Template arrangement of \{\text{Ni}^3(\mu_3-\text{OH})(\text{SO}_4)(\text{R}-\text{NO})_2\}^+ \text{fragments around Na}^+ \text{cations: An unprecedented} \{\text{Ni}^{12}\text{Na}\} \text{unit linked by oximate and sulfate bridges}

Jordi Esteban $^a,⁎$ , Mercè Font-Bardia $^b,c$ , Albert Escuer $^a,⁎$

a Departament de Química Inorgànica, Universitat de Barcelona, Av. Diagonal 645, Barcelona 08028, Spain
b Departament de Mineralogia, Cristal·lografia i Dipòsits Minerals, Universitat de Barcelona, Martí Franqués s/n, 08028 Barcelona, Spain
c Unitat de Difracció de R-X, Centre Científic i Tecnològic de la Universitat de Barcelona (CCiTUB), Universitat de Barcelona, Solé i Sabaris 1-3, 08028 Barcelona, Spain

⁎ Corresponding authors. Tel.: +34 934039144; fax: +34 934907725.
E-mail address: jordi.esteban@qi.ub.edu (J. Esteban).

Keywords: Supramolecular Template synthesis Sulfato complexes Metallamacrocycle Magnetic measurements
A novel \(-\text{Ni}_{12}\text{Na}_2\text{-Ni-}\) chain has been characterized from the reaction between 2-pyridylcyanoxime, \((\text{pyC}\{\text{CN}\}\text{NOH})\), and nickel(II) sulfate. The template synthesis around a Na\(^+\) cation gives an unprecedented arrangement of four nickel triangles coordinated to the central sodium ion by sulfato bridges.
The use of 2-pyridyloximate ligands and paramagnetic first-row transition metal ions has been a growing field in the last years due to their ability to generate stable polynuclear compounds with a wide range of nuclearities [1]. Among them, 2-pyridylcyanoxime ligand, pyC{CN}NOH, Scheme 1, has proven to possess unique reactivity that arises from the coordination of the cyano substituent to the vicinal C-atom to the oximate function, which gives a much more acidic oxime (3–5 units of pKa with respect to ligands with other substituents) [1], and has lead to unique topologies, as we have reported in the previous copper [2], nickel [3] and manganese [4] studies. One of the specific properties of this ligand is that, as has been recently reported, it is prone to generate isolated triangular clusters with \{Ni3(μ3-OH)(R-NO)3\}^2+ core [3].

Although sulfate anions present great coordinative possibilities (they can bind up to 10 metal ions) [5], and have shown interesting properties in different fields such as catalysis, medicinal, bioinorganic and environmental chemistry [5], its use in coordination chemistry is limited and currently, only six entries were found in CCDC containing the simultaneous sulfate and oximate bridges being practically all of them NiII derivatives such as Ni4 [6], two Ni5 [7], a family of Ni6 [8] and one Ni8 [9] clusters. In this work we have explored the combination of the pyC{CN}NOH ligand and sulfate anions with the aim of triggering the aggregation of preformed smaller species into new high-nuclearity clusters; and we report the synthesis, characterization and magnetic study of a \{−Ni12Na2-Ni−\}_n chain with the formula \[\text{[Ni13Na2(H2O)2(MeOH)14(OH)4(pyC{CN}NO)8(SO4)8\cdot solven}(1\cdot \text{solvent})\] in which four \{Ni3(μ3-OH)(SO4)(R-NO)2\}^+ triangles template around a central Na(1) ion. This fragment links a peripheral Na(2) cation and the chain is the result of further linkage of the \{Ni12Na2\} units by one additional bridging NiII cation.

Noteworthy, the \{Ni13Na2\} fragment is the largest oximate–sulfate cluster and the second highest nuclearity in Ni-oximate chemistry (only surpassed by a family of Ni14 clusters [10]) and in Ni-sulfate chemistry (just outstripped by one Ni30 compound [11]).

Reaction of nickel sulfate and 2-pyridyloximate (2:1 ratio) in methanolic solution and NaOH as base yields compound 1 by slow evaporation [12,13]. Compound 1 consists of one central Na(1) cation surrounded by four \{Ni3(OH)(pyC{CN}NO2)(SO4)(MeOH)2(H2O)\}−triangles and a second Na(2) cation linked by a sulfato bridge. One additional nickel atom links the \{Ni12Na2\} units generating a onedimensional \{−(Ni12Na2)-Ni\}_n system. The four triangular subunits are not crystallographically equivalent but their bond parameters are very similar and to simplify the discussion only one of them will be described in detail. The triangular subunit formed by Ni(1,2,3) is defined by one central μ3-OH ligand, two oximate and one sulfato bridges that determine the main plane of the triangle, Fig. 1 top. The two sides defined by the oximate bridges show close bond parameters (Ni–O(1a)/Ni bond angles are 106.8(2) and 109.5(2)° and Ni⋯Ni distances of 3.274(1) and 3.325(1) Å) whereas the parameters for the side defined by the sulfato bridge are 123.3(2)° and 3.585(1) Å, respectively. Ni–N–O–Ni torsion angles are 7.8(5) and 17.9(5)°. One capping tridentate sulfate ligand links three axial coordination sites and the coordination spheres of the nickel atoms are completed by solvent molecules except for O(10) atom, which comes from one sulfate of the neighbor triangle. The O(10) atom is equivalent to O(33): they both bridge two triangles and link the central Na(1) cation.

The four linked triangles are arranged in a roughly S4 symmetry around the central Na(1) cation, Fig. 1 bottom, determining the tridecanuclear \{Ni12Na2\} unit. The sodium cation is linked by four pentadentate 4.2210 sulfates resulting in a girobifastigium coordination polyhedron (Johnson 26) [15], Fig. 2. The fourNa–O distances of the central square plane, O(10,12,28,33), are comprised in the 2.277–2.328 Å range whereas the other four sites O(9,15,26,34), related by an S4 axis, exhibit larger bond distances in the 2.710–2.871 Å range. Focusing in the environment of the sodium atom, its coordination can
alternatively be described as the center of a 16-MC8 metallacrown formed by four nickel atoms, four sulfurs and eight oxygen donors, Fig. 2.

The discrete \{Ni\textsubscript{12}Na\textsubscript{2}\} units are linked to the Ni(13) atom. This nickel atom exhibits a Ni\textsubscript{6} coordination environment that arises from four methanol molecules and two trans 4.1111 sulfate anions that generate the final 1D \{-(Ni\textsubscript{12}Na\textsubscript{2})-Ni-\}_n system, Fig. 3.

Factors that lead to the stabilization of 1 are the combination of the properties of the chosen reagents. In fact, other 2-pyridyloximes with R=H,Me or Ph instead of the nitrile function do not tend to give triangular clusters and when combined with sulfato ligand give a variety of Ni\textsubscript{6} topologies. A second feature is related with the great coordinative flexibility of the sulfato ligand, which exhibits their 4.2110, 4.1111 and 3.1110 modes coordinating Ni\textsuperscript{II} and Na\textsuperscript{+} cations, Scheme 1. The sodium cation plays a crucial role in the syntheses of 1 as a templating agent. Noteworthy, reaction performed employing Et\textsubscript{3}N as base does not give isolable compounds whereas the same reaction with CsOH as base leads to the equivalent compound with Cs\textsuperscript{+} instead of the central Na\textsuperscript{+} cation.

The temperature dependence of the χ\textsubscript{MT} product of compound 1 is plotted in Fig. 4 [16]. The room temperature χ\textsubscript{MT} value is 14.2 K cm\textsuperscript{3} mol\textsuperscript{-1}, which decreases gradually on cooling, down to 1.8 K cm\textsuperscript{3} mol\textsuperscript{-1} at 2 K.

In view of the negligible magnetic exchange promoted by sulfato anions [5] no intertriangle interactions were considered and thus the fitting of the experimental data was done using the conventional analytical equation derived from the two-J Hamiltonian:

\[
H = -J_1 (S_1 \cdot S_2 + S_2 \cdot S_3) - J_2 (S_1 \cdot S_3)
\]

Considering four triangles plus one isolated Ni\textsuperscript{II} for molar formula. Best fit parameters obtained were \(J_1 = -22.8(4)\) cm\textsuperscript{-1}, \(J_2 = -14.3(2)\) cm\textsuperscript{-1} and \(g = 2.204(5)\).

According to DFT calculated correlation for μ\textsubscript{3}-OH/NO bridges as superexchange pathway presented in a previous paper [3a], the main factor that contributes to tune the AF interaction are the Ni–O–Ni bond angles involving the central μ\textsubscript{3}-OH bridge. The estimated J value for an average Ni–O–Ni angle of ~108° would be around ~25 cm\textsuperscript{-1} in excellent agreement with the estimated value of J1. The weaker interaction, mediated by the countercomplementary SO\textsubscript{4} 2−/OH bridges, should be mainly attributed to the interaction mediated by the Ni–O–Ni pathway with a bond angle of 123.4(2)°. Ground state for a triangular arrangement of Ni\textsuperscript{II} cations depends on the J2/J1 ratio, being S = 1 for ratios comprised between 0 and 0.5 and S = 0 for ratios larger than 0.5 (which is a frustration point). The J2/J1 ratio for 1 is around 0.62 and the ground state of each triangle is S=0. Thus, the low χ\textsubscript{MT} value at 2 K can be rationalized like four S = 0 triangles plus one isolated Ni\textsuperscript{2+} atom.

In conclusion, the employment of 2-pyridylcianoxime ligand with nickel sulfate in the presence of sodium cations has lead to one 1D system containing four triangular units template around the sodium cation resulting in \{Ni\textsubscript{12}Na\textsubscript{4}\} fragments. Compound 1 provides a new example of the unusual reactivity of 2-pyridylcianoxime and the relevant and poorly explored role of the sulfato ligands to generate large nuclearity clusters.
Funds from the Ministerio de Economia y Competitividad Project CTQ2012-30662 are acknowledged.
A.E. is thankful for the financial support from the Excellence in Research ICREA-Academia Award.
REFERENCES

[12] Reaction of Ni(SO4)·6H2O (0.280 g, 1 mmol) with 2-pyridylcyanoxime (0.073 g, 0.5 mmol) an NaOH (0.040 g, 1 mmol) in 20 mL of methanol yields compound 1 by slow evaporation as orange bricks. Anal. calcd for dried C70H96N24Na2Ni13O60S8 (1): C, 25.48; H, 2.94; N, 10.19; S, 7.77%. Found: C, 25.0; H, 3.1; N, 9.8; S, 7.6 %. Relevant IR bands (cm−1): 3315(br), 2226(w), 1603(m), 1468(s), 1432(w), 1303(w), 1266(w), 1224(m), 1142(s), 1107(s), 1037(m),...
Reaction performed with CsOH instead NaOH yields the equivalent compound as tin needles (not adequate for X-ray determination) with the same IR spectra. Infrared spectra (4000–400 cm$^{-1}$) were recorded from KBr pellets on a Brucker IFS-125 FT-IR spectrophotometer.

[13] Data for compound 1 was measured from orange crystals at 273 K and $\lambda = 0.71073$ Å using a Bruker APEX-II CCD diffractometer with graphite monochromator. Crystal data and structural parameters for 1: [C$_{70}$H$_{96}$N$_{24}$Na$_{2}$Ni$_{13}$O$_{60}$S$_{8}$], MW: 3299.39, triclinic space group P-1, $a = 14.0686(18)$ Å, $b = 22.314(3)$ Å, $c = 29.223(4)$ Å, $\alpha = 93.991(2)^{\circ}$, $\beta = 103.354(2)^{\circ}$, $\gamma = 108.295(2)^{\circ}$, $V = 8373.6(2.18)$ Å$^3$, $Z = 2$, $D_c = 1.306$ g·cm$^{-3}$, $\mu$(Mo–K$\alpha$) = 1.605 mm$^{-1}$, $T = 273(2)$ K, 34,029 reflections measured, 17,825 independent reflections ($R_{int} = 0.0782$), final $R_1[\sigma(I)] = 0.0622$ and final $wR_2 = 0.1569$. Program SQUEEZE, part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data; as consequence methanol and water molecules around Na(2) were not determined. CCDC 972518.

[14] Harris notation, referred as X.Y$_1$Y$_2$Y$_3$…Y$_n$, where X is the overall number of metals bound by the whole ligand and each value of Y refers to the number of metal ions attached to the different donor atoms. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules, hence here O before N. R.A. Coxall, S.G. Harris, D.K. Henderson, S. Parsons, P.A. Tasker, R.E.P. Winpenny, Chem. Soc. Dalton Trans. (2000) 2349–2356.


[16] Magnetic susceptibility measurements were carried out on polycrystalline samples using a Quantum Design MPMS-5 SQUID susceptometer working in the range 2–300 K under magnetic fields of 0.3 T (300–30 K) and 0.03 T (30–2 K) to avoid saturation effects. Diamagnetic corrections were estimated from Pascal tables.
Legends to figures

Scheme 1. Left, pyC\{CN\}NOHligand and the coordinationmode for pyC\{CN\}NO−present in this communication, in Harris notation [14]. Right, sulfate coordinationmodes presented in this work. Color code: NiII, green; O, red, N, blue; S, orange; Na+ purple.

Figure 1. Top, labeled plot of a Ni3 triangular subunit. Bottom, view along the pseudo-S4 axis of the \{Ni12Na\} unit of compound 1.

Figure 2. Left, environment of the central Na(1) cation generating the girobifastigium coordination polyhedron. Right, View of the 16-MC8 metallacrown generated around the Na+cation.

Figure 3. View of the \{−Ni12Na2-Ni−\}n chain showing the bridging Ni(13) ion and the position of Na(2) linked to one of the 4.1111 sulfates.

Figure 4. χMT product vs. T for compound 1. Solid line shows the best obtained fit. Inset: coupling scheme for each of the triangles (see text).
SCHEME 1

[Diagram showing molecular structures with labels and numerical codes]
FIGURE 1