

The title compound (I) crystallizes in the orthorhombic space group $P2_12_12$ ($a=10.7028 \text{ \AA}$, $b=12.8508 \text{ \AA}$, $c=6.5844 \text{ \AA}$, $V=905.62 \text{ \AA}^3$) at 298 K (phase I). The Ti complex resides on a two-fold axis with $Z'=0.5$. Complex (I) undergoes two sharp enantiotropic phase transitions upon cooling. The first transformation occurs at 293 K to yield a unit cell with a doubled c axis ($a=10.5539 \text{ \AA}$, $b=12.8757 \text{ \AA}$, $c=13.0817 \text{ \AA}$, $V=1777.66 \text{ \AA}^3$) at 175 K and the orthorhombic space group $P2_12_12_1$ (phase II). The doubling of the unit cell volume results in the addition of a translational component to the two-fold rotational symmetry in the c direction, and now the complex is in a general position. The second transition takes place at 147 K to convert the single crystal into a merohedrally twinned crystal with two monoclinic components of half the size ($a=10.5529 \text{ \AA}$, $b=12.7403 \text{ \AA}$, $c=6.5486 \text{ \AA}$, $\beta=92.327^\circ$, $V=879.71 \text{ \AA}^3$) at 100 K) in the monoclinic space group $P2_1$ (phase III). The Ti complex remains in a general position. The concomitant phase transition and twinning necessarily result in the loss of symmetry along the a and c axes and can be thought of as taking the b axis in phase II and "pulling" (shifting) it in the positive direction to generate the twinning in phase III (see diagram). The unique angle widens as the temperature is lowered. The variable temperature study of the selected crystal was conducted in an automated mode on a Bruker SMART APEX2 diffractometer with Cu $K\alpha$ radiation while the exact transition temperatures were manually pinpointed with Mo $K\alpha$ radiation. The molecular symmetry evaluations and exact refinement procedures are also discussed.

Keywords: Polymorphism, Twinning, Solid phase transitions

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Knowledge-based design of host-guest interactions in wheel-and-axle inorganic diols

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We are interested in the design of hybrid organic-inorganic wheel-and-axle systems (waad) with flexible dynamic frameworks that can create pores "on demand" to accommodate small guest molecules [1-3]. A reversible dynamic reorganization between the waad non-solvate and solvate phases requires two conditions: (i) a low cost structural rearrangement between two states represented by the initial close (self-mediated) and the final open (guest-mediated) host frameworks, (ii) an easily accessible migration path for the outgoing and incoming guest molecules. Palladium complexes of triarylcarbinol ligands have shown suitable structural requisites to give reversible host-guest properties [2, 3]. New iminic ligands designed on this basis result very promising promoters of potentially bistable supramolecular architectures based on metallo-organic supramolecular building units as wide as 40 Å (Figure).

References

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Keywords: host-guest complexes, supramolecular assemblies, crystal engineering

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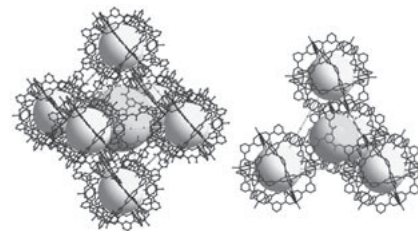
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A designed metal-organic framework based on a metal-organic polyhedron

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Metal-organic frameworks (MOFs) based on metal-organic polyhedra (MOPs) might provide efficient ways for the construction of designed porous MOFs, because MOPs themselves have their inherent cavities. We have prepared a (3,24)-connected MOF, $[Zn_{24}(L)_8(H_2O)_{24}]_n$, using a C_3 symmetric tritopic ligand, 5,5',5''-[1,3,5-benzenetriyltris(carbonylimino)]tris-1,3-benzenedicarboxylic acid (H6L). The carboxylate groups of 1,3-benzenedicarboxylate unit of the ligand can be combined with Zn^{2+} ion to form paddle wheel secondary building units, $Zn_2(COO)_4$, which produce an edge-directed corner-linked metal-organic cuboctahedron (MOC). The planar C_3 symmetric tritopic character of the ligand can force all of the resulting MOCs to a triangular arrangement for a cubic close packing (CCP) arrangement at all 24 edges of the cuboctahedron. This CCP arrangement of the MOCs led to additional superoctahedral and supertetrahedral cavities. Though the (3,24)-connected MOF represents the highest connected network topology presently known for frameworks corresponds to ~71% of the total crystal volume.



Keywords: metal-organic framework, metal-organic polyhedra, metal-organic cuboctahedron

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Properties of metal-organometallic frameworks derived from facially η^6 metalated terephthalates

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Interest in the design and synthesis of metal-organometallic

frameworks has grown drastically over the past few years. The use of multifunctional ligands, such as organometallic complexes, permits the introduction of other functionalities within the frameworks. We have synthesized and characterized a series of metal-organometallic framework (MOMF) materials, derived from simple [CpFe-(η^6 -arene-carboxylate)] bridging ligands. Depending on the reaction conditions, solid state structures ranging from simple 1D polymer chains to three dimensional square grid structures have been obtained. For example, the reaction of Ni(NO₃)₂·6H₂O with [CpFe]⁺-metalated 1,4-benzenedicarboxylic acid (1) results in [Ni₃(1-H)₄(H₂O)₂(μ -H₂O)₂][NO₃]₂, a 3D framework material constructed of square grid nickel-carboxylate networks that are interconnected in the third dimension through additional nickel ions. The synthesis, structure and characterization of these materials will be presented.

Keywords: coordination polymers, framework structures, ferrocene derivatives

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Cis-trans isomerizations and rearrangements during hydrothermal synthesis of metal carboxylates

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Hydrothermal conditions provide clean routes for the synthesis of new hybrid organic-inorganic frameworks. However, at elevated temperature and pressure, it is possible to induce reactions in the organic ligand used. For example, carboxylic acids may undergo isomerization, rearrangements, decompositions, hydrogen abstractions, etc. Unsaturated carboxylic acids may, additionally, suffer dimerization, oligomerization, or polymerization. Even though the hydrothermal reaction may not lead to the desired compound, it may produce an interesting derivative not accessible by other means. For instance, reaction at 160 °C during 48 h of *cis*-4-cyclohexene-1,2-dicarboxylic acid with Ca(OH)₂ afforded *cis*-4-cyclohexene-1,2-dicarboxylato)calcium(II), [CaC₈H₈O₄]. However, when using BaCO₃, under the same conditions, a product which contains the original ligand in the *trans* conformation, diaquabis(*trans*-cyclohex-4-ene-1-carboxylic-2-carboxylato)barium(II), [Ba(C₈H₉O₄)₂(OH₂)₂], is obtained. Other reactions which involve partial decomposition and rearrangement of the organic moiety, leading to mixed ligand compounds will be discussed. We thank R. Benson (Rigaku-USA) and M. Pink (Indiana University), for support with data collection. This work was funded by FONACIT-Venezuela, through grant LAB-97000821.

Keywords: cis-trans isomerization, hydrothermal synthesis, metal carboxylates

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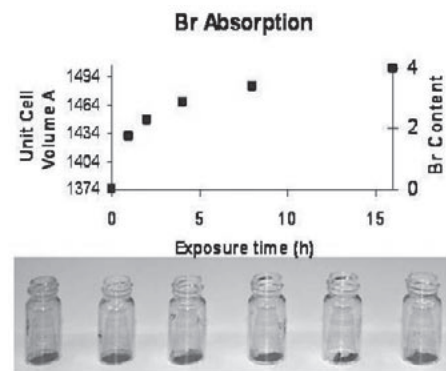
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Real crystal engineering: Solid state reactions in metal-organic compounds

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The results of our recent solid state reaction studies applied to the synthesis of hybrid organic-inorganic crystalline solids are presented. Development of methods suitable to prepare solid solutions are reported that allow control of their unit cell dimensions and polymorphism. Mechanochemical reactions are shown to be excellent alternatives to traditional solution methods in preparing coordination polymers and metal-organic hydrogen-bonded networks. Similar products can be prepared by gas-solid methods such as hydrochlorination or dehydrochlorination of crystalline precursors. In some cases reactions proceed under topochemical control to give different products. Precise control over unit cell metrics can be achieved by solid-gas halogen-exchange reactions that enable the modification of the unit cell volume, whilst the formation of a two-metal solid solution allows the coordination geometry of one metal to constrain the other and hence the resulting crystal structure and symmetry. Combined, these methods offer promise helping to control composition, polymorphism and unit cell dimension of the crystal species considered: real crystal engineering.



Keywords: crystal engineering, solid state reactions, polymorphism

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Design of supramolecular complexes: From concept to crystal structures

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In order to understand the hydrogen bond interaction between an active pharmaceutical ingredient (API) and its receptor, we have investigated small complexes with structurally similar bonding patterns. The co-crystallization of specific supramolecular complexes is not a straightforward procedure. The process, from the pre-selection of potential candidates to the successful co-crystallization of small receptor/ligand models, should not be left to chance. Therefore we have developed a concept for designing these structures. After selection of model compounds with complementary functional groups, we calculate the structures and energies of a multitude of alignments (constellations) by means of our force-field program MOMO [1]. These calculations are time-consuming if the molecules possess a number of torsional degrees of freedom and are thus able to adopt different conformations. Various analytical tools are used to identify the intermolecular hydrogen-bond interactions (especially IR spectroscopy and powder diffraction). The most promising combinations are then selected for further co-crystallization experiments. We have studied many different hydrogen-bond arrangements between at least two acceptor or donor groups at each molecule, advancing our examination to three hydrogen bonds with diverse hydrogen-bonding patterns. We are not only interested in forming the desired hydrogen bonds but also how to prevent undesired ones. The prerequisite for this is a thorough consideration