

isotropic after all.

In conclusion, the thermal behaviours of SA and ESA are quite similar indeed, despite some minor differences in their packings, which appears to confirm our previous hypothesis, given in [2], regarding the geometrical reasons for the  $\beta$  to  $\alpha$  transition.

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#### MS25 P04

**Cobalt cations distribution in fully dehydrated CoX zeolite studied by XRD and XAS** Elena Borissenko<sup>a</sup>, Florence Porcher<sup>a</sup>, Mohamed Souhassou<sup>a</sup>, I-Jui Hsu<sup>b</sup>, Yu Wang<sup>b</sup>, Claude Lecomte<sup>a</sup>, <sup>a</sup>*Laboratoire de Cristallographie et Modélisation des Matériaux Minéraux et Biologiques, LCM3B UMR 7036, CNRS - Université Henri Poincaré, BP 239, 54506 Vandœuvre-lès-Nancy, France.* <sup>b</sup>*Department of Chemistry, National Taiwan University, Taipei, Taiwan.*

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The numerous applications of natural/synthetic zeolites as catalysts, ion exchangers and for gas separation rely on their porous crystal structure (sieving effect) together with their electrostatic properties (distribution of cations/acid sites). The zeolites hosting transition-metal cations have interesting catalytic activity and are already used, for example, in oxidation reactions of organic compounds. Stable complexes formed by insertion of pyridine-based molecules in transitional-metal zeolites (like (bpy)<sub>3</sub>@zeolite CoX) have been evoked to exhibit remarkable magnetic properties [1]. In both cases, the macroscopic properties rely on the interactions of the guest molecules with the zeolite framework and cations and the precise knowledge of the crystal structures of these compounds is, therefore, of prime interest. However, most of these structures are not well known because of the difficulty to grow single crystals for XRD measurements, and of the disorder caused by partial cation exchange and hydration.

In this context, the crystal structure of fully dehydrated but partially exchanged Na<sub>13</sub>Co<sub>32</sub>X zeolite has been determined from single crystal and powder XRD. All the charge compensating cations were located in the structure (Sites I, I', II, III). The interpretation of a weak electron density peak close to Site I' found in XRD Fourier maps, but hardly assignable to Co<sup>2+</sup> cation on the basis of XRD data was ascertained by X-ray Absorption Spectroscopy (XAS) (NSRRC, Taiwan). The combination of EXAFS and XRD analyses also indicates that the Co cations sitting in site I are involved in a distorted hexagonal antiprism (result also supported by Monte Carlo calculations [2]).

The migration of cations and the drastic structural modifications endured by the framework over dehydration were also studied from 3 partially hydrated crystals. The comparison of CoX dehydrated structure to the native NaX and other ion-exchanged dehydrated M<sup>n+</sup> zeolite X structures evidences a relationship between these structural modifications and the nature of the charge compensating cation and its shielding by water molecules.

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#### MS25 P05

**Synthesis and structural characterization of new organic-inorganic hybrids based on polyoxometalates.** Mongi Debbabi<sup>a</sup>, Hafedh Driss,<sup>a,b</sup> and René Thouvenot,<sup>b</sup>

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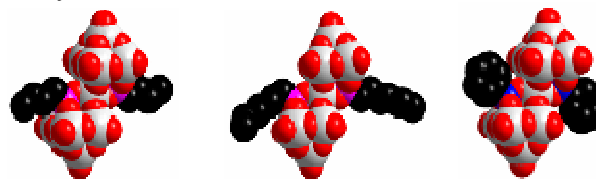
**Keywords:** Hybrid anion, polyoxometalate, Lindqvist structure.

Polyoxometalates (POMs) constitute an unprecedented class of compounds in terms of number and structural diversity. They exhibit remarkable chemical and physical properties and are of great interest in different fields such as medicine, biology, catalysis, material sciences, chemical analysis. Derivatization with organic groups attached covalently to the metal centers [1], [2] or electrostatically [3] to the periphery constituted by the oxo groups of the POM can alter the properties of POMs towards increased or decreased activity, efficacy and specificity in catalysis. The focus of this work is a new type of undeca-transition metaloxo anion cluster (polyoxometalate) derivatized with organophosphonyl groups NbW<sub>10</sub>O<sub>38</sub>(RP)<sub>2</sub><sup>3-</sup>. These compounds are resulting from reaction of organophosphonic dichloride RPOCl<sub>2</sub> (R = Et, Pr, Bu, Hexyl, Heptyl, Cyclohexyl, Ph) with monosubstituted isopolyanion NbW<sub>5</sub>O<sub>19</sub><sup>3-</sup>. These new polyoxometalates have been characterized by infrared and Raman spectroscopy, multinuclear <sup>31</sup>P and <sup>183</sup>W NMR, and X-ray crystallography. The anion is built-up from an {Nb(RPO)<sub>2</sub>} group linking two W<sub>5</sub>O<sub>18</sub> subunits which can be viewed as lacunary derivatives of the NbW<sub>5</sub>O<sub>19</sub> structure. Infrared spectrums of all hybrid anions are very similar, except in the organic groups part.

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Space-filling representation of anion NbW<sub>10</sub>O<sub>38</sub>(RP)<sub>2</sub><sup>3-</sup> respectively R=Bu, Heptyl, =Ph  
C: black, O: red, W,Nb: light grey, P: bleu