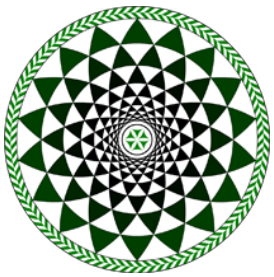

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Charge-transfer magnetic (H₃O)[Ni^{III}(cyclam)][M^{II}(C (M = Ru, Os) chains based on extraordinary redox couples

Tuesday, July 7, 2015 8:30 PM (1h 30m)

The [Ni^{II}(cyclam)]²⁺ complex (cyclam = 1,4,8,11-tetraazacyclotetradecane) has been widely employed as a building block in the construction of bimetallic assemblies and afforded several structurally dynamic guest-sensitive CN-bridged molecular magnets [1,2]. This complex can be easily oxidised to the relatively stable [Ni^{III}(cyclam)]³⁺ unit (s = ½) which we used to construct a new class of molecular magnets. The combination of [Ni^{III}(cyclam)]³⁺ with diamagnetic [Fe^{II}(CN)₆]⁴⁻ leads to the formation of the molecular (H₃O)[Ni^{III}(cyclam)][Fe^{II}(CN)₆]·5H₂O chain. The compound exhibits dehydration-induced reversible charge-transfer in the Ni^{III}-Fe^{II} couple, which results in the formation Ni^{II} (s = 1) and Fe^{III} (s = ½). The process is reflected in the change of magnetic properties - the increase of the magnetic susceptibility value and appearance of ferromagnetic interactions at low temperatures. This observation prompted us to combine [Ni(cyclam)]³⁺ with the related hexacyanometallates(II): [Ru^{II}(CN)₆]⁴⁻ and [Os^{II}(CN)₆]⁴⁻. In this way new 1D systems have been obtained: (H₃O)[Ni^{III}(cyclam)][M^{II}(CN)₆]·5H₂O, where M^{II} = Ru (1) or Os (2). 1 and 2 are isomorphic with the Fe-based analogue and show paramagnetic behaviour because of the separation of the paramagnetic Ni^{III} centres by diamagnetic low-spin Ru^{II} and Os^{II}, respectively. After dehydration the increase of the χT value in the high-temperature limit indicates that the charge-transfer process takes place with the formation of paramagnetic Ru^{III} or Os^{III} (s = ½) and Ni^{II} (s = 1). However, in contrast to Ni-Fe analogue, at low temperature a significant decrease of χT is observed, which suggests the presence of antiferromagnetic interactions through the CN bridges. The use of the [Ni^{III}(cyclam)]³⁺ building block allowed us to construct a new class of charge-transfer-active molecular magnets, based on unusual Ni^{III/II}-Ru^{II/III} and Ni^{III/II}-Os^{II/III} redox couples.

[1] B. Nowicka, M. Bałanda, M. Reczyński, A. M. Majcher, M. Kozieł, W. Nitek, W. Łasocha and B. Sieklucka, Dalton Trans., 2013, 42, 2616-2621.
[2] B. Nowicka, M. Reczyński, M. Rams, W. Nitek, M. Kozieł and B. Sieklucka, CrystEngComm, 2015, 17, 3526-3532.

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