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Novel tellurium halides Te_2Cl_2 and Te_2Br_2

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Novel Te_2Cl_2 and Te_2Br_2 were prepared by the reaction of Li_2Te and TeX_4 and characterized by mass spectroscopy and ^{125}Te NMR spectroscopy, and by successful syntheses of 1,2-Te_2S_5 and 1,2-Te_2Se_5.

Disulfur and diselenium dihalides are relatively stable[1] and form a useful class of reagents for many synthetic applications. The existence of mixed selenium–sulfur dihalides has also been reported.[1l,2] Here we describe a facile synthesis of Te_2Cl_2 and Te_2Br_2 that have turned out to be surprisingly stable,† though the phase diagrams of the Te–$TeCl_4$ and Te–$TeBr_4$ systems do not give any indications about the existence of Te_2Cl_2 and Te_2Br_2.[4] The closest known tellurium halides of this type are polymeric $(Te_2Cl)_x$, $(Te_3Cl_2)_x$ $(Te_2Br)_x$ and $(Te_2I)_x$.[5]

Te_2Cl_2 and Te_2Br_2 were prepared by reducing elemental tellurium with superhydride and treating the resulting telluride with appropriate tellurium tetrahalogenide [eqn. (1)].‡

$$\mathrm{Te} \xrightarrow{\mathrm{LiBHEt_3}} 1/x\mathrm{Te}_x^{2-}$$

$$\mathrm{Te}_x^{2-} + x\mathrm{TeX}_4 \rightarrow x\mathrm{Te}_2\mathrm{X}_2 + 2x\mathrm{X}^- \ (\mathrm{X = Cl,\ Br}) \qquad (1)$$

Ditellurium dichloride was obtained as a yellow liquid, and ditellurium dibromide as an orange–red liquid. Both Te_2Cl_2 and Te_2Br_2 should be stored under an inert atmosphere. Te_2Br_2 however, is stable for hours at room temperature. Te_2Cl_2 is not as stable as Te_2Br_2, but it can also be stored for hours, especially in organic solutions. Chlorinated solvents, however, should be avoided.

Both Te_2Cl_2 and Te_2Br_2 exhibit one major ^{125}Te resonance in their respective NMR spectra (Fig. 1).§ The ^{125}Te chemical shift of Te_2Cl_2 in CS_2 is at 1336 ppm and that of Te_2Br_2 at 1253 ppm. The chemical shift of Te_2Cl_2 in toluene is 1297 ppm.[3] The ^{125}Te chemical shifts of the two species bear a relationship that is expected from the comparison with the ^{77}Se chemical shifts of Se_2Cl_2 and Se_2Br_2.¶ The appearance of only one resonance in the spectra of both compounds indicate an open-chain X–Te–Te–X structure rather than a branched $X_2Te{=}Te$ structure. One minor signal was observed in both spectra (Fig. 1). The chemical shift of this resonance varies (820–880 ppm) and its intensity relative to that of the main resonance increases as a function of time and implies the decomposition of Te_2Cl_2 and Te_2Br_2. We have previously made a tentative assignment of a weak resonance observed at 849 ppm in the S–Se–Te melt at 145 °C to Te_8.[6] It is possible that the decomposition of Te_2X_2 (X = Cl, Br) produces Te_8.‖

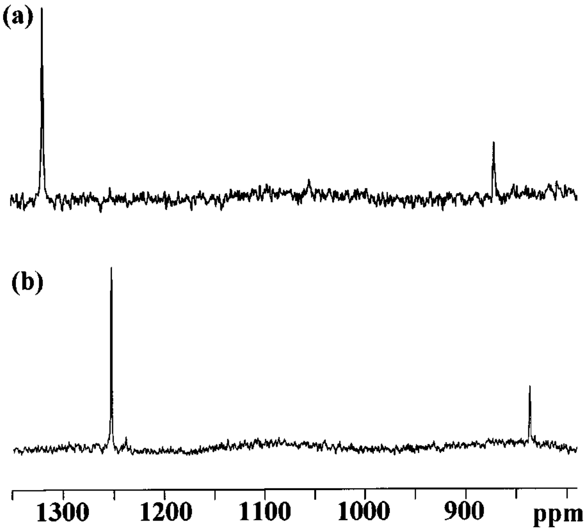

Fig. 1 ^{125}Te NMR spectra of (a) Te_2Cl_2 and (b) Te_2Br_2 in CS_2.

The mass spectra of Te_2Cl_2 and Te_2Br_2 are shown in Fig. 2.** The observed isotopic distribution for the molecular ion of Te_2Cl_2 as well as those for its fragments are in a good agreement with the calculated distributions. A reasonable fragmentation that exhibits the expected isotopic distributions could also be deduced in the mass spectrum of Te_2Br_2, though we did not observe the molecular ion.

It is well established that $[Ti(C_5H_5)_2S_5]$ and $[Ti(C_5H_5)_2Se_5]$ react with S_2Cl_2 or Se_2Cl_2 to produce cyclic seven-membered chalcogen compounds (S_7, 1,2-Se_2S_5 and 1,2,3,4,5-Se_5S_2, Se_7, respectively).[7] These titanocene reagents can be used to further verify the identities of Te_2Cl_2 and Te_2Br_2. We present here the preparation of 1,2-Te_2S_5 and 1,2-Te_2Se_5 [eqn. (2)] by treating Te_2Cl_2 with $[Ti(C_5H_5)_2E_5]$ (E = S, Se) in CS_2 in an analogous manner as described previously for 1,2,3,4,5-Se_5S_2.[8]††

$$[\mathrm{Ti(C_5H_5)_2E_5}] + \mathrm{Te_2X_2} \rightarrow 1{,}2\text{-}\mathrm{Te_2E_5} + [\mathrm{Ti(C_5H_5)_2X_2}] \qquad (2)$$

Only one ^{125}Te NMR resonance is observed in spectra of both compounds. The signal at 1732 ppm is assigned to 1,2-Te_2S_5 and that at 1724 ppm to 1,2-Te_2Se_5. The latter resonance is

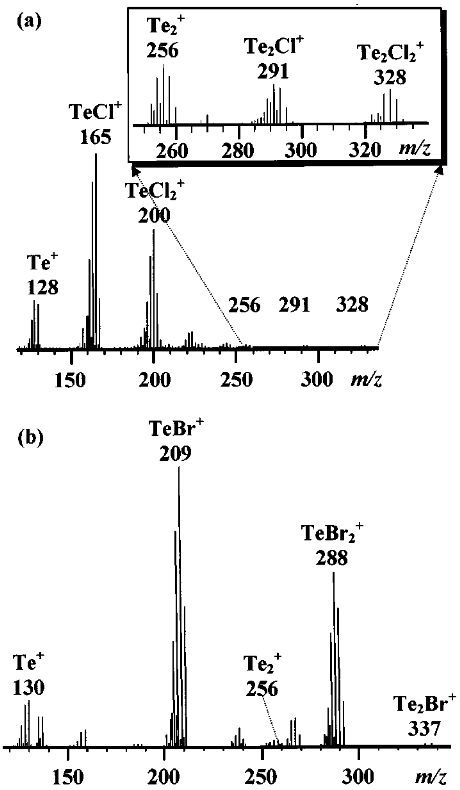

Fig. 2 12 eV mass spectra of (a) Te_2Cl_2 and (b) Te_2Br_2.

expectedly upfield, since selenium is less electronegative than sulfur.[11] The ^{77}Se NMR resonances of 1,2-Te_2Se_5 are 1040, 1019 and 982 ppm (intensity ratio 2:1:2). These signals are consistent with the ^{77}Se chemical shifts of 1,2,3,4,5-Se_5S_2[12] and imply that 1,2-Te_2Se_5 is also fluxional. It should be noted that Te_2Br_2 is less reactive than Te_2Cl_2.

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Notes and references

† Preliminary information on Te_2Cl_2 has been reported previously.[3]

‡ All reactions were carried out under a dry argon atmosphere. $LiBHEt_3$ (15.7 cm^3, 15.7 mmol, 'Super-Hydride' 1 M in THF) and elemental tellurium (1.00 g, 7.84 mmol) were stirred for 15 min under slight warming. The solution was cooled to room temperature and the solution of $TeCl_4$ (2.11 g, 7.84 mmol) or $TeBr_4$ (3.51 g, 7.84 mmol) in 50 cm^3 of THF was added dropwise. The solution was filtered and solvent removed under a dynamic vacuum. The product was dissolved in CS_2 to remove LiX, elemental tellurium, and the unreacted TeX_4 (yields in both cases *ca.* 40% based on the initial amount of TeX_4).

§ The ^{77}Se and ^{125}Te NMR spectra were recorded at 300 K on a Bruker DPX 400 spectrometer (76.311 and 126.241 MHz for ^{77}Se and ^{125}Te, respectively). D_2O was used as an external ^{2}H lock and saturated D_2O solutions of SeO_2 and H_6TeO_6 as external references. The ^{77}Se and ^{125}Te chemical shifts were reported relative to neat Me_2Se and Me_2Te, respectively [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$; $\delta(Me_2Te) = \delta(H_6TeO_6) + 712$].

¶ The ^{77}Se chemical shift in Se_2Cl_2 is 1271 ppm and that in Se_2Br_2 1171 ppm.[2b]

‖ To test this assignment Te_2Cl_2 was reacted with $[Ti(MeC_5H_4)_2(\mu\text{-}Te_2)_2Ti(MeC_5H_4)]$ (molar ratio 2:1) in CS_2. This reaction is expected to form Te_8. We observed a single ^{125}Te resonance at 868 ppm.

** EI-MS mass spectra of Te_2Cl_2 and Te_2Br_2 were recorded using a Kratos MS 80 spectrometer at 12 eV electron energy.

†† 0.26 g of $[Ti(C_5H_5)_2S_5]$[9] or 0.44 g of $[Ti(C_5H_5)_2Se_5]$[10] (0.77 mmol) was dissolved in 50 cm^3 of CS_2. Te_2Cl_2 (0.25 g; 0.77 mmol) in 10 cm^3 of CS_2 was added into this solution that was subsequently cooled down to −78 °C to precipitate 1,2-Te_2E_5 and $[Ti(C_5H_5)_2Cl_2]$. After filtration and redissolving of $[Ti(C_5H_5)_2Cl_2]$ in $CHCl_3$, the remaining product was dried *in vacuo* [yields 0.11 g (34.2%) and 0.31 g (47.6%) for Te_2S_5 and Te_2Se_5, respectively].

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