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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including torsion angles and contact distances, have been deposited with the IUCr (Reference: BK1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bustos, C., Manzur, C., González, H., Schreberg, R., Carrillo, D., Bois, C., Jeannin, Y. & Gouzerh, P. (1991). *Inorg. Chim. Acta*, **185**, 25–31.
- Carrillo, D., Gouzerh, P. & Jeannin, Y. (1985). *Nouv. J. Chim.* **9**, 749–755.
- Carrillo, D., Robert, F. & Gouzerh, P. (1992). *Inorg. Chim. Acta*, **197**, 209–215.
- Debenjak, B., Bustos, C., Carrillo, D., Robert, F. & Gouzerh, P. (1992a). *Bol. Soc. Chil. Quím.* **37**, 105–113.
- Debenjak, B., Bustos, C., Carrillo, D., Robert, F. & Gouzerh, P. (1992b). *Polyhedron*, **11**, 2321–2326.
- Henderson, B. A., Leigh, G. J. & Pickett, C. J. (1983). *Adv. Inorg. Radiochem.* **27**, 197–203.
- Leigh, G. J. (1992). *Acc. Chem. Res.* **25**, 177–181.
- Li-Kao, J., Bustos, C., Carrillo, D., Robert, F. & Gouzerh, P. (1993). *Transition Met. Chem.* **18**, 265–270.
- Palanca, P., Picher, T., Sanz, V., Gómez-Romero, P., Llopis, E., Domenech, A. & Cervilla, A. (1990). *J. Chem. Soc. Chem. Commun.* pp. 531–533.
- Sheldrick, G. M. (1991). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Siemens (1991). *P3/P4-PC Diffractometer Program*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

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$[(\eta^6-C_6H_3Me_3)Ru(D-pen)]_2Cl_2 \cdot 4H_2O$

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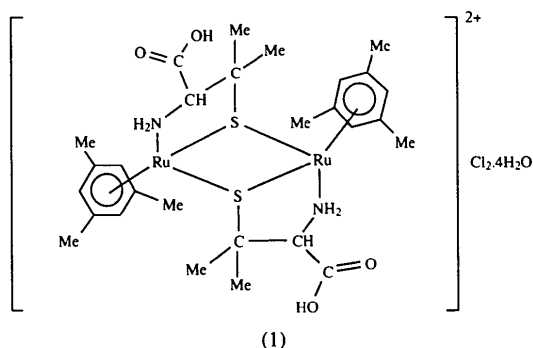
Abstract

The structure of the title compound, bis[μ -D-3-mercaptopivalinato(1-)]- $1\kappa N, 1:2\kappa^2 S; 2\kappa N, 1:2\kappa^2 S$ -bis[$(\eta^6$ -mesitylene)ruthenium] dichloride tetrahydrate, $[Ru_2(C_5-$

$H_{10}NO_2S)_2(\eta^6-C_9H_{12})_2]Cl_2 \cdot 4H_2O$, contains tridentate anionic amino acid ligands, where the S atoms adopt bridging positions between the two Ru atoms resulting in a near planar Ru—S—Ru—S ring. The coordination at each Ru atom is completed by an amino N atom of the chelating ligand and the η^6 -bonded mesitylene ring.

Comment

The determination of the structure of the title compound (1) was undertaken as part of a study of organometallic complexes with biologically important ligands (Carter, Davies, Fawcett & Russell, 1993). In particular, we have studied arene-ruthenium half-sandwich complexes, including amino acid complexes [(arene)Ru(aa)Cl] (aa = an anionic amino acid ligand) (Carter, Davies, Duffy, Fawcett & Russell, 1994) which contain a chiral metal centre.



Compound (1) is analogous to the η^6 -benzene-ruthenium(II)-l-penicillamine complex (2) reported by Sheldrick & Heeb (1989), the most significant difference being that compound (1) has four water molecules associated with each dimeric cation, where only one was found for (2). The central four-membered Ru—S—Ru—S ring, while essentially planar (Fig. 1) with deviations from the best least-squares plane of -0.15 for Ru(1), -0.15 for Ru(2), 0.38 for S(1) and 0.38 Å for S(2), is less so than that found by Sheldrick & Heeb (maximum deviation 0.009 Å). The Ru—S distances in the five-membered chelate rings [2.335 (3), 2.348 (3) Å] are shorter than the bridging Ru—S distances [2.394 (2), 2.401 (2) Å], as found for (2). The chelating rings have a *cis* arrangement which permits both chloride ions to form hydrogen bonds between the —OH group of one ligand and the —NH₂ group of the other. The O...Cl (2.874 , 2.917 Å) and the N...Cl (3.249 , 3.253 Å) distances are comparable with the distances found for a similar arrangement in compound (2). The chloride ions have further hydrogen-bond contacts with water molecules: Cl(1)...O(7) (3.273 Å) and Cl(2)...O(8) (3.235 Å) (Fig. 2). None of the H atoms of the —NH₂ or —OH groups or those of the water molecules were located with any certainty and were

excluded from the refinement. However, the arrangement of the O atoms of the water molecules is consistent with a continuous hydrogen-bonded chain with O...O distances in the range 2.768–2.979 Å. The three-dimensional hydrogen-bonded network is completed by contacts between the atoms O(5) and O(6) of the water molecules and the carbonyl atoms O(2) (2.825 Å) and O(3) (2.798 Å), respectively.

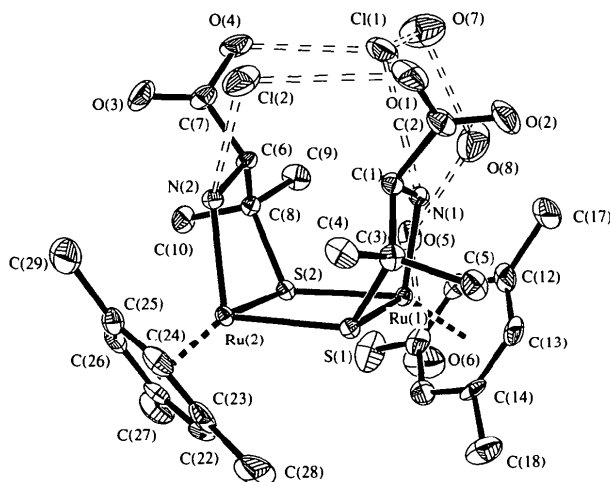


Fig. 1. A view (*SHELXTL/PC XP*; Sheldrick, 1991) of the title compound. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity.

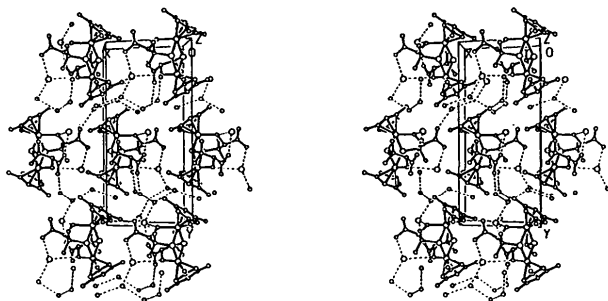


Fig. 2. Stereoview of the crystal packing (*SHELXTL/PC XP*; Sheldrick, 1991) of the title compound. The dashed lines indicate hydrogen-bond contacts. H atoms have been omitted for clarity.

Experimental

The complex was prepared by refluxing a 2:2:1 mixture of D-penicillamine, sodium methoxide and $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{RuCl}_2]_2$ in a 50:50 methanol/water solution for 3 h. The solution was rotary evaporated and the resultant solid was washed with ethanol and recrystallized from methanol/diethyl ether solution to give $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Ru}(\text{D-pen})]_2\text{Cl}_2$ in 53% yield. Crystals for the structure determination were grown from D_2O .

Crystal data

$[\text{Ru}_2(\text{C}_5\text{H}_{10}\text{NO}_2\text{S})_2\text{-}(\text{C}_9\text{H}_{12})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$

Mo $K\alpha$ radiation
 $\lambda = 0.7107 \text{ \AA}$

$M_r = 881.91$
Monoclinic
 $P2_1$
 $a = 10.060 (2) \text{ \AA}$
 $b = 19.793 (4) \text{ \AA}$
 $c = 10.251 (2) \text{ \AA}$
 $\beta = 118.9 (1)^\circ$
 $V = 1787 (1) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.638 \text{ Mg m}^{-3}$

Cell parameters from 46 reflections
 $\theta = 4\text{--}12.5^\circ$
 $\mu = 1.04 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
Block
 $0.38 \times 0.28 \times 0.19 \text{ mm}$
Orange

Data collection

Siemens *P4* diffractometer
 $\theta/2\theta$ scans
Absorption correction:
empirical
 $T_{\min} = 0.629$, $T_{\max} = 0.949$
4882 measured reflections
3947 independent reflections
3882 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0297$
 $\theta_{\max} = 27^\circ$
 $h = -11 \rightarrow 11$
 $k = -1 \rightarrow 24$
 $l = -1 \rightarrow 12$
3 standard reflections
monitored every 100 reflections
intensity decay:
insignificant

Refinement

Refinement on F
 $R = 0.0406$
 $wR = 0.0434$
 $S = 1.096$
3882 reflections
396 parameters
 $w = 1/[\sigma^2(F) + 0.00156F^2]$

$(\Delta/\sigma)_{\max} = 0.141$
 $\Delta\rho_{\max} = 1.83 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.04 \text{ e \AA}^{-3}$
Extinction correction: none
Atomic scattering factors from *SHELXTL* (Sheldrick, 1991)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ru(1)	0.1653 (1)	0.1859 (1)	-0.0123 (1)	0.021 (1)
Ru(2)	0.1710 (1)	0.0000	0.0082 (1)	0.021 (1)
S(1)	0.0820 (2)	0.0914 (2)	-0.1678 (2)	0.023 (1)
S(2)	0.2440 (2)	0.0953 (2)	0.1641 (2)	0.023 (1)
N(1)	0.3379 (6)	0.1838 (3)	-0.0770 (5)	0.025 (2)
C(1)	0.3372 (8)	0.1305 (4)	-0.1753 (7)	0.027 (3)
C(2)	0.4177 (11)	0.1583 (5)	-0.2593 (10)	0.044 (4)
O(1)	0.4895 (9)	0.1151 (4)	-0.2995 (8)	0.057 (3)
O(2)	0.4094 (9)	0.2168 (4)	-0.2901 (9)	0.064 (4)
C(3)	0.1765 (8)	0.1058 (4)	-0.2823 (7)	0.032 (3)
C(4)	0.1735 (10)	0.0386 (5)	-0.3578 (9)	0.041 (4)
C(5)	0.0832 (10)	0.1601 (5)	-0.3988 (8)	0.041 (3)
N(2)	0.4091 (6)	0.0003 (3)	0.0776 (5)	0.026 (2)
C(6)	0.5087 (7)	0.0549 (4)	0.1757 (7)	0.027 (2)
C(7)	0.6672 (9)	0.0253 (5)	0.2625 (9)	0.041 (3)
O(3)	0.6890 (7)	-0.0338 (4)	0.2962 (8)	0.058 (3)
O(4)	0.7815 (6)	0.0686 (4)	0.3064 (8)	0.058 (3)
C(8)	0.4495 (7)	0.0799 (3)	0.2804 (7)	0.024 (3)
C(9)	0.5236 (10)	0.1467 (5)	0.3568 (9)	0.046 (4)
C(10)	0.4669 (10)	0.0279 (5)	0.3968 (8)	0.041 (3)
C(11)	0.2052 (10)	0.2802 (5)	0.1226 (10)	0.039 (3)
C(12)	0.1773 (12)	0.2980 (5)	-0.0254 (12)	0.047 (5)
C(13)	0.0420 (12)	0.2767 (5)	-0.1461 (11)	0.044 (4)
C(14)	-0.0629 (9)	0.2363 (5)	-0.1314 (9)	0.037 (3)
C(15)	-0.0303 (11)	0.2168 (5)	0.0135 (11)	0.045 (4)
C(16)	0.1007 (12)	0.2418 (6)	0.1374 (10)	0.049 (4)
C(17)	0.2928 (15)	0.3384 (7)	-0.0455 (18)	0.080 (7)
C(18)	-0.2038 (11)	0.2126 (7)	-0.2669 (12)	0.068 (5)
C(19)	0.1222 (18)	0.2224 (8)	0.2870 (13)	0.085 (7)

C(21)	0.0616 (10)	-0.0479 (5)	0.1283 (9)	0.038 (3)
C(22)	-0.0488 (9)	-0.0275 (5)	-0.0146 (9)	0.039 (3)
C(23)	-0.0441 (11)	-0.0507 (6)	-0.1425 (10)	0.048 (4)
C(24)	0.0690 (12)	-0.0903 (5)	-0.1303 (10)	0.040 (4)
C(25)	0.1853 (10)	-0.1106 (6)	0.0110 (9)	0.038 (4)
C(26)	0.1762 (11)	-0.0884 (5)	0.1373 (10)	0.041 (4)
C(27)	0.0582 (14)	-0.0250 (7)	0.2639 (12)	0.066 (6)
C(28)	-0.1757 (11)	-0.0290 (8)	-0.2916 (11)	0.072 (5)
C(29)	0.3164 (14)	-0.1522 (8)	0.0254 (16)	0.074 (7)
C(1)	0.7013 (3)	0.1948 (2)	0.1479 (3)	0.063 (1)
C(2)	0.5501 (3)	-0.0149 (2)	-0.1469 (3)	0.064 (1)
O(5)	0.4318 (12)	0.3342 (7)	0.5649 (14)	0.111 (7)
O(6)	0.1312 (14)	0.3553 (7)	0.5493 (15)	0.125 (8)
O(7)	0.8359 (12)	0.3074 (7)	0.4140 (4)	0.111 (7)
O(8)	0.5919 (18)	0.3753 (8)	0.4177 (15)	0.126 (9)

Table 2. Selected geometric parameters (Å, °)

Ru(1)—S(1)	2.335 (3)	Ru(1)—S(2)	2.394 (2)
Ru(1)—N(1)	2.138 (7)	Ru(1)—C(11)	2.240 (10)
Ru(1)—C(12)	2.230 (11)	Ru(1)—C(13)	2.237 (9)
Ru(1)—C(14)	2.247 (8)	Ru(1)—C(15)	2.196 (13)
Ru(1)—C(16)	2.228 (13)	Ru(2)—S(1)	2.401 (2)
Ru(2)—S(2)	2.348 (3)	Ru(2)—N(2)	2.144 (6)
Ru(2)—C(21)	2.222 (11)	Ru(2)—C(22)	2.178 (10)
Ru(2)—C(23)	2.200 (9)	Ru(2)—C(24)	2.202 (10)
Ru(2)—C(25)	2.193 (11)	Ru(2)—C(26)	2.180 (10)
S(1)—C(3)	1.855 (9)	S(2)—C(8)	1.845 (6)
N(1)—C(1)	1.458 (10)	C(1)—C(2)	1.540 (15)
C(1)—C(3)	1.530 (9)	C(2)—O(1)	1.308 (15)
C(2)—O(2)	1.194 (14)	C(3)—C(4)	1.531 (13)
C(3)—C(5)	1.542 (11)	N(2)—C(6)	1.485 (9)
C(6)—C(7)	1.518 (10)	C(6)—C(8)	1.539 (12)
C(7)—O(3)	1.209 (13)	C(7)—O(4)	1.327 (11)
C(8)—C(9)	1.534 (11)	C(8)—C(10)	1.521 (12)
S(1)—Ru(1)—S(2)	78.1 (1)	S(1)—Ru(1)—N(1)	81.4 (2)
S(2)—Ru(1)—N(1)	101.5 (2)	S(1)—Ru(2)—S(2)	77.7 (1)
S(1)—Ru(2)—N(2)	101.4 (2)	S(2)—Ru(2)—N(2)	80.8 (2)
Ru(1)—S(1)—Ru(2)	102.1 (1)	Ru(1)—S(1)—C(3)	100.6 (3)
Ru(2)—S(1)—C(3)	118.2 (3)	Ru(1)—S(2)—Ru(2)	102.0 (1)
Ru(1)—S(2)—C(8)	118.0 (3)	Ru(2)—S(2)—C(8)	101.1 (2)
Ru(1)—N(1)—C(1)	119.7 (5)	N(1)—C(1)—C(2)	107.5 (7)
N(1)—C(1)—C(3)	112.1 (7)	C(2)—C(1)—C(3)	111.9 (6)
C(1)—C(2)—O(1)	117.5 (9)	C(1)—C(2)—O(2)	120.4 (11)
O(1)—C(2)—O(2)	122.0 (12)	S(1)—C(3)—C(1)	106.4 (5)
S(1)—C(3)—C(4)	107.2 (7)	C(1)—C(3)—C(4)	113.3 (7)
S(1)—C(3)—C(5)	106.9 (6)	C(1)—C(3)—C(5)	111.6 (7)
C(4)—C(3)—C(5)	111.0 (6)	Ru(2)—N(2)—C(6)	120.4 (5)
N(2)—C(6)—C(7)	106.8 (6)	N(2)—C(6)—C(8)	110.2 (6)
C(7)—C(6)—C(8)	111.5 (6)	C(6)—C(7)—O(3)	122.3 (8)
C(6)—C(7)—O(4)	116.2 (8)	O(3)—C(7)—O(4)	121.4 (7)
S(2)—C(8)—C(9)	107.0 (4)	S(2)—C(8)—C(9)	107.7 (5)
C(6)—C(8)—C(9)	112.2 (7)	S(2)—C(8)—C(10)	106.6 (6)
C(6)—C(8)—C(10)	113.1 (6)	C(9)—C(8)—C(10)	109.9 (6)
Ru(1)—C(11)—C(12)	70.7 (6)		

All H atoms bonded to C atoms were included in calculated positions (C—H = 0.95 Å) with a single fixed isotropic displacement parameter (0.06 Å²). No other H atoms were located or included in the refinement.

Cell refinement and data collection: *XSCANS* (Fait, 1991). Data reduction and structure solution: *SHELXTL/PC* (Sheldrick, 1991). Refinement: *SHELX76* (Sheldrick, 1976) and *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC XP*.

GC thanks the SERC for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: HU1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Carter, L., Davies, D. L., Duffy, K. T., Fawcett, J. & Russell, D. R. (1994). *Acta Cryst. C* **50**, 1559–1561.
- Carter, L., Davies, D. L., Fawcett, J. & Russell, D. R. (1993). *Polyhedron*, **12**, 1599–1602.
- Fait, J. (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
- Sheldrick, G. M. (1991). *SHELXTL/PC*. Release 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, W. S. & Heeb, S. (1989). *J. Organomet. Chem.* **377**, 357–366.

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The First Unsymmetrically Substituted Ring-Tilted Silicon-Bridged [1]Ferrocenophane

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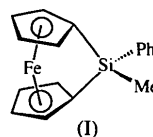
(Received 12 September 1994; accepted 19 October 1994)

Abstract

The structure analysis of the title compound, (1,1'-ferrocenediyl)methylphenylsilane, [Fe(C₁₇H₁₆Si)], is the first such study of an unsymmetrically substituted silicon-bridged [1]ferrocenophane. The strain present in this molecule results in a tilting of the cyclopentadienyl rings by 21.0 (2)° from being parallel.

Comment

As part of our overall program to investigate the structure/strain of [1]ferrocenophanes and the properties of poly(ferrocenylsilanes), we report here the first structural characterization of an unsymmetrically substituted silicon-bridged [1]ferrocenophane, [Fe{(η⁵-C₅H₄)₂SiMePh}], (I).



Although symmetrically substituted silicon-bridged [1]ferrocenophanes have been known for almost twenty years (Osborne & Whiteley, 1975; Stoeckli-Evans, Osborne & Whiteley, 1976; Finckh, Tang,