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Study of antimony carboxylates as dopants for zinc oxide varistors

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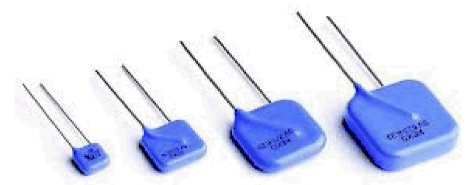
Introduction

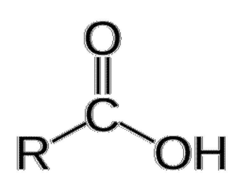
Varistors are used to protect electronic components. These are not for startup surges, overcurrent or sags but more for large spikes such as lightning strikes. Typically, these materials are composed of zinc oxides pressed into a disc; however, a a variety of other cations are doped into these materials to improve different properties.



Of these dopants, we are interested in adding Sb cations as they have demonstrated improved properties. To investigate the optimal percentage of Sb doping improved solubility in existing solution routes is necessary.

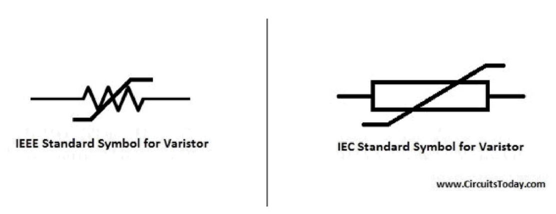
One ligand that has been understudied in Sb chemistry are the carboxylates. Carboxylates are of interest since the pendant chain can be easily modified to alter solubility and impact structure types, which play role in the final material properties.

Therefore, we undertook a systematic investigation of modifying a family of antimony alkoxides or $[Sb(OR)_3]$ (where OR = OCH_3, OCH_2CH_3, or $OCH(CH_3)_2$) with a series of sterically varied HORc (where ORc = O_2CH, O_2CCH_3, $O_2CCH(CH_3)_2$), $O_2CC(CH_3)_3$), or $O_2CCH_2C(CH_3)_3$)) to determine the various compounds that could be exploited for varistor applications.



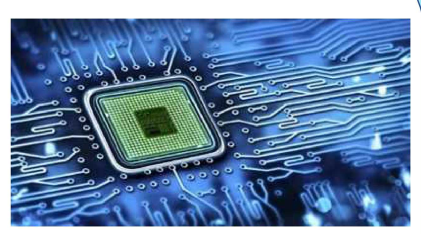
Varistors

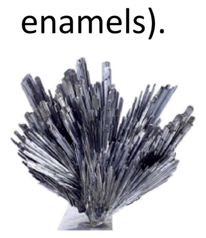
Varistors or voltage-dependent resistors are semiconductor diodes which apply resistance dependent on an applied voltage. These devices are used ensure optimal voltages are applied while compensating for over/under voltages. When needed, they shunt the excess current away from other sensitive components.



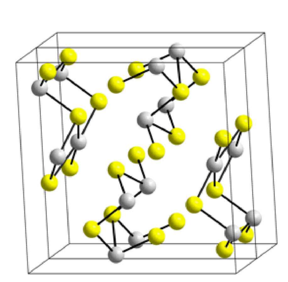
Antimony

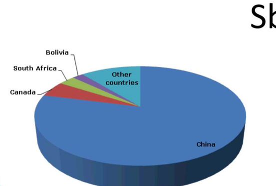
Antimony is a silver-colored semiconductor commonly used in a variety of applications: alloys for increased lead durability, batteries for low friction metals, flame-proofing materials (paints, ceramic enamels).





Antimony is found in over 100 different minerals but is mainly found as stibnite (Sb_2S_3, shown on left), thus the atomic symbol (Sb). Stibnite (shown to the right) adopts an As2S3 structure type where the Sb(III) centers are pyramidal and 3-coordinate. Stibnite is grey but turns black on oxidation to form antimony (III) oxide (Sb_2O_3). Sb adopts both the 3+ and 5+ oxidation state.

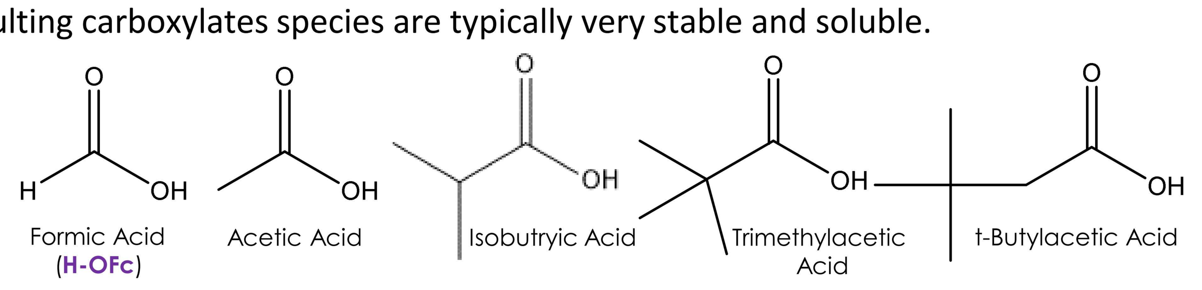




Despite being the 62nd most abundant element, antimony's coordination chemistry remains relatively unexplored. The majority of Sb is mined from China.

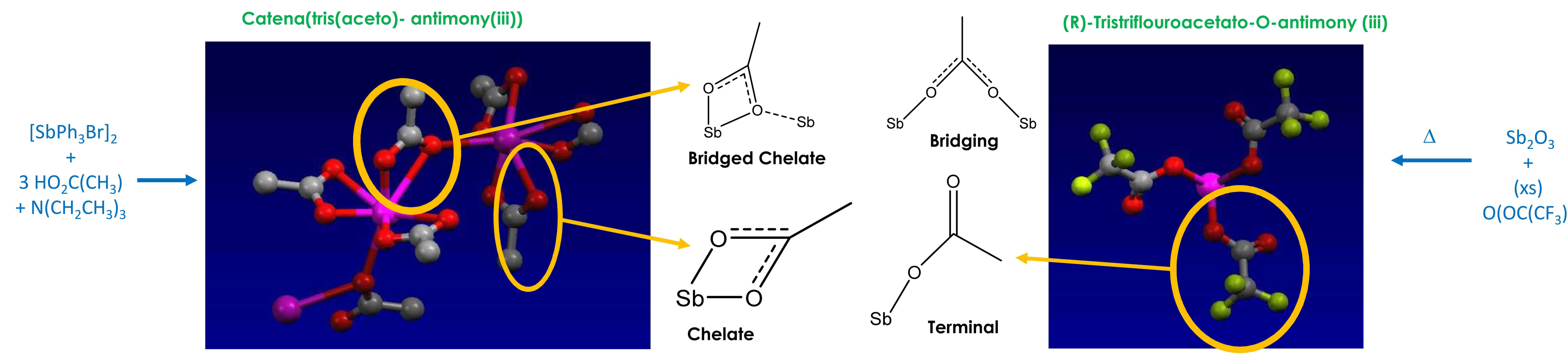
Carboxylates

Carboxylic acids (H-ORc) are organic compounds that contain both a carbonyl (C=O and a hydroxide (-OH) bound to the same carbon, along with an alkyl chain. The alkyl chain (R) can vary greatly in composition. When reacted with metals, the H is lost and the resulting carboxylates species are typically very stable and soluble.



We are interested in ORc because of the potential variability in steric bulk of the products will allow us to control the final properties (i.e., morphology, particulate size, etc.), especially the solubility.

Few structurally characterized antimony carboxylate complexes exist in literature.



Hall M, Sowerby DB. *J Chem Soc, Dalton Trans.* 1980:1292.

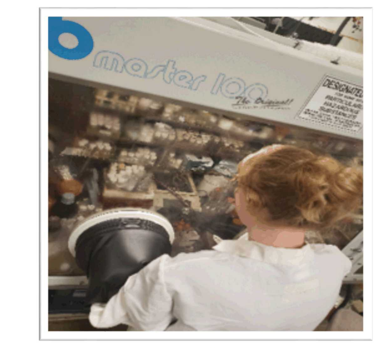
Bullivant DP, A. Dove MF, Haley MJ. *J Chem Soc, Dalton Trans.* 1980:105.

While there is little information available on antimony alkoxy carboxylates in the structure literature, other species have shown that the carboxylates can act as chelation, bridging, bridged chelation, and terminal configurations.

Inert Atmosphere Synthesis

Because the antimony precursors are air sensitive, it is essential to perform the reactions within a "clean" (inert) atmosphere.

Reaction synthesis took place under inert atmosphere in a glovebox.



Working in a Glove Box!

Working on a Schlenk line!

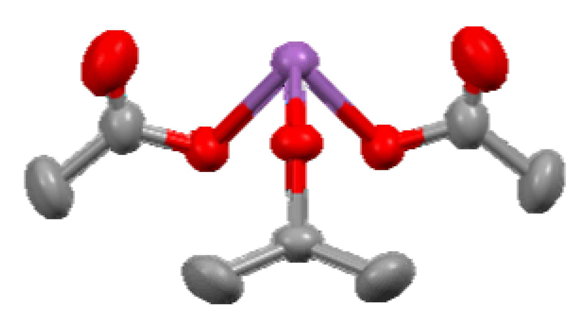
Inert Atmosphere synthesis uses argon and vacuum to keep water and air out.

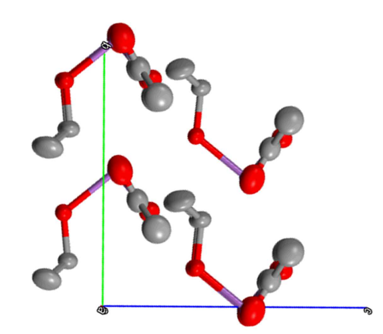
Reaction Crystallization and Characterization of Sb-carboxylates

$$Sb(OR)_3 + 3HO_2CR \xrightarrow{tol} Sb(O_2CR) + 3\ HOR$$

- (R)= H, Me, Bu, $(CH_3CH_2)_3C$, $(CH_3)_3CCH_2$), Pr^i
- (OR)=OMe, OEt, OPr^i, Cl

$$Sb(OPr^i)_3 + 3\ HOAc \xrightarrow{tol} [Sb(OAc)_2(OPr^i)] + 2\ HOPr^i + HOAc$$

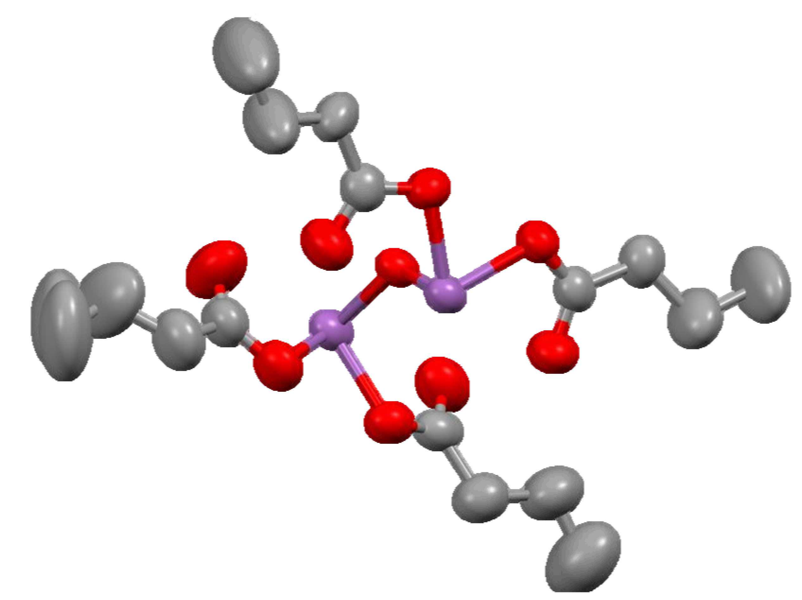


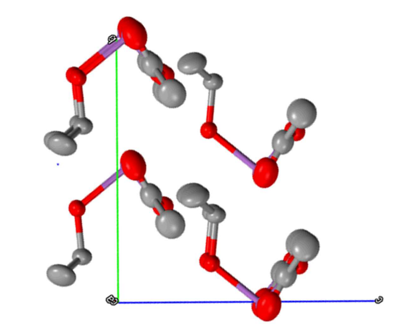


$[Sb(OAc)_2(OPr^i)]$

- Pseudo Tetrahedron
- Orthorhombic ($Cmc2_1$)
- Sb-OAc Bond Lengths: 2.053 Å
- Sb-OPr^i Bond Length: 1.989 Å

$$Sb(OPr^i)_3 + 3\ HOPc^n \xrightarrow{tol} [SbO(OPc^n)_2(\mu\text{-}O)]_2 + Pr^i(O)OPc^n$$





$[SbO(OPc^n)_2(\mu\text{-}O)]_2$

- Pseudo Tetrahedron
- Monoclinic ($p2_1/n$)
- Sb-OPc^n Bond Lengths: 2.05-2.06Å
- Sb-O Bond Length: 1.94 Å

Methods of Characterization

Single Christal X-Ray Diffraction (SCXRD)

Crystallography studies the formation processes that produce crystals and the structural and identifying details of the crystal. In the case of Single Crystal X-Ray Diffraction, x-rays are generated in a cathode ray tube, heating a filament to produce electrons and accelerating those electrons with an applied voltage. These electrons impact with the crystal produce x-ray spectra from the inner electron shells.

Infrared Spectroscopy is an analytical technique in which infrared radiation excites molecules into a higher vibrational state. Th wavelength of light absorbed by an a particular molecule is a function of the energy difference between the at-rest and vibrational states, which are shown as a spectra and analyzed to identify particular bonds within a molecule.

Fourier Transform Infrared Spectroscopy (FTIR)

Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance spectroscopy determines the number of protons in different environments of the compound. The oscillating magnetic field of the instrument induces a magnetic field within the sample which provides a spectra of different protons in different environments.

Summary and Conclusions

- synthesized two novel "Sr(OR)$_x$(ORc)$_y$" species.
- monomeric species isolated with 'small' acetate.
- oxide formed for OPc^n reaction lead to dimerization.
- compounds soluble in most organic solvents.

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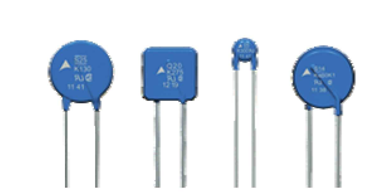
Future Directions

Looking forward:

- determine oxide source
- vary stoichiometry (and nuclearity?)
- Fully characterize compounds
- evaluate products in existing system
- generate Zn/Ab single source precursors



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