Synthesis and structure of $\{[\mathrm{Gd(OSO)_3(\mu\text{-}F_2AsF_4)_{6/2}}]\cdot 0.25\mathrm{SO_2}\}_m$

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Oxidation of lanthanide metals with AsF_5 in liquid SO_2 yields the corresponding polymeric $\{[M(SO_2)_n](AsF_6)_3\}_m$ (1a–j, M = Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb) where the metal centres are bridged by AsF_6 units; the X-ray crystal structure of the Gd complex 1g is reported.

The synthesis of sulfur dioxide–metal hexafluoroarsenates by oxidation of metals (M = Mn, Fe, Co, Ni, Cu, Cd, Mg) with AsF_5 in liquid SO_2 is described in the literature.[1–4] Due to the poorly coordinating solvent SO_2 and the weakly interacting counter ions AsF_6^- the metal centres in these complexes are almost 'naked'. Even very weak σ-donors (*e.g.* OPF_3, NSF_3, NSF)[5–7] can be added.

According to literature reports the highly reactive lanthanide metals undergo a redox reaction when treated with SO_2 in Me_2SO yielding mostly unidentified product mixtures.[8] In liquid SO_2 itself, at low temperatures, redox reactions with the solvent are very slow; at −25 °C with AsF_5 **1a–j** were isolated in 10–50% yield. (Scheme 1).†

In reaction (1), no hexafluoroarsenates were isolated at higher temperatures, probably as a result of passivation of the metal surface. Compounds of type **1** are also formed from $LnCl_3$ and $AgAsF_6$ together with other products,[9] but purification is more difficult.

$$2\,\mathrm{Ln} + 9\,\mathrm{AsF_5} \xrightarrow[-25\,^{\circ}\mathrm{C},\ 3\ \mathrm{weeks}]{\mathrm{SO_2}} 1/m\,\{[\mathrm{Ln(SO_2)}_n](\mathrm{AsF_6})_3\}_m + 3\,\mathrm{AsF_3} \tag{1}$$

1a–j: Ln = Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb

$$\mathrm{LnF_3} + \mathrm{AsF_5} \xrightarrow[\text{room temp.}]{\mathrm{SO_2}} \text{very slow reaction} \tag{2}$$

Scheme 1

Žemva and coworkers have isolated $LnF_3\cdot 2AsF_5$, $2LnF_3\cdot 3AsF_5$, $LnF_3\cdot 2BF_3$ and $2LnF_3\cdot 3BF_3$ from LnF_3 and $AsF_5(BF_3)$ in anhydrous HF.[10–12] A tris(hexafluoroarsenate) could only be isolated from LaF_3, the best fluoride base in this

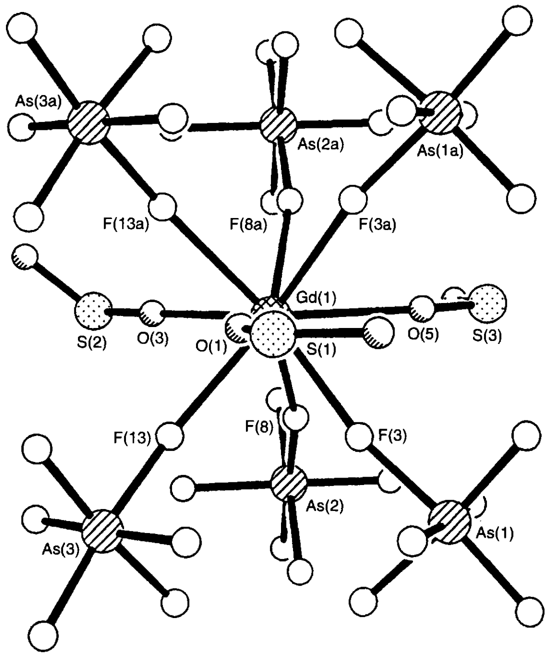

Fig. 1 Structure of the cation of **2g** with selected bond distances (pm) and angles (°): Gd–F 233.0(8)–234.2(7), Gd–O 243(2)–245(1), S–O_{br} 141(2)–143(1), S–O_t 139(6)–140.4(5); O–Gd–O 119.3(6)–121.0(6), O–S–O 113(4)–117.4(10); Φ(F3) 42.6, Φ (F8) 43.1, Φ (F13) 44.5 (Φ: angle between the Gd centre and the middle of the triangular faces)[17]

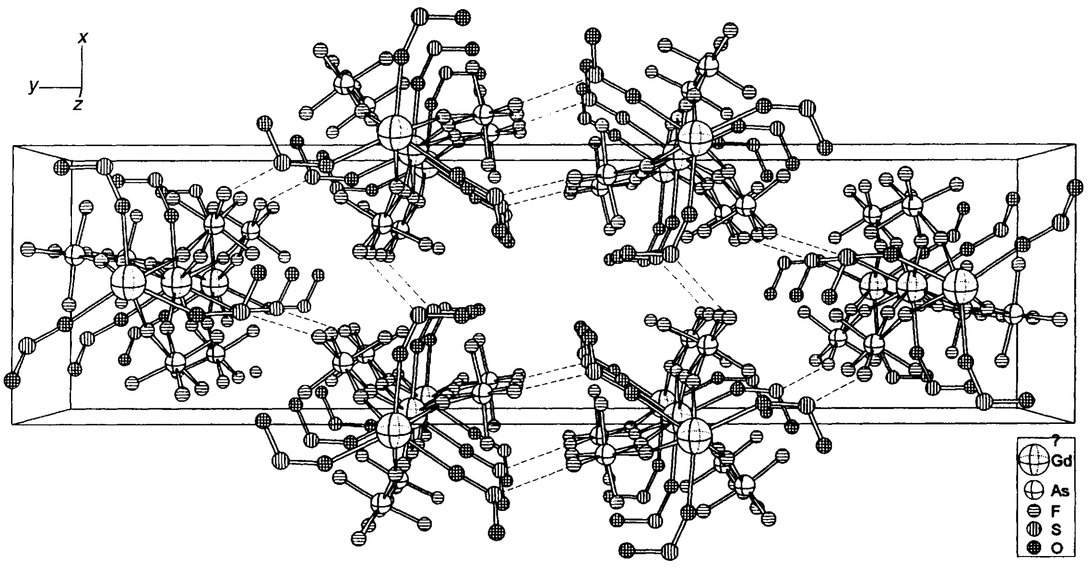

Fig. 2 Representation of the crystal packing of **2g**

series.[13] If the trifluorides are stirred with an excess of AsF_5 ($LnF_3:AsF_5 = 1:4–5$) in liquid SO_2, very little reaction is observed even after some weeks.

Salts **1** are stable at low temperature but at room temperature are only stable in an atmosphere of SO_2. In vacuum, rapid loss of SO_2 and much more slowly, of AsF_5 occurs. This reaction is reversible. Compounds **1** were characterised by elemental analysis and IR spectroscopy;‡ the X-ray crystal structure of the Gd derivative **1g** is shown in Fig. 1, Fig. 2 shows the packing in the crystal.§

Crystals of **1g** are orthorhombic in space group *Pbam* with $Z = 4$. The Gd ions are nine-coordinate with the fluoride atoms of the AsF_6^- ions occupying the corners of the surrounding trigonal prism, the rectangular faces of the prism are capped by OSO ligands. Stacks are formed by connection of the Gd^{III} ions to the edges of AsF_6^- octahedra. These are interconnected by weak fluoride bridges between the AsF_6^- octahedra and the sulfur centres (F···S 290–340 pm) of the coordinated SO_2 ligands. (Fig. 2). By this interaction $(\text{–GdFAsFSO–})_n$ rings ($n = 2,3,4$) are formed from which channels are created. In the largest of the channels is inserted additional SO_2.

Preliminary results show that compounds **1** are excellent starting materials for extended coordination chemistry, *e.g.* NSF_3, $OPCl_3$, CH_3CN may be introduced as ligands.

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Footnotes

† *Preparation of* **1**: 20 ml of SO_2 were condensed onto 1–2 g of pure metal powder or filings at −196 °C in a thick-walled Schlenk vessel,[14] then an excess of AsF_5 was added. *Direct* contact of gaseous AsF_5 with the metal powder must be avoided owing to vigorous reaction and possible combustion. After 2–3 weeks, insoluble by-products were separated by filtration, and volatiles were removed at −20 °C under vacuum. The products were further purified by recrystallisation from SO_2–AsF_5 at room temp. **1a** (50%), **1b–e** (30–40%), **1f–i** (20–30%) and **1j** (10%) were isolated as long needles. With the exception of **1d** (pale green), **1e** (pale violet), and **1i** (pale pink) the compounds are colourless. **1g**: IR (Nujol, Kel-F mull): 1336vs, 1156vs, 765s, 738vs, 680s, 548m, 524m, 516 (sh) cm^{-1}. Elemental analysis. Calc. As, 24.1; F, 36.7; S, 11.2. Found: As, 23.8; F, 36.7; S, 11.35%.

‡ **1a–j** show the characteristic ν_{as} and ν_{sym} for the SO_2 ligand at 1333–1336 and 1151–1156 cm^{-1} respectively and these are almost independent of the central atom despite the large differences in the ionic radii (*e.g.* La^{III} 135.6, Yb^{III} 118.2 pm for coordination number nine).[15]

§ *Crystal data* for $As_3F_{18}GdO_6S_3 \cdot 0{,}25SO_2$: orthorhombic, space group *Pbam*, $a = 956.5(2)$, $b = 3659.7(8)$, $c = 579.40(10)$ pm, $U = 2.0282(7)$ nm^3, $Z = 4$, $D_c = 3.053$ g cm^{-3}, $\mu = 8.644$ mm^{-1}, $F(000) = 1716$, crystal dimensions 0.4 × 0.15 × 0.1 mm. 1967 reflections collected with $2.7 < \theta < 25.0°$, 1967 unique used in the structural analysis. The data set was collected on a Siemens P4 diffractometer using Mo-Kα radiation ($\lambda = 71.073$ pm) at 173 K. The structure was solved by direct methods.[16] All atoms were refined anisotropically. An empirical absorption correction using ψ-scans was applied. The refinement (200 parameters) converged with $wR2 = 0.1358$ ($R1 = 0.0656$) and final difference electron density maxima and minima of 1906 and −1429 e nm^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/269.

References

1 P. A. W. Dean, *J. Fluorine Chem.*, 1975, **5**, 499.

2 C. D. Desjardins and J. Passmore, *J. Fluorine Chem.*, 1975, **6**, 379.

3 L. C. Damude and P. A. W. Dean, *J. Organomet. Chem.*, 1979, **168**, 123.

4 R. Hoppenheit, W. Isenberg and R. Mews, *Z. Naturforsch. Teil B*, 1982, **37**, 1116.

5 R. Mews, *J. Chem. Soc., Chem. Commun.*, 1979, 278.

6 U. Behrens, R. Hoppenheit, W. Isenberg, E. Lork, J. Petersen and R. Mews, *Z. Naturforsch., Teil B*, 1994, **49**, 238.

7 B. Buß, P. G. Jones, R. Mews, M. Noltemeyer and G. M. Sheldrick, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 231; G. Hartmann, P. G. Jones, R. Mews and G. M. Sheldrick, *Z. Naturforsch., Teil B*, 1980, **35**, 1191.

8 W. D. Harrison, J. B. Gill and D. C. Goodall, *J. Chem. Soc., Chem. Commun.*, 1976, 540.

9 $Cl_3AsO \cdot AsF_5$ was isolated from the reaction of $PrCl_3$ and $AgAsF_6$: J. Petersen, E. Lork and R. Mews, *Chem. Commun.*, 1996, 1897.

10 M. Fele-Beuermann, S. Miličev and B. Žemva, *13th Int. Symp. Fluorine Chem.*, Bochum 1991, Abstracts, p. 325; *J. Fluorine Chem.*, 1992, **59**, 329.

11 K. Lutar, M. Fele-Beuermann and S. Miličev, *14th Int. Symp. Fluorine Chem.*, Yokohama 1994, Abstracts, p. 2.

12 Z. Mazej, K. Lutar and B. Žemva, *11th Eur. Symp. Fluorine Chem.*, Bled, 1995, Abstracts p. 129.

13 NdF_3 reacts with SbF_5 to give $Nd(SbF_6)_3$: A. F. Clifford, H. C. Beachell and W. M. Jack, *J. Inorg. Nucl. Chem.*, 1957, **5**, 57.

14 G. Hartmann, R. Froböse, R. Mews and G. M. Sheldrick, *Z. Naturforsch., Teil B*, 1982, **37**, 1234.

15 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

16 Structure solution and graphics, Siemens SHELXTL-Plus: G. M. Sheldrick, Release 4.0 for Siemens R3 Crystallographic Research Systems, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1989; structure refinement: SHELXL-93, G. M. Sheldrick, University of Göttingen.

17 M. C. Favas, D. C. Kepert, J. M. Patrick and A. H. White, *Aust. J. Chem.*, 1983, **36**, 483.

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