

Synthesis and Characterization of Homo and Hetero Multi-Nuclear Complexes of Platinum Group Metals with Some New Tetrasubstituted Thioethene Derivatives

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The new tetra-substituted thioethene derivatives $R_2C=CR_2$ ($R =$ xanthate, dithiocarbamate, dithiophosphate) react with one or mixture of two of the salts $NiCl_2 \cdot 6H_2O$, Na_2PdCl_4 and K_2PtCl_4 in 1 : 2 or 1 : 4 (ligand to metal) molar ratio, respectively, to yield homo or hetero multi-nuclear complexes of the general formula $MM'LCl_4$ and $M_2M'_2LCl_8$, where $M \neq M'$ or $M = M' = Ni, Pd, Pt$. The complexes were characterized by their elemental analyses, IR and UV-vis. spectroscopy, conductivity and magnetic measurements. Conductivity data in DMSO and acetonitrile showed that some of the complexes are non-conductive assigning the formulae $[MM'LCl_4]$ or $[M_2M'_2LCl_8]$ and some of them are 1 : 4 conductive assigning the formulae $[MM'L]Cl_4$ or $[M_2M'_2LCl_4]Cl_4$. Explanations for the structural elucidation of these complexes are given and discussed.

INTRODUCTION

In our previous communications about the synthesis of the new tetra-substituted thioethene $R_2C=CR_2$, where $R =$ xanthate, dithiocarbamate and dithiophosphate (Scheme 1), we have given a brief survey about some similar ligands and their transition metal complexes¹. As an extension to our comprehensive studies on platinum and palladium complexes with sulphur containing ligands²⁻⁵, we are presenting here the reaction of these ligands (Scheme 1) with the salts $NiCl_2 \cdot 6H_2O$, Na_2PdCl_4 and K_2PtCl_4 in 1 : 2 or 1 : 4 ligand-to-metal molar ratio. A careful survey of the literature reveals that neither the free ligands nor their metal complexes have been previously synthesized.

EXPERIMENTAL

¹H NMR spectra of the ligands were measured using Hitachi Perkin-Elmer 60 MHz instrument for solutions of the ligands in DMSO-d₆ using SiMe₄ as internal standard. IR spectra were recorded on a Perkin Elmer 580B IR spectrophotometer in the range 4000–200 cm⁻¹ using Nujol mulls and CsI discs. Elemental analyses were carried out on a CHN analyser, type 1106 (Carlo Erba) at the University of Mosul, Iraq. Conductivity measurements were made on 10⁻³ M solutions of the complexes in DMSO and acetonitrile at room temperature (25°C) using conducti-

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vity meter model PCM3-Jenway. Electronic spectra were recorded on a Shimadzu UV-vis spectrophotometer UV-160 for 10^{-3} M solutions of the complexes in acetonitrile at 25°C using 1 cm quartz cell. Magnetic measurements were carried out at 25°C by the Faraday method on the solid complexes in a pyrex tube using Bruker B.M. 6 instrument.

K_2PtCl_4 , $PdCl_2$ and $NiCl_2 \cdot 6H_2O$ were used as supplied by Fluka. Potassium derivatives of xanthate⁶, dithiocarbamate⁷ and dithiophosphate⁸ were prepared by reported methods.

Preparation of the ligands

The tetra-substituted thioethene ligands, $R_2C=CR_2$, where r = xanthate, dithiocarbamate and dithiophosphate derivatives were prepared as outlined in a scheme in our previous article¹. The general method of the preparation is as follows:

Potassium salt of xanthate, dithiocarbamate and dithiophosphate derivative (0.04 mol) was treated with tetrachloroethene (0.01 mol) in ethanol (40 mL), and the mixture was heated under reflux for 6–8 h. After cooling to room temperature, KCl was removed by filtration. The resulting solution was reduced in volume to *ca.* 10 mL and on cooling the solution, the solid thus formed was filtered off, washed several times with water, ethanol and dried under vacuum for several hours. In all cases, the products can be recrystallized from *n*-propanol.

Preparation of the complexes

A. Homo, di- and tetra-nuclear metal complexes

1. **Nickel complexes:** The salt $NiCl_2 \cdot 6H_2O$ (0.47 g, 2 mmol) or (0.95 g 4 mmol) was dissolved in hot *n*-butanol (15 mL). The resulting solution was added slowly with stirring to a solution of the ligand $R_2C=CR_2$ (1 mmol) in *n*-butanol (15 mL). The mixture was refluxed on an oil bath for *ca.* 5 h, then the solution was allowed to cool to room temperature. The solid thus formed was filtered off, washed twice with hot *n*-butanol (5 mL), followed by ether (2×10 mL) and dried under vacuum for *ca.* 3 h.

2. **Palladium complexes:** The salt $PdCl_2$ (0.355, 2 mmol) or (0.710 g, 4 mmol) which was used as a solution of sodium tetrachloropalladate (II) [prepared by heating $PdCl_2$ and NaCl in 1 : 2 molar ratio in distilled water (5 mL) until all $PdCl_2$ dissolved and a red-brown solution formed]⁹, was added to a solution of the ligand $R_2C=CR_2$ (1 mmol) in ethanol (15 mL). A rapid formation of a coloured precipitate was observed. The mixture was then stirred at room temperature for *ca.* 2 h to ensure completion of the reaction. The solid thus obtained by filtration was washed twice with water (10 mL), ethanol (2×10 mL) and ether (10 mL), then dried under vacuum for *ca.* 3 h.

3. **Platinum complexes:** These were prepared by a similar method to that used for palladium complexes above, using the following materials:

The salt K_2PtCl_4 (0.83 g, 2 mmol or 1.66 g, 4 mmol) dissolved in distilled water (15 mL) was added to a solution of the ligand $R_2C=CR_2$ (1 mmol) in ethanol (15 mL).

B. Hetero, di- and tetra-nuclear metal complexes

1. Nickel-palladium complexes: The salt $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.235 g, 1 mmol or 0.470 g, 2 mmol) was dissolved in hot n-butanol (10 mL). This was added slowly with stirring to a solution of the ligand (1 mmol) in n-butanol (15 mL), and the resulting mixture was refluxed for *ca.* 4 h. To this mixture was added a solution of Na_2PdCl_4 (prepared as in A-2 above) (1 or 2 mmol) in distilled water (10 mL), gradually, with continuous stirring. Sufficient amount of 2-methoxyethanol was added to produce a homogeneous solution. The mixture was stirred at room temperature for *ca.* 2 h. The precipitate thus formed was filtered off, washed with warm water (10 mL), n-butanol (5 mL) and ether (10 mL), then dried under vacuum for *ca.* 3 h.

2. Nickel-platinum complexes: These were prepared by a similar method to that used for nickel-palladium complexes above using the following materials:

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.235 g, 1 mmol or 0.470 g, 2 mmol), in hot n-butanol (10 mL), the ligand (1 mmol) in n-butanol (15 mL) and K_2PtCl_4 (0.41 g, 1 mmol or 0.830 g, 2 mmol) in distilled water (10 mL).

3. Palladium-platinum complexes: The salt K_2PtCl_4 (0.415 g, 1 mmol) or (0.830 g, 2 mmol) was dissolved in distilled water (10 mL) and added gradually to a solution of the ligand (1 mmol) in ethanol (15 mL). To this was added a solution of Na_2PdCl_4 (prepared as in A-2 above) (1 or 2 mmol) in distilled water (10 mL). The mixture was stirred with gentle heating for *ca.* 3 h, during which time a precipitate started to deposit. This was cooled to room temperature and the solid filtered off, washed with warm water (20 mL), ethanol (10 mL) and ether (10 mL), then dried under vacuum for *ca.* 3 h.

RESULTS AND DISCUSSION

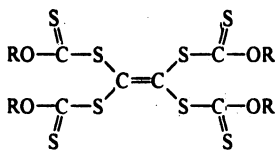
The tetra-substituted thioethene ligands (Scheme 1) have been prepared by one step reaction of tetrachloroethene with the respective potassium salts of xanthate, dithiocarbamate and dithiophosphate¹. On the basis of elemental analyses, IR and UV-vis spectral data, as well as the ¹H NMR data (which reveal the presence of the signals:

$\delta(\text{CH}_3)$ for $\text{L}^1, \text{L}^4, \text{L}^5, \text{L}^9, \text{L}^{10}$ and L^{11} at 1.0–1.5 ppm; $\delta(\text{N}-\text{CH}_3)$ for L^4, L^8 and L^{10} at 2.7–2.9 ppm; $\delta(\text{CH}_2)$ for $\text{L}^1, \text{L}^2, \text{L}^9$ and L^{10} at 2.0–2.9 ppm; $\delta(\text{CH}_2)_n$ for $\text{L}^1, \text{L}^2, \text{L}^4, \text{L}^7, \text{L}^{10}$ and L^{11} at 3.8–4.2 ppm; $\delta(\text{CH})$ for $\text{L}^4, \text{L}^5, \text{L}^7, \text{L}^{10}$ and L^{11} at 3.6–6.0 ppm; $\delta(\text{NH}_2)$ for L^2 at 1.5 ppm and $\delta(\text{Ph})$ for L^3 and L^6 at 6.8–8.3 ppm). These ligands have symmetric structures.

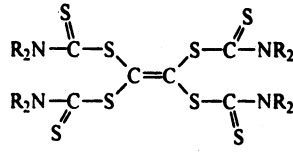
The reaction of these multidentate ligands with the salts $\text{NiCl}_2 \cdot \text{H}_2\text{O}$, Na_2PdCl_4 and K_2PtCl_4 gives products with metal-to-ligand ratios of 2 : 1 or 4 : 1. According to the physico-chemical data of the prepared complexes, their structures can be arranged in several categories (Scheme 2). The physical properties of the complexes are listed in Tables 1 and 2.

Xanthate complexes

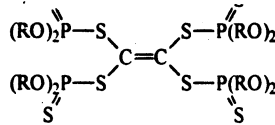
Homo and hetero di- and tetra-nuclear complexes were obtained from the coordination of the ligands L^1-L^4 in tetradentate or even octadentate fashions, *e.g.*, complexes (1), (2) and (4), (6), (12), respectively (Scheme 2).



- L1 : R = n-butyl
 L2 : R = 3-aminopropyl
 L3 : R = 2,4-dinitrophenyl
 L4 : R = N,N-dimethylaminoisopropyl

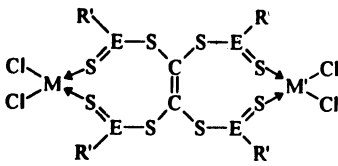


- L5 : R = isopropyl
 L6 : R = phenyl
 L7 : R = allyl
 L8 : R = methyl



- L9 : R = ethyl
 L10 : R = N,N-dimethylaminoisopropyl
 L11 : R = *iso*-butenyl

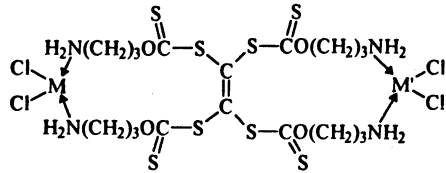
Scheme 1. The tetra-substituted thioethene ligands used in this study

**E = C****Complex**

- L1, M = M' = Pd.....(1)
 L4, M = M' = Pt.....(10)
 L4, M = Ni, M' = Pt.....(11)
 L5, M = Ni, M' = Pt.....(13)
 L6, M = Pd, M' = Pt.....(14)
 L8, M = Ni, M' = Pd.....(19)

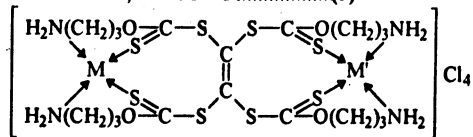
E = P

- L9, M = Pd, M' = Pt.....(20)
 L10, M = M' = Ni.....(21)



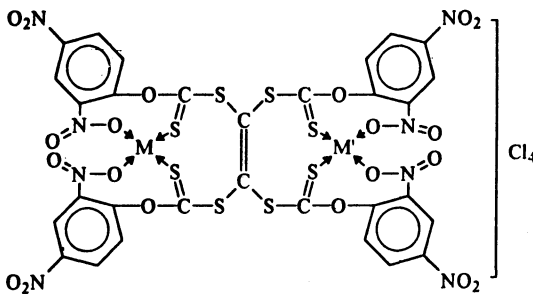
- L2, M = M' = Pd.....(2)

- L2, M = M' = Pt.....(3)



- L2, M = Ni, M' = Pd.....(4)

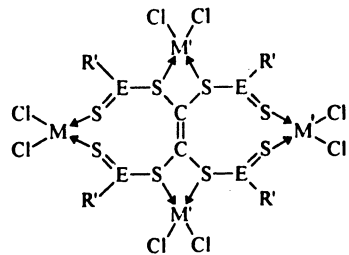
- L2, M = Pd, M' = Pt.....(5)



- L3, M = M' = Ni.....(6)

- L3, M = Ni, M' = Pd.....(7)

- L3, M = Ni, M' = Pt.....(8)

**E = C**

- L4, M = M' = Pd.....(12)

- L6, M = M' = Pt.....(15)

E = P

- L10, M = Pd, M' = Pt.....(22)

- L11, M = M' = Pt.....(23)

Scheme 2. The suggested structures of some complexes (for Ni, tetrahedral; and for Pd or Pt, square-planar). For the structures of complexes (9), (16), (17) and (18), see text.

TABLE-1
THE PROPERTIES OF HOMO AND HETERO DI- AND TETRA-NUCLEAR METAL
COMPLEXES OF THE LIGANDS (L¹-L¹¹)

Seq.	Complex (Colour)	m.p. (°C) (dec.)	Analyses, Found (Calcd.)%			μ_{eff} (B.M.)	Conductivity Λ ohm ⁻¹ cm ² mol ⁻¹	
			C	H	N		DMSO	CH ₃ CN
1.	[PdPtL ¹ Cl ₄] (Light brown)	>360	24.7 (24.8)	3.5 (3.4)	-	1.00	14.9	4.0
2.	[Pd ₂ L ² Cl ₄] (Light brown)	292-294	22.0 (22.0)	3.5 (3.3)	5.6 (5.7)	0.00	3.5	6.0
3.	[Pt ₂ L ² Cl ₄] (Light gray)	350-352	18.0 (18.7)	2.85 (2.8)	4.7 (4.8)	0.67	6.1	2.0
4.	[NiPtL ² Cl ₄] (Deep red)	333-335	21.0 (21.1)	3.3 (3.1)	5.4 (5.5)	3.14	275	496
5.	[PdPtL ² Cl ₄] (Light gray)	320-323	20.0 (20.2)	3.05 (3.0)	5.0 (5.2)	0.00	316	507.3
6.	[Ni ₂ L ³ Cl ₄] (Yellow green)	295-297	27.0 (27.2)	1.1 (0.9)	8.8 (8.5)	6.16	200	515
7.	[NiPdL ³ Cl ₄] (Deep green)	320-322	26.0 (26.3)	1.0 (0.9)	8.2 (8.2)	3.67	28	64
8.	[NiPtL ³ Cl ₄] (Khaki)	318-320	25.0 (24.7)	1.0 (0.8)	7.7 (7.7)	3.72	285	570
9.	[Pd ₂ Pt ₂ L ³ Cl ₄] (Deep red)	343-345	22.0 (21.45)	0.9 (0.7)	6.7 (6.7)	6.10	276	535
10.	[Pt ₂ L ⁴ Cl ₄] (Red brown)	305-307	24.2 (24.6)	3.9 (3.8)	4.3 (4.4)	0.00	21.7	6.3
11.	[NiPtL ⁴ Cl ₄] (Maroon)	338-340	28.0 (27.5)	4.5 (4.2)	4.9 (4.9)	3.18	8.5	20
12.	[Pd ₄ L ⁴ Cl ₈] (Dark gray)	>360	21.6 (21.5)	3.1 (3.3)	4.1 (3.9)	0.00	10.5	24
13.	[NiPtL ⁵ Cl ₄] (Olive)	307-309	33.1 (32.9)	5.2 (5.0)	4.9 (5.0)	2.87	17.6	5.0
14.	[PdPtL ⁶ Cl ₄] (Lemon)	328-330	44.8 (44.8)	2.9 (2.8)	3.7 (3.9)	1.02	6.3	18.0
15.	[Pt ₄ L ⁶ Cl ₈] (Deep brown)	292-294	31.0 (31.3)	2.1 (1.9)	2.6 (2.7)	1.08	16.5	15.0
16.	[Pt ₂ L ⁷ Cl ₄] (Yellow)	200-201	29.0 (28.9)	3.4 (3.2)	4.3 (4.5)	0.76	8.0	4.0
17.	[NiPdL ⁷ Cl ₄] (Yellow green)	277-279	36.0 (35.25)	3.9 (3.9)	5.8 (5.5)	2.89	12.4	3.0
18.	[Pd ₄ L ⁷ Cl ₄] (Dark brown)	239-241	25.4 (25.25)	2.6 (2.8)	4.0 (3.9)	1.30	246.7	519
19.	[NiPdL ⁸ Cl ₄] (Khaki)	253-255	21.2 (20.7)	3.2 (2.95)	7.0 (6.9)	3.72	4.9	29
20.	[PdPtL ⁹ Cl ₄] (Light gray)	296-298	18.0 (17.9)	3.5 (3.3)	-	1.11	18.0	3.1
21.	[Ni ₂ L ¹⁰ Cl ₄] (Yellow green)	>360	33.9 (34.0)	6.6 (6.5)	8.5 (8.65)	4.57	18.5	29
22.	[Pd ₂ Pt ₂ L ¹⁰ Cl ₈] (Brown)	274-276	23.7 (23.9)	4.7 (4.5)	5.2 (5.3)	0.00	14.0	25.0
23.	[Pt ₄ L ¹¹ Cl ₈] (Maroon)	302-304	19.4 (20.0)	3.0 (2.75)	-	1.07	18.5	29

TABLE-2
 SELECTED IR BANDS (cm^{-1}) AND ELECTRONIC SPECTRA OF THE FREE LIGANDS (L^1L^{11}) AND OTHER COMPLEXES (1-23)

Compound Seq.	IR Spectra (cm^{-1}) ^a						UV-vis. Spectra			
	$\nu(\text{C}=\text{C})$ (A)	$\nu(\text{C}-\text{S})$ (A)	$\nu(\text{C}=\text{S})$ (A)	$\nu(\text{P}-\text{S})$ (A)	$\nu(\text{P}=\text{S})$ (A)	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{Cl})$	$\nu(\text{Others})$	$\lambda_{\text{max}}(\text{nm})$	$\epsilon_{\text{max}}(\text{cm}^{-1})$
L^1	1670 s	671 s	1023 m					248	40322	
(1)	1670 s (0)	661 s (-10)	999 m (-24)			355 w (Pd) 374 m (Pt)	300 w 325 w	447, 380 320, 249	22371, 26315, 31250, 40160	
L^2	1666 m	661 m	1000 m					250	40000	
(2)	1666 s (0)	660 m (-1)	1000 s (0)			378 m	302 w 323 w	3382 mb (N-H) 3370 mb (N-H), 533 m (Pd-N)	21551, 27932, 30303, 40983	
(3)	1666 m (0)	661 m (0)	1000 m (0)			390 m	307 w 327 w	3283 mb (N-H), 535 m (Pt-N)	25000, 29824 31847, 36231	
(4)	1666 s (0)	660 s (-1)	980 m (-20)			382 m (Ni) 370 w (Pt)		3261 sb (N-H), 466 w (M-N)	17717, 24285, 28985, 33333, 37037	
(5)	1666 m (0)	661 w (0)	985 m (-15)			352 w (Pd) 390 w (Pt)	305 w 323 w	3236 mb (N-H), 544 m (M-N)	25372, 28901, 30959, 34482	
L^3	1666 m	670 m	1000 s					293	34129	
(6)	1666 s (0)	670 m (0)	985 s (-15)			387 w		1165 s (N-O) 410 w (Ni-O)	726, 423 372, 296	13774, 23641, 26882, 33748
(7)	1666 m (0)	669 m (-1)	984 w (-16)			386 m (Ni) 352 w (Pd)	320 w	1175 s (N-O)	423, 372	23641, 26954
(8)	1666 m (0)	672 m (2)	970 w (-30)			390 w (Ni) 372 w (Pt)		1155 s (N-O) 420 w (M-O)	423, 372, 291	23641, 26954, 34246

Compound Seq.	IR Spectra (cm ⁻¹) ^a						UV-vis. Spectra			
	v(C=C) (Δ)	v(C-S) (Δ)	v(C=S) (Δ)	v(P-S) (Δ)	v(P=S) (Δ)	v(M-S) (Δ)	v(M-Cl)	v(Others)	λ _{max} (nm)	ε _{max} (cm ⁻¹)
(9)	1666 m (0)	654 w (-16)	986 w (-14)			395 m (Ni) 365 w (Pd)	310 w, 323 w, 334 w	1165 m (N-O) 429 w (M-O)	403, 345, 268	24875, 28985, 37313
L ⁴									287	34843
(10)	1642 s (-1)	666 w (0)	990 s (-15)			378 w	299 w 340 w		335, 319, 278	29850, 31348, 35971
(11)	1643 s (0)	645 m (-21)	985 s (-20)			382 m (Ni) 373 w (Pt)	302 w, 323 w, 339 w		641, 426, 371, 353, 269	15596, 23443, 26954, 28332, 37174
(12)	1642 m (-1)	647 w (-19)	975 s (-30)			356 m	335 m		412, 346, 293	24272, 28902, 34111
L ⁵									258	38759
(13)	1666 m (0)	653s (-12)	976 m (-33)			390 m (Ni) 365 w (Pt)	307 w, 323 w, 333 w		345, 291, 266	28985, 34246, 37594
L ⁶									237	42194
(14)	1666 m (1)	660 m (0)	1002 s (-16)			355 w (Pd) 375 w (Pt)	299 m 323 w		444, 380, 315, 342	22522, 26316, 31746, 41322
(15)	1665 m (0)	633m (-27)	999 s (-19)			365 w	306 w 323 w		445, 348, 304, 263	22472, 28735, 32895, 38023
L ⁷									237	42194
(16)	1666 m (-2)	670 m (0)	1018 m (1)			369 m	301 w 325 w	1509 m ^b (C=C)	391, 362, 302, 237	25579, 27624, 33113, 42194
(17)	1668 vs (0)	675 s (5)	990 s (-27)			390 m (Ni) 357 m (Pd)	302 w, 323 w, 340 w	1509 s ^b (C=C)	622, 389, 328	16073, 25706, 30487

Compound Seq.	IR Spectra (cm ⁻¹) ^a						UV-vis. Spectra			
	v(C=C) (A)	v(C-S) (A)	v(C=S) (A)	v(P-S) (A)	v(P=S) (A)	v(M-S) (A)	v(M-Cl) (A)	v(Others)	λ _{max} (nm)	ε _{max} (cm ⁻¹)
(18)	1668 m (0)	660 m (-10)	1000 s (-17)			360 w	303 w, 323 w, 334 w	1509 ^b (C=C)	529, 361, 335, 258	18882, 27700, 29824, 38759
L ⁸	1664 m	671 m	1008 s						228	43859
(19)	1665 m (1)	658 w (-13)	999 s (-19)			382 w (Ni) 365 w (Pd)	303 w, 328 w, 339 w		470, 384, 355, 316, 258	21249, 26042, 28246, 31546, 38759
L ⁹	1674 s	670 s		562 s	625 m				296	33783
(20)	1672 m (-2)	671 m (1)		561 m (-1)	601 s (-24)	369 m (Pd) 407 m (Pt)	295 w 319 w		398, 349, 323, 292	25125, 28653, 30908, 34246
L ¹⁰	1675 m	675 m		556 s	620 s				294	34013
(21)	1675 m (0)	675 m (0)		556 s (0)	599 m (-21)	381 m	330 w		345, 295, 255	28985, 33898, 39215
(22)	1676 m (1)	653 m (-22)		540 m (-16)	586 s (-34)	365 w (Pd) 408 m (Pt)	304 w 334 w		397, 335, 236	25188, 29851, 41841
L ¹¹	1672 m	660 m		545 s	610 vs				295	33898
(23)	1672 m (0)	648 m (-12)		520 s (-25)	613 m (3)	388 m	300 w 340 w	1518 m ^b (C=C)	341, 313, 278	29308, 31746, 35971

^aFor IR data: s, strong; m, medium; w, weak; b, broad bands. (A) = ν(complex) - ν(ligand)

^bFrequency for (C=C) aliphatic; allyl or isobutenyl species.

The IR spectra of the new ligands show bands at 3350, 1023–1002, 671–666, 1571 and 1361–1347 cm^{-1} attributed to $\nu(\text{NH}_2)^{10}$, $\nu(\text{C—S})$ and $\nu(\text{NO}_2)^{12}$, respectively. The lowering of the frequencies of these bands indicates that the amide-nitrogen, sulphur atoms and the oxygen attached to N (of NO_2 group) are involved in coordination. Further support for this coordination comes from the appearance of new bands at 525–490, 390–352 and 420–410 cm^{-1} which are assigned to $\nu(\text{M—N})$, $\nu(\text{M—S})$, and $\nu(\text{M—O})^{2,3,13,14}$, respectively. The absorption IR band of some of the complexes appearing at 330–305 cm^{-1} is attributed to $\nu(\text{M—Cl})^{15-17}$. Electronic spectra and magnetic measurements of the complexes are listed in Table-2, in which the values obtained indicate a square-planar geometry for Pd and Pt complexes, while indicating a tetrahedral geometry for Ni complexes. Conductivity measurements indicate that complexes (1)–(3), (7) and (10)–(12) are non-conductive while complexes (4)–(6), (8) and (9) are 1 : 4 conductive in both solvents, DMSO and acetonitrile^{18,19}. According to the spectral data and conductivity measurements of the complexes with the ligands $\text{L}^1\text{--L}^4$, one can suggest five structures for these complexes (Scheme 2), except for complex (9), *i.e.*, $[\text{Ni}_2\text{Pd}_2\text{L}^3\text{Cl}_4]\text{Cl}_4$ in which we believe that the two Ni ions are bonded tetra-coordinatively with two S (of $\text{C}=\text{S}$) and two O (of NO_2) in both sides [like, *e.g.*, complex (6)], and the two Pd ions bonded coordinatively with two S (of C—S) in both sides, and two chlorides are attached to each Pd ion [like, *e.g.*, complexes (12)]. This could be reversed for Pd and Ni, respectively.

Dithiocarbamate complexes

The analytical data showed that the reactions of Ni(II), Pd(II) and Pt(II) with the dithiocarbamate ligands $\text{L}^5\text{--L}^8$ produce 2 : 1 and 4 : 1 metal-to-ligand complexes. These air-stable complexes are non-hygroscopic and soluble in DMSO and acetonitrile. The IR spectral data of the free ligands showed bands at 1018–1009, 1666–1660 and 675–650 cm^{-1} which assigned to $\nu(\text{C}=\text{S})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C—S})$, respectively. The lowering of the frequency of these bands indicates that sulphur atoms are involved in the coordination (Scheme 2). This has been substantiated by the appearance of a new band at 370–365 cm^{-1} which is assigned to $\nu(\text{M—S})^{13}$. The electronic spectra together with the magnetic measurements of the complexes of the ligands $\text{L}^5\text{--L}^8$ (Table-2) assign square-planar geometry around Pd(II) and Pt(II) ions²⁰, while Ni(II) complexes assign a tetrahedral geometry around nickel ion. Conductivity measurements indicate that complexes (13)–(17) and (19) are non-conductive while complex (18) is 1 : 4 conductive in both solvents, DMSO and acetonitrile. According to the spectral data and conductivity measurements, one can suggest two types of structures; complexes (13), (14) and (19) share one type and complex (15) shares another type (Scheme 2). Concerning complexes (16) and (17) we believe that the allyl double bond, rather than $\text{C}=\text{S}$, shares the coordination with the metal ion in both sides with two chlorides of both metals in a non-conductive fashion. On the contrary, for complex (18), *i.e.*, $[\text{Pd}_4\text{L}^7\text{Cl}_4]\text{Cl}_4$, we believe that two Pd(II) ions are bonded tetra-coordinatively with two S (of $\text{C}=\text{S}$) and two $\text{C}=\text{C}$ (of the allyl) on both sides [like, *e.g.*, complex (6)], and the remaining two Pd(II) ions are bonded coordinatively with two S (of C—S) on both sides, together with two chlorides on each palladium [like, *e.g.*, complex (12)].

Dithiophosphate complexes

The analytical data showed that the reaction of metal ions with the dithiophosphate ligands L^9-L^{11} produce again 2 : 1 and 4 : 1 metal-to-ligand complexes. The IR spectral data of the free ligands appearing at 625–612, 1675–1672 and 661–650 cm^{-1} are assigned to $\nu(\text{P}=\text{S})^{21}$, $\nu(\text{C}=\text{C})$, and $\nu(\text{P}-\text{S})$, respectively. The lowering of the frequencies of these bands indicates that sulphur atoms are involved in the coordination (Scheme 2). Bonding of sulphur atoms with the metal ions has been further investigated by the appearance of a new band at 408–369 cm^{-1} which is assigned to $\nu(\text{M}-\text{S})$.¹³ The electronic spectra together with the magnetic measurements of the complexes of the ligands L^9-L^{11} (Table 2) assign square-planar geometry around Pd(II) and Pt(II) ions, while a tetrahedral arrangement around Ni(II) ion is found. Conductivity measurements indicate that none of the complexes (20)–(23) are conductive in both solvents DMSO and acetonitrile. According to all data obtained concerning these complexes, one can suggest that complexes (20) and (21) share one type of structures and complexes (22) and (23) share another type of structures (Scheme 2).

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