C(15)	−0.0664 (4)	0.4203 (3)	0.2798 (2)	3.24 (8)
C(16)	−0.1667 (4)	0.3702 (4)	0.3334 (2)	3.99 (10)
C(17)	−0.3154 (5)	0.4535 (5)	0.3484 (2)	5.12 (14)
C(18)	−0.3617 (4)	0.5904 (5)	0.3077 (2)	5.62 (14)
C(19)	−0.2679 (5)	0.6409 (4)	0.2559 (3)	5.19 (12)
C(20)	−0.1148 (5)	0.5590 (3)	0.2406 (2)	4.33 (10)
C(21)	0.2218 (4)	0.2996 (3)	0.3686 (2)	3.02 (8)
C(22)	0.3406 (4)	0.1870 (3)	0.4057 (2)	3.17 (8)
C(23)	0.4148 (4)	0.1894 (3)	0.4741 (2)	3.66 (10)
C(24)	0.3698 (5)	0.3046 (4)	0.5051 (2)	4.57 (11)
C(25)	0.2472 (6)	0.4147 (5)	0.4693 (3)	6.84 (17)
C(26)	0.1717 (6)	0.4137 (4)	0.4009 (2)	5.83 (14)
C(27)	0.1447 (4)	−0.0875 (3)	0.1786 (2)	3.85 (10)
C(28)	0.2846 (7)	−0.1228 (5)	0.1238 (3)	7.19 (20)
C(29)	−0.0071 (6)	−0.0545 (5)	0.1336 (3)	6.59 (17)
C(30)	0.1631 (5)	−0.2171 (4)	0.2447 (3)	5.18 (13)

Table 2. *Selected geometric parameters (Å, °)*

Rh(1)—P(1)	2.492 (1)	P(1)—C(15)	1.815 (3)
Rh(1)—C(27)	2.216 (3)	P(1)—C(21)	1.822 (3)
Rh(1)—N(1)	1.934 (3)	N(1)—O(1)	1.367 (3)
Rh(1)—N(2)	1.973 (2)	N(2)—O(2)	1.293 (4)
Rh(1)—N(3)	1.930 (3)	N(3)—O(3)	1.361 (3)
Rh(1)—N(4)	1.982 (2)	N(4)—O(4)	1.281 (4)
P(1)—C(9)	1.810 (3)		
N(1)—Rh(1)—N(2)	78.4 (1)	N(4)—Rh(1)—C(27)	89.9 (1)
N(3)—Rh(1)—N(4)	78.8 (1)	P(1)—Rh(1)—C(27)	174.2 (1)
P(1)—Rh(1)—N(1)	90.2 (1)	Rh(1)—P(1)—C(9)	109.1 (1)
P(1)—Rh(1)—N(2)	87.3 (1)	Rh(1)—P(1)—C(15)	115.4 (1)
P(1)—Rh(1)—N(3)	92.4 (1)	Rh(1)—P(1)—C(21)	122.2 (1)
P(1)—Rh(1)—N(4)	95.8 (1)	C(9)—P(1)—C(15)	106.9 (1)
N(1)—Rh(1)—C(27)	90.0 (1)	C(9)—P(1)—C(21)	102.0 (1)
N(2)—Rh(1)—C(27)	87.1 (1)	C(15)—P(1)—C(21)	99.7 (1)
N(3)—Rh(1)—C(27)	87.4 (1)		

The H(O1) and H(O3) atoms were fixed at their observed positions (from difference synthesis). All other H atoms were fixed at their calculated positions. Each H-atom displacement parameter was fixed at 0.5 Å^2 greater than the B_{eq} value of the atom to which it is bonded.

Data collection: Syntex $P2_1$ diffractometer software. Cell refinement: Syntex $P2_1$ diffractometer software. Data reduction: *XP*21 (Pavelčík, 1987). Program(s) used to solve structure: *NRC Crystallographic Programs for the IBM*360 *System* (1970). Program(s) used to refine structure: *NRC Crystallographic Programs for the IBM*360 *System* (1970).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: HR1052). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tris(1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane-*S*,*S′*)ruthenium(II) Bis(hexafluorophosphate)–Water–Methanol (1/2/1)

ALEXANDER J. BLAKE,*† CHRISTIAN RADEK AND MARTIN SCHRÖDER†

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland. E-mail: a.j.blake@nott.ac.uk

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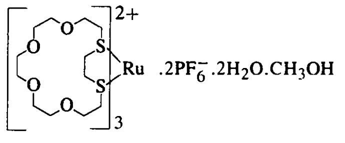
Abstract

In the title complex, $[Ru(C_{12}H_{24}O_4S_2)_3](PF_6)_2.2H_2O.CH_3OH$, the Ru^{II} ion lies on a crystallographic threefold axis and is coordinated to three symmetry-equivalent macrocyclic ligands *via* their S donor atoms [Ru—S 2.3620 (9) and 2.3859 (9) Å]. The macrocycle adopts a typical bidentate chelating coordination mode with S donors in *exo* and O donors in *endo* orientations.

Comment

Mixed O/S ionophores such as $[15]aneS_2O_3$ (1,4,7-trioxa-10,13-dithiacyclopentadecane) and $[18]aneS_2O_4$ (1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane) provide atoms with contrasting donor properties within the same macrocyclic framework (Blake, Radek & Schröder, 1995). We have been interested in the coordination chemistry of these ligands with a range of metal ions (Blake, Reid & Schröder, 1990; Blake, Gould, Radek & Schröder, 1994, 1995; Bell, Blake, Gould, Parsons, Radek & Schröder, 1995) and have found that metal ions such as Ru^{II} and Pd^{II} adopt exclusively *exo* bidentate coordination modes *via* the S donors. The O donors normally remain *endo* orientated and the cavity is partially occupied by the ethylene bridge between the S donors. The structure of $[Ru([18]aneS_2O_4)_3](PF_6)_2.2H_2O.CH_3OH$, (I), displays the same chelating mode, with three $[18]aneS_2O_4$ ligands coordinated to each Ru^{II} ion.



(I)

The geometric features of the Ru—S environment [Ru—S 2.3620 (9) and 2.3859 (9) Å and chelating S—Ru—S 87.24 (3)°] are similar to those of other Ru^{II}

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† Present address: Department of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England.

complexes with $[15]aneS_2O_3$ and $[18]aneS_2O_4$, such as $[RuCl(PPh_3)([15]aneS_2O_3)]^+$ (Blake, Reid & Schröder, 1990), $[RuCl_2(PPh_3)_2([15]aneS_2O_3)]$, $[RuCl(PPh_3)([18]aneS_2O_4)]^+$, $[Ru(C_5H_5)(PPh_3)([18]aneS_2O_4)]^+$, $[RuCl(C_6H_6)([18]aneS_2O_4)]^+$ and $[RuCl(C_{10}H_{14})([15]aneS_2O_3)]^+$ (Bell, Blake, Gould, Parsons, Radek & Schröder, 1995).

The mean ligand C—C, C—O and C—S bond lengths of 1.505 (5), 1.425 (5) and 1.825 (4) Å, respectively, correspond closely with values found in analogous compounds (Blake, Reid & Schröder, 1990; Bell, Blake, Gould, Parsons, Radek & Schröder, 1995). The ligand adopts a conformation in which all four O donors are in *endo* and the two S donors are in *exo* orientations. The macrocyclic cavity is consequently partially occupied by the ethylene bridge of the SCH_2CH_2S moiety, which prevents further coordination by the O-atom donors (Fig. 1).

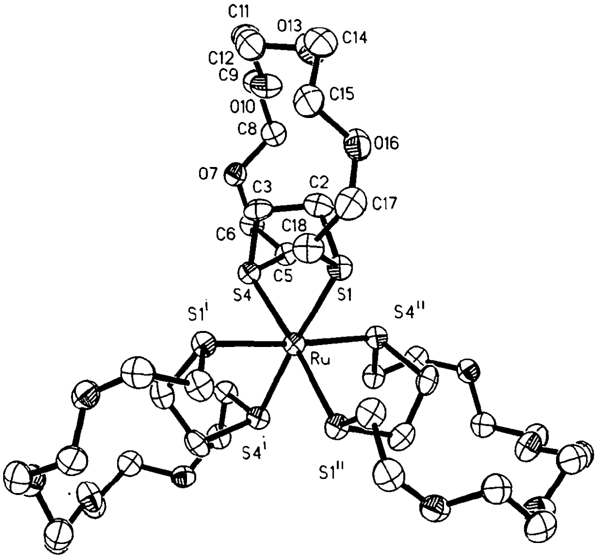

Fig. 1. A view of the $[Ru([18]aneS_2O_4)_3]^{2+}$ cation with the atom-numbering scheme adopted. H atoms have been omitted for clarity and displacement ellipsoids enclose 50% probability surfaces. Note that ligand atoms are numbered and connected in numerical order. [Symmetry codes: (i) $-y, x-y, z$; (ii) $y-x, -x, z$.]

The overall stoichiometry comprises two PF_6^- anions, two water molecules and one methanol molecule per $[Ru([18]aneS_2O_4)_3]^{2+}$ cation. The methanol and one of the water molecules were each found to occupy their sites partially.

Experimental

The macrocyclic ligand $[18]aneS_2O_4$ was prepared according to the published method of Bradshaw, Hui, Chan, Haymore, Izatt & Christensen (1974). Treatment of $[18]aneS_2O_4$ (0.296 g, 1.0 mmol) with $RuCl_3.xH_2O$ (0.104 g, 0.5 mmol) in 25 ml of CH_3OH/H_2O (1:1, *v*/*v*) yielded a dark brown solution. The reaction mixture was heated and refluxed for 24 h during which time the colour changed from dark brown through blue to dark green. Addition of $K_2C_2O_4$ (0.092 g, 0.5 mmol) as a reducing agent and excess NH_4PF_6 afforded a yellow solution from which both colourless ($K_2C_2O_4$ and NH_4PF_6) and yellow (product) crystals precipitated; the latter were isolated manually. Fast-atom bombardment (FAB) mass spectrum (3-noba): m/z 1135; calculated for $[^{101}Ru(C_{12}H_{24}O_4S_2)_3(PF_6)]^+$ 1135.

Crystal data

$[Ru(C_{12}H_{24}O_4S_2)_3](PF_6)_2.$-
$2H_2O.CH_4O$
$M_r = 1348.19$
Trigonal
$R\bar{3}$
$a = 18.629\ (2)$ Å
$c = 29.863\ (5)$ Å
$V = 8975\ (2)$ Å^3
$Z = 6$
$D_x = 1.496$ Mg m^{-3}
$D_m = 1.49$ Mg m^{-3}
D_m measured by flotation in
$CHCl_3$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28
reflections
$\theta = 15$–$16°$
$\mu = 0.617$ mm^{-1}
$T = 150.0\ (2)$ K
Tablet
0.74 × 0.62 × 0.39 mm
Yellow

Data collection

Stoe Stadi-4 four-circle
diffractometer
Learnt-profile (Clegg, 1981)
ω scans
Absorption correction:
none
3380 measured reflections
2608 independent reflections
2270 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0241$
$\theta_{max} = 22.49°$
$h = -16 \rightarrow 19$
$k = -15 \rightarrow 20$
$l = 0 \rightarrow 32$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0361$
$wR(F^2) = 0.1275$
$S = 1.039$
2577 reflections
224 parameters
H atoms riding with $U_{iso}(H)$
$= 1.2U_{eq}(C)$; water and
methanol H atoms not
located

$w = 1/[\sigma^2(F_o^2) + (0.060P)^2$
$+ 42.41P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.30$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
from *International Tables*
for Crystallography (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ru	0	0	0.212934 (15)	0.0246 (2)
S1	−0.03570 (6)	0.08846 (6)	0.25311 (3)	0.0310 (3)
C2	−0.1241 (2)	0.0783 (2)	0.22131 (12)	0.0350 (9)
C3	−0.1797 (2)	−0.0089 (2)	0.20558 (13)	0.0352 (9)
S4	−0.12261 (5)	−0.04416 (5)	0.17105 (3)	0.0284 (3)
C5	−0.1080 (2)	0.0156 (2)	0.11998 (11)	0.0304 (8)
C6	−0.1817 (2)	−0.0284 (2)	0.08861 (12)	0.0341 (9)

O7	−0.25629 (15)	−0.0360 (2)	0.10615 (8)	0.0344 (6)
C8	−0.2629 (2)	0.0368 (2)	0.09855 (13)	0.0388 (9)
C9	−0.3345 (3)	0.0285 (3)	0.12513 (13)	0.0429 (10)
O10	−0.3113 (2)	0.0412 (2)	0.17101 (9)	0.0463 (7)
C11	−0.3774 (3)	0.0283 (3)	0.19959 (15)	0.0492 (11)
C12	−0.3526 (3)	0.0325 (3)	0.24726 (14)	0.0489 (11)
O13	−0.2887 (2)	0.1141 (2)	0.25859 (9)	0.0466 (7)
C14	−0.2766 (3)	0.1267 (3)	0.30565 (13)	0.0454 (10)
C15	−0.2263 (3)	0.0931 (3)	0.32697 (14)	0.0441 (10)
O16	−0.1412 (2)	0.1448 (2)	0.31542 (9)	0.0410 (7)
C17	−0.0892 (3)	0.1173 (3)	0.33456 (14)	0.0450 (10)
C18	−0.0846 (3)	0.0502 (3)	0.30735 (12)	0.0373 (9)
P1	0	0	0	0.0292 (5)
F11	0.00286 (14)	0.07149 (13)	0.03095 (7)	0.0409 (5)
P2	0	1/2	0	0.0540 (5)
F21	0.0927 (2)	0.5565 (2)	0.01702 (12)	0.0826 (9)
F22	−0.0266 (2)	0.4535 (2)	0.04606 (11)	0.0844 (10)
F23	−0.0216 (2)	0.5671 (2)	0.01779 (13)	0.0868 (11)
O1*W*	1/3	2/3	0.0703 (4)	0.158 (4)
O2*W*†	0.5770 (13)	0.8251 (13)	0.1388 (7)	0.150 (7)
O1*M*†	0.4050 (12)	0.8616 (12)	0.1196 (6)	0.135 (6)
C2*M*†	0.4388 (15)	0.8224 (15)	0.1073 (8)	0.110 (7)

† Occupancy of 0.33.

Table 2. *Selected geometric parameters (Å, °)*

Ru—S1	2.3859 (9)	C8—C9	1.492 (6)
Ru—S4	2.3620 (9)	C9—O10	1.421 (5)
S1—C18	1.820 (4)	O10—C11	1.416 (5)
S1—C2	1.827 (4)	C11—C12	1.487 (6)
C2—C3	1.500 (6)	C12—O13	1.426 (5)
C3—S4	1.824 (4)	O13—C14	1.424 (5)
S4—C5	1.827 (3)	C14—C15	1.503 (6)
C5—C6	1.520 (5)	C15—O16	1.425 (5)
C6—O7	1.424 (4)	O16—C17	1.423 (5)
O7—C8	1.440 (5)	C17—C18	1.528 (6)
S4^{i}—Ru—S4	94.55 (3)	O7—C8—C9	108.2 (3)
S4^{i}—Ru—S1	175.66 (3)	O10—C9—C8	108.3 (3)
S4—Ru—S1	87.24 (3)	C11—O10—C9	112.7 (3)
S4—Ru—S1^{i}	81.36 (3)	O10—C11—C12	110.3 (4)
S1—Ru—S1^{i}	96.94 (3)	O13—C12—C11	110.8 (3)
C18—S1—C2	100.0 (2)	C14—O13—C12	112.9 (3)
C3—C2—S1	111.9 (3)	O13—C14—C15	115.4 (3)
C2—C3—S4	110.9 (3)	O16—C15—C14	109.3 (3)
C3—S4—C5	100.8 (2)	C17—O16—C15	112.8 (3)
C6—C5—S4	111.5 (2)	O16—C17—C18	114.0 (3)
O7—C6—C5	113.6 (3)	C17—C18—S1	112.0 (3)
C6—O7—C8	112.8 (3)		
C18—S1—C2—C3	−80.6 (3)	C9—O10—C11—C12	173.2 (3)
S1—C2—C3—S4	−58.0 (3)	O10—C11—C12—O13	66.2 (5)
C2—C3—S4—C5	−72.4 (3)	C11—C12—O13—C14	165.8 (3)
C3—S4—C5—C6	−86.3 (3)	C12—O13—C14—C15	79.8 (4)
S4—C5—C6—O7	65.4 (4)	O13—C14—C15—O16	73.7 (5)
C5—C6—O7—C8	84.1 (4)	C14—C15—O16—C17	179.7 (3)
C6—O7—C8—C9	−169.9 (3)	C15—O16—C17—C18	84.3 (4)
O7—C8—C9—O10	73.6 (4)	O16—C17—C18—S1	65.4 (4)
C8—C9—O10—C11	−175.4 (3)	C2—S1—C18—C17	−82.4 (3)

Symmetry code: (i) $-y, x-y, z$.

A crystal suitable for single-crystal X-ray diffraction studies was mounted on a glass fibre and placed in the stream of an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986).

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1354). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[1-hydroxy-2(1*H*)-pyridinethionato-*O*,*S*]-palladium(II)

Bao-Lin Song,[a] Ren-Gen Xiong,[a] Hong Wang,[a] Jing-Lin Zuo,[a] Xiao-Zeng You,[a] Hoong-Kun Fun[b]* and Kandasamy Sivakumar[b]†

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing University, Nanjing 210093, People's Republic of China, and* [b] *X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: hkfun@usm.my*

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Abstract

In the structure of the title compound, $[Pd(C_5H_4NOS)_2]$, the Pd atom is coordinated by a slightly distorted planar array of two S and two O atoms; the two 1-hydroxy-

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† On leave from the Department of Physics, Anna University, Madras 600 025, India.

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