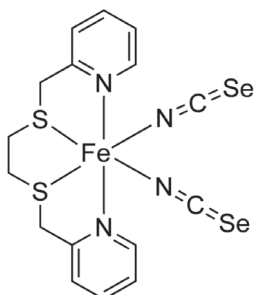


**MS27-03** **Four-Site Cooperative Spin Crossover in Polymorphs of a Mononuclear Fe(II) Complex.** Andrew D. Bond,<sup>a</sup> Anders Lennartson,<sup>a</sup> Stergios Piligkos,<sup>b</sup> Christine J. McKenzie<sup>a</sup> <sup>a</sup>University of Southern Denmark, Odense, Denmark, <sup>b</sup>University of Copenhagen, Denmark  
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Four-site cooperative spin crossover (SCO) in a mononuclear Fe(II) complex has been observed for the isoselenocyanate complex  $[(bpte)Fe^{II}(NCSe)_2]$  ( $bpte = S,S'$ -bis(2-pyridylmethyl)-1,2-thioethane). The compound has been characterised in four polymorphic crystalline phases. One is SCO-inactive ( $\beta$  phase), one exhibits one-step SCO ( $\gamma$  phase) and two exhibit four-site cooperative SCO ( $\alpha$  and  $\delta$  phases) as a function of temperature. Crystal structures have been determined over the temperature range 300–100 K for all four polymorphs, and at intervals of 5 K for the most interesting  $\alpha$  and  $\delta$  phases. Of the five potentially addressable local spin configurations in a four-site cooperative system, four are observed as ordered crystal structures amongst the polymorphs. The  $\delta$  phase exhibits a remarkable ordered 1HS:3LS structure (HS = high-spin Fe(II), LS = low-spin Fe(II)) below *ca* 130 K, which establishes conclusively the four-site cooperative nature of the system. The  $\alpha$  and  $\delta$  phases are polytypes, but it is difficult to link conclusively the associated two-dimensional structural similarity with the four-site cooperativity.



**Keywords:** spin crossover; polymorphism; magnetism

**MS27-04** **Synthesis and crystal structure of few new decavanadates.** Wiesław Łasocha<sup>ab</sup>, Anna Szymańska<sup>a</sup>, Wojciech Nitek<sup>b</sup>, Alicja Rafalska-Łasocha<sup>b</sup>, J.Haber Institute of Catalysis PAS, Kraków, Niezapominajek 8, Poland, <sup>b</sup>Faculty of Chemistry Jagiellonian University, Kraków, Poland,  
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Vanadates and peroxovanadates are used as valuable catalysts. They can be also applied in medicine thanks to their enzyme-imitative properties. During our studies of new peroxo-vanadates and poli-vanadates we have synthesized three new compounds which belong to the group of deca-vanadates: two organic decavanadates and a rubidium decavanadate. The obtained compounds have the same, island-like type of anion, which is built of  $VO_6$  octahedra. The structure of deca-vanadates can be described on the basis of the structures of b-octamolybdates. If in a -octamolybdate anion, Mo(VI) ions are replaced by V(V) ions  $V_8O_{26}^{-12}$  ions will be obtained. When to the  $V_8O_{26}^{-12}$  ion two  $VO_6$  octahedra (or  $VO_3^{3+}$  after removal of the redundant O atoms) are attached  $V_{10}O_{28}^{-6}$  anion is created. The syntheses were carried out in 30%  $H_2O_2$ . After crystallization, which lasted several days, deca-vanadates without  $O_2^{2-}$  groups were obtained. Explanation of this phenomenon will be the subject of our further research.

Lattice parameters and chemical formulas of the obtained compounds:

1.  $Rb_6V_{10}O_{28} \cdot 8H_2O$ :  $P2_1/c$ , 13.974, 10.595, 34.291 Å, 90, 97.437, 90°,  $V = 5034.23 \text{ Å}^3$ ,  $Z = 6$ .
2. 5(1-ammoniumpropane)( $H_3O^+$ ) $V_{10}O_{28} \cdot H_2O$ , P-1, 14.507, 15.502, 15.858 Å, 88.22, 81.53, 83.94°,  $V = 3507.21 \text{ Å}^3$ ,  $Z = 3$ ,
3. 2(1,2-diammoniumpropane).2( $H_3O^+$ ) $V_{10}O_{28} \cdot 4H_2O$ , P-1, 8.636, 10.394, 10.959 Å, 68.86, 78.92, 66.99°,  $V = 843 \text{ Å}^3$ ,  $Z = 1$ .

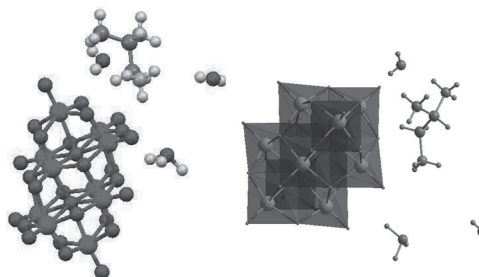


Fig. 1. Asymmetric unit of compound 3.

Properties and geometry of the synthesized compounds will be compared with the properties and structures of several decavanadates described in a comprehensive survey recently published [1]. The investigated compounds form complex structures often with several molecules in an asymmetric unit. For example, in the structure of the decavanadate denoted above as 2, the channels with dimensions of about  $\sim 10 \text{ Å}$  exist between the inorganic anions. Results of powder diffraction investigations of rubidium and cesium decavanadates indicate that both salts are probably isostructural. Purity of the obtained phases and thermal stability of all investigated compounds were also examined by means of powder diffractometry.

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- [1] N. Bosnjakovic-Pavlovic, J. Prevost, A. Spasojevic-de Bire. (2011) Cryst. Growth Des., 11, 3778–3789.

**Keywords:** vanadates, crystal structure analysis, powder diffraction