



Solvent-induced Transformations in Ferromagnetically Coupled

[Ni₄L₄] Cluster

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To date several magnetic systems with SMM-type behaviour based on polynuclear complexes of the Mn, Fe, Ni, V and Co or mixed metals have been described. Their synthesis poses a number of challenges, often related with inability to predict the exact cluster structure due to potentially variable outcomes of self-assembly process. Owing to a wide range of their potential applications, *e.g.* in data storage, memory devices, switches and sensors, considerable attention has been devoted to the targeted synthesis of such systems. The importance and great influence of the solvent on modulation of the SMM's magnetic features was first described in 1999 by Olivier Khan¹, who introduced the concept of a "magnetic sponge" to describe magnetic materials that can reversibly release and reabsorb both coordinated and uncoordinated solvent molecules. Importantly, it was shown that these processes are accompanied by the structural changes related to a cleavage/formation of the coordination bonds which subsequently also affect the magnetic properties.^{2,3} Among different cluster types that can exhibit SMM features, cubane-like magnetic clusters with [Ni₄(μ₃-O)₄] core are especially well-studied class. The cubane-like core of nearly all investigated tetranuclear Ni(II) complexes includes four identical μ₃-O bridges originating from -OH or -OR moieties. Previous studies have unveiled that the symmetry of [Ni₄O₄] core and the differences in the Ni-μ₃-O-Ni angles play a crucial role in the intramolecular magnetic interactions. Namely, it was shown that the ferromagnetic interactions are associated with the core angles close to 90°, whereas the antiferromagnetic interactions involve larger angles. This was also corroborated by the latest investigation of [Ni₄L₄(solv)₄] type of complexes which exhibit a switching of the spin ground state from S = 4 to S = 0 at ambient temperature, triggered by the reversible exchange of the coordinated solvent molecules (MeOH *vs.* H₂O).⁴ Although the structural alterations induced by such solvent exchange were subtle, substantial changes of the physical and chemical properties have been established.

Our latest investigations were directed to synthetic procedures, interconversion scenarios of reabsorption and exchanging solvent molecules, structural and magnetic studies of a new family of Ni(II) compounds based on cubane-like clusters. Depending on synthetic conditions different cubane-like clusters [Ni₄L₄(ROH)₄], [Ni₄L₄(H₂O)₂], [Ni₄L₄(ROH)₂(R'OH)₂] and [Ni₄L₄(ROH)₂] (H₂L = tridentate Schiff base ligand, *N*-(2-hydroxy-5-methylphenyl)salicylideneimine, R = -CH₃, -C₂H₅, -C₃H₇, -C₄H₉ i -C₅H₁₁) were isolated. The exhibited solvent-induced transformations of the clusters have been studied by SCXRD (at 150 K and at 296 K) and PXRD, TG/DSC, DVS, SQUID magnetometry, Hot-stage microscopy, IR as spectroscopic method and quantum chemical calculations. All experiments are showed possibility to come again to the well-defined initial state exposing clusters to methanol vapours, in turn.

Do danas je u literaturi opisano nekoliko SMM (*single molecule magnets*) magnetskih sustava građenih od polinuklearnih kompleksa Mn, Fe, Ni, V ili Co. Razvoj sintetskih postupaka koji bi vodili nastanku klusterskih molekula ciljanih magnetskih svojstava i građe predstavlja veliki izazov budući da ovi sustavi nalaze primjenu u elektornici, na pr. u sustavima za pohranu podataka, sensorima, memorijskim jedinicama. Utjecaj otapala na promjenu magnetskih svojstava kod molekulskih magneta prvi puta je opisao 1999. O. Khan¹ koji je opisujući utjecaj reverzibilne izmjene otapala na magnetska svojstva uveo koncept "magnetske spužve". Navedeni procesi praćeni su i strukturnim promjenama uslijed pucanja i nastajanja koordinativnih veza što upućuje na usku povezanost strukture s magnetskim svojstvima. Od u literaturi opisanih klusterskih sustava interesantnu skupinu čine klasteri nikla(II) koji sadrže $[\text{Ni}_4(\mu_3\text{-O})_4]$ jezgru. Ovi spojevi pobuđuju pažnju zbog svoje građe ali i zbog magnetskih svojstava.

Istraživanja su pokazala da simetrija $[\text{Ni}_4\text{O}_4]$ jezgre kao i Ni- μ_3 -O-Ni kutevi igraju presudnu ulogu u intramolekulskim magnetskim interakcijama.^{2,3} Također je ustanovljeno da su feromagnetske interakcije prisutne u slučaju kada su kutevi unutar tetranuklearne jezgre oko 90°, dok do antiferomagnetskih interakcija dolazi pri višim vrijednostima kuteva. Najnovija istraživanja klastera ovog tipa upućuju na moguću izmjenu osnovnog spinskog stanja Ni(II) iz $S = 4$ u $S = 0$ pri sobnoj temperature pod utjecajem reverzibilne izmjene molekula otapala.⁴

Naša istraživanja su pokazala kako sintetski uvjeti utječu na nastanak klastera opće formule $[\text{Ni}_4\text{L}_4(\text{ROH})_4]$, $[\text{Ni}_4\text{L}_4(\text{H}_2\text{O})_2]$, $[\text{Ni}_4\text{L}_4(\text{ROH})_2(\text{R}'\text{OH})_2]$ i $[\text{Ni}_4\text{L}_4(\text{ROH})_2]$. Također je ustanovljena mogućnost reverzibilne izmjene koordiniranog i kristalizacijskog otapala što je praćeno i reverzibilnom promjenom magnetskih svojstava. Klasteri su priređeni u reakcijama Ni(II) acetat s *N*-(2-hidroksi)-5-metilfenil)salicilaldiminom, H_2L , ($\text{L}^2 = \text{C}_6\text{H}_5(\text{O})-\text{C}=\text{N}-(\text{O})\text{C}_6\text{H}_4\text{CH}_3$) i upotrebom različitih alkohola kao otapala (ROH, R = -CH₃, -C₂H₅, -C₃H₇, -C₄H₉ i -C₅H₁₁). Opažene promjene pod utjecajem reverzibilne izmjene otapala praćene su metodama termičke analize (TG/DSC), difrakcije rentgenskih zraka na monokristalnim i praškastim uzorcima, (SCXRD i PXRD), spektroskopskim metodama te SQUID metodom mjerenja magnetske susceptibilnosti.