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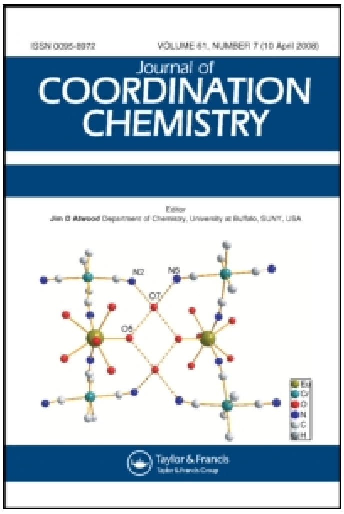

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SEVEN-COORDINATE PYRIDINE-2-THIONE AND PYRIMIDINE-2-THIONE COMPLEXES OF MOLYBDENUM (II) TUNGSTEN (II)

Paul K. Baker[a]; Steven Hughes[a]
[a] Department of Chemistry, University of Wales, Bangor, Gwynedd, UK

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SEVEN-COORDINATE PYRIDINE-2-THIONE AND PYRIMIDINE-2-THIONE COMPLEXES OF MOLYBDENUM (II) TUNGSTEN (II)

PAUL K BAKER* and STEVEN HUGHES

Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, UK

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Equimolar quantities of $[WI_2(CO)_3(NCMe)_2]$ and pyridine-2-thione (pySH) or pyrimidine-2-thione (pymSH) react in CH_2Cl_2 at room temperature to give the dimeric complexes $[\{W(\mu\text{-}I)I(CO)_3(pySH)\}_2]$ (**1**) or $[\{W(\mu\text{-}I)I(CO)_3(pymSH)\}_2]\cdot 1/2CH_2Cl_2$ (**2**), respectively. Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with two equivalents of pySH (for M = Mo only) or pymSH in CH_2Cl_2 afforded the bis(ligand) complexes $[MoI_2(CO)_3(pySH)_2]$ (**3**), $[MoI_2(CO)_3(pymSH)_2]$ (**4**) or $[WI_2(CO)_3(pymSH)_2]\cdot CH_2Cl_2$ (**5**) respectively. Reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of PPh_3 or one equivalent of $Ph_2P(CH_2)_nPPh_2$ (n = 1 to 6) in CH_2Cl_2 at room temperature, followed by an *in situ* reaction with one equivalent of pySH yielded the cationic complexes $[WI(CO)_3(PPh_3)_2(pySH)]I$ (**6**) or $[WI(CO)_3\{Ph_2P(CH_2)_nPPh_2\}(pySH)]I$ (**7→12**), respectively.

KEYWORDS: molybdenum, tungsten, pyridine-2-thione, pyrimidine-2-thione, seven-coordination

INTRODUCTION

Several biologically important compounds exhibit tautomeries of the type-NH-C(X)-$\rightleftharpoons$N = C(XH)-(where X = O or S). Examples include the pyrimidine and purine bases and their thiolated nucleoside analogues. In view of this, there is considerable interest in the coordination chemistry of tautomeric thiones.[1] Two of the simplest and most versatile examples of heterocyclic thiones are pyridine-2-thione (pySH) and pyrimidine-2-thione (pymSH), which can be represented by the resonance forms shown in Figure 1.

The thiol tautomer (I), is considered to be of some importance in dilute cyclohexane solution,[2] and the thione tautomer (II) which is dominant in more polar solvents such as acetone and methanol.[3] Electronic[4,5] and infrared[6] studies suggest that the thione form is overwhelmingly preferred for pySH and, to a lesser extent, pymSH in most situations. The neutral ligand pySH could coordinate to a transition metal centre by one of four coordination modes, namely two for the thiol form (S or N bonded) and two for the thione form (S or N bonded). Previous studies[1,7,8] have shown that pySH coordinates exclusively *via* the S atom in the thione form.

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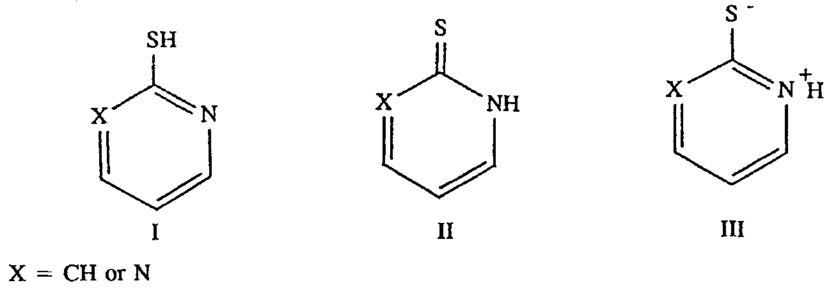

Figure 1 Resonance forms of pyridine-2-thione (pySH) and pyrimidine-2-thione (pymSH).

In order to further study the coordination chemistry of pyridine-2-thione and pyrimidine-2-thione we herein report the preparation and characterisation of the first examples of seven-coordinate molybdenum(II) and tungsten(II) complexes containing pySH or pymSH as ligands.

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EXPERIMENTAL

The syntheses and purifications of the complexes described in this paper were carried out under an atmosphere of dry nitrogen using standard Schlenk line techniques. All solvents were dried over phosphorus pentoxide (P_4O_{10}) distilled, and degassed before use. The starting complexes [$MI_2(CO)_3(NCMe)_2$] (M = Mo or W) were prepared according to the literature method.[9] All chemicals were obtained from commercial sources and used without further purification.

Elemental analyses (C, H and N) were determined using a Carlo Erba Elemental Analyser MOD 1106 with helium as the carrier gas. Iodide was determined by chemically-suppressed ion chromatography using a Dionex 2000i/SP Ion Chromatography system with conductivity detection. An IonPac AS4A analytical column was used for the separation of anions. The column comprised 15 micron polystyrene/divinylbenzene substrate agglomerated with anion exchange latex that is fully aminated. A $NaHCO_3$ (1.7 mM), Na_2CO_3 (1.8 mM) eluant, at a flow rate of 2 cm^3 min^{-1}, was used for the separation and elution of iodide. Potassium iodide was used for the preparation of standards for calibration. All standards and samples were prepared in the same matrix (0.1 M $NaHCO_3$). Tungsten was determined, on acid-digested complex, in solution by AAS using a Thermo Jarrell Ash Video 11E atomic absorbtion spectrophotometer. Tungsten was determined at a wavelength of 255.1 nm with Smith-Hieftje ('pulsing-lamp') background correction. A fuel-rich nitrous oxide-acetylene (N_2O/C_2H_2) flame was used for atomisation. Merck 'Spectrosol' tungsten standard solution (1000 mg dm^{-3}) was used as a stock solution for the preparation of standard solutions. All standard solutions, samples and blank solutions were prepared in an identical acid matrix. Similarly, molybdenum was analysed by flame AAS at a wavelength of 313.3 nm, again with Smith-Hieftje background correction, and with a fuel-rich, nitrous oxide-acetylene flame for atomisation.

^1H NMR spectra were recorded on a Bruker AC 250 NMR spectrometer referenced against tetramethylsilane as internal standard. Infrared spectra were either recorded in $CHCl_3$, as thin films between NaCl plates, or as nujol mulls, on a Perkin Elmer 1600 FTIR spectrophotometer. Molar conductance measurements were made using a standard laboratory conductivity meter, Jenway model 4070, referenced against a 10^{-3} M solution of KCl. All measurements were made in acetone under a nitrogen atmosphere at 25°C. Magnetic susceptibility measurements were obtained using a standard Johnson Matthey laboratory magnetic susceptibility balance.

[{W(μ-I)I(CO)$_3$(pySH)}$_2$] (1)

To $[WI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3, with continuous stirring, was added pyridine-2-thione (0.092 g, 0.828 mmol). After 2 hrs the solution was filtered through celite to remove insoluble material. Removal of solvent *in vacuo* followed by washing with diethyl ether (Et_2O) afforded a dark brown solid, $[\{W(\mu\text{-}I)I(CO)_3(pySH)\}_2]$ **(1)**, which was recrystallised from CH_2Cl_2; (yield = 0.31 g, 30%).

[{W(μ-I)I(CO)$_3$(pymSH)}$_2$]·1/2 CH$_2$Cl$_2$ (2)

To $[WI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3) with continuous stirring, was added pyrimidine-2-thione (0.093 g, 0.828 mmol). After 30 min. a wine-red precipitate was formed. Removal of solvent by syringe followed by washing with CH_2Cl_2/Et_2O yielded a deep-red solid, $[\{W(\mu\text{-}I)I(CO)_3(pymSH)\}_2]\cdot 1/2CH_2Cl_2$ **(2)**; (yield = 0.3 g, 27%).

[MoI$_2$(CO)$_3$(pySH)$_2$] (3)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.97 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring, was added pyridine-2-thione (0.215 g, 1.94 mmol). The solution turned dark-brown. After 1 hr, a dark brown/black precipitate was formed. Removed of solvent by syringe, followed by washing with Et_2O, yielded a dark brown solid as product, $[MoI_2(CO)_3(pySH)_2]$ **(3)**; (yield = 0.42 g, 66%).

[MoI$_2$(CO)$_3$(pymSH)$_2$] (4)

To $[MoI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.97 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring, was added pyrimidine-2-thione (0.217 g, 1.94 mmol). After 1 hr, a dark brown precipitate was formed. Removal of solvent by syringe, followed by washing with Et_2O, afforded a dark-brown solid, $[MoI_2(CO)_3(pymSH)_2]$ **(4)**; (yield = 0.4 g, 63%).

A similar reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of pymSH in CH_2Cl_2 at room temperature for 2 hrs. gave the brown solid, $[WI_2(CO)_3(pymSH)_2]\cdot CH_2Cl_2$ **(5)**. See Table 1 for physical and analytical data.

[WI(CO)$_3$(PPh$_3$)$_2$(pySH)]I (6)

To $[WI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring, was added PPh_3 (0.434 g, 1.65 mmol). The solution immediately turned green. After 10 min. pyridine-2-thione (0.092 g, 0.828 mmol) was

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Table 1 Physical and analytical data[a] for the pyridine-2-thione and pyrimidine-2-thione complexes of molybdenum(II) and tungsten(II).

	Complex	Colour	Yield (%)	W (%)	Mo (%)	Found (calcd.)% C	H	N	I^b (%)	I^{-b} (%)
(1)	$[(\mathrm{W}(\mu\text{-}\mathrm{I})\mathrm{I}(\mathrm{CO})_3(\mathrm{pySH})\}_2]$	Dark Brown	30			14.8 (15.2)	1.0 (0.8)	2.4 (2.2)		
(2)	$[\{\mathrm{W}(\mu\text{-}\mathrm{I})\mathrm{I}(\mathrm{CO})_3(\mathrm{pymSH})\}_2]\cdot\frac{1}{2}\mathrm{CH_2Cl_2}$	Deep Red	27	27.1 (18.1)		13.4 (13.3)	0.7 (0.7)	4.5 (4.3)		
(3)	$[\mathrm{MoI_2(CO)_3(pySH)_2}]$	Dark Brown	66		14.4 (14.6)	24.3 (23.8)	2.0 (1.5)	4.3 (4.3)		
(4)	$[\mathrm{MoI_2(CO)_3(pymSH)_2}]$	Dark Brown	63		13.9 (14.6)	20.1 (20.1)	1.5 (1.2)	9.1 (8.5)		
(5)	$[\mathrm{WI_2(CO)_3(pymSH)_2}].\mathrm{CH_2Cl_2}$	Brown	65	22.8 (22.1)		16.4 (17.3)	1.2 (1.2)	7.3 (6.7)		
(6)	$[\mathrm{WI(CO)_3(PPh_3)_2(pySH)}]\mathrm{I}$	Orange	68			47.2 (45.7)	3.4 (3.1)	1.2 (1.2)	21.5 (21.9)	
(7)	$[\mathrm{WI(CO)_3(dppm)(pySH)}]\mathrm{I}$	Orange	71			39.5 (39.0)	3.0 (2.7)	1.9 (1.4)		
(8)	$[\mathrm{WI(CO)_3(dppe)(pySH)}]\mathrm{I}$	Gold	78			39.8 (39.6)	3.1 (2.8)	1.6 (1.4)		
(9)	$[\mathrm{WI(CO)_3(dppp)(pySH)}]\mathrm{I}$	Brown	35			39.7 (40.2)	3.3 (3.0)	1.0 (1.3)	25.2 (24.3)	11.9 (12.2)
(10)	$[\mathrm{WI(CO)_3(dppb)(pySH)}]\mathrm{I}$	Brown	81			41.4 (40.8)	3.7 (3.1)	1.0 (1.3)		11.1 (12.0)
(11)	$[\mathrm{WI(CO)_3(dpppe)(pySH)}]\mathrm{I}$	Brown	75			42.4 (41.4)	3.6 (3.3)	1.2 (1.3)	23.9 (23.7)	12.2 (11.8)
(12)	$[\mathrm{WI(CO)_3(dpph)(pySH)}]\mathrm{I}$	Brown	62			42.2 (42.0)	3.6 (3.4)	1.4 (1.3)	24.2 (23.3)	11.3 (11.7)

[a] Calculated values are shown in parentheses (Analytical errors I and I^- = 3%; W and Mo = 5%). [b] The uncoordinated iodide, I^-, analysis was carried out in less than 1 min. in 0.1 M $NaHCO_3$ by ion chromatography, and the total, I, was analysed as iodide after 7 days in the same matrix.

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added *in situ*. The solution turned red. After 1 hr, the solution was filtered through celite to remove insoluble material and the solvent was removed *in vacuo*. Washing with Et_2O yielded an orange solid, $[WI(CO)_3(PPh_3)_2(pySH)]I$ **(6)**; (yield = 0.65 g, 68%).

$[WI(CO)_3(dppm)(pySH)]I$ (7)

To $[WI_2(CO)_3(NCMe)_2]$ (0.5 g, 0.828 mmol) dissolved in CH_2Cl_2 (15 cm^3), with continuous stirring, was added $Ph_2P(CH_2)PPh_2$ (dppm) (0.38 g, 0.828 mmol). The solution immediately turned red. After 10 min., pyridine-2-thione (0.092 g, 0.828 mmol) was added *in situ*. The solution turned brown. After stirring for 1 hr, the solution was filtered through celite, followed by the solvent being removed *in vacuo*. Washing with Et_2O yielded an orange solid, $[WI(CO)_3(dppm)(pySH)]I$ **(7)**; (yield = 0.6 g, 71%).

Similar reactions of $[WI_2(CO)_3(NCMe)_2]$ with an equimolar amount of $Ph_2P(CH_2)_nPPh_2$ (n = 2 → 6), in CH_2Cl_2 at room temperature, followed by an *in situ* reaction with one equivalent of pySH gave the cationic complexes $[WI(CO)_3\{Ph_2P(CH_2)_nPPh_2\}(pySH)]I$ **(8 → 12)**. See Table 1 for physical and analytical data.

RESULTS AND DISCUSSION

The starting materials used for this research, namely $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W)[9] are prepared by reacting the zero-valent complexes *fac*-$[M(CO)_3(NCMe)_3]$ (prepared *in situ* by reacting $[M(CO)_6]$ in refluxing acetonitrile[10]) with one equivalent of I_2 at 0°C. The reactions of $[WI_2(CO)_3(NCMe)_2]$ with one equivalent of pySH or pymSH in CH_2Cl_2 at room temperature gave the dimeric complexes $[\{W(\mu\text{-}I)I(CO)_3(\text{pySH or pymSH})\}_2]$ **(1** and **2)**. The complexes were characterised by elemental analysis {C, H, N and W (for pymSH)} (Table 1), infrared (Table 2), and ^1H NMR spectroscopy (Table 3). Both complexes **(1)** and **(2)** are reasonably stable in the solid state when stored under

Table 2 Infrared data[a,b] for the pyridine-2-thione and pyrimidine-2-thione complexes of molybdenum(II) and tungsten(II), cm^{-1}.

Complex	$\upsilon(C\equiv O)$	$\upsilon(C=C/C=N)$	$\upsilon(C=S)$
(1)[a]	2039(ms), 1964(s), 1938(s)	1584(m)	1138(m)
(2)[a]	2033(s), 1952(s), 1892(s)	1587(s)	1185(s)
(3)[a]	2075(m), 1975(ms), 1929(s)	1582(ms)	1125(m)
(4)[a]	2060(m), 1966(ms), 1911(s)	1587(ms)	1188(ms)
(5)[a]	2032(s), 1954(s), 1892(s)	1587(ms)	1188(ms)
(6)[b]	2019(s), 1936(s), 1846(s)	1606(m), 1587(s)	1113(ms)
(7)[b]	2032(s), 1946(s), 1863(s)	1605(m), 1581(s)	1126(m)
(8)[b]	2030(s), 1946(s), 1859(ms)	1605(m), 1586(ms)	1128(m)
(9)[b]	2018(2), 1944(s), 1851(s)	1603(m), 1587(m)	1126(m)
(10)[b]	2015(s), 1919(s), 1842(s)	1602(m), 1586(ms)	1131(m)
(11)[b]	2021(s), 1921(s), 1846(s)	1602(mw), 1588(m)	1120(m)
(12)[b]	2021(s). 1920(s), 1846(s)	1602(mw), 1588(m)	1120(m)

[a] Spectra were recorded as nujol mulls; [b] Spectra were recorded in $CHCl_3$ as thin films between NaCl plates; s = strong; ms = medium-strong; m = medium; mw = medium-weak.

Table 3 ^{1}H NMR data for the ligands pySH and pymSH, and the complexes **(1)**, **(2)** and **(12)**.

Complex, pySH or pymSH	^{1}H(δ)ppm
pySH[a]	14.15 (brs, pySH-NH); 7.60 (m, pySH-H^6, pySH-H^3); 7.40 (t, pySH-H^4, J_{HH} = 7 Hz); 6.80 (t, pySH^5, J_{HH} = 7 Hz)
pymSH[a]	8.55 (d, pymSH-H^6, pymSH-H^4, J_{HH} = 7 Hz); 7.05 (t, pymSH-H^5, J_{HH} = 7 Hz)
(1)[b]	8.30 (d, pySH-H^6); 7.55 (t, pySH-H^4); 6.95 (t, pySH-H^5); 6.90 (d, pySH-H^3)
(2)[c]	9.50 (m, pymSH-H^6); 9.05 (dd, pymSH-H^4); 7.70 (t, pymSH-H^5); 5.65 (s, CH_2Cl_2)
(12)[d]	14.60 (brs, 1H, pySH-NH); 7.95 (m, 2H, pySH-H^6, pySH-H^3); 7.80-7.60 (brm, 20H, Ph-H); 7.55 (m, 1H, pySH-H^4; 7.05 (t, 1H, pySH-H^5, J_{HH} = 7 Hz); 2.35 (m, 4H, PCH_2CH_2); 1.30 (brs, 8H, PCH_2CH_2)

[a] The ^{1}H NMR spectra for the ligands pySH and pymSH were recorded in $CDCl_3$ at +25°C. [b] The ^{1}H NMR spectrum for Complex **1** was recorded in D^6-dimethylsulphoxide at +25°C. [c] The ^{1}H NMR spectrum for complex **2** was recorded in $CDCl_3$ at +25°C. [d] The ^{1}H NMR spectrum for complex **12** was recorded in d^6-acetone at +25°C.

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nitrogen, however, they rapidly decomposed when exposed to air in solution. Complexes **(1)** and **(2)** are fairly soluble in methanol and dimethylsulphoxide, sparingly soluble in acetone and CH_2Cl_2, and insoluble in hydrocarbon solvents and diethyl ether. Although a number of attempts were made to prepare analogous molybdenum complexes they were considerably less stable than their tungsten analogues.

The infrared spectra of **(1)** and **(2)** exhibit three strong carbonyl stretching bands indicating the presence of at least three non-equivalent carbonyl ligands in these complexes. Both complexes exhibited skeletal ν(C = C/C = N) stretching vibrations at 1584 cm^{-1} **(1)** and 1587 cm^{-1} **(2)**, respectively. These values are $\approx$20 cm^{-1} lower in frequency than those of the neutral uncoordinated ligands[6] and are evidence of a lowering of the bond-order in the ring structure as a result of coordination of the ligand to the tungsten atom. The neutral ligand, pySH, is known to exist predominantly in the thione form.[1,6,8] The thiocarbonyl (C = S) stretching band in the neutral ligand, in solution, is $\approx$1143 cm^{-1}.[6] The thiocarbonyl stretching band of the coordinating ligand in complex **(1)** was observed at 1138 cm^{-1}, inferring that the neutral ligand coordinates in the thione form with the ring nitrogen protonated in preference to sulfur.

The ^{1}H NMR spectrum of complex **(1)** exhibited four resonances in the heterocyclic region corresponding to ring protons; these resonances were shifted to lower-field with respect to the uncoordinated ligand, pySH. The ring NH resonance was unobserved for complexes **(1)** and **(2)** which is probably due to a combination of quadrupolar broadening in the NH signals and the relatively weak ^{1}H NMR spectra obtained for these two complexes. The ^{1}H NMR spectrum of complex **(2)** showed three resonances in the heterocyclic region, at 7.7, 9.05 and 9.5 ppm downfield from tetramethylsilane. These resonances were all shifted to lower-field with respect to the uncoordinated pymSH ligand (Table 3). This indicates deshielding as a result of ligand coordination. Moreover, the ^{1}H NMR spectrum shows a resonance at 5.6 ppm which suggests this complex is a $1/2CH_2Cl_2$ solvate, which is also confirmed by repeated elemental analyses of the complex.

The neutral ligand, pySH, reportedly coordinates exclusively as a monodentate ligand through the S atom in the thione mode.[8] Reaction of $[WI_2(CO)_3(NCMe)_2]$ with one equivalent of pySH most likely proceeds by a dissociative mechanism involving concomitant displacement of one of the two labile acetonitrile ligands, with coordination of the pySH ligand (S-bonded). This intermediate rapidly loses the second labile acetonitrile ligand to form the dimeric product $[\{W(\mu\text{-}I)I(CO)_3(pySH)\}_2]$. The ability of seven-coordinate tungsten(II) carbonyl halide complexes to undergo dimerisation by formation of halide bridges has been well documented.[11,12] The X-ray crystal structure of $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ has been determined by Cotton and co-workers[13] and shown to have bromide bridges. It seems highly likely that complex **(1)** {and possibly complex **(2)**} contains iodide bridges. Each tungsten atom in $[\{W(\mu\text{-}Br)Br(CO)_4\}_2]$ is in a capped-octahedral environment with carbonyl ligands capping each octahedral face.[13] It may be that complexes **(1)** and **(2)** exhibit this geometry, as shown in Figure 2.

An interesting characteristic of the coordination chemistry of the neutral pySH ligand is its ability to participate in intramolecular hydrogen-bonding with coordinated halide atoms in the inner coordination sphere of transition metal complexes.[8,14] It maybe that complexes **(1)** and **(2)** contain hydrogen bonds, as shown in Figure 2. It is possible for complex **(2)** to possess a similar structure to that proposed for complex **(1)**; however it could be that this complex could be a seven-coordinate monomer with the pymSH ligand coordinating in the bidentate mode to the tungsten atom through the sulfur and second of the ring nitrogen atoms.

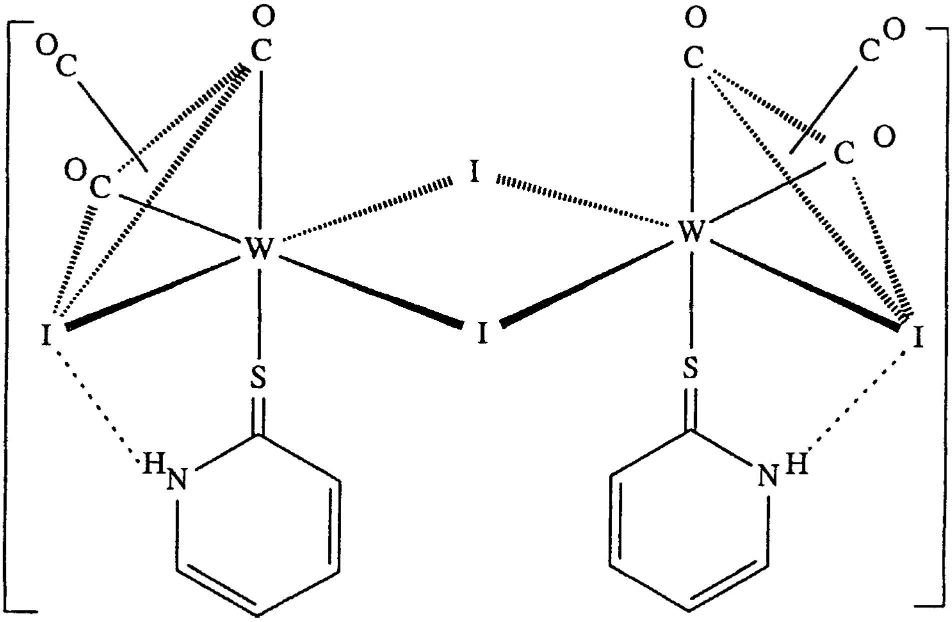

Figure 2 Possible structure for the complex $[\{W(\mu\text{-}I)I(CO)_3(pySH)\}_2]$ **(1)**, showing proposed hydrogen bonding between the protons on the ring nitrogen of the pyridine-2-thione ligands and the non-bridging iodine atoms in the equatorial girdle.

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Reaction of $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with two equivalents of pySH (for M = Mo only) or pymSH in CH_2Cl_2 at room temperature gave the nitrile displaced products $[MoI_2(CO)_3(pySH)_2]$ **(3)** or $[MI_2(CO)_3(pymSH)_2]$ **(4)** and **(5)** respectively. Complexes **(3)**, **(4)** and **(5)** as expected exhibited three carbonyl bands in their infrared spectra (Table 2). The thiocarbonyl stretching bands for **(3)**, **(4)** and **(5)** were observed at 1125, 1188 and 1188 cm^{-1}, respectively, which indicates that the ligand is attached in the monodentate thione mode. Unfortunately, these complexes were all generally insoluble in both polar and non-polar solvents, and hence no satisfactory ^1H NMR spectra were obtained. However, the presence of CH_2Cl_2 was observed in a very weak ^1H NMR spectrum of the tungsten complex $[WI_2(CO)_3(pymSH)_2]\cdot CH_2Cl_2$ **(5)**.

Reaction of $[WI_2(CO)_3(NCMe)_2]$ with two equivalents of PPh_3 or one equivalent of $Ph_2P(CH_2)_nPPh_2\{n = 1$ (dppm), n = 2 (dppe), n = 3 (dppp), n = 4 (dppb), n = 5 (dpppe), n = 6 (dpph)$\}$ in CH_2Cl_2 at room temperature followed by an *in situ* reaction with one equivalent of pySH gave the cationic complexes $[WI(CO)_3(PPh_3)_2(pySH)]I$ **(6)** or $[WI(CO)_3\{Ph_2P(CH_2)_nPPh_2\}(pySH)]I$ **(7→12)** in good yield. Complexes **(6→12)** have been characterised by elemental analysis (C, H, N and in selected cases I; Table 1), infrared spectroscopy (Table 2), and in selected cases by ^1H NMR spectroscopy (Table 3), and molar conductivity measurements (Table 4). Complexes **(6)→(12)** are reasonably stable when stored in the solid state under nitrogen. However, they decompose rapidly when exposed to air in solution. They are soluble in acetone and methanol, sparingly soluble in CH_2Cl_2, and insoluble in hydrocarbon solvents and diethyl ether.

The infrared spectra of complexes **(6→12)** all exhibited three strong carbonyl stretching bands, indicating the presence of three non-equivalent carbonyl ligands. Each complex also showed two skeletal $\nu(C = C/C = N)$ stretching bands in the region 1581–1602 cm^{-1}, which was due to the presence of the ring structures of the neutral phosphine donor ligands and pySH. Each complex showed a thiocarbonyl (C = S) stretching band in the region 1120–1131 cm^{-1}, consistent with pySH bonding in the thione mode.[6] Molar conductance measurements (Table 4) and iodide analysis by Ion Chromatography (Table 1) confirmed these complexes as 1:1 electrolytes, with an iodide anion in the outer coordination sphere. Iodide determined after < 1 min. in 0.1 M $NaHCO_3$ was approximately half that after 7 days in 0.1 M $NaHCO_3$ (Table 1) for complexes **(9)**, **(11)** and **(12)**, and is consistent with a mono-iodide displaced product. Iodide analysis after < 1 min in 0.1 $NaHCO_3$ solution should detect only labile iodide ions present in the outer coordination sphere of these complexes assuming that no significant decomposition of complex occurred during this short time in solution. Iodide determined after 1 week, however, was expected to yield total iodide analysis due to complex decomposition by displacement of coordinated iodine atoms from the inner coordination sphere. Molar conductance values for complexes **(9)** and **(12)**, Table 4

Table 4 Molar Conductance values[a] for complexes **(9)** and **(12)**.

Complex	Molar Conductance/$10^4 m^2 \Omega^{-1} mol^{-1}$
(9)	123
(12)	138

[a] Measurements are for a 1×10^{-3} mol dm^{-3} concentration of the complexes in acetone under a nitrogen atmosphere at 25°C.

were in the range expected for a 1:1 electrolyte, *i.e.*, 100–140 × 10^4 m^2 Ω^{-1} mol^{-1} in acetone.

The ^1H NMR spectrum of complex **(12)** exhibited five resonances in the heterocyclic region, *ca* 7.05–7.95 ppm downfield from tetramethylsilane, corresponding to ring protons. A broad singlet ring NH resonance was observed at 14.6 ppm downfield from tetramethylsilane. This very low field NH resonance, which was not concentration dependent, is taken as evidence for intramolecular hydrogen-bonding in this complex,[1,8,14] similar to that proposed for complex **(1)** (see Figure 2) forming a pseudo-chelate ring. Several unsuccessful attempts were made to grow single crystals for X-ray crystallography. However, since the majority of seven-coordinate complexes of molybdenum(II) and tungsten(II) have capped octahedral geometry[15,16] the most likely structure of complex **(12)** is shown in Figure 3.

The bis (triphenylphosphine) complex **(6)** was very much less stable with respect to complexes **(7)**→**(12)**, most probably due to the chelate effect. All of these complexes were rather unstable to disproportionation, possibly involving re-attack by the iodide atom in the outer coordination sphere. Attempts to synthesise the analogous pymSH complexes were unsuccessful. Although reactions certainly occurred, no satisfactory elemental analyses were obtained and these complexes were all very unstable and disproportionated in solution. Magnetic susceptibility measurements on complexes **(8)** and **(12)** showed these complexes to be diamagnetic, which is consistent with these compounds obeying the effective atomic number rule.

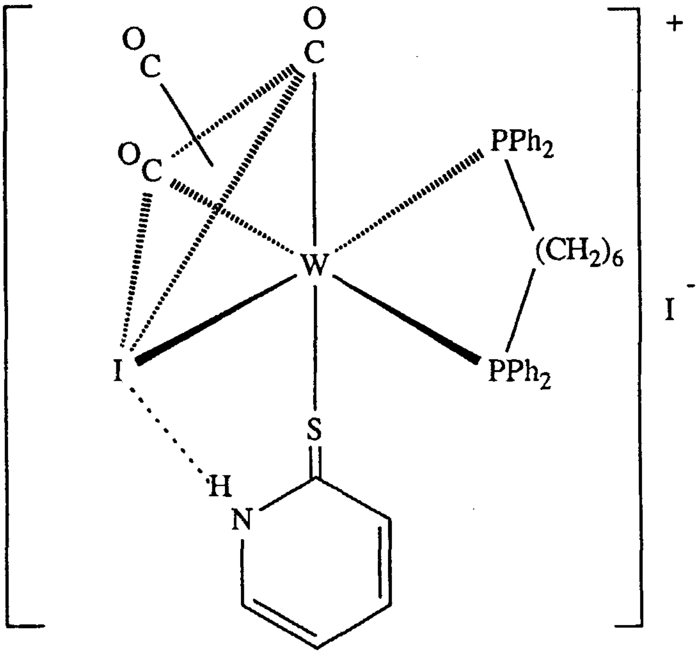

Figure 3 Possible structure for the complex $[WI(CO)_3(dpph)(pySH)]I$ **(12)**.

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