

$b = 9.6565(5)$, $c = 23.2828(11)$ Å, $\beta = 111.637(8)^\circ$, $V = 4759.6(4)$ Å³, space group $C2/c$. The 3.3% reduction in unit cell volume is explained in terms of water loss, rearrangement of the water structure and coordination about the mobile Co atom.

Keywords: cubane, modulation, magnetism

MS66.P03

Acta Cryst. (2011) A67, C638

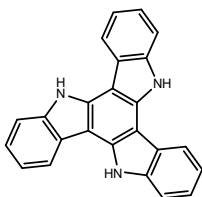
Semiconducting triindoles: Crystallographic packing vs electrical performance

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The field of organic electronics has experienced an enormous development over the past ten years and today we can consider it a mature field. Devices such as OLEDs, OFETs or photovoltaic cells are already reaching the market. These devices have in common that their performance depends on how efficiently charge carriers move in the organic active layers. Important advances achieved in this field have been therefore connected to the enhancement of the charge carrier mobility of the organic molecules which have reached values that can already compete with amorphous silicium.

In close relation with the supramolecular order, the highest charge carrier mobility is usually obtained in organic single crystals. Furthermore, organic single crystals offer an excellent opportunity to investigate structure-properties relationships and to elucidate charge transport mechanisms in organic materials, not yet fully understood.

In this context we have recently introduced heptacyclic 10,15-dihydro-5*H*-diindolo[3,2-*a*:3',2'-*c*]carbazole (triindole) as an interesting new organic semiconductor.



This molecule is an electron-rich heptacyclic platform with a high tendency to aggregate both in solution and in crystalline state. We have recently found that CH- π interactions have an important role in the self assembly of triindole-based molecules[2],[3]. Triindole-based single crystalline materials have been found to exhibit high hole mobilities (up to $\mu = 0.4$ cm² V⁻¹ s⁻¹) since they combine intrinsic electron donor properties with a highly ordered columnar packing that paves the way for increased charge carrier mobility due to favorable intermolecular π -orbitals overlap [1].

In this communication, we present how through an adequate functionalization we can modulate both the intermolecular interactions and the crystallographic packing, as could be determined through single crystal analysis of different derivatives. It will be shown how the crystallographic packing influences the electrical performance and the processability of these materials essential parameters towards their incorporation in devices.

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Keywords: organic, electronics, semiconductor

MS66.P04

Acta Cryst. (2011) A67, C638

Solid state transformation in coordination polymers with flexible ligands

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There is a growing interest in the nature of flexible and dynamic metal-organic frameworks (MOFs) owing to their potential applications as functional materials. Several examples of 'breathing' MOFs are known, in which structural changes occur without bond cleavage. In turn, few examples of MOFs in which the solid state transformation involves covalent bond breaking and formation are also known [1].

Herein, we report two new coordination polymers, {[Co(L)₂(OH₂)₂·2NO₃·2H₂O]_n} (1), and {[Co(L)₂(NO₃)₂]_n} (2), where L is the neutral N-donor ligand, 1,4-bis(triazolylmethyl)benzene. Remarkably, compound 1 is able to extrude the H₂O molecules (both solvated and coordinated) and transforms into compound 2 in the solid state. This process occurs on heating, with a consequent rearrangement of the 1D chains present in 1 into 2D layers. It is accompanied by a change in conformation of the flexible ligand, which implies breaking and formation of Co-N bonds. Such a change in conformation has been followed by spectroscopic techniques. Additionally, conversion of 1 into 2 also requires coordination of the NO₃ anions to the metal centers, which implies a substantial change in the Co^{II} environment that has been monitored by EPR.

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Keywords: MOF, flexible framework, molecular dynamics.

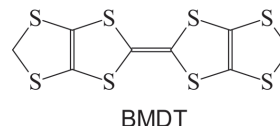
MS66.P05

Acta Cryst. (2011) A67, C638-C639

New molecular conductors with halogen substituted cobalt bis(dicarbollide) anions

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Radical cation salts and charge transfer complexes based on bis(ethyleneedithio)tetrathiafulvalene (ET) and its derivatives constitute a wide class of organic materials with transport properties ranging from insulating to superconducting.



Recently we started study of effect of different substituents in the iron group metal bis(1,2-dicarbollide) complexes on crystal packing and physical properties of their salts with radical cations – ET derivatives. In this report we describe synthesis, crystal structure and electrical conductivity of ET and BMDT salts of halogen substituted cobalt bis(dicarbollide) anion: (ET)[8,8',7)-(Cl₂(Cl_{0.09})-3,3'-Co(1,2-C₂B₉H₁₀)(1,2-C₂B₉H_{9.91})] (1) (ET)[8,(7),8'-Br_{0.75}(Cl_{0.25})Cl-3,3'-Co(1,2-C₂B₉H₁₀)₂] (2) and (BMDT-TTF)₄[8,8'-Br_{1.16}(OH)_{0.72}-3,3'-Co(1,2-C₂B₉H_{10.06})₂] (3).

The geometry of the [8,8',7)-(Cl₂(Cl_{0.09})-3,3'-Co(1,2-C₂B₉H₁₀)(1,2-

$C_2B_9H_{9.91}]^-$ anion in salt **1** presented in Figure 1. The dicarbollide ligands are mutually rotated by 180° producing *transoid* conformation.

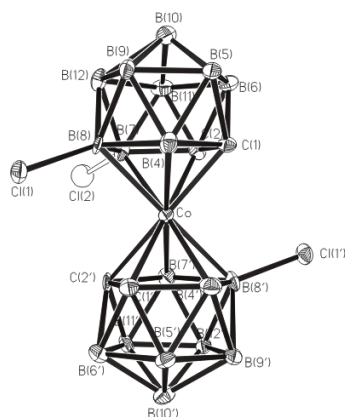


Fig. 1. The anion in (1). Hydrogen atoms omitted for clarity.

All radical cation salts prepared were found to be semiconductors, the room temperature conductivities are 2, 10^{-5} , $0.5 \Omega^{-1}cm^{-1}$, respectively.

Acknowledgements: The authors want to acknowledge Russian Foundation for Basic Research

Keywords: molecular conductors, X-ray study, materials

MS66.P06

Acta Cryst. (2011) A67, C639

Solvent-tuned Magnetic Behaviors of Manganese(III) Corroles

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Mn(tpfc) (tpfc = the trianion of 5,10,15-tri(pentafluorophenyl)corrole) is a good magnetic anisotropy motif. Compared to intense efforts on its catalytic performance [1, 2], rare research concentrates on its magnetic behaviors. We get three Mn(tpfc) solvates from methanol (**1**), ethyl acetate (**2**) and ethanol (**3**), respectively. Though they share the same magnetic repeating unit, they show quite different magnetic behaviors due to solvent-tuned different packing in crystal lattices. **1** and **2** are supramolecular 1D chains while **3** forms dimers. **1** with slow relaxation of magnetization below 2 K and magnetization hysteresis loop at 0.5 K is the first spin canted supramolecular single-chain magnet stemming from intermolecular $\pi-\pi$ interaction. **2** is an antiferromagnetic chain without ordering or slow magnetization relaxation down to 0.5 K while **3** shows field-induced single-molecule magnet-like behaviors below 2.5 K.

Such control of solvent on magnetic behaviors comes from different relative orientations of magnetic anisotropy axes induced by solvents and shows clear magneto-structural correlation.

We acknowledge the support of NSFC, the National Basic Research Program of China.

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Keywords: solvent, manganese, magnetism

MS66.P07

Acta Cryst. (2011) A67, C639

Multifunctional Gd^{III}-core nanoparticles directed by alkylnitrosopyrazolones

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The area of gadolinium(III) labelled nanoparticles for use as MRI contrast agents is rapidly increasing. They are usually envisaged as an inorganic nanoparticulate core of a Gd-containing species (i.e. Gd₂O₃) coated with a polymeric shell.[1] Our strategy consists in developing Gd(III) coordination clusters where specific organic molecules act as chelating and coating agent simultaneously. For this function we have selected a pyrazolone-derivative.

Pyrazolones constitute a wide family of organic heterocyclic compounds that are very relevant because of chemical, biological and medicinal points of view. The tautomerism that they exhibit, their use in dyes, as derivatizing agents in carbohydrate analysis and also as chelating ligands are among the most appealing chemical points of these heterocycles. Concerning their biological/medicinal aspects, two illustrative examples are the analgesic antipyrine still in use in several countries and Edaravone[®], a radical quencher that is used to treat brain ischemia.

Here we report the synthesis, crystal structure and magnetic properties of the complex [Gd₃L₁₁(μ₃-O)₂(H₂O)₂]-H₂O where L = 1-hexyl-3-phenyl-4-nitroso-5-pyrazolone. This compound is formed by nanoparticles of ca. 3.5 nm diameter that are stable in solution, a situation that has been confirmed by AFM studies. The luminescence of the nanoparticles has also been characterized.

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Keywords: nano, luminescent, gadolinium

MS66.P08

Acta Cryst. (2011) A67, C639-C640

Synthesis and structural characterization of [H₃N(CH₂)₄NH₃][Y(hedpH)][hedpH₂]

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We have recently reported the synthesis and crystal structure of a family of [H₃N(CH₂)₄NH₃]₂Ln[hedpH][hedpH₂], with Ln = La, Pr, Sm, Eu, Gd, Tb and Er [1, 2].

These phosphonates are based on 1-hydroxyethane-1,1-diphosphonic acid [hedpH₄, H₂O₃PC(OH)(CH₃)PO₃H₂], which has been widely used as a strong chelating agent in the preparation of functional