Contribution ID: **41** Type: **not specified**

Structural flexibility of CN-bridged magnetic networks based on planar cyclam complexes

Tuesday, July 7, 2015 12:00 PM (20 minutes)

Materials that respond to external stimuli in form of temperature, pressure, light or presence of guest molecules by changes in magnetic, optical or electrical properties can act as molecular switches and sensors. Molecular assemblies composed of metal ions and bridging ligands, which show sensitivity to external stimuli are often characterised by the flexibility of their coordination skeleton, which permits reversible structural changes. The design of structurally dynamic materials is a challenging task, since many factors from the coordination polyhedra and bridge geometry to subtle intermolecular interactions must be taken into account.
Tetradentate macrocyclic ligand 1,4,8,11-teraazacyclotertadecane (cyclam) has several features that make it a good building block for the construction of non-rigid coordination networks. It is one of the smallest ligands that can ensure planar coordination around the central atom, thus producing linear cationic connectors, which are bendable and take up relatively small space, leaving gaps for guest molecules in the structure. Moreover, aliphatic fragments of the macrocyclic ring afford only weak intermolecular interactions, which do not hinder distortions of the structure. We have characterised several cyano-bridged networks based on cationic cyclam complexes with various polycyanometallates [1]. They present different dimensionalities from 1D to 3D, but all of them uniformly show structural transformations and modification of magnetic properties in response to de-solvation, sorption of guest molecules or temperature changes.

[1] B. Nowicka, M. Rams, K. Stadnicka, B. Sieklucka; Inorg. Chem. 2007, 46, 8123; B. Nowicka, M. Bałanda, B. Gaweł, G. Ćwiak, A. Budziak, W. Łasocha, B. Sieklucka, Dalton Trans., 2011, 40, 3067; B. Nowicka, M. Bałanda, M. Reczyński, A. M. Majcher, M. Kozieł, W. Nitek, W. Łasocha, B. Sieklucka, Dalton Trans. 2013, 42, 2616; B. Nowicka, M. Reczyński, M. Rams, W. Nitek, M. Kozieł, B. Sieklucka, CrystEngComm, 2015, DOI: 10.1039/C5CE00287G.

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Session Classification: Molecular magnets