal oxidation states [1-3]. In coordination chemistry, dithiocarbamate act as ligands due to their selectivity and sensitivity to the reaction with transition and non-transition metal ions. They are also important from biological point of view since they were found to affect many biological processes [4,5]. Moreover, metal dithiocarbamate have diversified applications in the field of rubber chemistry as vulcanization accelerator and antioxidants [6]. Phosphines and diphosphines are important ligands in transition-metal catalyzed reactions and the electronic and steric effects of the phosphine have a promoted influence on the organic trans-formation that take place at the transition metal center [7,8].

In the present work we report the Synthesis and characterization of some new complexes obtained by the reactions of Zn(II) and Cd(II) salts with mixed ligands of dithiocarbamate and tertiary phosphine.

Experimental

IR-spectra were recorded on the (FTIR- 600 Spectrophotometer) in the (400-4000) cm^{-1} range using KBr discs. Micro elemental analysis (CHN) using (Euro EA 3000). Molar Conductivities for complexes were measured at 10^{-3} M solution in DMSO at 25°C using (Cond7110). Melting points were obtained using (Electro thermal9300). The ¹H-¹³P-NMR spectra were performed (solvent DMSO-d⁶) on (Brucker 400MHz), at the University of Sinop, Turkey.

Starting materials

All chemicals and phosphine ligands were commercial products and were used as supplied from Sigma-Aldrich and Alfa-Asercompanies

Preparation of ligand

barbituric acid bis (dithiocarbamate) (BADTC) was prepared by a previously described method [9].

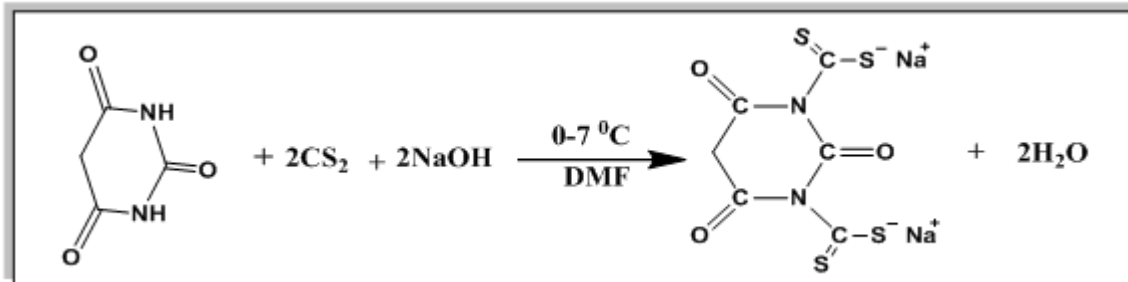


Table 1: chemical formula, CHN analysis and some physical properties of the BADTC ligand

Chemical formula	Color	Melting point/°C	Micro elemental analysis calculated (found)			
			C%	H%	N%	S%
C ₆ H ₂ N ₂ Na ₂ O ₃ S ₄ 324.31	Light orange	260-262	22.22 (22.61)	0.62 (0.55)	8.64 (8.12)	39.54 (38.91)

Synthesis of Dithiocarbamate complexes with phosphine

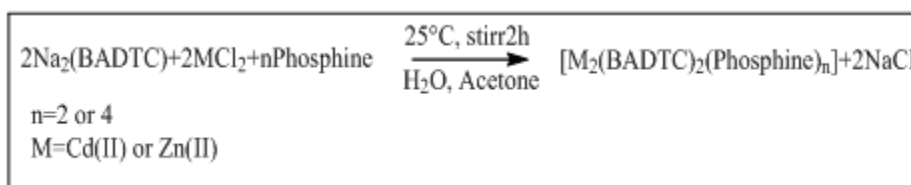
Synthesis of [Zn₂(BADTC)₂(dppp)₂]

This complex was synthesized by the following procedure:

A solution of ZnCl₂(0.03g,0.154mmol)in distilled water(5ml) was added toasolution of Na₂BADTC (0.025g,0.154 mmol) in distilled water (5ml).The mixture was stirred at room temperature for 1hour. The solution colour waschanged from colorless to white.Then the solution of dppp (0.5g,0.154 mmol) in 5ml of acetone was added. The mixture was left to stir for an2hour.As a consequence, awhite precipitate was formed, whichwas then filtered off and washed with a small amount of distilled water (3 times) and dried in an oven for 2 hour at 50 °C.

T

he rest of the complexes listed in (Table 2) were synthesized in the same way as mentioned above using a proper number of moles of the metal salts and ligands.



Antibacterial activity

All the newly synthesized compounds were evaluated in vitrofor antibacterial activity against gram positive (*Staphylococcus aureus*) and gram negative (*Escherichia Coli*) bacteria. The tested microorganisms were obtained from College of Science\Tikrit University. All the newly synthesized compounds were weighed and dissolved in dimethylsulphoxide (DMSO) to Prepare stock solution of (40µl) then diluted to prepare other concentration (0.1,0.001,0.0001) mg/ml by disk diffusion methodusing Mueller-Hinton agar(MH) (Difco, Detroit, MI) was employed as culture media[10].A 5 ml of compound solution prepared in DMSO was added in the cup under aseptic conditions using micropipette. A volume of 5ml of DMSO placed in one of the cups as ablank (negative control) and after 24-48 h of incubation at 37°C, the zones of inhibition were measured in mm. The activity was compared with a known antibiotic, Ciprofloxacin, Ampicillin and Amoxicillin.

RESULTS AND DISCUSSION

Physical and spectral techniques were used for the identification of synthesized complexes. The solid prepared complexes are soluble in some common solvents such as DMSO, DMF, THF. The molar conductivity values for all prepared complexes were in the range of (0.12-0.28) mole⁻¹,cm⁻¹ in DMSO solvent of 10⁻³ M at 25°C (Table 2) indicate that complexes are non-electrolyte[11]. This is consistent with the stoichiometry for the complexes [M₂(BADTC)₂ (Phosphine)_n]. The micro elemental analysis measurements for all complexes gave approximate values when are compared with theoretical values, (Table2) includes some physical properties and (CHN) results for the synthesized complexes.

Table 2: some physical properties , CHN values , conductance data and yield% of the complexes decomposition* Infrared spectra:-

The prominent infrared spectral data of prepared ligand and its complexes are given in (Table 3).

N O	Complexes	Color	M.P/°C	yield %	Molar cond./ mole ⁻¹ ,cm ⁻¹ hom	Micro elemental analysis calculated (found)		
						C%	H%	N%
1	[Zn ₂ (BADTC) ₂ (dppm) ₂]	White	(114-115)	78	0.13	15.14 (15.12)	3.32 (3.30)	3.85 (3.84)
2	[Zn ₂ (BADTC) ₂ (dppe) ₂]	White	(137-138)	80	0.12	51.79 (51.78)	3.53 (3.54)	3.77 (3.76)
3	[Zn ₂ (BADTC) ₂ (dppp) ₂]	White	(157-158)	68	0.15	52.42 (52.40)	3.73 (3.70)	3.70 (3.69)
4	[Zn ₂ (BADTC) ₂ (PPh ₃) ₄]	White	(174-175)	77	0.27	58.10 (58.8)	3.71 (3.70)	3.23 (3.20)
5	[Cd ₂ (BADTC) ₂ (PPh ₃) ₄]	White	(174-175)	66	0.28	55.11 (55.9)	3.52 (3.50)	3.06 (3.05)
6	[Cd ₂ (BADTC) ₂ (dppm) ₂]	White	(113-114)	70	0.26	48.04 (48.03)	3.12 (3.11)	3.61 (3.50)
7	[Cd ₂ (BADTC) ₂ (dppe) ₂]	White	(135-136)	72	0.18	48.70 (48.69)	3.32 (3.30)	3.55 (3.53)
8	[Cd ₂ (BADTC) ₂ (dppp) ₂]	White	(<300)*	75	0.19	49.35 (49.34)	3.51 (3.50)	3.49 (3.47)

The IR spectra of the complexes were compared with the free ligand spectrum in order to determine the coordination sites that may be involved in bonding .

In BADTC ,the infrared bands observed at 1668cm⁻¹,1537cm⁻¹,(1125 cm⁻¹)and(1107cm⁻¹)have been assigned to ν C=O, ν (C.....N) and ν (C.....S) respectively[9].

In IR spectra of all complexes , the C=O stretching vibration are shifted to higher values 1670-1691cm⁻¹,suggesting that the carbonyl group is not involved in bonding in coordination with central metal ion[12].

Also, the complexes spectra showed bands at 1550-1598 cm⁻¹ which is assigned to (C.....N) group and those values, indicating that (C.....N) group is not coordinated [13].

A noticeable shift to lower frequencies for bands of ν (C.....S) (991-1020) cm⁻¹ and (1101-1066)cm⁻¹ in the complexes were observed .

The (C.....S) frequencies can be used for distinguishing between the mono and bidentate binding of dithiocarbamate ligand with the metal ion , the presence of two (C.....S) bands in spectra of the complexes refer to monodentate coordination of dithiocarbamate ligand with the metal ion [14].

The new bands in the region (513-493 cm⁻¹)and (1406-1429 cm⁻¹)were assigned to ν (P-C) and ν (P-Ph) respectively indicating that phosphine ligands are coordinated with metal center [15].

Table 3: IR data of synthesized complexes and ligands(cm^{-1})

Seq.	Compounds	V(C-H) Arm.	V(C-H) Aiph.	V(C=O)	V(C=S)	ν	V(C-S)	V(P-Ph)	V(C-P)
	BADTC	3058m	2813m	1668m	1126m	1537w	1107m	————	————
1	$[\text{Cd}_2(\text{BADTC})_2(\text{dppp})_2]$	3055m	2906	1670w	1101m	1598s	993m	1406s	513m
2	$[\text{Cd}_2(\text{BADTC})_2(\text{dppe})_2]$	3022s	2929m	1668w	1088m	1577m	993w	1427s	505s
3	$[\text{Cd}_2(\text{BADTC})_2(\text{dppm})_2]$	3002m	2920w	1691w	1091m	1575w	995w	1429s	503m
4	$[\text{Cd}_2(\text{BADTC})_2(\text{pph}_3)_4]$	3001w	2945w	1685m	1086w	1558s	991m	1429s	549w
5	$[\text{Zn}_2(\text{BADTC})_2(\text{dppp})_2]$	3018s	2929s	1658m	1093s	1579m	997m	1423s	505s
6	$[\text{Zn}_2(\text{BADTC})_2(\text{dppe})_2]$	3008m	2925m 2806	1679w	1091m	1575m	995w	1429s	505s
7	$[\text{Zn}_2(\text{BADTC})_2(\text{dppm})_2]$	3004s	2918w	1691m	1095w	1570m	991w	1413s	493m
8	$[\text{Zn}_2(\text{BADTC})_2(\text{pph}_3)_4]$	3005w	2925w	1682s	1085w	1550s	994m	1422s	493s

NMR results

^1H -NMR spectrum of BADTC:-

The ^1H -NMR spectrum of the ligand Barbituric acid bis (dithiocarbamate) was measurement in DMSO-d^6 solvent and showed singlet at $\delta\text{H}(3.25)$ from the chemical shift and the integration this signal is assigned to (CH_2) protons, (figures 1) shows the spectra of $(\text{Na}_2\text{BADTC})$.

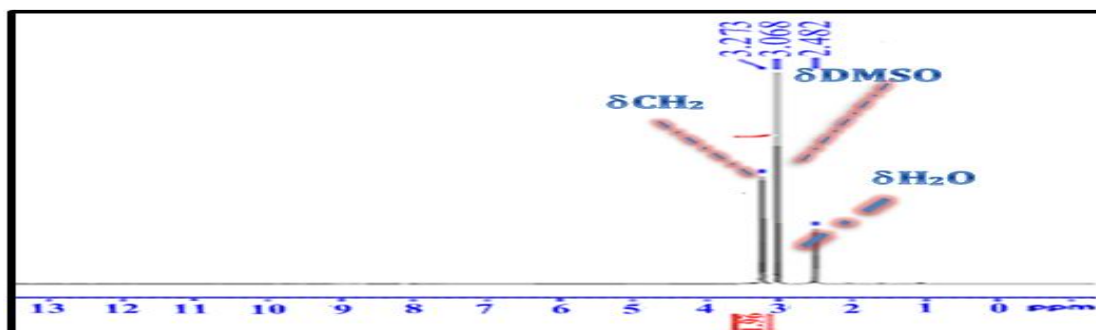


Figure 1: ^1H NMR spectrum of $(\text{Na}_2\text{BADTC})$

The ^1H and ^{31}P -NMR data for Some prepared complexes using DMSO-d^6 as a Solvent are given in (Table 4,5), and (figures 2,3) shows the spectra of $[\text{Zn}_2(\text{BADTC})_2(\text{dppp})_2]$ [16,17].

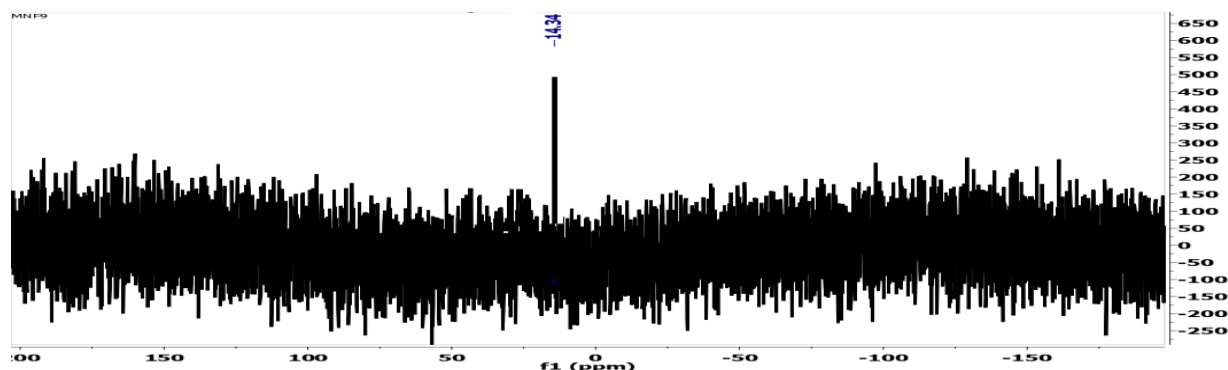


Figure 2: $\{^1\text{H}\}$ - ^{13}P NMR spectrum of complex $[\text{Zn}_2(\text{BADTC})_2(\text{dppp})_2]$

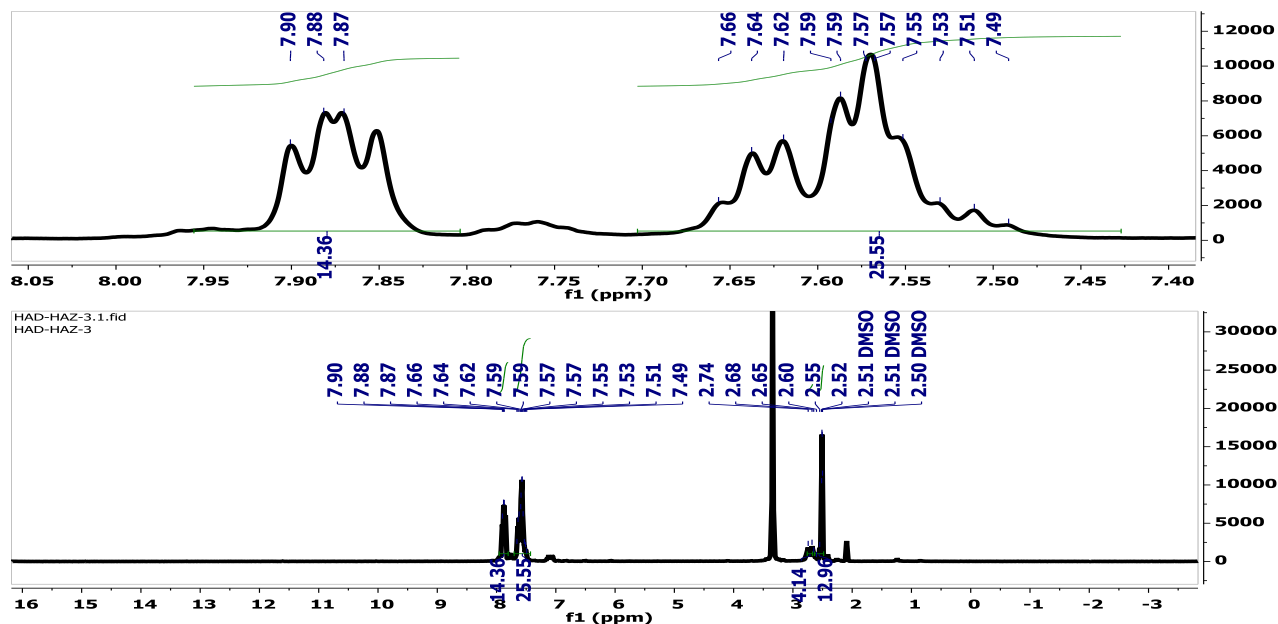


Figure 3: $^1\text{H-NMR}$ spectrum of $[\text{Zn}_2(\text{BADTC})_2(\text{dppp})_2]$

Table 4: $\{^1\text{H}\}$ - $^{31}\text{P-NMR}$ data of some prepared complexes

N0	Complex	δP	
1	$[\text{Zn}_2(\text{BADTC})_2(\text{dppm})_2]$	25.80	P-Zn
2	$[\text{Zn}_2(\text{BADTC})_2(\text{dppp})_2]$	14.34	P-Zn
3	$[\text{Cd}_2(\text{BADTC})_2(\text{dppm})_2]$	42.68	P-Cd

Measured in CDCl_3

Table 5: $^1\text{H-NMR}$ spectral data for some complexes

N0	Complexes
1-	$^1\text{H-NMR}(\text{DMSO-d}^6)$: $\delta 7.46-7.55(23\text{H, Phos})$ and $\delta 7.78-7.85(16\text{H, Phos})$ for 8 aromatic, $\delta 1.73(8\text{H, } 2\text{CH}_2, \text{ligand phos})$, $\delta 2.70(4\text{H, CH}_2, \text{ligand BADTC})$.ppm.
2-	$^1\text{H-NMR}(\text{DMSO-d}^6)$: $\delta 7.46-7.57(23\text{H, phos})$ and $\delta 7.57-7.81(16\text{H-phos})$ for 8 aromatic, $\delta 1.95(2\text{CH}_2, \text{ligand dppp})$, $\delta 2.92(\text{CH}_2, \text{ligand BADTC})$.ppm

Anti-bacterial activity

The synthesized dithiocarbamate ligand and its complexes were tested against two types of bacteria *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative). DMSO was used as solvent and as a control. The concentration of the compound in this solvent were (1×10^{-4}) , (1×10^{-3}) and (1×10^{-2}) mg/ml. The disc sensitivity test method was used, the incubation was held for 24 hours at 37°C . The measured inhibition zones against amounts of growth of two types of bacteria are summarized in (Table 6) and (Figure 4) show the inhibition zone of the complex $[\text{Zn}_2(\text{BADTC})_2(\text{dppp})_2]$.

The results revealed that some of the metal complexes have nearly the same activity or to be more active in comparison with the ligands and that means upon complexation.

Antibiotics have been used are: Ciprofloxacin, Ampicillin, Amoxicillin

Table 6: Results of antibacterial study of complexes and prepared ligands

Seq	Comp. No.	Conc. mg/ml	<i>Pseudomonas aeruginosa</i>	<i>Staphylococcus aureus</i>
(-)=	B.ADTC	1×10^{-4}	-	+
		1×10^{-3}	-	+
		1×10^{-2}	+	+
1	[Zn ₂ (B.ADTC) ₂ (dppm) ₂]	1×10^{-4}	+	-
		1×10^{-3}	++	+
		1×10^{-2}	++	+
2	[Cd ₂ (B.ADTC) ₂ (dppp) ₂]	1×10^{-4}	+	-
		1×10^{-3}	++	+
		1×10^{-2}	+++	+
3	[Cd ₂ (B.ADTC) ₂ (dppe) ₂]	1×10^{-4}	-	+
		1×10^{-3}	+	++
		1×10^{-2}	+	+++
4	[Zn ₂ (B.ADTC) ₂ (dppe) ₂]	1×10^{-4}	-	+
		1×10^{-3}	-	++
		1×10^{-2}	+	++

inhibition

(+) = Inhibition of 5 - 15 mm diameter

(++)=Inhibition of 2 - 15 mm diameter

(+++)=Inhibition of 25 to 35 mm diameter

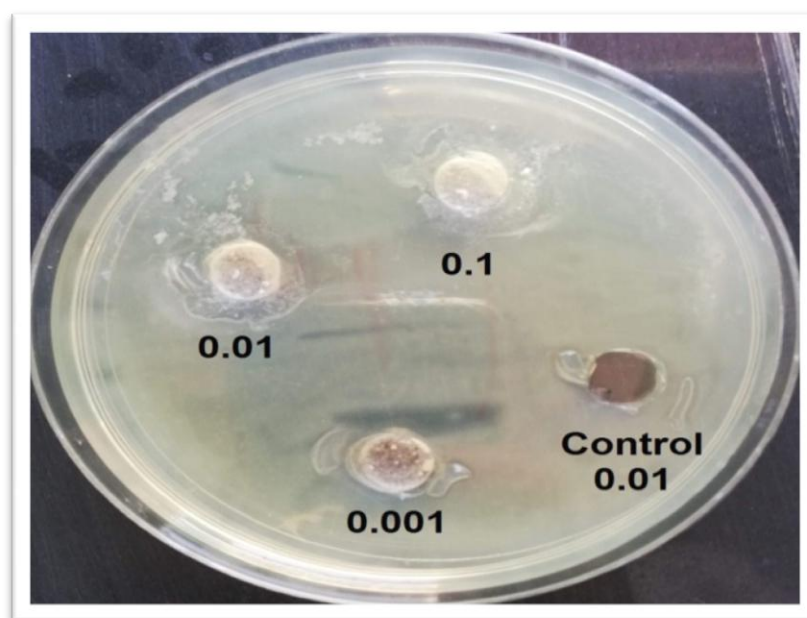


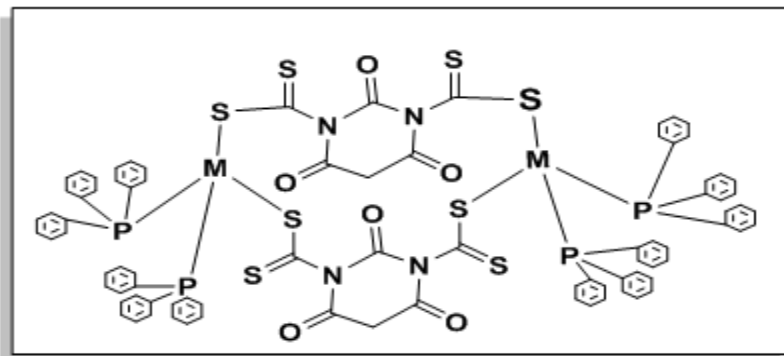
Figure 4: The inhibitionzone of the complex [Zn₂ (BADTC)₂ (dppp)₂] against bacteria *Pseudomonas aeruginosa*

Conclusions

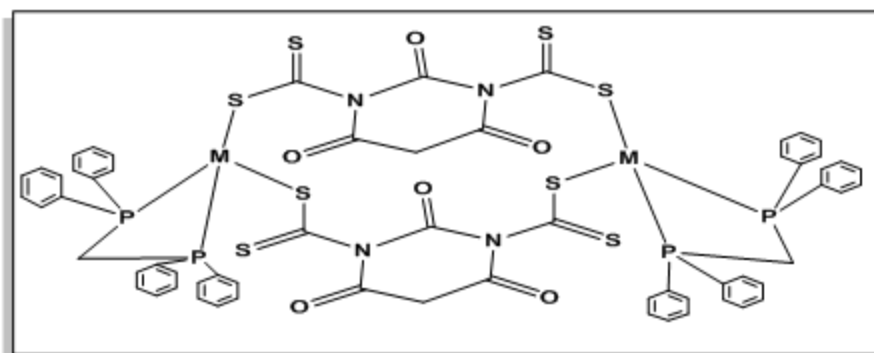
Based on analytical and spectral results, the BADTC acts as a monodentate ligand via the use of FT-IR apparatus which is bonded with the metal ions through a single sulfur atom while phosphine ligands is coordinated with the metal ions in a different modes. *pph₃* was coordinated as a monodentate ligand, *dppm* coordinate through one phosphine atom behaved and *dpe* and *dppp* behaved as a bidentate ligands.

The geometrical structures for synthesized complexes can be proposed as follows:

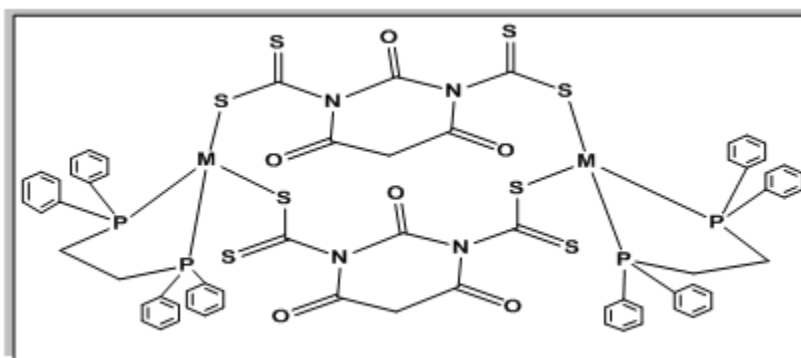
*Tetrahedral structure for Zn(II), Cd(II) complexes



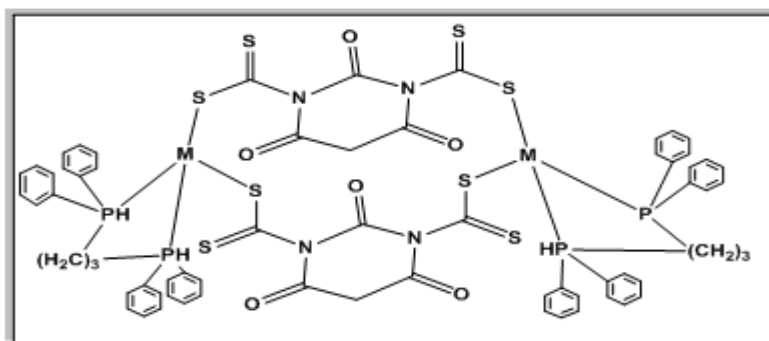
$[M_2(BADTC)_2(PPh_3)_4]$



$[M_2(BADTC)_2(dppm)_2]$



$[M_2(BADTC)_2(dppe)_2]$



$[M_2(BADTC)_2(dppp)_2]$

REFERENCES

- [1] G. Hogarth "Metal –dithiocarbamate complexes: chemistry and biological activity " mini reviews in medicinal chemistry ,12,1202-1215(2012).
- [2] G. Hogarth, "Transition metal dithiocarbamates"*Prog. Inorg. Chem.*, 53, 71(2005).
- [3] P.J.Heard"Main group dithiocarbamate complexes" *Prog. Inorg. Chem.* 53,1-69,(2005).
- [4] Z. F. Dawood, T. J. Mohammed and M. R. Sharif, " New nickel(II) complexes with benzilbis (semicarbazone) and dithiocarbamate ligands" .*Iraqi J. Veterinary Sci.*, 23, (2009).
- [5] N. Manav, A. K. Mishra and N. K. Kaushik, " In vitro antitumor and antibacterial studies of some Pt(IV)dithiocarbamate complexes " *Spec. Chim. Acta*, A 65, (2006).
- [6] G. D. Thorn, R. A. Ludwig, "The Dithiocarbamates and Related Compounds", Elsevier publishing Co., New York, (1962).
- [7] D.C. Gilheany, C.M. Mitchell, In *The chemistry of organophosphorus compounds*, F.R. Hartley, Ed.; J. Wiley and Sons: New York, Vol. 1(1990).
- [8] B.Cornils , A.W. Herrmann, *Aqueous phase organometallic catalysis*, Wiley-VCH :Weinheim (Chapter 3.2), (1998).
- [9] A.Q.Abdulsatter.,M.Y.Mohammed.,"Synthesis and Characterization binuclear complexes with dithiocarbamate ligands derived from barbituric acid and thiobarbituric acid"*International Journal of Enhanced Research in Science, Technology& Engineering*,7(4),2319-7463,(2018).
- [10] N.Kurtoglu,"Synthesis, characterization, chelation with transition metal ions, andantibacterial and antifungal studies of the 4-[E-phenyldiazenyl]-2-[(E)-(phenylimino) methyl] phenol dye " *Journal of th Serbian Chemical Society.* 74(8-9):917-926(2009)
- [11] W.J.Geary, "The Use of Conductivity Measurements Inorganic Solvents for Characterization of Coordination Compounds".*J.Coord. Chem. Rev.*7(1):81-122(1971).
- [12] H. Khan., A.Badshah. Murtaz Get al., " Synthesis, characterization and anticancer studies of mixed ligand dithiocarbamate palladium(II)complexes " *European Journal of medicinal chemi-stry*", (46), (9),.4071-4077, (2011).
- [13] R.Abu-El-Halawa ,S.A.Zabin"Removal efficiency of Pd,Cd,Cu and Zn from polluted water using dithiocarbamate ligands" *Journal of Taibah University for Science*, 11,57-65(2017)
- [14] I.A.Mustafa, and Amer .A.Taqa ,Coordination compounds of tin and bismuth complexes of tin (IV) and bismuth(III) with N,N-dialkyldithiocarbamates, *Synth.React.Inorg .Met.Org.Chem .*, (31),.4,517-526(2001).
- [15] A.S.M.AL-Janabi,S.A.Ahmed and S.A.O.Ahmed"Synthesis and characterization of mercury (II) mixed ligands complexes derived from 5-(4-pyridyl)-1,3,4-oxadiazole-2-thione with tertiary phosphines ligands"*Krikuk University Journal / Scientific Studies (KUJSS)* Volume 12,Issue 2, March (2017).
- [16] O.Amin, L. Al-Hayaly, S,Al-Jibory and T.AL-Allaf "Hetrobimetallic complexes of palladium (II) and platinum(II) bridgedby the ligand 5-phenyl-1,3,4-oxadiazde-2-thione"*polyhedron*,23,2013-2020(2004).
- [17] S.Al-Jibori,A.AL.Zaubai,M.MohammedandT,Al.Allaf- "Mixed ligand palladium (II) and platinum(II)complexes of tertiary diphosphines and benz-1,3-imidazoline-2-thione,benz-1,3-oxazoline-2-thione or benzo-1,3-thiazoline-2-thione" *Trans.Met.Chem* ,32:281-286(2007).