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RESEARCH PAPER

Synthesis and characterization complexes of bis (2-mercaptobenzimidazole) mercury (II) with transition metal (Ni (II), Pd (II), and Pt (II))

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A B S T R A C T:
Treatment of 2-Mercaptobenzimidazol (HL) with the mercuric acetate ($Hg(OAc)_2$) give the complex$[Hg(L)_2]$ **(1).** Then the multinuclear complexes of the type $[M_2Hg_2(L)_4Cl_4]$ were prepared through the reaction of complex **(1)** with each of $NiCl_2.6H_2O$, $PdCl_2$ and $PtCl_2$ in (2:2) molar ratio. All complexes were described using infrared spectra, Proton Nuclear Magnetic Resonance , Carbon 13- Nuclear Magnetic Resonance , ultraviolet-visible, atomic absorption spectroscopy, CHNS analysis, molar conductivity, determination of Chloride Percentage and magnetic susceptibility measurements.The heterocyclic ligand is expected to be coordinated to two or single metal atom through the nitrogen atom and sulphur atom or by only sulphur atom.

KEY WORDS: 2-Mercapto benzimidazole: Ni (II), Pd (II), Pt (II), Hg(II).
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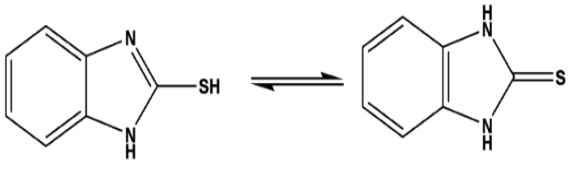
INTRODUCTION :

The coordination chemistry of heterocyclic thiones has attracted a large attention for their potentially ambidentate or multi-group donor capacity. Either the exocyclic S or heterocyclic N(or S)atoms are ready for connected to form complexes with transition metals and the possibility exists that coordination with harmful metal ions in an organism could occur (Rafael et al., 2002).

Heterocyclic compounds that containing thiones form complexes with many metal ions and this have been known for many years ago (Aranzazu et al., 2006).

They are characterized by thione-thiol tautomerism (Rapper et al., 1984). Transformation thiol to thione is significant from the point of heterocyclic compound (Obot et al., 2014). Those ligands which containing sulphur, especially thiolates, are widely applied as briding ligands in the design of transition-metal (Shan et al., 2010), Structure (1)



thiol form thione form

Structure (1) Tautomerism of benzimidazole-2-thione to thiol

1. MATERIALS AND METHODS

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All materials ($NiCl_2.6H_2O$, Palladium (II) chloride, Platinum (II) chloride, 2-Mercaptobenzimidazol (HL)) were obtained from Yahoo Chem. China. The Shimadzu infrared spectrophotometer in the range 400-4000 cm^{-1} was used to record the infrared (IR) spectra through using KBr discs. Furthermore, for detecting the Far IR spectra, the pye Unicam 300s was used in the range 200-4000 cm^{-1} by means of CsI discs. Additionally, to detect the (^1H, and ^{13}C)-NMR spectra, we used a Bruker 300 MHZ Ultra-shied. While an Ultraviolet-Visible spectrometer, AE-UV1609 (UK) CO was utilized to record Electronic spectra. To measure the conductivity of all complexes, we used a conductivity meter 4200 (0.93 cell constant) (UK). Elemental Analyzer, Atomic absorption spectra were recorded on a pye unicam sp(flam-AAS). The Magnetic susceptibility data were measured on a Bruker BM6 instrument at 25 ^oC following the faraday method.

1.1 Synthesis of $[Hg(L)_2]$ Complex (1)

A solution (Zora et al., 2002) of 2-mercaptobenzimidazloe (HL) (0.4g, 2.73 mmol) in 30 ml of MeOH was added slowly to a solution of mercuric acetate ($Hg(OAc)_2$) (0.4 g, 1.26 mmol) in 30 ml of MeOH solution. Then filtered off the colorless crystalline that formed, after that cleaned with cold MeOH and dried in air. (Formula: $C_{14}N_4H_{10}S_2Hg$, Yield: 0.5g, 80%, d.p.:252-255 ^oC, Color: White)

1.2 Preparation of $[M_2Hg_2(L)_4Cl_4]$ Complexes (2,3,4)

This type of the complexes (Butrus et al., 2012) were prepared by reaction (2mmol) of metal chloride salts with (0.4g) $NiCl_2.6H_2O$ dissolved in 10ml of ethanol, and (0.3g) $PdCl_2$, (0.5g) $PtCl_2$ was suspended in 10ml methanol to a solution include (0.99g,2mmol) $[Hg(L)_2]$ in 10ml of DMSO , the blend was stirred at 25^oC for four days. The coloured precipitation was formed, filtered-off, washed with di ethyl ether and dried in an oven at 50 ^oC. (formula: $C_{28}H_{20}N_8S_4Hg_2Ni_2Cl_4$, Yield: 1g, 40% , d.p..: 261-265 ^oC, Color: Orange, $C_{28}H_{20}N_8S_4Hg_2Pd_2Cl_4$, Yield: 1.1g, 38.4% , d.p..: 272-275 ^oC, Color: Brown, $C_{28}H_{20}N_8S_4Hg_2Pt_2Cl_4$, Yield: 1.1g, 39.2% , d.p..: 255-260 ^oC, Color: Green).

Table(1) Physical parameters(such as colors, molecular weight, melting points, yield) for the prepared complexes **.**

No.	Complexes symbol	Color	M.Wt g/mol	d.p.(°C)	Yield %
1	$[Hg(L)_2]$	White	498	252-255	80
2	$[Ni_2Hg_2(L)_4Cl_4]$	Orange	1252	261-265	40
3	$[Pd_2Hg_2(L)_4Cl_4]$	Brown	1350.6	275-272	38.4
4	$[Pt_2Hg_2(L)_4Cl_4]$	Green	1526	260-255	39.2

Table (2) Elemental analysis for the prepared complexes **.**

No.	Complexes symbol	C	H	N	S	Hg	Ni	Pd	Pt	Cl
1	$[Hg(L)_2]$	---	---	---	---	---	---	---	---	---
2	$[Ni_2Hg_2(L)_4Cl_4]$	26.7 (25.98)	1.5 (1.77)	8.9 (8.87)	10.1 (10.30)	31.9 (31.38)	9.3			11.3 (11.5)
3	$[Pd_2Hg_2(L)_4Cl_4]$	24.8 (23.91)	1.4 (1.52)	8.2 (8.27)	9.4 (9.55)	29.7 (29.81)		15.7		10.5 (10.61)
4	$[Pt_2Hg_2(L)_4Cl_4]$	22 (21.88)	1.3 (1.29)	7.3 (7.39)	8.3 (8.48)	26.2 (---)			25.5	9.3 (9.6)

2. RESULTS AND DISCUSSION

2.1 Analysis of elements for prepared complexes

The elemental analysis data of the C, H, N, S, Ni, Pd, Pt, Hg and Cl of the prepared complexes are presented in Table 1. These data are in consistent with the propose stoichiometry's. Table 1 shows physical parameters such as colors, molecular weight and melting points of the prepared complexes.

2.2 Ultraviolet-visible and Magnetic Susceptibility of the Prepared Complexes

For all complexes, the uv.vis spectra were done in DMSO (10^{-3} M) solution at 25 ^{o}C.

The electronic spectrum of complex (1) **$[Hg(L)_2]$** two bands observed at (37037 and 32258) cm^{-1}, these transitions bands were attributed to Metal-ligand charge transfer transitions of Hg(II) in linear geometry (Kennedy et al., 1972).

The electronic spectrum of complex (2) **$[Ni_2Hg_2(L)_4Cl_4]$** Ni^{+2} gave two high intensity bands at 18518cm^{-1} and 22300 were attributed to transitions $^1A_1g \longrightarrow {}^1A_2g$ and $^1A_1g \longrightarrow {}^1B_1g$ respectively, both transitions are in a square planar geometry. Other high energy band keep an eye on at 37037 cm^{-1} which assigned to $Ni^{+2} \longrightarrow$ C=N charge transfer transition (Sutton , 1968, Leka et al., 2005, AI-Adeli, 2009, Mohammed et al., 2011, Nanhai et al., 2001, Tariq, 2013).

The ultra-visible spectrum of complex(3) **$[Pd_2Hg_2(L)_4Cl_4]$**, Pd^{+2} gave three spin allowed transitions at 18181cm^{-1}, 22321 cm^{-1} and 25000 cm^{-1} were attributed to $^1A_1g \longrightarrow {}^1A_2g$, $^1A_1g \longrightarrow {}^1B_1g$ and $^1A_1g \longrightarrow {}^1Eg$ transitions respectively. Other high energy band observed at 31250 cm^{-1} is assigned to $Pd^{+2} \longrightarrow$ C=N charge transfer transition, these transitions are reasonable to square planar geometry of the complexes (Sutton ,1968, Leka et al., 2005, Ali, 2007, Ibrahem et al., 2008).

The electronic spectrum of complex(4) **$[Pt_2Hg_2(L)_4Cl_4]$**; Pt^{+2} gave three high intensity bands at 18115 cm^{-1}, 20000 cm^{-1} and 23809 cm^{-1} were assigned to transitions $^1A_1g \longrightarrow {}^3B_1g$, $^1A_1g \longrightarrow {}^1A_2g$ and $^1A_1g \longrightarrow {}^1B_1g$ respectively,. Other high energy band appear at 34482 cm^{-1} are assigned to $Pt^{+2} \longrightarrow$ C=N charge transfer transition all transitions are attributed to square planar geometry of complexes (Kennedy et al., 1972, Sutton , 1968, Irshad et al., 2010).

The effective magnetic moment value of the prepared complexes (2,3,4) $[M_2Hg_2(L)_4Cl_4]$ are ($\mu_{eff.}$ =zero) B.M., which indicates that they are diamagnetic and have square planar geometry around M(II) where (M=Ni, Pd, Pt) (Butrus et al., 2012, Sutton , 1968, Irshad et al., 2010, Nikiforova et al., 2006, Khullar et al., 1975, James et al., 1993).

2.3 The Proton Nuclear Magnetic Resonance, Carbon 13 Nuclear Magnetic Resonance spectra of complexes (2, 3, 4)

The Proton Nuclear Magnetic Resonance spectra of prepared complexes were measured in d_6-DMSO solvent. The ^{1}H-NMR for aromatic ring protons were appeared at (δ =6.8-7.1) ppm, (δ =5.9-9.2) ppm and (δ =6.8-8.8) ppm for complexes Ni^{+2}, Pd^{+2} and Pt^{+2} respectively. The ^{1}H-NMR for (NH) amine protons were appeared at (δ =2.2) ppm, (δ =3.9-4.0) ppm and (δ =3.8-4.3) ppm for complexes Ni^{+2}, Pd^{+2} and Pt^{+2} respectively (Tariq, 2013, Mohammed et al., 2015), Table 3.

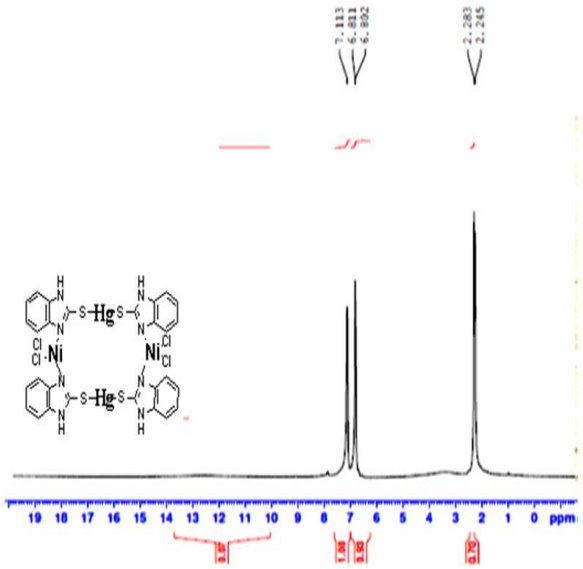

Figure 1: The ^{1}H-NMR of $[Ni_2Hg_2(L)_4Cl_4]$

Table (3) ^{1}H-NMR data for prepared complexes .

no.	Str. Formula	δ / ppm	no. Proton	Group
2	$C_{28}H_{20}N_8S_4Hg_2Ni_2Cl_4$	7.1-6.8	20H	4Ph
		2.2	4H	4NH
3	$C_{28}H_{20}N_8S_4Hg_2Pd_2Cl_4$	9.2-5.9	20H	4Ph
		4.0-3.9	4H	4NH
4	$C_{28}H_{20}N_8S_4Hg_2Pt_2Cl_4$	8.8-6.8	20H	4Ph
		4.3-3.8	4H	4NH

The nuclear magnetic resonance (^{13}C-NMR) of the prepared complexes in the solvent (d_6-DMSO) gave four singlet peaks (C1, C2, C3, C4) and each peak is equivalent to two atoms of carbon and to the presence of symmetry in the complexes as scale in Table 4.

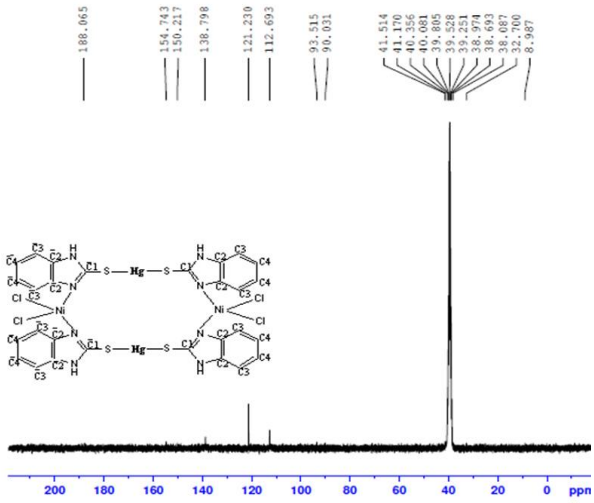

Figure 2: The ^{13}C-NMR of $[Ni_2Hg_2(L)_4Cl_4]$

Table (4) ^{13}C-NMR data for prepared complexes.

no.	Structure formula	δ/ppm	Group
2	$C_{28}H_{20}N_8S_4Hg_2Ni_2Cl_4$	150.217	C_1,C_1'
		138.798	C_2,C_2'
		112.693	C_3,C_3'
		121.230	C_4,C_4'
3	$C_{28}H_{20}N_8S_4Hg_2Pd_2Cl_4$	140.826	C_1,C_1'
		133.509	C_2,C_2'
		109.429	C_3,C_3'
		121.653	C_4,C_4'
4	$C_{28}H_{20}N_8S_4Hg_2Pt_2Cl_4$	153.597	C_1,C_1'
		---	C_2,C_2'
		112.520	C_3,C_3'
		122.891	C_4,C_4'

2.4 Infrared spectra for the ligand and prepared complexes

The spectra of the ligand exhibited band at 1514 cm^{-1} due to the **V**(C=N) group of the ligand and when the complexes were formed this spectra were shifted to higher or lower frequency in the range (1622-1490)cm^{-1} which indicate that the ligand was bonded to the metal ion through N atom of **V**(C=N)group (Kennedy et al., 1972, Mohammed et al., 2013, Anandarajagopal et al., 2010, Ganesh et al., 2011, Akira et al., 1970, Rehman et al., 2013), also the ligand showed band at (736)cm^{-1} due to the **V**(C-S) group of the ligand and this band was shifted to higher or lower frequency in the range (742-725)cm^{-1} during the complexes which indicate that the ligand was bonded to the metal ion through sulphur atom (Zora et al., 2002, Butrus et al., 2012, Irshad et al.,2010, Khullar et al.,1975) .The infrared spectra of the prepared complexes show band in the range (451-412) cm^{-1}, which are attributed to **V** (M-N) . On the other hand, it has been observed that in the spectra of all compounds, the bands at (310-290) cm^{-1} were assigned to V (Hg-S) (Carlo et al., 1977, Musa, 1998, Awaz, 2015). Also bands in the range (330-280) cm^{-1}, which are attributed to **V** (M-Cl) (Butrus et al., 2012, Oztekin et al., 2005, Nakamoto, 1997, Joseph et al., 2001).

2.5 Molar conductivity for the prepared complexes

At 25^{o}C the molar conductivities were measured for (10^{-3} M) solution in DMSO. From the obtained results it was concluded that the prepared complexes are non electrolytical complexes.

3. CONCLUSIONS

The current study includes synthesis of complexes of bis (2-mercaptobenzimidazole) mercury (II) with Ni (II), Pd (II), and Pt (II). From the magnetic susceptibility values, the geometry of the complexes were determined. The structure of Hg(II) complex was linear, whereas the a square planer is the geometry for the complexes of Ni(II), Pd(II) and Pt(II) metal ions. As stated by the molar conductivity data, it is recommended that the complexes are non-electrolyte.

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Conflict of Interest

There is no conflict of interest.

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