



Cadmium(II) Complexes Containing the Mixed Ligands Benz-1,3-Imidazoline -2-Thione, Benz-1,3-Oxazoline -2-Thione, Benz-1,3-Thiazoline -2-Thione, and Diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$, $n = 1-4$ or Triphenyl Phosphine

AHMED S. M. AL-JANABI^{1*} and SHIHAB A. O. AHMED²

¹Department of Biochemistry, College of Veterinary Medicine, University of Tikrit, Tikrit, (Iraq).

²Department of Chemistry, College of Science, University of Tikrit, Tikrit, (Iraq).

*Corresponding author: E-mail: a_sh200683@yahoo.com

(Received: July 20, 2011; Accepted: September 30, 2011)

ABSTRACT

Cadmium(II) complexes of the types $[\text{CdCl}_2(\text{LH})]$ (LH= benz-1,3-imidazoline -2-thione , benz-1,3-oxazoline-2-thione or benz-1,3-thiazoline-2-thione), have been prepared by the reaction of $[\text{HgCl}_2]$ with one mole proportion of the ligands LH. Reaction of $[\text{Cd}(\text{OAc})_2]$ with two mole proportion of LH in the presence Et_3N gave complexes of the type $[\text{CdL}_2]$. Treatment of $[\text{CdL}_2]$ with two mole proportion of PPh_3 or one mole proportion of the diphosphine $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n= 1-4$) gave tetrahedral complexes of the type $[\text{CdL}_2(\text{PPh}_3)_2]$, $[\text{CdL}_2(\mu\text{-diphos})_2]$ ($n=1$) or $[\text{CdL}_2(\text{diphos})]$ $n=2 - 4$ receptivity . The prepared complexes were characterized by elemental analysis, i.r., ^1H , $^{13}\text{C}\{-^1\text{H}\}$ and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. data.

Key words : Cadmium, Thione, Phosphine complexes.

INTRODUCTION

It is well that cadmium is a highly toxic metal and a potent carcinogen. However, its mechanism of action still unclear¹. Thiolate complexes are of great importance from a bioinorganic point of view, mainly due to the presence of thiolate donors in the coordination sphere of many metal ions in very diverse metalloproteins^{2,3}. Heterocyclic thione are among the ligand system used to mimic bio-relevant metal - sulfur interaction⁴⁻⁷. Chemical interest of thione lies in the fact that they are potentially ambidentate or multi- functional donors with exocyclic S and heterocyclic N available for coordination, their

biological interest arises from their structural analogy to thiolated nucleosides⁴⁻⁸.

Cadmium (II) halides form 1:1 and 1:2 complexes with neutral heterocyclic thione ligands⁹⁻¹². It was reported previously^{9,11,13} that the reaction of (LH); LH= benz-1,3-imidazoline -2-thione, benz-1,3-oxazoline -2-thione or benz-1,3-thiazoline -2-thione with $[\text{CdCl}_2]$ gave complexes of the type $[\text{CdX}_2(\text{LH})_2]$ [12], the heterocyclic thione (LH) behaves as a monodentate ligand coordinated through sulfur atoms while the halogen ligand was coordinated to cadmium(II) ions as bidentate bridging and monodentate.

However heterocyclic thiones form linear complexes of the type $[ML_2]$ (L = deprotonated thione ligands) [5, 10 - 12]. Mixed ligand complexes of heterocyclic thiones have been reported for several metal ions such as silver and rhodium¹³⁻¹⁶, while mixed ligands heterocyclic thiones(LH) and phosphines have been reported for several metal ions such as mercury, silver and rhodium¹⁷⁻²¹, complexes with cadmium seem unexplored²².

In the present work, we report the preparation of cadmium (II) complexes containing mixed ligand of heterocyclic thione (LH) fig. 1 (I) and diphosphines or triphenyl phosphine.

EXPERIMENTAL

General

The ¹H- and ¹³C- n.m.r spectra were recorded on Varian unity 500 and Gemini 2000 spectrometers respectively with CDCl₃ as solvent and Me₄Si as internal reference. ³¹P-{¹H} n.m.r spectra were recorded on Gemini 200 spectrometer with CDCl₃ as solvent and H₃PO₄(85%) as external reference. The n.m.r. spectra were determined at the Institute für Anorganische chemie, Martin – Luther-universität Halle- Witten-berg, Germany. I.r. spectra were recorded on a Shimadzu FT.IR. 8400 spectrometer in the 200 – 4000 cm⁻¹ range using CsI discs. Elemental analysis were carried out on a CHN analyzer type 1106 (Carlo-Erba). Melting points were measured on an electro thermal 9300 melting point apparatus.

Starting materials

The compounds [CdX₂] (X= Cl , OAc) , PPh₃, dppm, dppe, dppp, dppb, benz-1,3-imidazoline -2-thione, benz-1,3-oxazoline -2-thione and benz-1,3-thiazoline -2-thione were commercial products and were used as supplied, [Cd(bztzS)₂](3), [Cd(bzimSH)₂](4), [Cd(bzoxS)₂](5), were prepared according literature methods [12,].

Preparation of complexes

[CdCl₂(bztzSH)] (1)

A solution of bztzSH (0.137g, 0.82mmol) in EtOH (10cm³) was added to a solution of [CdCl₂] (0.15g, 0.82mmol) in EtOH(10cm³). The mixture was stirred at room temperature for 2h. The yellow solid thus formed was filtered off washed with EtOH,

dried under vacuum and recrystallized from Me₂CO (yield 90%). The following complexes [CdCl₂(bzimSH₂)](2), [CdCl₂(bzoxSH)](3), were prepared and isolated by a similar method.

[Cd (bztzS)₂] (4)

A solution of dppm (0.19g, 1.125mmol) in EtOH (15cm³) was added to solution of [Cd(oAc)₂] (0.15g , 0.563mmol) in EtOH(10cm³) in the presence of Et₃N (1.12g, 1.125mmole) The mixture was stirred at room temperature for 2h. The solid formed was filtered off washed with EtOH, CHCl₃, dried under vacuum and recrystallized from Me₂CO (yield 90%) . The following complexes [Cd(bzimSH)₂](5), [Cd(bzoxS)₂](6) were prepared and isolated by a similar method .

[Cd(bztzS)₂(μ-dppm)]₂(7)

A solution of dppm (0.087g ,0.225mmol) in CHCl₃(10cm³) was added to a hot solution of [Cd(bztzS)₂](4) (0.1g, 0.225mmol) in EtOH (15cm³). The mixture was stirred at room temperature for 2h. The yellow solid thus formed was filtered off washed with EtOH, dried under vacuum and recrystallized from CHCl₃(yield 82%). The following complexes [Cd(bztzS)₂dppe] (8), [Cd(bztzS)₂dppp] (9), [Cd(bztzS)₂dppb] (10) were prepared and isolated by a similar method.

[Cd(bzimSH)₂(μ-dppm)]₂(12)

A solution of dppm (0.093g ,0.243mmol) in CHCl₃(10cm³) was added to a warm solution of [Cd(bzimSH)₂](5)(0.1g, 0.243mmol) in EtOH (15cm³). The mixture was stirred at room temperature for 1.5h. The white solid thus formed was filtered off washed with EtOH, dried under vacuum and recrystallized from CHCl₃(yield 79%). The following complexes [Cd(bzimSH)₂dppe](13), [Cd(bzimSH)₂dppp](14), [Cd(bzimSH)₂dppb] (15) were prepared and isolated by a similar method.

[Cd(bzoxS)₂(μ-dppm)]₂(17)

A solution of dppm (0.093g ,0.242mmol) in CHCl₃(10cm³) was added to a hot solution of [Cd(bzoxS)₂](4) (0.1g, 0.242mmol) in EtOH (15cm³). The mixture was stirred at room temperature for 1h. The white solid thus formed was filtered off washed with EtOH, dried under vacuum and recrystallized from CHCl₃(yield 78%). The following complexes [Cd(bzoxS)₂dppe] (18),

[Cd(bzoxS)₂dppp] (19), [Cd(bzoxS)₂dppb] (20) were prepared and isolated by a similar method.

[Cd(bztzS)₂(PPh₃)₂] (11)

A solution of PPh₃ (0.21g, 0.450mmol) in EtOH (10cm³) was added to a warm solution of [Cd(bztzS)₂](4) (0.1g, 0.225mmol) in EtOH(10cm³). The mixture was stirred at room temperature for 1h. The yellow solid thus formed was filtered off washed with EtOH, dried under vacuum and recrystallized from CHCl₃ (yield 90%). The following complexes [Cd(bzimSH)₂(PPh₃)₂](16), [Cd(bzoxS)₂(PPh₃)₂](21) were prepared and isolated by a similar method .

RESULTS AND DISCUSSION

Synthesis of complexes

Mercapto-1,3-azole ligand (I) exist as two tautomeric conformations exhibiting thiol – thione isomers involving (-N=C-SH) and (-NH-C=S) group in the thiol – thione equilibrium. On deprotonation the resulting anions can also have thiol – thione isomerism (II) with negative charge is either on the thiol sulfur atom or the amide nitrogen atom.

Reaction of [CdCl₂] with heterocyclic thione ligands in ethanol solution (1 :1) molar ratio gave tetrahedral complexes of the type [CdX₂(LH)₂] [12]. The halogen was coordinated as a bidentate bridging and monodentate to cadmium (II) ions , while the heterocyclic thione (LH) behaves as monodentate ligand coordinated via sulfur atoms to cadmium(II) ion.

The deprotonated complexes of the type [CdL₂] were readily precipitated by reaction of [Cd(OAc)₂] with two mole proportion of LH in the presence Et₃N as a base. The thionate were coordinated as bidentate ligands to cadmium through sulfur atom of thiol group and nitrogen atom of the amide group [22].

Treatment of the cadmium(II) complexes of the type [CdL₂](4), (5),(6) [12] with one mole proportion of the diphosphines Ph₂P(CH₂)_nPPh₂ (n = 1-4) or two mole proportion of PPh₃ gave tetrahedral complexes of the [CdL₂(μ-Ph₂PCH₂PPh₂)₂](7),(12),(17) or the [CdL₂(Ph₂P(CH₂)_nPPh₂)₂] n=2-4 (8),(9),(10),(13), (14),(15),(18),

(19),(20) or the [CdL₂(PPh₃)₂](11),(16),(21). The anionic thionato ligands are coordinated as monodentate ligands, via sulfur atoms to cadmium(II) ion, while Ph₂(CH₂)_nPPh₂ (n=2-4) were coordinated as bidentate chelates, but Ph₂CH₂PPh₂ behaves as a bidentate bridging ligand, PPh₃ coordinated as monodentate ligands.

Characterization of complexes

The prepared complexes were identified by elements analysis, i.r. spectra and some of them by ³¹P-{¹H}, ¹H and ¹³C-{¹H} n.m.r. spectra and their data are listed in Tables 1-3.

Nuclear magnetic resonance

The ³¹P -{¹H}, ¹H and ¹³C-{¹H} n.m.r. data of some the prepared complexes are given in Table 3. The ³¹P-{¹H} n.m.r. spectra of complexes [CdL₂(μ-dppm)] { L=bztzS(7) and bimSH(12)}, showed a singlet for each at δP= 25.97 and 9.85 p.p.m respectively suggestion a single product. The positive values of the dP indicate that dppm behaves as a bidentate bridging²³⁻²⁴. This has been supported by ¹Hn.m.r. spectra of complexes (7) and (12) which showed a singlet at δH= 2.8 and 2.78 p.p.m respectively for the methylene group of the bridging dppm²⁵. On the bases of the above n.m.r. data and other identification data given in tables 1 and 2, the structure shown in Fig. 4 has been suggested

Reaction of [CdL₂] complexes one mole proportion of the Ph₂(CH₂)_nPPh₂ (n=2-4) gave a mononuclear chelate – diphosphines complexes of the types [CdL₂(Ph₂P(CH₂)_nPPh₂)₂] (n=2-4) (10), (13), (15), (18) and (19). The ³¹P-{¹H} n.m.r. spectra of complexes (10), (13), (15), (18) and (19). given a singlet each (table 3) indicating the presence of single chelated isomer for each. These conclusions have been supported by ¹H and ¹³C-{¹H} n.m.r. data are shown in tables 3. On the basis of these data and other identification data given in Tables 1 & 2 the tetrahedral structures shown in Fig. 5 have been suggested for these complexes.

Infrared spectra

The infrared spectra of compounds (1) – (21) recorded in the 4000 – 250 cm⁻¹ range showed the usual four thionamide bands required by the presence of the heterocyclic thione ligands. The shifts observed for these bands due to coordination

Table 1: Color, yield, m.p. and elemental analysis for complexes (1-21)

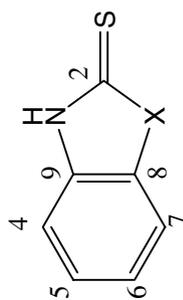
Seq.	Complexes	Color	M.p. (°C)	Yield %	Found (calc. %)		
					C	H	N
1	[CdCl ₂ (bztzSH)]	Yellow	240 ^a	90	25.21 (25.23)	1.52 (1.55)	3.91 (3.92)
2	[CdCl ₂ (bzoXSH)]	White	240 ^a	87	26.40 (26.42)	1.56 (1.63)	4.06 (4.11)
3	[CdCl ₂ (bzimSH ₂)]	White	250 ^a	79	25.21 (25.23)	1.93 (1.82)	8.14 (8.24)
4	[Cd(bztzS) ₂]	Yellow	179 – 181	90	25.21 (25.23)	1.92 (1.81)	6.25 (6.30)
5	[Cd(bzoXS) ₂]	White	187 – 190	76	25.21 (25.23)	1.64 (1.95)	6.39 (6.76)
6	[Cd(bzimSH) ₂]	White	159 – 161	72	25.21 (25.23)	2.36 (2.45)	13.65 (13.64)
7	[Cd(bztzS) ₂ (dppm)] ₂	Yellow	192 – 193	82	67.11 (67.02)	4.73 (4.79)	3.99 (3.86)
8	[Cd(bztzS) ₂ (dppe)]	Yellow	166-168	90	57.21 (57.37)	4.13 (4.11)	3.25 (3.26)
9	[Cd(bztzS) ₂ (dppp)]	Yellow	211- 213	72	57.80 (57.82)	4.33 (4.27)	3.29 (3.21)
10	[Cd(bztzS) ₂ (dppb)]	Yellow	162 – 164	79	60.01 (60.04)	4.93 (4.90)	1.99 (1.94)
11	[Cd(bztzS) ₂ (PPH ₃) ₂]	Yellow	231 – 233	90	62.21 (62.22)	4.21 (4.20)	2.59 (2.58)
12	[Cd(bzoXS) ₂ (dppm)] ₂	White	210 – 211	78	64.11 (64.14)	4.53 (4.59)	3.79 (3.70)
13	[Cd(bzoXS) ₂ (dppe)]	White	225 ^a	91	59.60 (59.60)	4.20 (4.27)	3.36 (3.39)
14	[Cd(bzoXS) ₂ (dppp)]	White	204- 205	82	60.20 (60.04)	4.43 (4.44)	3.39 (3.33)
15	[Cd(bzoXS) ₂ (dppb)]	White	132 – 134	90	61.43 (61.41)	5.03 (5.01)	2.01 (1.99)
16	[Cd(bzoXS) ₂ (PPH ₃) ₂]	White	171 – 174	93	65.81 (65.88)	4.67 (4.65)	1.79 (1.75)
17	[Cd(bzimSH) ₂ (dppm)] ₂	White	234 – 236	79	64.55 (64.36)	4.88 (4.87)	7.11 (7.41)
18	[Cd(bzimSH) ₂ (dppe)]	White	201 -204	81	59.74 (59.74)	4.53 (4.52)	6.83 (6.80)
19	[Cd(bzimSH) ₂ (dppp)]	White	128 – 131	89	60.22 (60.18)	4.70 (4.69)	6.69 (6.68)
20	[Cd(bzimSH) ₂ (dppb)]	White	124 - 126	85	61.51 (61.50)	5.20 (5.16)	3.97 (3.98)
21	[C(bzimSH) ₂ (PPH ₃) ₂]	White	145 - 146	72	65.91 (65.96)	4.73 (4.78)	3.59 (3.50)

a: decomposition

Table 2: I.R. spectra data (cm⁻¹) of the ligands and complexes (1-21)

v(C-O-C)sy, asy	v(P-C)	v(Cd-S)	v(C-H)	v(N-H)	Thioamide bands				Seq.	
					I	II	III	IV		
1090m, 820m			3072 w, 3022 w 3062w, 2970w 3080w	3112w 3199 w 3152w	667s 740m 650m	1015s 1010m 1362s	1319s 1240 m 1460s	1490s 1504m 1505s	bzizSH bzoxSH bzimSH ₂	
1093s , 825m			3083 w , 2927 w 3109w	3134w,br 3168w	720m 742s	1029s 1005m	1334m 1245m	1498s 1508s	1	
1095m, 815m		280 m	3078 w , 2983 w 3052 w, 2989 w 3054w, 2987w 3095w , 2974w	3182 w	690m 665s 740m	1352m 1010s 1010m	1460s 1289s 1240 m	1518s 1470s 1504m	2 3 4 5	
			3052 w 3058 m 3056 w 3058 w 3060 m 3056 w 3048 m 3053 w, 2891m 3058 w, 2972w 3057 m, 2987w 3056 w 3062 w, 2990 w 3054w, 2967w 3093w , 2974w 3063 m	3159w	675m 725 m 692 s 700m 690s 704m 734m 742s 746s 747s 740s	1352s 1025s 1018s 1020s 1018s 1023m 1000m 1003s 1000m 1010s 1010s	1421s 1338s 1300m 1350m 1352 w 1324m 1228m 1242s 1240m 1240m	1519s 1490m 1486m 1480m 1487m 1478s 1475m 1475m 1470m 1475m 1475m 1510m 1510m 1505m 1500s 1515m	6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21	
1085m, 825m 1090s, 830m 1095m, 825m 1095m, 815m 1080s, 820m	500 s 500 s 505 s 500 s 505 m 505m 505s 500s 505s 500s 490m 505s 500s 500s 505s	270m 270m 275m								

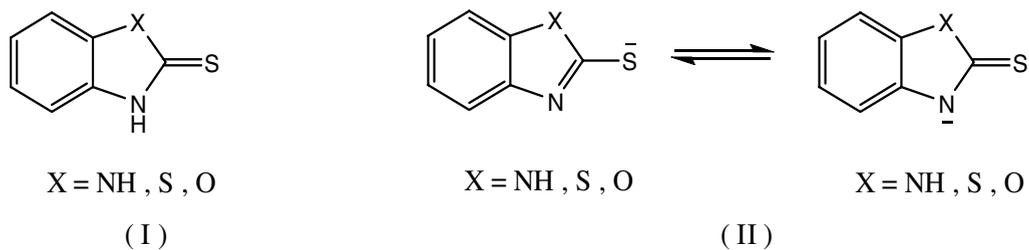
S = Strong , W = Weak , M = Medium , br = broad

Table 3: The ^{31}P -{1H}, 1H and ^{13}C -{1H} n.m.r. data(?P p.p.m) of some the prepared complexes a

δC_1^b	δC_9	δC_8	δC_7	δC_6	δC_5	δC_4	δC_2	δPhenyl	δCH_2	δP	Seq.	Complexes
	141.3	129.4	112.4	124.2	127.1	121.7	189.9					bztzSH
c	132.7	131.7	c	127.0	128.3	123.7		7.2 - 7.45	2.8	25.97	7	[Cd(bztzS) ₂ (dppm)] ₂
27.343 ^d	132.8	131.6	112.1	126.7	128.4	124.4	c	7.2 - 7.54	1.553 (4H)	-14.914	10	[Cd(bztzS) ₂ (dppb)]
									2.0 (4H)			
								7.05 - 7.65	2.6	33.78	13	[Cd(bzoxS) ₂ (dppe)]
								7.07-7.67	1.57 (2H)	33.4	14	[Cd(bzoxS) ₂ (dppp)]
									2.5 (4H)			
								7.2 - 7.73	2.78	29.85	17	[Cd(bzimSH) ₂ (dppm)] ₂
								6.74 - 7.63	2.88	33.52	18	[Cd(bzimSH) ₂ (dppe)]
								7.18 - 7.7	1.54(4H)	-14.24	20	[Cd(bzimSH) ₂ (dppb)]
									2.0 (4H)			

a- Measured in CDCl₃ unless stated otherwise, b- methylene carbon of the diphosphine

c- singlet was very weak , d- singlet



LH= bzimSH₂, X=NH ; bzoXSH X=O ; bztzSH X=S.

Fig. 1: The structure of thione ligands (LH)

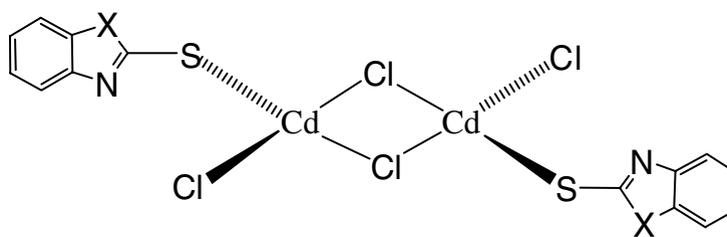


Fig. 2: The structure formula of the complexes [CdL₂(LH)]₂

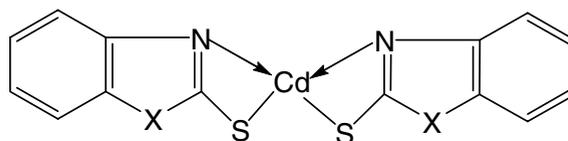


Fig. 3: The structure formula of the complexes [CdL₂]

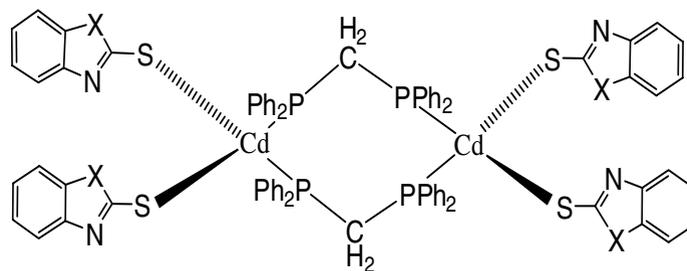
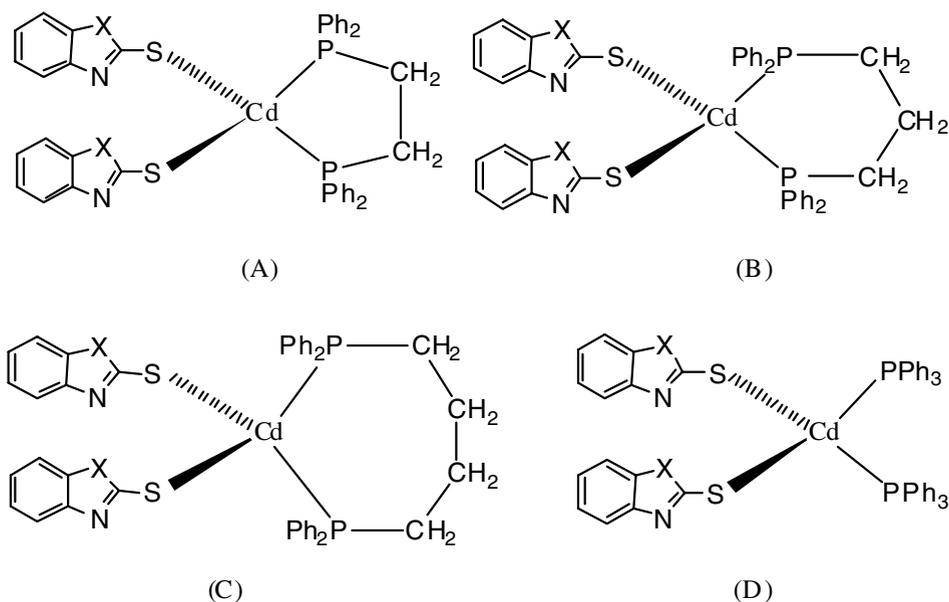


Fig. 4: The structure formula of the complexes [CdL₂(μ-dppm)]₂



LH= bzimSH₂, X=NH ; bzoSH X=O ; bztzSH X=S.
 (A) [CdL₂(dppe)] (B) [CdL₂(dppp)] (C) [CdL₂(dppb)] (D) [CdL₂(PPh₃)₂]

Fig. 5: The structure formula of the complexes

in comparison with the uncoordinated ligands with the lack of the $\nu(\text{SH})$ bands at ca 2500-2600 cm^{-1} , singlet the exclusive S- coordination mode of thione ligands. The ligand bzoSH showed $\nu(\text{COC})_{\text{sy}}$ and $\nu(\text{COC})_{\text{asy}}$ at 1080 and 820 cm^{-1} respectively. These bands were unaffected on complex formation¹⁶.

Moreover the spectra of compounds under investigation contain $\nu(\text{Cd-S})$ stretching vibrations observed in the 270 – 280 cm^{-1} range [23] and $\nu(\text{P-C})$ stretching vibrations observed in the 490 –505

cm^{-1} range [24] singlet the coordination of phosphines ligands

ACKNOWLEDGEMENTS

We thank Prof. Subhi A. Al-Jibori (Department of Chemistry, College of Science, University of Tikrit) and the NMR department of the Institute of Chemistry; Martin-Luther-University; Halle Germany for measuring the NMR spectra.

REFERENCES

- Ochoa P.A., Rodriguiz-Tapiador M.I., Alexadre S.S., Pastor C., Zamora F., *J. Inorg. Biochem.*, **99**:1540 (2005).
- Fleischer H., *Coord. Chem. Rev.* **249**: 799 (2005).
- Ahmed S., Isad A. A., Ali S., Al-Arfaj A. R., *Polyhedron*, **25**: 1646 (2006).
- Lobanna T. S., Butcher R. J., Hunter A. D., Zeller M., *Polyhedron*, **25**: 2775 (2006).
- Raper E. S., *Coord. Chem. Rev.*, **61**: 115 (1985).
- Raper E.S., *Coord. Chem. Rev.*, **129**, 91(1997) .
- Raper E.S., *Coord. Chem. Rev.*, **213**: 181 (2001).
- Beheshti A., Brooks N.R., Clegg W., Hyvadi R. *Acta. Crystallogr. Sec.*, **E 61**: 1383 (2005).
- Popovic Z., Soldin Z., Calogovic D.M.,

- Povlovic C.G., Giester G., Rajic M. *Europon J. Inorg. Chem.*, **2002**: 171 (2001).
10. Dean P.A., *Prog. Inorg. Chem.*, **24**:109(1978).
11. Graddon D.P., *Rev. Inorg. Chem.*, **4**: 211 (1982).
12. Bell N.A., William C., Constable C.P., Siman J.C., Ross H.W., Michael B., Mark E.L., Raper E.S., Sammon C.S., *Inorg. Chim. Acta.* **357**: 2091 (2004).
13. Wazeer M.I.M., Isab A.A., Fettouhi M. *Polyhedron.*, **26**: 1725 (2007).
14. Pert C., Tosi G., *Can. J. Chem.*, **55**: 1407 (1977).
15. Popovic Z., Matkovic - Galogolvic D., Soldin Z., Povlovic G., Davidovic N. Vikic- Topic D., *Inorg. Chem. Acta.*, **72**: 360 (2001).
16. Zugaj Z, Popovic Z., Mrvos-Seemek D., Bell-Czech., *Crysalloger. Association*, **5**: 322 (1998).
17. Al-Janabi A.S.M., Abdullah B.H., Al-Jibori S.A., *Orient. J. Chem.*, **25**(2): 277 (2009).
18. Mitchell R.W., Rudderick J.D., Wilkinson G.A., *J. Chem. Soc.*, **A**: 3224 (1971) .
19. Al-Jibori S.A., Al-Zaubi A.S.S., Mahammed M.Y., Al-Allaf T.A.K., *Trans. Met. Chem.*, **27**: 281 (2007) .
20. Hadjikakou S.K., Kubicki M., *Polyhedron*, **19**: 223 (2000).
21. Kamei T., Fujli T., Saotome M., *Jap. Appl. Chem. Abst.*, **107**: 220333d (1987).
22. Hunt C. T., Balch A. L., *Inorg. Chem.*, **20**: 2267 (1981).
23. Al-Jibori S. A., Abdullah I.A., Al-Allaf T.A.K., *Trans. Met. Chem.*, **32**: 398 (2007).
24. Al-Hayaly L. J., Abdullah B. H., Al-Dulaimi A. A. N., Al-Jibori S. A., *Orient. J. Chem.* **24**(2): 38 (2008).
25. Chatt .J, Duncanson L. A., *Nature*, **97**: 178 (1956).