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1,9-Dihydro-purine-6-thione Derivatives of the d^8–d^{10} Metal Ions (Pd^{II}, Pt^{II}, and Cu^{I}): Synthesis, Spectroscopy, and Structures

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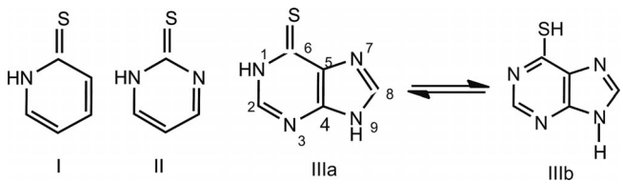
Abstract. Reaction of 1,9-dihydro-purine-6-thione ($puSH_2$) in presence of aqueous sodium hydroxide with $PdCl_2(PPh_3)_2$ suspended in ethanol formed $[Pd(\kappa^2\text{-}N^7,S\text{-}puS)(PPh_3)_2]$ (**1**). Similarly, complexes $[Pd(\kappa^2\text{-}N^7,S\text{-}puS)(\kappa^2\text{-}P,P\text{-}L\text{-}L)]$ (**2**–**4**) {L-L = dppm (*m* = 1) (**2**), dppp (*m* = 3) (**3**), dppb (*m* = 4) (**4**)} were prepared using precursors the $[PdCl_2(L\text{-}L)]$ {L-L = $Ph_2P\text{–}(CH_2)_m\text{–}PPh_2$}. Reaction of $puSH_2$ suspended in benzene with platinic acid, H_2PtCl_6, in ethanol in the presence of triethylamine followed by the addition of PPh_3 yielded the complex $[Pt(\kappa^2\text{-}N^7,S\text{-}puS)(PPh_3)_2]$ (**5**). Complexes $[Pt(\kappa^2\text{-}N^7,S\text{-}puS)(\kappa^2\text{-}P,P\text{-}L\text{-}L)]$ (**6**–**8**) {L-L = dppm (**6**), dppp (**7**), dppb (**8**)} were prepared similarly. The 1,9-dihydro-purine-6-thione acts as N^7,S-chelating dianion in compounds **1**–**8**. The reaction of copper(I) chloride [or copper(I) bromide] in acetonitrile with $puSH_2$ and the addition of PPh_3 in methanol yielded the same product, $[Cu(\kappa^2\text{-}N^7,S\text{-}puSH)(PPh_3)_2]$ (**9**), in which the halogen atoms are removed by uninegative N,S-chelating $puSH^-$ anion. However, copper(I) iodide did not lose iodide and formed the tetrahedral complex, $[CuI(\kappa^1\text{-}S\text{-}puSH_2)(PPh_3)_2]$ (**10**), in which the thio ligand is neutral. These complexes were characterized with the help of elemental analysis, NMR spectroscopy (^1H, ^{31}P), and single-crystal X-ray crystallography (**3**, **7**, **8**, **9**, and **10**).

Introduction

The chemistry of heterocyclic-2-thiones with the chemically active, –N(H)–C(=S)– ⇌ –N=C(–SH)– group, has been in the focus of several investigations owing to their interactions with transition, post-transition and main group metals, both as the neutral and deprotonated ligands, leading to the formation of monomers, dimers, oligomers, and polymers.[1–6] The coordination chemistry of pyridine-2-thione (pySH, structure I) / pyrimidine-2-thione (pymSH, structure II) (Scheme 1) with Pd^{II}, Pt^{II}, and Cu^{I} has been intensively studied.[1–19] These ligands generally formed mononuclear square-planar complexes with Pd^{II}/Pt^{II}, namely, $[Pd(\kappa^2\text{-}N,S\text{-}pyS)Cl(PPh_3)]$,[7] $[Pd(\kappa^1\text{-}S\text{-}pySH)_4]Cl_2$,[8] $[Pd(\kappa^2\text{-}N,S\text{-}pymS)(PPh_3)_2](ClO_4)$,[9] $[M(\kappa^1\text{-}S\text{-}pyS)_2(dppe)]$ (M = Pd, Pt),[10] $[Pt(\kappa^1\text{-}S\text{-}pyS)_2(PPh_3)_2]$,[11] $[Pt(PPh_3)_2(\kappa^2\text{-}N,S\text{-}pyS)](PF_6)\cdot CHCl_3$,[12] $[Pt(\kappa^1\text{-}S\text{-}pyS)_2(bipy)]$,[13] $[Pt(terpy)L)](ClO_4)$ (L = κ^1-S-pyS, κ^1-S-pymS)],[13] $[M(\kappa^2\text{-}N,S\text{-}pymS)(\kappa^1\text{-}S\text{-}pymS)(PPh_3)]$ (M = Pd, Pt),[14] and $[M(\kappa^1\text{-}S\text{-}pymS)_2(L\text{-}L)]$ (dppm Pt; dppe, Pd).[14] Likewise, copper(I) halides with pySH and pymSH have yielded mono- and dinuclear complexes, $[CuX(\kappa^1\text{-}S\text{-}pySH)(PPh_3)_2]$ (*X* = Cl, Br),[15,16] $[Cu_2Br_2(\kappa^2\text{-}\mu\text{-}S\text{-}pySH)_2(PPh_3)_2]$,[16] $[CuX(\kappa^1\text{-}S\text{-}pymSH)(PPh_3)_2]$,[17–20] and $[Cu_2(\kappa^2\text{-}\mu\text{-}I)_2(PPh_3)_2(\kappa^2\text{-}\mu\text{-}N,S\text{-}pymSH)]$.[20] Recently, copper(I) iodide with pySH, in presence of bis(diphenylphosphanyl)alkanes, has also formed a trinuclear complex, $[Cu_3I_3(\kappa^2\text{-}P,P\text{-}dppe)_3(\kappa^1\text{-}S\text{-}pySH)]$ {dppe = 1,2-bis(diphenylphosphanyl)ethane} and a polynuclear complex, $\{Cu_6(pySH)_6\}_n\cdot 2nCH_3CN$.[21]



Scheme 1. Molecular structures of thio ligands.

Apart from structure and bonding aspects, another impetus to pursue chemistry of heterocyclic-2-thiones lies in their biochemical applications.[1–6] Metal complexes are known to have applications, as antimetabolite and antitumor drugs, they also exhibit bacteriocidal and fungicidal activity.[22–24] Aurophosphine thiolate complexes have shown antiarthritic activity, and they are also used as anticancer drugs.[25–28]

There are a few complexes of 1,9-dihydro-purine-6-thione ($puSH_2$, structure IIIa and IIIb tautomers, Scheme 1), or its derivatives reported with these metals, namely, $[Pd(\kappa^2\text{-}N,S\text{-}puS\text{-}9\text{-}CH_2Ph)_2]\cdot L$ {L = $MeC(O)NMe_2$; κ^2-S,N-puS-9-CH_2Ph = 9-benzyl-6-mercaptopurine},[29] $[Cu^I_2Cl_2(\mu\text{-}Cl)_2(\kappa^1\text{-}S\text{-}puSH_3)_2]$, and $[Cu^I_2Cl_4(\kappa^2\text{-}\mu\text{-}S\text{-}puSH_3)_2]$ ($puSH_3^+$ is protonated $puSH_2$].[30,31] The coordination chemistry of 1,9-dihydro-

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purine-6-thione remains essentially unexplored and thus in this paper, reactions of 1,9-dihydro-purine-6-thione (structure III) with palladium(II), platinum(II), and copper(I) in the presence of mono- and di-tertiaryphosphines are described.

Experimental Section

Materials and Techniques: 1,9-Dihydro-purine-6-thione ($puSH_2$), bis(diphenylphosphanyl)methane (dppm), 1,3-bis(diphenylphosphanyl)-propane (dppp), PPh_3, and H_2PtCl_6 were procured from Sigma Aldrich Ltd. The 1,2-bis(diphenylphosphanyl)butane (dppb) was prepared by a reported method.[32] Palladium(II) complexes, namely, $PdCl_2(PPh_3)_2$ or $PdCl_2L$ (L = a diphosphine) were prepared by stirring $PdCl_2$ with a phosphine in 1:2 (PPh_3), or 1:1 (in case of diphosphines) molar ratios in acetonitrile for 5–6 h.[33] Copper(I) halides were prepared by reducing an aqueous solution of $CuSO_4{\cdot}5H_2O$ with SO_2 in the presence of stoichiometric amount of sodium halides in water.[34] The melting points were determined with a Gallenkamp electrically heated apparatus. C, H, N analyses were carried out with a thermoelectron FLASHEA1112 analyser. The ^{1}H NMR spectra of the complexes were recorded with an AL - 300 FT JEOL spectrometer operating at a frequency of 300 MHz using $CDCl_3$/[D_6]DMSO (15:1 ratio) with TMS as the internal reference. The ^{31}P NMR spectra were recorded with an AL - 300 FT JEOL spectrometer operating at a frequency of 121.5 MHz using $CDCl_3$/[D_6]DMSO (15:1 ratio) with H_3PO_4 as the external reference. The infrared spectra in the 4000–200 cm^{-1} (or 400 cm^{-1}) range were recorded using KBr pellets with a Pye Unicam SP-3–300 or FTIR NICOLET 320 fourier transform infrared spectrophotometer.

Synthesis of [Pd(κ^2-N,S-puS)(PPh_3)$_2$] (1): To the solid 1, 9-dihydro-purine-6-thione ($puSH_2$) (0.050 g, 0.0713 mmol) placed in a round bottomed flask was added a solution of sodium hydroxide (NaOH) (0.026 g) in distilled water (2 mL), which formed a clear light yellow solution. To this solution was added a suspension of $PdCl_2(PPh_3)_2$ (0.050 g, 0.0713 mmol) in ethanol, and the contents were stirred for 6 h. The reaction mixture was filtered to remove NaCl, and the yellow filtrate was allowed to crystallize at room temperature. The yellow crystals formed over a period of one week, which turned opaque in the absence of solvent. M.p. 240–250 °C. Yield: 60%. Anal. $C_{41}H_{32}N_4P_2SPd$: calcd. C 63.0; H 4.10; N 7.11%; found. C 62.1; H 4.00; N 7.01%. **IR** (KBr, main peaks): ν(C–C) + ν(C–N), 1555, 1440; ν (C–S), 860 s cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + [D_6]DMSO): δ = 7.68 (s, 1 H, H^8), 7.29 (s, 1 H, H^2), 7.20–7.47 (m, PPh_3) ppm. **^{31}P NMR**: δ = 26.5, –8.29 ppm.

Complexes 2–4 were prepared similarly.

Synthesis of [Pd((κ^2-N,S-puS)(dppm)] (2): A yellow compound (powder) formed on slow evaporation at room temperature. M.p. 260–270 °C. Yield: 70%. Anal. $C_{30}H_{24}N_4P_2SPd$: calcd. C 56.2; H 3.75; N 8.75%; found C 55.5; H 3.68; N 8.48%. **IR** (KBr, main peaks): ν(C–C) + ν(C–N), 1545, 1450; ν (C–S), 860 w cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + [D_6]DMSO): δ = 8.44 (s, 1 H, H^8), 7.88 (s, 1 H, H^2), 7.47 –7.68 (m, dppm) ppm. **^{31}P NMR**: δ = 27.8, 22.7 ppm.

Synthesis of [Pd(κ^2-N,S-puS)(dppp)] (3): Dark yellow crystals formed over a period of one week. M.p. 270–280 °C. Yield: 70%. Anal. $C_{32}H_{28}N_4P_2SPd$: calcd. C 57.4; H 4.18; N 8.37%; found C 57.12; H 4.08; N 8.02%. **IR** (KBr, main peaks): ν(C–C) + ν(C–N), 1537, 1481; ν (C–S), 836 m cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + [D_6]DMSO): δ = 8.45 (s, 1 H, H^8), 7.72(s, 1 H, H^2), 7.34–7.59 (m, dppp) ppm. **^{31}P NMR**: δ = 37.31, 34.45, 13.9 ppm.

Synthesis of [Pd(κ^2-N,S-puS)(dppb)] (4): A yellow compound (powder) formed over a period of one week. M.p. 280–290 °C. Yield: 70%. Anal. $C_{33}H_{30}N_4P_2PdS_2$: calcd. C 58.06; H 4.39; N 8.21%; found. C 58.00; H 4.35; N 8.35%. **IR** (KBr, main peaks): ν(C–C) + ν(C–N), 1550, 1440; ν (C–S), 810 s cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + [D_6]DMSO): δ = 8.46 (s, 1 H, H^8), 7.74 (s, 1 H, H^2), 7.43–7.65 (m, dppb) ppm. **^{31}P NMR**: δ = 32.08, 29.35, 9.39 ppm.

Synthesis of [Pt(κ^2-N,S-puS)(PPh_3)$_2$] (5): To the solid 1, 9-dihydro-purine-6-thione ($puSH_2$) (0.039 g, 0.116 mmol) suspended in dry benzene (5 cm^3) in a round bottomed flask was added a solution of platinic acid, H_2PtCl_6 (0.05 g, 0.116 mmol) in dry ethanol (15 cm^3) in the presence of Et_3N base (2 cm^3). The contents were stirred for 2 h until turbidity appeared and to this was added solid triphenylphosphine (PPh_3) (0.061 g, 0.232 mmol). The yellow solution was stirred overnight, and $Et_3NH^+Cl^-$ formed was filtered, and the filtrate was allowed to crystallize at room temperature. A yellow compound (powder) formed over a period of one week. M.p. 220–230 °C. Yield: 60%. Anal. $C_{41}H_{32}N_4PPtS_2$: calcd. C 55.4; H 3.46; N 6.53%; found C 55.21; H 3.25; N 6.22%. **IR** (KBr, main peaks): ν(C–C) + ν(C–N), 1560, 1440; ν(C–S), 810 s cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + [D_6]DMSO): δ = 8.5 (s, 1 H, H^8), 7.66 (s, 1 H, H^2), 7.40–7.60 (m, PPh_3) ppm. **^{31}P NMR**: δ = 31.24 ppm.

Complexes 6–8 were prepared similarly.

Synthesis of [Pt(κ^2-N,S-puS)(dppm)] (6): Yellowish orange compound (powder) formed over a period of one week. M.p. 230–240 °C. Yield: 70%. Anal. $C_{30}H_{24}N_4P_2PtS_2$: calcd. C 48.80; H 3.13; N 7.60%; found C 48.76; H 2.98; N 7.29%. **IR** (KBr, main peaks): ν(C–C) + ν(C–N), 1545, 1450; ν(C–S), 850w cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + [D_6]DMSO): δ = 8.45 (s, 1 H, H^8); 7.22 (s, 1 H, H^2), 6.50–6.90 (m, dppm) ppm. **^{31}P NMR**: δ = 32.46 ppm.

Synthesis of [Pt(κ^2-N,S-puS)(dppp)] (7): Dark yellow crystals formed over a period of one week and turned opaque in the absence of solvent. M.p. 260–270 °C. Yield: 70%. Anal. $C_{32}H_{28}N_4P_2PtS_2$: calcd. C 50.22; H 3.30; N 7.42%; found C 50.01; H 3.17; N 7.10%. **IR** (KBr, main peaks): ν(C–C) + ν(C–N), 1520, 1460; ν (C–S), 805 s, 850 m cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + [D_6]DMSO): δ = 8.50 (s, 1 H, H^8), 7.70 (s, 1 H, H^2), 6.50–7.51 (m, dppp) ppm. **^{31}P NMR**: δ = 29.98 ppm.

Synthesis of [Pt(κ^2-N,S-puS)(dppb)] (8) : Yellow crystals formed over a period of one week. M.p. 270–280 °C. Yield: 70%. Anal. $C_{33}H_{30}N_4P_2PtS_2$: calcd. C 51.3; H 3.89; N 7.26%; found C 50.95; H 3.35; N 7.35%. **IR** (KBr, main peaks): ν(C–C) + ν(C–N), 1550, 1445; ν (C–S), 850 w cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + [D_6]DMSO): δ = 8.50 (s, 1 H, H^8), 7.66 (s, 1 H, H^2), 6.64–7.62 (m, dppb) ppm. **^{31}P NMR**: δ = 34.58 ppm.

Synthesis of [Cu(κ^2-N,S-puSH)(PPh_3)$_2$]·CH_3OH (9): To a solution of CuCl (0.050 g,0.50 mmol) in dry acetonitrile (5 mL) was added a suspension of 1,9-dihydro-purine-6-thione ($puSH_2$) (0.085 g, 0.50 mmol) in dry acetonitrile (15 mL). The contents were stirred when an orange solid compound formed, which was suspended in MeOH (10 mL), and afterwards a solution of triphenylphosphine (0.132 g, 1.01 mmol) in MeOH (15 mL) was added. The mixture was stirred for 5–6 h and yellow crystals formed at room temperature after a few days. The crystals were solvent stored, which become opaque

in the absence of solvent. M.p.150–160 °C. Yield: 65%, Anal. $C_{42}H_{38}N_4OP_2SCu$: calcd. C 65.30; H 4.92; N 7.25%; found C 65.00; H 4.78; N 7.22%. **IR** (KBr, main peaks): ν(C–H), 3049; ν(C–C) + ν(C–N), 1596, 1481; ν(C–S), 790 s cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + $[D_6]$DMSO): δ = 8.14 (s, 1 H, H^8), 7.68 (s, 1 H, H^2), 7.23–7.55 (m, PPh_3) ppm. **^{31}P NMR**: δ = 26.98 ppm.

Compound **10** was prepared similarly.

Synthesis of $[CuI(\kappa^1\text{-S-puSH}_2)(PPh_3)_2]\cdot H_2O$ (10): Light yellow crystals formed over a period of one week. M.p. 240–250 °C. Yield 65%. Anal. $C_{41}H_{36}N_4OP_2SCuI$: calcd. C 55.62; H 4.07; N 6.33%; found C 55.5; H 4.08; N 6.80%. **IR** (KBr, main peaks): ν(C–H), 3049; ν(C–C) + ν(C–N), 1537, 1477; ν(C–S), 836 s cm^{-1}. **^{1}H NMR** (*J*, Hz, $CDCl_3$ + $[D_6]$DMSO): δ = 8.25(s, 1 H, H^8); 7.14 (s, 1 H, H^2), 6.36–6.82 (m, PPh_3) ppm. **^{31}P NMR**: δ = 31.80, 0.69 ppm.

X-ray Crystallography: The data for crystals of **3**, **8**, and **10** were measured with a Bruker AXS SMART Apex CCD employing graphite monochromated Mo-K_α radiator (λ = 0.71073 Å) using ω scan, whereas that of **7** and **9** were measured with a X-calibur, Ruby Gemini CCD from Oxford diffraction using ω scan and employing graphite monochromated Cu-K_α (1.5418 Å). The data were reduced using the programs SAINT (Bruker) and CRYSALIS (Oxford's diffractometer). The data were corrected for Lorentz and polarization effects. A multi-scan absorption correction was applied for crystals measured on the Bruker diffractometer employing SADABS[35] in SAINT, whereas an analytical absorption correction was used for the crystals measured with the Oxford diffractometer using CRYSALISPRO.[36] The structures were solved by direct methods with SHELXTL.[37] The refinement was done by using SHELXL-97.[38] All structures were refined anisotropically for all the non-hydrogen atoms using full-matrix least-squares refinement on F_o^2. Hydrogen atoms were fixed geometrically with their isotropic thermal parameters' value 1.2 times that of the carrier methylene or phenylene carbon atoms, except for those belonging to the solvent water molecule in complex **8** and the hydrogen atoms attached to the nitrogen in purine-6-thione in **9** and **10**. These were located from the difference Fourier and were refined isotropically. In **9** and **10** these N–H bond lengths were restrained to 0.88(2) Å and given an U_{iso} value of 1.2 times that of the carrying nitrogen atom. The unit cell parameters and other refinement data for various crystals are given in Table 1. Complexes **3** and **7** are isomorphous and isostructural.

The structure of complex **3** showed rotational disorder for the ligand puS^{2-}, which was resolved by splitting of all of these atoms into two components with an occupancy ratio of 84% to 16%. The equivalent bond lengths within the two moieties were restrained to be the same within a standard deviation of 0.02 Å and the ADPs of the equivalent atoms were set to be equal. The final model of complex **7** shows residual electron density peaks ranging from 7.0 to 3.0 e very close to Pt^{II} metal ion (ca. 0.8 Å), which may be due to series termination error as the data are properly corrected for the absorption correction. Complex **8** was crystallized with one water and one ethanol solvent molecule, whereas **9** has one methanol solvent molecule in the asymmetric unit.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-845050 (**3**), -845051 (**7**), -845052 (**8**), -845054 (**9**), and -845055 (**10**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Results and Discussion

Synthesis and IR Spectra

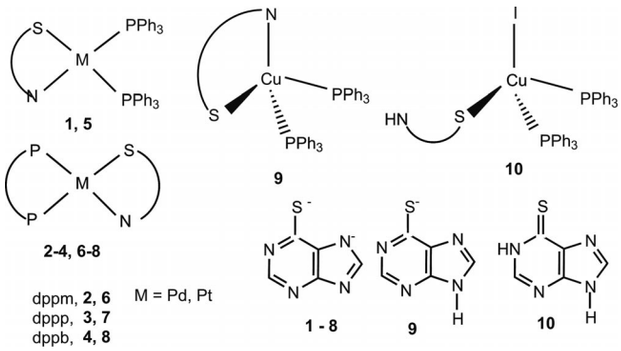
Complexes of 1,9-dihydro-purine-6-thione with Pd^{II}, Pt^{II}, and Cu^{I} are depicted below. For the preparation of complex

Table 1. Crystallographic data for complexes **3**, **7**, **8**, **9**, and **10**.

	3	**7**	**8**	**9**	**10**
Empirical formula	$C_{32}H_{28}N_4P_2PdS$	$C_{32}H_{28}N_4P_2PtS$	$C_{33}H_{30}N_4P_2PtS$ $C_2H_6OH_2O$	$C_{41}H_{33}CuN_4P_2SCH_4O$	$C_{41}H_{34}CuIN_4P_2S$
Formula weight (M)	668.98	756.67	771.70	771.30	867.16
T /K	100(2)	295(2)	295(2)	123(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1$	$P2_1/n$	$P2_1/n$
Unit cell dimensions /mm^3					
a /Å	10.6827(5)	10.7720(3)	10.9463(4)	9.1063(5),	11.2972(5)
b /Å	15.9905(8)	16.0467(4)	13.1054(5)	25.229(2)	14.6354(7)
c /Å	17.0646(8)	17.2701(4)	11.8560(4)	16.967(2)	22.5112(10)
α /°	90.0	90.00	90.0	90.0	90.0
β /°	104.757(1)	104.395(2)	99.629(1)	102.115(8)	98.931(1)
γ /°	90.0	90.00	90.0	90.0	90.0
V /Å^3	2818.9(2)	2891.50(13)	1676.85(11)	3811.2(6)	3676.9(3)
Z	4	4	2	4	4
λ /Å	Mo-K_α	Cu-K_α	Mo-K_α	Cu-K_α	MoK_α
$D_{calcd.}$ /mg·m^{-3}	1.576	1.740	1.528	1.344	1.567
μ /mm^{-1}	0.876	11.028	4.369	2.413	1.614
Unique reflections	6991	6035	5521	7979	8989;
R_{int}	0.0216	0.0706	0.0187	0.0377	0.0222
Reflections with $[I \geq 2\sigma(I)]$	6923	5592	5342	5888	8228
Final *R* indices $[I \geq 2\sigma(I)]$	*R*1 = 0.0623	*R*1 = 0.0975	*R*1 = 0.0340	*R*1 = 0.0577	*R*1 = 0.0277
	*wR*2 = 0.1277	*wR*2 = 0.2564	*wR*2 = 0.1078	*wR*2 = 0.1636	*wR*2 = 0.0717
R indices (all data)	*R*1 = 0.0627	*R*1 = 0.1018	*R*1 = 0.348	*R*1 = 0.0793	*R*1 = 0.0305
	*wR*2 = 0.1279	*wR*2 = 0.2611	*wR*2 = 0.1083	*wR*2 = 0.1961	*wR*2 = 0.0737

$[Pd(\kappa^2\text{-}N,S\text{-}puS)(PPh_3)_2]$ (**1**), $PdCl_2(PPh_3)_2$ was suspended in ethanol and reacted with 1,9-dihydro-purine-6-thione ($puSH_2$) in the presence of aqueous NaOH. It involved deprotonation of both NH hydrogen atoms of the purine ligand as well as removal of both chloride anions as NaCl salt and the thio ligand has bonded to the central metal atom as puS^{2-} dianion. Complexes $[Pd(\kappa^2\text{-}N^7,S\text{-}puS)(\kappa^2\text{-}P,P\text{-}L\text{-}L)]$ (**2**–**4**) were prepared similarly. In the preparation of complex **5**, reaction of H_2PtCl_6 in ethanol in the presence of Et_3N base with 1,9-dihydro-purine-6-thione suspended in dry benzene (2 cm^3) followed by addition of PPh_3 involving in situ reduction of Pt^{IV} to Pt^{II} and removal of hydrogen and halogen atoms as $Et_3NH^+Cl^-$ salt. Complexes $[Pt(\kappa^2\text{-}N^7,S\text{-}puS)(\kappa^2\text{-}P,P\text{-}L\text{-}L)]$ (**6**–**8**) were prepared similarly. Complexes **1** and **5** are similar to cations of $[Pd(\kappa^2\text{-}N,S\text{-}pymS)(PPh_3)_2](ClO_4)$[9] or $[Pt(\kappa^2\text{-}N,S\text{-}pyS)(PPh_3)_2](PF_6)\cdot CHCl_3$[12] having chelating thio ligands. Diphosphine complexes **2**–**4** and **6**–**8** have chelating 1,9-dihydro-purine-6-thiolate dianions and represent new type of heterocyclic –2-thiolate derivatives as in literature diphosphines have yielded only κ^1-S bonded complexes, namely, $[M(\kappa^1\text{-}S\text{-}pyS)_2(dppe)]$ (M = Pd, Pt)[10] and $[M(\kappa^1\text{-}S\text{-}pymS)_2(L\text{-}L)]$ (dppm Pt; dppe, Pd).[14] Both copper(I) chloride and copper(I) bromide with 1,9-dihydro-purine-6-thione lost halogen atoms and the thio ligand coordinated to Cu^I as anion in $[Cu(\kappa^2\text{-}N,S\text{-}puSH)(PPh_3)_2]\cdot CH_3OH$ (**9**), and there is no similar example of this type in copper-heterocyclic-2-thione chemistry.[1–6] Finally, copper(I) iodide, however, did not lose iodide and formed complex $[CuI(\kappa^1\text{-}S\text{-}puSH_2)(PPh_3)_2]\cdot H_2O$ (**10**), which is more common stoichiometry as observed in $[CuX(\kappa^1\text{-}S\text{-}pySH)(PPh_3)_2]$ (X = Cl, Br)[15,16] and $[CuX(\kappa^1\text{-}S\text{-}pymSH)(PPh_3)_2]$ (X = Cl, Br, I).[17–20]

Complexes **1**–**8** did not show signals in their IR spectra due to the ν(N–H) stretching frequency (free 1,9-dihydro-purine-6-thione, ν(N–H) = 3431 cm^{-1}), which revealed that this thio ligand is coordinating to the central Pd/Pt metal atoms as dianion probably through N^7,S donor atoms. In complexes **9** and **10**, the ν(N–H) bands appeared in the region of 3382–3440 cm^{-1}. The ν(C–S) bands in all complexes show low energy shifts to 790–860 cm^{-1} as compared to that in free ligand at 868 cm^{-1}supporting coordination through sulfur donor atoms.



Structures of Complexes

The important bond parameters for compounds **3**, **7**–**10** are given in Table 2. Complexes **1**, **2**, **4**, **5**, and **6** were crystalline powders, but single crystals could not be obtained.

Table 2. Selected bond lengths /Å and bond angles /° of complexes **3** and **7**–**10**.

3			
P(1)–Pd(1)	2.2981(12)	Pd(1)–S(1)	2.4157(14)
P(2)–Pd(1)	2.2484(11)	Pd(1)–S(1B)	2.631(9)
Pd(1)–N(1)	2.066(4)	Pd(1)–N(1B)	1.899(19)
C(31)–S(1)	1.760(5)	C(31B)–S(1B)	1.758(17)
P(1)–Pd(1)–S(1)	170.60(4)	N(1)–Pd(1)–S(1)	86.10(12)
P(2)–Pd(1)–N(1)	172.77(12)	P(2)–Pd(1)–S(1)	87.05(4)
P(2)–Pd(1)–P(1)	89.31(4)	N(1)–Pd(1)–P(1)	97.81(12)
N(1B)–Pd(1)–P2	109.1(6).	N(1B)–Pd(1)–P(1)	160.0(6)
P(1)–Pd(1)–S(1B)	80.77(16)	N(1B)–Pd(1)–S(1B)	81.5(6)
P(2)–Pd(1)–S(1B)	168.81(16)		
7			
Pt(1)–P(2)	2.286(3)	Pt(1)–S(1)	2.414(3)
Pt(1)–P(1)	2.243(3)	Pt(1)–N4A	2.107(12)
S(1)–C(1A)	1.744(13)		
P(2)–Pt(1)–S(1)	172.14(12)	N4A–Pt(1)–S(1)	86.3(4)
P(1)–Pt(1)–N4A	173.5(4)	P(1)–Pt(1)–S(1)	87.62(11)
P(2)–Pt(1)–P(1)	90.19(11)	P(2)–Pt(1)–N4A	96.1(4)
8			
Pt(1)–P(2)	2.277(2)	Pt(1)–S(4)	2.385(2)
Pt(1)–P(1)	2.256(2)	Pt(1)–N(1)	2.119(6)
S(4)–C(32)	1.735(9)		
P(2)–Pt(1)–S(4)	175.96(8)	N(1)–Pt(1)–S(4)	85.30(19)
P(1)–Pt(1)–N(1)	165.4(3)	P(1)–Pt(1)–S(4)	85.18(7)
P(2)–Pt(1)–P(1)	93.86(7)	P(2)–Pt(1)–N(1)	96.38(19)
9			
Cu(1)–N(1)	2.130(3)	Cu(1)–P(2)	2.263(1)
Cu(1)–P(1)	2.276(1)	Cu(1)–S(1)	2.439(1)
S(1)–C(1)	1.718(4)		
P(1)–Cu(1)–S(1)	101.79(4)	N(1)–Cu(1)–P(1)	108.61(11)
P(2)–Cu(1)–S(1)	117.80(4)	N(1)–Cu(1)–P(2)	108.14(10)
P(2)–Cu(1)–P(1)	125.80(4)	N(1)–Cu(1)–S(1)	88.20(10)
10			
Cu(2)–P(2)	2.2750(5)	Cu(2)–S(5)	2.3574(5)
Cu(2)–P(1)	2.2788(5)	Cu(2)–I(1)	2.6842(3)
S(5)–C(37)	1.6797(18)		
P(2)–Cu(2)–P(1)	121.761(19)	P(1)–Cu(2)–S(5)	107.999(18)
P(2)–Cu(2)–S(5)	101.321(18)	S(5)–Cu(2)–I(1)	108.719(14)
P(2)–Cu(2)–I(1)	112.338(15)	P(1)–Cu(2)–I(1)	104.207(14)

Palladium / Platinum Complexes

The crystal structure of complex $[Pd(\kappa^2\text{-}N^7,S\text{-}puS)(dppp)]$ (**3**) has shown that palladium is bonded to two phosphorus atoms of dppp ligand, one nitrogen and one sulfur atom of the thio ligand (Figure 1; disorder in the thio ligand). The dppp ligand is P,P-donor forming a six-membered chelate ring, and likewise 1,9-dihydro-purine-6-thiolate is N^7,S-donor (dianion) and forms a five-membered chelate ring. This coordination behavior is in contrast to that shown by η^1-S-bonded pyridine-2-thiolate in $[M(\kappa^1\text{-}S\text{-}pyS)_2(dppe)]$ (M = Pd, Pt),[10] or pyrimidine-2-thiolate in $[M(\kappa^1\text{-}S\text{-}pymS)_2(L\text{-}L)]$ (dppm Pt; dppe,

Pd).[14] The coordination pattern in **7** and **8** is similar (Figure 2 and Figure 3). The *trans* bond angles, P–M–N are 172.77, 173.5, and 165.4°, and likewise P–M–S bond angles (M = Pd, Pt) are 170.60, 172.13, and 175.96° in **3**, **7**, and **8**, respectively. This shows that dppb forming a seven-membered chelate ring in **8** makes the largest variation in the *trans* bond angles. These opposite bond angles (P–M–P and N–M–S) vary in the complementary fashion. The angles around central metal atoms reveal a distorted square-planar arrangement around a central metal atom. The M–P bond lengths *trans* to sulfur atoms are somewhat longer than the ones *trans* to M–N bond, probably due to the greater *trans* effect shown by the sulfur donor atom. The bond lengths (M–P, M–S, M–N) are similar to the literature values observed in the analogous complexes.[10,11,14]

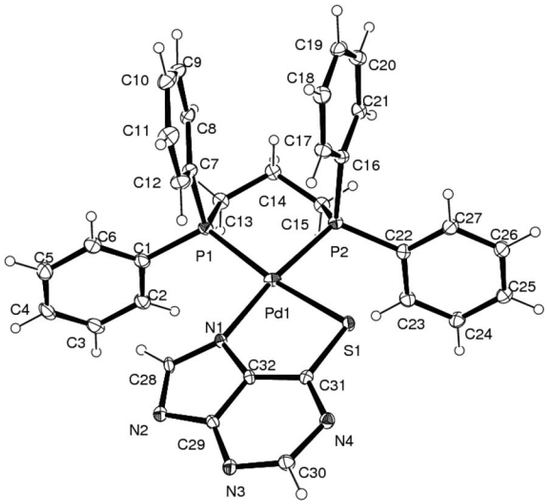


Figure 1. Molecular structure of [Pd(η^2-N^7,S-puS)(dppp)] (**3**). Only one part of the disordered atoms of purine-6-thione are shown.

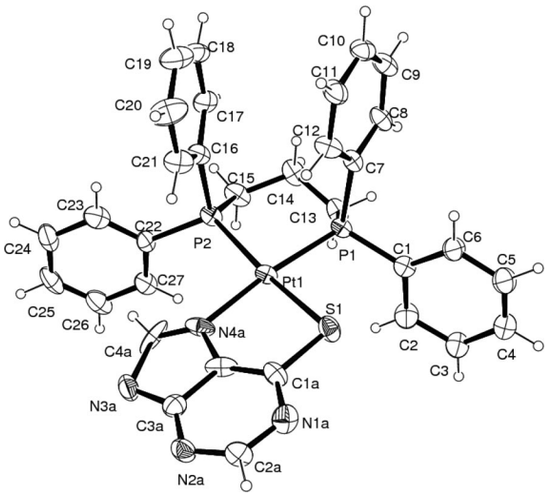


Figure 2. Molecular structure of [Pt(η^2-N^7,S-puS)(dppp)] (**7**).

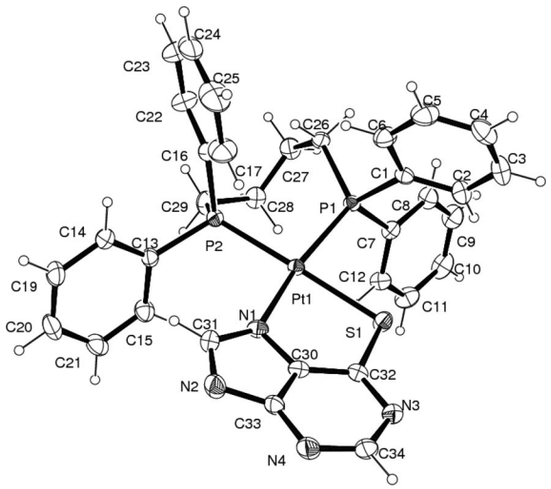


Figure 3. Molecular structure of [Pt(η^2-N^7,S-puS)(dppb)] (**8**). Solvent molecules are omitted for clarity.

Copper Complexes

Complex [Cu(κ^2-N^7,S-puSH)(PPh_3)$_2$]·CH_3OH (**9**) obtained using copper(I) chloride and 1,9-dihydro-purine-6-thione was same as that obtained using copper(I) bromide. The 1,9-dihydro-purine-6-thiolate is chelating to copper(I) by its N^7 and S donor atoms, whereas the other two positions are occupied by phosphorus donor atoms of two PPh_3 ligands. In this complex, copper(I) is coordinated to one nitrogen (N^7) atom, one sulfur ($puSH^-$ anion), and two phosphorus atoms of two triphenyl phosphine ligands (Figure 4). The angles around copper atom lie in the range of 88–127°, and reveal that the arrangement around copper is severely distorted tetrahedral (Table 2). In complex [CuI(κ^1-S-puSH$_2$)(PPh_3)$_2$] (**10**) copper is coordinated to one sulfur atom of neutral $puSH_2$, one iodine atom, and two phosphorus atoms of two triphenyl phosphine ligands (Fig-

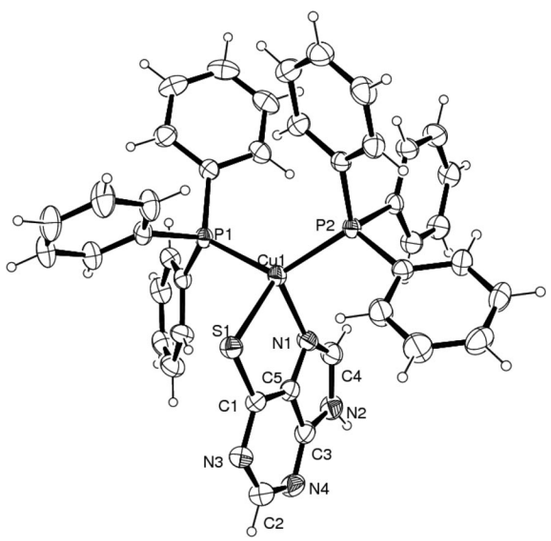


Figure 4. Molecular structure of [Cu(η^2-N^7,S-puSH)(PPh_3)$_2$]·CH_3OH (**9**). Solvent molecules are omitted for clarity.

ure 5). The angles around copper (101–122°) reveal a distorted tetrahedral structure. The Cu–S, Cu–N, and Cu–P bond lengths fall in the similar ranges as observed with copper complexes reported in the literature.[15–21]

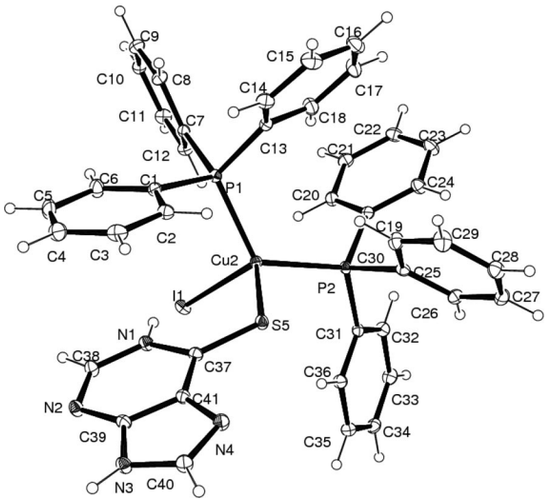


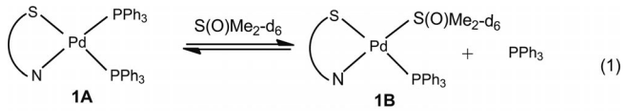
Figure 5. Molecular structure of [CuI(η^1-S-puSH$_2$)(PPh$_3$)$_2$] (**10**).

Variation in C–S Bond Lengths

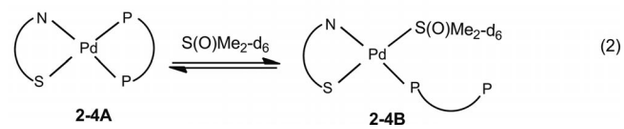
It is interesting to note that complexes **3**, **7**, and **8** have C–S bond lengths of 1.760(5), 1.744(13), and 1.735(9) Å, respectively, which are significantly longer than the C=S double bond length of 1.62 Å, but shorter than a C–S single bond length of 1.81 Å[39,40] suggesting partial double bond character in the C–S bonds. Likewise complex **9** has shown C–S bond length of 1.718 Å, which is shorter than the similar distances observed in complexes **3**, **7**, and **8**. Finally, complex **10** has shown a C–S distance of 1.680(2) Å. It is concluded that when the thio ligand coordinates as a neutral ligand, the decrease in C–S bond length is small (**10**), which increases when the ligand is uninegative (**9**) and it further increases when it is dinegative (**3**, **7**, and **8**).

NMR Spectroscopy

The ^{1}H NMR spectrum of purine-6-thione in [D$_6$]DMSO showed two signals at δ = 7.10 and 7.75 ppm due to H^2 and H^8 protons, respectively, which shifted to the low field region in complexes. The ligand did not show signals due to N–H^1 and N–H^9 protons probably due to quadrupolar nitrogen atoms and thus the same signals expected in complexes **9** (N–H^9) and **10** (N–H^1 and N–H^9) could not be observed. The phenyl proton signals of the phosphine groups showed up as multiplets in the broad range of 6.36–7.68 ppm. Complex **1** showed two ^{31}P NMR signals and it shows that this complex in the presence of [D$_6$]DMSO solvent forms more than one species (Equation (1)). The signal at δ = 26.5 ppm is assigned to species **1**A, whereas that at –8.25 ppm is assigned to species **1**B. The species **1**A and the solvent [D$_6$]DMSO are in equilibrium with species **1**B and free PPh$_3$. A similar situation is observed for compound **2** with a chelating dppm ligand (Equation (2)). Here dppm appears to recombine replacing [D$_6$]DMSO more quickly. Complexes **3** and **4** showed three signals each and it appears that due to the increased ring size of dppp and dppb ligands, the rate of recombination of pendant P-donor ends is slow. Complexes **5**–**9** showed one ^{31}P NMR signal each in the region of ca. 29–35 ppm with coordination shifts ($\Delta\delta$) in the range of ca. 32–40 ppm (Table 3). It revealed equivalent chemical environments around each phosphorus donor atom with more inert Pt–P bonds. Whereas complex **9** showed one ^{31}P NMR signal, there were two signals shown by complex **10**, probably due to formation of species similar to complex **1**.



(1)



(2)

Conclusions

1,9-Dihydro-purine-6-thione with Pd^{II}/Pt^{II} has formed a new type of neutral complexes of stoichiometry, [M(κ^2-N^7,S-puS)-L$_2$] {L$_2$ = 2PPh$_3$ (**1**, **5**); L$_2$ = Ph$_2$P–(CH$_2$)$_m$–PPh$_2$, m = 1, 3, 4 (**2**–**4** and **6**–**8**)}, in which the thio ligand is N,S-chelating as a dianion. In literature, Pd^{II}/Pt^{II} complexes are either ionic

Table 3. ^{31}P NMR spectroscopic data (δ in ppm) of complexes **1**–**10**.

Complex	δ_P	$\Delta\delta = \delta_C - \delta_L$	$\Delta\delta = \delta_C - \delta_L$ for other species	Remarks
1	26.5, –8.3	31.2	–3.6	species **1**A, **1**B
2	27.8, 22.7	32.4	27.4	species **2**A, **2**B
3	27.3, 34.5, 13.9	42.0	39.2, 18.6	species **3**A, **3**B
4	32.1, 29.4, 9.4	36.7,	34.1, 14.1	species **4**A, **4**B
5	31.2	35.9	–	single species
6	32.5	37.2	–	single species
7	30.0	31.7	–	single species
8	34.6	39.3	–	single species
9	27.0	31.7	–	single species
10	31.8, 0.7	36.5	5.4	two species

$[M(\kappa^2\text{-N,S-L}')L_2]^+$ {L_2 = $2PPh_3$,[9,12] or κ^1-S-bonded $[M(\kappa^1\text{-S-L}')_2L_2]$; L_2 = $Ph_2P\text{–}(CH_2)_2\text{–}PPh_2$}.[10,14] With copper(I) chloride/bromide, 1,9-dihydro-purine-6-thione formed the product $[Cu(\kappa^2\text{-N}^7\text{,S-puSH})(PPh_3)_2]$ (**9**) with N,S-chelating anion, and there is no similar example of this type in copper-heterocyclic thioamide chemistry. Finally with copper(I) iodide, 1,9-dihydro-purine-6-thione has formed a tetrahedral complex, $[CuI(\kappa^1\text{-S-puSH}_2)(PPh_3)_2]$ (**10**).

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