Notes

Crystal and Molecular Structure of $[AsPh_4][Ru(\text{DL-}MeSeCH_2CH_2SeMe)Cl_4]$†

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The structure of the title complex has been determined by single-crystal *X*-ray diffraction. The complex belongs to the space group $P2_1/a$ ($Z = 4$) and the data has been refined to $R = 0.042$ from 4 073 reflections $[F > 3\sigma(F)]$. The complex contains $[AsPh_4]^+$ cations and pseudo-octahedral *cis*-$[Ru(\text{DL-}MeSeCH_2CH_2SeMe)Cl_4]^-$ anions [Ru–Se 2.446(1), 2.457(1); Ru–Cl(*trans* Se) 2.386(2), 2.404(2); Ru–Cl(*trans* Cl) 2.344(2), 2.353(2) Å]. The diselenoether adopts the DL conformation, and is the first example of this invertomer to be structurally characterised.

Chelation of diselenoether ligands (RSe–SeR) to metals gives complexes $[M(RSe\text{–}SeR)L_n]$ (L = halide, carbonyl, *etc.*) which contain two isomeric forms of the ligand: *meso* (*syn* R groups) or DL (*anti* R groups). N.m.r. spectroscopic (^1H and ^{77}Se) studies reveal that both forms are usually present in solution in unequal amounts and that interconversion occurs by pyramidal inversion at selenium.[1–5] *X*-Ray studies have been reported for five complexes all containing *meso* invertomers, namely, $[Pd(Pr^iSeCH_2CH_2SePr^i)Cl_2]$,[6] $[Re(CO)_3I(MeSeCH_2CH_2SeMe)]$,[7] $[PtMe_3X(MeSeCHCHSeMe)]$ (X = Cl or I),[3] and $[Pt\{o\text{-}C_6H_4(SeMe)_2\}Cl_4]$ [5] and here we report the first structure containing a DL invertomer, $[Ru(MeSeCH_2CH_2SeMe)Cl_4]^-$.

Experimental

X-Ray Crystallography.—The title compound was prepared as described.[5] Air-stable brown crystals were obtained from CH_2Cl_2–hexane by vapour diffusion, and preliminary photographic *X*-ray studies established approximate cell dimensions and the crystal system. Accurate cell dimensions and intensity data taken at room temperature were recorded from a crystal (0.42 × 0.25 × 0.15 mm) mounted in a thin-walled glass capillary using an Enraf-Nonius CAD-4 diffractometer. The cell dimensions were obtained from 25 high-angle reflections and intensity data collected with graphite-monochromated Mo-K_α radiation. 5 845 Reflections were recorded by the θ—2θ scan technique [$1 < \theta < 25°$; *hkl*, *h*(−20 to 20), *k*(0—14), *l*(0—18)]. Systematic absences (*hkl*, none; *h*0*l*, $l \neq 2n$; 0*k*0, $k \neq 2n$) established the space group as $P2_1/a$ and removal of those systematically absent left 5 547 unique reflections. An empirical ψ-scan absorption correction was applied [transmission: 99.9 (max.), 82.3% (min.)] as well as Lorentz and polarisation corrections. Removing observations with $F < 3\sigma(F)$ and the 001 reflection (for instrumental reasons) left 4 073 reflections which were used in the structure analysis and refinement.

Crystal data. $C_{28}H_{30}AsCl_4RuSe_2$, $M = 842.27$, monoclinic, space group $P2_1/a$ (no.14), $a = 17.377(2)$, $b = 11.960(1)$, $c = 15.660(1)$ Å, $\beta = 103.85(1)°$, $U = 3\,160.0(8)$ Å^3, $Z = 4$, $D_c = 1.770$, D_m (flotation) = 1.77 g cm^{-3}, $F(000) = 1\,644$, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 41.2 cm^{-1}.

Table 1. Final atomic co-ordinates*

Atom	*x*	*y*	*z*
Ru	0.196 85(3)	0.436 61(4)	0.325 94(3)
As	0.158 66(4)	−0.076 10(5)	0.135 60(5)
Se(1)	0.247 98(5)	0.246 56(6)	0.322 12(5)
Se(2)	0.171 52(5)	0.398 70(7)	0.470 99(5)
Cl(1)	0.135 5(1)	0.616 0(1)	0.330 3(1)
Cl(2)	0.318 3(1)	0.504 0(2)	0.411 2(1)
Cl(3)	0.238 6(1)	0.472 3(2)	0.194 0(1)
Cl(4)	0.076 3(1)	0.358 1(2)	0.250 1(1)
C(11)	0.263 1(2)	−0.105 0(3)	0.201 7(3)
C(12)	0.323 5(2)	−0.027 9(3)	0.202 8(3)
C(13)	0.401 2(2)	−0.052 8(3)	0.247 4(3)
C(14)	0.418 4(2)	−0.154 9(3)	0.290 9(3)
C(15)	0.357 9(2)	−0.232 0(3)	0.289 8(3)
C(16)	0.280 3(2)	−0.207 1(3)	0.245 2(3)
C(21)	0.091 7(2)	−0.058 7(4)	0.212 9(3)
C(22)	0.123 2(2)	−0.049 6(4)	0.303 4(3)
C(23)	0.073 1(2)	−0.031 5(4)	0.359 6(3)
C(24)	−0.008 5(2)	−0.022 5(4)	0.325 4(3)
C(25)	−0.040 0(2)	−0.031 6(4)	0.234 9(3)
C(26)	0.010 0(2)	−0.049 7(4)	0.178 7(3)
C(31)	0.158 9(3)	0.056 7(3)	0.070 8(3)
C(32)	0.119 1(3)	0.150 9(3)	0.090 5(3)
C(33)	0.118 7(3)	0.249 2(3)	0.042 5(3)
C(34)	0.158 1(3)	0.253 3(3)	−0.025 3(3)
C(35)	0.197 9(3)	0.159 0(3)	−0.045 1(3)
C(36)	0.198 3(3)	0.060 7(3)	0.003 0(3)
C(41)	0.119 3(2)	−0.198 3(3)	0.060 4(3)
C(42)	0.104 8(2)	−0.298 6(3)	0.099 2(3)
C(43)	0.082 3(2)	−0.393 4(3)	0.047 4(3)
C(44)	0.074 3(2)	−0.387 9(3)	−0.043 3(3)
C(45)	0.088 7(2)	−0.287 5(3)	−0.082 2(3)
C(46)	0.111 2(2)	−0.192 7(3)	−0.030 3(3)
C(1)	0.363 6(6)	0.254 1(9)	0.342 5(9)
C(2)	0.238 8(9)	0.188 6(9)	0.436 6(7)
C(3)	0.230 7(11)	0.258 8(9)	0.498 3(8)
C(4)	0.062 2(7)	0.350 0(16)	0.456 7(7)

* Carbon atoms of the phenyl rings are labelled C(*ij*) where *i*(1—4) indicates the ring and *j*(1—6) the atoms within each ring.

The structure was solved using the centrosymmetric direct methods strategy available in SHELX. The solution with the higher figure of merit yielded the Ru, As, and Se atom positions, and Cl and C atoms were located by repeated structure factor and electron-density syntheses. Anisotropic atoms were introduced for non-carbon atoms and the phenyl rings treated as rigid groups. The carbon atoms of the selenoether ligand were found to have unusually large isotropic thermal parameters and

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† Tetraphenylarsonium tetrachloro(DL-2,5-diselenahexane-*Se,Se'*)ruthenate(III).

Supplementary data available (No. SUP 56544, 4 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 2. Selected interatomic distances (Å) and angles (°)

Ru–Se(1)	2.446(1)	Se(1)–C(1)	1.96(1)
Ru–Se(2)	2.457(1)	Se(1)–C(2)	1.96(1)
Ru–Cl(1)	2.404(2)	Se(2)–C(3)	1.96(1)
Ru–Cl(2)	2.353(2)	Se(2)–C(4)	1.95(1)
Ru–Cl(3)	2.386(2)		
Ru–Cl(4)	2.344(2)	C(2)–C(3)	1.31(2)
Se ··· Cl min.	3.18	Se(1) ··· Se(2)	3.463
max.	3.49		
Se ··· Cl min.	3.37	C(4) ··· Cl(4)	3.30
max.	3.54	C(1) ··· Cl(2)	3.33
Se(1)–Ru–Cl(2)	92.9(1)	Cl(1)–Ru–Cl(2)	91.2(1)
Se(1)–Ru–Cl(3)	87.6(1)	Cl(1)–Ru–Cl(3)	95.4(1)
Se(1)–Ru–Cl(4)	84.3(1)	Cl(1)–Ru–Cl(4)	91.3(1)
Se(2)–Ru–Cl(1)	87.7(1)	Cl(2)–Ru–Cl(3)	90.7(1)
Se(2)–Ru–Cl(2)	82.7(1)	Cl(3)–Ru–Cl(4)	93.0(1)
Se(2)–Ru–Cl(4)	93.3(1)	Se(1)–Ru–Se(2)	89.9(1)
Ru–Se(1)–C(1)	108.5(3)	C(1)–Se(1)–C(2)	99.9(6)
Ru–Se(1)–C(2)	101.3(3)	C(3)–Se(2)–C(4)	102.5(8)
Ru–Se(2)–C(3)	99.2(4)	Se(1)–C(2)–C(3)	119.5(8)
Ru–Se(2)–C(4)	109.6(3)	Se(2)–C(3)–C(2)	121.9(9)
As–C(11)	1.893(3)	C–As–C min.	107.3(2)
As–C(21)	1.882(3)	max.	111.2(2)
As–C(31)	1.885(3)	mean	110(1)
As–C(41)	1.898(3)		
Se(1)–C(2)–C(3)–Se(2)	34(1)		
C(1)–Se(1)–C(2)–C(3)	94(1)		
C(4)–Se(2)–C(3)–C(2)	82(1)		

when these were introduced as anisotropic atoms the thermal ellipsoids were seen to be aligned with the large displacements perpendicular to adjacent bonds reflecting either genuinely large thermal motion or more likely some static disorder in the ligand. There were no recognisable disordered sites for C atoms. There was some evidence for H atoms of the phenyl ring and these were introduced in calculated positions with a common refined thermal parameter, but no H atoms were included for methylene and methyl groups. Full-matrix least-squares refinement converged at $R = 0.042$ ($R' = 0.051$) {4 073 reflections, 158 parameters, anisotropic [Ru, As, Se, Cl, $C(H_2)$, $C(H_3)$] and isotropic [C(H), H] atoms, rigid C_6 groups [d(C–C) = 1.395 Å], $w = 1/[\sigma^2(F) + 0.0005F^2]$, phenyl H atoms [$d$(CH) = 1.0 Å], max. shift–error ratio 0.19}. A final difference synthesis showed all features in the range 0.84 to −0.57 e Å^{-3}. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX (Cl, C, H)[8] and ref. 9 (Ru, As, Se) and all calculations were performed using SHELX,[8] ORTEP,[10] and XANADU.[11] Final atomic co-ordinates are presented in Table 1.

Results and Discussion

The title complex contains $[AsPh_4]^+$ cations and pseudo-octahedral *cis*-$[Ru(DL\text{-}MeSeCH_2CH_2SeMe)Cl_4]^-$ anions. Selected bond lengths and angles are given in Table 2 and the anion is shown in the Figure. The only structurally characterised Ru^{III} complex which is directly comparable with the present anion is *cis*-$[Ru(H_2O)_2Cl_4]^-$[12] which has Ru–O 2.12(1), 2.11(1); Ru–Cl(*trans* Cl) 2.35(1), 2.36(1); and Ru–Cl(*trans* O) 2.32(1), 2.33(1) Å. Thus Ru–Cl(*trans* Cl) in this aqua complex and the title complex [2.353(2), 2.344(2) Å] are not significantly different but the Ru–Cl(*trans* Se) bonds [2.404(2), 2.386(2) Å] are longer ($\sim 7\sigma$) than Ru–Cl(*trans* O), consistent with the expected *trans* influence order $O < Cl < Se$. The anion has approximate C_2 symmetry and contains the DL conformation of the diselenoether ligand with a 'bite' (3.46 Å) a little shorter than in the only other example (*meso*) of this ligand (3.51 Å[7]). The C–C bond length is abnormally short for a single bond but this is an artefact of the calculation due to the disorder in the ligand.[13] The conformation of the five-membered ring is highly puckered both in this example and other compounds[6,7] where there is torsional freedom about the C–C bond. A comparison of the geometry of the present example and the previously determined structures[3,5–7] reveals* a complex picture from which no rationalisation of the detailed molecular geometry emerges. No satisfactory models have been developed which can predict the effects of such small energy differences. One interesting observation from Table 2 concerns the two smallest angles. Thus Cl(2)–Ru–Se(1) (92.9°) is adjacent to the small angle Se(1)–Ru–Cl(4) (84.3°) and presumably arises from non-bonded interaction with the methyl group on selenium [C(1) ··· Cl(2), 3.33 Å]. A similar effect is seen with the angles involving Se(2).

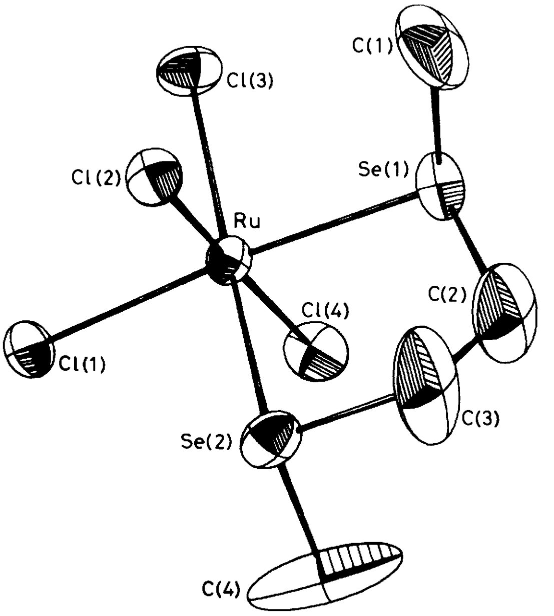

Figure. The anion of $[AsPh_4][Ru(DL\text{-}MeSeCH_2CH_2SeMe)Cl_4]$ showing the atom-numbering scheme and with thermal ellipsoids drawn with 40% probability boundary surfaces

The $[AsPh_4]^+$ ion has been found in many structures and the stereochemistry of EPh_4 (E = various Group 3—5B elements) discussed in detail.[14,15] In the present case there is no crystallographic symmetry and inspection of the CAsCC torsion angles gives no clear indication of S_4, D_2, or D_{2d} approximate point group symmetry.

Acknowledgements

We thank the S.E.R.C. and the University of Southampton for financial support (to E. G. H. and H. C. J. respectively) and Dr. D. C. Povey, University of Surrey, for the X-ray data collection.

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* Bond distances calculated from the published co-ordinates in ref. 7 did not agree with the reported values and the *a* cell dimension apparently should be 14.422 Å.

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Received 5th November 1985; *Paper* 5/1943