

## THE SYNTHESIS AND STRUCTURES OF SILVER COMPLEXES WITH TRIMERIC THIOFORMALDEHYDE AND TRIMERIC SELENOFORMALDEHYDE \*

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### Summary

The compounds  $\{[(\text{CH}_2\text{X})_3]_2\text{Ag}\}\text{AsF}_6$  ( $\text{X} = \text{S}, \text{Se}$ ) have been prepared from  $(\text{CH}_2\text{X})_3$  and  $\text{AgAsF}_6$  in liquid  $\text{SO}_2$  as minor and major products respectively. Both X-ray crystal structures were determined.  $\text{X} = \text{S}$ :  $P2_1/c$ ,  $a$  8.579(2),  $b$  20.618(4),  $c$  9.821(2) Å,  $\beta$  107.95(2)°,  $R = 0.078$  for 2439 reflections. The silver atom shows irregular trigonal coordination, with  $\text{Ag}-\text{S}$  2.515, 2.532, 2.764 Å; the extended cation structure is a chain polymer.  $\text{X} = \text{Se}$ :  $C2/c$ ,  $a$  28.80(4),  $b$  9.42(1),  $c$  22.40(4) Å,  $\beta$  137.4(1)°,  $R = 0.106$  for 1676 reflections. The structure contains isolated  $\{[(\text{CH}_2\text{Se})_3]_2\text{Ag}\}^+$  cations, all six selenium atoms coordinating silver ( $\text{Ag}-\text{Se}$  2.78–3.05 Å).

We have described in a previous paper [1] the reaction between  $\text{AgAsF}_6$  and trimeric thioformaldehyde in liquid  $\text{SO}_2$ ; the major product is  $\{[(\text{CH}_2\text{S})_3]_5\text{Ag}_2\}(\text{AsF}_6)_2 \cdot \text{SO}_2$ , and contains two independent silver ions with coordination number four and five respectively. Here we report the isolation and crystal structures of (i)  $\{[(\text{CH}_2\text{S})_3]_2\text{Ag}\}\text{AsF}_6$ , a minor product of the same reaction, and (ii)  $\{[(\text{CH}_2\text{Se})_3]_2\text{Ag}\}\text{AsF}_6$ , obtained as the major product of an analogous reaction. Other examples of complex formation in liquid  $\text{SO}_2$  have been reported by Mews [2], and other reactions involving  $\text{Ag}^+$  ions and thioformaldehyde by Weissflog [3].

### Experimental

The reactions were performed under nitrogen in pressure vessels and protected against light with aluminium foil.  $\text{SO}_2$  and  $(\text{CH}_2\text{S})_3$  were dried before use.

*Preparation of  $\{[(\text{CH}_2\text{S})_3]_2\text{Ag}\}\text{AsF}_6$ .* A mixture of 0.52 g (1.75 mmol)  $\text{AgAsF}_6$ , 0.48 g (3.48 mmol)  $(\text{CH}_2\text{S})_3$  and 20 cm<sup>3</sup> liquid  $\text{SO}_2$  at  $-80^\circ\text{C}$  was allowed to warm up slowly to room temperature, while stirring. After 72 h the residue was filtered off

\* Dedicated to Professor Harry Emeléus, on the occasion of his 80th birthday.

and the solution evaporated slowly to dryness, yielding 0.60 g of  $[(\text{CH}_2\text{S})_3]_5\text{Ag}_2(\text{AsF}_6)_2 \cdot \text{SO}_2$ . Part of the residue was dissolved in 20 ml liquid  $\text{SO}_2$ . After filtration and evaporation to dryness, a new crystalline product could be obtained (yield 0.30 g); it was sensitive to daylight but surprisingly stable to moisture, decomp.  $195^\circ\text{C}$ . (Found: C, 13.3; H, 2.1; F, 20.8; S, 33.7%.  $\text{C}_6\text{H}_{12}\text{S}_6\text{AgAsF}_6$  calcd.: C, 12.57; H, 2.11; F, 19.88; S, 33.55%). IR (Nujol mull): 1226w, 1163m, 908m, 740m, 728m, 700s, 395s  $\text{cm}^{-1}$ ; Raman: 803w, 748sh, 740m, 728m, 676s, 664s, 652s, 570w, 423s, 367w, 328w, 294s, 235w, 158s  $\text{cm}^{-1}$ .

The reaction of  $\text{AgAsF}_6$  and  $(\text{CH}_2\text{S})_3$  in a molar ratio of 1/4 results in the formation of  $[(\text{CH}_2\text{S})_3]_5\text{Ag}_2(\text{AsF}_6)_2\text{SO}_2$ .

*Preparation of  $[(\text{CH}_2\text{Se})_3]_2\text{Ag}(\text{AsF}_6)$ .* A mixture of 0.267 g (0.9 mmol) of  $\text{AgAsF}_6$  and 1.0 g (1.79 mmol) of  $(\text{CH}_2\text{Se})_3$  was cooled to  $-196^\circ\text{C}$  in a pressure flask and 25 ml of liquid  $\text{SO}_2$  were added. The flask was allowed to warm to room temperature and was stirred for an additional 12 h. The reaction mixture was filtered and concentrated over a period of 3 d until yellow crystals appeared. Yield 98%, m.p.  $132\text{--}135^\circ\text{C}$  (Found: C, 8.6, H, 1.4; F, 13.6  $\text{C}_6\text{H}_{12}\text{Se}_6\text{AgAsF}_6$  calcd.: C, 8.42; H, 1.40; F, 13.33%). IR (Nujol mull): 1328s, 1160w, 1150m, 1110m, 1045w, 970w, 818s, 720sh, 698vs, 630s, 520m, 392vs  $\text{cm}^{-1}$ .

#### *X-Ray structure determination of $[(\text{CH}_2)_3\text{S}]_2\text{Ag}(\text{AsF}_6)$*

A crystal  $0.6 \times 0.6 \times 0.2$  mm was mounted in a capillary and used to collect 3655 profile-fitted intensities [4] on a Stoe four-circle diffractometer (monochromated  $\text{Mo-K}_\alpha$  radiation,  $2\theta_{\text{max}}$   $50^\circ$ ). After Lorentz polarisation and absorption corrections.

TABLE I

ATOMIC COORDINATES ( $\times 10^4$ ) AND ISOTROPIC THERMAL PARAMETERS ( $\text{\AA}^2 \times 10^3$ ) FOR  $[(\text{CH}_2\text{S})_3]_2\text{Ag}(\text{AsF}_6)$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sup>a</sup></i>
Ag	5475(1)	2011(1)	1937(1)	105(1)
S(11)	2555(3)	1694(1)	1713(2)	45(1)
S(12)	4600(4)	1718(1)	4848(3)	58(1)
S(13)	4786(4)	564(1)	3039(3)	61(1)
S(21)	8304(3)	3211(1)	6796(3)	48(1)
S(22)	6318(3)	4349(1)	5153(3)	57(1)
S(23)	5939(3)	3024(1)	3865(3)	57(1)
C(11)	2671(12)	1901(5)	3551(10)	55(4)
C(12)	4647(14)	843(4)	4703(10)	57(4)
C(13)	2828(15)	831(5)	1859(12)	68(4)
C(21)	8245(14)	4068(4)	6313(13)	65(5)
C(22)	6130(12)	3885(4)	3601(10)	51(4)
C(23)	7973(11)	2854(4)	5072(10)	48(3)
As	365(1)	1032(1)	6884(1)	56(1)
F(1)	-1147(16)	1527(5)	6976(18)	199(9)
F(2)	1829(14)	536(5)	6824(15)	164(7)
F(3)	-848(17)	398(6)	6672(20)	203(10)
F(4)	-160(22)	1132(7)	5154(14)	214(9)
F(5)	1567(22)	1653(7)	6946(33)	328(19)
F(6)	761(30)	927(11)	8551(13)	319(14)

<sup>a</sup> Equivalent isotropic *U* defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor.

TABLE 2

BOND LENGTHS (Å) AND ANGLES (deg.) FOR  $[\{(\text{CH}_2\text{S})_3\}_2\text{Ag}]\text{AsF}_6^a$ 

Ag–S(11)	2.532(3)	Ag–S(23)	2.764(3)
Ag–S(21a)	2.515(3)	S(11)–C(11)	1.827(11)
S(11)–C(13)	1.795(10)	S(12)–C(11)	1.790(9)
S(12)–C(12)	1.812(10)	S(13)–C(12)	1.770(11)
S(13)–C(13)	1.808(11)	S(21)–C(21)	1.827(10)
S(21)–C(23)	1.787(10)		
S(22)–C(21)	1.791(10)	S(22)–C(22)	1.764(10)
S(23)–C(22)	1.811(9)	S(23)–C(23)	1.817(9)
S(11)–Ag–S(23)	100.6(1)	S(11)–Ag–S(21a)	153.4(1)
S(23)–Ag–S(21a)	103.7(1)	Ag–S(11)–C(11)	95.9(3)
Ag–S(11)–C(13)	98.5(4)	C(11)–S(11)–C(13)	100.8(5)
C(11)–S(12)–C(12)	101.1(5)	C(12)–S(13)–C(13)	100.4(5)
C(21)–S(21)–C(23)	99.7(5)	C(21)–S(21)–Ag(b)	103.9(4)
C(23)–S(21)–Ag(b)	95.9(3)	C(21)–S(22)–C(22)	101.3(5)
Ag–S(23)–C(22)	130.1(3)	Ag–S(23)–C(23)	102.0(3)
C(22)–S(23)–C(23)	99.9(4)	S(11)–C(11)–S(12)	114.3(6)
S(12)–C(12)–S(13)	113.9(6)	S(11)–C(13)–S(13)	115.1(6)
S(21)–C(21)–S(22)	115.1(5)	S(22)–C(22)–S(23)	113.3(6)
S(21)–C(23)–S(23)	112.3(6)		

<sup>a</sup> Symmetry operators: a,  $x, 1/2-y, -1/2+z$ ; b,  $x, 1/2-y, 1/2+z$ .

averaging equivalents gave 2899 unique reflections, 2439 of which with  $F > 4\sigma(F)$  were used for all calculations. Cell constants were refined from  $2\theta$  values of 44 reflections in the range  $20^\circ < 2\theta < 24^\circ$ .

*Crystal data:* monoclinic, space group  $P2_1/c$ ,  $a$  8.579(2),  $b$  20.618(4),  $c$  9.821(2) Å,  $\beta$  107.95(2)°,  $U$  1652.7 Å<sup>3</sup>,  $D_x$  2.30 g cm<sup>-3</sup>,  $Z$  = 4,  $\mu(\text{Mo-K}\alpha)$  4.0 mm<sup>-1</sup>.

The structure was solved by the heavy atom method and refined anisotropically to  $R$  = 0.078,  $R_w$  = 0.091 (weighting scheme  $w^{-1} = \sigma^2(F) + 0.0003F^2$ ). Hydrogen

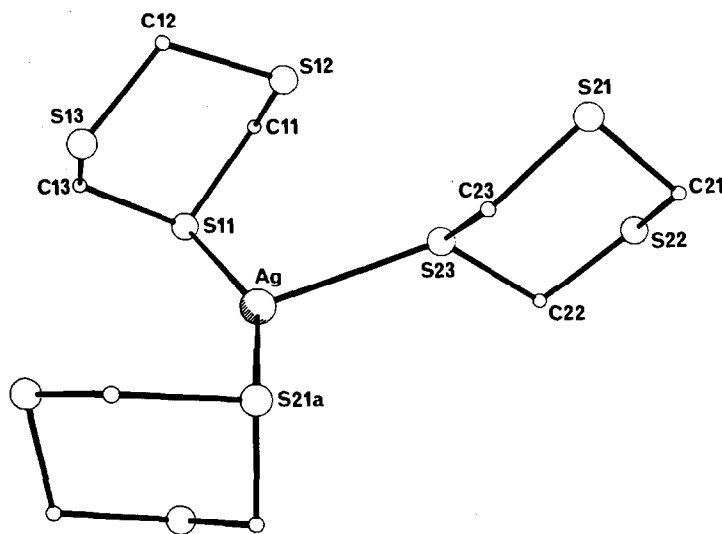


Fig. 1. The trigonally coordinated silver atom in  $[\{(\text{CH}_2\text{S})_3\}_2\text{Ag}]^+$ , showing the atom numbering scheme.

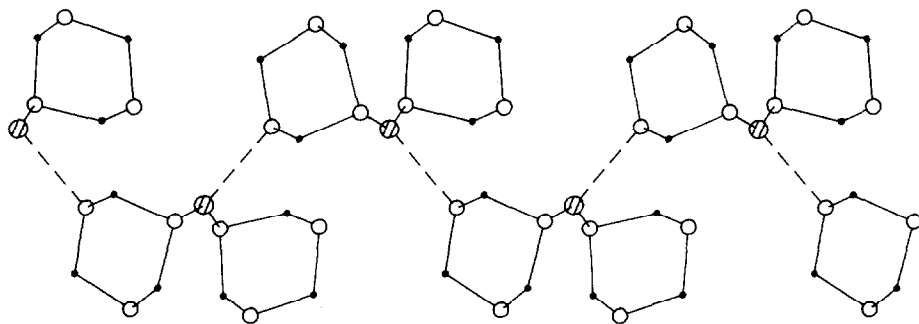


Fig. 2. Part of a chain polymer of  $[((\text{CH}_2\text{S})_3)_2\text{Ag}]^+$ ; view direction approximately along the  $a$  axis. The longer Ag-S bonds are indicated by dashed lines.

atoms were included in the refinement using a riding model. Final atom coordinates and derived parameters are given in Tables 1 and 2.

The silver atom is coordinated by the two sulphur atoms S(11), S(21a) to form a distorted linear unit (S-Ag-S  $153^\circ$ ). A further sulphur S(23) completes a distorted trigonal planar coordination (Fig. 1), but this Ag-S interaction is at  $2.76 \text{ \AA}$  ca.  $0.25 \text{ \AA}$  longer than the other two; there are no other Ag  $\cdots$  S contacts  $< 3.16 \text{ \AA}$ . Thus the structure may be considered to contain  $[((\text{CH}_2\text{S})_3)_2\text{Ag}]^+$  cations linked by the

TABLE 3

ATOMIC COORDINATES ( $\times 10^4$ ) AND ISOTROPIC THERMAL PARAMETERS ( $\text{\AA}^2 \times 10^3$ ) for  $[((\text{CH}_2\text{Se})_3)_2\text{Ag}]\text{AsF}_6$

	$x$	$y$	$z$	$U$
Ag	1881(2)	1410(4)	510(2)	102(3) <sup>a</sup>
Se(11)	404(2)	1021(5)	-1308(2)	80(3) <sup>a</sup>
Se(12)	1027(2)	-145(4)	551(2)	68(3) <sup>a</sup>
Se(13)	1614(2)	-1325(4)	-150(2)	61(3) <sup>a</sup>
Se(21)	1730(2)	4413(4)	485(3)	85(4) <sup>a</sup>
Se(22)	2845(2)	2575(5)	2290(2)	79(4) <sup>a</sup>
Se(23)	3056(2)	3040(5)	1067(3)	82(4) <sup>a</sup>
C(11)	272(18)	402(51)	-675(23)	100(13)
C(12)	1274(15)	-1760(39)	339(20)	65(9)
C(13)	790(15)	-729(40)	-1262(20)	73(10)
C(21)	2253(17)	4265(43)	1663(21)	82(11)
C(22)	3471(17)	3128(47)	2232(22)	86(11)
C(23)	2443(17)	4671(46)	602(24)	88(12)
As	1255(2)	3145(4)	2410(3)	72(3) <sup>a</sup>
F(1)	1354(19)	4685(29)	2224(27)	209(58) <sup>a</sup>
F(2)	1130(21)	1644(39)	2657(28)	240(60) <sup>a</sup>
F(3)	997(21)	2378(53)	1520(29)	250(68) <sup>a</sup>
F(4)	1473(19)	3824(55)	3276(22)	235(48) <sup>a</sup>
F(5)	2086(12)	2796(48)	3052(19)	189(33) <sup>a</sup>
F(6)	430(10)	3404(38)	1784(17)	161(26) <sup>a</sup>
S(1)	5000	0	5000	141(7)
S(2)	0	4953(32)	7500	170(9)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor.

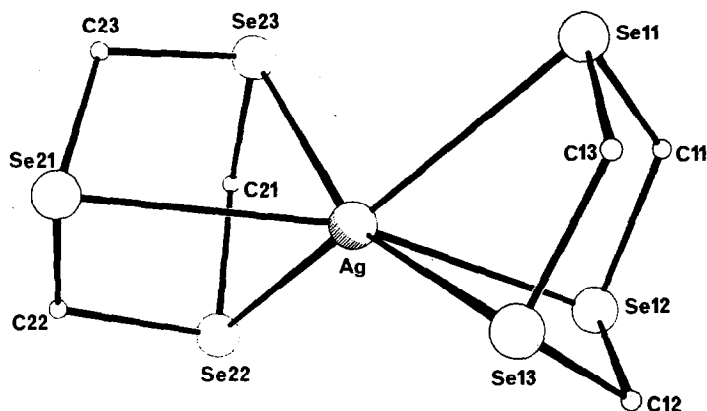


Fig. 3. The  $[(\text{CH}_2\text{Se})_3]_2\text{Ag}^+$  ion, showing the atom numbering scheme.

weak additional  $\text{Ag} \cdots \text{S}$  interaction to form polymeric chains, with two chains per cell parallel to the  $c$  axis (Fig. 2). The ion  $[(\text{CH}_2\text{S})_3]_2\text{Ag}_2^{2+}$  [1] also displays a wide range of  $\text{Ag}-\text{S}$  bond lengths (2.519–2.924 Å, shortest non-bonded distance 3.17 Å; we have arbitrarily regarded 3 Å as the maximum  $\text{Ag}-\text{S}$  bonding distance). The

TABLE 4

BOND LENGTHS (Å) AND ANGLES (deg.) FOR  $[(\text{CH}_2\text{Se})_3]_2\text{Ag}[\text{AsF}_6]$

$\text{Ag}-\text{Se}(11)$	3.05(1)	$\text{Ag}-\text{Se}(23)$	3.02(1)
$\text{Ag}-\text{Se}(12)$	2.92(1)	$\text{Ag}-\text{Se}(13)$	2.78(1)
$\text{Ag}-\text{Se}(21)$	2.86(1)	$\text{Ag}-\text{Se}(22)$	2.92(1)
$\text{Se}(11)-\text{C}(11)$	1.81(7)	$\text{Se}(11)-\text{C}(13)$	1.95(5)
$\text{Se}(12)-\text{C}(11)$	1.93(4)	$\text{Se}(12)-\text{C}(12)$	1.88(5)
$\text{Se}(13)-\text{C}(12)$	1.98(6)	$\text{Se}(13)-\text{C}(13)$	1.86(3)
$\text{Se}(21)-\text{C}(21)$	1.84(5)	$\text{Se}(21)-\text{C}(23)$	1.89(7)
$\text{Se}(22)-\text{C}(21)$	1.97(4)	$\text{Se}(22)-\text{C}(22)$	1.97(7)
$\text{Se}(23)-\text{C}(22)$	1.91(5)	$\text{Se}(23)-\text{C}(23)$	1.96(5)
$\text{Se}(12)-\text{Ag}-\text{Se}(11)$	66.6(2)	$\text{Se}(12)-\text{Ag}-\text{Se}(23)$	162.5(2)
$\text{Se}(13)-\text{Ag}-\text{Se}(11)$	67.1(2)	$\text{Se}(13)-\text{Ag}-\text{Se}(23)$	118.5(2)
$\text{Se}(21)-\text{Ag}-\text{Se}(11)$	92.9(2)	$\text{Se}(21)-\text{Ag}-\text{Se}(23)$	67.3(2)
$\text{Se}(22)-\text{Ag}-\text{Se}(11)$	149.1(2)	$\text{Se}(22)-\text{Ag}-\text{Se}(23)$	66.2(2)
$\text{Se}(12)-\text{Ag}-\text{Se}(13)$	69.1(2)	$\text{Se}(12)-\text{Ag}-\text{Se}(21)$	112.1(2)
$\text{Se}(13)-\text{Ag}-\text{Se}(21)$	158.2(2)	$\text{Se}(12)-\text{Ag}-\text{Se}(22)$	97.0(2)
$\text{Se}(13)-\text{Ag}-\text{Se}(22)$	133.4(2)	$\text{Se}(21)-\text{Ag}-\text{Se}(22)$	68.4(2)
$\text{Se}(11)-\text{Ag}-\text{Se}(23)$	130.4(2)	$\text{Ag}-\text{Se}(12)-\text{C}(11)$	85(2)
$\text{C}(11)-\text{Se}(11)-\text{C}(13)$	97(2)	$\text{C}(11)-\text{Se}(12)-\text{C}(12)$	96(2)
$\text{Ag}-\text{Se}(12)-\text{C}(12)$	85(2)	$\text{Ag}-\text{Se}(13)-\text{C}(13)$	91(1)
$\text{Ag}-\text{Se}(13)-\text{C}(12)$	87(1)	$\text{Ag}-\text{Se}(21)-\text{C}(21)$	87(1)
$\text{C}(12)-\text{Se}(13)-\text{C}(13)$	98(2)	$\text{C}(21)-\text{Se}(21)-\text{C}(23)$	99(2)
$\text{Ag}-\text{Se}(21)-\text{C}(23)$	89(1)	$\text{Ag}-\text{Se}(22)-\text{C}(22)$	90(1)
$\text{Ag}-\text{Se}(22)-\text{C}(21)$	83(1)	$\text{C}(22)-\text{Se}(23)-\text{C}(23)$	96(2)
$\text{C}(21)-\text{Se}(22)-\text{C}(22)$	95(2)	$\text{Se}(12)-\text{C}(12)-\text{Se}(13)$	114(2)
$\text{Se}(11)-\text{C}(11)-\text{Se}(12)$	122(3)	$\text{Se}(21)-\text{C}(21)-\text{Se}(22)$	117(3)
$\text{Se}(11)-\text{C}(13)-\text{Se}(13)$	116(2)	$\text{Se}(21)-\text{C}(23)-\text{Se}(23)$	116(3)
$\text{Se}(22)-\text{C}(22)-\text{Se}(23)$	113(2)		

ligands retain the chair conformation observed in the free ligand [5]. The  $\text{AsF}_6^-$  ions display large and anisotropic thermal parameters, possibly indicating some disorder. The thermal parameters of the silver atom are also rather large, as was observed in  $[(\text{S}_8)_2\text{Ag}]^+$  [6].

#### *X-Ray structure determination of $[\{(\text{CH}_2)_3\text{Se}\}_2\text{Ag}]\text{AsF}_6$*

Data were collected as for the sulphur analogue (see above) with the following differences:  $2\theta_{\text{max}} 45^\circ$ , 2757 reflections (2673 unique, 1676 observed). The crystal was of poor quality, showing wide and irregular profiles.

*Crystal data:* monoclinic,  $C2/c$ ,  $a$  28.80(4),  $b$  9.42(1),  $c$  22.40(4) Å,  $\beta$  137.4(1)°,  $U$  4113 Å<sup>3</sup>,  $Z = 8$ ,  $\mu(\text{Mo-K}\alpha)$  15.7 mm<sup>-1</sup>. In view of uncertainties regarding solvent of crystallisation (see below), we do not quote a crystallographic density.

The structure was solved by direct methods (to locate Ag, As and Se) and refined to  $R = 0.106$ ,  $R_w = 0.100$  (weighting scheme  $w^{-1} = \sigma^2(F) + 0.001 F^2$ ; Ag, Se. As and F anisotropic, C isotropic, H isotropic with riding model). Two substantial difference peaks on the special positions  $\frac{1}{2}, 0, \frac{1}{2}$  and  $0, y, \frac{3}{4}$  were interpreted as sulphur atoms of  $\text{SO}_2$  of crystallisation; these were refined isotropically. Several smaller difference peaks at distances of ca. 1.5 Å from S probably correspond to disordered O atoms, but could not be refined. The solvent sites may be partially occupied, since the solvent is easily lost, accounting for the poor quality of the crystals (cf. the elemental analysis, see above). Final atomic coordinates and derived parameters are given in Tables 3 and 4.

The silver atom is coordinated irregularly by all six selenium atoms of two ligands to form isolated  $[\{(\text{CH}_2\text{Se})_3\}_2\text{Ag}]^+$  units (Fig. 3); the sulphur and selenium analogues are thus not isostructural. The Ag–Se bond lengths lie in the range 2.78–3.05 Å; the next shortest Ag  $\cdots$  Se contact is 3.71 Å.

#### **Acknowledgements**

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