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polynuclear complexes

Unusual penta- and hexanuclear Ni(II)-based silsesquioxane

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Fine tuning of the reaction between alkali metal siloxanolate [PhSi(O)ONa]n and [Ni(NH₃)₆]Cl₂ allowed to design new hexa-

 $[(PhSiO_{1,5})_{1/2}(NiO)_{6}(H_{2}O)(DMSO)_{3}]$ (1) and pentanuclear $[(PhSiO_{1,5})_{1/2}(NiO)_{5}(NaOH)(DMF)_{7}]$ (2) cage-like silsesquioxanes. Their

specific structures were studied by single crystal X-ray diffraction and topological analysis. Compound 2 is the first example of pentanuclear "Cylinder"-like metallasilsesquioxane. Magnetic properties investigations demonstrate the presence of a



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Introduction

Metal-containing silsesquioxanes of polyhedral geometry, called also cage-like metallasilsesquioxanes (CLMSs), are an intensively studied class of molecular materials due to their unique ability to form unprecedented molecular architectures¹ and to exhibit high activity in different catalytic applications.^{1f,1g,2} In turn. CLMSs are attractive platforms for estimation of exchange interactions of metal ions, "trapped" in siloxane matrix,³ including rare case of CLMSs, containing metal ions in different oxidation states.⁴ Indeed, rational approaches (e.g. using of trisilanols^{1c} or non-condensed cubane silsesquioxanes^{1e} as initial reagents) allow to design isolated architectures of desired nuclearity and in controlled fashion containing transition metal ions or lanthanides assembled through the silicon atoms. Surprisingly, magnetic properties investigations on these materials are not abundant and we can cite here only few examples, including studies of Fe-^{3b-f, i}, Co-^{3e}, Cu-^{3g}, Mn-^{3h} or Cr-containing⁴ CLMSs. Recently, we reported the first example of a CLMS architecture displaying an unusual slow dynamic of the magnetization arising from the interaction between three crystallographically independent Co(II) ions arranged in a triangular fashion with a spin frustration giving rise to an appearance of a spin glass-like

Levitsky*^a



The most recent description of CLMS structures formation given in^{1g} postulates that aggregation of cage metallasilsesquioxane is governed by several factors, e.g. silicon/metal(s) ratio, nature of solvent(s), presence of monoor bidentate ligands. It is known that despite the kaleidoscopic variety in CLMS cores described to date (Cubane, Bird Cage, Lantern, Cooling Tower etc.), many of obtained CLMSs, including M(II) ions, belong to Cylinder family with two major types of nuclearity - 4 and 6.^{1g} We suggested that the use of synthetic approaches, mentioned above, let to obtain other forms of Prismatic CLMSs. Our first investigations were devoted to the synthesis of Ni(II)-containing CLMSs in the presence of different solvents. We were interested in such variation because recently some of us have shown that the nature of solvent molecules may highly influence structural parameters of Cu(II)-based CLMSs.^{2h} Consequently, we report here crystal structures and magnetic properties investigation of two new Cylinder Ni(II)-CLMSs of different nuclearity. A particular emphasis is given on the determination of the magnetic regime in these systems.

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Results and Discussion

Synthesis and Crystal Structure

The exchange reaction between sodium phenylsiloxanolate [PhSi(O)ONa]_n (formed in situ from PhSi(OEt)₃ and sodium hydroxide) and [Ni(NH₃)₆]Cl₂ precursors in two different solvents, DMSO and DMF, induces a formation of two new CLMSs of different nuclearity. In the first case, the hexanuclear $[(PhSiO_{1.5})_{12}(NiO)_6(H_2O)(DMSO)_9]$ **1** and in the second, the pentanuclear $[(PhSiO_{1,5})_{10}(NiO)_5(DMF)_7]$ 2 architectures were obtained with 43 % and 38 % yield, respectively (Scheme 1).



Figure 1. Schematic representation of the synthetic strategy employed for of designing hexanucelar [(PhSiO_{1.5})₁₂(NiO)₆(H₂O)(DMSO)₉] 1 and pentanuclear [(PhSiO_{1.5})₁₀(NiO)₅(DMF)₇] **2** phenylsilsesquioxanes.

Structural peculiarities of 1 and 2 were established by single crystals X-ray diffraction analysis. Compound 1 presents a typical^{1g} hexanuclear cylinder-like type of CLMSs molecular geometry (Figure 2, top). The main difference between compound 1 and early described hexanuclear cylindrical CLMSs^{1g} is the nature of the encapsulated entity. The inner void of 1 captures a water molecule (unfortunately, the hydrogen atoms bonded to the oxygen atoms cannot be located) instead of classically encapsulated agents, such as Cl .^{1g} The shortest intramolecular distance Ni...Ni is 2.92 Å. Crystal packing of 1 is shown on Figure 2 (bottom). The shortest intermolecular Ni- Ni distance (between the polynuclear complexes) is 13.44 Å. Additional discussion of structural parameters of 1 is provided below (Table 1).



Figure 2. Top. Molecular structure of hexanuclear $[(PhSiO_{15})_{12}(NiO)_6(H_2O)(DMSO)_9]$ CLMS **1**. Color code: Ni, green; O, red; Si, yellow. Phenyl groups at the silicon atoms and DMSO molecules are omitted for clarity. Bottom. Crystal packing of CLMS 1.

Similar synthesis in the DMF media leads to pentanuclear Cylinder [(PhSiO_{1.5})₁₀(NiO)₅(DMF)₇] CLMS **2** (Figure 3). The shortest intramolecular distance Ni...Ni is 2.70 Å. Crystal packing of 2 is shown on Figure 3 (bottom). The shortest intermolecular Ni- Ni distance (between the polynuclear complexes) is 10.34 Å. Noteworthy that compound 2 joins very rare family of pentanuclear CLMSs¹⁰ and is the first example of the Ni(II)-containing CLMS with the odd number of nickel atoms.



3 Top. Molecular structure of pentanuclear Figure [(PhSiO_{1 5})₁₀(NiO)₅(DMF)₇] CLMS **2**. Color code: Ni, green; O, red; Si, yellow, Na, orange. Phenyl groups at silicon atoms and molecules of solvates (DMF) are omitted in the sake of clarity. Bottom. Crystal packing of CLMS 2.

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An assembly of such non-trivial pentanuclear complexes became possible due to an involvement of DMF molecules, which are specific ligands with high basicity. Presumably, at the first stage of compound 1 formation, four molecules of DMF coordinate to sodium ion and, in the same time, to two Ni(II) ions of metallasilsesquioxane cyclic fragments. Thus, unusual synthone is formed, where coordination number of the sodium ion is increased to 6 (due to an additional coordination of Na^+ to oxygen atoms in Si-O-Ni moieties). Noteworthy, metallasilsesquioxane cycles in this synthone are oriented each to other by the angle of 107.6°, which corresponds to the inner angle value for the regular pentagon (108°) (Figure 4 A). It seems that further assembly, resulting in an arising of regular pentanuclear Cylinder-like cage, is strongly assisted by the presence of an OH⁻ counterion. The latter is situated in the inner void of cage and coordinates to Ni(II) ions (Figure 4, B). Three DMF molecules additionally coordinate three nickel ions, resulting in realization of an hexacoordinate environment of all Ni(II) sites.



Figure 4. Schematic representation of an assembly of pentanuclear $[(PhSiO_{1,5})_{10}(NiO)_5(DMF)_7]$ CLMS **2** assisted by DMF molecules.

A comparison of structural parameters of hexa- and pentanuclear complexes **1** and **2** is provided in Table 1. It should be noticed that the mean Ni...Ni distance in **2** is much shorter than the one observed for **1**. It is comparable to the distances observed for decanuclear nickel(II)-based CLMS, reported by some of us previously.¹¹

Table 1. Average values of selected bonds and interatomic distances in 1 and 2.

	1 (L = H ₂ O)	2 (L = OH), M= Na
NiNi	2.946(1)	2.7265(4)
Ni-O (siloxanolate atoms)	2.016(3)	2.0329(2)
Ni-L (encapsulated ligand)	2.938(7)	2.061(2)
Si-O (siloxanolate atoms)	1.598(3)	1.597(2)
Si-O (atoms of siloxane cycle)	1.630(3)	1.636(2)
M-O		2.394(2)

Also, taking in mind an importance of the mutual disposition of nickel(II)-containing complexes for magnetic behavior of synthesized complexes, we were interested in a topological analysis of CLMSs 1 and 2. Recently some of us reported the first example of such study on copper(II)-containing silsesquioxanes of different nuclearity.^{2h} Simplification of the molecular graph to obtain the graph of Ni-containing skeleton keeping the complexes connectivity was carried out with the ToposPro package.¹² Following the procedure of a metal complexes notation described previously¹³ one would obtain that penta- and hexanuclear compounds 1 and 2 form 4M5-1 and 5M6-1 discrete polynuclear complexes, respectively (Figure 4), in terms of the NDk-m notation.¹³ Here, N is a set of coordination numbers of topologically non-equivalent nodes (N = 2 for 2-connected nodes), D is the dimensionality (D = Mfor discrete polynuclear complexes), k is the number of metal atoms in the polynuclear complexes (k = 5 or 6), and m is a classification number to distinguish topologically distinct polynuclear complexes with equal NDk parameters.

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Figure 5. The Ni-containing polynuclear complexes connected by the oxygen bridged atoms in (a) **1** and (b) **2** and the graphs for the corresponding polynuclear complexes' connectivity (c, d).

Based on a database of topological representations of polynuclear nickel compounds¹⁴ containing 318 compounds and 126 different topological motifs, only two and four compounds with the 4M5-1 and 5M6-1 topologies, respectively, were published before. The family of 4M5-1 polynuclear complexes contains also $[Ni_5(\mu_5-S)(\mu_3-S)_2(\mu_2-S)(\mu_3-S)_2(\mu_2-S)(\mu_3-S)_2(\mu$ $CH_{3}COO)(PPh_{3})_{5}PF_{6}C_{7}H_{8}O.5CH_{2}Cl_{2}^{15}$ and $[Ni_{5}(\mu-SSi^{t}Bu_{3})_{5}(\mu_{5}-$ S)].¹⁶ The hexanuclear nickel(II)-containing polynuclear complexes of the 5M6-1 topology were found also in $[Ni_6(\mu_6 - \mu_6)]$ $S(\mu-S)_2(\eta^3-allyl)_6]^{17}$ $[Ni_6(\mu_6-Hal)(\mu_3-Hal)_2(\mu-Hal)_6(\mu-phip)_3]$ (phip = 3,5-bis(2,6-diisopropylphenyliminoacetyl)-1H-pyrazole; Hal = Cl_{1}^{18} Hal = Br^{19} and $[Ni_6(amox)_6(\mu_6-O)(\mu_3-OH)_2]Cl_2 \cdot 6H_2O$ (amox = 4-amino-4-methyl-2-pentanone oxime).²⁰ Thus, μ_5 or μ_6 coordination in the nickel polynuclear complexes is possible for Hal⁻, S²⁻ and O²⁻ anions.

Thus, the use of different solvent media, when corresponding solvent could play an assisting role in the cage formation, lets us to design hexa **1**- and (for the first time) pentanuclear **2** Ni(II)-based CLMSs. It was shown that hexagon-like disposition of nickel ions in **1** is characterized by longer Ni...Ni distances that found in pentagon-like organisation of nickel ions in **2**.

Magnetic properties investigations

The magnetic properties of compounds **1** and **2** were investigated using SQUID magnetometry.



Figure 6. Temperature dependence of χT under a 1000 Oe DC magnetic field for **1** and **2**. Inset: Field dependence of the magnetisation performed at 1.8 K for **1** and **2**.

Compound **1** exhibits the χT value of 11.06 cm³.K.mol⁻¹ at 300 K, which is higher than the theoretical value of 8.26 cm³.K.mol⁻¹ expected for six high-spin independents square pyramidal Ni^{II} ions.²¹ This discrepancy could arise from the occurrence of ferromagnetic interactions which are still operative at room temperature. The thermal dependence of χT reveals an increase when the temperature decreases until reaching a maximum at 10 K with a χT value of 45.00 cm³.K.mol⁻¹. This confirms the occurrence of ferromagnetic interactions between the Ni²⁺ ions, although the value is considerably higher than the value of 23.15 cm³.K.mol⁻¹ expected for S = 6 species that would result from a ferromagnetic coupling between all Ni²⁺ ions. Such deviation may be rationalized through the presence of intermolecular dipolar interactions mediated, for example, through the π -stacking. Below 10 K, a decrease of χT occurs and most likely originates from the zero-field splitting. The field dependence of the magnetization at 1.8 K (Inset of Figure 6) leads to a value of 8.50 μ_{B} under 70 kOe, although the system does not reach a clear saturation, indicating the presence of a magnetic anisotropy. In order to probe the occurrence of a slow relaxation of the magnetization, the zero-field cooled/field cooled (ZFC/FC) procedure was performed. In the ZFC experiment, the sample was cooled in the absence of a static magnetic field and the magnetization was then recorded as a function of temperature under a 50 Oe magnetic field. The FC magnetization data were collected after cooling the sample with the same field. The ZFC curve shows a narrow peak with a maximum at $T_{max} = 6.2$ K, while the FC curve increases. The ZFC/FC curves coincide for high temperatures and begin to separate at 7 K (Figure 7). An increasing of the applied dc field induces a shift of the ZFC curve maximum towards lower temperature. Consequently, a clear magnetic irreversibility occurs which is characteristic of the presence of a slow relaxation of the magnetization. This behavior is confirmed by monitoring the relaxation dynamics of the magnetization with AC magnetic measurements.

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Figure 7. ZFCcurves with various applied magnetic fields for **1** and FC curve for a 50 dc field.

The temperature dependence of the in-phase (χ') and the out-ofphase (χ'') components of the alternating current susceptibility were measured in the zero-dc field and reveals a frequency dependence indicating an occurrence of a slow relaxation of the magnetization (Figure 8). The maxima of χ'' shift to higher temperatures as the frequency increases. For instance, χ' exhibits a maximum at 7.2 K, while the maximum of χ'' is observed at 6.4 K with a 100 Hz frequency. Additionally, the χ'' intensity increases with frequencies up to 100 Hz before decreasing for higher values. The frequency dependence of the ac susceptibilities can originate from either a Single-Molecule Magnet or a spin glass-like behavior. The frequency dependence of the ac susceptibility show very broad peaks (Figure S1) that indicates a distribution of the relaxation time. Similarly, the Cole-Cole plots (Figure S2) show curves that deviate strongly from perfect semo-circles expected in the case of a narrow distribution of relaxation process. Such wide distribution of relaxation processes may originate from a spin-glass behavior which is further confirmed by calculating the Mydosh parameter φ (φ = $(T_{max} - T_{min})/(T_{max} \times \log v_{max} - \log v_{min}))$, which indicates the amplitude of the out-of-phase peaks' shift with frequency. This parameter is equal to 0.049, which is lower than the values observed for classical superparamagnets (> 0.1) and suggests the occurrence of a spin glass behavior. This is further confirms when looking at the Arrhenius law, $\tau = \tau_0 exp(U_{eff}/k_BT)$, where U_{eff} is the average energy barrier for the reversal of the magnetization, τ_0 is the attempt time and k_B is the Boltzmann constant. The best Arrhenius law fit of the blocking temperatures obtained from the χ'' maxima for different observation times $\tau = 1/2\pi v$ (with v being the frequency of the oscillating field) gives the U_{eff} and τ_0 values equal to 300.89 K and 3.55.10⁻²³ s, respectively. The τ_0 value obtained is clearly too low than those expected for pure superparamagnetic systems $(10^{-8}-10^{-1})$ ¹² s) and has not a physical meaning.



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Figure 8. Temperature dependence of the in-phase (χ') (top) and out-of-phase susceptibilies (χ'') (bottom) under a zero dc-field for **1**.

To check the occurrence of a spin glass-like behaviour, of the temperature dependence of the AC susceptibilities (at the frequency of 500 Hz) were measured for the different dc fields (Figure 9). The peak's maxima and intensities of both, the in-phase and the out-of-phase susceptibilities shift to lower temperature with increasing fields.

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Figure 9. Temperature dependence of the in-phase (a) and out-ofphase susceptibilities (b) measured with various dc magnetic fields for **1**.



Figure 10. Field dependence of the temperature maximum of χ'' as a function of the magnetic field (Almeida-Thouless line) for **1**.

The temperature maximum of χ'' decreases linearly with $H^{2/3}$ which corresponds to the Almeida-Thouless line and is frequently associated with a spin glass-like behavior (Figure 10).^{5,22} Extrapolation at H = 0 Oe gives a freezing temperature of 6.7 K, close to the value for the maximum of the ZFC curve of 6.2 K (Figure 7). Consequently, compound **1** clearly shows a spin glass-like behavior.

The magnetic behaviour of compound 2 reveals also the presence of the spin glass-like behaviour. The experimental room temperature γT value of compound **2** is equal to 6.02 cm³.K.mol⁻¹, which is slightly higher than the one of 5.51 cm³.K.mol⁻¹ expected for the five independent octahedral Ni(II) sites (S = 1, g = 2.1). Upon cooling, χT continuously decreases to reach a small plateau around 12 K (1.63 cm³.K.mol⁻¹) before strongly decreasing to a value of 1.00 cm³.K.mol⁻¹ at 1.8 K (Figure 6). While the former decrease originates from dominant antiferromagnetic interactions between the spin carriers, the decrease at low temperature may be imputed to the occurrence of a zero-field splitting and/or intermolecular dipolar interactions. The presence of a plateau with a non-zero value of the γT product may indicate the occurrence of a spin frustrated system in accordance with the topology of the polynyclear complex. The field dependence of the magnetization at 1.8 K reveals a fast increase at low fields before showing a linear dependence to reach the value of 1.43 μ_{B} under a 70 kOe field (Inset of Figure 6). To probe the occurrence of a spin glass behavior, the dynamic behavior was studied with alternating current (AC) measurements. The temperature dependence of the in-phase (χ') and the out-ofphase (χ'') susceptibilities reveal a clear frequency dependence. While the maximum of χ' shifts to higher temperature with increasing frequencies, no maximum can be observed for γ'' in the temperature range available (Figure 11). This precludes an in-depth analysis of the relaxation mechanisms. However, it can be observed than the intensity of the out-of-phase signal increases with frequency, which does not correspond to what is usually observed for pure superparamagnetic systems and suggests also the presence of a spin glass-like behavior.

Consequently, the spin glass-like behavior observed in 1 and 2 may originate from: (i) the freezing of the spins in each individual CLMS molecule, which may be caused by a particular arrangement of the Ni(II) ions in hexa- and pentagonal topology, and/or (ii) the presence of dipolar interactions between the CLMS molecules. Indeed, a particular geometrical arrangement of Ni(II) ions linked through two types of bridging oxygen atoms including peripheral and central ones may lead to different magnetic exchange pathway resulting in a spin frustration (see Figures 2-3). Such a phenomenon has previously been observed in the case of Co(II)-based triangular CLMS presenting a relatively large inter-complex separation of 14.5 Å. The shortest intermolecular Ni...Ni distances is equal to 13.54 and 10.34 Å for 1 and 2, respectively. For this reason, it is reasonable to conclude that in the case of 1, the observed spin glass-like regime originates rather from a spin frustration in each complex, even if we cannot completely exclude an influence of dipolar interactions, while for compound 2, the dipolar interactions play more important role, as previously observed in a trinuclear nickel (II) based complex.23

10 Hz

100 Hz 500 Hz

1000 Hz

1500 Hz





3

Conclusions

0.00

2

New hexanuclear $[(PhSiO_{1.5})_{12}(NiO)_6(H_2O)(DMSO)_9]$ 1 and pentanuclear [(PhSiO_{1.5})₁₀(NiO)₅(NaOH)(DMF)₇] 2 nickel(II)based silsesquioxanes have been obtained by an exchange reaction between a sodium phenylsiloxanolate [PhSi(O)ONa]_n and NiCl₂•6NH₃ in the presence of DMSO in the first and DMF molecules in the second case. We demonstrated that the role of solvent during the synthesis is crucial for the nuclearity of the final compound. Thus, this approach allow us to design for the first time the first example of an unusual pentanuclear cage-like Ni(II)-based silsesquioxane CLMS. The representation of the pentanuclear complex assembly, implying a coordination of the DMF molecules was proposed. Both compounds were studied by X-ray diffraction and topological analysis. Magnetic properties investigations revealed the presence of a slow relaxation of the magnetization in both cases induced by a spin glass-like behavior which concomitantly originates from both, the spin frustration in each polynuclear complex, and dipolar interactions between the CLMSs molecules.

Starting materials and physical measurements

The solvents (Merck) and other chemicals (Sigma-Aldrich) were used without further purification

Synthesis

[(PhSiO_{1,5})₁₂(NiO)₆(H₂O)(DMSO)₉] 1:

PhenyltriethoxysilanePhSi(OEt)₃ (1 g, 4.16 mmol) water (0.149 g, 8.28 mmol), sodium hydroxide (0.166 g, 4.15 mmol) in 18 ml of MeOH were placed into flask, provided by magnetic stirrer and condenser. After total dissolution of sodium hydroxide mixture was heated at reflux for 2 hours, then cooled down to room temperature. Afterwards 55 ml of DMSO and nickel hexamine chloride $Ni(NH_3)_6Cl_2$ (0.482 g, 2.08 mmol) were added at once. The reaction mixture was brought to reflux along with simultaneous partial distillation of the solution. As 15 mL of solvents were distilled off, the rest of reaction mixture was heated under reflux for 3.5 h, then cooled to room temperature. After overnight stirring the mixture was filtered into an evaporation flask. The flask was equipped with a septum and needle to allow solvents to evaporate under a slow current of nitrogen. Immediately after yellow-colored crystals began to form, the flask was transferred to the cool place and stored there until the crystal fraction growth (~ 3 weeks) ceased, as visually determined. A few selected single crystals were used for the X-ray study (for details, see below). Yield: 0.26 g, 38%; elemental analysis calcd (%) for $[(PhSiO_{1.5})_{12}(NiO)_6(H_2O)]$: Ni 17.46, Si 16.71; found (in a vacuum-dried sample): Ni 17.29, Si 16.45.

[(PhSiO_{1,5})₁₀(NiO)₅(NaOH)(DMF)₇] 2:

Phenyltriethoxysilane PhSi(OEt)₃ (1 g, 4.16 mmol) water (0.149 g, 8.28 mmol), sodium hydroxide (0.166 g, 4.15 mmol) in 18 ml of MeOH were placed into flask, provided by magnetic stirrer and condenser. After total dissolution of sodium hydroxide mixture was heated at reflux for 2 hours, then cooled down to room temperature. Afterwards 55 ml of DMF and nickel hexamine chloride Ni(NH₃)₆Cl₂ (0.482 g, 2.08 mmol) were added at once. The reaction mixture was brought to reflux along with simultaneous partial distillation of the solution. As 15 mL of solvents were distilled off, the rest of reaction mixture was heated under reflux for 3.5 h, then cooled to room temperature. After overnight stirring the mixture was filtered into an evaporation flask. The flask was equipped with a septum and needle to allow solvents to evaporate under a slow current of nitrogen. Immediately after yellow-colored crystals began to form, the flask was transferred to the fridge and stored there until the crystal fraction growth (~ 2 weeks) ceased, as visually determined. A few selected single crystals were used for the X-ray study (for details, see below). Yield: 0.30 g, 42%; elemental analysis calcd (%) for [(PhSiO_{1.5})₁₀(NiO)₅(NaOH)]: Ni 17.21, Si 16.47; found (in a vacuum-dried sample): Ni 17.09, Si 16.29.

IR studies

IR studies were carried out using Nujol mulls on a Nicolet 6700 FTIR spectrometer in the 4000–600 cm⁻¹ range. Set of signals for **1-2**: 1120 cm⁻¹ (vPh–Si), 940–1100 cm⁻¹ (v^{as}Si–O, v^{as}Si–O–

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Si), 900 cm⁻¹ (v^{as} Si–O in Si–O–M fragment), 720–680 cm⁻¹ (σ C–H of mono-substituted phenyl group).

Magnetic measurements

Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer working between 1.8 and 350 K with the magnetic field up to 7 Tesla. The data were corrected for the sample holder and the diamagnetic contributions calculated from the Pascal's constants.

X-ray

X-ray diffraction studies were carried out on Bruker APEX DUO at 120 K (**1**) and Bruker Smart APEX II (**2**). The structures were solved by direct method and refined in anisotropic approximation against F^2 . The crystal structure contains strongly disordered solvents molecules; their contribution to diffraction intensities was excluded using SQUEEZE procedure implemented in PLATON software.²⁴ All calculations were carried out with SHELX²⁵ and OLEX2²⁶ software. The experimental parameters and crystal data for **1** and **2** are summarized in Table 2

Table 2. Crystal data and experimental parameters ofthe structures 1 and 2.

	1	2
Formula	$\begin{array}{c} C_{90}H_{112}Ni_6O_{34}S_9\\Si_{12}\end{array}$	$\begin{array}{c} C_{81}H_{100}N_7NaNi_5\\ O_{28}Si_{10} \end{array}$
Mass	2715.68	2217.11
Space group	P21/c	P21/c
Z	4	4
a, Å	23.0693(3)	20.1408(17)
b, Å	21.9189(3)	18.6886(16)
c, Å	23.4492(3)	27.306(2)
β, °	90.1120(10)	92.703(2)
V, Å ³	11857.2(3)	10266.8(15)
d _{calc} , g·cm ⁻³	1.521	1.434
μ, cm ⁻¹	42.99	10.95
F(000)	5616	4596
2θ _{max} , °	132	52
Reflections collected	86444	133509
Independent reflections	20537	31342
Independent reflections (I>2σ(I))	18211	23643
Parameters	1371	1203
R ₁ [I>2σ(I)]	0.0591	0.0450

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wR ₂ [all reflections]	0.1727	0.1303
GOF	1.033	1.101
Residual electron density $e \cdot Å^{-3}(\rho_{min}/\rho_{max})$	2.670/-1.183	1.714/-0.719

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