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Binuclear complexes of rhodium(II) bridged by anionic $\widehat{NS}$ ligands and X-ray crystal structure of tetrakis(μ-5-methylthio-2-mercaptothiadiazolinato)triphenylphosphinodirhodium*

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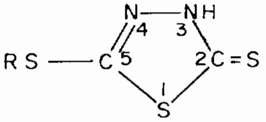
Abstract

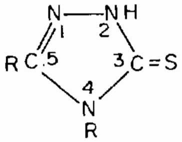
Reactions of the binuclear complex $[Rh(OCOCH_3)_2]_2$ with bifunctional anionic heterocyclic ligands such as 5-substituted 2-mercaptothiadiazolines, 4,5-substituted 3-mercaptotriazoles or thiazolidine-2-thione in the presence of a base yield the binuclear complexes $Rh\{\mu\text{-}(\widehat{NS})_2(OCOCH_3)_2\}\cdot 2L$ where $\widehat{NS}$ is the monoanionic group listed and L = PPh_3, $P(OR)_3$ or Py. With a large excess of the anionic ligand, fully substituted products of the type $[Rh(\mu\text{-}\widehat{NS})_2]_2L$ are obtained. These complexes are characterized by IR, ^1H NMR and electronic spectroscopy. The structure of the 3-mercapto-5-methylthio-1-2-thiadiazolinate bridged rhodium complex $[Rh(DMTH)_2]_2PPh_3$ has been determined by X-ray crystallography. This compound, $C_{30}H_{27}N_8PS_{12}Rh_2$, formula weight = 1121.2, crystallizes in the space group $P2_1/a$ with $a = 20.403(2)$, $b = 9.752(2)$, $c = 23.176(1)$ Å, $\beta = 112.77(1)°$, $V = 4252.0(5)$ Å^3, $Z = 4$. The prominent feature of this compound is the bridging arrangement in which all four sulfur atoms and a triphenylphosphine group are bound to one rhodium while the other rhodium atom is bound equatorially to four nitrogen atoms, the axial position being vacant. The Rh–P distance is 2.350(2) Å, with the Rh(1)–Rh(2)–P angle of 174.1(1)°. The geometry around Rh(2) is distorted octahedral, while that around Rh(1) is square-pyramidal. The Rh(1)–Rh(2) distance is 2.603(1) Å.

Introduction

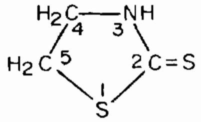
The synthesis and characterization of a large number of dirhodium(II) complexes with bridging carboxylate ions and neutral axial ligands have been reported [1, 2]. Several 2-oxopyridinate [3–5], acetamidate [6, 7] and benzamidate [8] dirhodium(II) complexes have also been synthesized and structurally determined. Dirhodium(II) complexes with axially and equatorially non-equivalent rhodium atoms containing bridging ω-caprolactum ions and one axially bound caprolactum ligand have been reported by Bear and co-workers [9]. There are few reports of partial replacement of acetate ligands in $Rh_2(OCOR)_4$ using other bridging anionic ligands [10]. With the intention of synthesizing Rh–Rh bonded complexes containing bridging heterocyclic anionic ligands, we herein report partial as well as complete replacement of carboxylate ions in the $Rh_2(OCOCH_3)_4$ complex. The axial ligands used are PPh_3, $P(OR)_3$ and Py; and the bridging anions are heterocyclic ligands containing nitrogen and an exocyclic thiocarbonyl group. The following heterocyclic ligands were used for the present study.



5-Alkylthiothiadiazoline-2-thione where R = CH_3 (1), CH_3CH_2 (2) or C_3H_7 (3)



4,5-Substituted 1,2,4-triazoline-2-thione where R = CH_3, C_6H_5 or $CH_2CH_2C_6H_5$



Thiazolidine-2-thione

Experimental

Reactions were carried out by using freshly dried, distilled and degassed solvents under an atmosphere

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of pure, dry nitrogen. IR spectra were recorded as Nujol mulls or KBr pellets on a Perkin-Elmer 599 IR spectrophotometer and NMR spectra on a Bruker WH 90 spectrophotometer.

Thiazolidine-2-thione was purchased from Aldrich Chemical Co. Thiadiazolinethione [11], 1,2,4-triazolinethiones [12] and Rh$_2$(OCOCH$_3$)$_4$·2CH$_3$OH [13] were prepared by reported methods. The ligands PPh$_3$, P(OCH$_3$)$_3$, P(OC$_3$H$_7^i$)$_3$ and Py were purchased from standard suppliers.

Preparation of bis(μ-acetato)bis(μ-5-methylthio-2-mercapto-1,3,4-thiadiazole)bis-triphenylphosphinodirhodium(II)

The sodium derivative of the ligand was prepared by stirring the ligand (0.328 g, 2 mmol) and oil-free sodium hydride (0.048 g, 2 mmol) in ether (25 ml) for 4 h. The ether was removed and the sodium derivative was suspended in benzene (50 ml), to which Rh(OCOCH$_3$)$_4$(CH$_3$OH)$_2$ (0.506 g, 1 mmol) and PPh$_3$ (0.524 g, 2 mmol) were added, and refluxed for 16 h. The contents were centrifuged and the clear benzene solution was concentrated to produce deep brown crystals which were washed with petroleum ether and dried *in vacuo*. The product was recrystallized from a methanol–petroleum ether mixture.

Other bis-substituted complexes were prepared similarly (Table 1).

Preparation of tetra(μ-5-methylthio-2-mercapto-1,3,4-thiadiazole)triphenylphosphinodirhodium(II)

The sodium derivative of the ligand was prepared from 5-alkylthiothiadiazoline-2-thione (1.8 g, 11 mmol) and NaH (0.264 g, 11 mmol), dissolved in ethanol (60 ml) and refluxed along with Rh$_2$(OCOCH$_3$)$_4$(CH$_3$OH)$_2$ (0.50 g, 1 mmol) for 72 h. Triphenylphosphine (0.524 g, 2 mmol) was added and the mixture was stirred for 2 h. The product was collected by filtration, washed with methanol and dried *in vacuo*.

Other tetra-substituted products were prepared similarly (Table 1).

X-ray data collection and analysis

Deep brown crystals of C$_{30}$H$_{27}$N$_8$PS$_{12}$Rh$_2$ were grown from benzene. Accurate unit cell parameters were determined by a least-squares fit of 20 machine centered reflections $30 < 2\theta < 57°$. Data were collected on a Nonius CAD-4F-11M single crystal X-ray diffractometer by using Cu Kα radiation ($\lambda = 1.5418$ Å). Three standard reflections {7, 2, 4; 12, 0, −2; 7, 4, −7} measured after every hour showed 4% variation in average intensity. Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. Scattering factors were taken from International Tables for X-ray Crystallography [14]. The structure was solved by direct methods using MULTAN-78 [15]. Block diagonal least-squares refinement LALS [16] of scale factor, positional and anisotropic thermal parameters for non-

TABLE 1. Rhodium(II) complexes of alkyl-thiadiazoles, -thiolatotriazoles and -thiolatothiazolidines

Compound no.	Compound[a]	Yield (%)	Melting point (°C)	Elemental analysis (%)			
				C	H	N	P
1	Rh$_2$(OCOCH$_3$)$_2$(CH$_3$DMTD)$_2$(PPh$_3$)$_2$	50	170	47.13(47.01)	3.66(3.57)	4.82(4.77)	5.67(5.28)
2	Rh$_2$(OCOCH$_3$)$_2$(isopropylDMTD)$_2$(PPh$_3$)$_2$	53	155	48.67(48.78)	4.27(4.06)	4.88(4.55)	5.23(5.04)
3	Rh$_2$(OCOCH$_3$)$_2$(butylDMTD)$_2$(PPh$_3$)$_2$	55	160	49.92(49.60)	4.08(4.29)	4.86(4.45)	4.46(4.92)
4	Rh$_2$(OCOCH$_3$)$_2$(butylDMTD)$_2$(POPh$_3$)$_2$	60	90	46.46(46.08)	3.76(3.98)	4.36(4.13)	4.47(4.57)
5	Rh$_2$(OCOCH$_3$)$_2$(CH$_3$DMTD)$_2$(Py)$_2$	48	>200	29.99(29.70)	2.36(2.72)	10.88(10.39)	
6	Rh$_2$(OCOCH$_3$)$_2$(C–Ph–N–Phtriazole)$_2$(PPh$_3$)$_2$	47	>250	60.92(60.35)	4.37(4.14)	6.66(6.21)	4.10(4.58)
7	Rh$_2$(OCOCH$_3$)$_2$(CCH$_3$–NCH$_3$triazole)$_2$(PPh$_3$)$_2$	62	>250	51.92(52.17)	4.36(4.34)	7.69(7.60)	5.45(5.61)
8	Rh$_2$(OCOCH$_3$)$_2$(C–CH$_3$NPhentriazole)$_2$(PPh$_3$)$_2$	45	90	57.22(57.94)	4.69(4.67)	6.82(6.54)	4.53(4.82)
9	Rh$_2$(OCOCH$_3$)$_2$(C–PhNPhentriazole)$_2$(PPh$_3$)$_2$	54	97	61.87(61.36)	4.19(4.54)	5.33(5.96)	4.68(4.40)
10	Rh$_2$(OCOCH$_3$)$_2$(C–PhN–CH$_3$triazole)$_2$(PPh$_3$)$_2$	59	>220	56.96(56.67)	4.57(4.23)	6.03(6.84)	5.46(5.04)
11	Rh$_2$(OCOCH$_3$)$_2$(thiazolidinethione)$_2$[P(OPr$_3$)]$_2$	60	>250	34.94(34.42)	5.39(5.73)	2.06(2.86)	6.11(6.35)
12	Rh$_2$(OCOCH$_3$)$_2$(thiazolidinethione)$_2$(Py)$_2$	63	>250	33.63(33.42)	3.09(3.06)	7.53(7.79)	
13	Rh$_2$(CH$_3$DMTD)$_4$(PPh$_3$)	51	>250	32.45(32.14)	2.44(2.41)	10.10(10.00)	2.64(2.76)
14	Rh$_2$(isopropylDMTD)$_4$(PPh$_3$)	55	>250	37.33(37.01)	3.27(3.49)	9.33(9.09)	2.34(2.51)
16	Rh$_2$(C–PhN–triazole)$_4$(PPh$_3$)	61	>250	60.69(60.16)	3.21(3.72)	11.77(11.38)	2.23(2.10)
17	Rh$_2$(C–CH$_3$NCH$_3$triazole)$_4$(PPh$_3$)	56	>250	41.44(41.63)	3.69(3.97)	17.72(17.14)	3.39(3.16)
18	Rh$_2$(C–PhNCH$_3$triazole)$_4$(PPh$_3$)	59	>250	52.93(52.76)	3.56(3.82)	13.56(13.68)	2.34(2.52)
19	Rh$_2$(thiazolidinethione)$_4$[P(OPr)$_3$]	62	>250	28.67(28.44)	4.33(4.17)	6.17(6.32)	3.23(3.49)
20	Rh$_2$(thiazolidinethione)$_4$(PPh$_3$)	45	>250	38.62(38.29)	3.48(3.29)	5.77(5.95)	3.48(3.29)

[a] Abbreviations: CH$_3$DMTD = 5-methylthiothiadiazolinethione; isopropylDMTD = 5-isopropylthiothiadiazolinethione; butylDMTD = 5-butylthiothiadiazolinethione; C–Ph–N–Phtriazole = C-phenyl *N*-phenyltriazolinethione; C–CH$_3$–N–CH$_3$triazole = C-methyl *N*-methyl triazolinethione; C–Ph–N–Phentriazole = C-phenyl *N*-phenethyltriazolinethione; Py = pyridine; P(OPr)$_3$ = triisopropyl phosphite.

hydrogen atoms was carried out. Coordinates of hydrogen atoms were geometrically determined and held fixed during refinement. Each H atom was assigned the same temperature factor as the atom to which it was bonded. The H atom scattering contribution was included in all subsequent calculations. The Cruick Shank's weighting scheme of the type $w=[a+b|F_o|+c|F_o|^2]^{-1}$ with $a=11.48, b=1.0, c=0.0044$ was applied. The refinement converged to $R=0.063$, $R_w=0.070$. The crystal data, data collection and refinement parameters are summarized in Table 2. The final atomic coordinates are given in Table 3, and Table 4 gives bond lengths and bond angles. Figure 1 shows the perspective view of the molecule along with the crystallographic numbering.

Results and discussion

Dirhodium tetraacetate reacts with sodio derivatives of $\widehat{NS}$ heterocyclic ligands in a 1:2 mole ratio in the presence of Lewis bases (L) such as PPh_3, $P(OR)_3$ and Py to form mixed binuclear complexes of the type $Rh_2(OCOCH_3)_2(\widehat{NS})_2(L)_2$.

$$Rh_2(OCOCH_3)_4+2Na(\widehat{NS})+2PPh_3 \longrightarrow$$
$$Rh_2(OCOCH_3)_2(PPh_3)_2(\widehat{NS})_2+2NaOCOCH_3$$

TABLE 2. Crystal and refinement data

Molecular formula	$C_{30}H_{27}N_8PS_{12}Rh_2$
Formula weight	1121.2
Crystal dimensions (mm)	0.57×0.15×0.06
Crystal colour	deep brown
Space group	$P2_1/a$
a (Å)	20.403(2)
b (Å)	9.752(2)
c (Å)	23.176(1)
β (°)	112.77(1)
Cell volume (Å)^3	4252.0(5)
Z	4
$F(000)$	2240
D_{calc} (gm/cm^3)	1.75
Temperature (K)	293
Radiation	nickel filtered Cu Kα ($\lambda=1.5418$ Å)
μ (Cu Kα) (cm^{-1})	123.3
Scan technique	$\omega/2\theta$
Scan speed (° min^{-1})	1
Scan width (°)	0.80+0.35 tgθ
Scan range (°)	$0<\theta<60.0$
Total no. unique reflections	6718
Cut off observed data	$3\sigma(I)$
No. observed reflections	4505
No. parameters refined	478
R[a] and R_w[b]	0.063 and 0.070

[a] $R=(\Sigma||F_o|-k|F_c||)/\Sigma|F_o|$. [b] $R_w=[\Sigma w(|F_o|-k|F_c|)^2/\Sigma|F_o|^2]^{1/2}$; $w=[a+b|F_o|+c|F_o|^2]^{-1}$; $a=11.48$, $b=1.0$ and $c=0.0044$.

TABLE 3. Atomic coordinates (×10^4) (×10^5 for Rh) and equivalent isotropic thermal parameters for non-hydrogen atoms with e.s.d.s in parentheses

	x	y	z	B_{eq} (Å^2)[a]
Rh(1)	14139(3)	12176(7)	67294(3)	2.41(2)
Rh(2)	25196(3)	6656(6)	77404(3)	2.33(3)
P	3485(1)	363(2)	8699(1)	2.27(9)
S(1)	2745(1)	3057(2)	7852(1)	3.21(10)
S(2)	1634(1)	5194(2)	7766(1)	3.63(11)
S(3)	122(2)	6118(3)	7071(1)	5.19(13)
S(4)	1754(1)	688(3)	8298(1)	2.95(10)
S(5)	261(1)	−443(3)	7882(1)	3.71(11)
S(6)	−1106(2)	−1044(3)	6730(1)	4.78(14)
S(7)	2269(1)	−1685(2)	7541(1)	3.01(10)
S(8)	1585(1)	−3271(3)	6341(1)	3.82(11)
S(9)	576(2)	−3188(3)	4993(1)	5.69(14)
S(10)	3166(1)	479(3)	7082(1)	3.77(11)
S(11)	3138(1)	2522(3)	6087(1)	3.79(11)
S(12)	2184(2)	4590(4)	5120(1)	5.79(14)
N(1)	1364(4)	3088(7)	7079(3)	3.1(3)
N(2)	722(4)	3793(7)	6883(3)	3.1(3)
N(3)	760(4)	480(7)	7114(3)	2.8(3)
N(4)	85(4)	89(8)	6748(3)	3.0(3)
N(5)	2063(4)	1974(7)	6333(3)	3.0(3)
N(6)	1825(4)	2961(8)	5866(3)	3.6(3)
N(7)	1432(4)	−694(8)	6402(3)	3.1(3)
N(8)	1003(4)	−1049(8)	5785(3)	3.3(3)
C(1)	1909(5)	3667(9)	7533(3)	3.1(4)
C(2)	783(5)	4924(10)	7203(4)	3.3(4)
C(3)	−520(7)	5521(14)	6345(6)	7.2(6)
C(4)	953(5)	278(9)	7729(4)	3.1(4)
C(5)	−250(5)	−414(10)	7075(4)	3.4(4)
C(6)	−1366(9)	−1156(29)	7350(8)	12.3(8)
C(7)	1753(5)	−1745(10)	6759(4)	3.0(4)
C(8)	1032(5)	−2359(10)	5690(4)	3.5(4)
C(9)	−31(7)	−1896(14)	4558(6)	6.1(6)
C(10)	2738(4)	1641(9)	6506(4)	2.8(4)
C(11)	2333(6)	3331(12)	5700(4)	4.1(5)
C(12)	2997(7)	4563(18)	5022(6)	9.6(6)
C(13)	3355(5)	977(10)	9396(4)	3.0(4)
C(14)	3035(5)	2212(11)	9390(4)	4.0(5)
C(15)	2993(6)	2777(12)	9934(5)	5.4(5)
C(16)	3264(6)	2020(13)	10482(4)	5.7(5)
C(17)	3565(6)	778(14)	10491(4)	5.7(5)
C(18)	3610(5)	196(12)	9952(4)	4.2(4)
C(19)	4307(5)	1249(10)	8793(4)	3.2(4)
C(20)	4660(5)	2102(9)	9299(4)	3.3(4)
C(21)	5283(6)	2761(12)	9361(5)	4.3(5)
C(22)	5567(6)	2616(12)	8917(5)	4.6(5)
C(23)	5232(6)	1744(15)	8408(5)	5.5(5)
C(24)	4614(5)	1049(13)	8341(5)	4.9(5)
C(25)	3745(5)	−1431(9)	8882(4)	3.0(4)
C(26)	4410(6)	−1926(11)	8960(4)	4.6(5)
C(27)	4557(6)	−3338(13)	9061(5)	6.0(5)
C(28)	4028(8)	−4199(14)	9073(6)	6.2(7)
C(29)	3372(7)	−3715(12)	9013(5)	5.2(6)
C(30)	3235(6)	−2333(10)	8913(4)	3.8(4)

[a] $B_{eq}=\frac{4}{3}(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta)$.

The bis-acetato dirhodium complexes are dark brown in colour. The thiazolinemercapto complexes are partially soluble in chloroform and dichloromethane and insoluble in hexane but the other complexes containing

TABLE 4. Bond distances (Å) and bond angles (°) with e.s.d.s in parentheses

Bond distances			
Rh(1)–Rh(2)	2.603(1)	Rh(1)–N(1)	2.015(7)
Rh(1)–N(3)	2.002(7)	Rh(1)–N(5)	2.020(8)
Rh(1)–N(7)	2.018(7)	Rh(2)–P	2.350(2)
Rh(2)–S(1)	2.372(2)	Rh(2)–S(4)	2.382(3)
Rh(2)–S(7)	2.355(2)	Rh(2)–S(10)	2.379(3)
P–C(13)	1.834(9)	P–C(19)	1.822(10)
P–C(25)	1.830(9)	S(1)–C(1)	1.685(10)
S(2)–C(1)	1.748(9)	S(2)–C(2)	1.741(10)
S(3)–C(2)	1.718(11)	S(3)–C(3)	1.782(14)
S(4)–C(4)	1.703(9)	S(5)–C(4)	1.732(10)
S(5)–C(5)	1.753(9)	S(6)–C(5)	1.729(11)
S(6)–C(6)	1.716(18)	S(7)–C(7)	1.709(8)
S(8)–C(7)	1.736(9)	S(8)–C(8)	1.739(9)
S(9)–C(8)	1.722(9)	S(9)–C(9)	1.780(14)
S(10)–C(10)	1.711(9)	S(11)–C(10)	1.720(9)
S(11)–C(11)	1.727(12)	S(12)–C(11)	1.757(11)
S(12)–C(12)	1.761(16)	N(1)–N(2)	1.390(11)
N(1)–C(1)	1.325(11)	N(2)–C(2)	1.308(12)
N(3)–N(4)	1.364(10)	N(3)–C(4)	1.339(10)
N(4)–C(5)	1.297(13)	N(5)–N(6)	1.388(10)
N(5)–C(10)	1.317(12)	N(6)–C(11)	1.290(15)
N(7)–N(8)	1.400(9)	N(7)–C(7)	1.321(11)
N(8)–C(8)	1.301(13)	C(13)–C(14)	1.368(15)
C(13)–C(18)	1.412(12)	C(14)–C(15)	1.408(15)
C(15)–C(16)	1.386(15)	C(16)–C(17)	1.355(19)
C(17)–C(18)	1.408(14)	C(19)–C(20)	1.391(12)
C(19)–C(24)	1.427(14)	C(20)–C(21)	1.381(16)
C(21)–C(22)	1.369(16)	C(22)–C(23)	1.399(16)
C(23)–C(24)	1.386(18)	C(25)–C(26)	1.385(16)
C(25)–C(30)	1.386(15)	C(26)–C(27)	1.410(16)
C(27)–C(28)	1.376(21)	C(28)–C(29)	1.375(23)
C(29)–C(30)	1.378(15)		
Bond angles			
Rh(2)–Rh(1)–N(1)	89.2(2)	Rh(2)–Rh(1)–N(3)	91.1(2)
Rh(2)–Rh(1)–N(5)	89.6(2)	Rh(2)–Rh(1)–N(7)	90.7(2)
N(1)–Rh(1)–N(3)	90.0(3)	N(1)–Rh(1)–N(5)	89.8(3)
N(1)–Rh(1)–N(7)	177.0(3)	N(3)–Rh(1)–N(5)	179.3(3)
N(3)–Rh(1)–N(7)	87.0(3)	N(5)–Rh(1)–N(7)	93.2(3)
Rh(1)–Rh(2)–P	174.1(1)	Rh(1)–Rh(2)–S(1)	87.7(1)
Rh(1)–Rh(2)–S(4)	87.9(1)	Rh(1)–Rh(2)–S(7)	88.7(1)
Rh(1)–Rh(2)–S(10)	86.6(1)	P–Rh(2)–S(1)	87.9(1)
P–Rh(2)–S(4)	88.5(1)	P–Rh(2)–S(7)	95.9(1)
P–Rh(2)–S(10)	97.3(1)	S(1)–Rh(2)–S(4)	94.1(1)
S(1)–Rh(2)–S(7)	175.3(1)	S(1)–Rh(2)–S(10)	90.7(1)
S(4)–Rh(2)–S(7)	88.7(1)	S(4)–Rh(2)–S(10)	172.5(1)
S(7)–Rh(2)–S(10)	86.1(1)	C(13)–P–C(19)	100.4(4)
C(13)–P–C(25)	103.7(4)	C(19)–P–C(25)	104.8(4)
C(1)–S(2)–C(2)	89.2(4)	C(2)–S(3)–C(3)	100.8(6)
C(4)–S(5)–C(5)	88.3(5)	C(5)–S(6)–C(6)	102.7(8)
C(7)–S(8)–C(8)	88.1(5)	C(8)–S(9)–C(9)	101.7(6)
C(10)–S(11)–C(11)	87.6(5)	C(11)–S(12)–C(12)	101.2(6)
N(2)–N(1)–C(1)	116.4(7)	N(1)–N(2)–C(2)	111.1(7)
N(4)–N(3)–C(4)	115.4(7)	N(3)–N(4)–C(5)	112.2(7)
N(6)–N(5)–C(10)	114.7(7)	N(5)–N(6)–C(11)	110.3(8)
N(8)–N(7)–C(7)	114.2(7)	N(7)–N(8)–C(8)	111.4(7)
S(1)–C(1)–S(2)	123.8(5)	S(1)–C(1)–N(1)	126.5(7)
S(2)–C(1)–N(1)	109.7(6)	S(2)–C(2)–S(3)	121.2(6)
S(2)–C(2)–N(2)	113.6(7)	S(3)–C(2)–N(2)	125.0(7)
S(4)–C(4)–S(5)	123.4(5)	S(4)–C(4)–N(3)	126.0(7)
S(5)–C(4)–N(3)	110.6(6)	S(5)–C(5)–S(6)	124.4(6)
S(5)–C(5)–N(4)	113.5(7)	S(6)–C(5)–N(4)	122.0(8)
S(7)–C(7)–S(8)	121.9(5)	S(7)–C(7)–N(7)	126.2(7)
S(8)–C(7)–N(7)	111.9(7)	S(8)–C(8)–S(9)	120.5(6)
S(8)–C(8)–N(8)	114.3(7)	S(9)–C(8)–N(8)	125.2(8)
S(10)–C(10)–S(11)	124.1(5)	S(10)–C(10)–N(5)	124.0(7)
S(11)–C(10)–N(5)	111.9(6)	S(11)–C(11)–S(12)	124.4(7)
S(11)–C(11)–N(6)	115.4(8)	S(12)–C(11)–N(6)	120.1(8)
P–C(13)–C(14)	120.7(7)	P–C(13)–C(18)	119.9(7)
C(14)–C(13)–C(18)	119.3(9)	C(13)–C(14)–C(15)	122.0(10)
C(14)–C(15)–C(16)	118.2(10)	C(15)–C(16)–C(17)	120.5(11)
C(16)–C(17)–C(18)	122.2(11)	C(13)–C(18)–C(17)	117.7(9)
P–C(19)–C(20)	122.5(7)	P–C(19)–C(24)	119.5(7)
C(20)–C(19)–C(24)	118.0(9)	C(19)–C(20)–C(21)	121.5(9)
C(20)–C(21)–C(22)	120.9(10)	C(21)–C(22)–C(23)	119.0(11)
C(22)–C(23)–C(24)	121.2(11)	C(19)–C(24)–C(23)	119.3(10)
P–C(25)–C(26)	123.0(7)	P–C(25)–C(30)	117.6(7)
C(26)–C(25)–C(30)	119.4(9)	C(25)–C(26)–C(27)	119.7(10)
C(26)–C(27)–C(28)	118.8(11)	C(27)–C(28)–C(29)	121.9(13)
C(28)–C(29)–C(30)	118.6(12)		

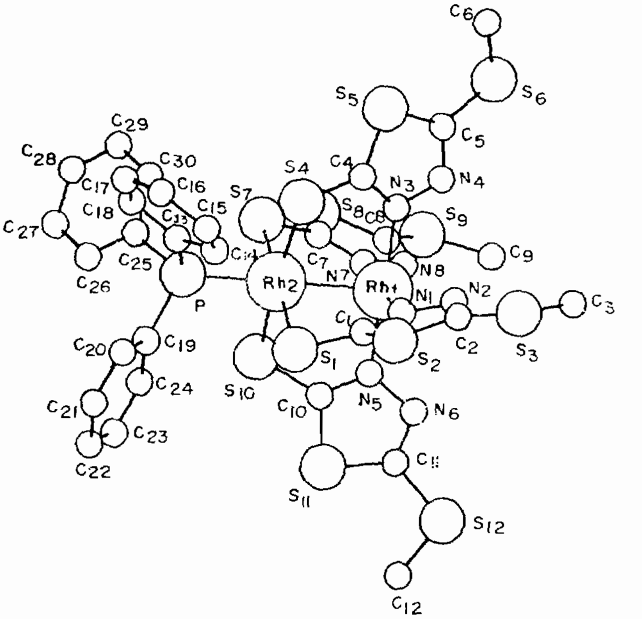

Fig. 1. A perspective view of the molecule along with the crystallographic numbering.

thiazolinemercapto and triazolinethiolato ligands are insoluble in chloroform and alcohol.

Replacement of all the acetate groups by $(\overset{\frown}{NS})$ containing ligands was carried out by refluxing $Rh_2(OCOCH_3)_4$ with a large excess of the sodium derivative of the ligand in ethanol for 72 h. In the same reaction, PPh_3 was added to produce a mono adduct $[(\overset{\frown}{NS})_4Rh_2(PPh_3)]$.

$$Rh_2(OCOCH_3)_4 + 4Na(\overset{\frown}{NS}) + PPh_3 \longrightarrow$$
$$Rh_2(\overset{\frown}{NS})_4(L) + 4NaOCOCH_3$$

The products isolated are air stable, orange to brown crystalline solids which show low solubility in chloroform, dichloromethane and are insoluble in light petroleum.

The IR spectra of bis-acetato complexes show a strong absorption band around 1550–1580 cm^{-1} due to $\nu_{as}(OCO)$ which is at a lower frequency than that found for $Rh_2(OCOCH_3)_4$ at 1588 cm^{-1} [17]. In the spectra of $Rh_2(\widehat{NS})_4L$, $\nu(OCO)$ is absent indicating complete replacement of the acetate groups.

The ligands show a medium broad band at 3100–3200 cm^{-1} in the solid state due to ν(N–H) which suggests that they exist in the thioketo form. In all the complexes a medium band is seen at 1480 cm^{-1} due to ν(C=N) as a result of thioenolization followed by metal complex formation (Table 5). This indicates the bidentate nature of the ligands in the complexes.

The stretching frequency, ν(Rh–Rh) has been identified in the laser Raman spectrum of the dirhodium triazolinemercaptotriphenylphosphine complexes at 287 cm^{-1} whereas in dirhodium tetraacetate with triphenylphosphine as axial ligands ν(Rh–Rh) is at 289 cm^{-1} [18].

The electronic absorption spectra of the complexes and free ligands were measured in chloroform. Apart from the ligand centered intense bands between 250 and 300 nm, the spectra of the complexes show characteristic bands around 300–350 nm and a shoulder at 500 nm due to $\sigma(Rh\text{–}Rh) \rightarrow \sigma^*(Rh\text{–}Rh)$ transition. The spectrum of $Rh_2(OCOCH_3)_4 \cdot H_2O$ contains two maxima at 450 and 600 nm [19].

Comparison of ^1H NMR spectra of the ligands and the corresponding complexes show the $\widehat{NS}$ coordination and replacement of the acetate groups. In the case of bis-acetate complexes, the acetate CH_3 groups resonate around δ 1.7–2.1 as singlets. In the case of tetrakis complexes, this signal is absent. The resonance due to the NH proton is also absent in all the complexes. Other ligand peaks are seen at their respective positions (Table 5).

Thus, on the basis of IR, laser Raman, ^1H NMR and UV spectral data, it is observed that both the rhodium atoms in bis-acetate complexes are hexacoordinated with a Rh–Rh bond.

The X-ray diffraction study of a crystal of tetra-μ(5-methylthio-2-mercapto-1,3,4-thiadiazolinato)triphenylphosphinodirhodium(II) revealed that all four sulfur atoms are bonded to Rh(2), whereas the Rh(1) atom is bonded equatorially to the four nitrogen atoms of the bridging ligands. The average Rh–N distance is 2.014(7) Å. A similar arrangement has been observed in the crystal structure of $Rh_2(tCl)_4(tClH)$ and $Rh_2(tCl)_4(CO)$ [9].

The axial position of Rh(2) is occupied by a triphenylphosphine group while that of Rh(1) is vacant [9]. The average Rh–S equatorial distance is 2.372(2) Å, which is relatively short compared to other compounds that have been reported (2.449–2.551 Å) [1, 20], but is comparable to $Rh_2(tCl)_4(tClH)$ [9] where Rh–S = 2.354 Å. The title compound contains a slightly longer metal–metal bond (Rh(1)–Rh(2) = 2.603(1) Å) which is comparable to other tetrabridged dirhodium(II) complexes $Rh_2(OSCCH_3)_4(HSOCCH_3)_2$ (2.550(1) Å) [21] and $Rh_2[OSC(CH_3)_3]_4 \cdot 2PPh_3$ (2.584(1) Å) [22]. Rh(1) exhibits a square-pyramidal coordination with

TABLE 5. IR (cm^{-1}) and ^1H NMR (chemical shift, ppm) spectral data for new binuclear rhodium(II) complexes

Compound no.	$\nu_{as}CO_2$	C=N	CH_3CO	$C\text{–}CH_3/S\text{–}CH_3$	$N\text{–}CH_3$	CH_2	CH	Aromatic protons
1	1550	1480	2.15	2.55				7–7.8
2	1550	1480	2.00	0.25d			3.75m	6.25–7.9
3	1550	1480	1,8	0.7–1.8		3.05, 4.7		7.0–7.9
4	1590	1490	1.9	0.7–1.9		3.05, 4.7		6.75–7.5
5	1590	1495	insoluble					
6	1590	1480	insoluble					
7	1590	1485	2.2	2.31		3.2		7.0–8.1
8	1570	1480	2.0	1.68		2.93, 3.87		6.85–7.3
9	1580	1480	1.77			2.82, 3.95		6.6–8.0
10	1580	1480	1.75			3.4		7.0–8.0
11	1580	1480	2.0	1.3d		3.2, 3.9	4.75	
12	1580	1480	1.9			3.2, 3.8		7.2–8.0, 9.3–9.35
13		1480		2.5				7.1–7.75
14		1480		1.3			3.71	7.1–7.9
15		1480		0.7–1.8		3.1		7.2–8.0
16		1480						6.5–8.0
17		1480	insoluble					
18		1480	insoluble					
19		1510	insoluble					
20		1490		1.25		3.2, 3.5, 3.9	4.6	

angles ranging from 87.0 to 93.2°, while Rh(2) has a distorted octahedral coordination with angles in the range 86.1–88.7°. The metal–metal bond is bridged by four 5-methylthio-2-mercapto-1,3,4-thiadiazole ligands in a 'cisoid' arrangement. A similar coordination and arrangement has been found in $Rh_2[OSC(CH_3)_3]_4 \cdot 2PPh_3$ [22] (angles vary from 87 to 93°). The average 'torsion angle' S–Rh–Rh–N of the ligand is 23.8°, which is comparable to 21.1° of $Rh_2(tCl)_4(tClH)$ [9]. Four five-membered chelate rings are formed by way of coordination: Rh(1), N(5), C(10), S(10), Rh(2); Rh(1), N(7), C(7), S(7), Rh(2); Rh(1), N(1), C(1), S(1), Rh(2) and Rh(1), N(3), C(4), S(4), Rh(2).

A packing diagram viewed down the *b* axis is shown in Fig. 2. The following are the intermolecular contacts having values below 3.500 Å: S(2)...S(7) (x, $1+y$, z) (3.431(4)); S(3)...C(5) (x, $1+y$, z) (3.468(9)); C(2)...S(8) (3.50(1)); Rh(1)...C(9) ($-x$, $-y$, $1-z$) (3.285(8)); N(4)...C(9) ($-x$, $-y$, $1-z$) (3.46(1)); N(8)...C(9) ($-x$, $-y$, $-z$) (3.41(1)); N(8)...C(12) ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $-z$) (3.31(1)). The molecules are packed in the crystal through van der Waals contacts.

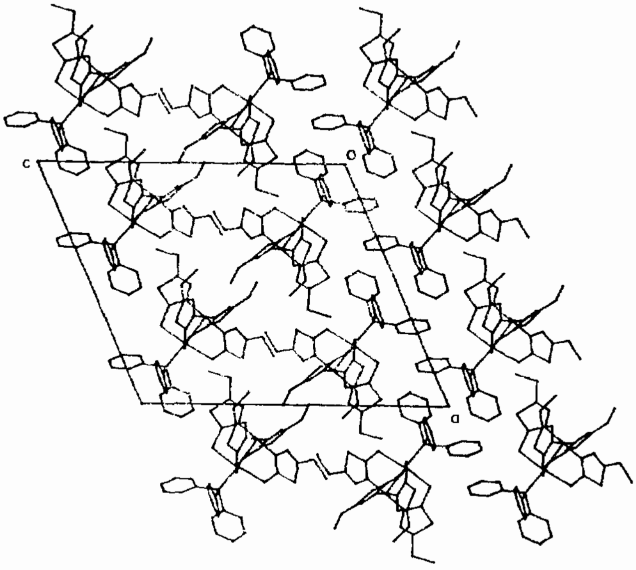

Fig. 2. The molecular packing viewed down *b*.

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