POLAR AND NON-POLAR POLYTYPOIDS BASED ON THE SAME POLYMER BACKBONE

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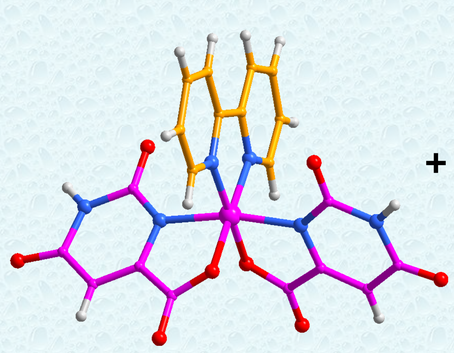
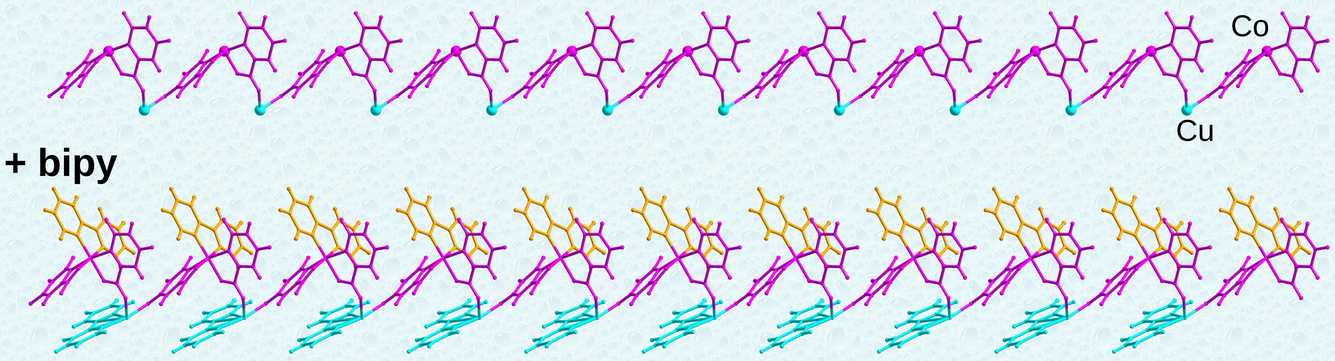
Physical properties such as **piezoelectricity, pyroelectricity** and **ferroelectricity** require the solids that possess them to be **polar**. That fact is one motivation for studying the factors that cause a specific 1D polymer to organize into crystalline solids with polar directions.

A 1D polymer with the $\{[Cu(bipy)][Co(orotate)_2(bipy)]\}_n$ backbone presents both polar and centric modifications in crystalline solids, producing polytypoids (analogous to polytypes but with differences in chemical composition) that provide a useful vehicle for a comparative study of the role of non-covalent interacions in producing the arrangements of these 1D polymers in their respective solids.

The 1D backbone is formed by Cu^{II} and Co^{III} centers bridged by orotate groups. Each metal is also coordinated to one 2,2´-bipyridine ligand.



+ Cu^{II} + bipy

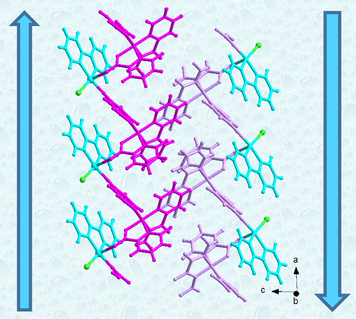


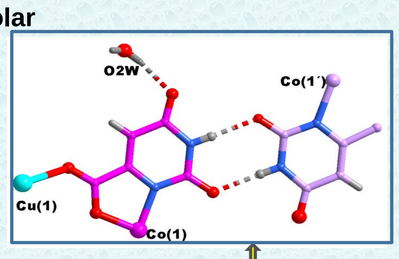
Orotate groups bonding cobalt and copper atoms

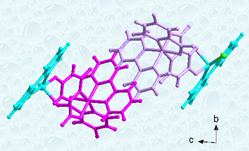
Backbone showing the bipy ligands bonded to cobalt (**orange**) and copper (**blue**)

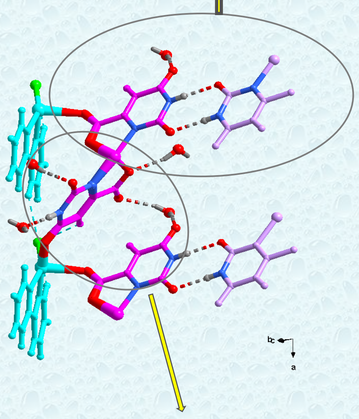
$\{[CuClbipy][Co(orotate)_2bipy]\}_n$

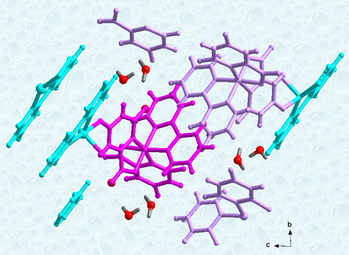
Space Group: P-1
Neutral, Non-Polar

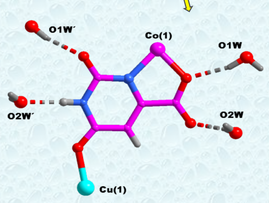


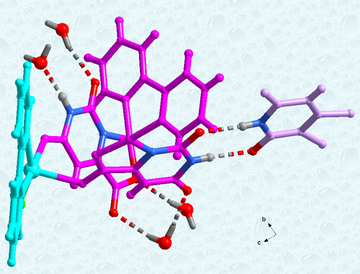


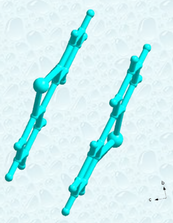












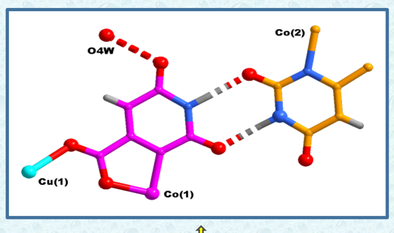
π–π interaction
only in the centrosymmetric structure

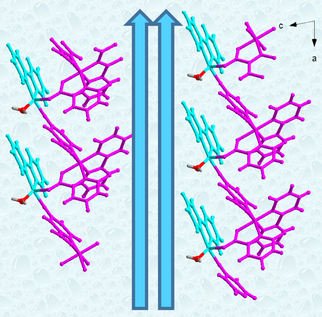
The cobalt part of a **polymer** and its **symmetry relatives** in different colors

$[Co(orotate)_2bipy]_n\{[Cu(OH)bipy][Co(orotate)_2bipy]\}_n$

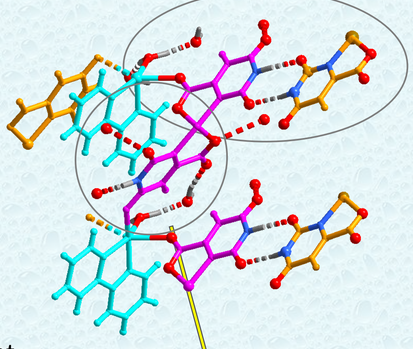
Space Group: P1
Cationic, Polar

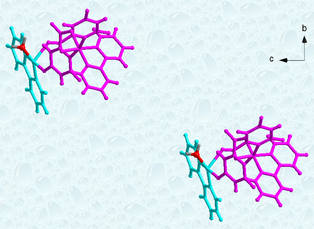
Self-recognition of the HNCO fragment $R_2^2(8)$ One of the orotate groups **Both structures**



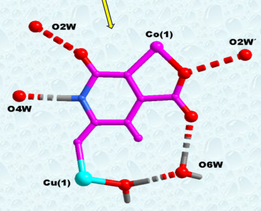


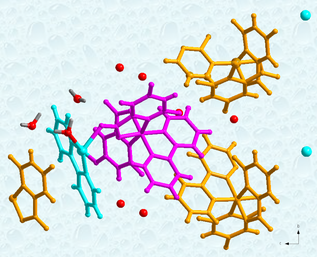
Non-covalent interactions of a section of the chain





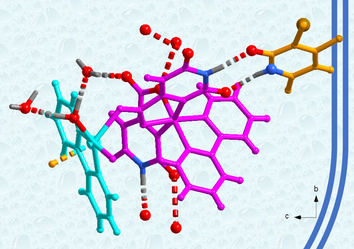
Detail of the non-covalent interactions of the second orotate group.
The presence of water bonded to Cu modifies some of the hydrogen bonds.





Conclusion

The HNCO $R_2^2(8)$ self-recognition pattern, which is a strong synthon, is centrosymmetric and is present in both solids.
In the neutral polymer, it forms between two chains ➡ thus the chains as a whole are also centrosymmetrically related.
In the cationic polymer, the $R_2^2(8)$ pattern is formed between the polymer and the anion; no center of symmetry is present.



The cobalt part of a **polymer** and the **counterion** in different colors

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