



	Experiment title: Structural investigation of dye modified mordenite	Experiment number: 01-02-622
Beamline: BM01A	Date of experiment: from: 23 July 2003 to: 26 July 2003	Date of report: 2004-03-03
Shifts: 9	Local contact(s): Prof. Vladimir DMITRIEV (e-mail: dmitriev@esrf.fr)	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Petra Simoncic*, Nicola Döbelin*, Thomas Armbruster

Laboratory for chem. and mineral. Crystallography

University of Bern

Freiestr.3

3012 Bern

Switzerland

Purpose: The aim of this study was a structural characterisation of different dye loaded, synthetic mordenite single crystals (preferred molecules sites, disorder). These dye-zeolite host-guest systems have applications as artificial antenna systems, where the dye mimic the role of chlorophyll in natural plants. Different dyes have been incorporated in various zeolites [1] (zeolite L, zeolite Y, and ZSM-5), but little is known about geometrical arrangement of the dyes in the zeolite channels.

In a preceding experiment (01-02-609) a data set of a thionine-loaded mordenite crystal was measured at room temperature. Although the orthorhombic symmetry of mordenite already limits disorder of the enclosed molecules, the structural refinement of thionine-mordenite showed distinct disorder of the organic molecule along axis of the large 12-membered ring channel. To obtain more reliable structural data, experimental settings were modified: (1) diffraction data of dye loaded mordenite single crystals were collected at 120 K to reduce disorder effects, (2) data of selenium-modified mordenite sample was measured (also at 120 K) to compare Se-sites in the mordenite channels with S-sites of the sulphur containing dye molecules. Cationic thionine blue $C_{12}H_9N_3S^+$, methylene blue $C_{16}H_{18}N_3S^+$, DAMS $C_{16}H_{19}N_2^+$ have been used for dye incorporation by ion exchange [2]. Elemental selenium and sulphur was induced in Na-mordenite by gas phase.

Experiment at BM1A

8 data sets of 6 different samples were collected:

- 1) Self-synthesised Na-mordenite single crystal ($Na_6Al_6Si_{42}O_{96} \times H_2O$) (1 data set)
- 2) Self-synthesised, partially exchanged Thionine-mordenite single crystal ($Na_x(C_{12}H_9N_3S)_{1-x} Si_{42}O_{96} \times H_2O$) (1 data set)
- 3) Self-synthesised, partially exchanged Methylene blue-mordenite single crystal ($Na_x(C_{16}H_{18}N_3S)_{1-x} Si_{42}O_{96} \times H_2O$) (2 data sets)
- 4) Self-synthesised, partially exchanged DAMS-mordenite single crystal ($Na_x(C_{16}H_{19}N_2^+)_{1-x} Si_{42}O_{96} \times H_2O$) (1 data set)
- 5) Self-synthesised, Na-mordenite single crystal with incorporated elemental selenium ($(Na_6Al_6Si_{42}O_{96} \times Se_{7.9})$) (2 data sets)
- 6) Self-synthesised, Na-mordenite single crystal with incorporated elemental sulphur ($(Na_6Al_6Si_{42}O_{96} \times nS)$) (1 data sets)

All samples were mounted on glass needles. Data collection was performed in dose mode for all crystals at room temperature with a wavelength of 0.7995 Å using the MAR image plate. All samples were cooled at 120 K by an conventional liquid-N₂ device during the data collection. All structures were refined in space group Cc.

Structural study of Se-modified Na-mordenite is submitted to "Microporous mesoporous materials" [3]:

Abstract: "Single crystals of self-synthesized mordenite-Na were used for incorporation of elemental selenium. The mordenite sample was first dehydrated at 280 °C and selenium was subsequently incorporated as gas-phase at 450 °C until mordenite changed colour to bright orange. Se-loaded mordenite was quantitatively determined by electron-microprobe analyses yielding Na₆Al₆Si₄₂O₉₆ × [Se_{7.9}]. X-ray data collection of mordenite-Na and Se-loaded mordenite-Na single-crystals were performed at 120 K with synchrotron radiation ($\lambda = 0.79946$ Å) using the single-crystal diffraction line at SNBL (ESRF, Grenoble) where diffracted intensities were registered with a MAR image plate. The structures of both mordenite-Na and Se-mordenite-Na were refined in monoclinic space group Cc converging at R1 = 5.25% (mordenite-Na) and R1 = 6.65% (Se-mordenite-Na). A strongly broadened Raman band at ca. 254 cm⁻¹ confirmed the existence of Se-chains in the 12-membered channels along the c-axis. Several, low-populated, disordered Se chains with a length up to 10 Å and 7 Se atoms were located in the large mordenite channel. During structure refinement nearest and next nearest neighbor Se-Se distances were fixed at 2.33 Å and 3.62 Å, respectively. Other distances and angles remained unconstrained. Because of electrostatic interaction with the framework and influence of extraframework occupants such as Na⁺ and H₂O molecules, the chains show different geometrical Se arrangement with highly variable dihedral angles. Any other Se species such as Se₆ or Se₈ rings were neither confirmed by structure refinement nor by Raman spectroscopy. There was no indication of a trigonal Se chain geometry within the 12-membered ring channel."

Dye-loaded mordenite samples:

The unit cell constants of all dye-loaded structures showed a significant change due to the molecule incorporation. All incorporated dye molecules have similar dimensions (15 - 17 Å length, 7 Å height). Compared with the channel aperture (6.5 × 7 Å), this allows only a limited position for the molecules in the 12-membered channel. Because the mordenite framework is flexible to a certain degree, the unit cell is expanded in a-direction and shortened in b-direction. The easiest way to localize the molecule site in the channel is to determine the position of the sulphur site, which is the heaviest atom within the molecule (thionine, methylene blue). By comparison of the difference fourier map of the 12-membered ring channel section down the c-axis (Fig. 1), it is obvious that the S atom has a similar position as the selenium sites in the Se-modified mordenite [2]. A highlighted on the thionin molecule, it is obvious that the molecule has 3 degrees of freedom to rotated within the channel, if the sulphur site is assumed as fixed: (1) rotation around the a-axis, (2) rotation around the b-axis and (3) rotation around the c-axis (Fig. 2). Maximal rotation angles are limited by the channel wall oxygens. Despite of this limitation, a slight rotation of about 10° in each direction is possible resulting in disorder and less defined sites of the other molecule atoms. Additionally disorder along the channel axis is also observed.

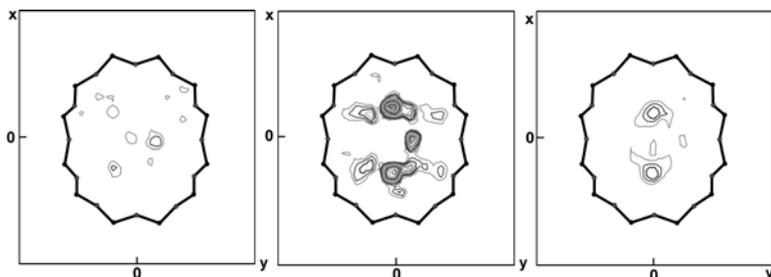


Fig. 1: Difference Fourier maps of Na-mordenite, Se-modified Na-mordenite and thionin-modified mordenite at 120 K. (001) section of 12-membered ring channel, contours at 0.25 Å² for all maps. 1. (from left) Na-mordenite: only weak electron density within the channel. 2. Se-modified mordenite: Strong electron density peaks belonging to Se sites. 3. Thionin-modified mordenite: Electron density similar to Se-modified mordenite, shifted $\pm x$ from the center of the channel.

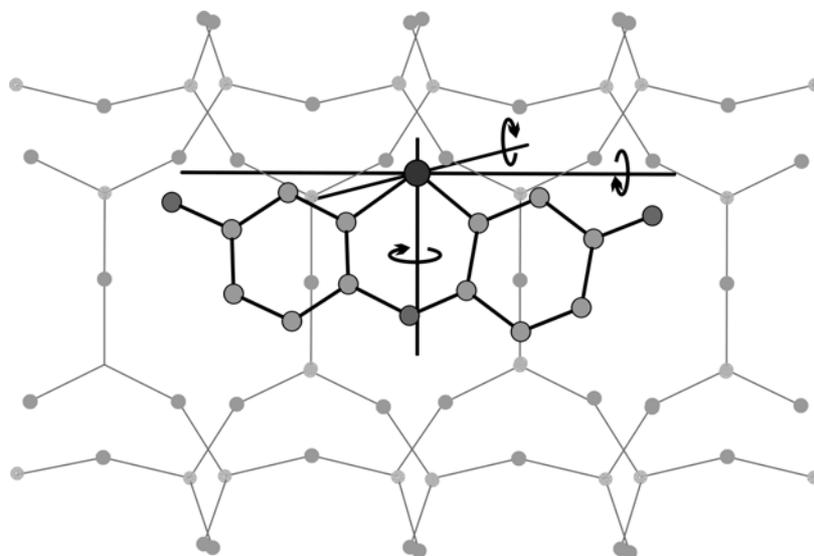


Fig. 2: 12-membered ring channel with thionin molecule (schematically) and degrees of freedom of the molecule.

- [1] Calzaferri G., Pauchard M., Maas H., Huber S., Khatyr A., Schaafsma T. (2001) *J. Mater. Chem.*, 12(1), p 1-13
- [2] Simoncic, P., and Armbruster, T. (2002) *Zeolite '02*, Book of Abstracts, 336
- [3] Simoncic, P., and Armbruster, T. (2004) *Micro Meso Materials* (submitted)