[30] A detailed experimental description of the synthesis of **3** will be published elsewhere.
[31] Unfortunately the small crystal size of the 1:1 complexes did not permit X-ray structure analysis.
[32] Differential scanning calorimetry measurements were performed on a Perkin-Elmer DSC-7 with a 10 K min^{-1} scan rate. GPC analyses were obtained on an HPLC system utilizing an Altex Model 110A pump, a Rheodyne model 7125 injector with a 100 μL injection loop, through two American Polymer Standards 10 micron mixed bed columns, and a Knauer differential-refractometer. The molecular weights and polydispersities are reported versus monodisperse polystyrene standards. Microscopic observations of the textures were made using a Zeiss Universal Polarizing Microscope equipped with a Minolta camera. Powder X-ray diffraction measurements were performed by using a SCINTAC INC., USA XDS-2000 instrument equipped with a high-temperature attachment.
[33] Triphenylene **1** displayed discotic hexagonal liquid crystalline mesophase behavior. The polarized optical micrographs showed fan-shaped textures characteristic of discotic hexagonal mesophases.
[34] If phase separation instead of mixing had taken place, signals characteristic of the single compounds would have been detected.
[35] A small excess of a component can be detected in the DSC through the signals characteristic of the single compounds.

$(PhTe)_3^-$: The Anionic Tellurium Analogue of I_3^-**

Anna C. Hillier, Sung-Ying Liu, Andrea Sella,* and Mark R. J. Elsegood

The chemistry of tellurium is an intriguing area for solid-state chemists, and numerous unexpected examples of structures not easily rationalized by simple models of bonding have come to light.[1] Tritelluride units are a recurring motif in this chemistry, although these are often found as part of polymeric networks in which the interatomic interactions may be thought of as being supported by the network. Such structures are often related to those of the polyhalides, in particular I_3^-; the direct analogue, the Te_3^{4-} ion, remains elusive.[2, 3] The classic bent hypervalent Zintl ion Te_3^{2-} was first isolated by Corbett and Cisar in 1977.[4–6] A cluster containing the linear selenium analogue Se_3^{4-} has been reported where the Se_3 unit forms part of an overall Sm_3Se_{11} cluster.[7] A formal (but cationic) triiodide analogue, pentamesityltritellurium, was synthesized recently by addition of a Te_1 cation to a Te_2 unit.[8] We now report the preparation of the corresponding *anionic* analogue of triiodide by the direct addition of diphenylditelluride to a tellurolate anion formed by reduction with divalent samarium.

Reductive cleavage of dichalcogenides RQQR (Q = S, Se, Te) is a convenient method for the synthesis of lanthanide chalcogenolates.[9–13] Reaction of diphenylditelluride (0.5 molar equiv) with $[Sm(Tp^{Me,Me})_2]$[14, 15] ($Tp^{Me,Me}$ = hydrotris(3,5-dimethylpyrazolyl)borate) in toluene gave an orange solution, from which **1** could be isolated as a bright orange powder [Eq. (1)]. Complex **1** gives a simple ^1H NMR spectrum similar to that observed for $[Sm(Tp^{Me,Me})_2(OTf)]$ ($Tf = F_3CSO_2$) at room temperature.[16] The *ortho* hydrogen atoms of the phenyl group are significantly deshielded by the paramagnetic samarium center, suggesting a close interaction between the tellurium atom and the metal.

$$[Sm(Tp^{Me,Me})_2] + 0.5\,PhTePh \rightarrow \underset{\mathbf{1}}{[Sm(Tp^{Me,Me})_2(TePh)]} \qquad (1)$$

Addition of a 1.5-fold excess of PhTeTePh to $[Sm(Tp^{Me,Me})_2]$ resulted in the formation of an orange solution, from which a moderately air sensitive deep red powder of stoichiometry $[Sm(Tp^{Me,Me})_2(TePh)_3]$ (**2**) was isolated [Eq. (2)]. Compound **2** could also be prepared by addition of PhTeTePh to a solution of **1**.

$$[Sm(Tp^{Me,Me})_2] + 1.5\,PhTeTePh \rightarrow \underset{\mathbf{2}}{[Sm(Tp^{Me,Me})_2(TePh)_3]} \qquad (2)$$

The ^1H NMR spectrum of **2** was similar to that of **1**. The chemical shifts of the phenyl protons were, however, normal and apparently unaffected by the paramagnetic samarium center. The spectrum was temperature invariant, consistent with a symmetrical and nonfluxional coordination sphere around the metal. These observations are in agreement with a saltlike formulation, implying a six-coordinate metal center analogous to that in $[Sm(Tp^{Me,Me})_2]BPh_4$.[17] The ^{125}Te spectrum of **2** at room temperature consists of a single peak at $\delta = 415$, which is very similar to the chemical shift of diphenylditelluride ($\delta = 422$). Although there was a considerable temperature dependence of the signal, no broadening of the signal was observed down to −80 °C.

Compound **2** was crystallized in both unsolvated (**2a**) and solvated forms (**2b**) from toluene. The structures show similar gross features, but only **2b** will be discussed here as the quality of the dataset for **2a** was marginal. The asymmetric unit consists of well-separated ions $[Sm(Tp^{Me,Me})_2]^+$ and $[Te_3Ph_3]^-$ (Figure 1) and half a molecule of toluene. No significant intermolecular or interionic contacts were noted. The cation is six-coordinate and similar to those in $[Sm(Tp^{Me,Me})_2]I$ and $[Sm(Tp^{Me,Me})_2]BPh_4$,[17] and the average Sm–N bond length (245(5) pm) is typical of this kind of system.

The $[Te_3Ph_3]^-$ anion is very slightly bent (∢(Te-Te-Te) 172.92(3)°), consistent with the VSEPR prediction. This is in contrast to the diorganyltritellurides, which show significant

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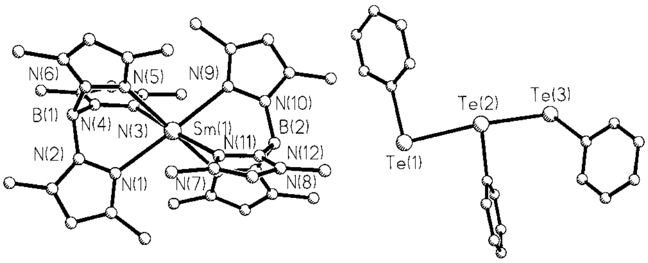

Figure 1. Ball-and-stick view of the cation and anion units in **2b.** Selected bond lengths [pm] and angles [°]: Te(1)–Te(2) 311.2(1), Te(2)–Te(3) 293.9(1); Te(1)-Te(2)-Te(3) 172.92(3).

bending at the central tellurium atom (100–103°),[18, 19] and the recently reported $[\{(Mes)_2Te\}_2Te(Mes)]^+$ cation (159.51 (3)°; Mes = 2,4,6-$Me_3C_6H_2$).[8] The anion of **2** is unsymmetrical with Te–Te bond lengths of 293.9(2) and 311.3(1) pm. Both distances are significantly longer than in singly bonded compounds such as organoditellurides RTeTeR (typically 269–275 pm),[11, 20–23] in the Te_2^{2-} bridging group of $[(SmCp^*_2)_2(\mu\text{-}Te_2)]$ (277.3(1) pm),[24] in the tritellurides $[\{(Me_3Si)_3Si\}_2Te_3]$ (271.0(1) pm)[18] and $[(2\text{-pyrPh})_2Te_3]$ (277.6(1) pm, pyr = pyridyl),[19] in the crown-shaped Te_8 rings of Cs_3Te_{22} (280(2) pm),[25] and in elemental tellurium itself (283.45(8) pm).[26] Rather, the Te–Te distances are comparable to those observed in the pentamesitylditellurium cation (304.91(10) and 297.91(10) pm)[8] and in the linear polyiodide analogue Te_5^{4-} present in NaTe (282–308 pm).[27] A similarly long Te–Te distance is also found in the complex $[Ru_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}TePh)_2(\mu\text{-}PhTeTePh)]$ with an intact bridging ditelluride moiety (290.1(3) pm).[28]

The asymmetry of the ion, suggesting a neutral diphenylditelluride unit bound to a phenyltellurolate anion, is reminiscent of the triiodide ion, which has been isolated in both symmetrical[29] and unsymmetrical structures,[30] depending upon the countercation. This analogy is further supported by the fact that we have also prepared the corresponding triiodide $[Sm(Tp^{Me,Me})_2]I_3$ (**3**) by the reaction of $[Sm(Tp^{Me,Me})_2]$ with excess iodine in toluene.

It is quite suprising to us that the $(TePh)_3^-$ anion has not been reported previously since it appears to be so easy to prepare in high yield. We assume that it is simply stabilized in the solid state by the presence of the large $[Sm(Tp^{Me,Me})_2]^+$ cation. Experiments are in progress to verify whether the $(TePh)_3^-$ anion can be isolated after reduction with alkali metals in the presence of crown ethers. Preliminary experiments suggest, however, that sulfur and selenium analogues cannot be prepared analogously.

Experimental Section

1: $[Sm(Tp^{Me,Me})_2]$ (100 mg, 0.13 mmol) and Te_2Ph_2 (27 mg, 0.065 mmol) were stirred in toluene at room temperature. The purple solid dissolved to give a red-orange, slightly turbid solution, which was filtered to give a clear deep red solution. The volume was reduced to 10 mL, and the solution cooled slowly to −20 °C to give dark red crystals of **1**. Yield: 66 mg (54 %). X-ray quality crystals were obtained by slow cooling of a solution in toluene. Elemental analysis calcd for $C_{36}H_{49}N_{12}B_2SmTe$: C 48.32, H 5.42, N 16.63; found: C 48.71, H 5.37, N 16.40; ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = -0.695$ (s, 18 H; 3-Me), 2.13 (s, 18 H; 5-Me), 5.465 (s, 6 H; CH), 7.35 (m, 2 H; *o*-Ph), 7.49 (m, 1 H; *p*-Ph), 9.47 (d, 2 H; *o*-Ph); IR (KBr): $\tilde{\nu} = 2554\,cm^{-1}$ (BH).

2: Compound **2** was prepared according to a procedure analogous to that of **1** using Te_2Ph_2 (83 mg, 0.20 mmol). Yield: 72 mg (41 %). X-ray quality crystals were obtained by slow cooling of a solution in toluene. Elemental analysis calcd for $C_{48}H_{59}N_{12}B_2SmTe_3$: C 42.33, H 4.38, N 12.37; found: C 43.28, H 4.36, N 12.50; ^{1}H NMR (300 MHz, C_6D_6, 20 °C, TMS): $\delta = -0.99$ (s, 18 H; 3-Me), 3.08 (s, 18 H; 5-Me), 5.53 (s, 6 H; CH), 7.19 (m, 5 H; Ph); ^{13}C NMR (100.16 MHz, C_6D_6, 20 °C, TMS): $\delta = 11.3$ (q, 3 or 5 Me), 14.2 (q, 5 or 3 Me), 105.4 (d, C-H), 128.1 (d, Ph), 129.3(s, Ph), 137.6 (d, Ph), 139.0 (d, Ph), 145.5 (s, C(3) or C(5)), 149.4 (s, C(5) or C(3)); ^{125}Te NMR (126.38 MHz, [D$_8$]toluene, 20 °C, Me_2Te): $\delta = 415$ (s); IR (KBr): $\tilde{\nu} = 2554\,cm^{-1}$ (BH).

3: To a purple slurry of $[Sm(Tp^{Me,Me})_2]$ (100 mg, 0.13 mmol) in toluene at room temperature was added a solution of iodine (51 mg, 0.2 mmol). An immediate color change from purple to orange was observed along with the formation of an orange precipitate. The toluene was removed under reduced pressure, and the orange solid redissolved in dichloromethane. Addition of diethyl ether resulted in precipitation of the product. The mixture was allowed to settle for 1 h, the yellow supernatant was decanted, and the orange brown powder (**3**) was dried at room temperature under dynamic vacuum. Yield: 104 mg (71 %). Elemental analysis calcd for $C_{36}H_{49}N_{12}B_2SmI_3$: C 32.02, H 3.94, N 14.93; found: C 31.73, H 3.83, N 14.59; ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): $\delta = -2.57$ (s, 18 H; 3-Me), 4.03 (s, 18 H; 5-Me), 5.21 (s, 6 H; CH); ^{13}C NMR (100.16 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 9.3$ (q; 3 or 5 Me), 15.3 (q; 5 or 3 Me), 102.1 (d; C-H), 144.0 (s; C(3) or C(5)), 147.6 (s; C(5) or C(3)); IR (KBr): $\tilde{\nu} = 2554\,cm^{-1}$ (BH).

X-ray structure analysis: **2a**: $C_{48}H_{59}B_2N_{12}SmTe_3$, red crystal, 0.31 × 0.23 × 0.17 mm, $M_r = 1358.84$, monoclinic, space group $P2_1/c$, $a = 8.7348(11)$, $b = 14.035(2)$, $c = 43.857(13)$ Å, $\beta = 88.751(2)°$, $V = 5372.8(19)$ Å^3, $Z = 4$, $F(000) = 2636$, $\rho_{calcd} = 1.680\,g\,cm^{-1}$, $\mu(Mo_{K\alpha}) = 2.734\,mm^{-1}$, $2\theta_{max} = 46°$, $T = 160$ K. A total of 8941 reflections were collected on a Stoe-Siemens four-circle diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$), ω/θ scans, and on-line profile fitting.[31] Data were corrected for Lp effects and for absorption by ψ scans (transmission: 0.654–0.485). The structure was solved by direct methods and refined by full-matrix least squares on F^2 to $wR2 = 0.2637$ for 7343 independent data and 607 parameters; $R = 0.0884$. Hydrogen atoms were included in a riding model. The largest features in the final electron density map within +2.35 and −2.35 e Å^{-3} were close to heavy atoms. Programs: Bruker AXS SHELXTL (structure solution and refinement), Stoe DIF4 (data collection), and local programs.

2b: $C_{48}H_{59}B_2N_{12}SmTe_3 \cdot 0.5\,C_7H_8$, red crystal, 0.17 × 0.16 × 0.04 mm, $M_r = 1404.91$, monoclinic, space group $P2_1/n$, $a = 8.6288(5)$, $b = 13.8812(8)$, $c = 46.185(3)$ Å, $\beta = 95.031(2)°$, $V = 5510.6(6)$ Å^3, $Z = 4$, $F(000) = 2736$, $\rho_{calcd} = 1.693\,g\,cm^{-1}$, $\mu(Mo_{K\alpha}) = 2.668\,mm^{-1}$, $2\theta_{max} = 50°$, $T = 160$ K. A total of 38653 reflections were collected on a Bruker AXS SMART CCD area detector diffractometer with narrow frames (0.3°) using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data corrections as for **2a** (transmission: 0.901–0.660). The structure was solved by direct methods (refinement and treatment of hydrogen atoms as for **2a**). $wR2 = 0.1249$ (9707 unique data), 634 parameters, $R = 0.0788$. The largest features in the final electron density map within +2.32 and −2.32 e Å^{-3} were close to heavy atoms. Programs: Bruker AXS SMART and SAINT for data collection and reduction, SHELXTL, and local programs.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114734 (**2a**) and CCDC-114735 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] a) P. Böttcher, *Angew. Chem.* **1988**, *100*, 781 – 794; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 759 – 772; b) M. A. Ansari, J. A. Ibers, *Coord. Chem. Rev.* **1990**, *100*, 223 – 266.
[2] M. G. Kanatzidis, *Angew. Chem.* **1995**, *107*, 2281 – 2283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2109 – 2111.
[3] Q. Liu, N. Goldberg, R. Hoffmann, *Chem. Eur. J.* **1996**, *2*, 390 – 397.
[4] A. Cisar, J. D. Corbett, *Inorg. Chem.* **1977**, *16*, 623.
[5] J. Shreeve Keyer, C. Warren, S. Dhingra, R. Haushalter, *Polyhedron* **1997**, *16*, 1193 – 1199.
[6] R. Zagler, B. Eisenmann, H. Schafer, *Z. Naturforsch. B* **1987**, *42*, 151 – 156.
[7] W. J. Evans, G. W. Rabe, M. A. Ansari, J. W. Ziller, *Angew. Chem.* **1994**, *106*, 2200 – 2201; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2110.
[8] J. Jeske, W.-W. du Mont, P. G. Jones, *Angew. Chem.* **1997**, *109*, 2304; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2219 – 2221.
[9] A. Strzelecki, C. Liker, B. Helsel, T. Utz, M. Lin, P. Bianconi, *Inorg. Chem.* **1994**, *33*, 5188 – 5194.
[10] K. Mashima, Y. Nakayama, T. Shibahara, H. Fukumoto, A. Nakamura, *Inorg. Chem.* **1996**, *35*, 93.
[11] J. Becker, J. Bernstein, M. Dayan, L. Shahal, *Chem. Commun.* **1992**, 1048 – 1049.
[12] M. Berardini, J. Lee, D. Freedman, J. Lee, T. J. Emge, J. G. Brennan, *Inorg. Chem.* **1997**, *36*, 5772 – 5776.
[13] D. Freedman, T. J. Emge, J. G. Brennan, *J. Am. Chem. Soc.* **1997**, *119*, 11114 – 11115.
[14] G. H. Maunder, A. Sella, D. A. Tocher, *Chem. Commun.* **1994**, 885 – 886.
[15] J. Takats, X. W. Zhang, V. W. Day, T. A. Eberspacher, *Organometallics* **1993**, *12*, 4286 – 4288.
[16] S.-Y. Liu, G. H. Maunder, A. Sella, M. Stephenson, D. A. Tocher, *Inorg. Chem.* **1996**, *35*, 76 – 82.
[17] J. Takats, personal communication.
[18] F. Sladky, B. Bildstein, C. Rieke, A. Gieren, H. Betz, T. Hübner, *Chem. Commun.* **1985**, 1800 – 1801.
[19] T. A. Hamor, N. Al Salim, A. A. West, W. R. McWhinnie, *J. Organomet. Chem.* **1986**, *310*, C5-C7.
[20] G. Llabres, O. Dideberg, L. Dupont, *Acta Crystallogr. Sect. B* **1972**, *28*, 2438 – 2442.
[21] M. R. Spirlet, G. Van de Bossche, O. Dideberg, L. Dupont, *Acta Crystallogr. Sect. B* **1979**, *35*, 1727 – 1735.
[22] D. J. Sandman, L. Li, S. Tripathy, J. C. Starck, L. A. Acampora, B. M. Foxman, *Organometallics* **1994**, *13*, 348 – 353.
[23] A. Edelmann, S. Brooker, N. Bertel, M. Noltemeyer, H. W. Roesky, G. M. Sheldrick, F. T. Edelmann, *Z. Naturforsch. B* **1992**, *47*, 305 – 309.
[24] W. J. Evans, G. W. Rabe, J. W. Ziller, R. J. Doedens, *Inorg. Chem.* **1994**, *33*, 2719 – 2726.
[25] W. S. Sheldrick, M. Wachhold, *Angew. Chem.* **1995** *107*, 490; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 450 – 451.
[26] P. Cherin, P. Unger, *Acta. Crystallogr.* **1967**, *23*, 670 – 675.
[27] P. Böttcher, R. Keller, *J. Less-Common Met.* **1985**, *109*, 311 – 321.
[28] H. Matsuzaka, T. Ogino, M. Nishio, Y. A. Noshibashi, S. Uemura, M. Hidai, *Chem. Commun.* **1994**, 223 – 224.
[29] R. C. Mooney-Slater, *Acta Crystallogr. B* **1959**, *12*, 187 – 196.
[30] H. A. Tasmin, K. H. Bozwijk, *Acta Crystallogr.* **1955**, *8*, 59 – 60.
[31] W. Clegg, *Acta Crystallogr. Sect. A* **1981**, *37*, 22.

Enzymatic Regeneration of 3′-Phosphoadenosine-5′-Phosphosulfate Using Aryl Sulfotransferase for the Preparative Enzymatic Synthesis of Sulfated Carbohydrates

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Sulfotransferases comprise a family of enzymes that catalyze the transfer of a sulfo group (SO$_3$$^-$) from the cofactor 3′-phosphoadenosine-5′-phosphosulfate (PAPS, **1**) to an acceptor molecule. Sulfotransferases mediate the sulfation of different classes of substrates such as carbohydrates, proteins, and steroids for a variety of biological functions including signaling and modulation of receptor binding.[1, 2] Within the past three years many new sulfotransferases have been identified and cloned.[3] A facile means to produce large amounts of sulfated product and efficient sulfotransferase assays are essential for the biological study of these enzymes and their sulfated products.

The cofactor PAPS, the universal sulfate donor and source of sulfate for all sulfotransferases, is a highly expensive and unstable molecule that has been an obstacle to the large-scale production of enzymatically sulfated products.[4] Product inhibition by adenosine 3′,5′-diphosphate (PAP, **2**) has also been a limiting factor to large-scale applications.[5, 6] We reported the first enzymatic regeneration of PAPS based on a multienzyme system coupled with *Rhizobium* Nod factor sulfotransferase (NodST) for the enzymatic synthesis of *N*,*N*′-diacetylchitobiose 6-sulfate.[6] While application of the cloned enzymes used in this recycling system serve as a facile and efficient means to synthesize PAPS on a large scale, we have developed here a simpler, one-enzyme regeneration system using a recombinant rat liver aryl sulfotransferase IV (AST IV; Scheme 1). This enzyme, when coupled to a sulfotransferase of choice, transfers a sulfo group (SO$_3^-$) from *p*-nitrophenyl sulfate (**3**) to PAP.[7] This system averts product inhibition by PAP while regenerating PAPS in situ and can be monitored quantitatively by measurement of the absorbance of released *p*-nitrophenol (**4**) at 400 nm. Additionally, this recycling system can be modified to serve as a continuous spectrophotometric assay for the activity of any sulfotransferase enzyme. The most common assay of sulfotransferase activity involves monitoring the transfer of radioisotopic sulfate from [^{35}S]PAPS to the product by thin-layer or paper chromatography using end-point methods.[8] These assays are expensive and often imprecise.[9] Demonstrated here is the use of this one-enzyme PAPS regeneration system for the synthesis of *N*,*N*′,*N*″-triacetylchitotriose 6-sulfate (**5**) and of a continuous, colorimetric, coupled-enzyme assay of NodST to determine the substrate specificity of this enzyme.

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