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Acta Cryst. (2008). A64, C414**Synthesis and spectroscopic characterization of high-spin iron(III) oxalato porphyrin complex**

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The metalloporphyrins serves as models for the active sites and formed of a heme (protoporphyrinIX of iron(II)). The porphyrin complex of iron(III) present an anionic ligand, this new complex is not known in the literature. The preparation and characterization of the (oxalato) complex is described. The synthesis procedure utilizes the crown(18-C-6) to solubilize potassium oxalate. This compound has been characterized by UV-vis, IR and ^1H NMR spectroscopies. In electronic spectroscopie, our derivative presents a strip of Soret to 415 nm and a strip to 509 nm. These values are very near of those of the porphyrins iron(III) complex to high-spin ($S = 5/2$). The IR data show the existence of two epaulements 1672 cm^{-1} and 1664 cm^{-1} that one can assign to the $\nu_1(\text{C}=\text{O})$ and a second 1385 cm^{-1} assigned to the $\nu_2(\text{C}-\text{O})$ vibration of the ligand oxalate[1]. Many works of the ^1H NMR on porphyrins iron(III) complex show that in the case of the méso-porphyrins, the protons β -pyrrolic is very sensitive to the state of spin of the iron(III)[2]. The ^1H NMR is a spectroscopic method of choice to determine the state of spin of the complex of iron(III) [2]. The derivatives of iron(III) high-spin ($S = 5/2$) with the méso-porphyrins present in ^1H NMR spectroscopie of the proton of the resonance peaks β -pyrrolic a lot of deblind ([70,100]ppm). Proton NMR data for the isolated product is in accordance with high-spin ($S = 5/2$) ferric porphyrin species. The X-ray molecular structure of this species has been also determined. The iron atom is hexa-coordinated by the four nitrogen atoms of the pyrrol rings and the two oxygen atoms of the ligand group.

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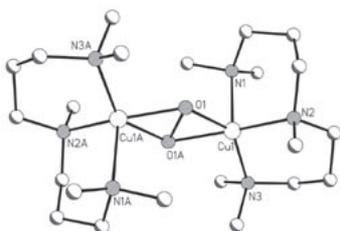
Keywords: metalloporphyrins, oxalato-complexes, ^1H NMR

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Acta Cryst. (2008). A64, C414**X-ray diffraction study of a low-temperature copper(I)/dioxxygen adduct: A solid solution**

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Single crystals of $[\{\text{Cu}(\text{MeAN})\}_2(\text{O}_2)]_2(\text{SbF}_6)_2$ have been isolated at -80°C and studied via X-Ray diffraction. The results suggest the presence of a Cu_2O_2 core that is "intermediate" in structure between that known for well established side-on $\mu:\eta^2:\eta^2$ -peroxo-dicopper(II) and bis- μ -oxodicopper(III) species;¹ these isomers possess very different Cu-Cu and O-O distances. Whereas resonance Raman spectra indicate that both are present in solution, the X-Ray data describe an average



of both forms that exist as a solid solution. EXAFS data in support of this conclusion and the ability of single-crystal diffraction studies to adequately differentiate the side-on peroxo from the bis- μ -oxo species are discussed. Additionally, the techniques used to prepare the sample at low-temperatures for the diffraction experiment are described.

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Keywords: copper-dioxygen complex, bio-inorganic, low-temperature

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Acta Cryst. (2008). A64, C414**Synthesis and crystal structure of methylammonium bis(citrato)borate**

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A new complex $\text{CH}_3\text{NH}_3[(\text{C}_6\text{H}_6\text{O}_7)_2\text{B}]$ (**I**) has been synthesized and its X-ray investigation has been carried out in order to extend the investigations of bis(citrato)borate structures containing alkylammonium cations – LH^+ $[(\text{C}_6\text{H}_6\text{O}_7)_2\text{B}] \times n\text{H}_2\text{O}$, $\text{L} = (\text{CH}_3)_2\text{NH}$ (**II**), $\text{L} = (\text{C}_2\text{H}_5)_2\text{NH}$ (**III**), $\text{L} = (\text{C}_2\text{H}_5)_3\text{N}$, $n = 1$ (**IV**). In the crystals **I** the spiran-type complex anion are formed by two citric acid molecule residues coordinated to the BO_4 tetrahedron. The bonds $\text{B}-\text{O}(\text{carb.})$ (av. $1.492(2)\text{ \AA}$) are longer than bonds $\text{B}-\text{O}(\text{hydr.})$ (av. $1.455(2)\text{ \AA}$). The two chelate rings are planar and approximately perpendicular ($87.8(1)^\circ$). In citric acid residues the average bond lengths are: in the terminal carboxyl groups $\text{C}-\text{OH}$ $1.314(3)\text{ \AA}$, $\text{C}=\text{O}$ $1.203(3)\text{ \AA}$; in the central carboxyl groups $\text{C}-\text{O}(\text{H})$ $1.313(2)\text{ \AA}$, $\text{C}=\text{O}$ $1.215(2)\text{ \AA}$; $\text{C}(\text{sp}^3)-\text{O}(\text{H})$ $1.422(1)\text{ \AA}$. The $\text{C}(\text{sp}^2)-\text{C}(\text{sp}^3)$ bonds are $1.505(3)\text{ \AA}$ and $1.531(3)\text{ \AA}$ long in average, respectively. In methylammonium cation the bond length $\text{N}(\text{sp}^3)-\text{C}(\text{sp}^3)$ is $1.436(5)\text{ \AA}$, the $\text{N}-\text{H}$ bonds are $0.96(3)\text{ \AA}$ in average; the individual values of $\text{H}(\text{C})-\text{N}-\text{H}$ angles are within $100.2^\circ - 116.3^\circ$. The hydrogen bond system includes seven independent hydrogen bonds. The crystal structures of **I**, **II** and **IV** are lamellar, structure of **III** – three-dimensional. The comparative crystal chemical analysis of the crystal structures of **I** – **IV** shows that substitution of hydrogen atoms in the ammonium cation by alkyl-groups causes the changes in the density, crystal symmetry, spatial package of crystal structures and hydrogen bond systems. Crystals are triclinic, sp. gr. centrosymmetric: $a=8.973(2)$, $b=10.104(1)$, $c=10.723(1)\text{ \AA}$, $\alpha=66.894(1)$, $\beta=85.347(1)$, $\gamma=84.991(2)^\circ$, $V=889.6(2)\text{ \AA}^3$, $Z=2$; $R=0.0473$.

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2. I.Zviedre, S.Belyakov, *Latv. Khim. Zh.* (2007) No 3, pp. 237-248.

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Keywords: boron compounds, coordination compounds, X-ray analysis

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Acta Cryst. (2008). A64, C414–415**Crystal structure, magnetic and dielectric property of linear chain rhodium(I)-semiquinonato complex**

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Recently, multiferroic materials exhibiting ferromagnetic and ferroelectric properties have attract much attention because of the control of a magnetism by an electric field and/or the control of an electric polarization by a magnetic field.¹ We are studying the syntheses and the correlation between crystal structures and solid-state properties of a series of linear chain rhodium(I)-semiquinonato complexes from the viewpoint of the development of multifunctional materials based on the frontier orbital control.² Here we report the crystal structure, magnetic and dielectric properties of a linear chain rhodium(I)-semiquinonato complex, [Rh(3,6-DBSQ-4,5-(MeO)₂)(CO)₂] (**1**) (3,6-DBSQ-4,5-(MeO)₂ = 3,6-di-*tert*-butyl-4,5-dimethoxy-1,2-benzosemiquinonato). Complex molecules of **1** are stacked by the Rh-Rh interactions to form a linear chain structure. This compound undergoes first-order phase-transition in the temperature range of 208-224 K. Magnetic property changes from an antiferromagnetic interaction (room temperature (RT) phase) to a ferromagnetic one (low temperature (LT) phase, $\theta = +64$ K). This compound undergoes a magnetic phase-transition to the metamagnet in which the interchain interaction is a ferromagnetic whereas the intrachain interaction is antiferromagnetic ($T_N = 13.8$ K). Furthermore, the real part, ϵ' , of dielectric constant along 1-D chain in the RT phase shows the large value of 1000-2500 depending on the measuring frequency. ϵ' decreases rapidly with first-order phase-transition and takes a temperature-independent value of ca. 160 in the LT phase. *P-E* hysteresis measurement to reveal the ferroelectricity of this compound is now in progress.

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Keywords: crystal structure and properties, ferromagnetism, dielectric properties

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Magnetic and structural properties of some triazole metal complexes

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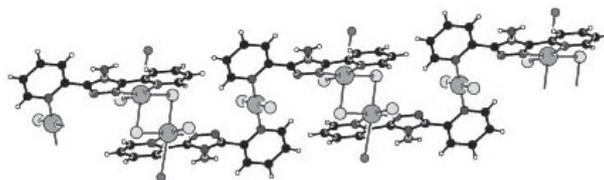
1,2,4-triazole and triazole derivatives have shown to be good bridging ligands between 3d transition metals and the magnetic complexes thus achieved have shown several magnetic properties ranging from strong antiferromagnetic to ferromagnetic coupling [1]. Also, low spin to high spin transitions, induced by temperature changes, have been observed in polymeric Fe-triazole chains [2]. We have synthesised three new metal complexes mixing 4-amino-3,5-di-2-pyridil-4H-1,2,4-triazole with copper and manganese chloride, using different solvents. The ditriazole-dibenzoato-Cu(II) and the triazole-aqua-manganese complex, both triclinic, crystallize with the metal atoms in octahedral environments, four nitrogen atoms in the equatorial plane and two oxygen atoms in the axial positions. The copper chloride complex, monoclinic, shows the formation of chains running along the [101] direction. The chains consist of alternating dimers/monomers. The structural and magnetic results will be presented.

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Keywords: metal complex, coordination, magnetic

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Construction molecular magnet with porosity, chirality from [Fe(C₂O₄)Cl₂]_n with cation templet

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One-dimensional antiferromagnetic [Fe(C₂O₄)Cl₂]_n which merged from [CrMn(C₂O₄)₃]_n and FeCl₄⁻ is a good anion for conductive molecular magnet as weak-ferromagnetic conductor and weak-ferromagnetic insulator [1-5]. Three kinds configurations of [Fe(C₂O₄)Cl₂]_n chain in the molecular crystal have been found depending on cation templet: the first one is zigzag chain, the second one is boat-shape chain, the third one is a chiral chain which produce chiral magnet from achiral ligands. A molecular magnets of [Fe(C₂O₄)Cl₂]_n with porosity was got. Their crystal structures and physical properties were studied.

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Keywords: dual-function molecular crystal, molecular magnet, chiral magnet