Complexes of Pyridine-2-thiol With Some Transition Metals †

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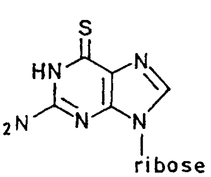
Pyridine-2-thiol (LH) complexes of iron(II), cobalt(II), nickel(II), copper(II), copper(I), rhodium(II), and palladium(II) have been prepared and characterised by infrared and electronic spectroscopy and by magnetic susceptibility measurements. With the exception of $PdL_2(LH)$ all the complexes have unidentate pyridine-2-thiol, most of them showing an N–H stretching frequency confirming other evidence that the donor atom is sulphur.

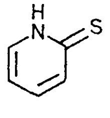
THE first metal complex [1] of pyridine-2-thiol (LH), $RuL_2(PPh_3)_2$, was formulated as a chelate, despite the short bite of the ligand, and this structure was confirmed by *X*-ray diffraction.[2] A similar iridium complex containing bidentate pyridine-2-thiolato-groups has also been prepared.[3]

In extending studies of the complexing by this ligand we were encouraged by interest [4] in the complexing of thiolated nucleosides such as 6-thioguanosine (I) which has NH and sulphur in the 1 and 6 positions.

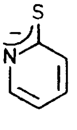
A brief note has recently appeared,[5] where, using 6-mercaptopurine blocked at the 9-position by a benzyl substituent to simulate a riboside, a palladium complex was prepared and shown to involve bonding at the sulphur and the N(7) donor atoms. Since pyridine-2-thiol exists as the tautomer,[6] it is best named as a thione, (II); it provides thus a model for the sulphur and N(1) donor atoms in (I). Pyridine-2-thiol (it is more convenient to call it this) has three potential bonding forms, since co-ordination can occur either through the sulphur or nitrogen donor atoms or through both as in (III).



(I)



(II)



(III)

As this work was being completed, the reaction of the ligand with some metal ions was described,[7] but there is only a small overlap with the cobalt(II) and nickel(II) complexes as will be noted later.

RESULTS

Iron(II).—Iron(II) halides react readily with pyridine-2-thiol in anhydrous media (an ethanol–2,2-dimethoxypropane mixture) to yield complexes of stoicheiometry $FeX_2(LH)_2$ ($X = Cl, Br$). The complexes are paramagnetic and have values of μ_{eff}, 5·03 and 4·92 B.M. respectively (297 K), consistent with tetrahedral co-ordination,[8] although distortion in octahedral iron(II) complexes can lower the magnetic moment sufficiently to cause some doubt if assignment is made on this basis alone.[9]

The electronic spectrum exhibits a broad, split, band

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† No reprints available.

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at 4·90 and 5·62 kK (X = Cl, Br) which can be assigned to the $^5T_2\leftarrow{}^5E$ transition of a tetrahedral iron(II) species. A similar transition occurs at 4·65 and 5·78 kK in the $[Fe(NCS)_4]^{2-}$ anion[10] (Table 1).

At 77 K the Mössbauer spectrum is a doublet, of isomer shift 0·87 mm s^{-1} and quadrupole splitting 3·48 mm s^{-1} (relative to metallic iron). This is in the region expected for tetrahedral iron(II) with sulphur ligands.[11] In addition there is a small, somewhat broad, peak with an isomer shift of 0·29 mm s^{-1}. On raising the temperature to 300 K this splits into a well resolved doublet of isomer shift 0·39 mm s^{-1} and quadrupole splitting 0·51 mm s^{-1}. On re-cooling to 77 K a spectrum identical with the original is obtained, and this remains essentially unchanged down to 4·2 K. The 300 K spectrum was unchanged when the complex was set aside in air for a week, and the additional doublet is most likely to be due to some phase change caused by the initial cooling to 77 K. In the spectra at 77 and 4·2 K there is a very weak magnetically split component, probably due to an impurity.

TABLE 1

Selected i.r.,* far-i.r.,† and electronic reflectance spectra ‡ for pyridine-2-thiol complexes

	I.r. data §		Far-i.r. data			Electronic reflectance spectra	
Complex	ν(N–H)	ν(C⁚S)	ν(M–X) [c]	ν(M–S) [c]	Others [c]	Band	Assignment
$FeCl_2(LH)_2$	3162	1126	311, 281m	223m		4·90, 5·62	$^5T_2\leftarrow{}^5E$
$FeBr_2(LH)_2$	3150	1118	242, 226m	*b*		4·90, 5·62	$^5T_2\leftarrow{}^5E$
$CoCl_2(LH)_2$	3150	1125	303, 287m	220m	264m	4·90, 5·88	$^4T_1(F)\leftarrow{}^4A_2$
						13·89, 15·62, 16·67	$^4T_1(P)\leftarrow{}^4A_2$
$CoBr_2(LH)_2$	3145	1120	230br, s	*b*	255vw	5·32, 7·27, 7·94	$^4T_1(F)\leftarrow{}^4A_2$
						13·90, 15·87	$^4T_1(P)\leftarrow{}^4A_2$
$CoI_2(LH)_2$ [d]	3140	1115	210, 191s	226s	156, 90m	5·13, 5·99, 7·25	$^4T_1(F)\leftarrow{}^4A_2$
						20·41, 22·73	Charge transfer
$NiCl_2(LH)_2$	3160	1132	298vs, 260s	236m		(8·33) 9·30 (10·53)	$^3T_{2g}\leftarrow{}^3A_{2g}$
						14·30	$^3T_{1g}\leftarrow{}^3A_{2g}$
						22·73	$^3T_{1g}(P)\leftarrow{}^3A_{2g}$
						15·62	$^1E_g\leftarrow{}^3A_{2g}$
$NiBr_2(LH)_2$	3150	1130	233vs	*b*	205, 211, 225w	(7·69) 8·77, 9·80	$^3T_{2g}\leftarrow{}^3A_{2g}$
						(12·90) 14·29	$^3T_{1g}\leftarrow{}^3A_{2g}$
						21·20	$^3T_{1g}(P)\leftarrow{}^3A_{2g}$
$NiI_2(LH)_2$ [d]	3140	1119	193s, 168m	218s	281m, 144s	5·40	
						(6·94) 7·94	$^3T_{2g}\leftarrow{}^3A_{2g}$
						12·58, 13·70	$^3T_{1g}\leftarrow{}^3A_{2g}$
						20·83	$^3T_{1g}(P)\leftarrow{}^3A_{2g}$
$NiCl_2(LH)_4$	3160	1132	242m	218m	287w	6·06, 8·33	$^3T_{2g}\leftarrow{}^3A_{2g}$
						10·31	$^1E_g\leftarrow{}^3A_{2g}$
						13·70	$^3T_{1g}\leftarrow{}^3A_{2g}$
						21·74	$^3T_{1g}(P)\leftarrow{}^3A_{2g}$
$NiBr_2(LH)_4$	3068	1138, 1127	Not co-ord.	*a*		8·84	
						20·00	$\nu_2(^1A_{2g}\leftarrow{}^1A_{1g})$
$NiI_2(LH)_4$	3130	1118	Not co-ord.	218m	272, 242w	8·84	
						20·83	$\nu_2(^1A_{2g}\leftarrow{}^1A_{1g})$
$CuCl(LH)_3$	3130	1130	251m	242m	211, 205m		
$CuBr(LH)_2$	3140	1118, 1125	*a*	242m	219m, 211w		
$CuI(LH)_2$ [d]	*a*	*a*	*a*	243m	206, 93, 56m		
$Pd(LH)_4Cl_2,EtOH$	3090	1125	Not co-ord.	328s			
$PdL_2(LH)$	*a*	*a*		362, 333s	255w		
$Ag(LH)_4BF_4$	3170	1123		252, 243s			
$Ag(LH)_2ClO_4$	*a*	*b*		278s			
$Rh_2(OAc)_4(LH)_2$	3175	1120		340s	219m		
$Cu(phen)_2(LH)(ClO_4)_2$	3175	*b*		243m	297, 275, 206m	11·43	

* Nujol mulls, KBr plates, in cm^{-1}. † 450—200 cm^{-1}, Polythene plates; Vaseline mulls. ‡ 4—25 kK. § Ring breathing mode 990 ± 6 cm^{-1}. Thioamide bands,[14,15] not assigned.

[a] Not observed. [b] Obscured. [c] s, Strong; m, medium; w, weak; br, broad; v, very. [d] Measured down to 20 cm^{-1}.

Using the temperature dependence of the quadrupole splitting the degree of distortion, Δ, in the *e* levels can be obtained in a manner similar to that for $FeCl_4^{2-}$.[12,13] Δ is *ca.* 735 cm^{-1}, and this large distortion is probably due to the large bulk of the ligand; it is comparable with the distortions in thioacetamide and thiourea complexes of iron(II).[11]

The i.r. spectrum (4000—200 cm^{-1}) gives little information as to the bonding, as the various ring modes which are diagnostic proved difficult to assign with any certainty (Table 1). However the presence of an N–H stretch in both chloride and bromide strongly suggests sulphur co-ordination, with the ligand in the thione form.

In the far-i.r. region, ligand vibrations can be easily identified by their lack of sensitivity toward changes of halogen, and the bands at 442 and 358 cm^{-1} (X = Cl), and 437 and 356 cm^{-1} (X = Br) are assigned to ligand modes, or modes of predominantly ligand character.

The two M–X stretching bands are consistent with a

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[15] C. N. R. Rao, R. Venkataraghavan, and T. R. Kasturi, *Canad. J. Chem.*, 1964, **42**, 36.

tetrahedral $MX_2(LH)_2$ system (Table 1) and the band at 223 cm^{-1} ($X = Cl$) is in the region expected for an Fe–S stretching mode.[16]

The compounds decompose slowly during several months even under dry oxygen-free conditions. They are immediately solvolysed by water and are insoluble in non-polar solvents such as dichloromethane, benzene, and petroleum. They dissolve in solvents of high co-ordinating ability such as dimethyl sulphoxide, where there is evidence for some dissociation ($\Lambda = ca.\ 50\ \Omega^{-1}\ mol^{-1}\ cm^{-2}$).

No complexes of the type $FeX_2(LH)_4$ could be obtained even using ligand to metal ratios $>6:1$. The non-existence of the 4 : 1 species when compared with the well known $FeX_2(pyridine)_4$, is probably due to the size difference of the ligands, rather than to electronic factors.

Cobalt(II).—The complexes $CoX_2(LH)_2$ ($X = Cl, Br, I$) were prepared from ethanolic solutions of the ligand and the corresponding metal halide. No dehydrating agent was necessary, and no difference was observed in the complexes if anhydrous salts were used instead of hydrated salts. Kennedy and Lever [7] have reported the preparation of these complexes and we are in broad agreement with the spectral data they report.

The electronic spectra obtained differ slightly in band positions from those reported, but this is most probably due to the difference between transmission [7] and diffuse reflectance spectra, which is significant, especially below 5 kK.

In the far i.r. region both Co–I stretches can be assigned at 210 and 191 cm^{-1}, corresponding to the Co–Cl stretches in $CoCl_2(LH)_2$ at 303 and 287 cm^{-1}.

Nickel(II).—With a 2 : 1 ratio of ligand to metal the complexes $NiX_2(LH)_2$ ($X = Cl, Br, I$) were obtained whereas a 4 : 1 or 6 : 1 ratio gave the compounds $NiX_2(LH)_4$ ($X = Cl, Br, I$). Intermediate ratios such as 2·5 : 1 or 3 : 1 inevitably led to mixtures of products and it is probable that the yellow and green mixtures reported by Lever [7] in some of his preparations are due to formation of complexes intermediate in composition between $NiX_2(LH)_2$ and $NiX_2(LH)_4$.

The series $NiX_2(LH)_2$ are green ($X = Cl, Br$) or brown ($X = I$) and their susceptibilities of 3·37 ($X = Cl$), 3·36 ($X = Br$), and 3·43 B.M. ($X = I$) are not definitive as to octahedral *vs.* tetrahedral co-ordination.

The electronic spectra are probably more in agreement with an octahedral co-ordination around the nickel but in the absence of ε values it is difficult to be certain; oscillator strengths and band intensities are not necessarily related in reflectance spectra and thus correlation of band intensities is not possible.

Comparison of the far-i.r. spectra allows of complete assignment of the halogen modes, the two bands for $X = Cl, I$ being consistent with a tetrahedral $NiX_2(LH)_2$ system rather than the alternative LH bridged octahedral system; this would be expected to show only one Ni–X stretch.

The data obtained are not definitive of the co-ordination type and it would certainly be unwise to use transmission or reflectance electronic spectra as the deciding factor.

With a 4 : 1 ratio of ligand to metal, complexes of stoicheiometry $NiX_2(LH)_4$ ($X = Cl, Br, I$) were obtained.

With $X = Cl$ the complex was mustard yellow and had $\mu_{eff} = 3{\cdot}16$ B.M. (294·5 K) typical of octahedral nickel. The electronic spectrum was consistent with this, showing the expected three spin-allowed bands at 8·33 ($^3T_{2g}\leftarrow{}^3A_{2g}$), 13·70 ($^3T_{1g}\leftarrow{}^3A_{2g}$), and 21·74 kK [$^3T_{1g}(P)\leftarrow{}^3A_{2g}$]. A band at 10·31 kK is tentatively assigned to the spin-disallowed $^1E_g\leftarrow{}^3A_{2g}$ transition, which is frequently observed.

The occurrence of only a single ν(Ni–Cl) at 242 cm^{-1} in the far i.r. region indicates a *trans*-octahedral structure for the complex.

The compounds $NiX_2(LH)_4$ ($X = Br, I$) are red-brown and dark green respectively, and show very different magnetic and spectral properties to $NiCl_2(LH)_4$. Both complexes are diamagnetic indicating a spin-singlet ground term characteristic of square Ni^{II}. The complexes are soluble in solvents such as pyridine or dimethyl sulphoxide giving conductivities at 10^{-3}M of *ca.* 60—80 Ω^{-1} mol^{-1} cm^{-2} apart for $X = Br$ in pyridine, which gave a conductivity of $<10\ \Omega$ mol^{-1} cm^{-2}. For the species which give conducting solutions the cations $[Ni(LH)_4(py)_2]^{2+}$ or $[Ni(LH)_4(Me_2SO)_2]^{2+}$ are presumably formed.

The electronic spectra of the complexes have the $^1A_{2g}\leftarrow{}^1A_{1g}$ transition at 20·00 ($X = Br$) and 20·83 kK ($X = I$) but the lower-energy band commonly seen in NiS_4^{2+} systems [17] is absent as the band at 8·84 kK in both compounds is probably too low to be assigned to this. A sharp band at 6·04 kK ($X = Br$) and 6·02 kK ($X = I$) is almost certainly vibrational in origin, probably an overtone of the ν(C–H) at *ca.* 3·0 kK.

Consistent with the above interpretation the complexes $NiX_2(LH)_4$ ($X = Br, I$) show no bands attributable to either ν(Ni–Br) or ν(Ni–I) in the far infrared region (450—200 cm^{-1}).

Nickel is the only metal investigated which gives both 2 : 1 and 4 : 1 complexes. A rationalisation in terms of ligand-field stabilisation energies is possible. Nickel(II) has the highest negative ΔH for the transformation tetrahedral$\rightarrow$octahedral [18] calculated in terms of LFSE. Since the other parameters involved probably change uniformly from metal to metal, it is likely that the LFSE's involved do play an important role in the determination of the stereochemistry involved. Consistent with this explanation is the non-existence of Mn^{2+} complexes with pyridine-2-thiol, no reaction being observed even under vigorous conditions.

Copper(I). Copper(I) chloride and bromide react readily as ethanolic suspensions with LH to give complexes of stoicheiometry $CuCl(LH)_3$ and $CuBr(LH)_2$. As expected, the complexes (d^{10}) are diamagnetic and show no bands in the electronic spectrum apart from high-

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energy charge-transfer bands. The complexes are doubtless tetrahedral.[19]

CuI did not react directly with the ligand but $CuI(LH)_2$ could be prepared by adding a methanolic solution of the pyridine-2-thiol containing potassium iodide to a suspension of copper(II) sulphate in methanol, in presence of sulphur dioxide.

The complexes are bright orange, due to charge-transfer absorption.

Silver(I).—With silver(I) tetrafluoroborate the complex $Ag(LH)_4BF_4$ was obtained whereas with $AgClO_4$ the complex $Ag(LH)_2ClO_4$ was isolated. The i.r. spectrum indicates ionic perchlorate, although there is some slight splitting of ν_3; ν_4 is not observed.

Palladium(II) *and Rhodium*(II).—The interaction of $PdCl_2$ with the ligand in refluxing ethanol led to the complex $Pd(LH)_4Cl_2$,EtOH. The orange complex dissolved in water and in methanol in which it gave a conducting solution. The conductivity ($\Lambda = 120\ \Omega^{-1}$ mol^{-1} cm^{-2}; $c\ 10^{-3}$M) was much lower than that expected for a 2 : 1 electrolyte, however, the range in methanol being generally 160—220 Ω^{-1} mol^{-1} cm^{-2}.[20] Analogous behaviour has been noted for the similar complex $Pt(LH)_4Cl_2$.[7] An absorption at 328 cm^{-1} in the far-infrared spectrum may be an indication that there is some degree of Pd–Cl bonding, although it is considered more likely to be a mode of primarily metal–ligand character.

Displacement of co-ordinated acetate occurs with palladous acetate, $[Pd(CO_2Me)_2]_3$, and the complex $PdL_2(LH)$, evidently five-co-ordinate, is obtained. The diamagnetic complex is red, due to charge-transfer absorptions, and is very soluble in chloroform and dichloromethane. At 35 °C, no ^{1}H n.m.r. signal could be detected in $CDCl_3$, but on cooling to −60 °C some broad resonance was observed from τ 2·5 to 3·2. This behaviour is probably due to a rapid exchange process. Indeed similar behaviour has been noted in the complex $Pt(Et_2NCS_2)_2(PMePh_2)$,[21] and in $Pt(SnCl_3)_5^{3-}$ no tin resonance could be detected.[22]

With the dimeric $Rh_2(OAc)_4$, no displacement of co-ordinated acetate was achieved and the adduct $Rh_2(OAc)_4$,2LH was obtained. The complex was purple-brown and had an i.r. spectrum similar to that of $Rh_2(OAc)_4$ with additional bands due to the co-ordinated pyridine-2-thiol. Adducts of $Rh_2(OAc)_4$ with many ligands have been prepared and it has been suggested that the colour of the adduct can be used to distinguish between sulphur and oxygen donor atoms,[23] as oxygen donor ligands produced green adducts and sulphur donor ligands orange or red adducts. There is more range in the colour of adducts with nitrogen donor ligands so assignment of the donor atom in $Rh_2(OAc)_4$,2LH from the colour of the adduct is not feasible. However, the presence of a strong band in the far-i.r. spectrum at 375 cm^{-1}, the correct region for ν(Rh–S), strongly suggested sulphur bonding of the ligands.

Attempts to prepare a pyridine-2-thiolato-complex from $Rh_2(OAc)_4$ were unsuccessful because the bite of the ligand as an anion is insufficient to bridge two metal atoms, which it would be required to do in this case as $Rh_2(OAc)_4$ contains a rhodium–rhodium bond.

Interaction with Copper(II).—Copper(II) chloride and bromide reacted with pyridine-2-thiol in ethanol to give yellow species which were diamagnetic and which had stoicheiometry CuCl(LH) and $CuBr_2(LH)_2$. Pyridine-2-thiol could reduce Cu^{II} to Cu^{I} by being oxidised itself to the disulphide, and the chloride complex is probably a genuine copper(I) species, probably with bridging halogen atoms. It is difficult to rationalise the bromide complex being diamagnetic with its formulation as a copper(II) complex. The differences in stoicheiometry between the copper(I) complexes derived directly from copper(I) and those derived from copper(II) were independent of the ratio of ligand : metal in the reactions. The different complexes obtained probably reflect the two distinct ways by which the complexes are formed. Starting with copper(I), a complex of stoicheiometry $CuCl(LH)_3$ is not unexpected because of the almost inevitable preference of copper(I) for a tetrahedral environment. With the complexes derived from copper(II), it may well be that reduction to copper(I) occurs after co-ordination of the ligand to the metal, so that the stoicheiometry adopted by the complex reflects more the reaction of a copper(II) species.

Copper(II) nitrate, sulphate, acetate, and perchlorate also gave insoluble yellow species. The sulphate and nitrate had stoicheiometry $CuSO_4,1\frac{1}{2}LH$ and $Cu(NO_3)_2,1\frac{1}{2}LH$ and their i.r. spectra indicated co-ordination of the anions. The sulphate complex had $\mu_{eff} = 0{\cdot}45$ B.M. and possessed a rather featureless e.s.r. spectrum consistent with a polymeric structure ($g = 2{\cdot}013$). The acetate reacted to give an extremely insoluble species containing no acetate; it presumably contains ionised pyridine-2-thiol. It had the stoicheiometry $(CuL)_n$. Because of their insolubility and intractable nature the complexes were not studied further.

Although thiourea reduces copper(II) to copper(I), copper(II) complexes containing co-ordinated thiourea can be isolated by using copper(II) perchlorate stabilised by co-ordination to 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy).[24] With $Cu(phen)_2(ClO_4)_2$ the complex $Cu(phen)_2(LH)(ClO_4)_2$ was isolated by allowing the stabilised species to react with the ligand in ethanol. The complex has a normal magnetic moment for copper(II) and has an electronic spectrum consistent with a five-co-ordinate species.

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EXPERIMENTAL

Microanalyses by the Microanalytical Laboratory, Imperial College.

I.r. spectra (4000—450 cm^{-1}) were taken on a Perkin-Elmer 457 spectrophotometer; far-i.r. spectra (450—200 cm^{-1}) on a Perkin-Elmer 325 spectrophotometer, and (200—20 cm^{-1}) on a Beckman FS 720 Fourier spectrophotometer.

Magnetic moments were measured at room temperature using the Evans' modification [25] of the Gouy–Rankine balance. The balance was calibrated using the compound $HgCo(NCS)_4$.

Diffuse reflectance spectra were measured in the region 4—25 kK on a Cary 14 R spectrophotometer using a Cary 1411 diffuse reflectance accessory.

Dried solvents of reagent grade were used in all reactions, but reactions were not carried out under an inert atmosphere unless specifically stated.

Analytical data are collected in Table 2.

TABLE 2

Analytical data

Compound	Found (%)			Required (%)		
	C	H	N	C	H	N
$FeCl_2(LH)_2$	34·8	2·9	8·2	34·4	2·9	8·0
$FeBr_2(LH)_2$	27·4	2·4	6·4	27·4	2·3	6·4
$CoCl_2(LH)_2$	34·3	3·0	7·8	34·1	2·8	8·0
$CoBr_2(LH)_2$	27·7	2·2	6·2	27·2	2·3	6·4
$CoI_2(LH)_2$	23·2	1·9	5·5	22·4	1·9	5·2
$NiCl_2(LH)_2$	34·2	2·6	8·1	34·1	2·8	8·0
$NiBr_2(LH)_2$	28·0	2·5	6·5	27·2	2·3	6·3
$NiI_2(LH)_2$	21·9	1·8	5·0	22·4	1·9	5·2
$NiCl_2(LH)_4$	41·7	3·7	9·9	41·8	3·5	9·8
$NiBr_2(LH)_4$	36·5	3·1	8·6	36·2	3·0	8·4
$NiI_2(LH)_4$	32·5	3·0	7·5	31·7	2·6	7·4
$CuCl(LH)_3$	42·0	3·6	9·5	41·7	3·5	9·5
$CuBr(LH)_2$	32·8	3·0	7·2	32·8	2·7	7·7
$CuI(LH)_2$ [a]	29·4	2·4	6·9	29·1	2·4	6·8
$Cu(phen)_2(LH)(ClO_4)_2$	46·8	2·9	9·4	47·4	2·9	9·5
$Ag(LH)_4BF_4$	37·7	3·2	8·5	37·6	3·1	8·8
$Ag(LH)_2ClO_4$	27·1	2·3	6·2	27·9	2·3	6·5
$Pd(LH)_4Cl_2,EtOH$	40·2	3·9	8·9	39·6	3·9	8·4
$PdL_2(LH)$	40·5	3·1	9·2	41·2	3·4	9·6
$Rh_2(OAc)_4(LH)_2$	33·3	3·6	4·2	32·5	3·3	4·2

[a] I: Found, 31·6%; Required, 30·8%.

Dichlorobis(pyridine-2-thiol)iron(II).—Iron(II) dichloride tetrahydrate (0·5 g) was dissolved under nitrogen in a mixture of ethanol (30 ml) and 2,2-dimethoxypropane (10 ml) which had been degassed with nitrogen. Iron wire (*ca.* 2 g) was added along with conc. hydrochloric acid (*ca.* 0·2 ml) to provide a reducing system. The flask was sealed and shaken periodically until the solution was colourless. The solution was filtered into a solution of pyridine-2-thiol (0·56 g) in ethanol (15 ml). The yellow *powder* which precipitated was filtered off under nitrogen, washed with ethanol (2 × 10 ml) and diethyl ether (2 × 10 ml), and dried *in vacuo* over silica gel (0·82 g, 93%).

Dibromobis(pyridine-2-thiol)iron(II).—This reaction was carried as that described above, except that the iron(II) bromide was prepared from an excess of iron wire and 40% aqueous hydrobromic acid (yield, 0·63 g, 72%).

Dichloro-, Dibromo-, and Di-iodo-bis(pyridine-2-thiol)-cobalt(II).—A solution of the halide (2 mmol) in ethanol (10 ml) was added to a solution of the ligand (4 mmol) in ethanol (15 ml). The *complexes* that immediately precipitated were filtered off, washed with ethanol (2 × 10 ml) and diethyl ether (2 × 10 ml), and dried in *vacuo* over silica gel. The yields were essentially quantitative.

Dichloro-, Dibromo-, and Di-iodo-bis(pyridine-2-thiol)-nickel(II).—These compounds were prepared in an analogous way to the cobalt(II) complexes. The yields were quantitative.

Dichlorotetrakis(pyridine-2-thiol)nickel(II).—A solution of nickel(II) chloride hexahydrate (2 mmol) in ethanol (10 ml) was added to the ligand (8 mmol) in ethanol (20 ml). The yellow *complex* which quantitatively precipitated was collected, washed with ethanol and ether, and dried *in vacuo* over silica gel.

Tetrakis(pyridine-2-thiol)nickel(II) *Dibromide and Di-iodide.*—This reaction was carried out as that for the chloride above, except that the nickel(II) iodide was formed *in situ* by mixing equivalent solutions of nickel(II) chloride and sodium iodide in ethanol and filtering off the precipitated sodium chloride after cooling the solution to −30 °C. The yields of the *complexes* were *ca.* 80%.

Chlorotris(pyridine-2-thiol)copper(I) *and Bromobis(pyridine-2-thiol)copper*(I).—To a suspension of the copper(I) halide (5 mmol) in ethanol (25 ml) was added a solution of the ligand (15 mmol for chloride, 10 mmol for bromide) in ethanol (30 ml) and the solution was vigorously stirred. The halide dissolved immediately to give an orange solution and after 25 s the *complexes* precipitated as bright orange powders. They were filtered off and washed with ethanol and diethyl ether. The yields were *ca.* 75%.

Iodobis(pyridine-2-thiol)copper(I).—Sulphur dioxide was bubbled through a solution of copper(II) sulphate pentahydrate (0·5 g) in methanol (35 ml) and a solution of pyridine-2-thiol (0·7 g) and sodium iodide (0·7 g) in methanol (35 ml) was added. An orange precipitate formed immediately and the solution was stirred for a further 10 min to complete the reaction. The orange *complex* was filtered off, washed with ethanol and ether, and dried *in vacuo* (0·7 g, 67%).

Tetrakis(pyridine-2-thiol)silver(I) *Tetrafluoroborate.*—Silver(I) tetrafluoroborate (0·5 g) in ethanol was added slowly to a solution of pyridine-2-thiol (0·28 g) in ethanol (15 ml) with stirring. An initial precipitate redissolved and the solution was filtered free from any solid which remained (an oily deposit often remains at this stage). When set aside, the solution deposited pale yellow *needles* of the compound. These were collected, washed with a little cold ethanol and ether, and dried *in vacuo* (0·35 g, 46%).

Bis(pyridine-2-thiol)silver(I) *Perchlorate.*—Pyridine-2-thiol (0·32 g) in ethanol (20 ml) was slowly added to a solution of silver(I) perchlorate (0·3 g) in ethanol (20 ml). A pale yellow precipitate formed immediately. It was filtered off, washed with ethanol (2 × 10 ml) and ether (2 × 10 ml), and dried *in vacuo* (0·3 g, 50%).

Tetrakis(pyridine-2-thiol)palladium(II) *Dichloride.*—Palladium(II) chloride (0·5 g) dissolved in the minimum of hot ethanol was added to a hot solution (60°) of pyridine-2-thiol (0·63 g) in ethanol (15 ml). As the solution was cooled, the orange *compound* precipitated. It was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* over silica gel (0·8 g, 71%).

Bis(pyridine-2-thiolato)(pyridine-2-thiol)palladium(II).—Palladous acetate (0·2 g) in hot (60°) benzene (30 ml) was added to pyridine-2-thiol (0·48 g) in boiling benzene (50 ml). As the solution was cooled, the red *complex* precipitated. It was washed with a little benzene and ether and dried *in vacuo* (0·35 g, 90%).

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[25] D. F. Evans, *J. Chem. Soc.* (*A*), 1967, 1670.

Tetra-μ-acetato-bis(pyridine-2-thiol)dirhodium(II).— Rhodium(II) acetate (0·5 g) was dissolved in the minimum of boiling methanol and pyridine-2-thiol (0·25 g) in methanol (25 ml) was added. The initial green solution immediately turned red on the addition of the ligand and deposited the purple-brown *complex* on cooling. It was filtered off, washed with methanol and ether, and dried *in vacuo*. More complex could be obtained by reducing the volume of the solution and cooling to −40 °C (0·4 g, 60%).

Bis(1,10-*phenanthroline*)(*pyridine-2-thiol*)*copper*(II) *Perchlorate*.—Bis(1,10-phenanthroline)copper(II) perchlorate[26] (0·4 g), dried *in vacuo* over silica gel, was suspended in ethanol (30 ml) and pyridine-2-thiol (0·1 g) in ethanol (15 ml) was added. The suspension was stirred for 4 h; the precipitated solid was filtered off, washed with ethanol and ether, and dried *in vacuo* to give the green-brown *complex* (0·2 g, 45%).

We thank the S.R.C. for a studentship and Johnson Matthey Limited for the loan of palladium and rhodium.

[3/860 *Received, 25th April, 1973*]

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[26] A. A. Schilft and R. C. Taylor, *J. Inorg. Nuclear Chem.*, 1959, **9**, 211.