The Nature of Chalcogen-Bonding-Type Tellurium–Nitrogen Interactions: A First Experimental Structure from the Gas Phase

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Dedicated to Professor Thomas M. Klapötke on the occasion of his 60th birthday

Abstract: (C$_6$F$_5$)Te(CH$_2$)$_3$NMe$_2$ (1), a perfluorophenyltellurium derivative capable of forming intramolecular N···Te interactions, was prepared and characterized. The donor-free reference substance (C$_6$F$_5$)TeMe (2) and the unsupported adduct (C$_6$F$_5$)(Me)Te·NMe$_2$Et (2b) were studied in parallel. Molecular structures of 1, 2 and 2b were determined by single-crystal X-ray diffraction and for 1 and 2 by gas-phase electron diffraction. The structure of 1 shows N···Te distances of 2.639(1) Å (solid) and 2.92(3) Å (gas). Ab initio plus NBO and QTAIM calculations show significant charge transfer effects within the N···Te interactions and indicate a-hole interactions.

In 1990 Singh et al. reported the existence of special N···Te interactions in tellurium(IV) derivatives with benzylamine ligands in the solid phase. In the stabilizing effect was demonstrated by Hammerl et al. for the same benzylamine derivatives and Rakesh et al. crystallized a system containing N···Te–Cl units with a stronger interaction between nitrogen and tellurium atoms (2.355(3) Å in ClTe(o-C$_6$H$_4$)-CH$_2$NMe$_2$). In fact, the investigated systems describe donating interactions between the heavy atom tellurium and the nitrogen atom, but a substantial proof in the gas phase is still missing to exclude pure solid-state effects.

For this purpose we now prepared (N,N-dimethylanilino)perfluorophenyltelluride (1) (Scheme 1). Its $^{125}$Te-$^1$H NMR spectrum shows a triplet ($J_{Te-H}$ = 64 Hz) at 353 ppm. The fact that the $^{125}$Te-$^1$H NMR resonance of Te(C$_6$F$_5$)$_2$ is a quintet at 305 ppm allows to conclude the tellurium atom in 1 to be weakly coordinated in solution— intra- or intermolecularly—by an electronnegative element such as nitrogen.

Suitable crystals for X-ray diffraction (XRD) of 1 were obtained by sublimation. Its molecular structure in the solid state (Figure 1) shows a N···Te distance of 2.639(1) Å. The distance from Te1 to the ipso-carbon atom C1 of the perfluorophenyl unit is 2.189(1) Å; this is rather long compared to bis(perfluorophenyl)ditelluride at 2.124(1) Å and bis(perfluorophenyl)telluride at 2.101(6) Å and is explicable by population of the antibonding Te1–C1 orbital by the donating nitrogen function in the NBO picture. As expected, the angle C1-Te1-C7 at 91.3(1)$^\circ$ is close to 90$.^\circ$ The angle C1-Te1–N1 at 166.4(1)$^\circ$ deviates slightly from the expected 180$^\circ$ for chalcogen bonding, likely due to ring restrictions.

The measured N···Te distance is more than one Å shorter than the sum of the van der Waals radii ($\sum r_{vdW}$ = 3.65 Å). The normalized contact distance, that is, the measured distance divided by the $\sum r_{vdW}$ at 0.72 describes the interaction more properly.