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Crystal and molecular structures of three $[Rh_2(O(E)CR)_4(C_5H_5N)_2]$ compounds (E = S, R = CMe_3, Ph; E = O, R = Ph)

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Abstract

The structures of two rhodium(II)tetramonothiocarboxylate compounds have been determined by single crystal X-ray diffraction. Only two previous studies on the structures of closely related compounds of this type have appeared in the literature. In each compound $[Rh_2(OSCR)_4(C_5H_5N)_2]$ (R = CMe_3 (**1**), Ph (**2**)) the $[Rh_2(OSCR)_4]$ core is centrosymmetric with each metal ion coordinated by two oxygen and two sulfur donor atoms. The two Rh–Rh bond lengths, 2.514(1) Å (**1**) and 2.521(1) Å (**2**), are appreciably greater than those observed in compounds with a $[Rh_2(O_2CR)_4]$ core. The structure of the tetracarboxylate compound, $[Rh_2(O_2CPh)_4(C_5H_5N)_2]$ (**3**), has also been determined in order that detailed comparisons can be made between strictly analogous carboxylate and thiocarboxylate compounds. Crystallographic data: **1**: space group $C2/c$, $a = 19.579(9)$, $b = 10.326(3)$, $c = 18.156(9)$ Å, $\beta = 90.32(4)°$, $V = 3671$ Å^3, $Z = 4$, $R = 0.0566$; **2**: space group $P2_1/n$, $a = 10.816(3)$, $b = 14.873(4)$, $c = 11.534(3)$ Å, $\beta = 104.23(3)°$, $V = 1798$ Å^3, $Z = 2$, $R = 0.0602$; **3**: space group $P2_1/n$, $a = 10.049(3)$, $b = 10.441(2)$, $c = 17.356(4)$ Å, $\beta = 99.12(2)°$, $V = 1798$ Å^3, $Z = 2$, $R = 0.0431$.

Introduction

Many dinuclear compounds of rhodium(II) have been reported in the literature. The single most extensively studied group have undoubtedly been the dirhodium tetracarboxylate molecules [1–3] which have been examined by a wide range of structural and spectroscopic techniques, and have been the subject of numerous theoretical calculations [4–12]. It is perhaps surprising then that relatively little work has appeared on the closely related compounds containing monothiocarboxylate bridging ligands [13–17]. Compounds containing the $[Rh_2(OSCR)_4]$ core were first reported by Russian workers in 1975 [13]. The products obtained from the reaction of $[Rh_2(O_2CH)_4]$ with an excess of a monothiocarboxylic acid at elevated temperatures, were identified as $[Rh_2(OSCR)_4(HOSCR)_2]$, in which neutral molecules of the acid occupy the axial coordination sites of the metal ions. The axial ligands were readily replaced by a variety of Lewis bases [14]. Recently [17] an alternative synthetic strategy which involves the room temperature reaction of the monothiocarboxylic acids with $[Rh_2(O_2CCH_3)_2\{Ph_2P(C_6H_4)\}_2]$ has been described, and provides a more facile route to the triphenylphosphine adducts of the $[Rh_2(OSCR)_4]$ core. Many of these compounds have only been characterised by IR and electronic spectroscopy [13, 14], although a few have been studied by cyclic voltammetry [17]. Surprisingly, although over forty $[Rh_2(O_2CR)_4L_2]$ molecules have been crystallographically characterised, only two of the dirhodium tetramonothiocarboxylates have been studied by single crystal X-ray diffraction [15–17].

In this paper we describe the crystal structure determination of two dirhodium tetramonothiocarboxylate compounds, $[Rh_2(OSCCMe_3)_4(C_5H_5N)_2]$ (**1**) and $[Rh_2(OSCPh)_4(C_5H_5N)_2]$ (**2**), and compare and contrast the details of their structures with those of the two reported related compounds. Comparisons are also drawn with structural data previously published on $[Rh_2(O_2CR)_4L_2]$ molecules. The structure of $[Rh_2(O_2CPh)_4(C_5H_5N)_2]$ (**3**) is reported so that definitive comparisons can be made with **2**.

Experimental

Materials

Compounds **1** and **2** were prepared by addition of pyridine to suspensions of $[Rh_2(OSCCMe_3)_4(HOSCCMe_3)_2]$ and $[Rh_2(OSCPh)_4(HOSC-$

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Ph)$_2$], respectively [13, 14]. Compound **3** was obtained by ligand exchange reaction with rhodium(II) tetraacetate [18–21]. X-ray quality crystals were obtained by the slow evaporation of dichloromethane/hexane solutions.

X-ray crystallographic procedures

The molecular structures of **1**, **2** and **3** were obtained by the application of the general procedures described previously [22, 23]. The general method is described in outline below and various crystal parameters and basic information pertaining to data collection and refinement are summarised in Table 1.

A crystal of an appropriate size was mounted on a glass fibre. All geometric and intensity data were taken from the crystal using an automated four-circle diffractometer (Nicolet R3mV) equipped with graphite monochromated Mo Kα radiation. The crystal orientation matrix and unit cell parameters were obtained from the setting angles of accurately located reflections in the range $7 \leqslant 2\theta \leqslant 30°$. Data were collected in the range $5 \leqslant 2\theta \leqslant 50°$ using the ω–2θ technique. Three standard reflections were remeasured every 97 scans and showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections were applied.

Each molecule sits on the inversion centre at the origin and therefore each asymmetric unit contains only one half of the dimeric formula unit. The structures were solved by the Patterson method and developed using alternating cycles of least-squares refinement and difference Fourier synthesis. Hydrogen atoms were not included in the refinement. In the final cycles all non-hydrogen atoms were refined anisotropically. A weighting scheme was applied to each data set (see Table 1).

Fractional atomic coordinates for **1**, **2** and **3** are presented in Tables 2, 3 and 4, respectively. Geometric data is presented in Tables 5, 6 and 7. Crystallographic calculations used the SHELXTL PLUS program package [24].

TABLE 1. Crystallographic data for [$Rh_2(OSCCMe_3)_4(C_5H_5N)_2$] (**1**), [$Rh_2(OSCPh)_4(C_5H_5N)_2$] (**2**) and [$Rh_2(O_2CPh)_4(C_5H_5N)_2$] (**3**)

	1	2	3
Formula	$C_{30}H_{46}O_4S_4N_2Rh_2$	$C_{38}H_{30}O_4S_4N_2Rh_2$	$C_{38}H_{30}O_8N_2Rh_2$
Space group	$C2/c$	$P2_1/n$	$P2_1/n$
a (Å)	19.579(9)	10.816(3)	10.049(3)
b (Å)	10.326(3)	14.873(4)	10.441(2)
c (Å)	18.156(9)	11.534(3)	17.356(4)
α (°)	90.0	90.0	90.0
β (°)	90.32(4)	104.23(3)	99.12(2)
γ (°)	90.0	90.0	90.0
V (Å^3)	3671	1798	1798
Z	4	2	2
$F(000)$	1944	916	852
D_{calc} (g/cm^3)	1.77	1.69	1.57
Crystal size (mm)	0.06×0.30×0.30	0.20×0.28×0.28	0.10×0.30×0.70
μ(Mo Kα) (cm^{-1})	9.90	11.69	9.55
Data collection instrument		Nicolet R3m/V	
Radiation		Mo Kα(λ=0.71073 Å)	
Orientation reflections (used for unit cell determination)			
no.	30	50	30
range (2θ)	$19 \leqslant 2\theta \leqslant 28$	$7 \leqslant 2\theta \leqslant 29$	$21 \leqslant 2\theta \leqslant 29$
Temperature (K)		292	
Indices measured	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$
Unique data	3251	3093	3165
No. unique with $I \geqslant 3.0\sigma(I)$	2841	2475	2824
Trans. Factors: max., min.	92.3, 78.7	88.0, 73.5	96.1, 84.5
No. of parameters	190	226	226
R^a	0.0566	0.0602	0.0431
R_w^{b}	0.0649	0.0610	0.0474
Weighting scheme, w^{-1}	$\sigma^2(F)+0.001207F^2$	$\sigma^2(F)+0.001262F^2$	$\sigma^2(F)+0.001043F^2$
Largest shift/e.s.d., final cycle	0.001	0.002	0.06
Largest peak (e/Å^3)	1.2	0.98	1.1

[a] $R=\Sigma|[F_o-F_c]|/\Sigma F_o$. [b] $R_w=\Sigma(|[F_o-F_c]|w^{1/2})/\Sigma(F_o w^{1/2})$.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å} \times 10^3$) for $[Rh_2(OSCCMe_3)_4(C_5H_5N)_2]$ (1)

	x	y	z	U_{eq}
Rh(1)	557(1)	441(1)	235(1)	34(1)
S(1)	0(1)	1344(2)	1196(1)	56(1)
S(2)	396(1)	2277(2)	−431(1)	56(1)
O(1)	767(2)	−1251(5)	828(3)	58(2)
O(2)	1108(3)	−402(5)	−618(3)	58(2)
N(1)	1575(3)	1166(5)	645(3)	40(2)
C(1)	383(3)	−2227(7)	829(4)	42(2)
C(2)	677(4)	−3426(7)	1192(5)	51(2)
C(3)	1217(5)	−3958(10)	663(6)	81(4)
C(4)	121(6)	−4473(7)	1353(6)	75(4)
C(5)	1012(6)	−2995(9)	1962(6)	87(4)
C(6)	845(3)	−1060(6)	−1116(4)	38(2)
C(7)	1333(3)	−1593(7)	−1703(4)	48(2)
C(8)	1435(6)	−487(9)	−2270(5)	79(4)
C(9)	2007(4)	−1921(11)	−1313(5)	77(4)
C(10)	1043(4)	−2803(8)	−2097(5)	62(3)
C(11)	2101(4)	340(7)	669(5)	53(3)
C(12)	2749(4)	749(9)	899(6)	67(3)
C(13)	2857(4)	2014(9)	1113(6)	68(3)
C(14)	2297(4)	2842(7)	1098(6)	66(3)
C(15)	1675(4)	2393(7)	852(5)	54(3)

Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å} \times 10^3$) for $[Rh_2(OSCPh)_4(C_5H_5N)_2]$ (2)

	x	y	z	U_{eq}
Rh(1)	305(1)	271(1)	1068(1)	31(1)
S(1)	−1696(2)	808(2)	854(2)	49(1)
S(2)	−174(2)	−1096(1)	1710(2)	47(1)
O(1)	862(6)	1518(4)	560(5)	48(2)
O(2)	2195(5)	−157(4)	1319(5)	43(2)
N(1)	841(7)	829(4)	2925(6)	42(2)
C(1)	−2564(8)	592(5)	−545(7)	38(3)
C(2)	−3865(8)	995(5)	−917(8)	42(3)
C(3)	−4297(10)	1329(7)	−2066(9)	59(4)
C(4)	−5455(9)	1767(8)	−2427(9)	66(4)
C(5)	−6232(10)	1814(8)	−1636(11)	70(4)
C(6)	−5861(9)	1472(8)	−481(10)	68(4)
C(7)	−4638(9)	1076(6)	−122(9)	54(3)
C(8)	−679(8)	−1766(5)	502(7)	37(3)
C(9)	−975(8)	−2739(5)	684(7)	37(3)
C(10)	−1765(10)	−3193(6)	−236(10)	60(4)
C(11)	−1998(13)	−4106(7)	−140(12)	79(5)
C(12)	−1414(17)	−4547(7)	900(13)	97(7)
C(13)	−586(16)	−4098(7)	1849(11)	92(6)
C(14)	−367(11)	−3192(6)	1748(9)	63(4)
C(15)	96(9)	804(7)	3672(8)	52(3)
C(16)	423(12)	1241(7)	4784(9)	67(4)
C(17)	1543(11)	1708(7)	5099(8)	61(4)
C(18)	2337(10)	1726(7)	4334(9)	61(4)
C(19)	1950(9)	1283(6)	3246(8)	50(3)

Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å} \times 10^3$) for $[Rh_2(O_2CPh)_4(C_5H_5N)_2]$ (3)

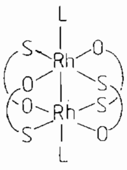
	x	y	z	U_{eq}
Rh(1)	869(1)	433(1)	485(1)	28(1)
O(1)	−174(3)	2118(3)	392(2)	37(1)
O(2)	1792(3)	−1312(3)	515(2)	43(1)
O(3)	1866(3)	978(3)	−402(2)	36(1)
O(4)	−245(3)	−151(3)	1304(2)	39(1)
N(1)	2467(4)	1164(4)	1436(2)	42(1)
C(1)	−1262(5)	2196(4)	−78(2)	35(1)
C(2)	−1968(5)	3451(4)	−132(3)	40(2)
C(3)	−1393(6)	4508(4)	273(4)	51(2)
C(4)	−2031(7)	5700(5)	186(5)	67(3)
C(5)	−3238(9)	5828(6)	−303(4)	82(3)
C(6)	−3865(10)	4738(7)	−698(5)	98(3)
C(7)	−3227(7)	3558(6)	−601(4)	77(2)
C(8)	1342(5)	729(4)	−1093(2)	33(1)
C(9)	2072(5)	1199(4)	−1722(3)	38(1)
C(10)	3246(5)	1910(5)	−1544(3)	46(2)
C(11)	3857(6)	2422(6)	−2152(3)	56(2)
C(12)	3300(6)	2217(6)	−2923(3)	61(2)
C(13)	2123(7)	1503(7)	−3092(3)	67(2)
C(14)	1520(6)	987(6)	−2495(3)	52(2)
C(15)	2168(6)	2116(6)	1899(4)	67(2)
C(16)	3025(8)	2418(9)	2587(4)	95(3)
C(17)	4179(9)	1764(9)	2772(5)	99(3)
C(18)	4540(9)	824(8)	2283(6)	108(4)
C(19)	3613(7)	554(5)	1620(5)	78(3)

Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Results and discussion

Compounds **1** and **2** were obtained by stirring suspensions of $[Rh_2(OSCR)_4(HOSCR)_2]$ in methanol with an excess of pyridine. The red solids precipitated immediately from solution and were recrystallised from mixtures of dichloromethane and hexane.

When four asymmetric ligands, such as monothiocarboxylates, bridge across two metal centres then the potential exists for the formation of up to four geometric isomers (**I–IV**). Although examples of all four isomers are known the most prevalent is isomer **II** [25–29]. The reasons behind this observation are not well understood except at the most simplistic of levels.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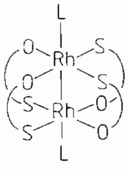
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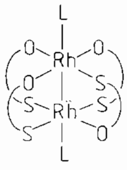
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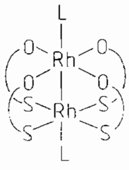
IV

Both compounds **1** and **2** crystallise with the centrosymmetric 2:2 coordination exemplified in **II**, and illustrated in Figs. 1 and 2. Each rhodium ion is bound by two oxygen and two sulfur atoms in the

TABLE 5. Bond distances and angles for $[Rh_2(OSCCMe_3)_4(C_5H_5N)_2]$ (**1**)

Bond lengths (Å)			
Rh(1)–S(1)	2.266(2)	Rh(1)–S(2)	2.268(2)
Rh(1)–O(1)	2.091(5)	Rh(1)–O(2)	2.085(6)
Rh(1)–N(1)	2.253(5)	Rh(1)–Rh(1A)	2.514(1)
S(1)–C(6A)	1.689(6)	S(2)–C(1A)	1.687(7)
O(1)–C(1)	1.259(8)	O(2)–C(6)	1.240(9)
N(1)–C(11)	1.339(9)	N(1)–C(15)	1.335(9)
C(1)–C(2)	1.513(10)	C(1)–S(2A)	1.687(7)
C(2)–C(3)	1.536(13)	C(2)–C(4)	1.565(12)
C(2)–C(5)	1.603(13)	C(6)–C(7)	1.540(10)
C(6)–S(1A)	1.689(6)	C(7)–C(8)	1.551(12)
C(7)–C(9)	1.533(11)	C(7)–C(10)	1.545(11)
C(11)–C(12)	1.399(11)	C(12)–C(13)	1.378(13)
C(13)–C(14)	1.391(12)	C(14)–C(15)	1.378(11)
Bond angles (°)			
S(1)–Rh(1)–S(2)	90.1(1)	S(1)–Rh(1)–O(1)	92.3(2)
S(2)–Rh(1)–O(1)	176.6(1)	S(1)–Rh(1)–O(2)	177.4(2)
S(2)–Rh(1)–O(2)	91.3(2)	O(1)–Rh(1)–O(2)	86.2(2)
S(1)–Rh(1)–N(1)	92.3(2)	S(2)–Rh(1)–N(1)	91.1(1)
O(1)–Rh(1)–N(1)	86.3(2)	O(2)–Rh(1)–N(1)	85.5(2)
S(1)–Rh(1)–Rh(1A)	89.3(1)	S(2)–Rh(1)–Rh(1A)	90.2(1)
O(1)–Rh(1)–Rh(1A)	92.3(1)	O(2)–Rh(1)–Rh(1A)	92.9(1)
N(1)–Rh(1)–Rh(1A)	178.0(1)	Rh(1)–S(1)–C(6A)	109.9(2)
Rh(1)–S(2)–C(1A)	109.1(2)	Rh(1)–O(1)–C(1)	123.6(5)
Rh(1)–O(2)–C(6)	123.7(4)	Rh(1)–N(1)–C(11)	118.7(4)
Rh(1)–N(1)–C(15)	122.4(4)	C(11)–N(1)–C(15)	118.9(6)
O(1)–C(1)–C(2)	115.3(6)	O(1)–C(1)–S(2A)	124.4(5)
C(2)–C(1)–S(2A)	120.2(5)	C(1)–C(2)–C(3)	106.4(7)
C(1)–C(2)–C(4)	112.4(6)	C(3)–C(2)–C(4)	110.7(7)
C(1)–C(2)–C(5)	107.8(6)	C(3)–C(2)–C(5)	111.4(7)
C(4)–C(2)–C(5)	108.1(7)	O(2)–C(6)–C(7)	116.3(6)
O(2)–C(6)–S(1A)	124.1(5)	C(7)–C(6)–S(1A)	119.6(5)
C(6)–C(7)–C(8)	106.3(6)	C(6)–C(7)–C(9)	107.3(6)
C(8)–C(7)–C(9)	110.8(7)	C(6)–C(7)–C(10)	112.3(6)
C(8)–C(7)–C(10)	109.6(7)	C(9)–C(7)–C(10)	110.5(7)
N(1)–C(11)–C(12)	121.1(7)	C(11)–C(12)–C(13)	120.4(8)
C(12)–C(13)–C(14)	117.2(8)	C(13)–C(14)–C(15)	119.9(8)
N(1)–C(15)–C(14)	122.5(7)		

Atoms labelled 'A' are generated by crystal symmetry.

TABLE 6. Bond distances and angles for $[Rh_2(OSCPh)_4(C_5H_5N)_2]$ (**2**)

Bond lengths (Å)			
Rh(1)–S(1)	2.262(3)	Rh(1)–S(2)	2.266(2)
Rh(1)–O(1)	2.079(6)	Rh(1)–O(2)	2.092(6)
Rh(1)–N(1)	2.236(7)	Rh(1)–Rh(1A)	2.521(1)
S(1)–C(1)	1.686(8)	S(2)–C(8)	1.690(8)
O(1)–C(8A)	1.248(10)	O(2)–C(1A)	1.244(11)
N(1)–C(15)	1.317(13)	N(1)–C(19)	1.347(11)
C(1)–C(2)	1.493(11)	C(1)–O(2A)	1.244(11)
C(2)–C(3)	1.385(13)	C(2)–C(7)	1.390(15)
C(3)–C(4)	1.382(14)	C(4)–C(5)	1.386(17)
C(5)–C(6)	1.390(16)	C(6)–C(7)	1.414(14)
C(8)–C(9)	1.508(11)	C(8)–O(1A)	1.248(10)
C(9)–C(10)	1.366(12)	C(9)–C(14)	1.414(12)
C(10)–C(11)	1.391(14)	C(11)–C(12)	1.376(18)
C(12)–C(13)	1.401(18)	C(13)–C(14)	1.378(14)
C(15)–C(16)	1.404(13)	C(16)–C(17)	1.367(16)
C(17)–C(18)	1.375(17)	C(18)–C(19)	1.387(13)
Bond angles (°)			
S(1)–Rh(1)–S(2)	93.7(1)	S(1)–Rh(1)–O(1)	89.4(2)
S(2)–Rh(1)–O(1)	176.2(2)	S(1)–Rh(1)–O(2)	176.7(2)
S(2)–Rh(1)–O(2)	88.6(2)	O(1)–Rh(1)–O(2)	88.2(2)
S(1)–Rh(1)–N(1)	89.4(2)	S(2)–Rh(1)–N(1)	92.7(2)
O(1)–Rh(1)–N(1)	85.0(2)	O(2)–Rh(1)–N(1)	88.0(2)
S(1)–Rh(1)–Rh(1A)	89.6(1)	S(2)–Rh(1)–Rh(1A)	90.4(1)
O(1)–Rh(1)–Rh(1A)	91.9(2)	O(2)–Rh(1)–Rh(1A)	92.8(2)
N(1)–Rh(1)–Rh(1A)	176.8(2)	Rh(1)–S(1)–C(1)	109.3(3)
Rh(1)–S(2)–C(8)	108.2(3)	Rh(1)–O(1)–C(8A)	123.6(5)
Rh(1)–O(2)–C(1A)	122.3(5)	Rh(1)–N(1)–C(15)	124.0(5)
Rh(1)–N(1)–C(19)	117.0(6)	C(15)–N(1)–C(19)	118.7(7)
S(1)–C(1)–C(2)	117.5(6)	S(1)–C(1)–O(2A)	125.7(6)
C(2)–C(1)–O(2A)	116.6(7)	C(1)–C(2)–C(3)	119.4(9)
C(1)–C(2)–C(7)	121.5(8)	C(3)–C(2)–C(7)	119.0(8)
C(2)–C(3)–C(4)	121.6(10)	C(3)–C(4)–C(5)	118.5(10)
C(4)–C(5)–C(6)	122.2(10)	C(5)–C(6)–C(7)	117.6(11)
C(2)–C(7)–C(6)	120.9(9)	S(2)–C(8)–C(9)	119.2(6)
S(2)–C(8)–O(1A)	125.2(6)	C(9)–C(8)–O(1A)	115.6(7)
C(8)–C(9)–C(10)	118.7(7)	C(8)–C(9)–C(14)	120.6(7)
C(10)–C(9)–C(14)	120.5(8)	C(9)–C(10)–C(11)	120.8(9)
C(10)–C(11)–C(12)	118.8(10)	C(11)–C(12)–C(13)	121.5(10)
C(12)–C(13)–C(14)	119.4(10)	C(9)–C(14)–C(13)	119.1(9)
N(1)–C(15)–C(16)	121.9(9)	C(15)–C(16)–C(17)	119.1(11)
C(16)–C(17)–C(18)	119.5(9)	C(17)–C(18)–C(19)	118.3(9)
N(1)–C(19)–C(18)	122.5(10)		

Atoms labelled 'A' are generated by crystal symmetry.

equatorial coordination plane, while the other two sites on the metal are occupied by one pyridine ligand and a second metal ion. The angles between adjacent donor atoms in the metals' coordination sphere lie in the ranges 85.5–92.9° and 85.5–93.7° for **1** and **2**, respectively. Thus the geometry about each metal centre is that of a distorted octahedron. The rhodium–rhodium distances are 2.514(1) Å for **1**, and 2.521(1) Å for **2**. The small difference in bond lengths is statistically significant and is due to the relative electronic effects of the two different substituent groups on the bridging carboxylate ligands since it has been demonstrated on a number of previous occasions that increasing the electron withdrawing power of substituents on the bridging ligand gives rise to a lengthening of metal–metal distances [1, 30, 31]. Although there is an inverse correlation between the rhodium–rhodium and rhodium–nitrogen distances the two Rh–N distances in this pair of compounds are indistinguishable. There are also no meaningful differences in rhodium–sulfur or rhodium–oxygen distances. The new structural data can be usefully compared with that already reported on $[Rh_2(OSCMe)_4(HOSCMe)_2]$ [15, 16] and $[Rh_2(OSCCMe_3)_4(PPh_3)_2]$ [17]. Comparison of the structural data for **1** with that for $[Rh_2(OSCCMe_3)_4(PPh_3)_2]$ reveals that replacement of the pyridine axial ligands by the better donor ligand, triphenylphosphine, results in an increase in the rhodium–rhodium bond length to 2.584(1) Å. The difference in the two bond lengths, 0.070 Å, is dramatic, and is appreciably greater than that observed in the pair of closely related dirhodium te-

TABLE 7. Bond distances and angles for $[Rh_2(O_2CPh)_4(C_5H_5N)_2]$ (3)

Bond lengths (Å)			
Rh(1)–O(1)	2.041(3)	Rh(1)–O(2)	2.040(3)
Rh(1)–O(3)	2.046(3)	Rh(1)–O(4)	2.038(3)
Rh(1)–N(1)	2.247(4)	Rh(1)–Rh(1A)	2.402(1)
O(1)–C(1)	1.259(5)	O(2)–C(1A)	1.258(5)
O(3)–C(8)	1.258(5)	O(4)–C(8A)	1.259(5)
N(1)–C(15)	1.341(8)	N(1)–C(19)	1.310(8)
C(2)–C(2)	1.487(6)	C(1)–O(2A)	1.258(5)
C(2)–C(3)	1.385(7)	C(2)–C(7)	1.395(8)
C(3)–C(4)	1.397(8)	C(4)–C(5)	1.372(10)
C(5)–C(6)	1.422(11)	C(6)–C(7)	1.387(11)
C(8)–C(9)	1.490(7)	C(8)–O(4A)	1.259(5)
C(9)–C(10)	1.387(7)	C(9)–C(14)	1.387(6)
C(10)–C(11)	1.407(8)	C(11)–C(12)	1.384(7)
C(12)–C(13)	1.389(9)	C(13)–C(14)	1.390(8)
C(15)–C(16)	1.394(9)	C(16)–C(17)	1.340(12)
C(17)–C(18)	1.383(13)	C(18)–C(19)	1.390(11)
Bond angles (°)			
O(1)–Rh(1)–O(2)	175.5(1)	O(1)–Rh(1)–O(3)	90.5(1)
O(2)–Rh(1)–O(3)	89.6(1)	O(1)–Rh(1)–O(4)	88.9(1)
O(2)–Rh(1)–O(4)	90.7(1)	O(3)–Rh(1)–O(4)	175.6(1)
O(1)–Rh(1)–N(1)	93.6(1)	O(2)–Rh(1)–N(1)	90.9(1)
O(3)–Rh(1)–N(1)	94.6(1)	O(4)–Rh(1)–N(1)	89.8(1)
O(1)–Rh(1)–Rh(1A)	87.8(1)	O(2)–Rh(1)–Rh(1A)	87.7(1)
O(3)–Rh(1)–Rh(1A)	88.0(1)	O(4)–Rh(1)–Rh(1A)	87.6(1)
N(1)–Rh(1)–Rh(1A)	177.0(1)	Rh(1)–O(1)–C(1)	119.3(3)
Rh(1)–O(2)–C(1A)	119.4(3)	Rh(1)–O(3)–C(8)	118.6(3)
Rh(1)–O(4)–C(8A)	119.5(3)	Rh(1)–N(1)–C(15)	119.3(3)
Rh(1)–N(1)–C(19)	120.8(4)	C(15)–N(1)–C(19)	119.1(5)
O(1)–C(1)–C(2)	117.1(4)	O(1)–C(1)–O(2A)	125.8(4)
C(2)–C(1)–O(2A)	117.1(4)	C(1)–C(2)–C(3)	120.9(4)
C(1)–C(2)–C(7)	119.1(4)	C(3)–C(2)–C(7)	120.0(5)
C(2)–C(3)–C(4)	120.5(5)	C(3)–C(4)–C(5)	120.0(6)
C(4)–C(5)–C(6)	120.0(7)	C(5)–C(6)–C(7)	119.4(8)
C(2)–C(7)–C(6)	120.0(6)	O(3)–C(8)–C(9)	116.7(4)
O(3)–C(8)–O(4A)	126.2(4)	C(9)–C(8)–O(4A)	117.1(4)
C(8)–C(9)–C(10)	120.9(4)	C(8)–C(9)–C(14)	119.2(4)
C(10)–C(9)–C(14)	119.8(5)	C(9)–C(10)–C(11)	119.6(4)
C(10)–C(11)–C(12)	120.6(5)	C(11)–C(12)–C(13)	119.2(5)
C(12)–C(13)–C(14)	120.5(5)	C(9)–C(14)–C(13)	120.3(5)
N(1)–C(15)–C(16)	120.9(6)	C(15)–C(16)–C(17)	118.9(8)
C(16)–C(17)–C(18)	121.0(7)	C(17)–C(18)–C(19)	116.5(8)
N(1)–C(19)–C(18)	123.4(7)		

Atoms labelled 'A' are generated by crystal symmetry.

tracarboxylate compounds $[Rh_2(O_2CMe)_4(C_5H_5N)_2]$ 2.396(1) Å [32] and $[Rh_2(O_2CMe)_4(PPh_3)_2]$ 2.451(1) Å [33]. The rhodium–rhodium distance in the compound $[Rh_2(OSCMe)_4(HOSCMe)_2]$, 2.550(3) Å, in which the axial monothiocarboxylic acid ligands are bound to the axial sites of the metal via the sulfur atom, is intermediate between that observed for the pyridine and tertiary phosphine adducts. The variations in rhodium–rhodium bond lengths observed through this series of four tetramonothiocarboxylate compounds reflects the relative donor effects of the axial ligands but is also subtly influenced by the electron withdrawing/releasing properties of the substituents on the bridging ligands.

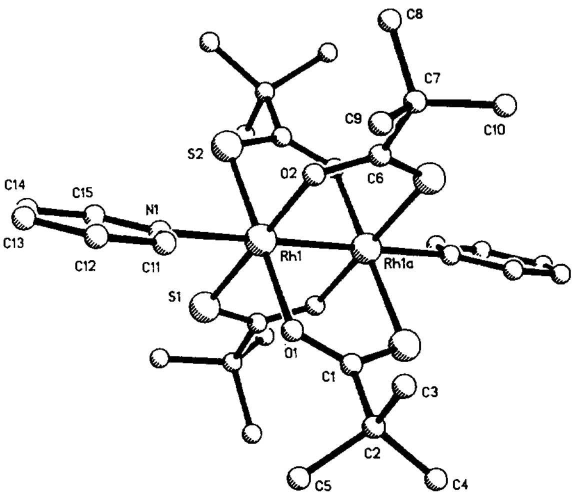

Fig. 1. Molecular structure of $[Rh_2(OSCCMe_3)_4(C_5H_5N)_2]$ (1) showing the atom numbering scheme adopted. Atoms labelled 'a' generated by the symmetry operator −*x*, −*y*, −*z*.

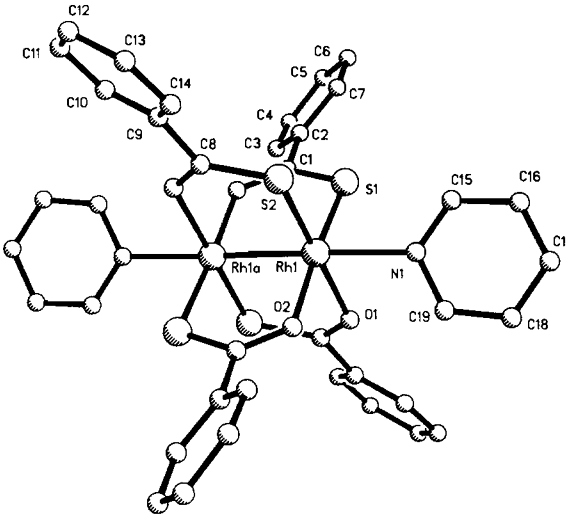

Fig. 2. Molecular structure of $[Rh_2(OSCPh)_4(C_5H_5N)_2]$ (2) showing the atom numbering scheme adopted. Atoms labelled 'a' generated by the symmetry operator −*x*, −*y*, −*z*.

As no precise carboxylato analogue of any of the four monothiocarboxylates had been structurally characterised we thought it important that at least one such compound should be studied. The compound selected to be studied by X-ray diffraction was $[Rh_2(O_2CPh)_4(C_5H_5N)_2]$ (3). The gross structure of 3, which is not isomorphous with 2, is closely similar to that of numerous other dimetal tetracarboxylate compounds and is shown in Fig. 3. The rhodium–rhodium distance, 2.402(1) Å, is appreciably less than that found for 2. However, the shorter metal–metal bond is not accompanied by a signifi-

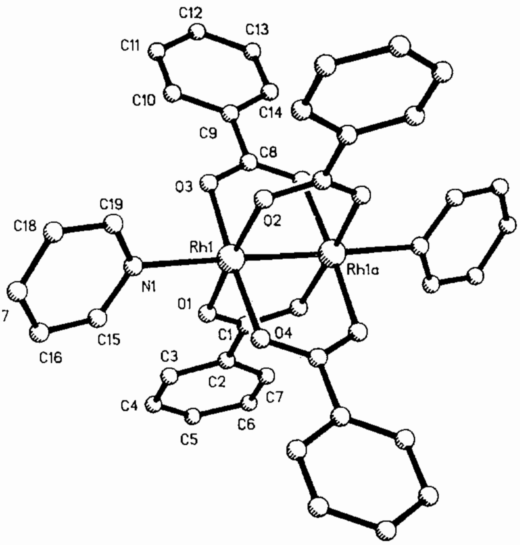

Fig. 3. Molecular structure of $[Rh_2(O_2CPh)_4(C_5H_5N)_2]$ (**3**) showing the atom numbering scheme adopted. Atoms labelled 'a' generated by the symmetry operator $-x$, $-y$, $-z$.

cantly longer Rh–N bond (2.247(4) Å). Indeed the length of rhodium–pyridine bonds is remarkably invariant throughout a wide range of compounds with many different ligands bridging the rhodium–rhodium bond (e.g. $[Rh_2(O_2CMe)_4(C_5H_5N)_2]$ [32], $[Rh_2(HNOCPh)_4(C_5H_5N)_2]$ [27] and $[Rh_2(O_2CMe)_2\{PhP(C_6H_4)\}_2(C_5H_5N)_2]$ [34]). In none of the three compounds described in this report is there a significant twisting about the rhodium–rhodium bond. In **3** the two independent torsion angles are 0.2 and 0.5°, while in the thiocarboxylato compounds they are 2.4 and 1.4° in **1** and 2.3 and 3.0° in **2**. The principle differences between the structures of **2** and **3** lie in the orientation of the phenyl substituent groups on the bridging ligands. In **3** the mean plane of each phenyl ring is almost coincident with that of the 'CO_2; moiety to which it is bound. The angles between these mean planes are only 5.8 and 6.6°. In contrast in the thiocarboxylato compound **2** both phenyl rings are substantially rotated away from that near coplanar arrangement. The plane defined by the atoms C2–C3–C4–C5–C6–C7 makes an angle of 37.8° with that defined by S1–C1–O2A, while the plane defined by the atoms C9–C10–C11–C12–C13–C14 makes an angle of 23.6° with the plane defined by S2–C8–O1A. This latter observation was somewhat surprising and although it may only be a result of the crystal packing forces alternative explanations cannot be excluded.

Our research into this neglected area of the chemistry of metal–metal bonded dimers is continuing and the results of further studies will be reported in due course.

Supplementary material

Tables of anisotropic thermal parameters and observed and calculated structure factors are available from the authors on request.

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