Ni$_4$Na$_2$-Phenyldilsesquioxane: Synthesis, Structure, and Slow Dynamic Behaviour

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EXPERIMENTAL SECTION

Materials.
Phenyltrimethoxygermane was purchased from ABCR as used as received.

Synthesis
PhGe(OMe)$_3$ (2.00 g, 8.2 mmol) was dissolved in 45 mL of ethanol. Then 0.33 g (8.2 mmol) of NaOH was added, and the resulting mixture was heated to reflux for 2.5 h. Afterward 0.76 g (3.30 mmol) of Ni(NH$_3$)$_6$Cl$_2$ was added at once. The resulted mixture was heated to reflux for 12 h. Filtration of the mixture from insoluble part gave yellow-colored solution. Slow evaporation of solvents (ethanol/methanol) gave in 10 days crystalline material. Several crystals (yellow-green prisms) were used for the single crystal X-ray diffraction analysis. Anal. calcd for C$_{60}$H$_{50}$Ge$_{10}$Na$_2$Ni$_4$O$_{20}$: Ge, 34.62; Ni, 11.19; Na, 2.19. Found (using XRF VRA-30 spectrometer for vacuum-dried sample): Ge, 34.50; Ni, 11.06; Na, 2.12. Yield 0.64 g (30%).

IR spectrum (Fig. S8) was recorded on Shimadzu IR Prestige21 FTIR spectrometer in KBr pellets. UV−vis absorption spectrum (Fig. S8) was recorded on a Varian Cary 50 spectrophotometer in cells with 10 mm optical path lengths.

Crystal Data for C$_{42}$H$_{65}$Ge$_5$Na$_2$Ni$_2$O$_{18}$ ($M = 1361.30$ g/mol): monoclinic, space group P2$_1$/n (no. 14), a = 15.328(3) Å, b = 22.205(4) Å, c = 16.163(3) Å, $\beta = 102.383(3)^\circ$, $V = 5373.0(15)$ Å$^3$, $Z = 4$, $T =$ 120 K, $\mu$(MoKα) = 3.519 mm$^{-1}$, $D_{calc} = 1.683$ g/cm$^3$, 93790 reflections measured (3.668$^\circ \leq \Theta \leq 61.016^\circ$), 16377 unique ($R_{int} = 0.0990$, $R_{sigma} = 0.0723$) which were used in all calculations. The final $R_1$ was 0.0794 ($1 > 2\sigma(I)$) and $wR_2$ was 0.2012 (all data). Single crystals of C$_{42}$H$_{65}$Ge$_5$Na$_2$Ni$_2$O$_{18}$ were green prisms. X-ray dataset was measured on Bruker APEX-II CCD diffractometer at 120 K. Using Olex2,$^{51}$ the structure was solved with the olex2.solve$^{52}$ structure solution program using Charge Flipping and refined with the ShelXL$^{53}$ refinement package using Least Squares minimisation.
Comparison of structural parameters of Ge-based ligands of \( \text{Ni}_2\text{Na}_2 \) and \( \text{Fe}_3\text{Na}_5 \)-based phenylgermaniumsesquioxanes

Table S1

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<thead>
<tr>
<th></th>
<th>Ni (this work)</th>
<th>Fe (ref. 9a)</th>
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<tbody>
<tr>
<td>Ge-O(Ni)</td>
<td>1.71 – 1.74 Å</td>
<td>Ge-O(Fe)</td>
</tr>
<tr>
<td>Ge-O(Ge)</td>
<td>1.76 – 1.78 Å</td>
<td>1.73 – 1.77 Å</td>
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<tr>
<td>( \angle ) Ge-O-Ge</td>
<td>120.5 - 126.3°</td>
<td>Ge-O(Ge)</td>
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<td></td>
<td></td>
<td>1.75 – 1.78 Å</td>
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<td></td>
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<td>( \angle ) Ge-O-Ge</td>
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<td></td>
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<td>120.5 – 126.3°</td>
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Figure S1. General scheme for the synthesis of 1.

Figure S2: Left: Temperature dependence of $\chi T$ under a 1000 Oe DC field. Right: Field dependence of the magnetization at 1.8 K.
**Figure S3:** Hysteresis loop at 1.8 K

**Figure S4:** ZFC/FC curves obtained with an applied magnetic fields a dc field of 100 Oe. The ZFC curve shows the presence of two maxima, $T_{\text{max}}$, located around 4.5 and 10.5 K respectively. On the other hand, the FC curve continuously increases and separate from the ZFC curve around 13 K, which corresponds to an irreversible temperature $T_{i\text{rr}}$. Hence, these results confirm the presence of a magnetic irreversibility, which could originate from a slow relaxation of the magnetization.
Figure S5: Temperature dependence of relaxation time for 1.

Note that fitting of the relaxation time by using the critical scaling law of the spin dynamics, $\tau = \tau_0 [T_g/(T_{\text{max}} - T_g)]^{z_v}$ (where $T_g$ is the glass temperature, and $z_v$ is a critical exponent) did not give the satisfactory results. The best obtained parameters are: $T_g = 5.07$ K and $z_v = 3.2$ (LT process) and $T_g = 6.71$ K and $z_v = 14.2$ (HT process). For both of them, the $z_v$ critical exponent is found slightly out of the range to what is expected for spin glass systems ($4 < z_v < 12$).

Figure S6: Temperature dependence of the in-phase and out-of-phase susceptibilities measured with various dc magnetic fields for 1.
**Figure S7**: Field dependence of the temperature maximum of $\chi''$ as a function of the magnetic field (Almeida–Thouless line) for the LT process.

**Figure S8**: IR spectrum of 1
Figure S9. UVvis spectrum of 1

