En-Type Ligands as Dimensional Reduction Agents in Coordination Polymers containing Dicarboxylic Acids.

THE 2ND INTERNATIONAL ONLINE CONFERENCE ON CRYSTALS 2020

MARIUS KREMER

MARIUS.KREMER@RWTH-AACHEN.DE

Contents

1. The concept of classic dimensional reduction.
2. The “new” concept of dimensional reduction through en-type ligands.
3. Examples

1. Classic dimensional reduction.

“Organic chemists have at their disposal a vast library of reaction schemes for performing specific structural transformations. […] In stark contrast, solid-state chemists have in their grasp only a few generalizable reaction schemes with which to modify the structure of an inorganic solid in a manner that might be predicted a priori.“

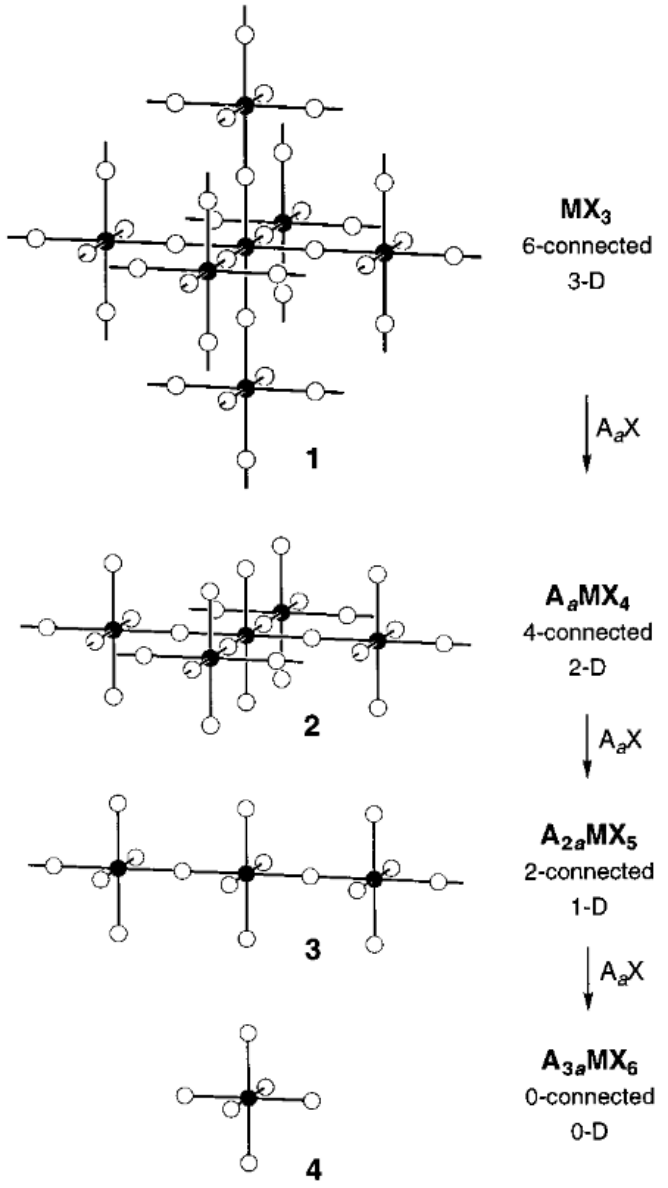
Eric G. Tulsky and Jeffrey R. Long: Dimensional Reduction: A Practical Formalism for Manipulating Solid Structures. Chem. Mater. 2001, 13 (4), 1149–1166

Concept:

"Dimensional reduction is set forth as a general formalism describing how the metal−anion (M−X) framework of a parent compound, MX_x, is dismantled upon reaction with an ionic reagent A_aX to form a child compound $A_{na}MX_{x+n}$."

$$MX_x + nA_aX \longrightarrow A_{na}MX_{x+n}$$

binary parent — dimensional reduction agent — ternary child



Eric G. Tulsky and Jeffrey R. Long: Dimensional Reduction: A Practical Formalism for Manipulating Solid Structures. Chem. Mater. 2001, 13 (4), 1149–1166

Benefits:

- Design prediction of inorganic compounds.
- Reduction of dimensionality while maintaining coordination and connectivity of the metal centres.

But:

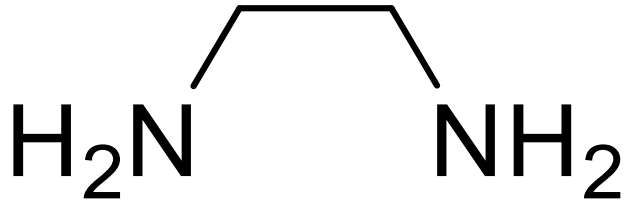
- All examples provided by Tulsky and Long are purely inorganic frameworks.

What about Metal-Organic Coordination Polymers?

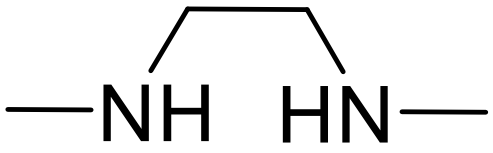
2. Dimensional reduction through en-type ligands.

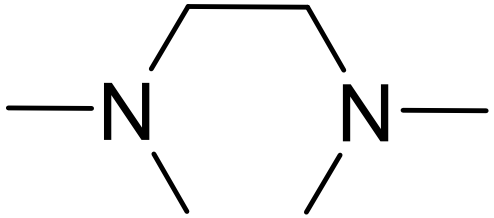
En-type ligands:

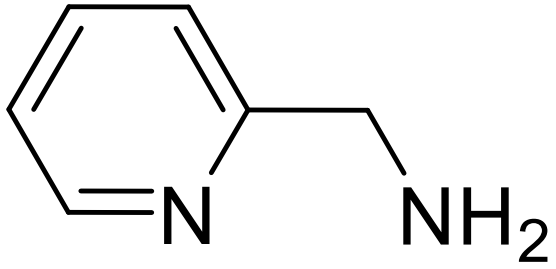
- Ethylenediamine (abbr. en) is a bidentate chelating ligand popular in coordination chemistry.

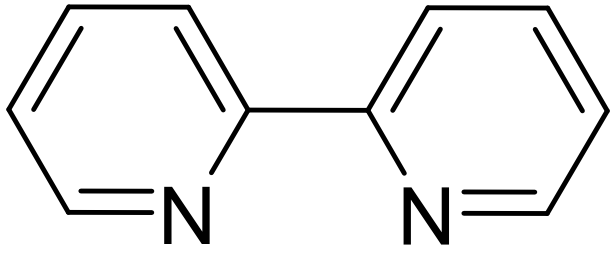


- Other ligands sharing the same bidentate coordination site are referred to as en-type ligands.









Concept:

- Addition of en-type ligands to coordination polymers of dicarboxylic acids leads to reduction of dimensionality by a degree of one.
- The en-type ligands coordinate as chelate.
- En-type ligands can either be added during the framework synthesis, or as past synthetic treatment of the coordination polymer.

Benefits:

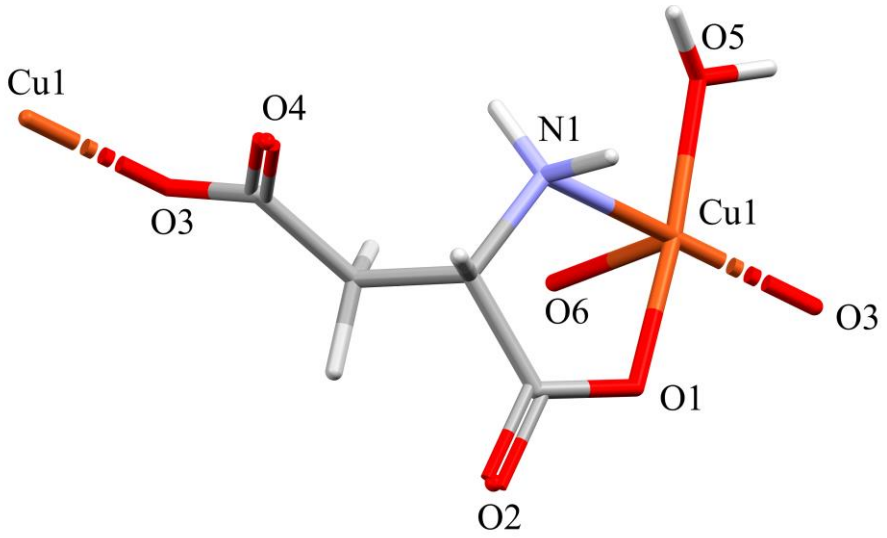
- Extension of the concept of dimensional reduction to include metal-organic compounds.
- Reduction of dimensionality drastically increases solubility.
- Allows for better crystallisation.

But:

- Addition of blocking ligands changes the coordination of metal centres.
- Concept has only been tested on a narrow field of compounds so far.
- Different Ligands have to be tested for each reaction to find the right one.
- Only 1D and 2D structures investigated so far.

3. Examples

3.1 Copper(II)aspartate

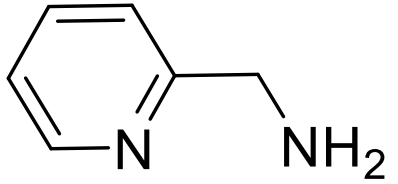


$[Cu(II)(asp)(H_2O)_2]_n^1$

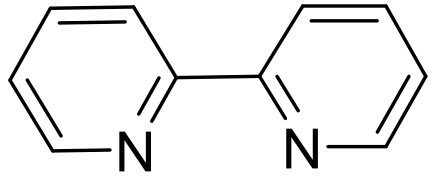
R. Calvo, C. A. Steren, O. E. Piro, T. Rojo, F. J. Zuniga, E. E. Castellano, *Inorg. Chem.* **1993**, *32* (26), 6016-6022.

$[Cu(II)(asp)(AMPY)(H_2O)]$ x 0.6 H_2O

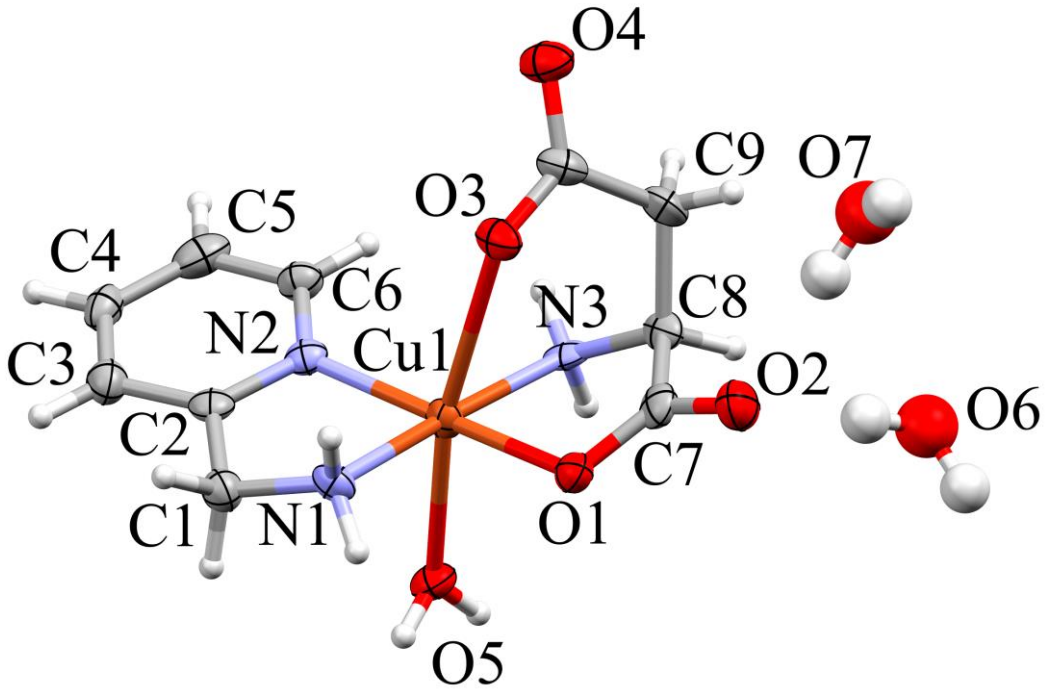
+ Aminomethylpyridin (AMPY)



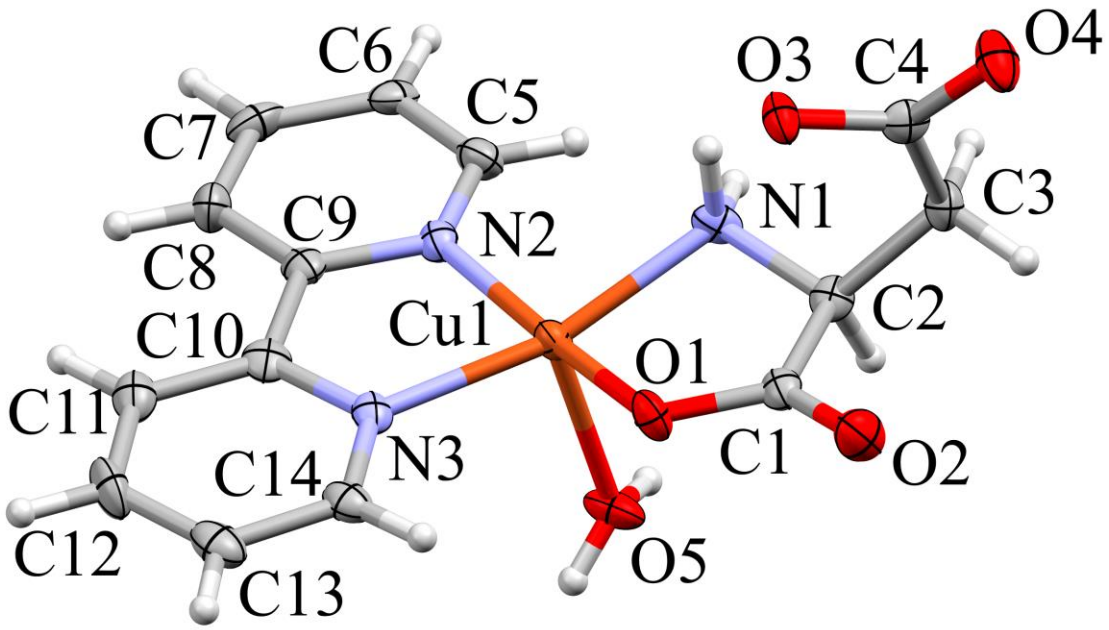
+ 2,2'-Bipyridine (2,2'-BIPY)



$[Cu(II)(asp)(BIPY)(H_2O)]$

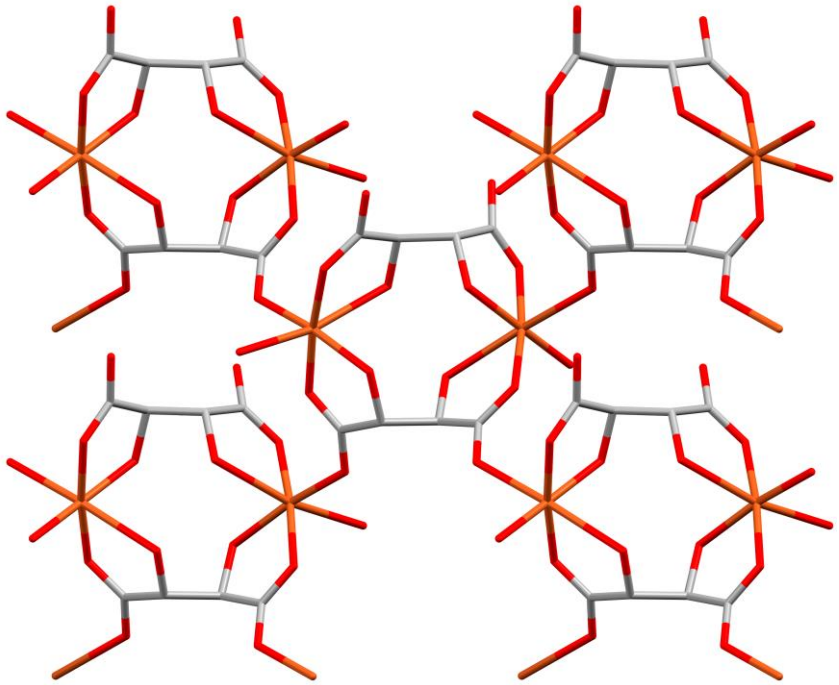


[Cu(II)(asp)(AMPY)(H_2O)] x 0.6 H_2O

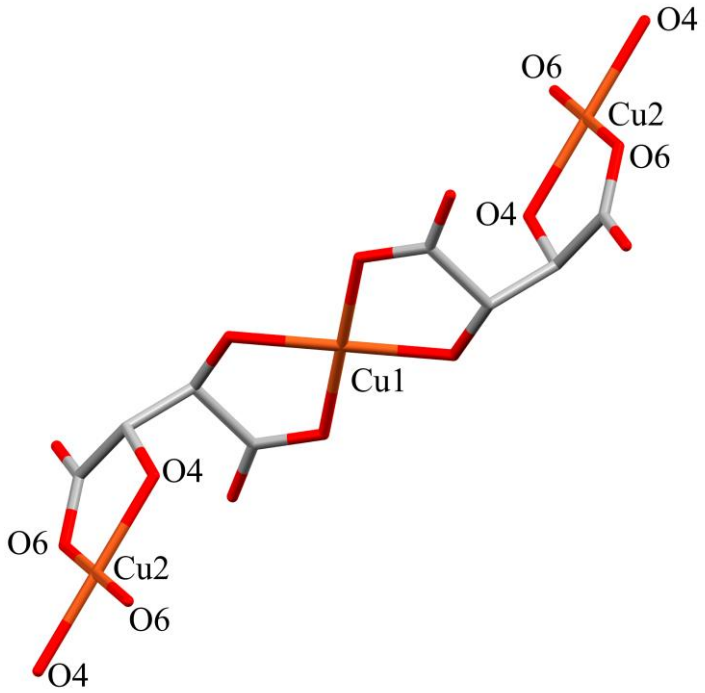


[Cu(II)(asp)(BIPY)(H_2O)]

3.2 Copper(II)tartrate



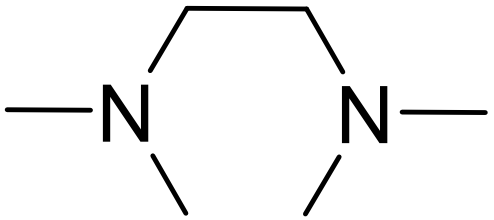
$[Cu(\text{D}-\text{tart})]_n^2$



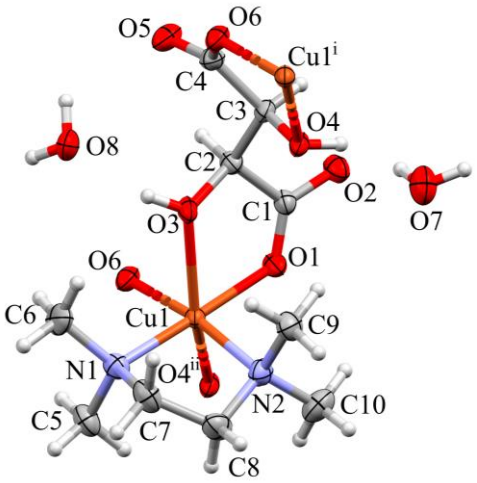
$[Cu(meso-\text{tart})]_n^1$

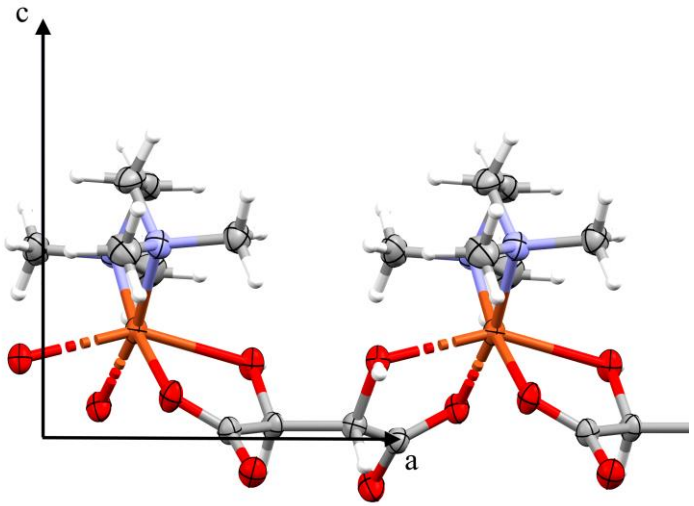
C. K. Prout, J. R. Carruthers, F. J. C. Rossotti, *J. Chem. Soc. A* **1971**, 3336-3342.

$[Cu(D-tart)]_n^2$



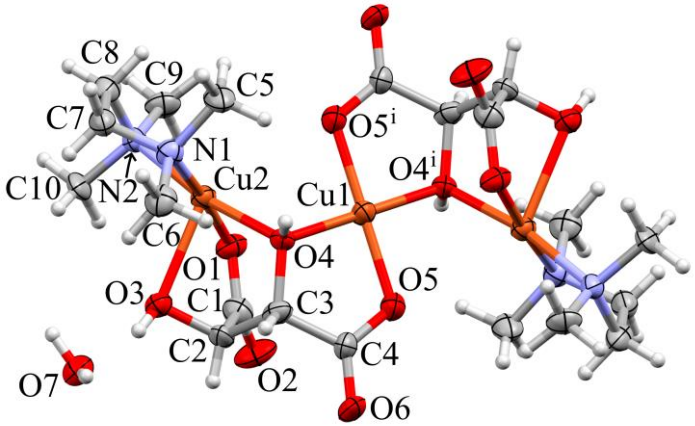
+Tetramethylethylendiamin
(TMEDA)





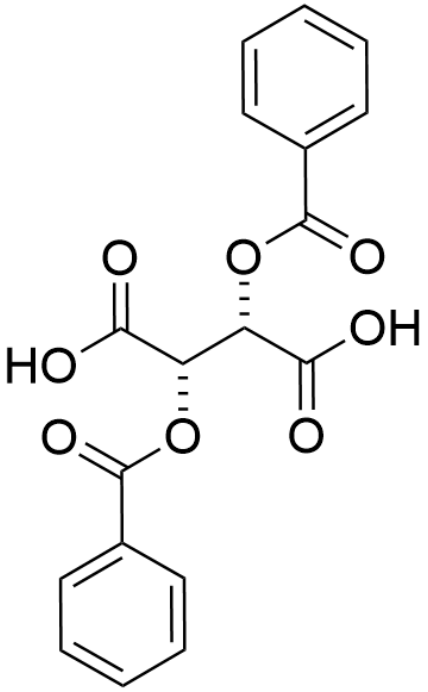
$[Cu(D-tart)(TMEDA)]_n^1$ x 2 H_2O

$[Cu(meso-tart)]_n^1$

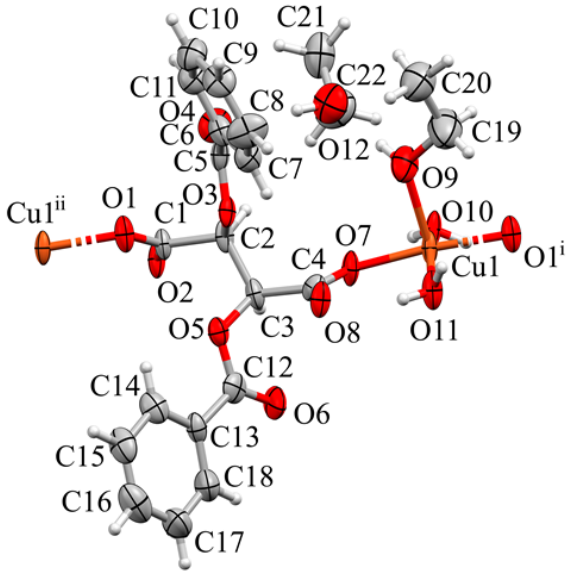


$[Cu_3(meso\text{-}tart)_3(TMEDA)_2]$ x 2 H_2O

3.3 Copper(II)-dibenzoyl-tartrate

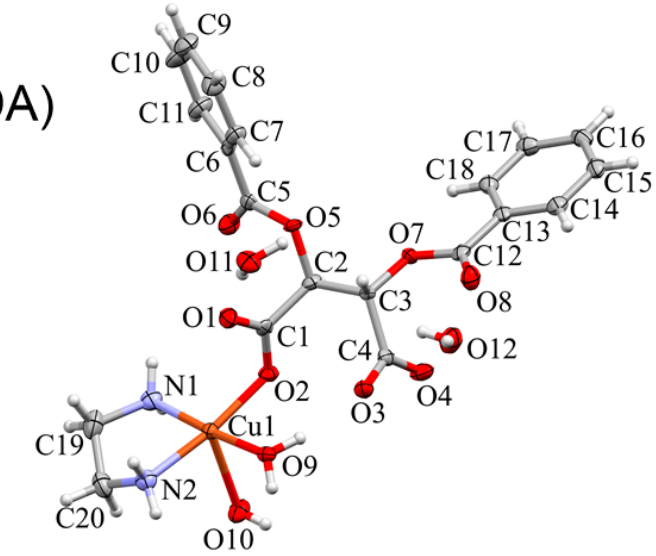


+Cu(II)



+Ethylenediamine (EDA)

H_2N NH_2



Dibenzoyl-tartaric acid

$[Cu(D\text{-}dbta)(EtOH)(H_2O)_2]_n^1$ x EtOH

$[Cu(dbta)(EDA)(H_2O)_2]$ x 2 H_2O

Summary

Parent compound (dimensionality)		**en-type ligand**	**Child compound (dimensionality)**	
Copper aspartate	1D (chain)	AMPY	[Cu(II)(asp)(AMPY)(H_2O)] x 0.6 H_2O	0D (discrete)
Copper aspartate	1D (chain)	BIPY	[Cu(II)(asp)(BIPY)(H_2O)]	0D (discrete)
Copper D-tartrate	2D (layer)	TMEDA	$[Cu(D\text{–tart})(TMEDA)]_n^1$ x 2 H_2O	1D (chain)
Copper *meso*-tartrate	1D (chain)	TMEDA	[Cu_3(*meso*-tart)$_3$($TMEDA)_2$] x 2 H_2O	0D (trinuclear)
Copper dbta	1D (chain)	EDA	[Cu(dbta)(EDA)($H_2O)_2$] x 2 H_2O	0D (discrete)

Thank you for your attention!

CONTACT ME FOR ANY QUESTIONS.