Lecture Plan

- Synthesis, structure and properties of tetrasulfur tetranitride.
- Halogen: their occurrence, electronic configuration and physical properties.
- Reactivity of halogens.
- Reaction of halogen with hydrogen, oxygen, water and alkalies.

Tetrasulfur tetranitride

- Tetrasulfur tetranitride S_4N_4 is binary sulfur nitride, gold-poppy colored solid.
- It contains sulfur in its +3 oxidation state. It also contains nitride ions.
- Nitrogen and sulfur have similar electronegativity and often form extensive families of covalently bonded structures.

Tetrasulfur tetranitride: Structure

- S_4N_4 has an unusual "extreme cradle" structure.
- It can be viewed as a derivative of a hypothetical eight-membered ring of alternating sulfur and nitrogen atoms.
- Single crystal X-Ray diffraction revealed that pairs of sulfur atoms across the ring are separated by 2.586 Å, resulting in a cage-like structure.

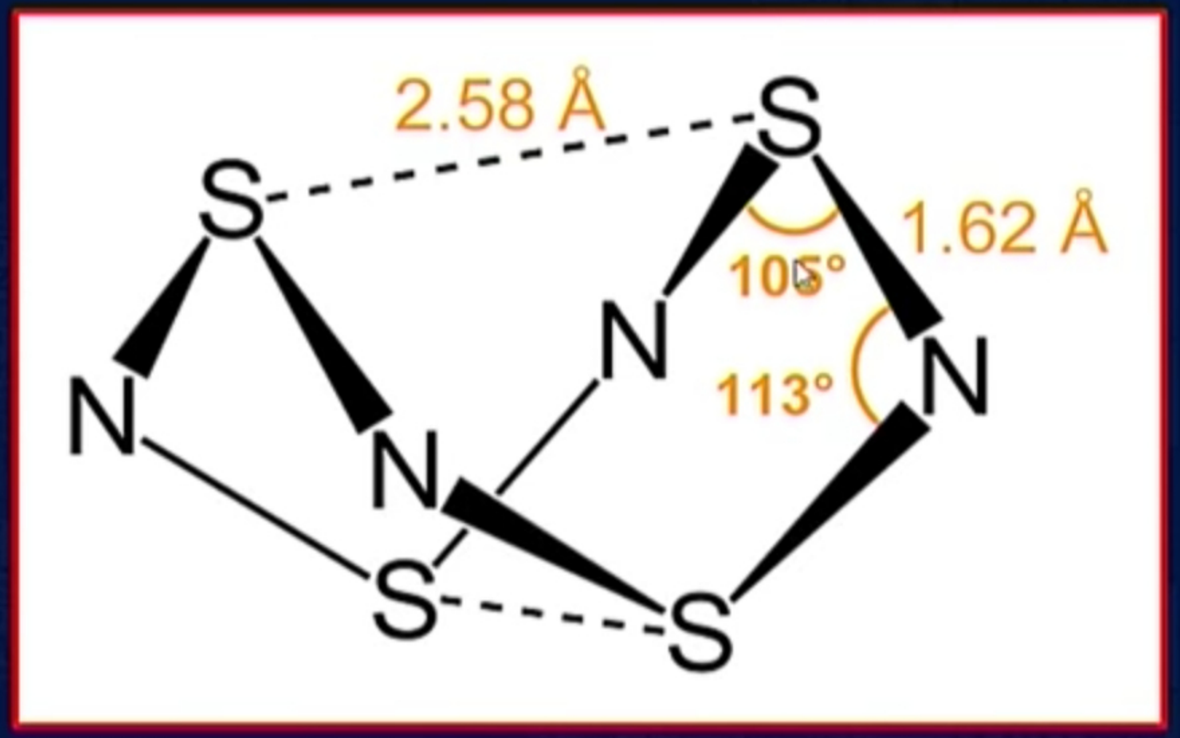
Tetrasulfur tetranitride: Structure

- The bonding in S_4N_4 is considered to be delocalized, as bond distances between neighboring sulfur and nitrogen atoms are almost the same.

Tetrasulfur tetranitride: Structure

- Average S-N bond length is 1.62 Å.
- Since sum of the covalent radii for S and N is 1.78 Å, the S-N bond seem to have some double bond character.
- Single bond distance S-S is 2.08 Å, thus it is a weak bond.
- The structure is a heterocyclic ring; having a cage like structure.

Tetrasulfur tetranitride: Structure



Tetrasulfur tetranitride:Synthesis

- Tetrasulfur tetranitride S_4N_4 is prepared by reaction of sulfurmonochloride with ammonia

$$6\ S_2Cl_2 + 16\ NH_3 \rightarrow S_4N_4 + S_8 + 12\ NH_4Cl$$

- Another synthesis use sulfur monochloride and NH_4Cl.

$$4\ NH_4Cl + 6\ S_2Cl_2 \rightarrow S_4N_4 + 16\ HCl + S_8$$

Tetrasulfur tetranitride: Properties

- Tetrasulfur tetranitride S_4N_4 is stable to air.
- Its melting point is 178 ^0C.
- S_4N_4 has been shown to co-crystallize with benzene.

Tetrasulfur tetranitride: Properties

- Tetrasulfurtetranitride S_4N_4 is thermochromic, changing from pale yellow below −30 °C to orange at room temperature to deep red above 100 °C.
- The endothermic enthalpy of formation originates in the difference in energy of S_4N_4 compared to its highly stable decomposition products:

$$2\ S_4N_4 \rightarrow 4\ N_2 + S_8$$

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Tetrasulfur tetranitride: Properties

- Because one of its decomposition products is a gas, S_4N_4 is an explosive.
- Small samples can be detonated by striking with a hammer.
- It is soluble in carbon disulfide, benzene, dioxane.

Tetrasulfurtetranitride: Properties

- It got much attention because of precursor to an unusual polymer called polythiazyl, $(SN)_x$. Polythiazyl is a bronze colored shiny solid with metallic appearance.
- Polythiazyl was the first conductive inorganic polymer. Polythiazyl conducts electricity and conductivity increases as the temperature decreases. It become superconductor at 0.26K.