Notes

$[RhPd_2(pyS)_4(\eta^3\text{-}C_4H_7)_2][BF_4]$:† Synthesis and *X*-Ray Structure of a Mixed-metal Trinuclear Complex containing Two μ_3-Pyridine-2-thionato (pyS) Ligands

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The complex $[Rh^{III}(pyS)_3(pySH)]$, containing two chelating pyridine-2-thionato (pyS) ligands, one monodentate S-bonded pyridine-2-thionato ligand, and one monodentate S-bonded 1*H*-pyridine-2-thione (pySH) ligand, reacts with triethylamine and two equivalents of the 2-methylallyl complex $[Pd(\eta^3\text{-}C_4H_7)S_2][BF_4]$ (S = solvent = H_2O or acetone) to yield the trinuclear compound $[Rh^{III}(pyS)_2(\mu_3\text{-}pyS)_2\{Pd^{II}(\eta^3\text{-}C_4H_7)\}_2][BF_4]$, (**1**). The structure of (**1**), determined by single-crystal *X*-ray diffraction, contains two chelating pyridine-2-thionato ligands at rhodium and two which bridge all three metal atoms as part of a bicyclic cage. None of the metal atoms is within bonding distance. The structure may be regarded as containing the cyclic bidentate ligand $[Pd_2(\mu\text{-}pyS)_2(\eta^3\text{-}C_4H_7)_2]$ chelated to the group $[Rh^{III}(pyS)_2]^+$ through two sulphur atoms.

The pyridine-2-thionate (pyridine-2-thiolate, C_5H_4NS) anion displays an unusual flexibility as a ligand since it has been found to co-ordinate as a monodentate ligand through the sulphur atom,[1-3] as a bridging ligand through both sulphur and nitrogen and also through sulphur alone,[4,5] and as a chelating ligand with a very short 'bite'.[1,2,6] Recently we reported a series of rhodium(III) complexes containing 1*H*-pyridine-2-thione and its conjugate anion as the sole ligands.[2] In these compounds there is potential for further co-ordination to Lewis acids (metal ions) using the available lone pairs on sulphur and/or nitrogen atoms to give oligomeric metal systems. The generation of dinuclear and trinuclear systems in a controlled way is of considerable current interest.[7]

Results and Discussion

Reaction of $[Rh(pyS)_3(pySH)]$ (pySH = 1*H*-pyridine-2-thione) in dichloromethane with NEt_3 to generate the anion $[Rh(pyS)_4]^-$ *in situ* and subsequent treatment of this anion with two equivalents of the cationic complex $[Pd(\eta^3\text{-}C_4H_7)S_2][BF_4]$ (S = solvent), formed in a dichloromethane–acetone mixture as solvent, affords a moderate yield (81%) of the trinuclear mixed-metal complex $[Rh(pyS)_2(\mu_3\text{-}pyS)_2\{Pd(\eta^3\text{-}C_4H_7)\}_2][BF_4]$, (**1**) (Scheme). Recrystallisation from a dichloromethane–diethyl ether mixture gave salmon pink crystals of (**1**) which were analytically and spectroscopically pure. The ^1H n.m.r. spectrum shows that the 2-methylallyl ligands are equivalent but unsymmetrical (see Experimental section for data). The aromatic signals indicate the presence of two equally populated sites for the pyridine-2-thionato ligands. Integration gives a ratio of 2:1 for the pyS to C_4H_7 ligands consistent with the formulation we have given. In CD_3CN solution the ^1H n.m.r. spectrum does not change appreciably up to 80 °C indicating that the molecule is rigid up to this temperature.

Table 1. Selected bond distances (Å) and angles (°) for $[Rh(pyS)_4\{Pd(C_4H_7)\}_2][BF_4]$, (**1**)

S(3)–Pd(1)	2.373(4)	N(4)–Pd(1)	2.150(8)
C(21)–Pd(1)	2.163(10)	C(22)–Pd(1)	2.143(9)
C(23)–Pd(1)	2.142(10)	S(4)–Pd(2)	2.361(4)
N(3)–Pd(2)	2.130(7)	C(25)–Pd(2)	2.123(9)
C(26)–Pd(2)	2.169(9)	C(27)–Pd(2)	2.180(9)
S(1)–Rh	2.394(4)	S(2)–Rh	2.371(4)
S(3)–Rh	2.327(4)	S(4)–Rh	2.324(4)
N(1)–Rh	2.070(8)	N(2)–Rh	2.078(7)
C(1)–S(1)	1.751(10)	C(6)–S(2)	1.745(10)
C(11)–S(3)	1.779(9)	C(16)–S(4)	1.774(9)
average C–C	1.38		
average C–N	1.34		
Pd(1) ··· Pd(2)	2.963(4)	Pd(1) ··· Rh	3.920(4)
Pd(2) ··· Rh	3.929(4)		
N(4)–Pd(1)–S(3)	99.2(3)	N(3)–Pd(2)–S(4)	97.7(3)
S(2)–Rh–S(1)	161.2(1)	S(3)–Rh–S(1)	88.6(2)
S(3)–Rh–S(2)	103.4(2)	S(4)–Rh–S(1)	104.6(2)
S(4)–Rh–S(2)	90.1(2)	S(4)–Rh–S(3)	90.0(2)
N(1)–Rh–S(1)	68.9(3)	N(2)–Rh–S(2)	68.9(3)
Rh–S(3)–Pd(1)	113.0(2)	C(11)–S(3)–Pd(1)	104.5(3)
C(11)–S(3)–Rh	100.0(3)	Rh–S(4)–Pd(2)	114.0(2)
C(16)–S(4)–Pd(2)	104.8(3)	C(16)–S(4)–Rh	98.8(3)

Spectroscopic data were inadequate to provide a satisfactory structure so a single-crystal *X*-ray diffraction study was undertaken. The structure of (**1**) is shown in Figure 1 and selected bond lengths and angles in Table 1. The molecule contains an approximate C_2 axis bisecting the S(4)–Rh–S(3) angle which is consistent with the ^1H n.m.r. spectra. Two pyS ligands are chelating at Rh, essentially the same as in the starting compound $[Rh(pyS)_3(pySH)]$.[2] The other two pyS ligands bridge the three metal atoms. These are not joined by metal–metal bonds; the intermetal distances are too great [Pd(1) ··· Pd(2) 2.963(4), Rh ··· Pd(1) 3.920(4), Rh ··· Pd(2) 3.929(4) Å].[8] The Rh–N and Rh–S distances are in the ranges observed in the parent molecule.[2] Also the Pd–N and Pd–S distances are similar to those reported for other related compounds.[9] The stereochemistry about rhodium is distorted octahedral whereas that around palladium is approximately

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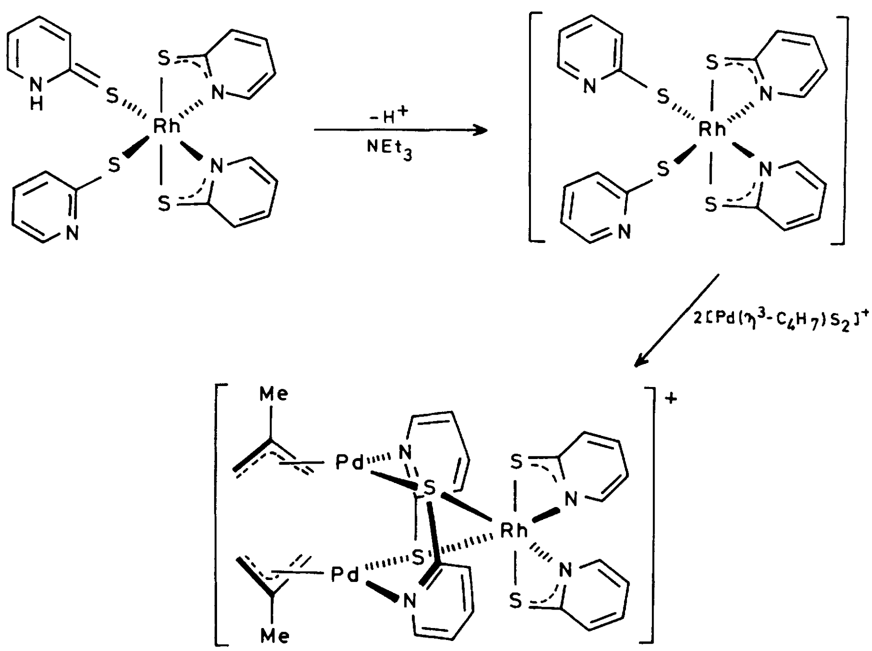
† 1,2-Bis(η^3-2-methylallyl)-3,3-bis(1*H*-pyridine-2-thionato-*N*,*S*)-μ_3-[1*H*-pyridine-2-thionato-*N*(Pd^1),*S*(Pd^{2}Rh^3)]-μ_3-[1*H*-pyridine-2-thionato-*N*(Pd^2),*S*(Pd^{1}Rh^3)]dipalladium(II)rhodium(III) tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



(1)

Scheme. S = solvent

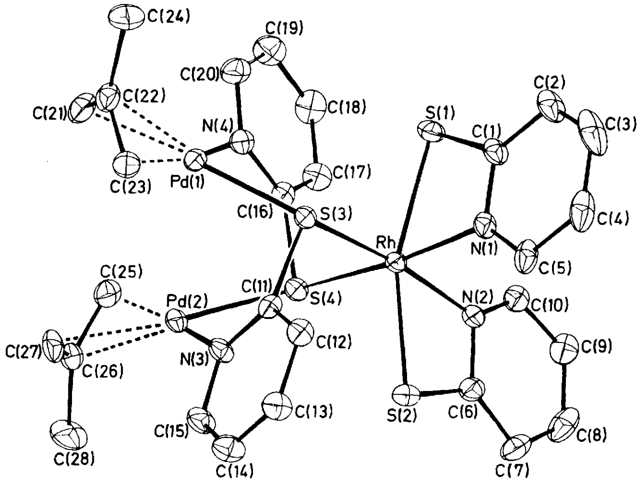


Figure 1. Molecular structure of the cation $[Rh(pyS)_4\{Pd(C_4H_7)\}_2]^+$, (1)

square planar consistent with the retention of the original oxidation states. The geometry of the $RhPd_2(\mu_3\text{-}pyS)_2$ group of atoms can be described as bicyclic (not counting the pyridine rings) with an isosceles triangle of metal atoms capped above and below by the μ_3-pyS ligands.

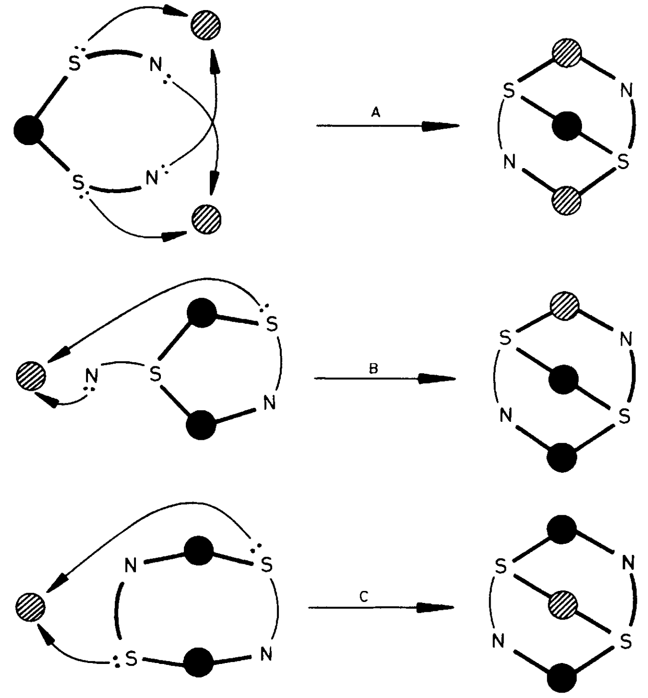


Figure 2. Diagrammatical representation of various ways of forming the $M_3(\mu_3\text{-}pyS)_2$ cage by adding metal atoms ▨ to compounds with metal atoms ● already co-ordinated to pyS ligands

Each palladium atom has been incorporated by co-ordinating to the nitrogen atom of one monodentate pyS ligand and the sulphur atom of the other. This is represented diagramatically in Figure 2 as process A. The same cage system might also be generated by processes B and C in Figure 2. Process B has been found for the formation of $[Rh_3(pyS)_2(CO)_6][ClO_4]$ in which the $Rh_3(pyS)_2$ framework is like that in (**1**) except that all the metal atoms are square planar. We have found examples of process C in the addition of metal cations to $[Pd_2(pyS)_2(\eta^3\text{-}C_4H_7)_2]$, reactions that will be reported elsewhere. With this final example in mind, we can see that compound (**1**) could be considered as a complex of the type $[Rh(pyS)_2Y]^+$ (Y = chelate) in which the neutral chelating ligand is the eight-membered cyclic molecule $[Pd_2(\mu\text{-}pyS)_2(\eta^3\text{-}C_4H_7)_2]$.

Table 2. Fractional atomic co-ordinates (× 10^4) for [Rh(pyS)$_4${Pd(C$_4$H$_7$)}$_2$][BF$_4$], **(1)**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pd(1)	6 563.2(2)	4 097.1(3)	5 079.4(3)	C(8)	5 758(4)	8 869(6)	2 227(6)
Pd(2)	7 169.9(2)	5 275.8(4)	4 504.0(3)	C(9)	5 465(3)	8 156(6)	1 947(5)
Rh	6 021.0(2)	6 447.1(3)	4 218.6(3)	C(10)	5 518(3)	7 411(5)	2 447(5)
S(1)	5 379(1)	5 489(1)	3 852(1)	C(11)	6 831(2)	6 148(4)	5 901(4)
S(2)	6 474(1)	7 766(1)	4 503(1)	C(12)	6 846(3)	6 735(5)	6 570(4)
S(3)	6 330(1)	5 542(1)	5 417(1)	C(13)	7 232(3)	7 269(5)	6 936(5)
S(4)	6 487(1)	5 778(1)	3 552(1)	C(14)	7 559(3)	7 198(6)	6 597(5)
F(1)	6 768(3)	9 429(5)	7 972(5)	C(15)	7 526(3)	6 611(6)	5 923(5)
F(2)	6 255(3)	8 869(4)	8 462(5)	C(16)	6 181(2)	4 768(5)	3 184(4)
F(3)	6 751(3)	7 944(5)	8 242(6)	C(17)	5 910(3)	4 723(6)	2 352(5)
F(4)	6 265(3)	8 530(7)	7 123(5)	C(18)	5 668(3)	3 996(7)	2 053(5)
N(1)	5 557(2)	6 920(4)	4 758(4)	C(19)	5 681(3)	3 267(7)	2 612(6)
N(2)	5 817(2)	7 372(4)	3 218(4)	C(20)	5 960(3)	3 331(5)	3 444(6)
N(3)	7 168(2)	6 086(4)	5 572(4)	C(21)	6 864(3)	2 762(6)	5 217(6)
N(4)	6 204(2)	4 062(4)	3 736(4)	C(22)	6 775(3)	3 006(6)	5 978(5)
C(1)	5 231(2)	6 295(6)	4 495(5)	C(23)	6 962(3)	3 824(6)	6 368(5)
C(2)	4 851(3)	6 364(8)	4 720(6)	C(24)	6 434(4)	2 488(8)	6 274(7)
C(3)	4 809(4)	7 024(11)	5 221(7)	C(25)	7 298(3)	4 328(5)	3 639(5)
C(4)	5 152(4)	7 697(8)	5 506(6)	C(26)	7 709(3)	4 692(5)	4 137(5)
C(5)	5 533(3)	7 617(6)	5 259(5)	C(27)	7 813(3)	4 612(6)	5 014(5)
C(6)	6 107(3)	8 058(5)	3 506(5)	C(28)	7 968(4)	5 295(8)	3 729(7)
C(7)	6 096(3)	9 835(6)	3 020(6)	B	6 504(5)	8 685(8)	7 945(7)

Experimental

The compounds [Rh(pyS)$_3$(pySH)][2] and [Pd$_2$Cl$_2$(η^3-C$_4$H$_7$)$_2$][10] were prepared as reported previously.

Synthesis of [Rh(pyS)$_4${Pd(C$_4$H$_7$)}$_2$][BF$_4$].—A mixture of [Rh(pyS)$_3$(pySH)] (0.100 g, 1.84 × 10^{-4} mol) and triethylamine (0.025 cm^3, 1.84 × 10^{-4} mol) in dichloromethane (10 cm^3) was stirred for 10 min. The compound Ag[BF$_4$] (0.071 g, 3.68 × 10^{-4} mol) was added to a solution of [Pd$_2$Cl$_2$(η^3-C$_4$H$_7$)$_2$] (0.072 g, 1.84 × 10^{-4} mol) in acetone (5 cm^3). After 5 min the precipitate of AgCl was filtered off and the rhodium- and palladium-containing solutions were mixed. The mixture became paler and was stirred for 1 h, filtered, and the product precipitated, by addition of diethyl ether, as a salmon-pink solid (0.143 g, 81%) (Found: C, 35.5; H, 3.2; N, 5.8. C$_{28}$H$_{30}$BF$_4$N$_4$Pd$_2$RhS$_4$ requires C, 35.3; H, 3.1; N, 5.8%). Recrystallisation by dissolving in dichloromethane and precipitating with diethyl ether gave well formed crystals suitable for *X*-ray structure determination. ^{1}H N.m.r. (200 MHz, 24 °C, CD$_2$Cl$_2$): δ 8.56 (d, H^6), 7.73 (m, H^3, H^4), 7.38 (t, H^5) (chelating pyS); δ 8.05 (d, H^6), 7.21 (m, H^4), 6.76 (t, H^5), 6.69 (d, H^3) (μ_3-pyS); δ 4.10(s), 3.54(s), 3.18(s), 2.38(s), 2.23 (s, Me) (2-methylallyl).

Crystallographic Studies.—Crystal data. C$_{28}$H$_{30}$BF$_4$N$_4$-Pd$_2$RhS$_4$, M = 863.3, monoclinic, a = 31.795(2), b = 14.692(3), c = 16.515(1) Å, β = 108.45(1)°, U = 7 317.9 Å^3, Z = 8, space group $C2/c$, D_c = 1.567 g cm^{-3}, F(000) = 3 429, λ = 0.710 69 Å, μ(Mo-K_α) = 12.2 cm^{-1}, crystal size 0.35 × 0.33 × 0.10 mm.

Data collection. Unit-cell parameters and intensity data were obtained by previously detailed procedures,[11] using a CAD4 diffractometer operating in the ω–2θ scan mode, with graphite monochromatised Mo-K_α radiation. A total of 6 844 unique reflections were collected ($1.5 \leqslant \theta \leqslant 25.0°$), the segment of reciprocal space scanned was: h 0 to 37, k 0 to 17, l −19 to 19. The reflection intensities were corrected for absorption, using the azimuthal-scan method;[12] maximum transmission factor 1.00, minimum value 0.95.

Structure solution and refinement. The structure was solved by routine heavy-atom methods, and refined by full-matrix least squares (SHELX 76[13]). All non-hydrogen atoms were refined with anisotropic coefficients. The final cycles of refinement included hydrogen atoms of the phenyl rings in calculated positions (C–H 0.96 Å), with their isotropic thermal parameters allowed to refine. Only the methyl hydrogen atoms of the 2-methylallyl ligands were included in the refinement (C–H 0.96 Å, U = 0.10 Å^2). The final values of R and R' were 0.040 and 0.046 respectively for the 419 variables and 4 667 data for which $F_o \geqslant 3\sigma(F_o)$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with the weight, w, being defined as $1/[\sigma^2(F_o) + 0.004{F_o}^2]$. A final difference map had peaks of up to 0.6 e Å^{-3} near the heavy atoms but was featureless elsewhere. Atomic scattering factors and anomalous scattering parameters were taken from refs. 14 and 15 respectively. All computations were made on a DEC VAX-11/750 computer. Atomic co-ordinates are given in Table 2.

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