

s9.m3.p29 Structure of an unusual copper-basket shaped assemblage. M. Cesario¹, R. Ziessel², T. Prangé³.

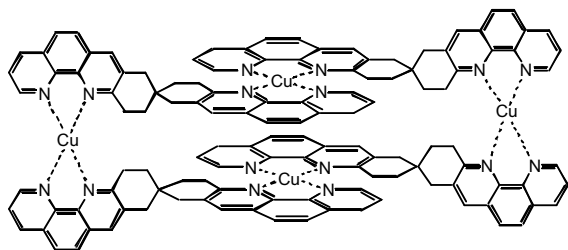
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Keywords: microcrystal, synchrotron, spiro-phenanthroline copper(I).

The self-assembly of metal cations with nitrogen heterocyclic bridging ligands is a central theme in supramolecular chemistry aimed at developing light-harvesting assemblies of electronically coupled metal centres. The ability of the spiro-phen ligand to control the assemblage is well suitable for the future preparation of multidimensional complexes displaying particular properties such as superexchange, electronic conductivity, energy concentrators.. etc.

The bis-spiro phenanthroline framework is a particularly promising candidate for use as a rigid and electronic spacer as judged by efficient photonic energy transfer found between two remote luminophoric metal centers.

Several trials with different counter ions were tested to prepare suitable monocrystals of the copper/bis-spiro phenanthroline complex. After numerous attempts, only micro crystals (0.1 x 0.1 x 0.01 mm) were obtained in the case of the PF₆⁻ salt. The diffraction data were recorded on the W32 beam line at the synchrotron facility LURE in Orsay at the maximum resolution of 1.1 Å (λ=0.964 Å).



The structure consists of a rigid sandwich of eight interlayer phenanthrolines clustering four copper ions, in a single compact supramolecular arrangement. The hexafluorophosphates counterions are just filling the channels in the packing with a high degree of freedom.

s9.m3.p30 Binary Crystals via Quasiracemates. R. Haerter, C. Hu, I. Kalf, X. Zheng, U. Englert, Institut für Anorganische Chemie, RWTH Aachen, Germany.

Keywords: molecular interactions, quasiracemates, packing.

In most cases¹ racemates of chiral objects pack in pairs of enantiomers related to each other by improper symmetry elements. Reasons for the preference for these racemic solids over conglomerates of enantiopure crystals have been critically reviewed².

The racemic molecular compound formed by enantiomeric pairs exhibits a local melting point maximum in a phase diagram. The formation of 1:1 molecular compounds has also been observed for closely related compounds of opposite chirality which are not enantiomers in a strict sense: An early example is represented by (+)-chlorosuccinic acid and (-)-bromosuccinic acid³. For systems of this type the term **quasi-racemates** has been coined by Fredga⁴. They were originally considered useful to probe the stereochemistry of organic compounds.

We are interested in these molecular compounds because they represent van der Waals crystals made up of components of similar size. We intend to compare the solid state structures of the quasiracemates to the structures of a) the individual enantiopure components and b) the true racemates formed by the constituents. The comparison will be based on simple space filling considerations such as molecular volume or packing coefficient and, possibly, lattice energy calculations⁵.

Our synthetic approach to the design of quasiracemic crystals is based on inert coordination compounds. Six-coordinated Co(III) complexes of the general formula [Co(dmGH)₂XL] with two chelating dimethylglyoximate (dmGH) ligands in the equatorial plane, a variable anionic ligand X in an apical position and a chiral substituent L in *trans* can satisfy several requirements:

The individual components of the binary crystals may be synthesized starting from commercial products. They are stable against air and moderate temperatures, do not racemize, and can be characterized by standard spectroscopic (IR, NMR) methods.

Due to the inert metal center Co(III) ligand exchange is relatively slow.

Variation of X allows to synthesize a group of different but structurally closely related compounds.

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