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Structural and magnetic variations in tetranuclear Ni^{II} clusters: the effect of the reaction solvent and ligand substitution on the product identity†

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Three structurally and magnetically different tetranuclear Ni^{II} complexes have been isolated and magnetically characterized, emphasizing the effect of reaction solvent and organic ligand substitution on the chemical identity of cluster compounds.

The synthesis of new polynuclear 3d-metal complexes (coordination clusters or simply clusters) is definitely one of the most fascinating areas of inorganic and coordination chemistry.[1] The interest mainly stems from the relevance of molecular cluster compounds in bioinorganic chemistry, catalysis, optics and magnetism.[2] Numerous synthetic strategies and approaches have been developed over the last three decades for the construction of structurally and physically novel 3d-metal clusters.[3] To this end, the self-assembly route has been proved to be the most fruitful one yielding high-nuclearity compounds with beautiful mosaics and impressive magnetic properties such as high-spin molecules,[4] single-molecule magnets (SMMs)[5] and magnetic refrigerants[6] for low-temperature cooling applications.

In general lines, self-assembly refers to the unpredictable, one-pot reaction of a metal ion precursor with a single bridging/chelating organic ligand or a combination of more than one such ligands. The unpredictable nature of this approach derives from the coordination affinity and versatility of the bridging organic ligand(s) and the flexibility of the 3d-metal ion toward various coordination geometries and topologies.[1] Hence, the choice of the polydentate organic bridging/chelating ligand is an important task, albeit not the only significant one, since this often dictates not only the topology and the number of metal ions present, but also the nature of the intramolecular magnetic exchange interactions.[7] Since 3d-metal cluster chemistry is relatively unpredictable, the products' identities often depend on many additional synthetic variables which are frequently ignored due to the need to

discover more new bridging/chelating ligands; such variables are usually the reaction solvent, temperature, "pH", metal-to-ligand ratio and the substitution of a given ligand type with donor- or non-donor R-groups.

Our groups have recently focused on the employment of polydentate chelating/bridging Schiff bases as a means of obtaining new polynuclear 3d-metal compounds with interesting magnetic properties. Of particular interest is the family of Schiff bases which are based on the scaffold of *N*-salicylidene-*o*-aminophenol (saphH$_2$, Scheme 1). This is due to the ability of the relatively soft N atom and the two hard, upon deprotonation, O atoms to bind to a single or multiple metal centers. We have recently reported the employment of saphH$_2$ in high nuclearity 3d/4f-metal cluster chemistry which has led to Mn$^{III}_4$Dy$^{III}_5$ and Mn$^{III}_4$Dy$^{III}_3$ complexes with unique topologies and SMM behaviors,[8] but we have been unsuccessful so far with the isolation of Ni^{II}/saphH$_2$ clusters.

Since then, we have been seeking new routes to Ni^{II} cluster compounds and we thus turned our attention into ring-substituted derivatives of saphH$_2$ with both donor and non-donor groups. We have initially decided to replace the H-atom at the position 4 of the *o*-aminophenol moiety with a methyl group aiming at the positive effect of the -CH$_3$ functionality on the crystallization of the resulting products. We have then attempted to replace the -OH donor group of the *o*-aminophenol moiety with a carboxylate (-COOH) functionality which could potentially coordinate to more metal centers than saphH$_2$ through the two O donor atoms and therefore foster formation of very high nuclearity metal species. In addition, we included a non-donor chloro group in place of a phenyl H atom at the position 5 which could, in principle, differentiate the electronic and steric properties, and hydrogen bonding effects. The resulting ligands *N*-salicylidene-4-methyl-*o*-aminophenol (samphH$_2$, Scheme 1) and *N*-salicylidene-2-amino-5-chlorobenzoic acid (sacbH$_2$, Scheme 1) have a limited previous

use in metal cluster chemistry restricted only to a recently reported Ni$_{11}$ compound featuring both Bu^{t}CH$_2$CO$_2$$^-$ and sacb^{2-} groups.[9] In the present work, we show how the thorough investigation of a reaction system can lead to three Ni$_4$ compounds with different structures and magnetic properties, emphasizing the effect of two synthetic variables on the products' identities.

Scheme 1 (top) Structural formulas and abbreviations of the ligands discussed in the text, and (bottom) their crystallographically established coordination modes in complexes **1**-**3**.

The reaction of [Ni$_2$(H$_2$O)(O$_2$CBu^t)$_4$(HO$_2$CBu^t)$_4$] precursor and samphH$_2$ in a 1:2 molar ratio in EtOH gave a brown solution that upon slow evaporation at room temperature gave olive-green crystals of [Ni$_4$(samph)$_4$(EtOH)$_4$]·0.7EtOH (**1**·0.7EtOH) in 35% yield.† Complex **1**·0.7EtOH crystallizes in the triclinic space group *P*-1 and has virtual S_4 symmetry. Its structure consists of four distorted octahedral Ni^{II} ions bridged together by four deprotonated μ$_3$-O atoms from the methyl-aminophenol part of four samph^{2-} ligands (Fig. 1); the latter are all binding in an η^1:η^1:η^3:μ$_3$ mode (Scheme 1). The tetranuclear cluster molecule has a distorted cubane {Ni$_4$(μ$_3$-OR)$_4$}$^{4+}$ core (Fig. S1) with the μ$_3$-O atoms occupying alternate vertices of the cube. Thus, the molecule consists of two interpenetrating concentric tetrahedra, one of four metal ions and the other of four triply bridging oxygen atoms. Peripheral ligation about the core is provided by four terminal EtOH molecules each lying on a Ni^{II} ion. The six faces of the cubane are not equivalent. Using the notation introduced by Williams, Decurtins and coworkers for cubanes,[10] we code **1** as a whole by Ni$_4$/2s$_4$/m$_4$. The symbol "s" indicates that the bridging atoms of samph^{2-} are supported, the number "2" designating that one arm of samph^{2-} links the bridging O atom to two terminal donor atoms (the imino N and phenolate O atoms); the abbreviation "m$_4$" indicates that four monodentate, terminal ligands (EtOH groups) complete the coordination spheres of the four Ni^{II} ions.

Within the concept of chemical reactivity on cluster compounds, an important synthetic factor that is worth investigating is the effect of the solvent on the structural identity of the complexes. The volatility, polarity, rigidity and coordination affinity of reaction solvents are some of the features which directly affect the identity of a product. To that end, the reaction that led to complex **1** has been repeated in DMF (instead of EtOH) under exactly the same conditions. The resulting dark orange solution afforded orange crystals of a new

[Ni$_4$(samph)$_4$(DMF)$_2$]·2DMF (**2**·2DMF) compound in the yield of 40%.† Complex **2**·2DMF crystallizes in the triclinic space group *P*-1. Its structure consists of centrosymmetric [Ni$_4$(samph)$_4$(DMF)$_2$] (Fig. 2) and solvate DMF molecules; the latter will not be further discussed. The four Ni^{II} ions are located at four vertices of a defective dicubane, i.e. two cubanes sharing a face [Ni(2)O(3)Ni(2′)O(3′)] and each missing one metal vertex. The Ni^{II} centers are bridged by two μ$_3$-O (O3, O3′) and four μ-O (O1, O1′, O2, O2′) atoms from two η^1:η^1:η^3:μ$_3$ and two η^2:η^1:η^2:μ$_3$ samph^{2-} ligands, respectively (Scheme 1). Thus, the core is {Ni$_4$(μ$_3$-OR)$_2$(μ-OR)$_4$}$^{2+}$ (Fig. S1), where RO$^-$ = samph^{2-}. Peripheral ligation is provided by two terminally bound DMF molecules on Ni2 and Ni2′ and the imino N atoms of four samph^{2-} ligands, each bound to a Ni^{II} ion. As a result, the latter atoms are six-coordinate and near-octahedral, whereas Ni1 and Ni1′ are five-coordinate with very distorted coordination geometries (τ = 0.43, where τ is 0 and 1 for perfect square-pyramidal and trigonal-bipyramidal geometries,[11] respectively).

Fig. 1 Labelled plot of complex **1** emphasizing the {Ni$_4$(μ$_3$-OR)$_4$}$^{4+}$ cubane core. Color scheme: Ni^{II} green, O red, N blue, C gray. H-atoms are omitted for clarity.

Fig. 2 Labelled plot of complex **2** emphasizing the $\{Ni_4(\mu_3\text{-}OR)_2(\mu\text{-}OR)_4\}^{2+}$ defective dicubane core. Color scheme as in Fig. 1. H-atoms are omitted for clarity. Symmetry operation for the primed atoms: 1-*x*, 2-*y*, -*z*.

Complex **2** can alternatively be described as containing a butterfly of Ni^{II} sites with the 'body' of the butterfly (Ni2 and Ni2′) bridged by two deprotonated μ_3-O atoms from two $\eta^1:\eta^1:\eta^3:\mu_3$ samph^{2-} ligands; these O atoms also bridge to Ni^{II} 'wing-tip' sites (Ni1 and Ni1′). Each of the four edges of the closed-type butterfly is bridged by one μ-O atom from two in total $\eta^2:\eta^1:\eta^2:\mu_3$ samph^{2-} ligands. In the crystal structures of both **1** and **2** there are no significant intermolecular H-bonding or π-π stacking interactions. There are four intramolecular H-bonds in **1** (Fig. S2, Table S5). **1** and **2** are the first cluster compounds bearing any form (neutral, singly- or doubly-deprotonated) of samphH$_2$.

The interesting behavior of the Ni^{II}/samphH$_2$ system prompted us to replace the samphH$_2$ Schiff base ligand with the closely-related, but with enhanced coordination capabilities, sacbH$_2$ ligand. Thus, the 1:2 reaction of [Ni$_2$(H$_2$O)(O$_2$CBu^t)$_4$(HO$_2$CBu^t)$_4$] and sacbH$_2$ in EtOH led to a dark green solution from which were isolated green crystals of a structurally different (compared to **1** and **2**) tetranuclear [Ni$_4$(sacb)$_4$(EtOH)$_4$]·6EtOH (**3**·6EtOH) compound in yields as high as 60%. Complex **3**·6EtOH crystallizes in the triclinic space group *P*-1 with the Ni$_4$ molecule lying on an inversion center located at the middle-point of the Ni2…Ni2′ vector (Fig. 3). The Ni$_4$ compound comprises a non-linear, zigzag array of four Ni^{II} atoms (Ni1-Ni2-Ni2′ = 108.56º) with each Ni$_2$ pair bridged by two μ-O atoms from the deprotonated alkoxido (O1, O1′, O11, O11′) and/or carboxylate (O12, O12′) functionalities of four sacb^{2-} ligands. The latter are of two types (Scheme 1): two are binding in an $\eta^2:\eta^1:\eta^1:\mu$ mode, acting as N,O,O-tridentate chelates to a Ni^{II} atom (Ni1, Ni1′) and simultaneously bridging an additional Ni^{II} atom (Ni2 or Ni2′) through the phenolate O atom, and the remaining two adopt the more complex $\eta^2:\eta^1:\eta^2:\eta^1:\mu_4$ binding mode, chelating the central Ni^{II} atoms and bridging all four metal ions through the phenolate and both carboxylate O atoms. Thus, the core of **3** is $\{Ni_4(\mu\text{-}OR)_6\}^{2+}$ (Fig. S1), with peripheral ligation provided by four terminal EtOH molecules. The central Ni2-O12-Ni2′-O12′ rhombus is strictly planar as a result of the inversion center, but the other two rhombs are quite distorted, with the Ni1-O1-Ni2-O11 torsion angle being 17.1º. The Ni^{II} atoms are all six-coordinate with distorted octahedral geometries. Finally, in the crystal structure of **3**·6EtOH there are H-bonding interactions between the carboxylate and phenolate moieties of sacb^{2-}, and the bound EtOH and lattice EtOH solvate molecules (Fig. S3, Table S6). In addition, weak π-π stacking interactions between the aromatic rings of sacb^{2-} ligands serve to link the Ni$_4$ clusters into a 2-D network (Fig. S4). Although there are hundreds of tetranuclear Ni^{II} complexes structurally and magnetically characterized, compound **3** is only the fourth example of a Ni$^{II}_4$ cluster with a zigzag topology.[12]

Variable-temperature dc magnetic susceptibility measurements were performed on freshly-prepared microcrystalline solids of **1**, **2**·DMF, and **3**·2EtOH in the temperature range 2.0-300 K; a dc field of 0.3 T was applied from 30 to 300 K and a weak dc field of 0.03 T was applied from 2 to 30 K to avoid saturation effects. The data are shown as $\chi_M T$ versus T plots in Fig. 4. The values of the $\chi_M T$ product at 300 K are 5.53 (**1**), 5.35 (**2**·DMF) and 5.80 (**3**·2EtOH) cm^{3}mol^{-1}K, slightly higher than the value of 4.84 cm^{3}mol^{-1}K (calculated with *g*=2.2) expected for four non-interacting Ni^{II} (*S* = 1) atoms. For the cubane and zigzag complexes, **1** and **3**·2EtOH, the value of $\chi_M T$ steadily increases in the 300-7 K and 300-17 K ranges, respectively, and then slightly (for **1**) or more rapidly (for **3**·2EtOH) decreases with decreasing T to reach the values of 6.68 (**1**) and 4.40 (**3**·2EtOH) cm^{3}mol^{-1}K at 2 K. For the defective dicubane complex **2**·DMF the magnetic response is distinctly different; the $\chi_M T$ product remains essentially constant in the 300-50 K region and then decreases sharply, reaching a value of 0.53 cm^{3}mol^{-1}K at 2 K. The data and shape of plots indicate predominant ferromagnetic (for **1** and **3**·2EtOH) and antiferromagnetic (**2**·DMF) exchange interactions, thus suggesting *S* = 4 and *S* = 0 ground state spin values, respectively.

Fig. 3 Partially-labelled representation of the structure of complex **3** emphasizing the $\{Ni_4(\mu\text{-}OR)_6\}^{2+}$ zigzag core. Color scheme as in Fig. 1; Cl cyan. H-atoms are omitted for clarity. Symmetry operation for the primed atoms: 1-*x*, 1-*y*, -*z*.

Fig. 4 $\chi_M T$ versus T plots of **1**, **2**·DMF, and **3**·2EtOH. The solid lines are the fits of the data; see the text for the fit parameters. (inset) *J*-coupling scheme employed for the elucidation of the magnetic exchange interactions in **1** (a) and **2/3** (b); see the text for the corresponding spin-Hamiltonians.

In order to quantify the nature of the magnetic exchange within **1-3**, theoretical expressions of χ_M as a function of T were derived and fitted to the experimental data. Structural data indicate that the core of complex **1** consists of a distorted cubane with different metric parameters in the six faces. However, opposite faces show similar Ni-O-Ni bond angles and thus, in order to reduce the number of coupling constants in the fitting process, only three coupling constants were employed according to the simplified coupling scheme shown in Fig. 4a (inset). The centrosymmetric complex **2** shows three sets of Ni-O-Ni bond angles and hence three coupling constants were applied according to Fig. 4b (inset). Complex **3** exhibits a different zigzag structure, but magnetically it can be reduced to the same coupling scheme as **2** (*vide infra*). On the basis of Fig. 4 (inset), the applied Heisenberg spin-Hamiltonians for complexes **1** and **2/3** are shown in Eqs 1 and 2, respectively.

$$\mathcal{H} = -J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) - J_2(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) - J_3(\hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3) \quad \text{(Eq. 1)}$$

$$\mathcal{H} = -J_1(\hat{S}_1 \cdot \hat{S}_2) - J_2(\hat{S}_1 \cdot \hat{S}_4 + \hat{S}_2 \cdot \hat{S}_3) - J_3(\hat{S}_1 \cdot \hat{S}_3 + \hat{S}_2 \cdot \hat{S}_4) \quad \text{(Eq. 2)}$$

The PHI program[13] was used to fit the susceptibility and magnetization data. Quality of the fits is quantified by the agreement factor R, defined as $(\chi_M T_{exp} - \chi_M T_{calc})^2/(\chi_M T_{exp})^2$. Preliminary fits for **1**, applying the spin-Hamiltonian of Eq. 1, were not satisfactorily and therefore the zero-field splitting parameter, D_{ion}, was included in the model. An excellent fit of the experimental data gave as best-fit parameters: $J_1 = -0.1$ cm^{-1}, $J_2 = +8.4$ cm^{-1}, $J_3 = +1.3$ cm^{-1}, $D = +3.8$ cm^{-1} and $g = 2.28$ ($R = 7.2 \cdot 10^{-5}$) for **1**; $J_1 = -10.0$ cm^{-1}, $J_2 = +14.9$ cm^{-1}, $J_3 = +10.4$ cm^{-1} and $g = 2.30$ ($R = 7.3 \cdot 10^{-6}$) for **2**; and $J_1 = +12.5$ cm^{-1}, $J_2 = -5.2$ cm^{-1}, $J_3 = +1.8$ cm^{-1} and $g = 2.35$ ($R = 6.7 \cdot 10^{-5}$) for **3**.

Magnetization versus field measurements were performed at 2 K and the corresponding plots (Fig. S5) show a continuous increase up to a non-saturated value equivalent to 7.0 and 7.2 electrons for **1** and **3**, respectively, and 3.6 electrons for **2**. These values are in agreement with the predominant ferro- and antiferromagnetic interactions observed in susceptibility measurements. To evaluate the accuracy of the susceptibility data, the magnetization data were also fitted using the spin-Hamiltonians expressed in Eqs. 1 and 2, and including the D_{ion} term. Best-fit parameters are: $J_1 = 0.0$ cm^{-1}, $J_2 = +9.4$ cm^{-1}, $J_3 = +2.4$ cm^{-1}, $D = +4.7$ cm^{-1} and $g = 2.24$ ($R = 1.5 \cdot 10^{-3}$) for **1**; $J_1 = -9.1$ cm^{-1}, $J_2 = +15.0$ cm^{-1}, $J_3 = +10.8$ cm^{-1}, $D = -0.98$ cm^{-1} and $g = 2.27$ ($R = 8.1 \cdot 10^{-6}$) for **2**; and $J_1 = +10.4$ cm^{-1}, $J_2 = -3.2$ cm^{-1}, $J_3 = +1.6$ cm^{-1}, $D = +3.9$ cm^{-1} and $g = 2.34$ ($R = 1.1 \cdot 10^{-4}$) for **3**, in good agreement with the susceptibility data. Both measurements confirmed an $S = 4$ ground state for **1**, an $S = 0$ ground state (population 80.3 %) for **2**, with very close in energy $S = 1$ (gap 2.0 cm^{-1}, population 19.0 %) and $S = 2$ (gap 6.6 cm^{-1}, population 0.7 %) excited states, and a quasi-frustrated situation for **3** with a mixture of all possible spin states ($S = 4$ to 0) being very close in energy and almost equally populated at 2 K (see the ESI). The $S = 4$ spin state for **3** is still not fully saturated under a 5 T field but it tends to saturate to 8 electrons at higher fields.

Rationalization of the magnetic interactions in zigzag Ni$_4$ compounds is unprecedented and thus urged us to further investigate the quasi-frustrated complex **3**. The J_3 coupling constant, which is associated with the next-nearest neighbor interactions of Ni1…Ni2′ and Ni1′…Ni2 mediated by the carboxylate functionality of sacb^{2-}, is undoubtedly necessary and cannot be ignored in order to avoid overparametarization effects. If J_3 was discarded from the fitting model, the ground state should be zero as the result of two external ferromagnetic Ni$_2$ pairs and a central, antiferromagnetically coupled Ni$_2$ pair; this is totally against the experimental susceptibility and magnetization data. Finally, none of the complexes show out-of-phase ac magnetic susceptibility signals down to 1.8 K, suggesting these are not SMMs.

The most important parameter in the magnetostructural correlation of tetranuclear clusters possessing the {Ni$_4$(μ_3-OR)$_4$}$^{4+}$ cubane or {Ni$_4$(μ_3-OR)$_2$(μ-OR)$_4$}$^{2+}$ defective dicubane cores has been reported to be the average Ni-O-Ni angle of the cubane faces.[10,14] A ferromagnetic exchange is expected for Ni-O-Ni angles lower than 99° and the positive coupling constant value increases as the angle decreases. On the other hand, Ni-O-Ni angles in the vicinity of, and larger than, 99° lead to antiferromagnetic interactions and the absolute value increases as the angle increases. The mean Ni-O-Ni angles for the three Ni$_2$ pairs described by J_1, J_2 and J_3 in **1** are 101.6°, 94.4° and 95.5°, respectively; thus, the J_2 coupling is predicted to be the most ferromagnetic, and indeed, it is. Clusters **2** and **3** possess diamagnetic and quasi-frustrated ground states, respectively, as a result of the highly competing ferromagnetic and antiferromagnetic interactions. The obtained signs of J constants for **2** agree with the corresponding Ni-O-Ni angles (J_1 for the Ni2…Ni2′ pair of a 99.4° mean angle, J_2 for the Ni1…Ni2 and Ni1′…Ni2′ pairs of a 97.5° mean angle, and J_3 for the Ni1…Ni2′ and Ni1′…Ni2 pairs of a 97.8° mean angle). The fact that the absolute values of J constants are very close to each other is reasonably attributed to the Ni-O-Ni angles which are close to the ferro-/antiferromagnetic border. In the case of the zigzag complex **3**, J_1 and J_2 constants were employed for the two outer (Ni1-Ni2 and Ni1′-Ni2′) and one central (Ni2-Ni2′) interactions with average Ni-O-Ni angles of 93.8° and 100.2°, respectively. Both J_1 and J_2 were reasonably found to be ferromagnetic and antiferromagnetic, respectively, according to the calculated mean angles.

Conclusions

In conclusion, we have reported three tetranuclear Ni^{II} complexes with cubane (**1**), defective dicubane (**2**) and rare zigzag (**3**) topologies, all resulted from similar one-pot reactions of a Ni^{II} precursor with structurally related Schiff base ligands. Besides the structural differences, complexes **1-3** show also variations in their magnetic behaviour; **1** is ferromagnetically coupled with an $S = 4$ ground state opposite to cluster **2** which possesses a diamagnetic ground state, and different than **3** which is a quasi-frustrated magnetic system with a mixture of spin states populated at very low

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temperatures. They key point of this work is the need to insist on the examination and trial of as many synthetic variables as possible in a given reaction system when seeking ways to isolate new polynuclear metal complexes. The search for completely new ligand types is not the only route to obtain structurally unique compounds; re-consideration and thorough investigation of various synthetic factors such as the reaction solvent and ligand substituent(s) can also offer alternative pathways for the emergence of beautiful and magnetically interesting 3d-metal clusters.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic data (CIF format), synthetic details, structural and magnetism text and figures for complexes **1-3**. See DOI: 10.1039/c000000x/

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GRAPHICAL ABSTRACT

Changes of the reaction solvent and organic ligand substituents in a general reaction system have led to three Ni^{II}_4 coordination clusters with different topologies and magnetic responses.

X = H
Y = Cl
Z = COOH
EtOH

$[Ni_2(H_2O)(O_2CBu^t)_4(HO_2CBu^t)_4]$ +

X = Me
Y = H, Z = OH
EtOH

X = Me, Y = H
Z = OH
DMF