Asian Journal of Chemistry Vol. 19, No. 2 (2007), 1334-1340

Platinum(II) Linkage Isomeric Complexes Containing Mixed Ligands 4,5-diphenyl-1,2,4-triazole-3-thione and Diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1,2 or3)

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Potassium salt of the ligand 4,5-diphenyl-1,2,4-triazole-3-thione (LK) reacts with K_2PtCl_4 to give *trans*-[PtL_2], in which (L) behaves as a bidentate chelating ligand coordinated to platinum through the nitrogen atom no.2 of the triazole ring and the sulphur of the thiolate group. Reaction of *trans*-[PtL_2] with the diphosphine $Ph_2P(CH_2)_n PPh_2$ (n = 1, 2 or 3) gave the mixed ligand complexes [PtL_2(diphos)]. The produced isomers are either a single isomer, the S,S-bonded (when n = 1 or 3) or a mixture of two linkage isomers, the S,S-bonded and the N,N-bonded isomers (when n = 2). However, a reaction of [$PtCl_2$(diphos)] with LK gave rather different isomers, two isomers in each case. The N,N- bonded and the N,S-bonded isomers, where n = 1 or 2 and the S,S-bonded and the N,S-bonded isomers where n = 3. The prepared complexes have been identified by elemental analysis, IR, UV/Vis, ^1H and ^{31}P NMR spectra. The ^{31}P NMR data have been used effectively to identify the produced linkage isomers.

Key Words: Platinum; Diphosphines; Triazole ligand; Complexes.

INTRODUCTION

There has been a considerable interest in the coordination chemistry of heterocyclic thiones and thiolates[1,2]. Mercaptotriazoles are an important class of well established biologically active compounds, some of which showed a broad spectrum of activity as fungicides, insecticides, acaricides and nematocides[3-9]. Others showed an *in vitro* activity against influenza and rhino viruses. It was found that metal complexes of such ligands exhibit the expected synergetic effect that was attributed to the effect of both heterocyclic ligand and the metal present in these complexes[9]. Coordination chemistry of mercaptotriazole ligands attracted much attention[8,10-15]. It

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was found that such ligands act as monodentate, bidentate or multidentate. The bidentate and multidentate mercaptotriazoles form more stable complexes[15,16].

However, phosphine metal complexes have received much attention due to their potential use as antitumour agents particularly 1,2-bis(diphenylphosphino) ethane and some of its analogous[17,18]. We expected that mixed ligands complexes of tertiary phosphines and mercaptotriazoles to be an important class of complexes and may exhibit the synergic effect that attributed to the mixed ligands. To the best of our knowledge no mixed ligand complexes of diphosphines and mercaptotriazole have been reported prior to the present work.

As a part of our systematic investigation on the coordination chemistry of compounds containing the thioamide group[19-21], we report here the synthesis and characterization of platinum(II) mixed ligand complexes of 4,5-diphenyl-1,2,4-triazole-3-thione (Fig.1) and the diphosphines $Ph_2P(CH_2)_nPPh_2$, where $n = 1, 2$ or 3.

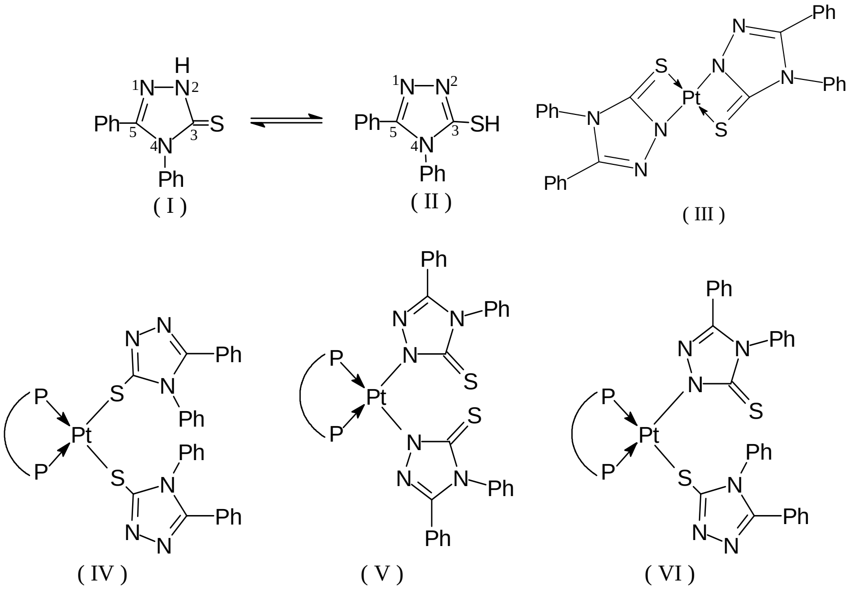
(I) (II) (III) (IV) (V) (VI)

Fig. 1. The ligand 4,5-diphenyl-1,2,4-triazole-3-thione (LH), its tautomeric forms (I) and (II) and the suggested structures of its complexes (III)-(VI), P···P = dppm, dppe and dppp.

EXPERIMENTAL

^1H and ^{31}P NMR spectra 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 200-4000 cm^{-1} range using CsI discs. Electronic spectra were obtained using a Jenway 6485 spectrphotometer. Elemental analyses were carried out on a CHN Analyzer, type 1106 (Carlo Erba). Melting points were measured on Toshinwal-Electrothermal melting point apparatus.

The compounds K_2PtCl_4, the diphosphines $PPh_2P(CH_2)_nPPh_2$ {n = 1 (dppm), 2 (dppe) or 3 (dppp)} were commercial products and used as supplied. The ligand 4,5-diphenyl-1,2,4-triazole-3-thione (LH) and its potassium salt (LK)[23] and *cis*-$[PtCl_2(DMSO)_2]$[24] were prepared according to a literature.

$[PtCl_2(dppm)]$: To a suspension of *cis*-$[PtCl_2(DMSO)_2]$ (0.05 g, 11.8 mmol) in chloroform (5 mL), a solution of dppm (0.046 g, 11.8 mmol) in chloroform (2 mL) was added with stirring. The mixture was heated on a steam bath until its volume was reduced to a half, the clear solution turned cloudy. The solvent was evaporated and the white residue was extracted with dichloromethane. The product was obtained as a white solid upon evaporation of all the solvent (yield 72 %).

Similarly, the complexes $[PtCl_2(dppe)]$and $[PtCl_2(dppp)]$ were prepared as white solids with yields of 74 and 77%, respectively.

***Trans*-$[PtL_2]$ (1):** A solution of potassium salt of 4,5-diphenyl-1,2,4-triazole-3-thione (LK) (0.14 g, 0.48 mmol) in distilled water (5 mL) was added, with stirring, to a solution of K_2PtCl_4 (0.1 g, 0.24 mmol) in distilled water (5 mL). The mixture was stirred for 3h to give a pale yellow solid which was filtered off, washed with water and dried in vacuum (yield 62 %).

Reaction of *trans*-$[PtL_2]$ with dppm: A solution of dppm (0.034 g, 0.088 mmol) in chloroform (3 mL) was added, with stirring, to a solution of *trans*-$[PtL_2]$ (0.062 g, 0.088 mmol) in chloroform (3 mL) to give a reddish-brown mixture. The mixture was refluxed on a water bath for 1h to give a pale yellow solution. The solvent was evaporated to dryness and the residue was washed with ether (8 mL) and dried under vacuum to give the product $[PtL_2(dppm)]$ (**2**) as a light brown solid (yield 55 %).

In a similar manner the complex *trans*-$[PtL_2]$ reacts with dppe and dppp to give the products $[PtL_2(dppe)]$ (**3**), as a mixture of two isomers (Table 4) and $[PtL_2(dppp)]$ (4) with yields of 41 and 45 %, respectively.

Reaction of $[PtCl_2(dppm)]$ with LK: A solution of LK (0.045 g, 0.154 mmol) in ethanol (5 mL) was added, with stirring, to a solution of $[PtCl_2(dppm)]$ (0.05 g, 0.077 mmol) in dichloromethane (10 mL) to give a light yellow mixture which was heated on a steam bath to reduce the volume. The mixture was set aside to evaporate at room temperature to give a yellow solid. This solid was extracted with dichloromethane (10 mL) then the solvent was evaporated at room temperature to give the product $[PtL_2(dppm)]$ (**5**) as a light powder (yield 74 %).

In a similar manner the analogue complexes [$PtCl_2$(dppe)] and [$PtCl_2$(dppp)] react with LK separately to give the products [PtL_2(dppe)] (**6**) and [PtL_2(dppp)] (**7**) with yields of 85 and 87 %, respectively. The products 5-7 consist of a mixture of two isomers each (Table 4).

RESULTS AND DISCUSSION

The prepared complexes were identified by elemental analysis, IR, UV/Vis, ^{1}H and ^{31}P NMR and the data are given in (Tables 1-4). The IR spectra of the complexes (Table-2) showed medium to strong bands at *ca.* 1590, 1370, 975 and 770 cm^{-1}, which may be assigned to thioamide vibrational bands I-IV, respectively[13]. Other bands due to the vibrations of C-H, N-N, P-C and metal-N or -P or -S are listed in (Table-2) and comparable well with those reported in our previous work[22].

The electronic spectral data of the complexes (Table-3) were in a good agreement with the suggested geometries for the four-coordinated metal centres being sequre-planar (Fig.1)[20].

TABLE-1
PHYSICAL PROPERTIES OF COMPLEXES 1–7

Seq.	Complex	Colour	Yield (%)	m.p. (ºC)	Found (Calcd.) (%)		
					C	H	N
1	*Trans*-[PtL_2]	pale yellow	62	238-242	47.8 (48.1)	3.0 (2.9)	11.9 (12.0)
2	[PtL_2(dppm)][a]	light brown	55	168-172	58.4 (58.7)	4.0 (3.9)	7.6 (7.8)
3	[PtL_2(dppe)][b]	Light brown	41	199-202	58.8 (59.0)	4.0 (4.0)	7.5 (7.7)
4	[PtL_2(dppp)][a]	light brown	45	200-203	59.2 (59.4)	4.1 (4.1)	7.5 (7.6)
5	[PtL_2(dppm)][c]	light yellow	74	190-192	58.4 (58.7)	3.7 (3.9)	7.6 (7.8)
6	[PtL_2(dppe)][c]	light yellow	85	180-184	58.8 (59.0)	4.0 (4.0)	7.5 (7.7)
7	[PtL_2(dppp)][d]	off white	87	197-201	59.0 (59.4)	4.1 (4.1)	7.4 (7.6)

a A single isomer in which L is S-bonded.
b A mixture of two linkage isomers in which L is N-bonded (60%) and S-bonded (40%).
c A mixture of two linkage isomers in which L is N-bonded (50%) and N,S-bonded (50%).
d A mixture of two linkage isomers in which L is S-bonded (15%) and N,S-bonded (85%).

Although the IR and UV/Vis spectral data gave some clue about the type of the products but more precise information could be obtained from the NMR data, especially significant is the ^{31}P NMR spectroscopy. However, the ^{1}H NMR spectra of the complexes revealed some signals due to the protons of CH_2 of the diphos ligands and C_6H_5 of both the thione and the diphos species (Table-4).

TABLE-2
IR SPECTRAL BANDS (cm^{-1}) OF THE LIGAND L, ITS POTASSIUM SALT (LK) AND COMPLEXES 1-7

Comp.	Thioamide bands				Others					
	I	II	III	IV	ν(C-H)	ν(N-N)	ν(P-C)	ν(M-N)	ν(M-P)	ν(M-S)
LH	1588s	1278s	975s	775vs	2980w 3080w	1490m	–	–	–	–
LK	1580m	1253m	975s	775s	–	–	–	–	–	–
1	1592s	1350m	975m	770s	2960w 3060w	1465m	–	520m		375m
2	1595s	1360s	975w	775s 750s	2940w 3040w	1470w	1075w	–	430w	350m
3	1595s	1360m	968m	770s 750s	2910w 3050w	1475m	1070m	530vs	440w	370w
4	1589s	1350m	968s	765s 740s	2920m 3030w	1470m	1065m	–	430m	370m
5	1592m	1370s	970m	775s 740s	2910w 3042w	1475m 1490m	1070m	550m	450w	375w
6	1592m	1360s	970w	770s 740s	2920w 3040m	1470m 1490m	1070m	530vs	440w	370w
7	1592m	1360w	975m	770s 740s	2900w 3030w	1468m	1070m	510vs	432m	370w

TABLE-3
ELECTRONIC SPECTRAL DATA[a] FOR COMPLEXES 1–7

Complex	ε^{b} ($x10^3$)	Band absorption		Assignments
		cm^{-1}	nm	
1	1.826	40486	247	CT
	1.750	33333	300	$^1A_1g \rightarrow {}^1Eg$
2	1.933	41322	242	CT
	2.598	28169	355	$^1A_1g \rightarrow {}^1Eg$
3	2.373	40486	247	CT
	1.827	32362	309	$^1A_1g \rightarrow {}^1Eg$
4	1.337	42194	237	CT
	1.350	28090	356	$^1A_1g \rightarrow {}^1Eg$
5	2.688	40486	247	CT
	1.781	25907	386	$^1A_1g \rightarrow {}^1B_1g$
6	2.795	40486	247	CT
	1.792	25840	387	$^1A_1g \rightarrow {}^1B_1g$
7	2.937	39526	253	CT
	1.783	26596	376	$^1A_1g \rightarrow {}^1B_1g$

[a]Measured in chloroform, [b]Molar extinction coefficient

^{31}P NMR spectrum of a reaction between *trans*-[PtL_2] and dppm revealed a singlet at δ P = -37.2 ppm associated with platinum satellites as a simple triplet with a ratio of 1:4:1 , J (Pt-P) = 2004 Hz, which assigned to a single product, identified as [PtL_2(dppm)] (Table 4). The negative value of the chemical shift (δ) indicates the chelating behaviour of the dppm ligand[25], while the low coupling constant (*J*) value indicates that the atom in *trans*-relationship to phosphorus is of a lower electronegativity value, *i.e.*, Sulphur[26,27]. In contrast, the reaction of [$PtCl_2$(dppm)] with the potassium salt of the ligand (LK) gave a rather different products. ^{31}P NMR spectrum of this reaction showed signals due to a mixture of two products with 1:1 ratio, identified as they are the two isomers, N,N-bonded and N,S-bonded triazole complexes. The spectrum showed a triplet with $\delta P = -47.3$ ppm and J (Pt-P) = 2747 Hz; a relatively high J value indicating that the atom in *trans*-relationship to phosphorus is of a higher electronegativity value, *i.e.*, nitrogen. The spectrum also showed an AX spin system with $\delta P_A = -50.3$ ppm, J (Pt-P) = 2561 Hz; $\delta P_X = -58.7$ ppm, J (Pt-P) = 2804 Hz. The AX system indicates that the two atoms in *trans*-relationship to phosphorus are different. The one with low J (Pt-P) value is in *trans*-relationship to sulphur while the other one with a relatively high J (Pt-P) value is in *trans*-relationship to nitrogen.

TABLE-4

^{31}P-{^1H} AND ^1H-{^{31}P} NMR DATA (δ ppm and J Hz) For Complexes 2–7

Complex	Seq.	^{31}P NMR					^1H NMR	
		δ P	Assignments	Proportion (%)	J (Pt-P)	$^2J(P_AP_X)$	δ CH_2	δ Ph
[PtL_2(dppm)][a]	2	-37.2	S,S-bonded	100	2004		3.8 e	7.0-8.1
[PtL_2(dppe)][a]	3	44.9	N-bonded	60	3081		2.25d	6.9-7.8
		47.1	S-bonded	40	2348			
[PtL_2(dppp)][a]	4	-4.1	S,S-bonded	100	2926		2.8e	6.9-7.8
[PtL_2(dppm)][b]	5	-47.3	N,N-bonded	50	2747		4.16	
		-50.3 P_A	S-bonded	50	2561	69	5.11	6.8-8.3
		-58.7 P_X	N-bonded		2804			
[PtL_2(dppe)][b]	6	45.0	N,N-bonded	50	3070			
		47.4 P_A	S-bonded	50	3038	6	2.23, 2.39	6.4-7.9
		35.4 P_X	N-bonded		3277			
[PtL_2(dppp)][b]	7	-4.1	S,S-bonded	15	2905		2.4, 2.8	
		-4.4 P_A	S-bonded	85	2905	30	3.0	6.5-7.9
		-13.3 P_X	N-bonded		3069			
[$PtCl_2$(dppm)][c]		-63.9			3083			
[$PtCl_2$(dppe)][c]		43.0			3634			
[$PtCl_2$(dppp)][c]		-4.9			3408			

[a] Prepared from reaction of *trans*-[PtL_2] and diphosphine.

[b] Prepared from [$PtCl_2$(diphosphine)] + 2LK.

[c] Data taken from references (28,29) and listed here for comparison.

[d] Doublet signal, [e] Broad signal.

The reaction between *trans*-[PtL_2] and dppe gave a mixture of two isomers, the N,N-bonded and the S,S-bonded triazole in a ratio of 3:2, respectively. In contrast, treatment of [$PtCl_2$(dppe)] with LK gave two isomers, the N,N-bonded and the N,S-bonded isomers in the ratio of 1:1 (Table-4).

Reaction of *trans*-[PtL_2] with dppp gave a single isomer identified as [PtL_2(dppp)], while its reaction [$PtCl_2$(dppp)]with LK gave two isomers, the S,S-bonded as the minor product (15 % proportion) and the N,S-bonded as the major product (85 % proportion). Since the type of isomer produced depends markedly on the type of reactants, it seems that the type of product is kinetically controlled rather than thermodynamically controlled.

ACKNOWLEDGEMENT

Dedicated to the memory of Professor Talal A.K. Al-Allaf.

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(*Received*: 28 December 2005; *Accepted*: 15 September 2006) AJC-5096