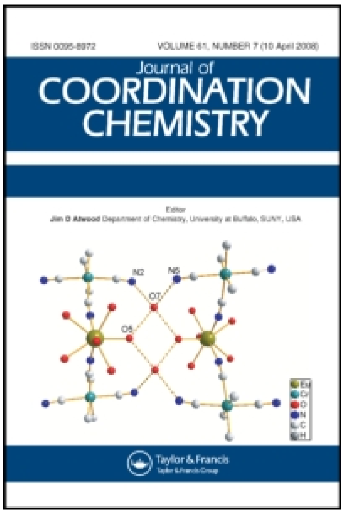

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Complexes of 1-hydroxopyridine-2-thione (LH) with Rh(III), Pd(II), Cd(II) and Hg(II): crystal structure of $Pd(L)_2 \cdot CHCl_3$

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Complexes of 1-hydroxopyridine-2-thione (LH) with Rh(III), Pd(II), Cd(II) and Hg(II): crystal structure of $Pd(L)_2 \cdot CHCl_3$

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The interactions of 1-hydroxopyridine-2-thione or 2-mercaptopyridine *N*-oxide (LH) with transition and d^{10} metal ions have been investigated. The complexes $[RhL_3]$ and $[ML_2]$ ($M = Pd$, Cd and Hg) were characterized by physicochemical and spectroscopic methods. The *bis*(1-oxopyridine-2-thionato)palladium(II) chloroform solvate crystallizes in space group $Pna2_1$ with $a = 9.1569(15)$, $b = 21.306(3)$, $c = 8.4618(14)$ Å, $Z = 4$. The structure can be described in terms of rows of *bis*(2-mercaptopyridine *N*-oxide) palladium(II) molecules which alternate with another row of molecules at an angle of approximately 24.9°. The coordination geometry about palladium(II) is nearly square-planar.

Keywords: 1-Hydroxopyridine-2-thione; Complexes; Crystal structure

1. Introduction

LH can bond to metal through its S and O atoms in a bidentate fashion or can also link two metal centers through its S in bridging mode and allows the isolation of low oligomeric compounds. Interest in thiolato transition metal complexes arises in part from the fact that the thiolato group mimics the ligation of cysteinyl residues in proteins [1]. Zhu *et al.* [2–5] found that some simple metal complexes, particularly those of palladium containing sulfur ligands, possess the ability of selective-hydrolytic cleavage of proteins and peptides. The regioselectivities of these hydrolyses vary with substrate. The mechanisms are complicated and it is not clear whether the palladium(II) activates the C–N bond, or delivers H_2O. Since structures with both Pd–S and Pd–O bonds in the same molecule are rare, more examples may help to elucidate the reaction mechanism. In addition, LH possesses antifungal and bactericidal activity and some metallic complexes containing L as a ligand were also found to be biologically active [6]. The present contribution reports the synthesis and characterization of new metal complexes containing 1-hydroxopyridine-2-thione which has been found to be a bifunctional ligand in its ligation to transition metals.

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2. Experimental

2.1. *Physical measurements*

Conductance measurements were made using a Wayne Kerr Universal Bridge. The conductivity cell was calibrated with aqueous KCl. IR spectra of the ligand and its metal complexes as KBr pellets were recorded in the 4000–400 cm^{-1} range with a Perkin-Elmer Series 2000 spectrophotometer. UV-Vis spectra were recorded using a Perkin-Elmer recording spectrometer. C, H, N and S were analyzed on a LECO CHNS 932 model microanalytical instrument. Cadmium(II) content was determined with a Perkin-Elmer atomic absorption spectrophotometer in solutions prepared by decomposition of the complex by conc. HCl and conc. HNO_3 (3 : 1) solution followed by dilution with water. Magnetic susceptibility was measured on a Johnson Matthey Susceptibility Balance at room temperature using mercury(II) tetrathiocyanato-cobaltate(II) as calibrant. ^1H NMR spectra were recorded on a Varian mercury-Vx 300 MHz instrument; samples were analyzed in dimethylsulfoxide-d_6 solutions.

2.2. *Materials*

A published method was used to prepare 1-hydroxopyridine-2-thione [7]. Solvents were distilled over appropriate drying agents prior to use. All other chemicals were commercial materials and of analytical grade. Unless otherwise stated the reactions were carried out under dry nitrogen.

2.3. *Preparation of RhL_3*

The rhodium(III) complex was prepared by mixing LH (3 mmol) with $RhCl_3$ (1 mmol) in dry ethanol (30 mL) with magnetic stirring for 24 h. This solution, after stirring, was left standing for evaporation of the solvent at room temperature, and in two weeks, a light brown solid was obtained. Yield 52%. Anal. Calcd for $[C_{15}H_{12}N_3O_3S_3Rh]$%: C, 37.43; H, 2.50; N, 8.73; S, 19.96. Found: C, 37.26; H, 2.81; N, 8.43; S, 19.58. No single crystals of the complex were obtained, even after several attempts.

2.4. *Preparation of $PdL_2 \cdot CHCl_3$*

The palladium(II) complex was synthesized by reaction of 2 mmol of a freshly prepared warm ethanolic solution of LH with a warm ammonia solution of $PdCl_2$ containing 1 mmol of the metal salt. A pale rose solid formed immediately, was filtered, washed with ethanol and ethyl ether, and dried in a desiccator over P_4O_{10}. Yield 75%. Anal. Calcd for $[C_{10}H_8N_2O_2S_2Pd]$%: C, 33.48; H, 2.23; N, 7.81; S, 17.86. Found: C, 33.40; H, 2.21; N, 7.77; S, 18.20. The solid (0.5 g) obtained was then dissolved in chloroform (10 mL) and left standing at room temperature during a week. Red crystals of $[C_{10}H_8N_2O_2S_2Pd] \cdot CHCl_3$ suitable for X-ray diffraction were obtained.

2.5. *Preparation of ML_2 (M = Cd, Hg)*

Metal(II) complexes were prepared by mixing HL (2 mmol) with MCl_2 (1 mmol) in dry ethanol (20 mL) with magnetic stirring at room temperature for 48 h. White solids of the complexes slowly precipitated. The complexes were filtered, washed with ethanol and ethyl ether, and dried in a dessicator over P_4O_{10}. Anal. Calcd for $[C_{10}H_8N_2O_2S_2Cd]$%: C, 32.93; H, 2.19; N, 7.68; S, 17.56; Cd, 30.85. Found: C, 33.40; H, 2.17; N, 7.72; S, 17.66; Cd, 31.15. Anal. Calcd for $[C_{10}H_8N_2O_2S_2Hg]$%: C, 26.51; H, 1.77; N, 6.19; S, 14.14. Found: C, 26.72; H, 2.12; N, 6.37; S, 14.35. The yields were quantitative. No single crystals of the complexes were obtained, even after several attempts.

2.6. *X-ray crystallography*

For X-ray structural determination a single crystal of dimensions $0.4 \times 0.3 \times 0.3\,\mathrm{mm}^3$ was sealed in a glass capillary. X-ray data were collected on a Siemens SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 45 kV and 40 mA. The data collection covered about 1.3 hemisphere of reciprocal space by a combination of three sets of exposures, each set having a different φ angle (0, 90, 180°) for the crystal and each exposure of 10 s covered 0.3° in ω to give a total of 1321 frames. The crystal-to-detector distance was 5.029 cm and the detector swing angle was −30°. Coverage of the unique set was over 99% complete. Crystal decay was monitored by repeating fifty frames from the initial set at the end of the data collection. Analysis of the duplicate reflections indicated that crystal decay was less than 2%. Unit cell parameters were determined by a least-squares fit of 921 reflections in the range $5.86° < 2\theta < 56.54°$. Absorption and other corrections were made using *SADABS* [8].

Preliminary positions for the non-hydrogen atoms were obtained with the direct methods routine of SHELXS-97 [9]. The refinement of atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms was carried out by full matrix least squares with SHELXL-97 [10]. Hydrogen atoms in the 2-mercaptopyridine *N*-oxide ligand were identified in the difference Fourier maps but were included in calculated positions using a riding model with aromatic C–H distances maintained at 0.93 Å. The isotropic thermal parameters for all hydrogen atoms were restricted to be equal to 1.2 times the U_{eq} of the parent carbon atom. As is common for chloroform containing complexes, the solvent is disordered. The refinement of the disordered model produced two positions for the chloroform molecule with occupancies of 0.48 and 0.52.

3. Results and discussion

Elemental analyses agree with the proposed formula of the complexes, which are colored, air-stable solids, soluble in DMSO and DMF, slightly soluble in MeCN and insoluble in MeOH and water. The experimental conductivity values measured in DMSO at room temperature fall in the range of non-electrolytes [11]. Attempts to form complexes of a well defined stoichiometry, in the above mentioned conditions, with silver(I), tin(II), platinum(II), iridium(III) and lead(II) were unsuccessful.

The IR spectral data for ligand and complexes have been assigned according to West and Frank [12] and reveal expected absorptions. Phenyl ν_{CH} vibrations are observed at 3000–3100 cm^{-1}. The absence of bands attributable to ν(O–H) confirms that the H is lost during reaction. Deprotonation of the ligand and subsequent coordination to the metals produce a shift of about 10–15 cm^{-1} for (N–O) to higher wavelengths with respect to the free ligand (1185 cm^{-1}). The absorptions in the free ligand at 835 and 712 cm^{-1}, attributable to δ(N–O) and ν(C–S), respectively, are shifted to lower wavelengths on coordination. This behavior is similar to that found in other compounds where the ligand is coordinated in the anionic form via O and S atoms, confirming bidentate ligand in all cases [13].

The UV–visible spectra of the ligand and its complexes in DMSO have two absorption maxima at 322 and 350 nm which have their origin in the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions within the organic ligand. The ground state of diamagnetic rhodium(III), $(t_{2g})^6$, is $^1A_{1g}$. The excited states, corresponding of $(t_{2g})^5(e_g)^1$ configuration, are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ in order of increasing energy. Hence, four bands are possible corresponding to the $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions. In the electronic spectrum of the complex, we observed two bands at 390 and 640 nm. The band at longer wavelength has been assigned to the spin allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition [14, 15]. The band at 390 nm has been assigned to the charge-transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbitals derived from the π^* level of the ligand, in accordance with the assignments made for other similar octahedral rhodium(III) complexes [16]. The ground state of diamagnetic palladium(II), $(e)^4(a_1)^2(b_2)^2$, is $^1A_1$. The excited states are $^1A_2$, $^1B_1$ and ^1E in order of increasing energy. The observed singlet-singlet absorptions and the assignments for the palladium(II) complex considering low spin *cis* square-planar C_{2v} geometry are 540 nm ($^1A_1 \rightarrow {}^1A_2$), 420 nm ($^1A_1 \rightarrow {}^1B_1$) and 380 nm, which may have charge transfer character.

The magnetic susceptibility measurements of dry solid samples measured using a digital balance at room temperature show that RhL_3 and ML_2 (M = Pd, Cd and Hg) complexes are diamagnetic, suggesting that the palladium(II) complex has square-planar structure.

The ^1H NMR spectra of complexes show that the singlet at 12.1 ppm of the free ligand is absent, indicating deprotonation and the ligand coordinated in the thionato form. Spectra of the complexes show four distinct, widely separated signals of equal intensity corresponding to the aromatic protons of the ligand moiety between 7.0 and 8.5 ppm, in agreement with the results reported by Davinson *et al.* [17].

3.1. *Crystal structure*

A search of the Cambridge Structural Database using ConQuest Version 1.4 [18] resulted in sixty-two reports of metal complexes with the 2-mercaptopyridine *N*-oxide ligand. The more closely related are palladium [19], nickel [20, 21], cobalt [22] and platinum [23]. The Pd complex reported ($P2_1/n$, unit cell parameters $a = 8.709(1)$, $b = 14.060(2)$, $c = 10.025(1)$ Å, $\beta = 96.79(1)°$) was prepared by three different routes using MeOH/MeCN in two synthesis and CH_2Cl_2 in one experiment, and recrystallizing from DMF in two of them. However, it does not contain solvent of crystallization. Similar to the previous structure [19], in *bis*(2-mercaptopyridine *N*-oxide) palladium(II) chloroform solvate, the Pd is nearly square-planar. An ORTEP drawing, including the atomic numbering scheme, is given in figure 1. The 2-mercaptopyridine *N*-oxide ligands coordinate *cis* with Pd–O distances of 2.036(3) and 2.040(3) Å and Pd–S distances of 2.2336(12) and 2.2361(13) Å. The bite angles S1–Pd1–O1 and S2–Pd1–O2 are 86.61(8) and 86.40(9)°, respectively.

Figure 2(a) shows a view of the structure down the *a*-axis, including the disordered chloroform molecules. A calculation using PLATON [24] of the per cent filled space without taking into consideration the chloroform molecules gave 52.8%. When the chloroform molecule is included, the calculated per cent filled space is 69.2% but after refinement of the disordered model, there are no solvent accessible voids.

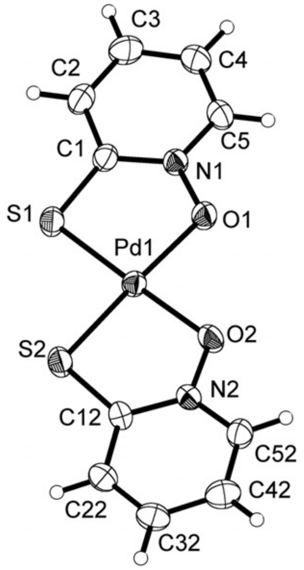

Figure 1. ORTEP view of the structure of PdL_2 including the atom numbering scheme.

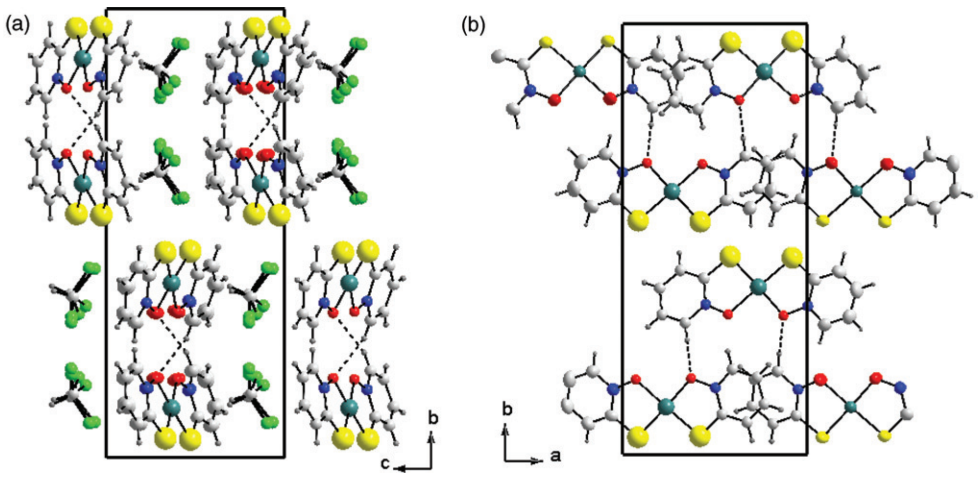

Figure 2. View of the (a) structure of *bis*(2-mercaptopyridine *N*-oxide)palladium(II)chloroform solvate down the *a* axis; (b) hydrogen bonding pattern in *bis*(2-mercaptopyridine *N*-oxide)palladium(II)chloroform solvate. Chloroform molecules were omitted for clarity.

Table 1. Crystallographic data for $[Pd(C_{10}H_8N_2O_2S_2)] \cdot CHCl_3$.

Empirical formula	$C_{10}H_8N_2O_2PdS_2 \cdot CHCl_3$
Formula weight	478.11
Crystal system	Orthorhombic
Space group	$Pna2_1$ (No. 33)
Unit cell parameters (Å)	
a	9.1569(15)
b	21.306(3)
c	8.4618(14)
V (Å^3)	1650.9(4)
Z	4
D_{calcd} (g cm^{-3})	1.924
$F(000)$	936
Scan type	ω scans
θ Min-max (°)	1.9, 28.3
Data set collected	$-12 \le h \le 11$; $-28 \le k \le 27$; $-6 \le l \le 11$
Number of reflections collected	9660
Unique data	2984
R_{int}/R	0.0459 (2984 refxs.)/0.02488
Observed data [$I > 2.0\sigma(I)$]	2842
Absorption correction	SADABS/$T_{min} = 0.514/T_{max} = 1.000$
$R(F)/wR(F^2)/S$	0.0316/0.0865/1.04
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.6303P]$ where $P = (F_o^2 + 2F_c^2)/3$
Max. and av. shift/error	0.00, 0.00
Flack × parameter	0.04(4)
Min. and max. resd. dens. (e Å^{-3})	−0.71, 071

Table 2. Selected bond lengths (Å) and angles (°) for $[Pd(C_{10}H_8N_2O_2S_2)] \cdot CHCl_3$.

Pd–O2	2.040(3)	S1–C1	1.725(5)
Pd–S1	2.2336(12)	S2–C12	1.727(5)
Pd–S2	2.2361(13)	O1–N1	1.360(5)
Pd–O1	2.036(3)	O2–N2	1.354(5)
S1–Pd–O1	86.61(8)	S1–Pd–O2	178.50(10)
S2–Pd–O1	177.98(10)	S2–Pd–O2	86.40(9)
O1–Pd–O2	91.92(12)	S1–Pd–S2	95.07(4)
Pd–S1–C1	97.65(15)	Pd–S2–C12	97.93(16)
Pd–O1–N1	114.8(2)	Pd–O2–N2	114.7(2)

The structure can be described in terms of rows of *bis*(2-mercaptopyridine *N*-oxide)palladium(II) molecules which alternate with another row of molecules at an angle of approximately 24.9° (figure 2b). The two rows interact via hydrogen bonds between C52–H52 and the O1 atom from a molecule at $1/2 + x$, $3/2 - y$, z [H52 ··· O1 2.4100 Å, C52 ··· O1 3.302(6) Å, C52–H52 ··· O1 162.00°] to form a ribbon which runs approximately along *a*. A similar ribbon repeats along *b* making an angle of 35.2° with the first one. When viewed down *a*, the rows form columns which intercalate with the disordered $CHCl_3$ molecules along the *c*-axis. An additional contact between the chloroform hydrogen and the S2 atom of a complex at $1 - x$, $1 - y$, $1/2 + z$ [H6B ··· S2 2.770 Å, C6B ··· S2 3.671(16) Å, C6B–H6B ··· S2 154.00°] is evident after refinement of the chloroform molecule in a disordered model. A summary of crystal data, data collection, and structure refinement results is presented in table 1. Selected bond distances and angles and potential hydrogen bonds, obtained with the program PLATON, are summarized in tables 2 and 3.

Table 3. Hydrogen bond geometry for $[Pd(C_{10}H_8N_2O_2S_2)] \cdot CHCl_3$. D represents the donor atom and A the acceptor atom.

D–H–A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (°)
C52–H52–O1^{i}	0.9300	2.4100	3.302(6)	162.00
C6B–H6B–S2^{ii}	0.9800	2.7700	3.671(16)	154.00

(i) $1/2+x$, $3/2-y$, z; (ii) $1-x$, $1-y$, $1/2+z$.

Supplementary material

File CCDC 283827 contains the crystallographic data for this article. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Rd, Cambridge CB2 1EZ, UK (Fax: +44(0)1223 336033; Email: deposit@ccdc.cam.ac.uk).

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