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Di- and trinuclear (η^6-arene)ruthenium(II) complexes containing bridging heterocyclic thioamides

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Abstract

Reaction of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{RuCl}_2]_2$ with the heterocyclic thioamides (L), 2-mercapto-1-methylimidazole (mmimH) or 4,5-diphenyl-2-mercaptoimidazole (dpmimH$_2$) in a 1:1 ratio in the presence of base leads to the formation of the dinuclear complexes $[\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2(\mu\text{-L})(\mu\text{-Cl})\text{Cl}]\text{Cl}$ (**3** and **4**). The [dpmimH]$^-$ ligand in **4** adopts a μ_2-(1κ^1S; 2κ^2N,S) bridging mode, as is also observed for one of the [mtz]$^-$ ligands (mtzH = 2-mercapto-2-thiazoline) in $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}_2(\mu\text{-mtz})_2\text{Cl}]\text{Cl}$ (**2**). In contrast, the second bridging [mtz]$^-$ ligand in **2** exhibits the μ_2-N,S coordination mode. The pentadentate [dpmimH$_{-1}$]$^{3-}$ ligand bridges three ruthenium atoms in the trinuclear complex $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_3\text{Ru}_3(\mu_3\text{-dpmimH}_{-1})(\mu\text{-Cl})\text{Cl}_2]$ (**6**), two of which via the μ_2-(1κ^1S; 2κ^2N,S) coordination mode displayed by **4**. A cyclometallation leads to the coordination of the third ruthenium atom through the second imidazole N atom and an *ortho*-C atom of the adjacent phenyl ring. The structures of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{mtzH})]$ (**1**), **2**, **4** and **6** were established by X-ray structural analysis.

Introduction

The coordination chemistry of heterocyclic thioamides such as 2-mercapto-2-thiazoline (mtzH) or 2-mercapto-1-methylimidazole (mmimH) is a topic of appreciable current interest [1–19]. These potentially ambidentate ligands display a structural analogy to thiolated nucleosides and pharmacological activity has been demonstrated for mmimH [1]. Copper(I) complexes, in which the neutral ligands coordinate through a terminal or bridging thione sulfur atom, have been extensively studied. Recently [mtz]$^-$, [mmim]$^-$ and the analogous anion [mbt]$^-$ (mbtH = 2-mercaptobenzothiazole) have been employed in a μ_2-N,S or μ_3-N,S bridging function in the construction of di-, tri- and tetranuclear complexes such as $[\text{Rh}(\mu\text{-mtz})(\text{CO})(\text{PPh}_3)]_2$ [4], $[(\text{COD})_2\text{Rh}_2(\mu_3\text{-mbt})_2\text{Ag}(\text{ClO}_4)]$ [20] (COD = 1,5-cyclooctadiene), $[\text{Rh}_3(\mu_3\text{-mbt})_2(\text{CO})_2(\text{PPh}_3)_2(\text{tfbb})][\text{ClO}_4]$ (tfbb = tetrafluorobenzobarrelene) [21] or $[\text{Cu}(\mu_3\text{-mmim})]_4$ [9]. As a result of their small angle of bite these anions are also capable of bridging metal–metal bonds in a μ_2-N,S fashion in clusters such as $[\text{Ir}(\mu\text{-mbt})\text{I}(\text{CO})_2]_2$, $[\text{Ir}_4(\mu\text{-mbt})_4(\text{I})_2(\text{CO})_8]$ [22] and $[\text{Ru}_2(\mu\text{-mtz})_2(\text{CO})_4(\text{PPh}_3)_2]$ [3]. An alternative bridging mode has recently been established in a polymeric cadmium(II) complex $[\text{Cd}(\mu\text{-mbt})_2]_n$ [23]. In this infinite chain, octahedrally coordinated cadmium atoms separated at a distance of 3.06 or 3.12 Å are linked via [mbt]$^-$ anions displaying a μ_2-(1κ^1S; 2κ^2N,S) coordination.

It is interesting that this coordination mode has not previously been observed in multinuclear transition metal complexes of five-membered heterocyclic thioamides. We have recently reported the preparation and structural characterisation of di- and tetranuclear (η^6-arene)ruthenium(II) complexes of various heteroaromatic nitrogen ligands such as pyrazole, 3-aminopyrazole, imidazole and adenine [24, 25]. In the present work we report an extension of these studies to (η^6-arene)ruthenium(II) complexes of the anions [mtz]$^-$, [mmim]$^-$, [dpmimH]$^-$ and [dpmimH$_{-1}$]$^{3-}$ (dpmimH$_2$ = 4,5-diphenyl-2-mercaptoimidazole). The number of previously characterised ruthenium(II) complexes of heterocyclic thioamides is limited. $[\text{Ru}(\text{dmtdH})_2(\text{CO})(\text{PPh}_3)_2]$ contains both a monodentate (κ^1S) and a bidentate (κ^2N,S) dmtdH anion (dmtdH$_2$ = 2,5-dimercapto-1,3,4-thiadiazole) [26]. Bidentate coordination of [mtz]$^-$ has also been proposed on the basis of spectroscopic studies for the mononuclear complexes $[\text{RuH}(\text{mtz})(\text{CO})(\text{PPh}_3)_2]$ and $[\text{Ru}(\text{mtz})(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]$ [27].

Experimental

^{1}H NMR spectra were recorded on Bruker WP 80 and AM 400 spectrometers at 20 °C; δ values are given in ppm. Elemental analyses were performed on a Carlo

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Erba 1106. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ were prepared as described previously [28, 29] from $RuCl_3 \cdot 3H_2O$, which was a gift from Degussa AG. 2-Mercapto-2-thiazoline, 2-mercapto-1-methylimidazole and 4,5-diphenyl-2-mercaptoimidazole were purchased from Janssen (mtzH, dpmimH_2) and Fluka (mmimH) and used as received.

Preparation of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)RuCl_2(mtzH)]$ *(1)*

A solution of 245 mg (0.4 mmol) of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ in 25 ml H_2O was added to 95 mg (0.8 mmol) of mtzH in 10 ml methanol. The solution was stirred for 2 h at r.t. and the solvent removed. **1** was recrystallised from CH_2Cl_2/hexane (yield 326 mg, 96%).

1: *Anal.* Found: C, 36.7; H, 4.6; N, 3.3; $M = 425.4$. Calc.: C, 36.7; H, 4.5; N, 3.3%. ^1H NMR (400 MHz, $CDCl_3$): δ 1.28 (d, 6H, CH_3(i-Pr) *p*-cymene), 2.22 (s, 3H, CH_3 *p*-cymene), 3.00 (sp, 1H, CH(i-Pr) *p*-cymene, 3.35, 3.85 (2t, 4H, CH_2 mtzH), 5.20, 5.40 (m, 4H, CH *p*-cymene), 9.95 (br, 1H, NH mtzH).

Preparation of $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mu\text{-}mtz)_2Cl]Cl$ *(2)*

A solution of 200 mg (0.4 mmol) of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in 20 ml H_2O was added to 95 mg (0.8 mmol) of mtzH in 5 ml methanol and 0.8 ml 1 M NaOMe. The red solution was stirred for 2 h at r.t., reduced in volume to 3 ml and set aside at 4 °C to yield red crystals of **4** within 24 h (yield 249 mg, 89%).

2$\cdot 2H_2O$: *Anal.* Found: C, 29.5; H, 2.8; N, 3.6; $M = 701.7$. Calc.: C, 30.8; H, 3.4; N, 4.0%. ^1H NMR (80 MHz, CD_3OD): δ 3.1–4.5 (mm, 8H, CH_2 mtz$^-$), 5.79 (s, 6H, CH C_6H_6), 6.09 (s, 6H, CH C_6H_6).

Preparation of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)_2Ru_2(\mu\text{-}mmim)(\mu\text{-}Cl)Cl]Cl$ *(3)*

A solution of 245 mg (0.4 mmol) of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ in 10 ml H_2O was added to 46 mg (0.4 mmol) of mmimH in 15 ml methanol and 0.4 ml 1 M NaOMe. The solution was stirred for 2 h at r.t. and reduced in volume to 3 ml. Addition of 20 ml diethyl ether led to the precipitation of **3** which was dried *in vacuo* (yield 167 mg, 59%).

3$\cdot H_2O$: *Anal.* Found: C, 40.7; H, 4.9; N, 4.2; $M = 708.1$. Calc.: C, 40.7; H, 5.0; N, 4.0%. ^1H NMR (80 MHz, $CDCl_3$): δ 0.85–1.35 (md, 12H, CH_3 (i-Pr) *p*-cymene), 1.85, 1.95 (2s, 6H, CH_3 *p*-cymene), 2.58–3.00 (2sp, 2H, CH(i-Pr) *p*-cymene), 4.10 (s, 3H, CH_3 mmim$^-$), 4.90–5.84 (mm, 8H, CH *p*-cymene), 6.88, 7.16 (2d, 2H, CH mmim$^-$).

Preparation of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)_2Ru_2(\mu\text{-}dpmimH)(\mu\text{-}Cl)Cl]Cl$ *(4)*

A solution of 245 mg (0.4 mmol) of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ and 101 mg (0.4 mmol) of dpmimH_2 in 25 ml ethanol and 0.2 ml 2 M KOH were stirred for 2 h at r.t. The solution was filtered and reduced in volume to 2 ml. Addition of 20 ml diethyl ether led to precipitation of **4** which was recrystallised from methanol (yield 138 mg, 42%).

4: *Anal.* Found: C, 49.4; H, 4.7; N, 3.4; $M = 828.3$. Calc.: C, 50.8; H, 4.8; N, 3.4%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.80–1.28 (md, 12H, CH_3(i-Pr) *p*-cymene), 2.00, 2.15 (2s, 6H, CH_3 *p*-cymene), 2.20–2.90 (2sp, 2H, CH(i-Pr) *p*-cymene), 4.85–6.10 (mm, 8H, CH *p*-cymene), 7.10–7.70 (m, 10H, CH dpmimH), 15.50 (br, 1H, NH dpmimH).

Preparation of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)_2Ru_2(dpmimH)_2Cl]Cl$ *(5)*

The preparation of **5** from 245 mg (0.4 mmol) of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ and 202 mg (0.8 mmol) of dpmimH_2 was performed under analogous conditions to **4** (yield 273 mg, 65%).

5: *Anal.* Found: C, 57.1; H, 4.8; N, 5.5; $M = 1044.1$. Calc.: C, 57.5; H, 4.8; N, 5.4%. ^1H NMR (400 MHz, $CDCl_3$): δ 0.88–1.14 (md, 12H, CH_3(i-Pr) *p*-cymene), 2.07, 2.09 (2s, 6H, CH_3 *p*-cymene), 2.28–2.90 (2sp, 2H, CH(i-Pr) *p*-cymene), 4.68–6.10 (mm, 8H, CH *p*-cymene), 7.25–7.66 (m, 20H, CH dpmimH$^-$), 12.78, 15.48 (2s, 2H, NH dpmimH$^-$).

Preparation of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)_3Ru_3(\mu_3\text{-}dpmimH_{-1})(\mu\text{-}Cl)Cl_2]$ *(6)*

245 mg (0.4 mmol) of $[(\eta^6\text{-}p\text{-}MeC_6H_4CHMe_2)_2RuCl_2]_2$ and 101 mg (0.4 mmol) of dpmimH_2 in 25 ml methanol and 0.4 ml 1 M NaOMe were stirred for 8 h at r.t. After removal of the solvent, 1 ml of CH_2Cl_2 was added and the solution filtered. 2 ml of H_2O/CH_3OH (1:2) were added and the solution set aside at −40 °C to yield deep red crystals of **6** (yield 81 mg, 28%).

6: *Anal.* Found: C, 51.5; H, 5.2; N, 2.7; $M = 1061.5$. Calc.: C, 50.9; H, 4.8; N, 2.6%. ^1H NMR (80 MHz, $CDCl_3$): δ 0.80–1.30 (md, 18H, CH_3(i-Pr) *p*-cymene), 1.95, 2.00, 2.20 (3s, 9H, CH_3 *p*-cymene), 2.25–3.80 (msp, 3H, CH(i-Pr) *p*-cymene), 4.80–6.04 (mm, 12H, CH *p*-cymene), 6.74–8.13 (m, 9H, CH dpmimH_{-1}).

X-ray structural analyses of 1, 2, 4 and 6

Crystal and refinement data are summarised in Table 1. Unit cell constants were determined in each case using 25 reflections ($15 \leqslant \theta \leqslant 20°$) centered on a Siemens P4 diffractometer using Mo Kα radiation. Intensity data were collected in the ω-scan mode for each of the compounds and corrected semi-empirically for absorption on the basis of ψ-scan data. The structures were refined by full-matrix least-squares with weights given by the expression $w = [\sigma^2(F_o) + pF_o^2]^{-1}$; values of p are given in Table 1. Difference syntheses revealed the positions of the following solvent molecules (the relevant

TABLE 1. Crystal and refinement data

Compound	**1**·CH_2Cl_2	**2**·$2H_2O$	**4**·$\frac{1}{2}CH_3OH$	**6**·$\frac{1}{2}H_2O$
Formula	$C_{13}H_{19}NS_2Cl_2Ru\cdot CH_2Cl_2$	$C_{18}H_{20}N_2S_4Cl_2Ru_2\cdot 2H_2O$	$C_{35}H_{39}N_2SCl_3Ru_2\cdot\frac{1}{2}CH_3OH$	$C_{45}H_{51}N_2SCl_3Ru_3\cdot\frac{1}{2}H_2O$
Space group	$C2/c$	$P2_1/n$	$P2_1/c$	$Pbcn$
a (Å)	22.455(5)	9.714(4)	19.578(4)	20.86(1)
b (Å)	8.822(3)	21.689(9)	18.035(4)	20.04(1)
c (Å)	22.778(6)	12.406(4)	10.755(3)	22.79(1)
β (°)	115.99(2)	112.44(3)	96.54(2)	90
V (Å^3)	4056(2)	2416(2)	3773(2)	9525(8)
Z	8	4	4	8
M (g cm^{-1})	510.3	701.7	844.3	1070.5
D_c (g cm^{-3})	1.67	1.93	1.49	1.49
Radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (cm^{-1})	14.8	18.0	10.8	11.7
Scan type	ω	ω	ω	ω
$2\theta_{max}$ (°)	55	50	50	45
Reflections collected	4709	4240	6650	6283
Reflections observed	3743	2589	4783	1754
Rejection criterion	$F_o^2\leqslant 2\sigma(F_o^2)$	$F_o^2\leqslant 2\sigma(F_o^2)$	$F_o^2\leqslant 2\sigma(F_o^2)$	$F_o^2\leqslant 3\sigma(F_o^2)$
R	0.034	0.060	0.038	0.112
R_w	0.035	0.055	0.040	0.110
p	0.0001	0.0002	0.0002	0.0002

compound is given in parentheses): CH_2Cl_2 (**1**), $2H_2O$ (**2**), $\frac{1}{2}CH_3OH$ (**4**) and $\frac{1}{2}H_2O$ (**6**). Site occupation factors of 0.5 were introduced for the disordered solvent molecules in the crystal lattices of **4** and **6**. Crystals of **6** were of mediocre quality, being characterised by a wide mosaic spread. As a result anisotropic temperature factors could only be introduced for the Ru, Cl and S atoms in this complex. In both **1** and **2** all non-hydrogen atoms could be refined anisotropically; in **4** all non-hydrogen atoms with the exception of the disordered methanol C and O atoms. Calculations were performed with the SHELXTL set of programmes (Siemens). Atom positional parameters with equivalent isotropic temperature factors are given in Table 2.

Results and discussion

Reaction of $[(\eta^6\text{-}p\text{-MeC}_6H_4CHMe_2)RuCl_2]_2$ with mtzH in H_2O/CH_3OH at a molar ratio 1:2 yields the monomeric complex **1**, in which the ligand is coordinated via its exocyclic thione sulfur atom S(7) (Fig. 1). Although, coordination of the ruthenium atom leads to a lengthening of the S(7)–C(7) bond from 1.671(7) in the free ligand [8] to 1.691(4) Å in **1**, this latter distance is still indicative of a pronounced degree of π-character, as is also apparent for the endocyclic S(8)–C(7) bond (1.729(4) Å). Both this and the second endocyclic S–C bond length (1.815(6) Å) are effectively unchanged in complex **1** in comparison to the free ligand (1.726(6) and 1.810(8) Å). The Ru–S(7) distance of 2.400(1) is similar to that of 2.385(5) Å observed for the monodentate dmtdH anion in $[Ru(dmtdH)_2(CO)(PPh_3)_2]$ [26].

The anion $[mtz]^-$ would be expected to exhibit an N,S coordination mode, either in a mononuclear complex through formation of a four-membered chelate ring or in a dinuclear complex by the adoption of a bridging function. Interestingly the reaction of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ with $[mtz]^-$ in H_2O/CH_3OH leads to the isolation of the same dinuclear complex $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mu\text{-mtz})_2Cl]Cl$ (**2**), irrespective of whether a 1:1 or 1:2 molar ratio of the starting compounds is employed. The observation of two singlets of identical integral height at $\delta = 6.05$ and 5.70 ppm for the benzene protons in the ^1H NMR spectrum of **2** (CD_3OD) indicates the presence of contrasting coordination spheres for the ruthenium atoms. As may be seen in the X-ray structure in Fig. 2, different coordination modes are adopted by the bridging $[mtz]^-$ anions in **2**. Both ligands exhibit a μ_2-N,S coordination mode, but for one ligand this is complemented by the formation of a four-membered chelate ring containing Ru(2). This means that this $[mtz]^-$ ligand assumes the μ_2-($1\kappa^1$S; $2\kappa^2$N,S) bridging mode, previously only observed in the polymeric cadmium(II) complex $[Cd(\mu\text{-mbt})_2]_n$ [23]. It is instructive to compare the molecular dimensions of the two $[mtz]^-$ ligands in **2**. Whereas the Ru(2)–S(1) bond distance of 2.395(3) Å is similar to that established for the mononuclear complex **1**, Ru(1)–S(5) is significantly shorter (2.361(3) Å) and Ru(2)–S(5) significantly longer (2.427(3) Å). Although the larger value of the latter bond distance may reasonably be attributed to strain within the effectively planar four-membered che-

TABLE 2. Atom positional parameters ($\times 10^4$) with equivalent isotropic temperature factors ($Å^2 \times 10^3$)

Atom	x/a	y/b	z/c	U
1				
Ru	1593(1)	3575(1)	3720(1)	31(1)
Cl(1)	1177(1)	3719(1)	2544(1)	59(1)
Cl(2)	2019(1)	1057(1)	3675(1)	46(1)
Cl(3)	1242(1)	3267(2)	642(1)	130(1)
Cl(4)	616(1)	6008(3)	788(1)	163(1)
S(7)	2633(1)	4640(1)	3870(1)	42(1)
S(8)	3541(1)	5005(1)	3257(1)	68(1)
C(1)	1554(2)	3071(4)	4635(2)	38(1)
C(2)	1776(2)	4561(4)	4657(2)	43(1)
C(3)	1409(2)	5625(4)	4166(2)	48(2)
C(31)	1663(3)	7219(5)	4180(3)	75(3)
C(4)	818(2)	5118(5)	3654(2)	50(2)
C(5)	581(2)	3601(5)	3636(2)	45(1)
C(6)	947(2)	2557(4)	4123(2)	38(1)
C(61)	746(2)	923(5)	4109(2)	50(2)
C(62)	431(3)	706(7)	4581(3)	80(3)
C(63)	301(3)	343(7)	3435(3)	72(3)
C(7)	2904(2)	4035(4)	3325(2)	39(1)
N(11)	2687(2)	2918(4)	2917(2)	51(1)
C(10)	2955(2)	2735(6)	2440(2)	59(2)
C(9)	3602(2)	3578(6)	2712(2)	57(2)
C(12)	1300(3)	4901(8)	1077(3)	116(4)
2				
Ru(1)	2090(1)	5841(1)	3159(1)	35(1)
Ru(2)	4744(1)	7159(1)	2566(1)	30(1)
Cl(1)	6(3)	6286(2)	3497(3)	57(1)
Cl(2)	2429(4)	729(2)	6123(3)	65(2)
S(1)	5877(3)	6481(2)	4189(3)	39(1)
S(2)	5792(3)	6599(2)	6517(3)	45(1)
S(5)	2291(3)	6823(1)	2408(3)	32(1)
S(6)	1720(3)	7664(2)	4321(3)	45(1)
N(4)	3521(10)	6187(4)	4787(8)	34(4)
N(8)	3910(10)	7667(4)	3614(8)	34(4)
C(1)	4834(12)	6399(5)	5039(9)	34(4)
C(2)	4377(14)	6261(7)	6915(10)	54(6)
C(3)	3023(13)	6181(7)	5788(10)	49(6)
C(5)	2706(12)	7389(5)	3517(9)	32(4)
C(6)	3256(14)	8194(7)	5066(12)	58(6)
C(7)	4307(14)	8189(6)	4410(10)	46(6)
C(11)	3258(17)	5375(7)	2252(15)	64(8)
C(12)	1736(19)	5417(7)	1471(12)	64(7)
C(13)	712(17)	5205(7)	1833(15)	71(7)
C(14)	1049(17)	4929(7)	2945(14)	67(8)
C(15)	2564(17)	4869(7)	3656(14)	69(7)
C(16)	3630(14)	5113(7)	3285(14)	59(7)
C(21)	6895(14)	7295(10)	2398(11)	69(7)
C(22)	6221(18)	7830(8)	2283(13)	59(7)
C(23)	4807(21)	7924(7)	1431(15)	72(9)
C(24)	4069(17)	7436(11)	744(13)	77(8)
C(25)	4752(18)	6866(8)	890(13)	63(8)
C(26)	6191(17)	6780(7)	1745(13)	55(7)
O(1)	8760(12)	564(5)	5219(10)	85(6)
O(2)	7718(15)	206(5)	1900(13)	124(9)
4				
Ru(1)	7346(1)	1258(1)	631(1)	34(1)
Ru(2)	5974(1)	527(1)	−1697(1)	43(1)
Cl(1)	6439(1)	334(1)	500(1)	50(1)
Cl(2)	5563(1)	1701(1)	−1066(2)	74(1)
Cl(3)	2418(1)	9816(1)	4871(2)	94(1)
S(2)	7054(1)	1198(1)	−1657(1)	38(1)
N(1)	7915(2)	428(2)	−196(4)	36(1)
N(3)	7961(2)	8(2)	−2095(4)	39(1)
C(2)	7674(2)	500(3)	−1379(5)	36(2)
C(4)	8416(2)	−412(3)	−1310(5)	38(2)
C(5)	8393(2)	−147(3)	−109(5)	37(2)
C(41)	8746(3)	−1066(3)	−1799(5)	45(2)
C(42)	8736(3)	−1747(3)	−1183(6)	61(2)
C(43)	9002(4)	−2377(4)	−1686(8)	83(3)
C(44)	9274(5)	−2333(5)	−2816(8)	95(4)
C(45)	9297(5)	−1666(5)	−3417(8)	93(4)
C(46)	9035(4)	−1024(4)	−2935(6)	70(3)
C(51)	8815(3)	−332(3)	1070(5)	40(2)
C(52)	9500(3)	−513(3)	1083(5)	45(2)
C(53)	9909(3)	−625(3)	2191(6)	57(2)
C(54)	9633(4)	−552(4)	3303(6)	66(3)
C(55)	8956(4)	−388(4)	3301(6)	64(3)
C(56)	8545(3)	−281(3)	2199(5)	51(2)
C(11)	7427(3)	2443(3)	696(6)	53(2)
C(12)	6878(3)	2243(3)	1336(6)	58(2)
C(13)	6970(3)	1731(3)	2316(6)	54(2)
C(131)	6381(4)	1451(5)	2983(7)	87(3)
C(14)	7632(3)	1430(3)	2626(5)	49(2)
C(15)	8172(3)	1638(3)	1960(5)	46(2)
C(16)	8083(3)	2149(3)	983(5)	49(2)
C(161)	8647(4)	2392(4)	214(8)	78(3)
C(162)	9187(4)	1829(5)	58(10)	120(5)
C(163)	8969(5)	3110(5)	736(11)	125(5)
C(21)	5189(3)	−342(4)	−1787(7)	62(3)
C(22)	4943(3)	243(4)	−2534(7)	66(3)
C(23)	5316(3)	548(4)	−3486(6)	64(2)
C(231)	5057(4)	1214(4)	−4233(8)	93(3)
C(24)	5944(3)	221(4)	−3640(6)	62(2)
C(25)	6193(3)	−387(4)	−2908(7)	61(2)
C(26)	5834(3)	−683(3)	−1963(7)	61(2)
C(261)	6080(4)	−1318(4)	−1115(10)	89(4)
C(262)	5716(5)	−2008(5)	−1618(14)	163(6)
C(263)	6859(4)	−1428(4)	−929(10)	102(4)
C(99)	3042(10)	3623(11)	2082(18)	116(6)
O(99)	3316(8)	3960(8)	1205(14)	144(5)
6				
Ru(1)	6367(2)	1309(2)	−1599(2)	61(2)
Ru(2)	5066(2)	1328(2)	−507(2)	61(2)
Ru(3)	5465(2)	3988(2)	−918(2)	51(2)
Cl(1)	6115(6)	817(6)	−657(6)	60(6)
Cl(2)	4642(8)	591(8)	−1249(6)	99(7)
Cl(3)	5184(6)	3777(8)	98(6)	83(7)
S(2)	5388(6)	1949(6)	−1360(6)	52(6)
N(1)	6567(20)	2160(19)	−1149(17)	57(13)
N(3)	6041(18)	3104(19)	−946(17)	53(12)
C(2)	6001(27)	2425(28)	−1099(22)	68(19)
C(4)	6715(22)	3248(24)	−845(21)	38(14)
C(5)	7066(20)	2687(24)	−999(20)	49(16)
C(41)	6864(24)	3889(25)	−653(19)	53(16)
C(42)	6342(23)	4331(23)	−590(19)	49(15)
C(43)	6419(21)	4995(22)	−359(17)	35(13)
C(44)	7043(24)	5173(23)	−183(20)	51(16)
C(45)	7559(25)	4794(27)	−290(22)	62(18)
C(46)	7502(26)	4153(28)	−457(23)	78(19)

(*continued*)

TABLE 2. (*continued*)

Atom	x/a	y/b	z/c	U
C(51)	7712(21)	2502(26)	−1004(22)	56(17)
C(52)	8106(24)	2922(25)	−1337(22)	55(17)
C(53)	8799(25)	2757(25)	−1420(22)	66(18)
C(54)	9000(21)	2166(24)	−1137(20)	39(15)
C(55)	8608(29)	1763(27)	−820(24)	81(19)
C(56)	7927(25)	1838(25)	−780(22)	61(17)
C(11)	6299(24)	1299(25)	−2524(25)	106(20)
C(12)	6108(23)	666(25)	−2338(22)	73(19)
C(13)	6448(27)	279(28)	−1935(24)	89(20)
C(131)	6141(32)	−391(31)	−1822(30)	157(32)
C(14)	7076(28)	476(27)	−1814(28)	133(28)
C(15)	7277(21)	1105(25)	−1999(21)	62(17)
C(16)	6915(23)	1509(24)	−2371(23)	73(18)
C(161)	7231(29)	2145(26)	−2577(29)	127(26)
C(162)	7636(37)	2020(37)	−3131(31)	185(36)
C(163)	6753(32)	2724(31)	−2651(32)	152(30)
C(21)	4890(25)	903(24)	392(20)	57(16)
C(22)	4320(29)	1030(27)	64(26)	105(22)
C(23)	4137(26)	1636(31)	−188(24)	95(22)
C(231)	3566(24)	1728(25)	−587(22)	79(19)
C(24)	4599(28)	2195(25)	−152(24)	68(18)
C(25)	5151(28)	2100(29)	174(27)	89(21)
C(26)	5304(23)	1461(28)	414(21)	66(18)
C(261)	5923(25)	1328(31)	737(23)	126(25)
C(262)	5830(30)	1378(32)	1407(24)	137(27)
C(263)	6487(29)	1790(30)	578(28)	128(26)
C(31)	5340(19)	3932(19)	−1844(18)	56(17)
C(32)	4745(18)	3747(22)	−1618(18)	50(14)
C(33)	4416(19)	4085(21)	−1175(18)	51(16)
C(331)	3832(19)	3722(22)	−946(20)	64(16)
C(34)	4671(21)	4697(21)	−998(20)	71(18)
C(35)	5225(19)	4931(20)	−1275(17)	39(14)
C(36)	5547(18)	4577(19)	−1713(16)	26(13)
C(361)	6128(19)	4916(21)	−1974(21)	85(20)
C(362)	6597(22)	4400(23)	−2232(20)	69(19)
C(363)	5915(23)	5486(23)	−2384(22)	80(19)
Ow(1)	6519(37)	3807(39)	917(34)	131(31)

late ring, it is interesting to note that the endocyclic Ru–S bond in [Ru(dmtdH)$_2$(CO)(PPh$_3$)$_2$] [26] is considerably longer (2.478(5) Å). The existence of pronounced ring strain is also underlined by a comparison of the S–C–N and Ru–N–C bond angles of 109.2(10) and 104.5(8) in the chelate ring with those of 130.6(9) and 126.5(9)°, respectively, for the apposite bond angles in the ligand displaying only the bridging μ_2-N,S coordination. The C(5)–S(5) bond is lengthened considerably in comparison to both the free ligand (1.671(7) Å) and the κ^1S coordinated ligand in **1** (1.691(4) Å). Indeed the bond length of 1.772(12) Å is now longer than that observed for the endocyclic C(5)–S(6) bond (1.731(14) Å) and is indicative of a much reduced degree of π-character. The analogous distances in the μ_2-N,S coordinated [mtz]$^-$ ligand are 1.728(14) and 1.765(11) Å.

The Ru(1)...Ru(2) distance in **2** is 3.675(1) Å. Closure of a second four-membered chelate ring would greatly

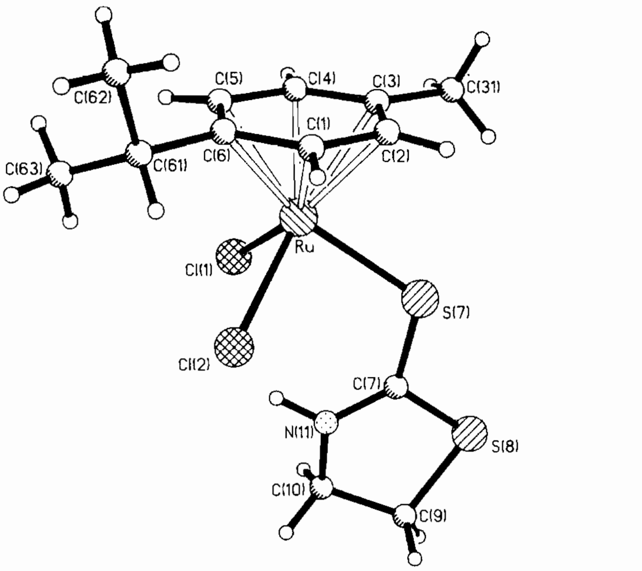

Fig. 1. Molecular structure of **1**. Selected bond distances (Å) and angles (°): Ru–Cl(1) 2.424(1), Ru–Cl(2) 2.439(1), Ru–S(7) 2.400(1), S(7)–C(7) 1.691(4), S(8)–C(7) 1.729(4), S(8)–C(9) 1.815(6), C(7)–N(11) 1.294(5), Cl(1)–Ru–Cl(2) 88.3(1), Cl(1)–Ru–S(7) 90.9(1), Cl(2)–Ru–S(7) 89.3(1), Ru–S(7)–C(7) 114.4(1), S(7)–C(7)–S(8) 119.1(2), S(7)–C(7)–N(11) 128.6(3).

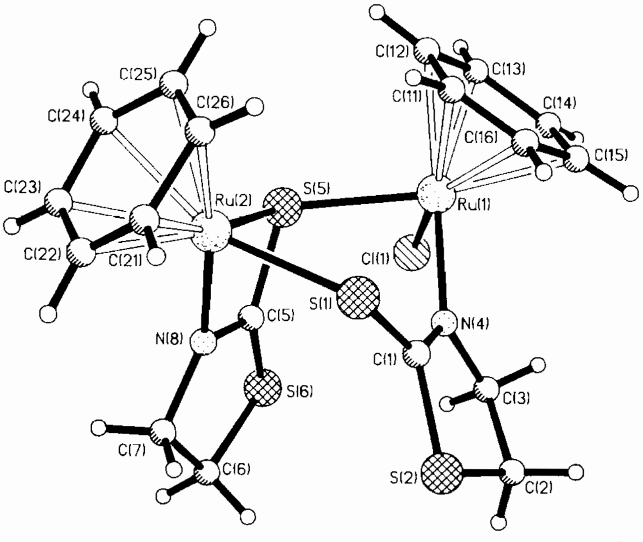

Fig. 2. Structure of the cation **2**. Selected bond distances (Å) and angles (°): Ru(1)–Cl(1) 2.419(4), Ru(1)–S(5) 2.361(3), Ru(1)–N(4) 2.104(8), Ru(2)–S(1) 2.395(3), Ru(2)–S(5) 2.427(3), Ru(2)–N(8) 2.090(11), S(1)–C(1) 1.728(14), S(2)–C(1) 1.765(11), C(1)–N(4) 1.277(15), S(5)–C(5) 1.772(12), S(6)–C(5) 1.731(14), S(6)–C(6) 1.829(13), C(5)–N(8) 1.280(15); S(5)–Ru(1)–N(4) 86.2(3), Ru(1)–N(4)–C(1) 126.5(9), S(1)–Ru(2)–S(5) 90.3(1), S(1)–Ru(2)–N(8) 87.9(3), S(5)–Ru(2)–N(8) 66.9(3), N(4)–C(1)–S(1) 130.6(9), C(1)–S(1)–Ru(2) 112.8(4), Ru(1)–S(5)–Ru(2) 117.8(1), Ru(1)–S(5)–C(5) 110.3(4), Ru(2)–S(5)–C(5) 78.7(4), S(5)–C(5)–N(8) 109.2(10), C(5)–N(8)–Ru(2) 104.5(8).

enhance the degree of steric strain in the dinuclear cation and may, therefore, reasonably be assumed to be energetically unfavourable. On the basis of the structure established for **2**, it seems probable that the μ_2-(1κ^1S; 2κ^2N,S) coordination mode will be preferred by bridging thioamides in dinuclear (η^6-arene)-ruthenium(II) complexes containing only one such ligand.

We were successful in characterising complexes of the type $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2(\mu\text{-L})(\mu\text{-Cl})\text{Cl}]\text{Cl}$ for both L = [mmim]$^-$ (**3**) and L = [dpmimH]$^-$ (**4**). An X-ray structural analysis of **4** confirmed the predicted bridging mode (Fig. 3). The central RuClRuS ring displays a folded conformation in which the atoms are ± 0.146 Å, respectively, from the best least-squares plane. As a result of the participation of the [dpmimH]$^-$ ligand in this strained four-membered ring system, **4** exhibits marked alterations in the dimensions of the Ru–S–Ru bridge in comparison to **2**. The Ru(1)–S(2) and Ru(2)–S(2) distances of 2.465(1) and 2.433(1) Å in **4** are both significantly longer than the analogous bond lengths in **2** (2.427(3) and 2.361(3) Å). At the same time the Ru–S–Ru angle narrows from 117.8(1) in **2** to only 103.3(2)° in **4**. The Ru(1)...Ru(2) distance of 3.700(1) Å is slightly longer than that of 3.675(1) Å in **2**. The C(2)–S(2) distance of 1.751(5) Å in **4** is also similar to that of 1.772(12) Å observed for the thione sulfur atom in **2**. In view of the similarity of the ^{1}H NMR spectra of **3** and **4** in CDCl_3, both of which confirm the presence of two non-equivalent *p*-cymene ligands, it seems reasonable to conclude that the [mmim]$^-$ ligand in **3** will also exhibit the μ_2-(1κ^1S; 2κ^2N,S) bridging mode characterised for [dpmimH]$^-$ in **4**.

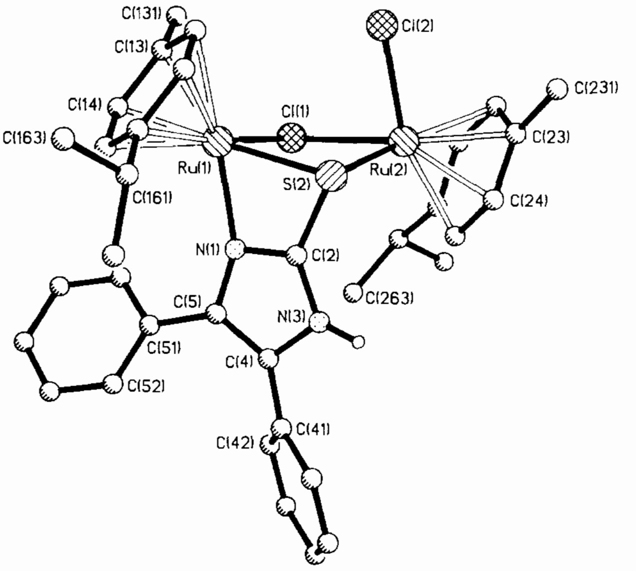

Fig. 3. Structure of the cation 3. Selected bond distances (Å) and angles (°): Ru(1)–Cl(1) 2.427(2), Ru(1)–S(2) 2.465(1), Ru(1)–N(1) 2.121(4), Ru(2)–Cl(1) 2.459(2), Ru(2)–Cl(2) 2.391(2), Ru(2)–S(2) 2.433(1), S(2)–C(2) 1.751(5), N(1)–C(2) 1.313(6), C(2)–N(3) 1.339(7), Ru(1)–Cl(1)–Ru(2) 98.5(1), Cl(1)–Ru(1)–S(2) 80.0(1), Cl(1)–Ru(1)–N(1) 84.7(1), S(2)–Ru(1)–N(1) 67.9, Cl(1)–Ru(2)–S(2) 80.0(1), Cl(1)–Ru(2)–Cl(2) 87.3(1), Cl(2)–Ru(2)–S(2) 82.8(1), Ru(1)–S(2)–C(2) 77.5(2), Ru(2)–S(2)–C(2) 103.3(2), Ru(1)–S(2)–Ru(2) 98.2(1), S(2)–C(2)–N(1) 113.7(4), Ru(1)–N(1)–C(2) 100.9(3).

Reaction of a 1:2 molar ratio of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ and [dpmimH]$^-$ in ethanol leads to the formation of the dinuclear complex $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2(\text{dpmimH})_2\text{Cl}]\text{Cl}$ (**5**). As for the [mtz]$^-$ complex **2**, the ^{1}H NMR spectrum (CDCl_3) indicates the presence of two non-equivalent η^6-arene ligands. The observation of NH proton resonances at 12.78 and 15.48 ppm is in accordance with the adoption of different coordination modes by the [dpmimH]$^-$ ligands. On the basis of the X-ray structure of **4**, for which an NH resonance at 15.50 ppm was recorded, it may be assumed that the μ_2-(1κ^1S; 2κ^2N,S) bridging mode will be exhibited by the second ligand in **5** (15.48 ppm). The analogy to **2** would suggest that the first ligand in **5** (12.78 ppm) will display the μ_2-N,S coordination mode. However, the spectroscopic data (IR, ^{1}H NMR) do not allow either a terminal κ^1S or a bridging μ_2-S coordination to be ruled out with certainty.

The reported synthesis of **4** was carried out in ethanol in the presence of base (KOH) followed by precipitation of the product with diethyl ether. During attempts to crystallise **4** we also performed the reaction of $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ with dpmimH_2 (1:1 molar ratio) at r.t. in methanol with NaOMe as base. In this case the solvent was subsequently removed and the product redissolved in 1 ml CH_2Cl_2. After addition of 2 ml $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (1:2) the solution was set aside at −40 °C to yield deep red crystals of the trinuclear complex $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)_3\text{Ru}_3(\mu_3\text{-dpmimH}_{-1})(\mu\text{-Cl})\text{Cl}_2]$ (**6**), the structure of which was established by X-ray analysis (Fig. 4). The poor quality of the available crystal prevents a detailed analysis of the bond lengths and angles in **6**. As in the dinuclear cation **4**, the ruthenium atoms Ru(1) and Ru(2) are bridged via a chloride ligand and $[\text{dpmimH}_{-1}]^{3-}$ in the μ_2-(1κ^1S; 2κ^2N,S) coordination mode. Complex **6** may, therefore, be regarded as the product of a cyclometallation reaction involving **4** and $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$, which leads to the additional coordination of N(3) and the phenyl carbon atom C(42). The trianion $[\text{dpmimH}_{-1}]^{3-}$ is pentadentate in **6**. The facile nature of the cyclometallation suggests that **6** should be capable of adopting a similar bridging function in further homo- and heteronuclear complexes.

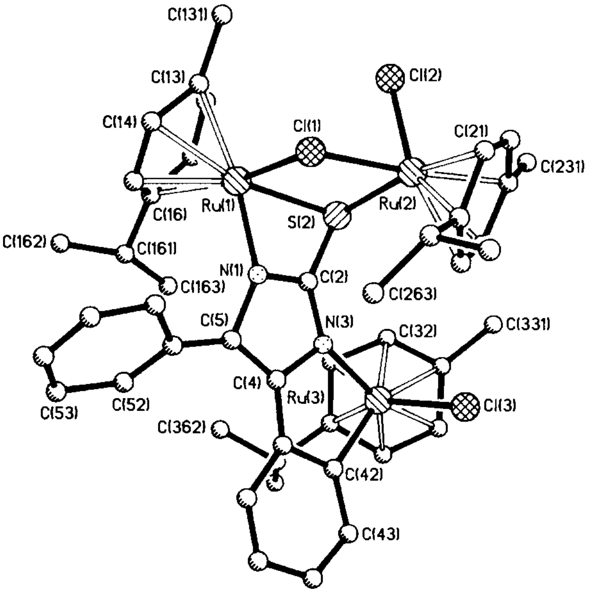

Fig. 4. Molecular structure of the trinuclear complex **6**.

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