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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 ν₁(C=O) and a second 1385 cm⁻¹ assigned to the ν₂(C-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.

[1]. Kazuo Nakamoto; *Infrared and Raman Spectra of Inorganic and Coordination Compound* (4th Edition), Wiley-Interscience ed., New-York (1986)

[2]. N. G. La. Mar, F. A. Walker, in "The porphyrins", (D. Dolphin, Ed), Academic Press, New York, (1979), 4,61.

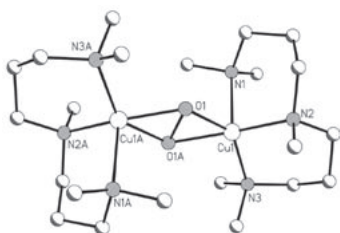
Keywords: metalloporphyrins, oxalato-complexes, ¹ H NMR

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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 Cu₂O₂ core that is "intermediate" in structure between that known for well established side-on μ:η²:η²-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.

1. Mirica, L. M.; Ottenwaelde, X.; Stack, T. D. P. *Chem. Rev.* 2004, 104, 1013-1045.

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 CH₃NH₃[(C₆H₆O₇)₂B] (**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⁺ [(C₆H₆O₇)₂B] × nH₂O, L = (CH₃)₂NH (**II**), L = (C₂H₅)₂NH (**III**), L = (C₂H₅)₃N, n = 1 (**IV**). In the crystals **I** the spiran-type complex anion are formed by two citric acid molecule residues coordinated to the BO₄ tetrahedron. The bonds B - O(carb.) (av. 1.492(2) Å) are longer than bonds B - O(hydr.) (av. 1.455(2) Å). The two chelate rings are planar and approximately perpendicular (87.8(1)°). In citric acid residues the average bond lengths are: in the terminal carboxyl groups C - OH 1.314(3) Å, C=O 1.203(3) Å; in the central carboxyl groups - C - O(H) 1.313(2) Å, C=O 1.215(2) Å; C(sp³) - O(H) 1.422(1) Å. The C(sp²) - C(sp³) bonds are 1.505(3) Å and 1.531(3) Å long in average, respectively. In methylammonium cation the bond length N(sp³) - C(sp³) is 1.436(5) Å, the N - H bonds are 0.96(3) Å in average; the individual values of H(C) - N - H angles are within 100.2° - 116.3°. 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) Å, α=66.894(1), β=85.347(1), γ=84.991(2)°, V=889.6(2) Å³, Z=2; R=0.0473.

1. I.Zviedre, V.K.Belskii, *Latv. Khim. Zh.* (2007) No 1, pp. 29-42.
2. I.Zviedre, S.Belyakov, *Latv. Khim. Zh.* (2007) No 3, pp. 237-248.
3. I.Zviedre, S.Belyakov, *Zh. Strukt. Khim.* (in press).

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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