Table 3. *Interatomic distances (Å) and angles (°) for complexes of the type* $MM'_2[Co(NO_2)_6]$

	$BaK_2[Co(NO_2)_6]$	$PbK_2[Co(NO_2)_6]$	$PbRb_2[Co(NO_2)_6]$
Co—N	2·010 (3)	2·024 (3)	2·046 (3)
N—O	1·250 (3)	1·236 (4)	1·243 (2)
Ba—O or Pb—O	2·864 (2)	2·782 (3)	2·814 (2)
K—O or Rb—O	3·107 (2)	3·054 (2)	3·096 (1)
O—N—O	116·6 (3)	117·2 (4)	116·7 (1)
Co—N—O	121·7 (2)	121·4 (2)	121·7 (1)

Co^{III} $(t_{2g})^6$ electron configuration to give the low-spin Co^{II} $(t_{2g})^6(e_g{}^*)^1$ configuration. In contrast, a difference as large as 0·21 Å occurs between low-spin $(t_{2g})^6$ $Co(H_2O)_6^{3+}$ and high-spin $(t_{2g})^5(e_g{}^*)^2$ $Co(H_2O)_6^{2+}$ (Beattie, Best, Skelton & White, 1981).

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Decaselenium Bis(fluorosulfate)

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Abstract. $Se_{10}[SO_3F]_2$, $M_r = 987·7$, orthorhombic, $P2_12_12_1$, $a = 8·627$ (1), $b = 13·114$ (3), $c = 15·135$ (3) Å, $U = 1712·3$ (6) Å^3, $Z = 4$, $D_x = 3·83$ Mg m^{-3}, $\lambda(Mo\ K\bar{\alpha}) = 0·71069$ Å, $\mu = 23·19$ mm^{-1}, $F(000) = 1752$, $T = 295$ K, $R = 0·0749$ for 1779 observed reflections. The structure contains Se_{10}^{2+} cations (of the bicyclo[4.2.2]decane type) and fluorosulfate anions. Se—Se bond lengths in the cation vary in length from 2·246 (5) to 2·450 (5) Å.

Introduction. S, Se and Te can be oxidized under suitable conditions to polyatomic cations such as S_8^{2+}, Se_{10}^{2+} and Te_4^{2+} (Gillespie, 1979). The structures of several of these cations in the solid state have been determined (Gillespie, 1979). In order to determine if these structures are maintained in solution ^{77}Se and ^{125}Te NMR studies have been carried out (Burns, Granger & Schrobilgen, 1978; Lassigne & Wells, 1978). During a continuation of these studies the precipitate obtained from the reaction of equimolar amounts of selenium, tellurium and arsenic penta-fluoride in SO_2 solution was dissolved in 30% oleum at room temperature in order to record the NMR spectrum. This solution deposited a large quantity of fine scarlet-red crystals, which were washed with liquid SO_2. A few red-brown crystals formed from the pale-green SO_2 washings. We report here the X-ray analysis of the red-brown crystals which shows that

they have the composition $Se_{10}[SO_3F]_2$ and contain the previously reported Se_{10}^{2+} cation (Burns, Chan, Gillespie, Luk, Sawyer & Slim, 1980) as a fluorosulfate salt. The other products obtained in this series of reactions have not yet been identified.

Experimental. Dark red-brown crystals of $Se_{10}[SO_3F]_2$ occur as blocks and needles. Crystals selected and sealed in Lindemann capillaries in a dry-box equipped with a microscope. Crystal 0·360 × 0·170 × 0·188 mm in the [100], [011] and [01$\bar{1}$] directions. Precession photographs used to obtain preliminary cell and space-group information. Accurate unit-cell dimensions by least-squares refinement of 2θ, ω and χ for 15 high-angle ($25 < 2\theta < 29°$) reflections on a Syntex $P2_1$ diffractometer, Mo $K\bar{\alpha}$ radiation. Data collected using θ:2θ scans over a range ($K\alpha_1 - 0·9°$) to ($K\alpha_2 + 0·9°$). Scan rates varied between 3·0 and 29·3° min^{-1} depending on intensity of preliminary count. Stationary background counts measured at each end of the scan, each for one quarter of the scan time. Three standard reflections obtained after every 67 reflections showed a gradual decrease in intensity with time. 4176 reflections (including standards) in the quadrants $h,k,\pm l$ with $2\theta < 55°$. Lorentz and polarization corrections were applied to all data after the measured intensities had been rescaled to allow for the crystal decomposition (max. rescale factor 1·15). The density was not deter-

mined because of the great sensitivity of the crystals to moisture. At a later stage in the refinement when the composition of the crystal had been ascertained absorption corrections were made using the program *ABSORB* (*XRAY* system, 1976), and a 7 × 10 × 10 grid. A^* values were found to vary from 13·93 to 62·13. Repeat measurements of the same reflection were then averaged. Exclusion of systematically absent and zero data then resulted in a data set of 3112 reflections of which 1779 were considered observed [$F > 6\cdot0\sigma(F)$]. Although the composition of the crystal was initially uncertain, the structure was solved using the direct-methods routines of the program *SHELX*76 (Sheldrick, 1976). The best E map gave several heavy-atom positions with consistent vectors in the Patterson function. Several cycles of least-squares and Fourier calculations then revealed the compound to be the fluorosulfate salt of the previously known Se_{10}^{2+} cation (Burns *et al.*, 1980). Atomic assignments were made on the basis of temperature-factor and bond-length–bond-angle considerations. Least-squares refinement of this model minimizing $w||F_o|-|F_c||^2$ converged to the residuals $R = 0\cdot0883$ (Se and S anisotropic) for the data uncorrected for absorption and $R = 0\cdot0749$ when absorption corrections had been applied. Introduction of a weighting scheme and further least-squares refinement converged (no shift/e.s.d. > 0·26) to the residuals $R = 0\cdot0749$ and $wR = 0\cdot0765$ and a structure-factor calculation using all the non-zero data gave $R = 0\cdot1211$. In the final cycle of refinement weights were calculated using the expression $w^{-1} = \sigma(F)^2 + 0\cdot005795F^2$ and a comparison of $\langle w||F_o|-|F_c||^2\rangle$ as a function of F_o and $\sin\theta$ after the use of this scheme showed no systematic trends. A final difference Fourier map contained a few small peaks close to some of the atoms in the second fluorosulfate group. No correction for secondary extinction. (Refinement of the alternative 'hand' gave $R = 0\cdot0779$ and $wR = 0\cdot0793$.) The present R factor (7·5%) although slightly higher than normal is reasonable for this type of compound, particularly in view of the slight decomposition of the crystal during data collection and the high absorption corrections applied to the data. Computer programs: *XRAY* system (1976) and *SHELX*76 on a Cyber computer.

Discussion. The final atomic coordinates are included in Table 1 and some bond-length and bond-angle information in Table 2. Figs. 1 and 2 give views of the Se_{10}^{2+} cation and the crystal packing respectively.†

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† Lists of structure factors and anisotropic thermal parameters and a full version of Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42480 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic positional* (×10⁴) *and thermal parameters* (×10³) *for* $Se_{10}[SO_3F]_2$ *(standard deviations in parentheses)*

	x	y	z	U or U_{eq}*(Å²)
Se(1)	8577 (4)	5019 (3)	6073 (2)	42 (2)
Se(2)	7503 (5)	6130 (3)	4967 (3)	53 (2)
Se(3)	5634 (5)	7012 (3)	5699 (3)	65 (3)
Se(4)	3384 (4)	6127 (3)	5301 (3)	49 (2)
Se(5)	2752 (4)	5324 (3)	6571 (2)	44 (2)
Se(6)	3763 (4)	3621 (3)	6374 (2)	36 (2)
Se(7)	5296 (4)	3807 (2)	5021 (2)	32 (2)
Se(8)	7660 (4)	3394 (2)	5529 (2)	36 (2)
Se(9)	6786 (4)	5203 (4)	7297 (2)	54 (2)
Se(10)	5850 (5)	3594 (4)	7391 (2)	54 (2)
S(1)	3929 (11)	5810 (6)	−870 (5)	37 (5)
S(2)	−193 (13)	−2323 (7)	−2739 (7)	52 (6)
O(11)	4829 (30)	6366 (20)	−1444 (15)	56 (7)
O(12)	4620 (38)	4905 (24)	−619 (19)	80 (9)
O(13)	3305 (30)	6328 (20)	−151 (15)	55 (7)
F(14)	2484 (30)	5457 (18)	−1429 (14)	67 (6)
O(21)	−228 (41)	−1841 (27)	−1888 (20)	84 (9)
O(22)	1236 (48)	−2287 (29)	−3191 (23)	96 (11)
O(23)	−1313 (86)	−1766 (53)	−3238 (45)	207 (27)
F(24)	−985 (105)	−3329 (68)	−2546 (47)	334 (41)

$$* \, U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

Table 2. *Bond distances* (Å) *and bond angles* (°) *in the* Se_{10}^{2+} *cation and fluorosulfate anions*

	$Se_{10}[SO_3F]_2$	$Se_{10}[SbF_6]_2$ (Burns *et al.*, 1980) Cation 1	Cation 2
Se(1)—Se(2)	2·405 (5)	2·410 (9)	2·437 (8)
Se(1)—Se(8)	2·418 (5)	2·413 (9)	2·425 (10)
Se(1)—Se(9)	2·423 (5)	2·456 (8)	2·398 (8)
Se(2)—Se(3)	2·273 (6)	2·265 (8)	2·254 (10)
Se(3)—Se(4)	2·340 (6)	2·347 (10)	2·356 (8)
Se(4)—Se(5)	2·259 (5)	2·266 (8)	2·258 (9)
Se(5)—Se(6)	2·416 (5)	2·431 (8)	2·445 (9)
Se(6)—Se(7)	2·450 (5)	2·422 (8)	2·388 (8)
Se(6)—Se(10)	2·369 (5)	2·413 (10)	2·428 (10)
Se(7)—Se(8)	2·246 (5)	2·254 (9)	2·259 (8)
Se(9)—Se(10)	2·263 (7)	2·246 (9)	2·234 (9)
Se(2)—Se(1)—Se(8)	99·8 (2)	101·7 (4)	100·0 (3)
Se(2)—Se(1)—Se(9)	103·1 (2)	99·8 (3)	101·7 (3)
Se(8)—Se(1)—Se(9)	98·0 (2)	96·7 (3)	98·8 (3)
Se(1)—Se(2)—Se(3)	104·0 (2)	103·6 (3)	103·7 (3)
Se(2)—Se(3)—Se(4)	102·2 (2)	102·0 (4)	102·7 (3)
Se(3)—Se(4)—Se(5)	102·3 (2)	104·0 (4)	104·0 (3)
Se(4)—Se(5)—Se(6)	103·8 (2)	105·9 (3)	104·5 (4)
Se(5)—Se(6)—Se(7)	101·8 (2)	100·8 (3)	103·8 (3)
Se(5)—Se(6)—Se(10)	102·0 (2)	101·7 (3)	99·6 (3)
Se(7)—Se(6)—Se(10)	97·7 (2)	97·3 (3)	98·9 (3)
Se(1)—Se(8)—Se(7)	101·6 (2)	102·3 (3)	102·5 (3)
Se(6)—Se(7)—Se(8)	100·4 (2)	102·5 (3)	101·5 (3)
Se(1)—Se(9)—Se(10)	100·6 (2)	102·3 (3)	102·8 (3)
Se(6)—Se(10)—Se(9)	102·5 (2)	102·1 (3)	102·9 (3)

Fluorosulfate anions

S(1)—O(11)	1·37 (3)	S(2)—O(21)	1·43 (3)
O(12)	1·38 (3)	O(22)	1·41 (4)
O(13)	1·39 (3)	O(23)	1·43 (7)
F(14)	1·58 (3)	F(24)	1·51 (9)
O(11)—S(1)—O(12)	113 (2)	O(21)—S(2)—O(22)	116 (2)
O(13)	117 (2)	O(23)	104 (3)
F(14)	105 (1)	F(24)	102 (3)
O(12)—S(1)—O(13)	112 (2)	O(22)—S(2)—O(23)	109 (3)
F(14)	104 (2)	F(14)	121 (4)
O(13)—S(1)—F(14)	105 (2)	O(23)—S(2)—F(24)	104 (4)

The structure determination established the composition of the crystals as the fluorosulfate salt of the decaselenium cation Se_{10}^{2+}. The hexafluoroarsenate, hexafluoroantimonate and tetrachloroaluminate salts of Se_{10}^{2+} have previously been reported and the crystal structure of the hexafluoroantimonate salt has been determined (Burns et al., 1980). The structure of the Se_{10}^{2+} cation in both the SO_3F^- and SbF_6^- salts may be described as a six-membered boat-shaped ring linked across the middle by a chain of four Se atoms, or as a bicyclo[4.2.2]decane-type structure (Gillespie, 1979). It is isostructural with the $Te_2Se_8^{2+}$ cation in $[Te_2Se_8]$-$[AsF_6]_2[SO_2]$ (Boldrini, Brown, Gillespie, Ireland, Luk, Slim & Vekris, 1976). Both chiral forms of the cations are present in $Se_{10}[SbF_6]_2$ and $[Te_2Se_8][AsF_6]_2[SO_2]$; the two enantiomorphs are related by the centers of symmetry in the space group $P2_1/c$. In the present structure only one enantiomorph is found in the noncentrosymmetric space group $P2_12_12_1$. Se—Se bond
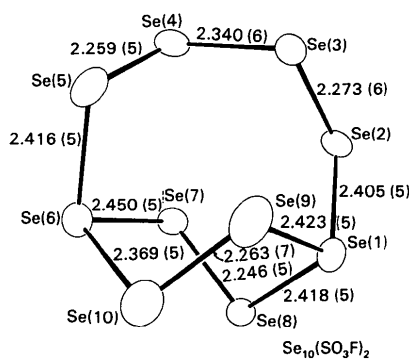
Table 3. *Some significant intra-ionic and inter-ionic contact distances* (Å)

Intra-cation	$Se_{10}[SO_3F]_2$	$Se_{10}[SbF_6]_2$ (Burns et al., 1980) Cation 1	Cation 2
Se(3)—Se(9)	3·530 (5)	3·386 (9)	3·405 (9) (3···8)
Se(4)—Se(7)	3·486 (5)	3·485 (9)	3·428 (9) (4···10)
Se(8)—Se(10)	3·233 (5)	3·301 (9)	3·372 (10) (7···9)

All other intra-cation Se···Se > 3·58 Å

Shortest Se···Se inter-cation
$Se_{10}[SO_3F]_2$:   Se(1)···Se(5)(x, y, −1 + z)   3·702 (5)

Shortest Se···O(F) contacts (<3·0 Å)
$Se_{10}[SO_3F]_2$:	2·79 (9)	[Se(9)···F(24)(1 − x, 1 + y, 1 + z)]
	2·89 (3)	[Se(7)···O(13)(1 − x, −$\frac{1}{2}$ + y, $\frac{1}{2}$ − z)]
	2·97 (3)	[Se(2)···O(12)($\frac{3}{2}$ − x, 1 − y, $\frac{1}{2}$ + z)]
	2·92 (2)	[Se(6)···O(13)(1 − x, $\frac{1}{2}$ + y, $\frac{1}{2}$ − z)]
	2·97 (3)	[Se(9)···O(11)(x, y, 1 + z)]

Fig. 1. *ORTEP* view (Johnson, 1965) of the Se_{10}^{2+} cation showing the atomic notation used in the structure determination as well as some principal bond lengths (Å).
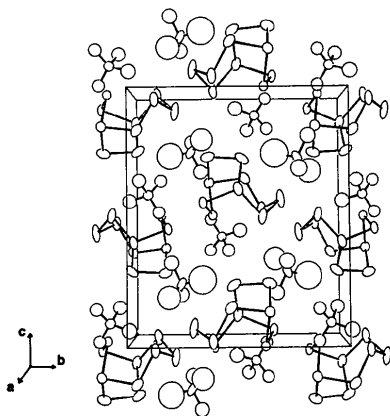

Fig. 2. The packing arrangement of $Se_{10}[SO_3F]_2$ as viewed down the a axis.

lengths and Se—Se—Se bond angles in the present cation are similar to those in the hexafluoroantimonate salt of Se_{10}^{2+} (Table 2). In both cations the bond distances vary over a wide range [2·246 (5) to 2·450 (5) Å] and the bonds are alternately long and short on moving away from the two three-coordinated atoms. The shortest of the Se—Se bonds have lengths similar to those in the Se_4^{2+} cation which nominally have a bond order of 1·25 (Cardinal, Gillespie, Sawyer & Vekris, 1982; Burns et al., 1980).

The dimensions of the two fluorosulfate anions (Table 2) show that both are slightly flattened tetrahedra with approximate C_{3v} symmetry. Bond lengths are similar to those observed in other examples of this anion (Gillespie, Kent & Sawyer, 1981). The thermal parameters indicate that the anion $[S(2)O_3F^-]$ is only weakly held in the lattice.

Some intra- and inter-cation Se···Se contact distances and some Se···F and Se···O anion—cation interactions are significantly shorter than the sum of the van der Waals radii (Se + Se = 3·80 Å; Se + F = 3·37 Å; Se + O = 3·42 Å) and are given in Table 3 (a full version of which has been deposited). As discussed elsewhere (Burns et al., 1980; Gillespie, 1979) the Se···Se contacts (3–9), 3·530 (5) Å, (4–7), 3·486 (5) Å, and (8–10), 3·233 (5) Å, may be regarded as weak bonding interactions. The transannular contact (8–10) is shorter and the contacts (3–9) and (4–7) somewhat longer than those in $Se_{10}[SbF_6]_2$ (Table 3). Many of the intermolecular Se···F contacts in the present structure are comparable in length to those in the $Se_{10}[SbF_6]_2$ structure; it is clear that they play a significant role in the stabilization of the cation in both salts. Contacts involving $S(2)O_3F^-$ are generally longer and weaker than those involving $S(1)O_3F^-$.

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Crystal Structure Determination of α-Aminoisobutyrato(α-Aib)–Transition-Metal Complexes. I. Structure of Bis(α-Aib)diaquanickel(II) Trihydrate (I) and Refinement of Bis(α-Aib)diaquanickel(II) Dihydrate (II)

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Abstract. (I): $[Ni(C_4H_8NO_2)_2(H_2O)_2].3H_2O$, $M_r = 353.01$, triclinic, $P\bar{1}$, $a = 8.262$ (2), $b = 9.717$ (2), $c = 11.441$ (2) Å, $\alpha = 103.36$ (2), $\beta = 110.32$ (1), $\gamma = 103.27$ (2)°, $V = 788.3$ (8) Å^3, $Z = 2$, $D_x = 1.49$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.197$ mm^{-1}, $F(000) = 372$, $T = 288$ K, $R = 0.045$ for 1838 unique reflections $[I > 3\sigma(I)]$ and 182 parameters. (II): $[Ni(C_4H_8NO_2)_2(H_2O)_2].2H_2O$, $M_r = 335.00$, monoclinic, $P2_1/c$, $a = 11.429$ (3), $b = 14.035$ (2), $c = 9.900$ (7) Å, $\beta = 108.67$ (4)°, $V = 1504$ (2) Å^3, $Z = 4$, $D_x = 1.48$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 1.248$ mm^{-1}, $F(000) = 704$, $T = 288$ K, $R = 0.085$ for 869 unique reflections $[I > 2\sigma(I)]$ and 104 parameters. In both compounds the complex displays approximate local C_2 symmetry with the twofold axis bisecting the angle subtended by the Ni^{2+} ion and the coordination water O atoms. Both structures are built from almost identical layers of molecules in which the Ni^{2+} ions lie on planes containing the two shortest Ni–Ni interatomic distances.

Introduction. Complexes of transition metals with amino acids have been extensively studied as models for the metal-binding sites in proteins (Freeman, 1973; Brill, 1977). The observation of magnetic phase transitions in some of these complexes, believed to be due to superexchange interactions through the net of hydrogen bonds commonly observed, added considerable interest to the study of new compounds and to the review of earlier data (Castellano, Nascimento & Calvo, 1982).

Attempts to obtain samples of the complex bis(α-Aib)diaquanickel(II) dihydrate (II) suitable for magnetic measurements produced crystals with unit-cell parameters essentially equal to those described by Noguchi (1962) and also others with different unit-cell parameters and crystal symmetry. A crystal structure determination showed this last compound to be $[Ni(\alpha\text{-Aib})_2(H_2O)_2].3H_2O$ (I). In spite of crystallizing in different space groups the structures turned out to be remarkably similar, displaying almost identical patterns of hydrogen bonds. To show this the structure of (II) was redetermined in order to locate its H atoms. Refinement of compound (II) and the crystal structure determination of (I) are reported below.