Asian Journal of Chemistry Vol. 9, No. 2 (1997), 187–194

Palladium(II) and Platinum(II) Complexes with Arylthioethenes

TALAL A.K. Al-ALLAF*, NABEEL H. BUTTRUS and PETER B. HITCHCOCK†
Chemistry Department, College of Sciences
University of Mosul, Mosul, Iraq

Di-, tri- and tetraarylthioethene derivatives prepared from di-, tri- and tetrahaloethenes and the respective thiophenols XC_6H_4SH($X = H$ or *o*-NH_2) have been isolated and reacted with $PdCl_2$ and K_2PtCl_4 in different molar ratios to yeld mono- or dinuclear Pd(II) and Pt(II) complexes of the general formula [$MLCl_2$] and [M_2LCl_4], respectively. The arylthioethene derivatives together with their complexes have been characterized physicochemically and spectroscopically. The X-ray single crystal structure of the free ligand *cis*-1,2-bis-(*o*-aminophenylthio)ethene is described.

INTRODUCTION

Transition metal complexes with sulphur-containing ligands were not uncommon in the 19th century; nevertheless, it was not until 1962, that three groups, independently, came to realize the unique nature of dithiolene compounds[1–3]. Complexes of 3,3-bis-(methylthio)-benzidine with Pd(II) chloride have been isolated and characterized[4]. Hartley *et al.*[5] prepared the planer complexes *cis*-[MLX_2], M = Pd or Pt; X = Cl, Br or I; L = $RS(CH_2)_n$ SR, *cis*-RSCH = CHSR (R = Me or Ph). $(RS)_4C_2$ (R = Me or Et) compounds were found to react with [$Pt(PEt_3)_2Cl_2$] to yield *cis*-and *trans*-[$(Et_3P)ClPt\{S(RS)C{=}C(SR)S\}PtCl(PEt_3)$][6].

Recently, Abel *et al.*[7] prepared the dinuclear Pt(IV) complexes [$(PtXMe_3)_2$ $\{(MeS)_2CHCH(SMe)_2\}$] by treating the mononuclear chelate complex [$(PtXMe_3)$ $\{(MeS)_2CHCH(SMe)_2\}$] with equimolar quantities of [$(PtXMe_3)_4$] (X = Cl or Br).

In view of these results and in continuation of our comprehensive studies on the Pd and Pt metal complexes with sulphur-containing[8, 9] and other various donating ligands[10–13], we have prepared some arylthioethene derivatives (1)–(5) (Scheme 1) and their [$MLCl_2$] and [M_2LCl_4] complexes, in which M = Pd or Pt.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer 580B IR spectrophotometer in the 4000-200 cm^{-1} range using Nujol mulls and CsI discs. Elemental analyses were carried out on a CHN Analyser, Type 1106 (Carlo Erba). Conductivity measure-

---

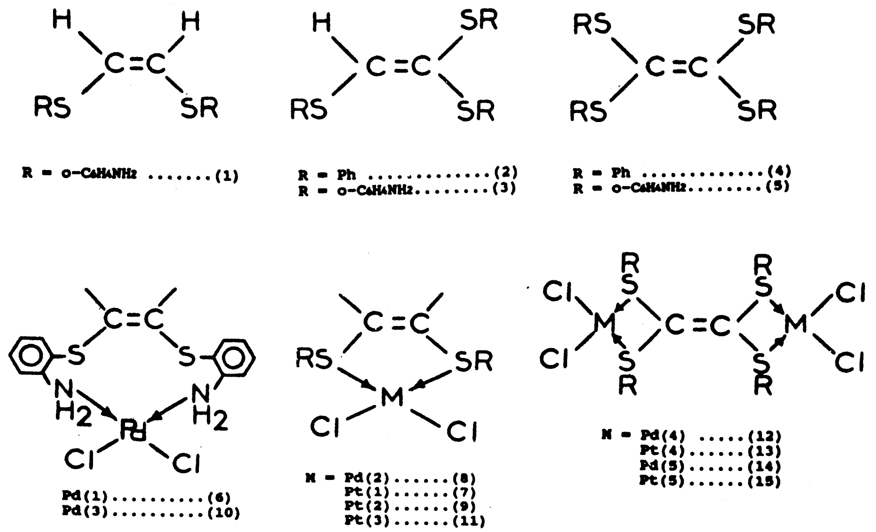
*Author to whom all correspondence should be addressed. Present address: Department of Chemistry, College of Science, Applied Science University, Amman-11931, Jordan.

†School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK.

ments were made on 10^{-3} M solutions of the complexes in DMF at ambient temperature using a conductivity meter model 4070 (Jenway). Electronic spectra were recorded on a Shimadzu UV.-vis spectrophotometer UV-160 for 10^{-3} M solutions of the complexes in DMF at 25°C, using a 1 cm quartz cell.

$K_2[PtCl_4]$ and $PdCl_2$ were used as supplied by Fluka.

The arylthioethene derivatives (Scheme 1) were prepared by using the following standard method[14].



Scheme 1. Ligands and possible structures for their Pd(II) and Pt(II) complexes

Cis-1,2-bis (*o*-aminophenylthio)-ethene (1)

1,2-Dibromoethene containing 66% of the *cis*-isomer, was boiled under reflux for *ca.* 5 h with an equivalent amount of *o*-aminothiophenol and KOH in ethanol. After cooling to room temperature, KBr was removed by filtration. The mixture was extracted with petroleum ether and the *cis*-isomer (product) was precipitated upon cooling; it was then recrystallized from *n*-propanol. The mother liquor yielded another crop of crystals upon standing in the refrigerator for few hours, with a different melting point. This was shown to be the *trans*-isomer product. Further investigations on this isomer were not carried out at this stage.

Tri-and tetra(arylthio)ethene (2)–(5).

The compounds were prepared similarly by treating equimolar quantities of thiophenoxide (prepared form equimolar quantities of KOH and XC_6H_4SH in EtOH) and 1,1,2-trichloroethene or 1,1,2,2-tetrachloroethene, and the mixture was boiled under reflux for *ca.* 6 h. After cooling to room temperature, KCl was removed by filtration. The resulting solution was reduced in volume to *ca.* 1/3, and on cooling left a white solid in the case of (2)–(4) and yellow cubic crystals in the case of (5). In all cases, the product can be crystallized from *n*-propanol.

[$MLCl_2$] and [M_2LCl_4] complexes

These complexes were prepared according to the following general procedure. K_2PtCl_4 or $PdCl_2$ (1 or 2 mmol) was dissolved or suspended in H_20 (10 cm^3) and a solution of the ligand (1 mmol) in MeOH (15 cm^3) was added; a rapid formation of precipitate was observed. The mixture was stirred under reflux for *ca.* 1 h to ensure completion of the reaction. The solid thus obtained was filtered off, washed with warm H_2O, MeOH, ether and dried under vacuum for several hours.

X-ray crystal structure determination

Optically clear, colourless needlelike crystals of the ligand (1) (Scheme 1) were grown up from EtOH. Crystal data, intensities measurments and structure refinement are summarized in Table 1. Unit cell parameters and diffracted

TABLE-1
CRYSTAL DATA AND REFINEMENT FOR
cis-1,2-Bis(*o*-AMINOPHENYLTHIO)-ETHENE (1)

Molecular formula	$C_{14}H_{14}N_2S_2$
Molecular weight	274.4
Crystal size (mm)	0.4 × 0.4 × 0.2
Crystal system	Monoclinic
Space group	$P2_1/C$ (No.14)
a (Å)	10.116 (5)
b (Å)	4.938 (2)
c (Å)	28.143 (9)
α (deg)	90
β (deg)	100.12 (3)
γ (deg)	90
Cell volume ($Å^3$)	1383.9
Z	4
D_{calc} ($g\ cm^{-3}$)	1.32
F (000)	576
λ (Å)	1.5418
μ (cm^{-1})	32.9
2θ range (deg)	25
Total reflections measured	2598
Unique reflections	2476
Significant reflections, $\|F^2\| > 2\sigma\|F^2\|$	1502
Rint	0.02
Absorption correction, max, min	1.3, 0.46 (DIFABS)
R (R′)	0.069 (0.094)
$(\Delta/\sigma)_{max}$	0.1
Max and min $\Delta\rho$ ($eÅ^{-3}$)	+0.28, −0.35

intensities were measured at room temperature on an Enraf-Nonius CAD_4 diffractometer using graphite monochromate CuKα. Data were collected for Lorentz and polarization effects and absorption (DIFABS)[15]. The structure was solved by direct methods (SHELEXS 86)[16] and subsequent Fourier syntheses and refined by full-matrix least-squares procedures using the Enraf-Nonius SDP programme package. The non-hydrogen atoms were refined anisotropically and the hydrogen positions were placed at calculated positions.

RESULTS AND DISCUSSION

Treatment of di-, tri- or tetrahaloethenes with sufficient amounts of a thiophenol derivative results in the isolation of the corresponding di-, tri- or tetraarylthioethenes (1)–(5) (Scheme 1). The physical properties of these ligands are listed in Table-2.

TABLE-2
PHYSICAL PROPERTIES OF THE FREE LIGANDS

Ligand[a]	Colour	m.p. (°C)	Found (Calcd.)%			Selected IR[b] bands (cm^{-1})		
			C	H	N	ν(N—H)	ν(C—S)	ν(C═C)
(1)	colourless	65–67	61.1	5.0	10.0	3380	644	1660
			(61.3)	(5.1)	(10.2)			
(2)	white	42–44	68.1	4.4	—	—	640	1650
			(68.2)	(4.5)	—			
(3)	colourless	65–67	60.4	4.7	10.5	3385	640	1666
			(60.5)	(4.8)	(10.6)			
(4)	colourless	58–60	67.5	4.4	—	—	640	1660
			(67.8)	(4.3)	—			
(5)	yellow	84–86	60.3	4.8	10.7	3380	650	1660
			(60.0)	(4.6)	(10.8)			

[a] For (1)–(5), see Scheme 1.
[b] In Nujol mulls.

Structure of (1)

The molecular structure of *cis*-1,2-bis-(*o*-aminophenylthio)-ethene (1) is shown in Fig. 1. Selected bond lengths and angles are given in Table-3; fractional atomic coordinates and equivalent isotropic thermal parameters are listed in Table-4. There is a slight twist along the S—C═C—S as shown by the torsion angle S(1)–C(1)–C(2)–S(2) of 2.9(7)Å. Also there are weak N—H . . . N hydrogen bonds between molecules related by the 2_1 screw along *b*-axis at which N(1)...N(2)′ is 3.176(7) Å and N(2). . .N(1)′ is 3.117(7) Å (′ is $\bar{\chi}$ 1/2 + y, 1/2 − Z).

The interatomic bond lengths and angles (Table 3) are generally within the expected limits. The C—S [1.750(5) and 1.761(6) Å] and C—N [1.38 g (7) and 1.303 (6) Å]bond lengths, respectively compare well with those of the complxes $[M\{o\text{-}(HN)SC_6H_4\}_3]$, (M = Re or Os)[17].

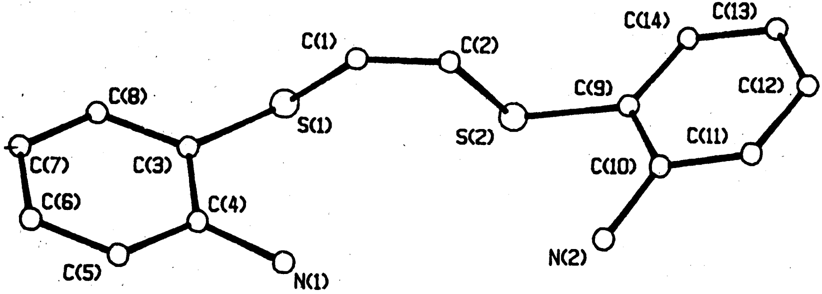


Fig. 1. Structure of *cis*-1,2-bi (*o*-aminophenylthio)ethene (1) with atomic numbering scheme

TABLE-3
SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (DEG) WITH E.S.D. IN PARENTHESES FOR (1)

Bonds:	
S(1)–C(1)	1.750(5)
S(2)–C(2)	1.761(6)
N(1)–C(4)	1.389(7)
C(1)–C(2)	1.308(7)
C(3)–C(8)	1.411(8)
C(9)–C(14)	1.383(8)
S(1)–C(3)	1.763(5)
S(2)–C(9)	1.767(6)
N(2)–C(10)	1.363(6)
S(3)–C(4)	1.395(8)
S(9)–C(10)	1.417(8)
Angles:	
C(1)–S(1)–C(3)	101.2(3)
S(1)–C(1)–C(2)	123.4(4)
S(1)–C(3)–C(4)	121.3(4)
C(4)–C(3)–C(8)	119.3(5)
S(2)–C(9)–C(10)	120.6(4)
C(2)–S(2)–C(9)	100.9(3)
S(2)–C(2)–C(1)	123.4(4)
S(1)–C(3)–C(8)	119.3(4)
N(1)–C(4)–C(3)	121.4(5)
S(2)–C(9)–C(14)	119.7(5)
N(2)–C(10)–C(9)	120.7(5)

TABLE-4

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($\times 10^3$)

	x	y	z	Ueq
S (1)	2942.1(15)	2101.1(32)	1748.4(5)	74(1)
S (2)	2801.9(14)	2120.1(33)	2890.8(5)	75(1)
N (1)	732 (4)	6384 (10)	1627 (2)	70(2)
N (2)	1114 (4)	6459 (10)	3559 (2)	79(3)
C (1)	3615 (5)	4694 (12)	2142 (2)	61(3)
C (2)	3587 (4)	4678 (11)	2604 (2)	61(3)
C (3)	2304 (5)	3956 (12)	1223 (2)	65(3)
C (4)	1287 (5)	5869 (13)	1218 (2)	68(3)
C (5)	803 (6)	7194 (14)	787 (2)	86(4)
C (6)	1278 (7)	6621 (16)	373 (2)	100(4)
C (7)	2278 (6)	4724 (16)	371 (2)	95(4)
C (8)	2774 (6)	3379 (14)	790 (2)	81(4)
C (9)	2992 (5)	3420 (13)	3484 (2)	70(3)
C(10)	2135 (5)	5499 (12)	3599 (2)	69(3)
C(11)	2326 (6)	6392 (15)	4077 (2)	86(4)
C(12)	3314 (6)	5284 (16)	4420 (2)	98(4)
C(13)	4116 (6)	3295 (17)	4303 (2)	102(4)
C(14)	3972 (6)	2370 (15)	3841 (2)	88(4)

*U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Palladium and platinum complexes

The ligands (1)–(5) react readily with 1 or 2 equivalent amounts of $PdCl_2$ or K_2PtCl_4 in aqueous methanolic solution at a reflux temperature resulting in the formation of highly intense (deep yellow to brown-black) complexes. The complexes are all powder, stable in air and insoluble in most organic solvents except for DMF and DMSO. The physical analyses of the complexes are in agreement with the suggested formulae of the complexes.

According to the IR spectral data, Pd and Pt complexes of these ligands can be arranged in three categories (Scheme 1): mononuclear complexes obtained from the coordination of the ligands (1)–(3) in a bidentate fashion. With Pd complexes, the ligands (1) and (3) were found to coordinate with Pd metal via H_2N donor site and this is clear from the drastic decrease of the absorption on NH_2 group, upon coordination, by 170 and 125 cm^{-1}, respectively (Table-2 and 5). On the contrary, the IR absorption of NH_2 group of the ligands (1) and (3) remains almost constant upon coordination with Pt metal, *i.e.*, the coordination had taken place *via* sulphur as the lignad (2) does with both Pd and Pt metals. Further support for this argument comes from the ν(C—S) mode of the ligands (1) and (3) which remains almost constant upon coordination with Pd metal

TABLE-5

THE PROPERTIES OF PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF THE LIGANDS (1)–(5)

Seq[a]	Complex[a] (Colour)	m.p. (C°) (dec.)	Found (Calcd.) %			Selected IR[b] bands (cm^{-1})[b]						UV-vis λ (nm)	Conductivity ohm^{-1} cm^2 mol^{-1} (DMF)
			C	H	N	ν(N—H)	ν(C—S)	ν(C═C)	ν(M═S)	ν(M═N)	ν(M—Cl)		
(6)	[Pd(1)Cl_2] (Brown)	>300	37.7 (37.6)	3.2 (3.1)	6.2 (6.3)	3210	630	1645	—	510	330, 310	268, 366	12
(7)	[Pt(1)Cl_2] (Brown-black)	280	31.0 (31.1)	2.8 (2.6)	5.3 (5.2)	3380	620	1640	440	—	340, 310	268, 375	10
(8)	[Pd(2)Cl_2] (Deep red)	>310	45.0 (45.2)	3.2 (3.0)	—	—	615	1620	441	—	340, 310	267, 379	30
(9)	[Pt(2)Cl_2] (Orange)	>350	39.0 (38.9)	2.5 (2.6)	—	—	610	1625	440	—	330, 310	270, 389	15
(10)	[Pd(3)Cl_2] (Brown)	340	39.2 (39.2)	3.0 (3.1)	13.5 (13.7)	3260	632	1630	—	510	340, 310	269, 385	35
(11)	[Pt(3)Cl_2] (Brown-black)	350	34.1 (34.0)	2.9 (2.7)	12.0 (11.9)	3380	610	1635	435	—	340, 310	270, 376	25
(12)	[Pd_2(4)Cl_4] (Deep red)	300	38.7 (38.7)	2.6 (2.5)	—	—	615	1630	450	—	330, 310	275, 400	20
(13)	[Pt_2(4)Cl_4] (Deep yellow)	>300	31.4 (31.5)	2.0 (2.1)	—	—	610	1630	440	—	330, 310	277, 393	18
(14)	[Pd_2(5)Cl_4] (Brown)	250	34.0 (33.8)	2.7 (2.6)	12.4 (12.1)	3380	620	1635	450	—	340, 310	272, 315, 405	55
(15)	[Pt_2(5)Cl_4] (Brown-black)	330	28.1 (28.2)	2.3 (2.2)	10.3 (10.1)	3380	620	1630	440	—	340, 310	273, 320, 410	50

[a] For (1)–(5) and (6)–(15), see Scheme 1.

[b] In Nujol mulls.

indicating N-bonding, while (as well as for the ligand (2)) decreases by *ca.* 30 cm^{-1} upon coordination with Pt metal indicating S-bonding (Scheme 1).

With the ligands (4) and (5), the matter is different, in which two moles of the salts $PdCl_2$ and K_2PtCl_4 were involved in the reaction with one mole of the ligand to give binuclear coordination complexes, most possibly via S—C—S linkage, forming four member chelate ring (Scheme 1). The elemental analyses clearly confirm the suggested formula and the IR spectral data again showed S-bonding with both Pd and Pt metals (Table-5).

Furthermore, the IR spectra showed bands in the 450–435 cm^{-1} and 510 cm^{-1} regions which tentatively assigned to ν(M—S) and ν(M—N), respectively. The IR spectra also showed, in all complexes, two medium intensity bands around 340 and 310 cm^{-1} assigned to ν(M—Cl) in a *cis*-arrangement[9–13].

The UV-vis spectra of the complexes showed bands at *ca.* 270 and 380 nm (Table-5) due to the thioethene ligand, plus a band at > 400 nm probably attributed to d-d transitions of the metal.

The molar conductivities of 10^{-3} M solutions of the complexes with ligands (1)–(4) indicate that all these complexes are non-electrolytes in DMF. On the contrary, both Pd and Pt complexes of the ligand (5) gave results consistent with a weak 1 : 1 electrolyte in DMF[18].

REFERENCES

1. G.N. Schrauzer and V.P. Mayweg, *J. Am. Chem. Soc.*, **84**, 221 (1962).
2. H.B. Gray and E. Billig, *J. Am. Chem. Soc.*, **85**, 2019 (1963).
3. J.A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).
4. N. Dunski and T.H. Crawford, *J. Inorg. Nucl. Chem.*, **31**, 2073 (1969).
5. F.H. Hartley, S.G. Murray, W. Levason, H.E. Soutter and C.A. McAuliffe, *Inorg. Chim. Acta*, **35**, 265 (1979).
6. B. Cetinkaaya, P.B. Hitchcock, M.F. Lappert, P.L. Pye and D.B. Shaw, *J. Chem. Soc. (Dalton Trans.)*, 434 (1979).
7. E. Abel, T.P.J. Coston, K.G. Orrell and V. Sik, *J.Chem. Soc. (Dalton Trans.)*, 49 (1990).
8. T. Al-Allaf, P.Castan, R. Turpin and S. Wimmer, *Transition Met. Chem.*, **17**, 579 (1992).
9. T.A.K. Al-Allaf, I.A. Mustafa and S.E. Al-Mukhtar, *Transition Met. Chem.*, **18**, 1 (1993).
10. S.A. Al-Jibori, Z.M. Kalay and T.A.K. Al-Allaf, *Transition Met. Chem.*, **19**, 293 (1994).
11. T.A.K. Al-Allaf, R.I. Al-Bayati and S.S. Younis, *Mu'tah J. Res. Stud.*, **9**, 33 (1994).
12. T.A.K. Al-Allaf and R.I. Al-Bayati, *Asian J. Chem.*, **7**, 465 (1995).
13. T.A.K. Al-Allaf and A.Z.M. Sheet, *Polyhedron*, **14**, 239 (1995).
14. C.A.L. Filgueiras, C.Celso, G.H. Coelho and B.F.G. Johnson, *Inorg. Nucl. Chem. Letters*, **17**, 283 (1981).
15. N. Walker and D. Stuart, *Acta Crystallogr.*, **39A**, 158 (1983).
16. G.M. Sheldrick, SHELXS-86, Programme for crystal structure determination, University of Gottingen, F.R.G. (1986).
17. A.A. Danopoulos, A.C.C. Wong and G. Wilkinson, *J. Chem. Soc. (Dalton Trans.)*, 315 (1990).
18. S.F.A. Kettle, Coordination Compounds, Nelson, London, pp. 186, 222 (1975).

(*Received*: 8 July 1996; *Accepted*: 4 November 1996) AJC-1178