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A synchrotron study of μ_3-chloro-tri-μ-chloro-μ_3-sulfido-hexakis(triphenylphospine)triruthenium(II)–tetrahydrofuran–water (1/1.25/0.75)

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The crystal structure of $[Ru_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3(\mu_3\text{-S})(PPh_3)_6]\cdot 1.25C_4H_8O\cdot 0.75H_2O$, has been determined using synchrotron radiation. The cluster complex contains a central six-membered ring of alternating Ru and Cl atoms. The core is completed by capping chloride and sulfide groups.

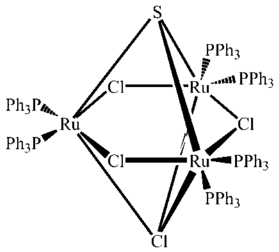
Key indicators

Single-crystal synchrotron study
T = 123 K
Mean σ(C–C) = 0.015 Å
Disorder in solvent or counterion
R factor = 0.089
wR factor = 0.243
Data-to-parameter ratio = 13.1

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

Comment

It is now well established that the reaction of metal halide complexes with $S[Si(CH_3)_3]_2$ produces metal sulfide clusters of high nuclearity. The ionic organometallic ruthenium sufide cluster complexes $[Ru_3S_2(p\text{-cymene})_3]^{2+}$ (p-cymene is 4-isopropyltoluene) (Lockemeyer, Rauchfuss & Rheingold, 1989) and $[\{RuCl(TMT)\}_3S]^+$ (TMT is tetramethylthiophene) (Lockemeyer, Rauchfuss, Rheingold & Wilson, 1989) have been prepared *via* this method from $[RuCl_2(p\text{-cymene})]_2$ and $[RuCl_2(TMT)]_2$, respectively. The neutral ruthenium sulfide clusters $[Ru_4S_6(PPh_3)_4]$, $[Ru_5S_6(PPh_3)_5]$ and $[Ru_6S_8(PPh_3)_6]$ have been prepared from the reaction of $[RuCl_2(PPh_3)_3]$ with NaSH or $S[Si(CH_3)_3]_2$ under various conditions (Eckermann *et al.*, 2002).



(I)

Small crystals of the title compound, (I), were isolated from the reaction of $[RuCl_2(PPh_3)_3]$ with $S[Si(CH_3)_3]_2$; it is thought to be an intermediate in the formation of halide-free cluster compounds. The poorly diffracting crystals did not yield sufficient data on a conventional laboratory diffractometer. A single-crystal structure of (I) (Fig. 1) was eventually obtained using synchrotron radiation at the ChemMatCARS facility of the Advanced Photon Source.

The core of the cluster consists of a flat six-membered ring of alternating Ru atoms and bridging chloro ligands. Additional μ_3-capping chloro and sulfido ligands, one on each side of the six-membered ring, complete the core. Each Ru centre is coordinated by two PPh_3 ligands and has distorted octahedral geometry with the bridging chloride occupying axial positions. Overall, the molecule has non-crystallographic C_{3v} symmetry. A similar core geometry has been observed in the cationic cluster $[Ru_3Cl_5((S)\text{-binap})_3]^+$ [binap is 2,2′-bis(-diphenylphosphino)-1,1′-binaphthyl] (Mashima *et al.*, 1991), which has two μ_3-chlorides capping a six-membered Ru_3Cl_3 ring. The cation of the organometallic ruthenium–sulfide cluster $[\{(TMT)RuCl\}_3S]^+$ also consists of a six-membered Ru_3Cl_3 ring which is capped by a μ_3–S atom (Lockemeyer, Rauchfuss, Rheingold & Wilson, 1989). The bond distances of (I) are in accord with equivalent bond distances in these related clusters.

Experimental

The title compound was prepared from the reaction of $[RuCl_2(PPh_3)_3]$ and $S[Si(CH_3)_3]_2$ in refluxing tetrahydrofuran for 16 h. After this time, the reaction was cooled to room temperature, the solution filtered and the solvent volume reduced *in vacuo* (*ca* 5 ml). Microcrystals suitable for single-crystal X-ray diffraction analysis were grown from the reaction solution at 243 K.

Crystal data

$[Ru_3Cl_4S(C_{18}H_{15}P)_6]\cdot$-
$1.25C_4H_8O\cdot 0.7H_2O$
$M_r = 2152.82$
Triclinic, $P\overline{1}$
$a = 14.183$ (4) Å
$b = 14.699$ (5) Å
$c = 25.814$ (9) Å
$\alpha = 91.904$ (11)°
$\beta = 92.328$ (11)°
$\gamma = 102.784$ (11)°
$V = 5239$ (3) Å^3

$Z = 2$
$D_x = 1.365$ Mg m^{-3}
Synchrotron radiation,
$\lambda = 0.5594$ Å
Cell parameters from 1021 reflections
$\theta = 2.3$–19.4°
$\mu = 0.37$ mm^{-1}
$T = 123$ (2) K
Prism, red
$0.08 \times 0.03 \times 0.02$ mm

Data collection

SMART 6000 detector mounted on a Bruker Kappa Platform
φ scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995; Sheldrick, 1996)
$T_{min} = 0.987$, $T_{max} = 0.995$
109758 measured reflections

15139 independent reflections
12160 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 19.0°$
$h = -14 \rightarrow 14$
$k = -16 \rightarrow 16$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.089$
$wR(F^2) = 0.243$
$S = 1.42$
15139 reflections
1156 parameters
H atoms constrained **OK?**

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 6P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.38$ e Å^{-3}
$\Delta\rho_{min} = -1.25$ e Å^{-3}

The asymmetric unit contains the complex cluster molecule (I) and four partially occupied tetrahydrofuran solvent sites. Additionally, there are four sites treated as partially occupied water O-atom sites, although they may be associated with further disordered and unresolved tetrahydrofuran sites. In general, the non-H-atom sites were modelled with anisotropic displacement parameters, and a riding atom model was used for the H atoms. The partially occupied non-H sites were modelled with isotropic displacement parameters. No H atoms were included in the model for the water sites.

Data collection: *SMART–KAPPA* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* for Windows (Molecular Structure Corporation, 1997), *Xtal*3.6 (Hall *et al.*, 1999), *ORTEP*II (Johnson, 1976) and *WinGX* (Farrugia, 1999); software used to prepare material for publication: *SHELXL*97.

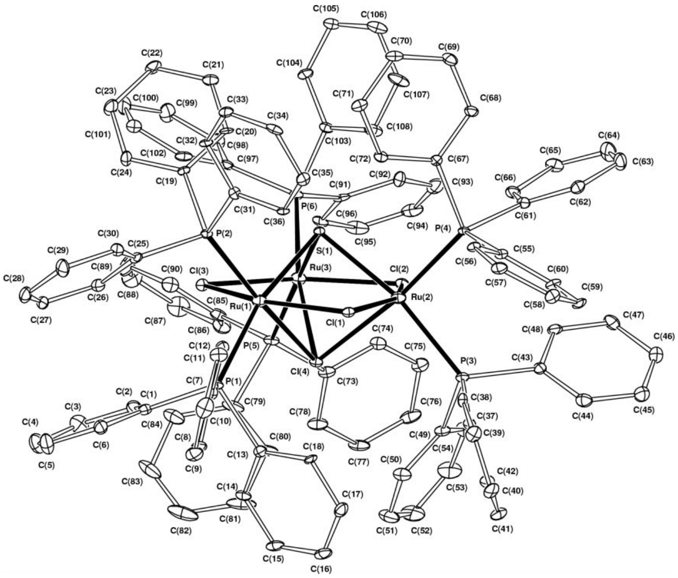


Figure 1

*ORTEP*II (Johnson, 1976; Hall *et al.*, 1999) projection of (I), with displacement ellipsoids shown at the 20% probability level.

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