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CHEMISTRY OF PYRIDINETHIOLS AND RELATED LIGANDS—4.[1] COMPLEXES OF BIS(PYRIDINE-2-THIOLATO- OR 1-OXOPYRIDINE-2-THIONE) RUTHENIUM(II) WITH BIS(DIPHENYLPHOSPHINO)ALKANES

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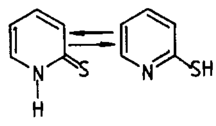
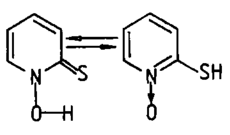
Abstract—A series of ruthenium(II) mixed-ligand complexes containing 2(1H)-pyridinethione (C_5H_5NS) or 1-hydroxypyridine-2-thione (C_5H_5NOS) and bis(diphenylphosphino) alkanes, $Ph_2P(CH_2)_mPPh_2$ ($m = 1$–4), and a tritertiaryphosphine, $(Ph_2PCH_2CH_2)_2PPh$ (triphos), of stoichiometry: RuA_2L (HA = C_5H_5NS or C_5H_5NOS; L = a di- or tri-tertiary phosphine) have been prepared. The complexes were obtained by the reactions of (i) RuL_nCl_2 [$n = 2$ for L ($m = 1$, 3) or $n = 1.5$ for L ($m = 4$)] with HA ligands in the presence of triethylamine, (ii) $RuA_2(PPh_3)_2$ with L ($m = 2$; triphos; HA = C_5H_5NS), or (iii) $RuCl_2(PPh_3)_3$ with C_5H_5NOS and L ($m = 2$; triphos) in the presence of triethylamine and characterized using analytical data, IR, far-IR, UV–vis, ^1H and ^{13}C NMR, and cyclic voltammetry. The geometry about Ru^{II} is distorted octahedral with S—Ru—S in the bent *trans*-configuration (S—Ru—S, *ca* 155°), with phosphines occupying *cis*-positions.

Ruthenium(II) chemistry continues to attract the attention of various research workers for a variety of reasons, such as the use of ruthenium(II) complexes in, for example, the conversion of solar energy into electrical energy, photodecomposition of water, catalysis, etc.[2-10]

There has been growing interest in preparing metal complexes containing anionic thiolates and bis(tertiaryphosphines).[11,12] From this laboratory, a series of mixed-ligand complexes of Cu^I, Cu^{II} and Fe^{III} containing 2(1H)-pyridinethione (hereafter C_5H_5NS; **I**), 1-hydroxypyridine-2-thione (hereafter C_5H_5NOS; **II**) and bis(diphenylphosphino) alkanes (**III**) have been reported.[1,13-15] It was observed that C_5H_5NS binds to Cu^I and Fe^{III} via its thione sulphur as a neutral ligand; while C_5H_5NOS behaved as an



I



II

$Ph_2P(CH_2)_mPPh_2$

III (m=1-4)

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oxygen and sulphur donor chelating anionic ligand, paving the way for stabilization of Cu^{II}–tertiary-phosphine.[1]

This paper reports the preparation of a series of ruthenium(II) complexes containing anionic ligands, $C_5H_4NS^-$ and $C_5H_4NOS^-$, and bis(diphenylphosphino)alkanes characterized using various techniques.

EXPERIMENTAL

Materials

The materials $RuCl_3 \cdot xH_2O$, PPh_3, $Ph_2P(CH_2)_mPPh_2$ ($m = 1$, 3) and $(Ph_2PCH_2CH_2)_2PPh$ were obtained from M/S Pressure Chemicals, Pittsburg, U.S.A. The tertiary phosphines for $m = 2$ and 4 were prepared from PPh_3 by the lithiation method.[16] The pyridine thiol ligands used were prepared by reported methods.[1,17] The solvents used were of analytical grade and used as such. The reactions were carried out under dry N_2.

Physical measurements

The elemental analyses for carbon, hydrogen and nitrogen were obtained from RSIC, Chandigarh. The electronic absorption spectra of the solutions of the compounds were recorded on a Shimadzu Graphicord 240-UV–visible spectrophotometer. The IR and far- IR spectra of the complexes (200–4000 cm^{-1}) were recorded using KBr pellets on Pye Unicam SP3-300 Infrared and Hitachi 270-50 spectrophotometers. The NMR (^1H, ^{13}C) spectra of the complexes in $CDCl_3$ were recorded using a Bruker AC 200 instrument at 200 MHz and 50 MHz frequency respectively, with TMS as the internal standard. The cyclic voltammograms of the complexes were recorded on a digital cyclic voltammeter (Micronics) using an (X: Y: t) recorder. The millimolar solutions of the complexes in acetonitrile–dichloromethane (1 : 1, v/v) were used with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The recording of the cyclic voltammograms was carried out under atmospheric conditions with a three-electrode assembly system consisting of a 3 mm diameter platinum disc as the working electrode, calomel with 0.1 M LiCl in methanol as the reference electrode and platinum wire as the counter electrode. Finally, the melting points of the samples were recorded using melting point tubes containing liquid paraffin and are uncorrected.

Table 1. The analytical data, physical properties and IR data (cm^{-1}) of the complexes[a, b]

Complex (m.p.,°C)	Analysis (%)[c] C	H	N	$\nu(C{=}S)$[d]	$\nu(N{-}O)$[d]	$\delta(N{-}O)$[d]
1 $Ru(C_5H_4NS)_2$(dppm)	(60.8)	(4.3)	(3.5)	1130s		
(240–242)	(59.6)	(4.0)	(4.0)			
2 $Ru(C_5H_4NS)_2$(dppe)	60.1	4.9	3.2	1130s		
(248–250)	(60.1)	(4.5)	(3.9)			
3 $Ru(C_5H_4NS)_2$(dppp)	60.5	3.9	3.7	1130s		
(258–260)	(60.6)	(4.6)	(3.8)			
4 $Ru(C_5H_4NS)_2$(dppb)	60.6	4.8	3.5	1130s		
(222–225)	(61.0)	(4.8)	(3.7)			
5 $Ru(C_5H_4NS)_2$(triphos)	61.2	5.1	2.3	1120s		
(232–235)	(61.8)	(4.8)	(3.3)	1140s		
6 $Ru(C_5H_4NOS)_2$(dppm)	56.7	4.2	3.1	1120	1090s	835s
(242–244)	(57.0)	(4.1)	(3.8)			
7 $Ru(C_5H_4NOS)_2$(dppe)	59.6	4.6	4.3	1120s	1090	830s
(255–257)	(58.0)	(4.3)	(3.7)			
8 $Ru(C_5H_4NOS)_2$(dppp)	59.0	3.7	3.4	1130s	1090s	820s
(230–231)	(60.6)	(4.4)	(3.7)	1140sh		840s
9 $Ru(C_5H_4NOS)_2$(dppb)	57.1	4.9	3.0	1135s	1090s	820s
(198–200)	(58.5)	(4.6)	(3.6)			
10 $Ru(C_5H_4NOS)_2$(triphos)	59.9	4.6	3.4	1120m	1100m	820m
(>250)	(59.6)	(4.6)	(3.2)	1140m	br	

[a] Ligand abbreviations: $Ph_2P(CH_2)_mPPh_2$, $m = 1$, dppm; $m = 2$, dppe; $m = 3$, dppp; $m = 4$, dppb; triphos = $(Ph_2PCH_2CH_2)_2PPh$.

[b] Complex **1** is orange; the others are yellow in colour.

[c] Expected values in parentheses.

[d] $\nu(C{=}S)$, 1138s cm^{-1}, C_5H_5NS; 1140s cm^{-1}, C_5H_5NOS. $\nu(N{-}O)$, 1090s. $\delta(N{-}O)$, 835s.

Synthesis of the complexes

The complexes were prepared by the following methods.

Method 1 : *preparation of* $Ru(C_5H_4NS)_2(dppm)$. To the orange solution of $Ru(dppm)_2Cl_2$[18] (0.940 g, 1 mmol) in degassed benzene (50 cm^3) was added the solid C_5H_5NS (0.220 g, 2 mmol) and Et_3N (1 cm^3). The contents were refluxed for a period of 12 h under dry N_2. The colour of the solution remained orange, the precipitated $Et_3NH^+Cl^-$ was filtered off and the filtrate concentrated to one-third of its initial volume. The addition of n-hexane (40 cm^3) formed a yellow coloured compound which was washed with diethyl ether and ethanol, and dried *in vacuo*. The starting complexes, $Ru(dppp)_2Cl_2$[18] and $Ru(dppb)_xCl_2$[19] ($x = 1.5$) were prepared by the reported methods. In the case of C_5H_5NOS complexes, the isolation after precipitation of $Et_3NH^+Cl^-$ was carried out as follows. Instead of adding n-hexane, the entire solvent was removed under reduced pressure and the compound was washed with dry diethyl ether three to four times and dried again. The complexes **3**, **4**, **6**, **8** and **9** were prepared similarly (see Table 1 for numbering scheme). The complexes were sensitive to air and light and were stored under an inert atmosphere.

Method 2: *preparation of* $Ru(C_5H_4NS)_2(dppe)$. To a solution of dppe (0.400 g, 1 mmol) in dry toluene (50 cm^3) was added the complex $Ru(C_5H_4NS)_2(PPh_3)_2$[17] (0.850 g, 1 mmol) and the contents were refluxed under N_2 for a period of about 48 h, followed by concentration to one-third of its initial volume. The addition of n-hexane (40

Table 2. The ^1H NMR data (ppm) of the complexes

Complex	Thiolate		Phosphine	Remarks
	H(6)	H(4)	—$(CH_2)_m$—	
1 $Ru(C_5H_4NS)_2(dppm)$	8.33 (3, 1H)	6.57 (t, 1H)	4.70 (t, 2H, $J = 8.35$ Hz)	PCH_2P
3 $Ru(C_5H_4NS)_2(dppp)$	7.44 (d, 1H)	6.09 (t, 1H)	2.27 (m)	$P(CH_2)_3P$
4 $Ru(C_5H_4NS)_2(dppb)$	7.58 (d, 1H)	6.12 (s, br, 1H)	2.27 (m)	$P(CH_2)_4P$
5 $Ru(C_5H_4NS)_2(triphos)$	8.34 (s, br, 1H)	6.61 (s, br, 1H)	1.58 (s, br) (A) 4.70 (m) (B)	(B) (B) PCH_2CH_2 ╲ PPh ╱ PCH_2CH_2 (A) (A)
6 $Ru(C_5H_4NOS)_2(dppm)$	8.33 (d, 1H)	6.60 (t, 1H)	4.70 (t, 2H, $J = 10.4$ Hz)	PCH_2P
8 $Ru(C_5H_4NOS)_2(dppp)$	7.60 (d, 1H)	6.30 (t, 1H)	2.11 (m)	$P(CH_2)_3P$
Ligands				
C_5H_5NS[a]	7.71 (s, br)	6.84 (t, br)		
C_5H_5NOS[b]	8.13 (d)	6.83 (s, br)		
$Ph_2PCH_2PPh_2$	—	—	2.80 (s, br)	PCH_2P
$Ph_2P(CH_2)_3PPh_2$	—	—	1.60 (m) (A) 2.19 (t) (B) ($J = 8.0$ Hz)	(B) (A) (B) $PCH_2CH_2CH_2P$
$Ph_2P(CH_2)_4PPh_2$	—	—	3.97 (t, $J = 13.4$ Hz)	$PCH_2CH_2CH_2CH_2P$
$(Ph_2PCH_2CH_2)_2PPh$	—	—	1.82 (m) 2.08 (m)	PCH_2CH_2 ╲ PPh ╱ PCH_2CH_2

[a] 7.44 [t, H(5)], 7.56 [d, H(3)], 12.8 (NH, br).

[b] 7.31 [t, H(5)], 7.65 [d, H(3)], 11.53 (OH, br).

cm^3) formed a yellow coloured compound which was filtered and washed using diethyl ether, acetone and methanol, and finally dried under reduced pressure. The compound was recrystallized from methanol–benzene (1 : 1, v/v). The complex **5** was prepared similarly but not washed with the solvents mentioned above; however, it was recrystallized from diethyl ether.

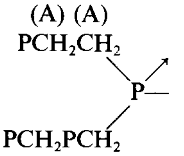
Method 3 : *preparation of* Ru(C_5H_4NOS)$_2$(dppe). To a solid mixture of Ru(PPh_3)$_3$$Cl_2$ (0.480 g, 0.5 mmol) and C_5H_5NOS (0.127 g, 1 mmol) in degassed benzene (60 cm^3) was added Et_3N (1 cm^3). The reaction mixture was refluxed for a period of 24 h under N_2, the colour of the solution changed from brown to orange and on cooling $Et_3NH^+Cl^-$ separated. The solid dppe (0.200 g, 0.5 mmol) was added to this orange coloured solution followed by further refluxing for a period of 12 h under N_2. The solution was cooled, filtered and concentrated under reduced pressure to one-third of its initial volume. The yellow coloured compound obtained by the addition of n-hexane (35 cm^3) was filtered, washed with diethyl ether and dried *in vacuo*. Complex **10** was obtained similarly.

RESULTS AND DISCUSSION

The elemental analyses reveal that the mixed-ligand complexes can be formulated as: RuA_2L [HA = C_5H_5NS or C_5H_5NOS; L = Ph_2P (CH_2)$_m$$PPh_2$ (m = 1–4), and ($Ph_2PCH_2CH_2$)$_2$PPh]. The complex Ru(C_5H_4NS)$_2$(dppe) could not be prepared by method 1 in view of the strong tendency of dppe to form the *trans*-octahedral complex, Ru(dppe)$_2$$Cl_2$, characterized by X-ray analysis only recently.[20] Thus, method 2 was followed for preparing dppe and triphos complexes with C_5H_5NS as the thiol ligand.

The $C_5H_4NS^-$ complexes turned green when their solutions were exposed to air in the presence of sunlight, probably undergoing oxidation, which is slow in the dark. The complexes of C_5H_5NOS are

Table 3. The ^{13}C NMR data (ppm) of the complexes

Complex	δ(thiolate) C(2)	C(6)	C(4)	Phosphine^a —(CH_2)$_m$— (J, Hz)	Remarks
1 Ru(C_5H_4NS)$_2$(dppm)	181.70	148.61	115.70	50.07 (t) (21.0)	PCH_2P
3 Ru(C_5H_4NS)$_2$(dppp)	180.72	146.38	115.25	19.06 (s) (A) 28.40 (t) (B) (17.00)	(B) (A) (B) $PCH_2CH_2CH_2P$
4 Ru(C_5H_4NS)$_2$(dppb)	181.53	146.64	115.23	23.42 (s) (A) 30.33 (t) (B) (13.90)	(B) (A) (A) (B) $PCH_2CH_2CH_2CH_2P$
5 Ru(C_5H_4NS)$_2$(triphos)	181.80	148.70	115.81	50.12 (t) (A) (20.85)	
6 Ru(C_5H_4NOS)$_2$(dppm)	181.77	148.65	115.77	50.10 (t) (20.75)	PCH_2P
Ligands					
dppm	—	—	—	27.84 (t) (22.50)	PCH_2P
dppp	—	—	—	22.40 (t) (A) (17.0) 29.62 (t) (B) (12.10)	(B) (A) (B) $PCH_2CH_2CH_2P$
dppb	—	—	—	38.82 (t) (43.85)	$PCH_2CH_2CH_2CH_2P$
Triphos	—	—	—	23.55 (m)	($Ph_2PCH_2CH_2$)$_2$PPh
C_5H_5NS	176.40	137.95	114.0		
C_5H_5NOS	166.40	132.37	113.9		

[a] J values in parentheses are ^{31}P–^{13}C coupling constants.

even more sensitive to air oxidation in the presence of sunlight. Whereas C_5H_5NS complexes remain stable in the solid state, the corresponding C_5H_5NOS complexes turn green even in the solid state in the presence of air and sunlight. Interestingly, $RuA_2(dppe)$($HA = C_5H_5NS$, C_5H_5NOS) were the most stable compared to other phosphine complexes. All the green materials (oxidized products) were ESR-active, but a detailed study of the nature of the products under different conditions was not undertaken. The complexes are soluble in CH_2Cl_2, $CHCl_3$, C_6H_6 and THF, and sparingly soluble in CH_3OH, C_2H_5OH and CH_3COCH_3.

Table 1 shows a decrease in the ν(C=S) frequency of complexes **1**–**4**, but the magnitude of the shift is lower than that observed in the analogous Cu^I complexes.[13, 14] In contrast, for $C_5H_4NOS^-$ complexes, the low-energy trends and splitting of the ν(C=S) peak take place and this trend is different from Cu^{II}–C_5H_4NOS–tertiary phosphine complexes,[1] where high energy shifts in ν(C=S) were observed. This difference indicates stronger interaction of thione sulphur with Ru^{II} vs Cu^{II}, as expected. However, the trends in ν(N—O) and δ(N—O) peaks are similar to those noted in Cu^{II} complexes.[1]

In the electronic absorption spectrum, C_5H_5NS in $CHCl_3$ shows a peak (medium) due to the C=S chromophore at 365 nm, which shifts to 320 nm after coordination to Ru^{II} in complexes **1**–**5**. Another peak of C_5H_5NS at 290 nm shifts to 240 nm.[13,14] Similarly, the dppm peak at 252 nm merges with the peak at 240 nm. The νC=S peak of C_5H_5NOS at 350 nm shifts to 320 nm in complexes **6**–**10**. The other ligand peak at 280 nm merges with the peak at 240 nm in the complexes.

The ^1H NMR spectra of the complexes (Table 2) confirm the deprotonation of C_5H_5NS and C_5H_5NOS ligands and subsequent coordination to the Ru^{II} metal centre via nitrogen, sulphur or oxygen, sulphur donor ends, respectively. The H(6) protons of complexes **1**, **5** and **6** show low-field shifts (Table 2) and the coordination shift ($\Delta\delta = 0.62$ ppm) is higher for complexes **1** and **5** than that for complex **6** ($\Delta\delta = 0.20$ ppm). For the other complexes (**3**, **4** and **8**) there are high-field shifts. The H(4) proton signal of the thiolate moieties also showed some high-field shifts. The CH_2 protons of complexes **1** and **6** showed a low-field triplet at δ 4.70 ppm (^{31}P, $I = \frac{1}{2}$, coupling); a similar trend was observed in complexes **3** and **8**, but to a much smaller extent. The increase in chain length from $(CH_2)_3$ to $(CH_2)_4$ leads to a high-field shift relative to the free ligands. In complex **5**, the CH_2 protons showed a well-defined triplet at δ 4.70 ppm (triplet at the same position where dppm complexes absorb) due to CH_2 protons of the coordinated $Ph_2PCH_2CH_2PPL$ moiety and a singlet at δ 1.9 (s, br) due to the uncoordinated $Ph_2PCH_2CH_2$ moiety.

Table 4. Cyclic voltammetric data (V) of some Ru^{II} complexes (room temperature, 25°C)

Complex[a]	E_a	E_c	$E_{\frac{1}{2}}$	Solvent
1	0.530	0.480	0.050	CH_2Cl_2–CH_3CN (1 : 1, v/v)
2	0.470	0.410	0.060	CH_2Cl_2
3	0.740	0.370	0.370	CH_2Cl_2–CH_3CN (1 : 1, v/v)
4	0.560	0.460	0.100	CH_2Cl_2–CH_3CN (1 : 1, v/v)
6	0.600	0.490	0.110	CH_2Cl_2–CH_3CN (1 : 1, v/v)
8	0.370	0.360	0.010	CH_2Cl_2–CH_3CN (1 : 1, v/v)
9	0.410	0.350	0.060	CH_2Cl_2–CH_3CN (1 : 1, v/v)

[a] Concentrations were 2×10^{-3} M for **1**, **3**, **4**, **8** and **9**, and 1×10^{-3} M for **2** and **6**. Scan rates were 100 mV s^{-1} for **1**–**4**, 80 mV s^{-1} for **6**, 200 mV s^{-1} for **8** and 320 mV s^{-1} for **9**.

In the $^{13}C\{^1H\}$ NMR spectra of complexes **1**, **3**, **4** and **5** (Table 3), the thione carbons C(2) undergo low-field coordination shifts ($\Delta\delta$) of 4.3–5.4 ppm. Similarly, the complex **6** shows a low energy shift of 15.37 ppm. This shows that the sulphur donor end of $C_5H_4NOS^-$ coordinates to Ru^{II} more strongly as compared to coordination by the sulphur of $C_5H_4NS^-$. Similarly, C(6) signals reveal coordination shifts of *ca* 9–11 ppm for the complexes **1**, **3**, **4** and **5** and of *ca* 16 ppm for complex **6**. This difference is attributed to: (i) the formation of a stable five-membered metallocyclic ring by C_5H_4NOS vs a strained four-membered ring by $C_5H_4NS^-$ and (ii) efficient $d\pi$ (Ru) to $\pi^*(C_5H_4NS^-)$ π-bonding as compared to lack of similar bonding in Ru–$C_5H_4NOS^-$ complexes.

The X-ray molecular structures of complexes **2** and **4** reveal their distorted octahedral structures.[21–23] The dppe forms a five-membered chelate ring, while dppb forms a seven-membered chelate ring. Finally, cyclic voltammograms of the complexes studied (Table 4) revealed reversible redox behaviour, probably involving the one-electron redox process:

$$Ru^{II} \rightleftharpoons Ru^{III}.$$

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