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Mononuclear and Heterobimetallic Complexes of Palladium(II) with 4,5-Diphenyl-1,2,4-triazole-3-thione

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The reaction of Na_2PdCl_4 with 4,5-diphenyl-1,2,4-triazole-3-thione (LH) in acetone gave *cis*-$[PdCl_2(LH)_2]$. Stirring *cis*-$[PdCl_2(LH)_2]$ in methanol gave a diamagnetic *cis*-$[PdL_2]$. Reaction of *cis*-$[PdL_2]$ with diphosphines gave diamagnetic complexes of the type $[PdL_2(\text{diphos})]$ where diphos = 1,2-*bis*(diphenylphosphino)methane (dppm), 1,2-*bis*(diphenylphosphino)ethane (dppe) or 1,2-*bis*(diphenylphosphino)-propane (dppp). The complexes *cis*-$[PdCl_2(LH)_2]$ and *cis*-$[PdL_2(\text{diphos})]$ have been used effectively to prepare bimetallic complexes of the type *cis*-$[Cl_2Pd(\mu\text{-}LH)_2M'Cl_2]$ where M´ = Co, Ni, Mn or $SnCl_2$ and $[(\text{diphos})Pd(\mu\text{-}L)_2M'Cl_2]$ where M´ = Co or Ni, the prepared complexes were characterized by elemental analysis, magnetic susceptibility, IR, UV-Vis, ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectral data.

Key Words: Palladium, Heterobimetallic, Phosphine, Triazole ligand, Complexes.

INTRODUCTION

Heterocyclic thiones and their complexes attract much attention[1-7] due to their biological and structural importance. Some research works involving coordination chemistry of mercaptotriazole ligands have already been published[8-11]. Interaction of some heavy metals with N,S-donor atoms have been recognized for their antineoplastic properties with the potential to develop metal based drugs[12,13]. However phosphine metal complexes have received much attention due to their potential use as antitumour agents particularly 1,2-*bis*(diphenyl phosphino) ethane and some of its analogous[14,15]. We expect that mixed ligands complexes of tertiary phosphines and mercaptotriazoles to be an important class of complexes and may

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exhibit the synergic effect that attributed to the mixed ligands. Metal complexes containg *bis*-tertiary phosphins and heterocyclic-2-thione are rare[16].

As part of our systematic investigation on the coordination chemistry of compounds containing the thioamide group[17-20], we report here the synthesis and characterization of some mononuclear palladium(II) mixed ligand complexes of 4,5-diphenyl-1,2,4-triazole-3- thione (LH) (Fig. 1) and the diphosphines $Ph_2P(CH_2)_nPPh_2$, where n = 1, 2 or 3. Further more we used the prepared mixed ligand complexes to build up some new type of heterobimetallic complexes bridged by L, *i.e.*, [(diphos)M(μ-L)$_2$M´Cl$_2$].

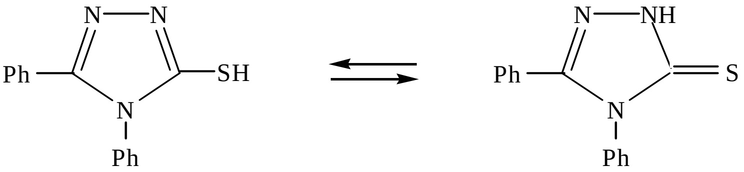

Fig. 1. 4,5-Diphenyl-1,2,4-triazole-3-thione

EXPERIMENTAL

^{31}P-{^1H} and ^1H-{^{31}P} were performed in the laboratories of Dr. Bob Moore II, University of Tennessee, Medical University, USA using Varian INOVA-500 MHz and of Prof. Dr. Dirk Steinborn, Martin Luther University Halle Wittenberg, Germany using Gemini 200 spectrometer.

IR spectra were recorded on a PYE-Unicam SP3-300s spectrophotometer in the 4000-200 cm^{-1} range using CsI discs. Electronic spectra were obtained using a Jenway 6485 spectrophotometer. Elemental analysis were carried out on a CHN Analyzer, type 1106 (Carlo Erba). Magnetic measurements were recorded on a Bruker BH6 instrument at room temperature following the Faraday method. Conductivity measurements were made on conductivity meter type CCMD 625. Melting points were measured on a Toshinwal Eelectrothermal melting point apparatus. The compounds K_2PtCl_4, $Na_2PdCl_4.3H_2O$, $MnCl_2.2H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $SnCl_4.5H_2O$, dppm, dppe and dppp were commercial products and used as supplied. The ligand 4,5-diphenyl-1,2,4-triazole-3-thione (LH) its potassium salt (LK)[21], *trans*-[$PdCl_2$(DMSO)$_2$], *cis*-[$PtCl_2$(DMSO)$_2$][22], were prepared according to the reported methods.

***cis*-[PdCl$_2$(LH)$_2$] (1):** A mixture of [Na_2PdCl_4].$3H_2O$ (0.38 g, 1.1 mmol) and LH (0.57 g , 2.2 mmol) in acetone (8 mL) was stirred at room temperature for *ca.* 24 h. The off white solid thus formed was filtered off washed with water (5 mL) three times then diethyl ether (5 mL) and dried in vacuum.

***cis*-[PdL$_2$] (2):** A suspension of *cis*-[$PdCl_2$(LH)$_2$] (0.1 g, 0.14 mmol) in methanol (14 mL) was stirred for *ca.* 3 d. The resulting clear red solution was filtered off. The filtrate was evaporated to dryness to give dark red solid.

***cis*-[$Cl_2Pd(\mu-LH)_2CoCl_2$].$2H_2O$ (3):** Solid $CoCl_2.6H_2O$ (0.03 g, 0.24 mmol) was added to a suspension of *cis*-[$PdCl_2(LH)_2$] (0.08 g, 0.12 mmol) in acetone (40 mL). The mixture was stirred at room temperature for *ca*. 7 d. The unreacted $CoCl_2$ was removed by filtration and the green filtrate was evaporated to dryness.

The complexes No. 4, 5 and 6 were prepared and isolated by a similar method.

[PdL_2(dppm)]$_2$ (7): A solution of dppm. (0.05 g, 0.12 mmol) in chloroform (5 mL) was added to a suspension of *cis*-[PdL_2] (0.07 g, 0.12 mmol) in chloroform (5 mL). The clear red solution was heated on steam bath for *ca*. 10 min, colour was changed to orange-red. Solvent was then left to evaporate at room temperature to give a reddish orange powder.

The complexes No. 8 and 9 were prepared and isolated by a similar method.

[(dppm)Pd(μ-L)$_2CoCl_2$].$2H_2O$ (10): This complex was prepared and isolated by a similar way to that used to prepare complex **3** using complex 7.

The complexes No. 10-15 were prepared and isolated by a similar method.

RESULTS AND DISCUSSION

Synthesis of the complexes

Treatment of Na_2PdCl_4 with 4,5-diphenyl-1,2,4-triazole-3-thions (LH) gave *cis*-[$PdCl_2(LH)_2$] on using acetone as a solvent. Stirring *cis*-[$PdCl(LH)_2$] in methanol for 3 d gave *cis*-[PdL_2]. Treatment of *cis*-[$PdCl_2(LH)_2$] with solid $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $MnCl_2.6H_2O$ or $SnCl_4.5H_2O$ in acetone yielded heterobimetalic complexes of the type [$Cl_2Pd(\mu-LH)_2M'Cl_2$]. Reaction of *cis*-[PdL_2] with the diphosphines (B), B = $Ph_2P(CH_2)_nPPh_2$ [n = 1; 1,2-*bis*(diphenylphosphino)methane (dppm), n = 2; 1,2-*bis*(diphenylphosphino)ethane (dppe), n = 3; 1,2-*bis*(diphenylphosphino)propane (dppp)] gave square planar complexes of the type [PdL_2(B)]$_2$ (B = dppm) or [PdL_2(B)] (B = dppe or dppp), which was a single linkage isomer in each case, This was the N,S–bonded isomer. Treatment of [PdL_2(B)] with solid $CoCl_2.6H_2O$ or $NiCl_2.6H_2O$ in chloroform yielded heterobimetalic complexes of the type [(B)Pd(μ-L)$_2M'Cl_2$].$2H_2O$.

Chractarization of the complexes

The complexes were identified by elemental analysis, IR, UV-Vis spectra, magnetic susceptibility conductivity measurements and some of them by $^{31}P-\{^1H\}$ and $^1H-\{^{31}P\}$ NMR and their data are listed in Tables 1-4.

The synthesized heterobimetalic complexes are stable in the solid state as well as in solution except for the cobalt complexes which showed some

TABLE-1

PHYSICAL PROPERTIES OF COMPLEXES **1-15**

Complex No.	Complex	Colour	Yield	Melting point (C°)[a]	Found (Calcd.) (%)		
					C	H	N
1	*cis*-$[PdCl_2(LH)_2]$	Off-white	61	265 – 268	48.9 (49.2)	3.0 (3.2)	11.9 (12.2)
2	*cis*-$[PdL_2]$	Deep red	80	268 – 272	54.7 (55.0)	3.2 (3.3)	13.5 (13.8)
3	*cis*-$[Cl_2Pd(\mu\text{-}LH)_2CoCl_2]\cdot 2H_2O$	Green	40	326[a]	40.0 (39.6)	2.8 (3.1)	10.0 (9.9)
4	*cis*-$[Cl_2Pd(\mu\text{-}LH)_2NiCl_2]\cdot 2H_2O$	Yellow	93	280 – 283	39.8 (39.6)	2.9 (3.1)	10.2 (9.9)
5	*cis*-$[Cl_2Pd(\mu\text{-}LH)_2MnCl_2]\cdot 2H_2O$	Orange yellow	66	256	41.2 (39.8)	3.0 (3.1)	10.2 (9.9)
6	*cis*-$[Cl_2Pd(\mu\text{-}LH)_2SnCl_4]$	Deep red	99	310	35.6 (35.6)	2.1 (2.3)	8.8 (8.9)
7	$[PdL_2(dppm)]_2$	Yellow	95	194 – 197	63.8 (64.0)	4.2 (4.2)	8.2 (8.4)
8	$[PdL_2(dppe)]$	Yellow	51	188 – 191	64.0 (64.3)	4.2 (4.3)	8.2 (8.3)
9	$[PdL_2(dppp)]$	Yellow	38	185 – 187	64.3 (64.6)	4.4 (4.5)	8.1 (8.4)
10	$[(dppm)Pd(\mu\text{-}L)_2CoCl_2]\cdot 2H_2O$	Green	95	178 – 182	54.8 (54.8)	3.8 (4.0)	7.4 (7.2)
11	$[(dppm)Pd(\mu\text{-}L)_2NiCl_2]\cdot 2H_2O$	Brown	86	202 – 204	54.5 (54.8)	3.8 (4.0)	7.5 (7.2)
12	$[(dppe)Pd(\mu\text{-}L)_2CoCl_2]\cdot 2H_2O$	Green	46	210 – 212	55.0 (55.2)	4.0 (4.0)	7.3 (7.2)
13	$[(dppe)Pd(\mu\text{-}L)_2NiCl_2]\cdot 2H_2O$	Olive-green	68	178 – 183	55.3 (55.2)	3.8 (4.1)	7.4 (7.2)
14	$[(dppp)Pd(\mu\text{-}L)_2CoCl_2]\cdot 2H_2O$	Pale-green	42	238 – 242	55.5 (55.5)	4.1 (4.2)	7.4 (7.1)
15	$[(dppp)Pd(\mu\text{-}L)_2NiCl_2]\cdot 2H_2O$	Grass-green	45	260 – 264	55.3 (55.6)	3.9 (4.2)	7.3 (7.1)

[a] complex melt with decomposition.

TABLE-2
IR SPECTRAL DATA[a] OF COMPLEXES **1–15**

Complex No.	Thioamide bands				Others								
	I	II	III	IV	ν(OH)	ν(NH)	ν(CH)	ν(M-N)	ν(M-S)	ν(M-Cl)	ν(C-P)	ν(M-P)	ν(N-N)
1	1580s	1325s	965s	765s, 720s	–	3060b	–	520s, 480m	–	290, 323s	–	–	1470s
2	1588m	1320s	965s	770s,	–	–	3040w	520m, 480m	380s, 455m	–	–	–	1465m
3	1610w	1330w	985s	775s	3380b	3120w	–	530m	385m	295w, 310s	–	–	1470s
4	1620s	1335s	970m	775vs, 725w	3400b	3100w	3020w	530m	350m	260m, 328w	–	–	1470m, 1490
5	1585s	1330vs	970s	765vs , 725s	3340m	3160s	3040w	520vs	380w	280w, 320m	–	–	1470s
6	1600m	1330m	980w	770vs, 720w	–	3140w	3020vw	540m	380w	310b	–	–	1470m, 1490m
7	1590s	1330s	972s	775vs, 740vs	–	–	2910w, 3060w	515s, 486m	385m	–	–	425m	1480s
8	1590w	1320m	968w	775vs, 750vs	–	–	2960w, 3020w	530s, 486m	390m	–	–	440m	1470s
9	1620w	1320s	975s	780s, 755vs	–	–	2900w, 3042w	520s	380m	–	–	428m	1470s
10	1590w	1330s	970w	775s, 740s	3480m	–	2920m, 3060w	505s	350w	305m, 320m	1075m	420w	1480s
11	1590m	1330s	970w	770s, 740s	3400b	–	2900w, 3050w	510s, 480s	378s	290w, 305w	1075m	420w	1475s, 1490s
12	1620w	1320m	980w	775s, 750s	3470b	–	2960w, 3040m	530s, 480s	390m	310s, 342w	1070m	440w	1470m, 1490w
13	1590m	1320vs	970m	775s, 750s	3420b	–	2900w, 3040w	530s, 485s	395w	290s, 310m	1070m	440w	1470m, 1490w
14	1590m	1330vs	970m	775s, 730s	3380b	–	2920m, 3050m	510s	380m	310vs, 325s	1070m	430w	1475m, 1490w
15	1610s	1325vs	985m	765s, 750s	3400b	–	2910w, 3050w	510vs	390m	300m, 320w	1075s	435m	1470w, 1490w

[a] For IR data (cm^{-1}); b: broad, m: medium, s: strong, w: weak bands

TABLE-3
ELECTRONIC SPECTRA, MAGNETIC MOMENTS AND MOLAR CONDUCTIVITY OF COMPLEXES **1–15**

Complex No.	λ_{max} (nm)	Assignment	μ_{eff} (BM)[a]	Δ_M(Ω^{-1}cm^{2}mol^{-1})
				CHCl$_3$
1	235	c.t.	0.2 Pd sq.pl.	0.6
	255	c.t.		
	360	$^1A_{1g} \rightarrow {}^1E_g$		
2	255	c.t.	0.2 Pd sq.pl.	1.4
	360	$^1A_{1g} \rightarrow {}^1E_g$		
	407	$^1A_{1g} \rightarrow {}^1B_{1g}$		
	452	$^1A_{1g} \rightarrow {}^1A_{2g}$		
3	232	c.t.	4.2 Pd sq.pl., Co o.h.	0.7
	344	$^1A_{1g} \rightarrow {}^1E_g$		
	450	$^1A_{1g} \rightarrow {}^1B_{1g}$		
	788	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$		
4	224	c.t.	2.7 Pd sq.pl., Ni o.h.	0.2
	241	c.t.		
	342	$^1A_{1g} \rightarrow {}^1E_g$		
	787	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$		
5	224	c.t.	6.0 Pd sq.pl., Mn o.h.	3.1
	241	c.t.		
	346	$^6A_{1g} \rightarrow {}^4T_{2g}(D)$		
	402	$^1A_{1g} \rightarrow {}^1B_{1g}$		
6	244	c.t.	0.2 Pd sq.pl., Sn o.h.	0.3
	345	$^1A_{1g} \rightarrow {}^1E_g$		
	410	$^1A_{1g} \rightarrow {}^1B_{1g}$		
7	250	c.t.	0.1 Pd sq.pl.	5.0
	356	$^1A_{1g} \rightarrow {}^1E_g$		
8	245	c.t.	0.1 Pd sq.pl.	1.0
	354	$^1A_{1g} \rightarrow {}^1E_g$		
	374	$^1A_{1g} \rightarrow {}^1B_{1g}$		
9	250	c.t.	0.2 Pd sq.pl.	2.3
	340	$^1A_{1g} \rightarrow {}^1E_g$		
	385	$^1A_{1g} \rightarrow {}^1B_{1g}$		
10	244	c.t.	4.7 Pd sq.pl., Co o.h.	1.2
	352	$^1A_{1g} \rightarrow {}^1E_g$		
	440	$^1A_{1g} \rightarrow {}^1B_{1g}$		
	631	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$		
11	243	c.t.	3.3 Pd sq.pl., Ni o.h.	1.7
	368	$^1A_{1g} \rightarrow {}^1E_g$		
	396	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$		
	788	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$		
12	228	c.t.	5.5 Pd sq.pl., Co o.h.	0.5
	248	c.t.		
	415	$^1A_{1g} \rightarrow {}^1B_{1g}$		
	638	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$		
13	242	c.t.	2.6 Pd sq.pl., Ni o.h.	4.1
	318	$^1A_{1g} \rightarrow {}^1E_g$		
	399	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$		
	410	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$		
14	245	c.t.	4.7 Pd sq.pl., Co o.h.	0.7
	355	$^1A_{1g} \rightarrow {}^1E_g$		
	630	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$		
15	243	c.t.	4.2 Pd sq.pl., Co o.h.	0.8
	265	c.t.		
	319	$^1A_{1g} \rightarrow {}^1E_g$		
	395	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$		

[a] Abbreviations sq.pl., o.h. and t.h., are for square planar, octahedral, tetrahedral environment, c.t. for charge transfer.

instability in aqueous or alcoholic solvents. For this reason, these solvents were avoided in the preparation and characterization of the cobalt complexes. The molar conductivities of the complexes in chloroform (Table-3) were too low to suggest that they are non-electrolytes[23].

IR spectra and magnetic moments: The IR spectra of the prepared complexes (Table-2) showed weak to strong bands at *ca*. 1590, 1330, 970 and 775 cm^{-1}, which may be assigned to the thioamide vibrational bands I, II, III and IV, respectively[24,25]. The IR spectra of the complexes **1-6** showed two medium to strong bands at around 323-290 cm^{-1} assigned to ν(Pd-Cl) in a *cis* geometry[26]. The Far IR spectrum of the Pd-Sn complex **6** showed a strong band at around 310 cm^{-1} assigned to ν(Sn-Cl)[20,27] overlapped with ν(Pd-Cl) bands. The IR spectra of the complexes **10-15** showed two medium intensity bonds at *ca*. 300, 320 cm^{-1} assigned to ν(M-Cl) (M = Co or Ni) in an octahedral environment (complexes 10-15)[20]. Other IR data are given in Table-2.

The magnetic susceptibility measurements for the prepared complexes (**1**, **2** and **6-9**) indicated that they are diamagnetic. The magnetic susceptibility values of the (Pd-Co) or (Pd-Ni) complexes (**3**,**4** and **10-15**) indicated that palladium has a square planar geometry. The magnetic susceptibility values for the other metals; cobalt was in the 4.2-4.7 B.M. suggesting an octahedral arrangement around cobalt, as compared with the reported values for octahedral complexes of cobalt(II) 4.7-5.2 B.M.[28,30]. For nickel(II) complexes the magnetic susceptibility values were in the 2.6-3.3 B.M. range. These values together with the spectral data suggests an octahedral arrangements around nickel(II)[17]. The magnetic susceptibility value for the manganese(II) (**5**) was 6.0 B.M. suggests an octahedral arrangements around manganese(II) as compared with the reported values for octahedral complexes of manganese(II) (5.5-6.0 B.M.)[28,30]. Other magnetic susceptibility values and assignments are given in Table-2.

^{31}P-{^{1}H} and ^{1}H-{^{31}P} NMR data: The ^{31}P-{^{1}H} and ^{1}H-{^{31}P} NMR data of some of the prepared complexes are given in Table-4.

The ^{31}P-{^{1}H} NMR spectrum of *cis*-$[PdL_2(dppm)]_2$ (**7**) showed an AX splitting system, doublet of doublets at δP 37.3 and 34.7 ppm with $^2J(P-P)$ = 56 Hz. The positive δP values indicate that dppm behaves as a bridging ligand[31]. The coupling between the two doublets indicating a single isomer and that the *trans* atoms are a sulfur and a nitrogen atoms. The ^{1}H-{^{31}P} NMR spectrum showed a singlet at δ H 1.8 ppm assigned for the methylene protons (CH_2) of the dppm ligand. The low chemical shift indicates that dppm behaves as a bridging ligand compared with that for the chelate δ H 4.4 ppm[31].

The ^{31}P-{^{1}H} NMR spectra of complexes *cis*-$[PdL_2(dppe)]$ (**8**) and *cis*-$[PdL_2(dppp)]$ (**9**) showed a doublet of doublets each, at δP 64.3, 63.4 and

10.3, 6.6 ppm with $^{2}J(P-P)$ of **7** and 35 Hz respectively. The doublet of doublets indicates a single isomer each with two different atoms sulfur and nitrogen bounded to palladium *trans* to phosphorus. Other NMR data are given in Table-4.

TABLE-4
$^{31}P-\{^{1}H\}$ AND $^{1}H-\{^{31}P\}$ NMR DATA (δ ppm and J Hz)[a]
OF SOME OF THE PREPARED COMPLEXES

Complex	Sequence	$^{31}P-\{^{1}H\}$		$^{1}H-\{^{31}P\}$		Comment
		ΔP	$^{2}J(P_A-P_X)$	δCH_2	δ Ph	
$[PdL_2(dppm)]_2$	7	37.3	56	1.8	6.8 – 8.8	S – bonded
		34.7				N – bonded
$[PdL_2(dppe)]$	8	64.3	7	3.2	6.5 – 7.9	S – bonded
		63.4				N – bonded
$[PdL_2(dppp)]$	9	6.6	35	2.0	6.4 – 8.0	N – bonded
		10.3	35	2.0	6.4 – 8.0	S – bonded

[a] Measured in $CDCl_3$ downfield from 85 % H_3PO_4.

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