

The first Crystalline Lewis Acid-Base Adducts between Tellurium Polycations and Cyanogen or TCNX Compounds in Liquid SO₂

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Introduction

Te_y[AsF₆]_{y/2}•xSO₂ with y = 4, 6 and x = 1, 1.5, 2, 4 are suitable compounds for ligand exchange reactions because of the substitutional lability of the Te...O-S-O coordinating bonds. We used neutral polynitriles with low lying HOMO orbitals as the exchanging ligand. The reaction of cyanogen with arsenic pentafluoride and tellurium in liquid SO₂ led to the formation of the first characterized Lewis acid-base complexes between a polynitrile and a polyatomic cation in [Te₄(C₂N₂)(AsF₆)₂] and [Te₆(C₂N₂)(AsF₆)₄]•0.5C₂N₂. These results became the starting point for further studies of Lewis acid-base complexes between TCNX compounds (TCNE, TCNQ, TCNB, TCNP, Tetracyanodithiin) and tellurium polycations (Te₄²⁺, Te₆⁴⁺). Up to now we characterized five compounds by single-crystal X-ray crystallography and Raman spectroscopy.

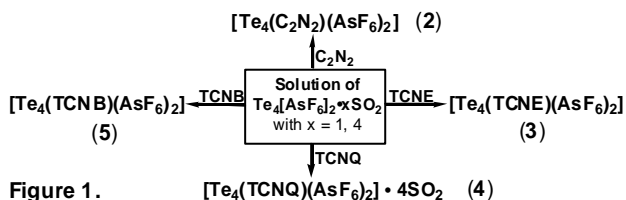
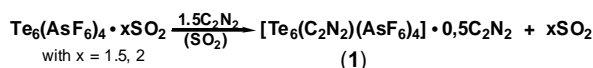


Figure 1.

Results and Discussion

The adducts (1), (2), (3), (4) and (5) were prepared from the reaction of excess polynitrile dissolved in liquid sulphur dioxide and a saturated solution of Te₄[AsF₆]₂ / Te₆[AsF₆]₄ in liquid sulfur dioxide. The tellurium cations were prepared using the literature procedure.¹ In these adducts the polynitriles bridge up to eight tellurium atoms by s coordination. Large polymeric and multidimensional aggregates with neutral TCNX ligands and different coordination behavior were formed. In compound (1) cyanogen is coordinated as a μ₂,²-ligand to an one-dimensional zigzag chain, in (2) as a μ₄,²-ligand to undulated layers. TCNE in (3) behaves like a μ₈,⁴-ligand towards Te₄²⁺ and undulated layers are built. Also TCNQ in (4) is a μ₈,⁴-ligand but with the square planar Te₄²⁺ cation a three-dimensional network is

formed. TCNB in (5) coordinates as a μ₄,²-ligand to form a one dimensional chain.

X-ray data collection was performed between -150°C and -100°C. The single crystals of all Lewis acid-base adducts were red colored.

The Te₄²⁺-TCNX adducts are sensitive towards hydrolysis and oxidation by air moisture and must be handled under dry conditions. Within two month in dry liquid SO₂ the adducts decompose to {Te₇[AsF₆]₂}_n and elimination of free polynitrile or in the case of the cyanogen adducts to an unknown (CN)_x polymer.

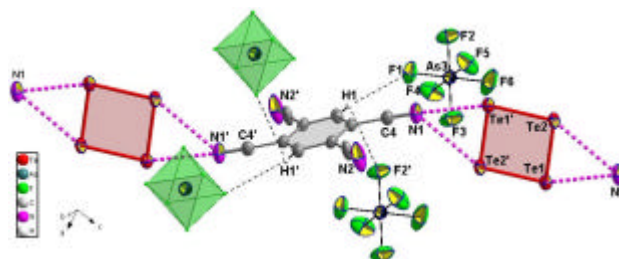


Figure 2. Chainlike structure of [Te₄(TCNB)(AsF₆)₂]. One TCNB unit is surrounded by two Te₄²⁺ cations and four [AsF₆]⁻ anions: Te...N contacts 2,909 Å and 3,282 Å, F...H distances 2,752 Å and 2,832 Å.

The existence of a significant s interaction between the CN groups of the TCNX moieties and the square planar Te₄²⁺ cation is indicated by the vibrational wave numbers of the symmetric CN stretching mode which were found to be shifted to higher wave numbers up to 22 cm⁻¹ with respect to the free nitrile.

Conclusion

From solution of tellurium polycationic clusters in liquid SO₂ and organic polynitriles crystalline coordination network compounds can be isolated. The weak coordinative Te...O-S-O are replaced by stronger Te...NC-R bonds.

Acknowledgements

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¹ J. Barr, R. Gillespie, G. Pez, P Ummat, *Inorg. Chem.* **1971**, 10,362.