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Tetraethylammonium dichlorotris(2,6-dimethylphenylsulfanyl-κS)ruthenium dichloromethane solvate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.049
wR factor = 0.084
Data-to-parameter ratio = 22.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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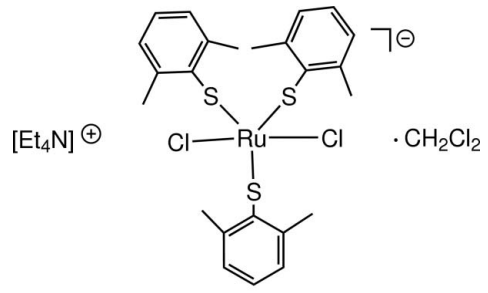
The title mononuclear ruthenium(IV) complex, $(C_8H_{20}N)[Ru(C_8H_9S)_3Cl_2]\cdot CH_2Cl_2$, contains the trigonal $\{Ru(Sxylyl)_3\}$ core (xylyl is 2,6-dimethylphenyl), with S—Ru—S angles in the range 118.07 (6)–123.45 (6)°. The coordination geometry of the central Ru atom is trigonal–bipyramidal, with two Cl atoms in the axial positions. The Ru—S and Ru—Cl bond lengths are 2.1918 (18)–2.2046 (19) and 2.378 (2)–2.385 (2) Å, respectively.

Comment

There has been continuing interest in the reactivity of coordinatively unsaturated ruthenium thiolate complexes as models for the active sites of heterogeneous catalysts (Topsoe & Clausen, 1984; Chianelli, 1984). While ruthenium(II) thiolate complexes are well documented, the ruthenium(IV) system has received rather less attention (Torrens, 2000). Ruthenium(IV) complexes that contain the characteristic trigonal–planar $\{Ru(SAr)_3\}^+$ core have been prepared from the reaction of ruthenium(IV) starting materials such as $[Et_4N][RuCl_5(CH_3CN)]$ or $K_2Ru(NO)Cl_5$ with a series of aromatic thiolate anions that are substituted in the 2- and 6-positions with methyl or isopropyl groups (Koch & Millar, 1983; Millar *et al.*, 1985; Soong *et al.*, 1988). Interestingly, complexes $[Ru^{IV}(SAr)_4(L)]$ (Ar = 2,3,5,6-tetramethylphenyl, 2,6-dimethylphenyl and 2,4,6-triisopropylphenyl; L = MeOH, MeCN and dimethyl sulfoxide) show unusual reactivity patterns that are dependent on the steric nature of the thiolate ligands (Soong *et al.*, 1988). For example, $[Ru(SAr)_4(MeCN)]$ reacts with CO to give a carbonyl complex $[Ru(SAr)_4(CO)]$ (Koch & Millar, 1983). A similar complex, $[Ru(SAr)_4(NO)]$, containing an [RuNO] centre may be obtained from the reaction of $[Et_4N][RuCl_5(CH_3CN)]$ with Li(S-2,4,6-^{i}Pr$_3$C$_6$H$_2$), as the [RuNO] coordination mode has been noted for its ability to persist during substitution and oxidation–reduction reactions (Soong *et al.*, 1988). σ-Acetylide complexes of ruthenium(IV) thiolates $[Et_3NH][Ru(SAr)_3(C{\equiv}CPh)Cl]$ (Ar = 2,6-Me$_2$C$_6$H$_4$) have been synthesized from $[Ru(SAr)_3(MeCN)Cl]$ and PhC≡CH in the presence of Et_3N as a base (Zhang *et al.*, 2002). In our research into the preparation of ruthenium complexes with sulfur and selenium donor ligands (Zhang *et al.*, 2001), we have synthesized high-valence ruthenium complexes with sterically bulky thiolate ligands (Zhang *et al.*, 2002) and have attempted to establish the structure of these complexes. In this paper, we report the structure of a ruthenium(IV) complex of a thiolate, *viz.* the title compound, $[Et_4N][Ru(Sxylyl)_3Cl_2]\cdot CH_2Cl_2$, (I) (xylyl = 2,6-dimethylphenyl).



(I)

The structure of (I) consists of discrete $[Et_4N]^+$ cations, $[Ru(Sxylyl)_3Cl_2]^-$ anions and dichloromethane solvent molecules. The coordination geometry of the central Ru atom in the anion is trigonal–bipyramidal, with two Cl atoms occupying the *trans* axial positions. The three S atoms and the Ru atom are coplanar, with an average deviation of 0.0315 Å from the least-squares plane. The two Ru—Cl bonds are almost perpendicular to the RuS_3 plane, with an average angle of 95.5°. The S—Ru—S bond angles range from 118.07 (6) to 123.45 (6)°. The Ru—S bond lengths in (I) (Table 1) are comparable with those in $[Ru(Sxylyl)_3(MeCN)Cl]$ (Zhang *et al.*, 2002) and $[Et_3NH][Ru(Sxylyl)_3(C{\equiv}CPh)Cl]$ (Zhang *et al.*, 2002). The *trans* Cl atoms and the central Ru atom are almost collinear, with a Cl1—Ru1—Cl2 angle of 178.33 (5)°. The two Ru—Cl bond distances are slightly shorter than those in the ruthenium(II)–sulfur complex $[(\eta^6\text{-}p\text{-cymene})RuCl(S_2CNMe_2)]$ [2.4276 (5) Å; Yao *et al.*, 2003) and in the ruthenium(IV)–thiolate complex $[Ru(Sxylyl)_3(MeCN)Cl]$ [2.437 (1) Å; Zhang *et al.*, 2002).

Experimental

Black crystals of the title complex were obtained as a by-product (*ca* 5% yield) from the reaction of $[Et_4N][RuCl_5(MeCN)]$ and sodium 2,6-dimethylthiophenol in a mixed methanol–acetonitrile (2:1) solvent, as described in our earlier report (Zhang *et al.*, 2002). The title complex was also synthesized from the reaction of $[Ru(Sxylyl)_3(MeCN)Cl]$ and $[Et_4N]\cdot Cl$ in 1:1 ratio in a tetrahydrofuran solution, according to the literature method of Satsangee *et al.* (2000). ^{1}H NMR ($CDCl_3$, δ, p.p.m.): 7.33 (*t*, 1H, H_p), 7.20 (*t*, 2H, H_p), 7.09 (*d*, 2H, H_m), 7.02 (*d*, 4H, H_m), 3.31 (*dt*, 8H, CH_3CH_2), 2.34 (*s*, 12H, Me), 2.22 (*s*, 6H, Me), 1.32 (*t*, 12H, CH_3CH_2). MS (FAB): *m*/*z* 583 (M^+ − [Et_4N] + 1), 512 (M^+ − [Et_4N] − 2Cl). Analysis calculated for $C_{32}H_{47}Cl_2NRuS_3\cdot CH_2Cl_2$: C 50.1, H 6.20, N 1.77%; found: C 50.8, H 6.13, N 1.74%.

Crystal data

$(C_8H_{20}N)[Ru(C_8H_9S)_3Cl_2]\cdot CH_2Cl_2$	D_x = 1.442 Mg m^{-3}
M_r = 798.78	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4257 reflections
a = 13.9279 (10) Å	θ = 2.3–25.0°
b = 12.4525 (16) Å	μ = 0.91 mm^{-1}
c = 21.2361 (13) Å	T = 293 (2) K
β = 92.162 (18)°	Needle, black
V = 3680.5 (6) Å^3	0.32 × 0.10 × 0.08 mm
Z = 4	

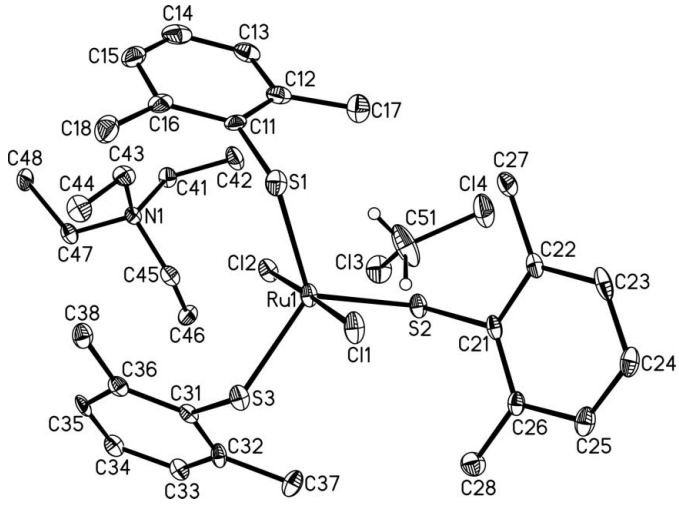


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms of the cation and anion have been omitted.

Data collection

Bruker SMART CCD area-detector diffractometer	8661 independent reflections
	3727 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.067
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	θ_{max} = 28.3°
	$h = -17 \rightarrow 7$
T_{min} = 0.744, T_{max} = 0.931	$k = -15 \rightarrow 16$
21935 measured reflections	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.049	$w = 1/[\sigma^2(F_o^2) + (0.0138P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.084	$(\Delta/\sigma)_{max} < 0.001$
S = 0.97	$\Delta\rho_{max}$ = 0.80 e Å^{-3}
8661 reflections	$\Delta\rho_{min}$ = −0.93 e Å^{-3}
389 parameters	

Table 1
Selected geometric parameters (Å, °).

Ru1—S2	2.1918 (18)	Ru1—Cl1	2.378 (2)
Ru1—S3	2.201 (2)	Ru1—Cl2	2.385 (2)
Ru1—S1	2.2046 (19)		
S2—Ru1—S3	118.07 (6)	S1—Ru1—Cl1	85.54 (5)
S2—Ru1—S1	118.05 (7)	S2—Ru1—Cl2	86.76 (4)
S3—Ru1—S1	123.45 (6)	S3—Ru1—Cl2	93.71 (5)
S2—Ru1—Cl1	93.54 (5)	S1—Ru1—Cl2	95.78 (5)
S3—Ru1—Cl1	84.70 (5)	Cl1—Ru1—Cl2	178.33 (5)

All H atoms were found in difference density maps, but were then placed in calculated positions (C—H = 0.93–0.97 Å) and included in the refinement using a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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References

Bruker (1998). *SMART* (Version 6.02a) and *SAINT-Plus* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.
Chianelli, R. R. (1984). *Catal. Rev. Sci. Eng.* **26**, 361–393.
Koch, S. A. & Millar, M. J. (1983). *J. Am. Chem. Soc.* **105**, 3362–3363.
Millar, M., O'Sullivan, T., de Vries, N. & Koch, S. A. (1985). *J. Am. Chem. Soc.* **107**, 3714–3715.
Satsangee, S. P., Hain, J. H. Jr, Cooper, P. T. & Koch, S. A. (2000). *Inorg. Chem.* **31**, 5160–5161.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Soong, S.-L., Hain, J. H., Millar, M. & Koch, S. A. (1988). *Organometallics*, **7**, 556–557.
Topsoe, H. & Clausen, B. S. (1984). *Catal. Rev. Sci. Eng.* **26**, 395–420.
Torrens, H. (2000). *Coord. Chem. Rev.* **196**, 331–352.
Yao, W.-R., Liu, Z.-H. & Zhang, Q.-F. (2003). *Acta Cryst.* E**59**, m303–m305.
Zhang, Q. F., Cheung, F. K. M., Wong, W. Y., Williams, I. D. & Leung, W. H. (2001). *Organometallics*, **20**, 3777–3781.
Zhang, Q. F., Lai, C. Y., Wong, W. Y. & Leung, W. H. (2002). *Organometallics*, **21**, 4017–4020.