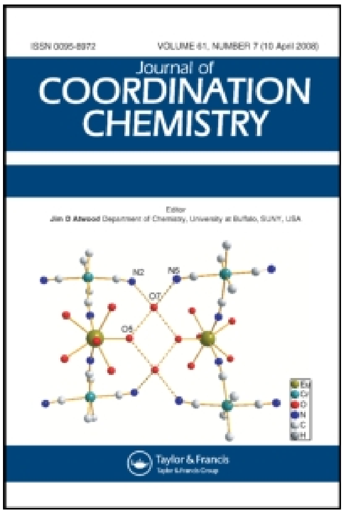

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Metal-Heterocyclic thione interactions-15 - reactivity of coordinated thiones of bis(pyridine- 2-thiolato- or 1-oxopyridine- 2-thiones)palladium(II)/platinum(II) towards divalent metal halides: synthesis of polynuclear complexes

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METAL–HETEROCYCLIC THIONE INTERACTIONS-15 – REACTIVITY OF COORDINATED THIONES OF BIS(PYRIDINE-2-THIOLATO- OR 1-OXOPYRIDINE-2-THIONES)PALLADIUM(II)/PLATINUM(II) TOWARDS DIVALENT METAL HALIDES: SYNTHESIS OF POLYNUCLEAR COMPLEXES

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Reactions of dinuclear tetrakis(pyridine-2-thiolato)dipalladium(II) or platinum(II), $M_2(C_5H_4NS)_4$, with divalent metal halides in organic solvents formed compounds of stoichiometry: $[M_2(C_5H_4NS)_4 \cdot (M'X_2)_2]$ {$M = Pd$, $M'X_2 = HgCl_2$ (**1**), $PtCl_2$ (**2**), $CdCl_2$ (**3**); $M = Pt$, $M'X_2 = HgCl_2$ (**4**)}. Similarly, bis(1-oxopyridine-2-thione)-palladium(II)/platinum(II) formed compounds: $[M(C_5H_4NOS)_2 \cdot M'X_2]$ {$M = Pd$, $M'X_2 = HgCl_2$ (**5**), $HgBr_2$ (**6**), HgI_2 (**7**), $CdCl_2$ (**8**), $PtCl_2$ (**9**); $M = Pt$, $M'X_2 = HgBr_2$ (**10**), HgI_2, (**11**)}. Compounds **1**–**11** have been characterized using elemental analysis, IR, far-IR, and NMR (^1H, ^{13}C) spectroscopy. Coordination to metal centers of $M'X_2$ occurs via coordinated sulfur. Possible structures are suggested. The crystallization of (**5**) in dimethyl sulfoxide formed crystals of $Pd(C_5H_4NOS)_2$ as revealed by X-ray crystallography.

Keywords: Pyridine-2-thiolato; 1-Oxopyridine-2-thione; Polynuclear complexes; Palladium(II); Platinum(II); X-ray structure

INTRODUCTION

The coordination chemistry of heterocyclic thiones containing chemically active, –N(H)–C(=S)– ↔ –N=C(–SH)– groups has been investigated intensively, particularly in the past two decades [1]. Interaction with metals takes place with neutral and deprotonated species via a variety of modes forming monomers, dimers and oligomers [1–3]. The simplest prototype of heterocyclic-2-thiones, i.e. pyridine-2-thione [hereafter C_5H_5NS, **I**] and its *N*-oxide analogue (hereafter C_5H_5NOS, **II**) have received more attention vis-à-vis other compounds of this class [1–6].

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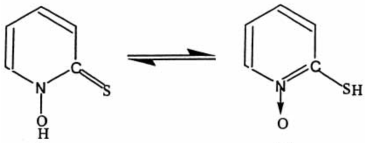
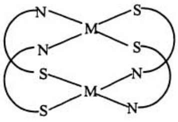
Generally monomeric compounds are formed by C_5H_5NS (**I**) and C_5H_5NOS (**II**) as well as by other heterocyclic thiones and the number of dinuclear and oligomers is limited [1]. In continuation of our interest in the interaction of metals with heterocyclic thiones, we recently reported monomeric complexes with palladium(II)/platinum(II) containing *S*-bonded anionic $C_5H_4NS^-$ and tertiary phosphines as co-ligands [2,6]. In the absence of tertiary phosphines, $M(C_5H_4NS)_2$ (M = Pd, Pt) exist as *N*,*S*-bridged $M_2(C_5H_4NS)_4$ dimers (structure **III**); in contrast, $M(C_5H_4NOS)_2$ (M = Pd, Pt) are *O*,*S*-bonded monomers (structure **IV**) [5]. In this article, reactions of $M_2(C_5H_4NS)_4$ and $M(C_5H_4NOS)_2$ with metal halides are reported in order to explore the reactivity of coordinated heterocyclic thiones.

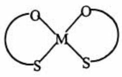
Ia **Ib**



IIa **IIb**



III



IV

EXPERIMENTAL

Materials and Techniques Used

$M_2(C_5H_4NS)_4$ and $M(C_5H_4NOS)_2$ (M = Pd, Pt) were prepared as described earlier [2,5]. The metal halides were procured from standard firms and used as such. The C, H and N elemental analyses were obtained with a Carlo-Erba 1108 microanalyser. Melting points were determined with a Gallenkamp electrically heated apparatus. Infrared spectra were recorded for KBr pellets (4000–400 cm^{-1}) or nujol mulls in polyethene sheets (500–100 cm^{-1}) on a Bruker IFS 66V spectrometer. NMR spectra were recorded in $CDCl_3$ using (i) Bruker AMX 300 spectrometer at 300.14 and 75.48 MHz (^1H and ^{13}C, respectively) with TMS as the internal reference. Tables I–III list IR and NMR data for the complexes.

Preparation of complexes

Compound **1** To a reddish-brown solution of $Pd_2(C_5H_4NS)_4$ (0.100 g, 0.150 mmol) in chloroform (20 cm^3) was added a solution of $HgCl_2$ (0.083 g, 0.300 mmol) in acetonitrile (20 cm^3) dropwise, with magnetic stirring, which was continued for 4 h. There was no precipitation; the contents were filtered and allowed to evaporate at room temperature.

TABLE I Main IR (cm^{-1}) peaks of compounds

Compound	*Formula*	*ν(C=S)*		
		Peak I	*Peak II*	*Peak III*
1	$Pd_2(C_5H_4NS)_4 \cdot (HgCl_2)_2$	1155s	1129m	
2	$Pd_2(C_5H_4NS)_4 \cdot (PtCl_2)_2$	1156s	1130m	
3	$Pd_2(C_5H_4NS)_4 \cdot (CdCl_2)_2$	1156m	1130m	
4	$Pt_2(C_5H_4NS)_4 \cdot (HgCl_2)_2$	1149s	1130m	
5	$Pd(C_5H_4NOS)_2 \cdot HgCl_2$	1177s	1160sh	1137s
6	$Pd(C_5H_4NOS)_2 \cdot HgBr_2$	1177s	1160sh	1136m
7	$Pd(C_5H_4NOS)_2 \cdot HgI_2$	1178s	1160sh	1136m
8	$Pd(C_5H_4NOS)_2 \cdot CdCl_2$	1180s	1161m	1140s
9	$Pd(C_5H_4NOS)_2 \cdot PtCl_2$	1176s	1160sh	1138s
10	$Pt(C_5H_4NOS)_2 \cdot HgBr_2$	1172m	1160sh	1139s
11	$Pt(C_5H_4NOS)_2 \cdot HgI_2$	1172m	1162sh	1140s

The solid obtained was dried *in vacuo*. Yield, 75%; m.p. (°C) 148−50 (dec.), analytical data (%), found, C, 19.1, H, 1.27, N, 4.24; calcd. for $C_{10}H_8N_2S_2Cl_2PdHg$, C, 20.1, H, 1.34, N, 4.68. IR data (cm^{-1}), 1651s, 1540s, 1468s, 1430s, 1155s, 1129m (νC=S), 1090s, 1054m, 771s, 727m, 617s, 566s, 339b (νPd–S), 227sb (νHg–Cl). Compounds **2** and **5** were prepared similarly.

Compound **2** Yield, 70%; m.p. (°C) >200; analytical data (%), found, C, 23.6, H, 1.84, N, 6.43; calcd. for $C_{10}H_8N_2S_2Cl_2PdPt$, C, 22.7, H, 1.74, N, 6.63. IR data (cm^{-1}), 1650m, 1584s, 1450s, 1417s, 1156s, 1130m (νC=S), 1089m, 1056s, 763s, 722m, 426s 393sb (νPd–S), 384s, 350s, 208b (νPt–Cl).

Compound **3** To a reddish-brown solution of $Pd_2(C_5H_4NS)_4$ (0.100 g, 0.150 mmol) in chloroform (20 cm^3) was added a solution of $CdCl_2$ (0.056 g, 0.300 mmol) in ethanol (20 cm^3) dropwise, with magnetic stirring, which was continued for 4 h. The solid obtained was filtered, washed with chloroform and dried *in vacuo*. Yield, 75%; m.p. (°C) >250; analytical data (%), found, C, 20.7, H, 1.78, N, 5.91; calcd. for $C_{10}H_8N_2S_2Cl_2PdCd$, C, 21.6, H, 1.44, N, 5.05. IR data (cm^{-1}), 1583s, 1556m, 1451s, 1417s, 1150m, 1130m (νC=S), 1088s, 1054m, 762m, 412m (νPd–S), 232s (νCd–Cl). Compounds **6**–**9** were prepared similarly.

Compound **4** To a yellow suspension of $Pt_2(C_5H_4NS)_4$ (0.100 g, 0.120 mmol) in acetonitrile (20 cm^3) was added a solution of $HgCl_2$ (0.065 g, 0.240 mmol) in acetonitrile (20 cm^3). The contents turn red; the solid was filtered, washed with acetonitrile and dried *in vacuo*. Yield, 75%; m.p. (°C) >250; analytical data (%), found, C, 17.9, H, 1.14, N, 4.15; calcd. for $C_{10}H_8N_2S_2Cl_2PtHg$, C, 17.5, H, 1.16, N, 4.08. IR data (cm^{-1}), 1592s, 1548m, 1462s, 1408s, 1149s (νC=S), 1096s, 1055s, 763s, 425w, 393sb (νPt–S), 295s (νHg–Cl).

Compound **5** Yield, 80%; m.p. (°C) 224–26; analytical data (%), found, C, 20.0, H, 1.06, N, 4.35; calcd. for $C_{10}H_0N_2O_2S_2Cl_2PdHg$, C, 19.1, H, 1.27, N, 4.44. IR data (cm^{-1}), 1598s, 1551m, 1461s, 1177s, 1160sh, 1137s (νC=S), 1087m (νN–O), 1042m, 827s (δN–O), 754s, 706m, 623m, 449s, 412s, 385s (νPd–S), 312s (νHg–Cl), 296s (νPd–O).

Compound **6** Yield, 80%; m.p. (°C) >230; analytical data (%), found, C, 17.0, H, 1.00, N, 3.84; calcd. for $C_{10}H_8N_2S_2O_2Br_2PdHg$, C, 16.7, H, 1.11, N, 3.89. IR data (cm^{-1}), 1597m, 1550m, 1461s, 1414s, 1177s, 1160m, 1136m (νC=S), 1087m (νN–O),

TABLE II ^{1}H NMR data (δ, ppm, *H*, Hz) of compounds

Compound	*H(6)*	*H(4)*	*H(3)*	*H(5)*
4	9.0dd ($J_5 = 6.1$, $J_4 = 1.0$)	7.6td ($J_{3,5} = 5.7$, $J_6 = 1.2$)	7.3dd ($J_4 = 8.3$, $J_5 = 0.9$)	7.2td ($J_{4,6} = 6.0$, $J_3 = 1.4$)
6	8.1d ($J_5 = 6.8$)	7.2td ($J_{3,5} = 7.6$)	7.5d ($J_4 = 6.8$)	6.9t ($J_{4,6} = 7.0$)
7	8.1dd ($J_5 = 6.1$, $J_4 = 0.8$)	7.2td ($J_{3,5} = 7.6$, $J_6 = 1.4$)	7.5dd ($J_4 = 8.7$, $J_5 = 1.8$)	7.00td ($J_{4,6} = 6.4$, $J_3 = 1.7$)
8	8.4d ($J_5 = 6.4$)	7.4td ($J_{3,5} = 7.7$, $J_6 = 1.2$)	7.6dd ($J_4 = 8.4$, $J_5 = 1.4$)	7.2td ($J_{4,6} = 6.9$, $J_3 = 1.7$)
9 *cis*	8.0t ($J_5 = 6.4$)	7.0m	7.8dd ($J_4 = 9.4$, $J_5 = 1.3$)	7.3m
9 *trans*	8.4d ($J_5 = 6.7$)	7.0m	7.7dd ($J_4 = 8.5$, $J_5 = 1.3$)	7.3m
10 *cis*	8.05d ($J_5 = 6.0$)	7.2m	7.7dd ($J_4 = 8.5$, $J_5 = 1.4$)	6.8m
10 *trans*	8.2d ($J_5 = 6.3$)	7.5m	7.5dd ($J_4 = 8.3$, $J_5 = 1.4$)	6.9m
11 *cis*	8.2d ($J_5 = 6.1$)	7.3m	7.7dd ($J_4 = 8.5$, $J_5 = 1.4$)	6.9m
11 *trans*	8.3d ($J_5 = 6.5$)	7.4m	7.6dd ($J_4 = 8.5$, $J_5 = 1.4$)	6.9m
$Pd_2(C_5H_4NS)_4$[a]	8.48d ($J_5 = 4.8$)	7.6m	7.6m	7.11m
$Pt_2(C_5H_4NS)_4$[a]	9.1d ($J_5 = 6.0$)	7.36t ($J_{3,5} = 7.6$)	7.2d ($J_4 = 8.1$)	6.9t ($J_{4,6} = 6.6$)
$Pd(C_5H_4NOS)_2$[a]	8.03d ($J_5 = 6.7$)	7.14td ($J_{3,5} = 7.2$, $J_6 = 1.1$)	7.39dd ($J_4 = 8.4$, $J_5 = 1.4$)	6.83td ($J_{4,6} = 6.9$, $J_3 = 1.6$)
$Pt(C_5H_4NOS)_2$[a]				
cis	7.9d ($J_5 = 7.0$)	–	7.5dd ($J_4 = 8.4$, $J_5 = 1.4$)	6.7t ($J_{4,6} = 7.0$, $J_3 = 1.6$)
trans	8.15d ($J_5 = 6.6$)	7.14td ($J_{3,5} = 7.8$, $J_6 = 1.3$)	7.46dd ($J_4 = 8.4$, $J_5 = 1.4$)	6.76td ($J_{4,6} = 6.9$, $J_3 = 1.6$)

[a] From reference [5].

TABLE III ^{13}C NMR data of (δ, ppm, *H*, Hz) of compounds

Compound	*C(2)*	*C(6)*	*C(4)*	*C(5)*	*C(3)*
4	176.8	149.7	137.4	128.1	121.1
7	156.7	138.2	131.2	128.1	119.8
8	156.6	138.2	131.2	128.1	119.7
9	155.3	138.4	132.3	127.2	120.5
	154.5	138.6	132.9	126.9	120.6
$Pd(C_5H_4NOS)_2$[a]	157.9	136.1	128.3	127.3	116.9

[a] From reference [5].

1042m, 827s (δN–O), 756s, 706m, 450s, 412s, 383s (νPd–S), 286s (νPd–O), 182s (νHg–Br).

Compound **7** Yield, 75%; m.p. (°C) >250; analytical data (%), found, C, 15.1, H, 0.76, N, 3.44; calcd. for $C_{10}H_8N_2O_2S_2I_2PdHg$, C, 14.8, H, 0.98, N, 3.44. IR data (cm^{-1}), 1597m, 1550s, 1460s, 1413m, 1178s, 1160w, 1136m (νC=S), 1086m (νN–O), 1041m, 826s (δN–O), 753s, 706m, 448s, 409s, 384s (νPd–S), 312m, 283s (νPd–O), 181s (νHg–I).

Compound **8** Yield, 78%; m.p. (°C) >250; analytical data (%), found, C, 20.8, H, 1.46, N, 5.00; calcd. for $C_{10}H_8N_2O_2S_2Cl_2PdCd$, C, 20.5, H, 1.36, N, 4.77. IR data (cm^{-1}), 1599m, 1549s, 1460s, 1415m, 1180s, 1161s, 1140m (νC=S), 1088m (νN–O), 1040w, 822m (δN–O), 747s, 441s, 391s (νPd–S), 293m (νPd–O), 227s (νCd–Cl).

Compound **9** Yield, 75%; m.p. (°C) >250; analytical data (%), found, C, 19.5, H, 1.55, N, 4.78; calcd. for $C_{10}H_8N_2O_2S_2Cl_2PdPt$, C, 19.2, H, 1.28, N, 4.48. IR data (cm^{-1}), 1660s, 1555s, 1464s, 1422m, 1176s, 1138s (νC=S), 1087w (νN–O), 1047s, 825s (δN–O), 764s, 462s, 395sb (νPd–S), 318sb, 287sb (νPd–O).

Compound **10** To a solution of $Pt(C_5H_4NOS)_2$ (0.100 g, 0.240 mmol) in acetonitrile (20 cm^3) was added a solution of $HgBr_2$ (0.080 g, 0.240 mmol) in ethanol (20 cm^3). The contents were stirred for 4 h and the solid obtained was filtered, washed with acetonitrile–ethanol mixture and dried *in vacuo*. Yield, 72%; m.p. (°C) >245d; analytical data (%), found, C, 14.5, H, 1.38, N, 3.34; calcd. for $C_{10}H_8N_2O_2S_2Br_2PtHg$, C, 14.9, H, 1.00, N, 3.46. IR data (cm^{-1}), 1601m, 1552m, 1461s, 1416m, 1172m, 1167sh, 1139s (νC=S), 1090m (νN–O), 1041w, 823m (δN–O), 757s, 385w, 344s (νPt–S), 302m (νPt–O), 253s, 198m (νHg–Br). The Compound **11** was prepared similarly.

Compound **11** Yield, 80%; m.p. (°C) >230d; analytical data (%), found, C, 12.7, H, 0.86, N, 2.84; calcd. for $C_{10}H_8N_2O_2S_2I_2PtHg$, C, 13.3, H, 0.89, N, 3.10. IR data (cm^{-1}), 1600m, 1551s, 1460s, 1416m, 1172m, 1140s(νC=S), 1089m (νN–O), 1040w, 821m (δN–O), 752s, 386w, 342s (νPt–S), 304w (νPt–O), 153m (νHg–I).

Crystal Structure Determination Crystal growth of $Pd(C_5H_4NOS)_2 \cdot HgCl_2$ (**5**) from dimethyl sulfoxide formed crystals of $Pd(C_5H_4NOS)_2$. A red prismatic crystal was mounted on a glass fibre and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least squares refinement of the diffraction data from 25 reflections in the range of $10.565 < \theta < 18.115$ degree on an Enraf Nonius CAD4 automatic diffractometer [7]. Data were collected at 293 K using Mo Kα radiation ($\lambda = 0.71073$ Å) and the ω scan technique and corrected for Lorentz and polarisation effects [8].

A semi-empirical absorption correction (ψ-scan) was made [9].

The structures were solved by Patterson and Fourier methods [10] which revealed the position of all non-hydrogen atoms and refined on F^2 by a full-matrix least squares procedure using anisotropic displacement parameters [11]. All hydrogen atoms were located from difference Fourier maps in their calculated positions (C–H, 0.93–0.97 Å) and were refined isotropically. Atomic scattering factors used from International Tables for X-ray crystallography [12] and molecular graphics from PLATON 98 [10]. A summary of the crystal data, experimental details and refinement results are listed in Table IV. Atomic positions for the nonhydrogen atoms are listed in Table VI.

TABLE IV Crystal data and structure refinement for $Pd(C_5H_4NOS)_2$ compound

Parameter	$Pd(C_5H_4NOS)_2$
Empirical formula	$C_{10}H_8N_2O_2S_2Pd$
Molecular weight	358.70
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	
a (Å)	8.698(2)
b (Å)	13.970(2)
c (Å)	9.957(2)
β (°)	96.68(2)
Volume $(Å)^3$	1201.7(4)
Z	4
Density (calculated) ($Mg\,m^{-1}$)	1.983
Absorption coefficient (μ) (mm^{-1})	1.880
$F(000)$	704
Crystal size, mm	$0.25 \times 0.15 \times 0.15$
$2\theta_{max}$ (°)	52.60
Index ranges	$0 \le h \le 10$; $0 \le k \le 17$; $-12 \le l \le 12$
Reflections collected	2604
Max. and min. transmission	0.966 and 0.931
Independent reflections (R_{int})	2444 (0.0265)
Reflections observed [$I > 2\sigma(I)$]	2444
Parameters	186
Goodness-of-fit on F^2	0.991
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0318$, $wR2 = 0.0687$
R indices (all data)	$R1 = 0.0730$, $wR2 = 0.0792$
Largest diff. peak and hole ($e\,Å^{-3}$)	0.482, −0.0536

TABLE V Atomic coordinates and equivalent isotropic displacement parameters

Atom	x/a	y/b	z/c	U_{eq} ($Å^2$)
Pd(1)	0.6021(1)	0.0645(1)	0.3511(1)	0.038(1)
S(1)	0.3990(1)	0.1390(1)	0.2382(1)	0.0 48(1)
S(2)	0.5211(1)	−0.0833(1)	0.2957(1)	0.051(1)
O(1)	0.7905(3)	0.0005(2)	0.4532(3)	0.047(1)
O(2)	0.6813(3)	0.1974(2)	0.4072(3)	0.048(1)
N(11)	0.5900(4)	0.2704(3)	0.3591(4)	0.040(1)
N(21)	0.7881(4)	−0.0961(2)	0.4557(3)	0.039(1)
C(12)	0.4561(5)	0.2549(3)	0.2771(4)	0.041(1)
C(13)	0.3698(5)	0.3352(4)	0.2303(5)	0.049(1)
C(14)	0.4180(6)	0.4251(4)	0.2662(5)	0.056(1)
C(15)	0.5535(6)	0.4368(4)	0.3526(5)	0.056(1)
C(16)	0.6380(6)	0.3597(3)	0.3968(5)	0.050(1)
C(22)	0.6678(5)	−0.1452(3)	0.3893(4)	0.041(1)
C(23)	0.6730(6)	−0.2444(3)	0.3993(5)	0.053(1)
C(24)	0.7948(6)	−0.2909(4)	0.4707(5)	0.054(1)
C(25)	0.9160(6)	−0.2374(3)	0.5331(5)	0.051(1)
C(26)	0.9117(5)	−0.1396(3)	0. 5259(4)	0.046(1)

RESULTS AND DISCUSSION

Synthesis and IR spectroscopy

Reactions of the dinuclear complexes $M_2(\eta^2\text{-}\mu\text{-N, S-}C_5H_4NS)_4$ (M = Pd, Pt) with divalent metal halides, $M'Cl_2$ (M′ = Pt, Hg, Cd) in organic solvents formed products of

TABLE VI Bond lengths (Å) and bond angles (°) for $Pd(C_5H_4NOS)_2$

Bond lengths			
Pd(1)–O(1)	2.033(3)	S(1)–C(12)	1.724(1)
Pd(1)–O(2)	2.036(3)	S(2)–C(22)	1.723(1)
Pd(1)–S(2)	2.230(1)	O(1)–N(21)	1.350(5)
Pd(1)–S(1)	2.237(1)	O(2)–N(11)	1.346(5)
Bond angles			
O(1)–Pd(1)–O(2)	92.1(1)	Pd(1)–S(2)–C(22)	98.0(2)
O(1)–Pd(1)–S(2)	86.0(1)	Pd(1)–O(1)–N(21)	115.8(2)
O(2)–Pd(1)–S(2)	177.9(1)	Pd(1)–O(2)–N(11)	115.3(2)
O(1)–Pd(1)–S(1)	178.2(1)	O(2)–N(11)–C(12)	121.4(4)
O(2)–Pd(1)–S(1)	86.3(1)	S(1)–C(12)–N(11)	119.3(3)
S(2)–Pd(1)–S(1)	95.7(1)	O(1)–N(21)–C(22)	120.6(4)
Pd(1)–S(1)–C(12)	97.7(2)	S(2)–C(22)–N(21)	119.3(3)

composition, $M_2(\eta^2\text{-}\mu\text{-N,S-}C_5H_4NS)_4\cdot M'_2X_4$ (**1**–**4**). Similarly, reactions of mononuclear complexes $M(\eta^2\text{-O,S-}C_5H_4NOS)_2$ with $M'X_2$ formed products of composition, $M(\eta^2\text{-O,S-}C_5H_4NOS)_2\cdot M'X_2$ (**5**–**11**). All the complexes prepared have poor solubility in common organic solvents such as ethanol, chloroform, benzene etc., but were soluble in DMSO. Due to poor solubility, NMR (^{1}H, ^{13}C) could not be recorded for all the complexes. The complexes were not stable in solvents such as DMSO, DMF etc. and our attempt to crystallise compound **5** formed crystals of $Pd(\eta^2\text{-O,S-}C_5H_4NOS)_2$ which was one of the decomposition products.

The IR spectral bands are listed in the experimental section; however, Table I contains the diagnostic νC=S peaks for ready comparison. The dinuclear $Pd_2(\eta^2\text{-}\mu\text{-N,S-}C_5H_4NS)_4$ [5] showed one νC=S peak at 1115 cm^{-1} and its adduct with $HgCl_2$, namely compound **1** showed two peaks at 1155s and 1129m (cm^{-1}); the behaviour of compounds **2**–**4** is similar. Since square planar Pd^{II} and Pt^{II} have poor tendency to extend coordination number, the $M'X_2$ molecules can coordinate to dinuclear $M_2(\eta^2\text{-}\mu\text{-}N,S\text{-}C_5H_4NS)_4$ via coordinated S atoms forming tetranuclear complexes (e.g. $III\cdot 2M'X_2$; coordinating via S atoms).

The compound $Pd(\eta^2\text{-}O,S\text{-}C_5H_4NOS)_2$ [5] shows νC=S peaks at 1177s and 1161s (cm^{-1}), which after reaction with $HgCl_2$ (compound **5**) showed clear change. Whereas the 1177s peak is unaffected, the other peak at 1161s (cm^{-1}) changes to a shoulder and a new peak appears at 1137s (cm^{-1}). The same behaviour is shown by the compounds **6**–**9**. The νN–O and δN–O do not show any significant changes (cf. Experimental section). Since $Pd(\eta^2\text{-}O,S\text{-}C_5H_4NOS)_2$ [5] exists as a monomer [13], the simplest way of its binding with $M'X_2$ molecules appears to be via coordinated S-atom. Finally $Pt(\eta^2\text{-}O,S\text{-}C_5H_4NOS)_2$ shows νC=S peak a 1168m, 1152sh and in its adducts (compounds **10** and **11**, Table I), three peaks occurred as for Pd(II) adducts, **5**–**9**. The structure $IV\cdot M'X_2$ (coordinating via S atoms) is suggested for compounds **5**–**11**.

NMR Spectroscopy

Among the polynuclear compounds **1**–**4**, only compound **4** showed sufficient solubility for recording its ^{1}H and ^{13}C NMR spectra (Tables II and III). The pyridyl ring protons H(6), H(4), H(3) and H(5) of $Pt_2(\eta^2\text{-}\mu\text{-}N,S\text{-}C_5H_4NS)_4$ showed a doublet, a triplet, a doublet and a triplet respectively and these protons in compound **4** appeared as a doublet of doublets, a triplet of doublets, a doublet of doublets and a triplet of doublets respectively. Similarly, the ^{13}C NMR spectrum of this compound showed C(2), C(6), C(4), C(5) and C(3) peaks at 176.8, 149.7, 137.4, 128.1 and 121.1 ppm respectively. Thus ^{1}H and ^{13}C NMR data clearly support the view that $C_5H_4NS^-$ moiety remains *N*,*S*-bridged as in the parent compound and that a dinuclear moiety binds to metal halides via coordinated S donor atoms only [1,5].

^{1}H NMR spectra of compounds **6**–**8** showed characteristic H(6), H(4), H(3) and H(5) peaks at positions relatively low-field as compared to the starting material $Pd(\eta^2\text{-O,S-}C_5H_4NOS)_2$ [5]. This low field shift supports coordination of $M'X_2$ molecules. ^{13}C NMR spectra of compounds **7** and **8** showed low-field shifts for all the pyridyl carbons except C(2) which showed a small high field shift. Since $Pt(\eta^2\text{-}O,S\text{-}C_5H_4NOS)_2$ showed *cis* and *trans* isomers as revealed by NMR [5], its adducts, namely, compounds **10** and **11** showed *cis* and *trans* isomers (Table II); the proton signals occurred at low field. In other words both *cis* and *trans* isomers are bonded to $M'X_2$ molecules via S donor atoms. Interestingly, the adduct $Pd(C_5H_4NOS)_2 \cdot PtCl_2$ showed two sets of proton and carbon NMR signals on the pattern shown by $Pt(C_5H_4NOS)_2$ as discussed above and it reveals that reaction of $Pd(C_5H_4NOS)_2$ with $PtCl_2$ rather involves rearrangement of $C_5H_4NOS^-$ moieties forming $Pt(C_5H_4NOS)_2 \cdot PdCl_2$ instead of the expected product $Pd(C_5H_4NOS)_2 \cdot PtCl_2$ **9**. This could be explained in terms of the enhanced ligand field stabilisation energy of Pt(II) complexes vis-à-vis that of Pd(II) complexes.

Crystal Structure of $Pd(\eta^2\text{-}O,S\text{-}C_5H_4NOS)_2$

Crystals of compound **5** from DMSO were studied using X-ray crystallography. Structural parameters of $Pd(C_5H_4NOS)_2$ are similar to those reported in literature [13]. The atom numbering scheme is shown in Fig. 1. Table IV contains a summary of the crystal data while the selected interatomic parameters are listed in Table V. Palladium is bonded to two oxygen and two sulfur atoms of two different $C_5H_4NOS^-$ moieties and the geometry around the metal center is square planar. As expected, $C_5H_4NOS^-$ acts as a *O*,*S*-chelating ligand with the central PdO_2S_2 core having a *cis* -disposition of O and S atoms.

The Pd–S bond lengths [2.230(1), 2.237(1) Å] are somewhat shorter while Pd–O bond distances [2.033(3), 2.036(3) Å] are longer than those reported in literature [Pd–S, 2.280–2.322 Å; Pd–O, 2.009 Å] [13]. The C–S distance [av. 1.724(1) Å] is significantly shorter than the sum of the covalent radii of C and S [1.79 Å] [14]. The N–O distances [1.346(5), 1.350(5) Å] are shorter than that (1.388 Å) found in Me_3NO where no π-bonding can occur [15]. These data indicate double bond character in the N–O and C–S bonds similar to that observed in Ag(I), Zn(II) and V(IV) compounds of the $C_5H_4NOS^-$ ligand [16].

The angles around Pd vary from 85 to 96°, the smallest being S(1)–Pd–S(2) and this distorts the square planar geometry. The bite angle O–Pd–S (*ca.* 86°) is somewhat larger than those found in Ag(I) (76°) and Zn(II) (82–85°) complexes [16]. The relatively large O–Pd–S bite angle leads to smaller Pd–S–C bond angles {97.71(15), 97.98(16)°} vis-à-vis those in Ag(I) complexes {100.4(1), 103.1(1)°}. The Pd–O–N bond angles {115.3(2), 115.8(3)°} are relatively rigid and are close to that in Ag(I) complex [16]. This difference in behaviour of M–S–C and M–O–N angles is attributed to larger angular flexibility of the S atom over the O atom.

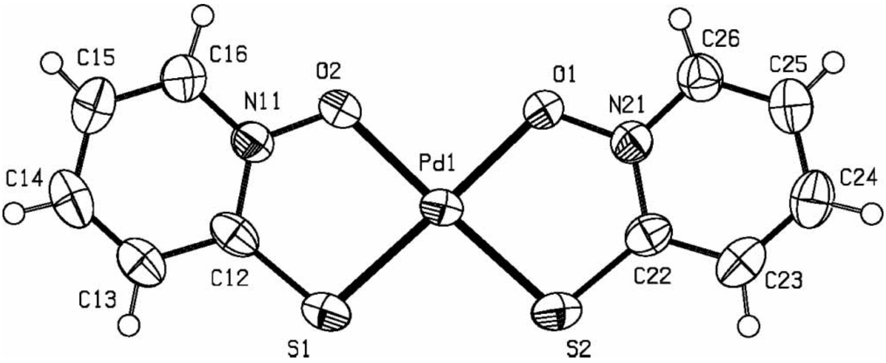


FIGURE 1 The structure of compound $Pd(C_5H_4NOS)_2$ showing atom numbering scheme.

The plane defined by $N^{11}C^{12-16}S^1O^1Pd^1$ makes an angle of 2.06° with the plane defined by $S^1S^2O^1O^2Pd^1$ which in turn makes an angle of 4.68° with the plane defined by $N^{21}C^{22-26}S^2O^2Pd^1$.

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Supplementary Data

Crystallographic information has been deposited with the Cambridge Data Centre as supplementary publication no. CCDC 211472. Information can be obtained from CCDC Deposit (deposit@ccdc.cam.ac.uk).

References

[1] (a) E.S. Raper, *Coord. Chem. Rev*. **61**, 115 (1985); (b) E.S. Raper, *Coord. Chem. Rev*. **153**, 199 (1996); (c) E.S. Raper, *Coord. Chem. Rev*. **129**, 91(1994); (d) E.S. Raper, *Coord. Chem. Rev*. **165**, 475 (1997).

[2] T.S. Lobana, Renu Verma, Geeta Hundal and A. Castineiras, *Polyhedron* **19**, 899 (2000) and references cited therein.

[3] (a) T.S. Lobana, Seema Paul and A. Castineiras, *Polyhedron* **16**, 4023 (1997); (b) T.S. Lobana, P.K. Bhatia and E.R.T. Tiekink, *J. Chem. Soc. Dalton Trans*. 749 (1989); (c) T.S. Lobana, P.K. Bhatia, D.C. Povey and G.W. Smith, *J. Cryst. and Spect. Res*. **21**, 9 (1991); (d) E.R.T. Tiekink, T.S. Lobana and R. Singh, *J. Cryst. and Spect. Res*. **21**, 205 (1991); (e) T.S. Lobana and P.K. Bhatia, *J. Chem. Soc. Dalton Trans*. 1407 (1992); (f) E. Horn, T.S. Lobana, R. Singh and E.R.T. Tiekink; *Z. Krist*. **205**, 291 (1993); (g) T.S. Lobana, Renu Verma, R. Singh and A. Castineiras, *Transition Met. Chem*. **23**, 25 (1998); (h) T.S. Lobana, Seema Paul and A. Castineiras, *J. Chem. Soc. Dalton Trans* 1819 (1999).

[4] T.S. Lobana and Seema Paul, *Transition Met. Chem*. **21**, 300 (1996) and references cited therein.

[5] T.S. Lobana and R. Verma, *Indian J. Chem. Sect A* **38A**, 592 (1999).

[6] T.S. Lobana, R. Verma and A. Castineiras, *Polyhedron* **17**, 3753 (1999).

[7] B.V. Nonius, CAD 4-Express Software, Ver. 5.1/1.2. (Enraf Nonius, Delft, The Netherlands, 1995).

[8] A.L. Spek, HELENA. A Program for Data Reduction of CAD4 data (University of Utrecht, The Netherlands, 1997).

[9] A.L. Spek, PLATON. A Multipurpose Crystallographic Tool (Utrecht University, Utrecht, The Netherlands, 1997).

[10] G.M. Sheldrick, *Acta Crystallgr*. **A46**, 467 (1990).
[11] G.M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures (University of Goettingen, Germany, 1997).
[12] International Tables for X-ray Crystallography, Vol. C, (Kluwer Academic Publishers, Dordrecht, The Netherlands 1995).
[13] J.C. Shi, T.B. Wen, Y. Zheng, S.J. Zhong, D.X. Wu, Q.T. Liu, B.S. Kang, B.M. Wu and T.C.W. Mak, *Polyhedron* **16**, 369 (1997).
[14] J.E. Huheey, E.A. Keiter and R.L. Keiter (Eds.), Inorganic Chemistry: Principles of Structure and Reactivity, 4th Edn. (Harper Collins College Publishers, New York, 1993).
[15] A. Caron, G.J. Palenik, E. Goldish and J. Donohue, *Acta Crystallogr*. **17**, 102 (1964).
[16] T.S. Lobana, S. Paul, G. Hundal and S. Obrai, *Transition Met. Chem*. **24**, 202 (1999) and references cited therein.