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Dirhodium(II,II) Tetra-acetate Complexes with Sulphur Donors. The Crystal Structure of $[Rh_2(O_2CMe)_4(L)_2]$ (L = *N,N*-Dimethylthioformamide or *N,N*-Dimethyl *O*-Ethylthiocarbamate)

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Abstract

The rhodium(II) complexes $[Rh_2(O_2CMe)_4(DMTC)]$ and $[Rh_2(O_2CMe)_4(L)_2]$, where L = DMTC ($EtOSCNMe_2$), DMTA ($MeSCNMe_2$), DMTF ($HSCNMe_2$), TBA ($PhSCNH_2$) and TAA (MeSCNHPh), have been prepared and characterized by infrared, ^{1}H NMR and electronic spectroscopy. The structures of $[Rh_2(O_2CMe)_4(DMTC)_2]$ (I) and $[Rh_2(O_2CMe)_4(DMTF)_2]$ (II) were determined by X-ray crystallography. Compound **I** is monoclinic, space group $P2_1/n$, with $a = 15.665(5)$, $b = 8.184(5)$ and $c = 21.976(5)$ Å, and $\beta = 106.76(3)°$; $D_c = 1.74$ g cm^{-3} for $Z = 4$. The structure was refined to $R = 0.048$ for 2385 observed reflections. Compound **II** is triclinic, space group $P\bar{1}$, with $a = 9.503(5)$, $b = 8.206(5)$, $c = 8.123(5)$ Å, $\alpha = 114.65(3)°$, $\beta = 105.21(3)°$ and $\gamma = 90.60(3)°$; $D_c = 1.87$ g cm^{-3} for one formula unit per unit cell. The structure was refined to $R = 0.030$ for 2445 observed reflections. Both compounds are binuclear complexes where two rhodium atoms, linked by four bridging acetato groups, form a strong direct metal–metal bond. The Rh–Rh distances are 2.409(1) Å in **I** and 2.418(1) Å in **II**. The strong *trans* influence of the Rh–Rh bond is reflected the weakness of the axial Rh–S bond (2.624 Å in **I** and 2.546(1) Å in **II**). Structural details of the dirhodium(II) tetraacetato moieties are fully equivalent in the two compounds. The colour of the complexes (green (**I**) and violet (**II**)) seems to depend on the Rh–S bond strength.

Introduction

Dirhodium(II) tetracarboxylates form generally 1:2 adducts with neutral ligands, in which the donor atoms lie approximately along the Rh–Rh axis of the bridging carboxylate cage [1–3]. Simple rhodium(II) carboxylates display significant antitumour properties [4], the most active species being rhodium(II) butyrate [5]. Moreover they bind reversibly sulphurated aminoacids [6] and inhibit the enzymes bearing essential sulphydryl groups [7]. Because antitumour activity often parallels toxicity, neutral or ionic sulphur donors are used as detoxicants against metal based drugs. As an example, thiocarbonyl donors show a protective effect on platinum-induced nephrotoxicity [8].

The coordination chemistry of rhodium(II) carboxylates with sulphur donors concerns mainly 1:2 adducts with thioethers [9–12] and dialkyl sulfoxides [10–17]. As regards thiocarbonyl donors, red or violet 1:2 adducts with thioacetamide, thiobenzamide and thiourea derivatives have been reported [18]. The colour of the rhodium(II) carboxylato adducts has been found to depend on the nature of the axial ligand, varying from pink to red for nitrogen donors and from orange to violet for sulphur donors. Conversely the blue or green colour is characteristic of oxygen ligands. An example of donor atom–colour correlation is shown by the ambidentate dimethyl sulfoxide, which is S-bound in the orange 1:2 complex with rhodium(II) propionate and O-bound in the blue trifluoroacetato analogue [17]. For this reason the colour of the product is sometimes used as a criterion to infer the coordination site in complexes with polydentate molecules. In previous papers we reported various platinum(II) and palladium(II) halide complexes with thiocarbonyl donors, some of them showing significant cytostatic activity against KB tumour cells [19–21]. On extending the study to rhodium(II) acetate, we observed that it reacts with thioamides yielding, as expected, violet dichloromethane solutions, whereas dark green solutions are obtained in the presence of the thiocarbamic ester DMTC ($EtOSCNMe_2$), which is S-bound in platinum, palladium and mercury complexes. Therefore it was worthwhile to determine the donor site of the potentially multidentate DMTC molecule.

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TABLE I. Infrared (cm^{-1}) and Electronic (nm) Spectral Data

Compound	3500–3100 cm^{-1}	1650–1500 cm^{-1}			400–300 cm^{-1}		λ_{max} (nm)[a]
$[Rh_2(O_2CMe)_4(MeOH)_2]$	3510sh, 3390sbr, 3258w	1637vvw	1583sbr		386ms	342m	539, 443
$[Rh_2(O_2CMe)_4(DMTC)_2]$			1596s	1552ms	381ms	332m	637, 387sh
$[Rh_2(O_2CMe)_4(DMTC)]$			1590sbr	1570sh	382ms	331m	640
$[Rh_2(O_2CMe)_4(DMTF)_2]$			1586s	1550s	$\left.\begin{matrix}383\\378\end{matrix}\right\}$s	332m	550, 455sh
$[Rh_2(O_2CMe)_4(DMTA)_2]$			$\left.\begin{matrix}1600\\1593\end{matrix}\right\}$s	1552sh 1539s	376ms	332w	565, 455sh
$[Rh_2(O_2CMe)_4(TBA)_2]$	3390m, 3310w, 3205m	1643ms	1590sbr		381ms	334m	525sh
$[Rh_2(O_2CMe)_4(TAA)_2]$	3425mbr, 3249s		1589s	1546m 1517m	374ms	$\left.\begin{matrix}333\\326\end{matrix}\right\}$m	540

[a] Solid samples in Nujol.

This paper reports the preparation and characterization of rhodium(II) acetate complexes with dimethylthioformamide (DMTF), dimethylthioacetamide (DMTA), thioacetanilide (TAA), thiobenzamide (TBA) and *N,N*-dimethyl *O*-ethylthiocarbamate (DMTC) and the crystal structure of $[Rh_2(O_2CMe)_4(DMTC)_2]$ (green) and $[Rh_2(O_2CMe)_4(DMTF)_2]$ (violet).

Experimental

Rhodium(III) chloride trihydrate (Ventron), *N,N*-dimethylthioacetamide (DMTA, ICN Biomedicals) and *N,N*-dimethylthioformamide (DMTF, EGA) were used as supplied. Thiobenzamide (TBA, EGA) was dissolved in diethylether and kept over anhydrous Na_2SO_4. The solvent was then removed under reduced pressure. *N*-Phenylthioacetamide (thioacetanilide, TAA, Janssen) was recrystallized from diethylether/n-pentane. *N,N*-Dimethyl *O*-ethylthiocarbamate (DMTC) was prepared as reported in ref. 22. The precursor complex $[Rh_2(O_2CMe)_4(MeOH)_2]$ was prepared by reduction of $RhCl_3 \cdot 3H_2O$ in an acetic acid/absolute ethanol solution containing sodium acetate. The crude product was recrystallized from boiling methanol [23–25].

Preparation of the Compounds

$[Rh_2(O_2CMe)_4(DMTC)_2]$

A benzene solution of DMTC (1.2 mmol in 4 cm^3) was added to a solution of $[Rh_2(O_2CMe)_4(MeOH)_2]$ in absolute ethanol (0.2 mmol in 4 cm^3). The dark green solution was allowed to evaporate slowly under dinitrogen flux to a final volume of 1 cm^3. Well shaped dark green crystals separated, which were decanted, washed with n-pentane and dried *in vacuo*. Yield, *ca.* 70%. *Anal.* Found: C, 30.38; H, 4.92; N, 4.03. Calc. for $C_{18}H_{34}N_2O_{10}Rh_2S_2$: C, 30.52; H, 4.84; N, 3.95%.

$[Rh_2(O_2CMe)_4(DMTC)]$

An excess of DMTC (0.9 mmol) was added to a $[Rh_2(O_2CMe)_4(MeOH)_2]$ solution in absolute ethanol (0.25 mmol in 4 cm^3) with vigorous stirring. The bluish-green solution decolourized gradually yielding an olive green powder (30 min) which was filtered, washed with ethanol and dried *in vacuo*. Yield, *ca.* 85%. *Anal.* Found: C, 27.17; H, 4.05; N, 2.44. Calc. for $C_{13}H_{23}NO_9Rh_2S$: C, 27.15; H, 4.03; N, 2.43%. The compound was also obtained either by addition of n-pentane to a dichloromethane solution containing $[Rh_2(O_2CMe)_4(MeOH)_2]$ (0.15 mmol) and DMTC (0.5 mmol) or by dissolving $[Rh_2(O_2CMe)_4(DMTC)_2]$ in benzene. The dark green solution separated the 1:1 adduct in a few minutes.

$[Rh_2(O_2CMe)_4(Thioamide)_2]$

The compounds have been prepared with *ca.* 90% yields by adding an ethanol solution of the appropriate ligand (0.3–0.4 mmol in 2 cm^3) to an ethanol solution of $[Rh_2(O_2CMe)_4(MeOH)_2]$ (0.1 mmol in 4 cm^3) with stirring (1 h). The solid samples were filtered, washed with absolute ethanol and dried *in vacuo*. Finally they were washed with abundant n-pentane.

$[Rh_2(O_2CMe)_4(DMTF)_2]$, reddish-violet. *Anal.* Found: C, 27.22; H, 4.33; N, 4.66. Calc. for $C_{14}H_{26}N_2O_8Rh_2S_2$: C, 27.11; H, 4.22; N, 4.52%.

$[Rh_2(O_2CMe)_4(DMTA)_2]$, grey. *Anal.* Found: C, 29.52; H, 4.59; N, 4.22. Calc. for $C_{16}H_{30}N_2O_8Rh_2S_2$: C, 29.64; H, 4.66; N, 4.32%.

$[Rh_2(O_2CMe)_4(TBA)_2]$, reddish-brown. *Anal.* Found: C, 37.04; H, 3.76; N, 4.02. Calc. for $C_{22}H_{26}N_2O_8Rh_2S_2$: C, 36.89; H, 3.66; N, 3.91%.

$[Rh_2(O_2CMe)_4(TAA)_2]$, reddish-violet. *Anal.* Found: C, 38.86; H, 4.19; N, 3.51. Calc. for $C_{24}H_{30}N_2O_8Rh_2S_2$: C, 38.72; H, 4.06; N, 3.76%.

Measurements

Infrared spectra were measured by using either a Perkin-Elmer 580B spectrophtometer (4000–400 cm^{-1}) or a Bruker FT-IR instrument (450–100 cm^{-1}) as Nujol mulls between KBr and polyethylene

TABLE II. ^1H NMR Data (ppm, $CDCl_3$, $T = 25$ °C)

Compound	$N(CH_3)_2$	NH	C(S)R	O_2CCH_3
$[Rh_2(O_2CMe)_4(DMTF)_2]$	3.56, 3.41		9.49	1.87
DMTF	3.27, 3.24		9.16	
$[Rh_2(O_2CMe)_4(DMTA)_2]$	3.78, 3.42		2.88	1.87
DMTA	3.46, 3.28		2.62	
$[Rh_2(O_2CMe)_4(TAA)_2]^a$		11.1	2.80	1.87
TAA^a		9.8, 8.9	2.71, 2.51	
$[Rh_2(O_2CMe)_4(DMTC)_2]$	3.54, 3.16		4.87^b	1.83
$[Rh_2(O_2CMe)_4(DMTC)]$	3.55, 3.18		4.90^b	1.88
DMTC	3.36, 3.11		4.50^b	

[a] The phenyl proton resonances are in the 7.0–7.7 ppm range. [b] Methylene proton signal of the OEt group. The related methyl proton signal is at 1.34 ppm.

TABLE III. Crystal and Intensity Data

Compound	$[Rh_2(O_2CMe)_4(DMTC)_2]$ (I)	$[Rh_2(O_2CMe)_4(DMTF)_2]$ (II)
Formula	$C_{18}H_{34}N_2O_{10}Rh_2S_2$	$C_{14}H_{26}N_2O_8Rh_2S_2$
Formula weight	708	620
Cell constants	$a = 15.665(5)$ Å $b = 8.184(5)$ Å $c = 21.976(5)$ Å $\beta = 106.76(3)°$ $V = 2698$ Å^3	$a = 9.503(5)$ Å $b = 8.206(5)$ Å $c = 8.123(5)$ Å $\alpha = 114.65(3)°$ $\beta = 105.21(3)°$ $\gamma = 90.60(3)°$ $V = 550$ Å^3
Density (calc.)	$D_c = 1.742$ g cm^{-3}	$D_c = 1.871$ g cm^{-3}
Molecules per cell	$Z = 4$	$Z^a = 1$
System	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Absorption (Mo Kα)	7.5 cm^{-1}	36.6 cm^{-1}
λ (Mo Kα)	0.7107 Å	0.7107 Å
Method	ϑ–2ϑ	ϑ–2ϑ
Scan speed	2°/min	2°/min
2ϑ limit	$2° < 2\vartheta < 50°$	$2° < 2\vartheta < 50°$
Number of reflexions	4404	3132
Number of observed reflexions (with $I > 3\sigma(I)$)	2385	2445
Correction applied	Lp, absorption [29]	Lp, absorption [29]
Final conventional R factor	0.048	0.030

[a] One formula unit, that is a dimeric molecule, is contained in the unit cell.

discs. ^1H NMR spectra were obtained by a Jeol FX 90 Q spectrometer and electronic spectra (Nujol mulls on paper) with a Beckman DK2A spectrophotometer. Data are reported in Tables I and II.

X-Ray Data

Crystals of maximum dimensions 0.2 mm were selected for the X-ray measurements. Data collection was made on a Philips diffractomer with the monochromatized Mo Kα radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal and intensity data are reported in Table III. The crystals are stable under irradiation. Solution of the structures was achieved by standard Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. Anisotropy was introduced for all non-hydrogen atoms. A fixed temperature factor of 0.07 Å^2 was assigned to the hydrogen atoms. The full-matrix least-squares refinement of scale factor, positional and thermal parameters was proceeded minimizing the function $\Sigma w(\Delta F)^2$ with $w = 1$. At convergence, the largest parameter shift on the refined parameters of the non-hydrogen atoms was 0.2σ. No significant residual of electronic density was observed in the final Fourier difference maps. Scattering factors for neutral atoms were taken from ref. 26, and those of Rh were corrected for the anomalous dispersion [27]. Calculations were done using the SHELX program system [28]. Final

TABLE IV. Atomic Parameters and Thermal Parameters for [$Rh_2(O_2CMe)_4(DMTC)_2$] (**I**)

Atom	x/a	y/b	z/c
Atomic coordinates[a]			
Rh1	0.80673(6)	0.02306(11)	0.60230(4)
Rh2	0.72817(6)	0.00349(11)	0.49084(4)
S1	0.9025(2)	0.0548(4)	0.7206(1)
O1	0.7762(5)	0.2314(9)	0.4804(4)
O2	0.8472(5)	0.2492(10)	0.5840(4)
O3	0.6934(5)	0.1196(10)	0.6158(4)
O4	0.6209(5)	0.1016(11)	0.5123(4)
O5	0.8405(5)	−0.0967(9)	0.4774(4)
O6	0.9122(5)	−0.0802(10)	0.5816(4)
O7	0.6851(5)	−0.2241(9)	0.5097(4)
O8	0.7578(6)	−0.2049(9)	0.6127(4)
C1	0.8234(8)	0.3033(13)	0.5289(7)
C2	0.8547(9)	0.4750(14)	0.5178(7)
C3	0.6250(7)	0.1356(13)	0.5674(6)
C4	0.5416(8)	0.1994(16)	0.5804(7)
C5	0.9065(7)	−0.1188(12)	0.5259(6)
C6	0.9880(8)	−0.1980(15)	0.5139(8)
C7	0.7068(9)	−0.2725(14)	0.5653(7)
C8	0.6701(10)	−0.4382(15)	0.5771(8)
O9	1.0000(6)	0.3114(10)	0.7034(4)
N1	0.8810(7)	0.3758(13)	0.7324(5)
C9	0.9286(8)	0.2562(15)	0.7186(5)
C10	0.9091(10)	0.5461(17)	0.7309(8)
C11	0.8005(10)	0.3487(23)	0.7512(8)
C12	1.0560(9)	0.2014(15)	0.6814(7)
C13	1.1204(10)	0.3018(17)	0.6609(8)
S2	0.1507(2)	0.5004(5)	0.8673(1)
O10	0.2342(6)	0.2484(10)	0.8311(5)
N2	0.1161(8)	0.1812(15)	0.8617(5)
C14	0.1668(9)	0.3009(16)	0.8538(6)
C15	0.1412(10)	0.0061(19)	0.8569(8)
C16	0.0398(10)	0.2075(22)	0.8841(8)
C17	0.3037(9)	0.3620(16)	0.8285(7)
C18	0.3703(10)	0.2663(19)	0.8070(9)
H21	0.8866	0.5299	0.5634
H22	0.8072	0.5598	0.4889
H23	0.9045	0.4454	0.4943
H41	0.5377	0.2513	0.6247
H42	0.5099	0.0809	0.5737
H43	0.5081	0.2789	0.5416
H61	0.9770	−0.2035	0.4632
H62	0.9922	−0.3205	0.5329
H63	1.0495	−0.1339	0.5357
H81	0.6240	−0.4721	0.5320
H82	0.6351	−0.4321	0.6128
H83	0.7224	−0.5285	0.5907
H101	0.9794	0.5715	0.7411
H102	0.8836	0.6040	0.7662
H103	0.8743	0.5931	0.6844
H111	0.7757	0.2258	0.7519
H112	0.7496	0.4232	0.7198
H113	0.8176	0.3992	0.7986
H121	1.0192	0.1272	0.6418
H122	1.0905	0.1232	0.7708
H131	1.1646	0.2257	0.6434
H132	1.1593	0.3802	0.6982
H133	1.0803	0.3757	0.6225

(continued)

TABLE IV. *(continued)*

Atom	x/a	y/b	z/c
H151	0.2003	0.0049	0.8412
H152	0.0859	−0.0531	0.8231
H153	0.1529	−0.0512	0.9028
H161	0.0147	0.0841	0.8756
H162	−0.0095	0.2917	0.8568
H163	0.0538	0.2356	0.9341
H171	0.2709	0.4561	0.7955
H172	0.3395	0.4171	0.8732
H181	0.4290	0.3278	0.8023
H182	0.3385	0.2012	0.7637
H183	0.3892	0.1809	0.8461

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal parameters $U_{i,j} \times 10^4$ [b]						
Rh1	293(5)	212(4)	364(6)	6(4)	95(4)	8(4)
Rh2	294(5)	217(4)	376(6)	5(4)	95(4)	−2(4)
S1	486(21)	439(19)	438(21)	7(16)	70(16)	−57(16)
O1	397(50)	276(42)	433(58)	87(41)	95(43)	−94(39)
O2	468(55)	243(42)	519(63)	−42(43)	127(47)	−23(39)
O3	354(51)	405(48)	411(55)	−32(41)	231(44)	31(41)
O4	319(51)	497(54)	435(62)	28(46)	49(43)	68(41)
O5	366(53)	365(47)	470(58)	−41(42)	150(46)	−26(40)
O6	329(49)	428(49)	427(57)	−31(43)	104(42)	57(39)
O7	306(50)	262(43)	627(68)	10(44)	122(45)	−34(37)
O8	573(61)	252(44)	469(61)	55(42)	164(49)	−5(43)
C1	343(73)	162(52)	575(94)	71(59)	114(66)	51(51)
C2	596(89)	178(59)	943(114)	16(68)	348(80)	−49(61)
C3	301(74)	257(59)	506(93)	130(59)	63(65)	11(52)
C4	367(79)	430(75)	831(113)	−76(75)	314(81)	24(64)
C5	274(69)	190(53)	599(94)	−30(56)	301(67)	−37(48)
C6	233(75)	406(73)	901(125)	−106(73)	309(70)	−53(57)
C7	483(86)	272(64)	511(98)	76(64)	165(73)	40(59)
C8	631(100)	327(72)	944(125)	93(76)	431(91)	−57(67)
O9	464(57)	366(47)	656(66)	−173(45)	219(49)	12(42)
N1	481(73)	496(69)	579(82)	−152(60)	175(61)	113(58)
C9	360(75)	431(67)	270(70)	−47(56)	84(56)	79(58)
C10	636(103)	523(92)	870(125)	−125(86)	257(90)	107(80)
C11	649(113)	914(127)	599(110)	−111(96)	255(88)	31(99)
C12	528(87)	310(65)	642(103)	0(64)	235(74)	3(62)
C13	568(102)	414(78)	965(137)	−122(84)	292(91)	−57(73)
S2	593(22)	568(22)	413(19)	19(20)	81(16)	34(21)
O10	668(70)	390(50)	760(73)	−101(51)	370(59)	−190(48)
N2	569(81)	579(75)	547(83)	−88(63)	195(65)	−190(65)
C14	542(92)	470(78)	363(84)	0(63)	18(69)	−139(69)
C15	803(112)	645(105)	781(111)	−12(96)	212(91)	−383(102)
C16	609(108)	817(116)	645(111)	−131(91)	227(89)	−299(92)
C17	471(85)	487(79)	572(97)	−37(71)	159(72)	−88(69)
C18	680(119)	624(101)	929(141)	−111(95)	406(104)	−119(88)

[a] Standard deviations on H coordinates are < 0.0020. [b] The anisotropic thermal parameters are in the form $T = \exp[-2\pi^2 \cdot (U_{ij}h_ih_ja^*_ia^*_j)]$.

atomic parameters are listed in Tables IV and V, bond distances and angles are reported in Tables VI and VII for $[Rh_2(O_2CMe)_4(DMTC)_2]$ (**I**) and in Table VIII for $[Rh_2(O_2CMe)_4(DMTF)_2]$ (**II**).

Results and Discussion

The thioamine complexes have been prepared with quantitative yields by adding an excess of the

TABLE V. Atomic Parameters and Thermal Parameters for $[Rh_2(O_2CMe)_4(DMTF)_2]$ (II)

Atom	x/a	y/b	z/c
Atomic coordinates[a]			
Rh1	0.61525(4)	0.57079(5)	0.62268(5)
S1	0.8617(1)	0.7226(2)	0.8720(2)
O1	0.7157(3)	0.3923(4)	0.4420(4)
O2	0.4989(3)	0.7388(4)	0.7874(4)
O3	0.6309(3)	0.7440(4)	0.5044(4)
O4	0.5832(3)	0.3881(4)	0.7243(4)
N1	0.9560(4)	0.7184(5)	1.2098(5)
C1	0.6402(4)	0.2794(5)	0.2800(5)
C2	0.7226(6)	0.1556(7)	0.1538(7)
C3	0.4696(4)	0.2732(5)	0.6409(6)
C4	0.4550(6)	0.1411(9)	0.7215(9)
C5	0.8555(5)	0.6706(6)	1.0455(6)
C6	1.0957(7)	0.8225(10)	1.2548(9)
C7	0.9367(7)	0.6594(9)	1.3509(8)
H21	0.6673	0.0531	0.0516
H22	0.7529	0.2034	0.1089
H23	0.8068	0.1283	0.2218
H41	0.3895	0.0444	0.6391
H42	0.3905	0.1498	0.7347
H43	0.4769	0.2175	0.8617
H51	0.7626	0.5984	1.0017
H61	1.1651	0.8020	1.3893
H62	1.1944	0.7962	1.2773
H63	1.0437	0.9185	1.2998
H71	0.8528	0.6038	1.3051
H72	0.9599	0.7786	1.4595
H73	1.0203	0.6108	1.3911

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal parameters $U_{i,j} \times 10^4$ [b]						
Rh1	260(1)	298(1)	234(1)	119(1)	47(1)	46(1)
S1	350(5)	504(6)	379(5)	180(5)	42(4)	6(5)
O1	327(14)	422(16)	355(15)	126(13)	101(12)	103(12)
O2	366(14)	398(15)	261(13)	72(11)	85(11)	61(12)
O3	368(15)	410(16)	382(15)	226(13)	69(12)	12(12)
O4	401(15)	431(16)	335(14)	239(13)	8(12)	21(12)
N1	389(19)	567(23)	355(18)	172(17)	33(15)	96(17)
C1	385(20)	340(19)	318(18)	145(15)	140(15)	69(15)
C2	473(26)	519(29)	432(25)	102(21)	220(21)	126(22)
C3	424(21)	351(19)	324(19)	174(16)	114(16)	79(16)
C4	677(34)	574(31)	505(29)	358(26)	78(26)	−69(28)
C5	330(20)	374(21)	405(22)	111(18)	81(17)	47(16)
C6	471(29)	933(54)	556(38)	282(34)	−120(28)	−200(31)
C7	562(31)	822(43)	477(30)	328(30)	117(25)	194(30)

[a] Standard deviations on H coordinates are < 0.0060. [b] The anisotropic thermal parameters are in the form $T = \exp[-2\pi^2(U_{ij}h_ih_ja^*_ia^*_j)]$.

appropriate ligand (*ca.* 4:1) to a solution of $[Rh_2(O_2CMe)_4(MeOH)_2]$ in absolute ethanol. The adduct colour is red or violet, except for the DMTA complex, which is grey in the solid state and forms violet dichloromethane solutions. In analogous conditions DMTC yields the olive green 1:1 adduct, insoluble in ethanol, whereas dark green crystals of $[Rh_2(O_2CMe)_4(DMTC)_2]$ are obtained by slow evaporation of a benzene/ethanol solution containing the methanol adduct and DMTC in molar ratio 1:6. When dissolved in benzene $[Rh_2(O_2CMe)_4(DMTC)_2]$ releases gradually one of the ligand molecules to give the insoluble 1:1 adduct. Conversely a dichloromethane solution of $[Rh_2(O_2CMe)_4(DMTC)_2]$ de-

TABLE VI. Bond Distances (Å) for **I**[a]

Rh(1)–Rh(2)	2.409(1)		
Rh(1)–S(1)	2.614(3)	Rh(2)–S(2)	2.634(4)
Rh(1)–O(2)	2.03(1)	Rh(2)–O(1)	2.05(1)
Rh(1)–O(3)	2.04(1)	Rh(2)–O(4)	2.04(1)
Rh(1)–O(6)	2.02(1)	Rh(2)–O(5)	2.04(1)
Rh(1)–O(8)	2.05(1)	Rh(2)–O(7)	2.06(1)
S(1)–C(9)	1.70(1)	S(2)–C(14)	1.69(1)
C(9)–N(1)	1.32(2)	C(14)–N(2)	1.30(2)
N(1)–C(10)	1.46(2)	N(2)–C(15)	1.50(2)
N(1)–C(11)	1.45(3)	N(2)–C(16)	1.43(3)
C(9)–O(9)	1.35(2)	C(14)–O(10)	1.36(2)
O(9)–C(12)	1.43(2)	O(10)–C(17)	1.44(2)
C(12)–C(13)	1.47(2)	C(17)–C(18)	1.49(2)
C(1)–O(1)	1.25(2)	C(5)–O(5)	1.27(2)
C(1)–O(2)	1.24(2)	C(5)–O(6)	1.24(2)
C(1)–C(2)	1.53(2)	C(5)–C(6)	1.54(2)
C(3)–O(3)	1.28(2)	C(7)–O(7)	1.24(2)
C(3)–O(4)	1.23(2)	C(7)–O(8)	1.24(2)
C(3)–C(4)	1.52(2)	C(7)–C(8)	1.54(2)

[a]e.s.d.s refer to the last significant digit.

composes on standing in air to give the blue insoluble species [$Rh_2(O_2CMe)_4(H_2O)_2$] and a solution of the 1:2 DMTC complex. As is shown in Table I, the absorption maxima in the electronic spectra of thioamide complexes are observed in the 520–570 nm range, and follow the wavelength order DMTA > DMTF > TAA > TBA, whereas the DMTC complex λ_{max} is at *ca.* 640 nm, at lower energy with respect to the methanol adduct value (593 nm). The trend in the electronic spectra could suggest coordination of DMTC through the oxygen atom, whereas IR and ^1H NMR spectra indicate that all ligands coordinate through sulphur.

In the 1500–1600 cm^{-1} region (Table I) the adducts present two strong absorptions, the one at *ca.* 1590 cm^{-1} due to the asymmetric stretching of the acetato CO_2 group and the other at *ca.* 1550 cm^{-1} due to the C–N bond stretch of the coordinated ligand. The ν(C–N) are in the free ligands at 1530 (DMTC), 1540 (DMTF) and 1510 (DMTA) cm^{-1} and shift to higher energies on coordination, as expected for S-bound moieties. The absorptions beyond 3000 cm^{-1} depend on the N–H bond stretching and $\delta(NH_2)$ is observed at 1643 cm^{-1} for the TBA complex. The bands at *ca.* 380 and 335 cm^{-1}, common to all complexes, are of the asymmetric and symmetric Rh–O bond stretching respectively, whereas below 300 cm^{-1} the adduct spectra contain very weak unassigned absorptions (cm^{-1}; DMTF: 134, 118; DMTA: 284, 126, 96; TBA: 177, 105, 89; DMTC: 205, 170).

TABLE VII. Bond Angles (°) for **I**[a]

Rh(2)–Rh(1)–S(1)	175.4(1)	Rh(1)–Rh(2)–S(2)	175.6(1)
Rh(2)–Rh(1)–O(2)	87.5(3)	Rh(1)–Rh(2)–O(1)	87.5(3)
Rh(2)–Rh(1)–O(3)	87.9(3)	Rh(1)–Rh(2)–O(4)	87.2(3)
Rh(2)–Rh(1)–O(6)	87.4(3)	Rh(1)–Rh(2)–O(5)	87.8(3)
Rh(2)–Rh(1)–O(8)	87.4(3)	Rh(1)–Rh(2)–O(7)	87.9(3)
S(1)–Rh(1)–O(2)	89.1(3)	S(2)–Rh(2)–O(1)	88.4(3)
S(1)–Rh(1)–O(3)	95.2(3)	S(2)–Rh(2)–O(4)	94.5(3)
S(1)–Rh(1)–O(6)	89.6(3)	S(2)–Rh(2)–O(5)	90.4(3)
S(1)–Rh(1)–O(8)	96.0(3)	S(2)–Rh(2)–O(7)	96.7(3)
Rh(1)–O(2)–C(1)	119(1)	Rh(2)–O(1)–C(1)	119(1)
Rh(1)–O(3)–C(3)	118(1)	Rh(2)–O(4)–C(3)	120(1)
Rh(1)–O(6)–C(5)	120(1)	Rh(2)–O(5)–C(5)	118(1)
Rh(1)–O(8)–C(7)	119(1)	Rh(2)–O(7)–C(7)	119(1)
Rh(1)–S(1)–C(9)	98.2(4)	Rh(2)–S(2)–C(14)	97.0(5)
O(1)–C(1)–O(2)	127(1)	O(5)–C(5)–O(6)	127(1)
O(1)–C(1)–C(2)	116(2)	O(5)–C(5)–C(6)	116(2)
O(2)–C(1)–C(2)	117(1)	O(6)–C(5)–C(6)	117(1)
O(3)–C(3)–O(4)	126(2)	O(7)–C(7)–O(8)	128(2)
O(3)–C(3)–C(4)	116(2)	O(7)–C(7)–C(8)	116(1)
O(4)–C(3)–C(4)	118(1)	O(8)–C(7)–C(8)	116(2)
S(1)–C(9)–N(1)	124(1)	S(2)–C(14)–N(2)	125(1)
S(1)–C(9)–O(9)	124(1)	S(2)–C(14)–O(10)	123(1)
O(9)–C(9)–N(1)	112(1)	O(10)–C(14)–N(2)	112(1)
C(9)–N(1)–C(10)	120(1)	C(14)–N(2)–C(15)	122(1)
C(9)–N(1)–C(11)	123(1)	C(14)–N(2)–C(16)	122(1)
C(10)–N(1)–C(11)	116(1)	C(15)–N(2)–C(16)	115(1)
C(9)–O(9)–C(12)	121(1)	C(14)–O(10)–C(17)	119(1)
O(9)–C(12)–C(13)	107(1)	O(10)–C(17)–C(18)	106(1)

[a]e.s.d.s refer to the last significant digit.

TABLE VIII. Bond Distances (Å) and Angles (°) for II[a]

Distances			
Rh(1)–Rh(1$^{\mathrm{I}}$)	2.418(1)	Rh(1)–O(2)	2.046(3)
Rh(1)–S(1)	2.546(1)	Rh(1)–O(3)	2.044(3)
Rh(1)–O(1)	2.045(3)	Rh(1)–O(4)	2.044(3)
C(1)–O(1)	1.26(1)	C(3)–O(3$^{\mathrm{I}}$)	1.26(1)
C(1)–O(2$^{\mathrm{I}}$)	1.27(1)	C(3)–O(4)	1.26(1)
C(1)–C(2)	1.51(1)	C(3)–C(4)	1.50(1)
S(1)–C(5)	1.648(5)	N(1)–C(6)	1.44(1)
C(5)–N(1)	1.32(1)	N(1)–C(7)	1.47(1)
Angles			
Rh(1$^{\mathrm{I}}$)–Rh(1)–S(1)	177.8(1)	S(1)–Rh(1)–O(1)	91.6(1)
Rh(1$^{\mathrm{I}}$)–Rh(1)–O(1)	87.2(1)	S(1)–Rh(1)–O(2)	93.0(1)
Rh(1$^{\mathrm{I}}$)–Rh(1)–O(2)	88.2(1)	S(1)–Rh(1)–O(3)	90.6(1)
Rh(1$^{\mathrm{I}}$)–Rh(1)–O(3)	87.5(1)	S(1)–Rh(1)–O(4)	94.1(1)
Rh(1$^{\mathrm{I}}$)–Rh(1)–O(4)	87.8(1)	Rh(1)–S(1)–C(5)	103.7(2)
S(1)–C(5)–N(1)	128.0(4)	C(5)–N(1)–C(7)	122.2(4)
C(5)–N(1)–C(6)	121.2(5)	C(6)–N(1)–C(7)	116.5(5)

[a] e.s.d.s refer to the last significant digit.

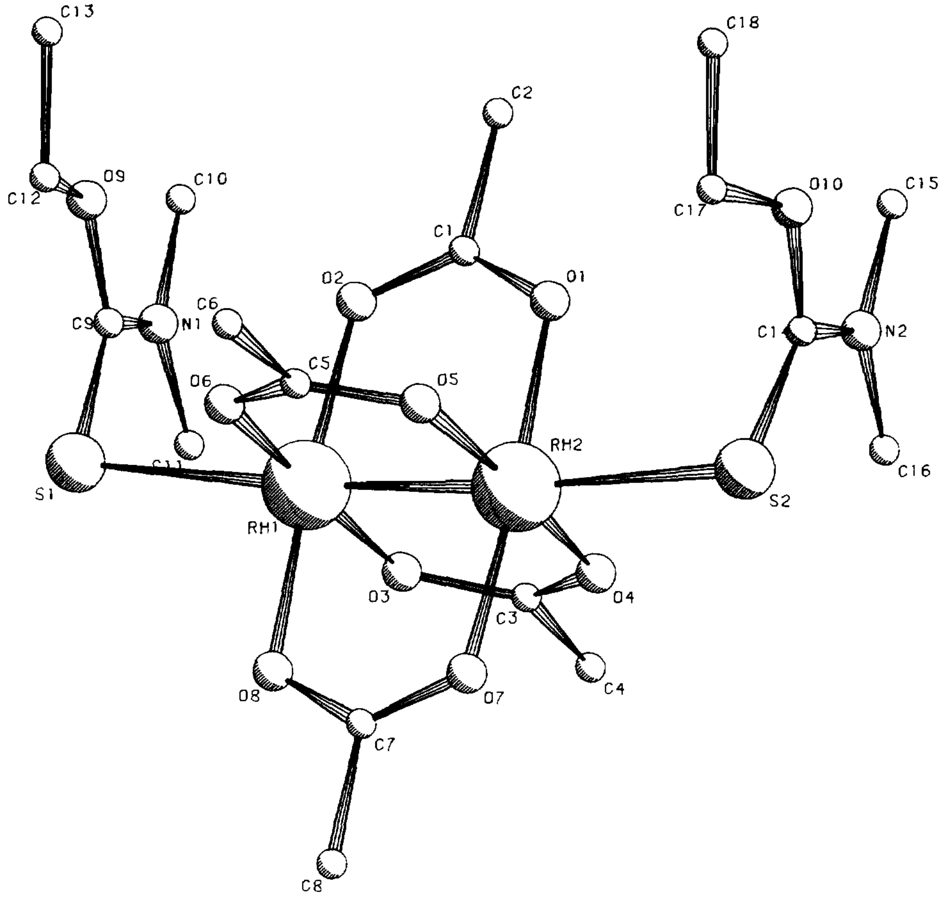

Fig. 1. The crystal structure of [$Rh_2(O_2CMe)_4(DMTC)_2$] (I).

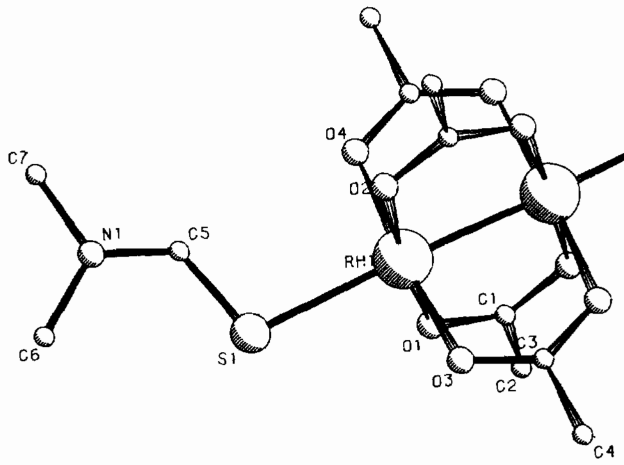

Fig. 2. The crystal structure of $[Rh_2(O_2CMe)_4(DMTF)_2]$ (II).

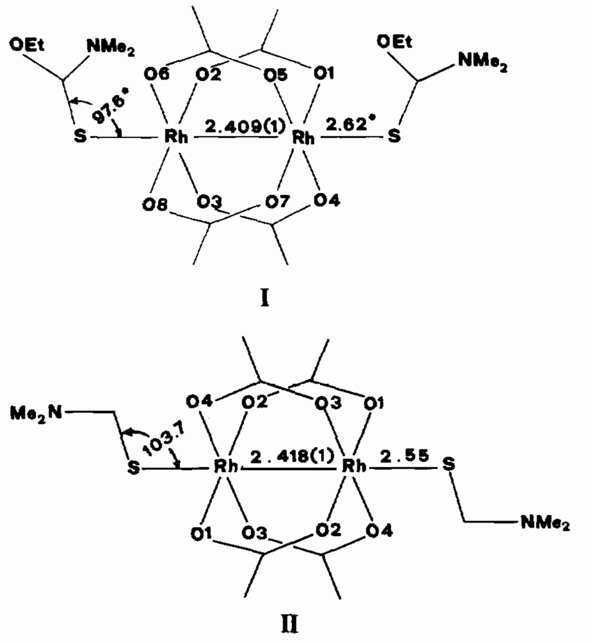

Fig. 3. Schematic drawing of the molecular structures. Asterisk indicates mean values.

The proton NMR spectra of the complexes (Table II) show the acetato proton signal at *ca.* 1.87 ppm. Owing to the barriers to rotation around the C–N bond, of the order of 100 kJ mol^{-1} in thioamides and 70 kJ mol^{-1} in thiocarbamic esters [30, 31] the free ligand molecules are planar. Consequently DMTF, DMTA and DMTC present two equally intense signals for the non-equivalent methyl groups bound to nitrogen. Due to the different substituents at the nitrogen atom, TAA is a mixture of both isomers having the phenyl group either in *syn* or in *anti* position with respect to the thiocarbonyl group. In fact the ^1H NMR spectrum contains two signals for either NH or $C(S)CH_3$ protons, the resonances at 2.71 and 8.9 ppm belonging to the major isomer (55%). A general downfield shift of the proton signals is observed on coordination and the increased C–N double bond causes a $N(CH_3)_2$ resonance separation larger than in free ligands. The presence of one signal for either NH or $C(S)CH_3$ indicates that in the complex $[Rh_2(O_2CMe)_4(TAA)_2]$ the ligand coordinates with one of the isomeric species.

The molecular structures of $[Rh_2(O_2CMe)_4(DMTC)_2]$ (I) and $[Rh_2(O_2CMe)_4(DMTF)_2]$ (II) are shown in Figs. 1 and 2 respectively. Regardless of the axial ligand, the structures of both octahedral rhodium(II) complexes are very similar: two metal atoms are linked by four bridging acetato groups forming a dimeric unit characterized by a direct Rh–Rh bond. It is noteworthy that the compounds crystallize in different crystal systems, despite the comparable crystal densities. $[Rh_2(O_2CMe)_4(DMTC)_2]$ is monoclinic and the asymmetric unit is represented by the dinuclear molecule; in this compound all structural details are singularly and independently determined. $[Rh_2(O_2CMe)_4(DMTF)_2]$ is triclinic and the molecule is centrosymmetric; in this case the asymmetric unit is one half of the dimer and all structural details are equal in pairs. The Rh–Rh distances in the two molecules (DMTC, 2.409(1) Å DMTF, 2.418(1) Å) are closely similar and fully comparable with the values observed in analogous complexes with axial sulphur donors (Me_2SO, 2.406(1) Å [12]; $PhCH_2SH$, 2.402(1) Å [32]; C_4H_8S, 2.413(1) Å [12]; PhSH, 2.402(1) Å [1]; $(PhCH_2)_2S$, 2.406(3) Å [9]). The strong *trans* influence of the metal–metal bond is reflected in the weakness of the axial Rh–S bonds, which are significantly longer than expected for a normal covalent bond. In fact the Rh–S length in the violet compound $[Rh_2(O_2CMe)_4(DMTF)_2]$ (2.546(1) Å) compares with the values in the adducts with axial ligand $PhCH_2SH$ (2.551(2) Å) [32], C_4H_8S (2.517(1) Å) [12], PhSH (2.548(1) Å) [1] and $(PhCH_2)_2S$ (2.561(5) Å) [9]. The corresponding distance in the green complex $[Rh_2(O_2CMe)_4(DMTC)_2]$ is the longest in the series, with a mean value of 2.624 Å. Because the structural details of the dirhodium(II) tetraacetato moieties are fully equivalent in the two compounds, the only cause of the observed difference in the Rh–S distances should lie in the nature of the ligand itself. As shown in Fig. 3, substitution of the strongly electronegative ethoxo group in **I** with the hydrogen atom in **II** results in a more pronounced double bond character of the C=S bond (1.65 Å in **II** *versus* 1.70 Å in **I**) and in an enlargement of about 6° of the Rh–S–C angle. Thus, the shorter Rh–S distance found in **II** is associated with the shorter C=S bond in the sulphur-donor ligand and could be in some way determined by it.

Finally, there is a difference between the molecules of the two compounds from a conformational point of view. As schematically shown in Fig. 3, the axial ligands are approximately oriented towards the same side of the binuclear cage in **I**, while they are rigorously centrosymmetric in **II** because of the presence of the crystallographic inversion center between the rhodium atoms.

The fact that λ_{max} of the low energy band in the electronic absorption spectra and the Rh–S distance correlate well in the DMSO (497 nm, 2.451 Å [10, 12]), DMTF (550 nm, 2.546 Å) and DMTC (637 nm, 2.624 Å) complexes suggests that the colour of the 1:2 rhodium(II) acetato adducts with sulphur donors depends on the Rh–S bond strength. If such a trend holds for all sulphur ligands, DMTA should be weakest donor among the thioamides reported in this paper.

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