

1 **Template arrangement of $\{\text{Ni}_3(\mu_3\text{-OH})(\text{SO}_4)(\text{R-NO})_2\}^+$ fragments around Na^+ cations: An**
2 **unprecedented $\{\text{Ni}_{12}\text{Na}\}$ unit linked by oximate and sulfate bridges**

3
4
5
6 Jordi Esteban ^{a,*}, Mercè Font-Bardia ^{b,c}, Albert Escuer ^{a,*}
7
8
9

10
11
12
13
14
15
16
17
18
19 a Departament de Química Inorgànica, Universitat de Barcelona, Av. Diagonal 645, Barcelona 08028,
20 Spain

21 b Departament de Mineralogia, Cristal·lografia i Dipòsits Minerals, Universitat de Barcelona, Martí
22 Franqués s/n, 08028 Barcelona, Spain

23 c Unitat de Difracció de R-X, Centre Científic i Tecnològic de la Universitat de Barcelona (CCiTUB),
24 Universitat de Barcelona, Solé i Sabarís 1-3, 08028 Barcelona, Spain

25
26
27
28
29
30
31
32 * **Corresponding authors.** Tel.: +34 934039144; fax: +34 934907725.

33 E-mail address: jordi.esteban@qi.ub.edu (J. Esteban).
34
35
36
37
38

39 **Keywords:** Supramolecular Template synthesis Sulfato complexes Metallamacrocycle Magnetic
40 measurements
41

42 **ABSTRACT**

43

44 A novel $\{-\text{Ni}_2\text{Na}_2\text{-Ni}\}_n$ chain has been characterized from the reaction between 2-pyridylcyanoxime,
45 (pyC{CN}NOH), and nickel(II) sulfate. The template synthesis around a Na^+ cation gives an
46 unprecedented arrangement of four nickel triangles coordinated to the central sodium ion by sulfato
47 bridges.

48

49

50

51

52 The use of 2-pyridyloximate ligands and paramagnetic first-row transition metal ions has been a
53 growing field in the last years due to their ability to generate stable polynuclear compounds with a wide
54 range of nuclearities [1]. Among them, 2-pyridylcyanoxime ligand, pyC{CN}NOH, Scheme 1, has
55 proven to possess unique reactivity that arises from the coordination of the cyano substituent to the
56 vicinal C-atom to the oximate function, which gives a much more acidic oxime (3–5 units of pKa with
57 respect to ligands with other substituents) [1], and has led to unique topologies, as we have reported in
58 the previous copper [2], nickel [3] and manganese [4] studies. One of the specific properties of this
59 ligand is that, as has been recently reported, it is prone to generate isolated triangular clusters with
60 $\{\text{Ni}_3(\mu_3\text{-OH})(\text{R-NO})_3\}^{2+}$ core [3].

61 Although sulfate anions present great coordinative possibilities (they can bind up to 10 metal ions) [5],
62 and have shown interesting properties in different fields such as catalysis, medicinal, bioinorganic and
63 environmental chemistry [5], its use in coordination chemistry is limited and currently, only six entries
64 were found in CCDC containing the simultaneous sulfate and oximate bridges being practically all of
65 them are NiII derivatives such as Ni4 [6], two Ni5 [7], a family of Ni6 [8] and one Ni8 [9] clusters.

66 In this work we have explored the combination of the pyC{CN}NOH ligand and sulfate anions with the
67 aim of triggering the aggregation of preformed smaller species into new high-nuclearity clusters; and we
68 report the synthesis, characterization and magnetic study of a $\{-\text{Ni}_{12}\text{Na}_2\text{-Ni}\}_n$ chain with the formula
69 $[\text{Ni}_{13}\text{Na}_2(\text{H}_2\text{O})_2(\text{MeOH})_{14}(\text{OH})_4(\text{pyC}\{\text{CN}\}\text{NO})_8(\text{SO}_4)_8]_n \cdot \text{solvent}$ (1·solvent) in which four
70 $\{\text{Ni}_3(\mu_3\text{-OH})(\text{SO}_4)(\text{R-NO})_2\}^+$ triangles template around a central Na(1) ion. This fragment links a
71 peripheral Na(2) cation and the chain is the result of further linkage of the $\{\text{Ni}_{12}\text{Na}_2\}$ units by one
72 additional bridging NiII cation.

73 Noteworthy, the $\{\text{Ni}_{13}\text{Na}_2\}$ fragment is the largest oximate–sulfate cluster and the second highest
74 nuclearity in Ni-oximate chemistry (only surpassed by a family of Ni14 clusters [10]) and in Ni-sulfate
75 chemistry (just outstripped by one Ni30 compound [11]).

76 Reaction of nickel sulfate and 2-pyridyloximate (2:1 ratio) in methanolic solution and NaOH as base
77 yields compound 1 by slow evaporation [12,13]. Compound 1 consists of one central Na(1) cation
78 surrounded by four $[\text{Ni}_3(\text{OH})(\text{pyC}\{\text{CN}\}\text{NO})_2(\text{SO}_4)_2(\text{MeOH})_2(\text{H}_2\text{O})]$ –triangles and a second Na(2)
79 cation linked by a sulfato bridge. One additional nickel atom links the $\{\text{Ni}_{12}\text{Na}_2\}$ units generating a
80 onedimensional $\{-(\text{Ni}_{12}\text{Na}_2)\text{-Ni}\}_n$ system. The four triangular subunits are not crystallographically
81 equivalent but their bond parameters are very similar and to simplify the discussion only one of them
82 will be described on detail. The triangular subunit formed by Ni(1,2,3) is defined by one central μ_3 -
83 OH ligand, two oximate and one sulfato bridges that determine the main plane of the triangle, Fig. 1 top.
84 The two sides defined by the oximate bridges show close bond parameters (Ni\O(1a)\Ni bond angles are
85 $106.8(2)$ and $109.5(2)^\circ$ and Ni···Ni distances of $3.274(1)$ and $3.325(1)$ Å) whereas the parameters for the
86 side defined by the sulfato bridge are $123.3(2)^\circ$ and $3.585(1)$ Å, respectively. Ni–N–O–Ni torsion angles
87 are $7.8(5)$ and $17.9(5)^\circ$. One capping tridentate sulfate ligand links three axial coordination sites and the
88 coordination spheres of the nickel atoms are completed by solvent molecules except for O(10) atom,
89 which comes from one sulfate of the neighbor triangle. The O(10) atom is equivalent to O(33): they both
90 bridge two triangles and link the central Na(1) cation.

91 The four linked triangles are arranged in a roughly S4 symmetry around the central Na(1) cation, Fig. 1
92 bottom, determining the tridecanuclear $\{\text{Ni}_{12}\text{Na}\}$ unit. The sodium cation is linked by four pentadentate
93 4.2210 sulfates resulting in a girobifastigium coordination polyhedron (Johnson 26) [15], Fig. 2. The
94 four Na–O distances of the central square plane, O(10,12,28,33), are comprised in the 2.277 – 2.328 Å
95 range whereas the other four sites O(9,15,26,34), related by an S4 axis, exhibit larger bond distances in
96 the 2.710 – 2.871 Å range. Focusing in the environment of the sodium atom, its coordination can

97 alternatively be described as the center of a 16-MC8 metallocrown formed by four nickel atoms, four
98 sulfurs and eight oxygen donors, Fig. 2.

99 The discrete $\{Ni_{12}Na_2\}$ units are linked to the Ni(13) atom. This nickel atom exhibits a NiO6
100 coordination environment that arises from four methanol molecules and two trans 4.1111 sulfate anions
101 that generate the final 1D $\{-(Ni_{12}Na_2)-Ni-\}_n$ system, Fig. 3.

102 Factors that lead to the stabilization of 1 are the combination of the properties of the chosen reagents. In
103 fact, other 2-pyridyloximes with R=H,Me or Ph instead of the nitrile function do not tend to give
104 triangular clusters and when combined with sulfato ligand give a variety of Ni6 topologies. A second
105 feature is related with the great coordinative flexibility of the sulfato ligand, which exhibits their 4.2110,
106 4.1111 and 3.1110 modes coordinating NiII and Na+ cations, Scheme 1. The sodium cation plays a
107 crucial role in the syntheses of 1 as a templating agent. Noteworthy, reaction performed employing Et3N
108 as base does not give isolable compounds whereas the same reaction with CsOH as base leads to the
109 equivalent compound with Cs+ instead of the central Na+cation.

110 The temperature dependence of the χ_{MT} product of compound 1 is plotted in Fig. 4 [16]. The room
111 temperature χ_{MT} value is 14.2 K cm³ mol⁻¹, which decreases gradually on cooling, down to 1.8 K cm³
112 mol⁻¹ at 2 K.

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

116

$$117 \quad H = -J_1 (S_1 \cdot S_2 + S_2 \cdot S_3) - J_2 (S_1 \cdot S_3)$$

118

119 considering four triangles plus one isolated NiII for molar formula. Best fit parameters obtained were J_1
120 = -22.8(4) cm⁻¹, J_2 = -14.3(2) cm⁻¹ and g = 2.204(5).

121 According to DFT calculated correlation for μ_3 -OH/NO bridges as superexchange pathway presented in
122 a previous paper [3a], the main factor that contributes to tune the AF interaction are the Ni\O\Ni bond
123 angles involving the central μ_3 -OH bridge. The estimated J value for an average Ni-O-Ni angle of
124 $\sim 108^\circ$ would be around -25 cm⁻¹ in excellent agreement with the estimated value of J_1 . The weaker
125 interaction, mediated by the countercomplementary SO₄ 2-/OH bridges, should be mainly attributed to
126 the interaction mediated by the Ni-O-Ni pathway with a bond angle of 123.4(2)°. Ground state for a
127 triangular arrangement of NiII cations depends on the J_2/J_1 ratio, being $S = 1$ for ratios comprised
128 between 0 and 0.5 and $S = 0$ for ratios larger than 0.5 (which is a frustration point). The J_2/J_1 ratio for 1
129 is around 0.62 and the ground state of each triangle is $S=0$. Thus, the low χ_{MT} value at 2 K can be
130 rationalized like four $S = 0$ triangles plus one isolated Ni²⁺ atom.

131 In conclusion, the employment of 2-pyridylcyanoxime ligand with nickel sulfate in the presence of
132 sodium cations has led to one 1D system containing four triangular units template around the sodium
133 cation resulting in $\{Ni_{12}Na\}$ fragments. Compound 1 provides a new example of the unusual reactivity
134 of 2-pyridylcyanoxime and the relevant and poorly explored role of the sulfato ligands to generate large
135 nuclearity clusters.

136 .

137

138 **ACKNOWLEDGMENTS**

139

140 Funds from the Ministerio de Economía y Competitividad Project CTQ2012-30662 are acknowledged.

141 A.E. is thankful for the financial support from the Excellence in Research ICREA-Academia Award.

142

143 **REFERENCES**

144

- 145 [1] C.J. Milios, T.C. Stamatatos, S.P. Perlepes, *Polyhedron* 25 (2006) 134–194.
- 146 [2] A. Escuer, G. Vlahopoulou, S.P. Perlepes, F.A. Mautner, *Inorg. Chem.* 50 (2011) 2468–2478.
- 147 [3] a) J. Esteban, E. Ruiz, M. Font-Bardia, T. Calvet, A. Escuer, *Chem. Eur. J.* 18 (2012) 3637–
148 3648; b) J. Esteban, M. Font-Bardia, A. Escuer, *Eur. J. Inorg. Chem.* (2013) 5274–5280.
- 149 [4] L. Alcazar, B. Cordero, J. Esteban, V. Tangoulis, M. Font-Bardia, T. Calvet, A. Escuer, *Dalton*
150 *Trans.* 42 (2013) 12334–12345.
- 151 [5] C. Papatriantafyllopoulou, E. Manessi-Zoupa, A. Escuer, S.P. Perlepes, *Inorg. Chim. Acta* 362
152 (2009) 634–650.
- 153 [6] E. Moushi, C.G. Efthymiou, S.P. Perlepes, C. Papatriantafyllopoulou, *Int. J. Inorg. Chem.*
154 (2011) 606271–606279.
- 155 [7] Z. Chen, M. Jia, Z. Zhang, F. Liang, *Cryst. Growth Des.* 10 (2010) 4806–4814.
- 156 [8] a) C. Papatriantafyllopoulou, G. Aromi, A.J. Tasiopoulos, V. Nastopoulos, C.P. Raptopoulou,
157 S.J. Teat, A. Escuer, S.P. Perlepes, *Eur. J. Inorg. Chem.* (2007) 2761–2774; b) C.G. Efthymiou,
158 A.A. Kitos, C.P. Raptopoulou, S.P. Perlepes, A. Escuer, C. Papatriantafyllopoulou, *Polyhedron*
159 28 (2009) 3177–3184.
- 160 [9] J. Esteban, A. Escuer, M. Font-Bardia, O. Roubeau, S.J. Teat, *Polyhedron* 52 (2013) 339–345.
- 161 [10] a) T.C. Stamatatos, K.A. Abboud, S.P. Perlepes, G. Christou, *Dalton Trans.* (2007) 3861–3863;
162 b) T.C. Stamatatos, A. Escuer, K.A. Abboud, C.P. Raptopoulou, S.P. Perlepes, G. Christou,
163 *Inorg. Chem.* 47 (2008) 11825–11838; c) J. Esteban, L. Alcázar, M. Torres-Molina, M. Monfort,
164 M. Font-Bardia, A. Escuer, *Inorg. Chem.* 51 (2012) 5503–5505.
- 165 [11] L. Dong, R. Huang, Y. Wei, W. Chu, *Inorg. Chem.* 48 (2009) 7528–7530.
- 166 [12] Reaction of Ni(SO₄)·6H₂O (0.280 g, 1 mmol) with 2-pyridylcyanoxime (0.073 g, 0.5 mmol) an
167 NaOH (0.040 g, 1 mmol) in 20 mL of methanol yields compound 1 by slow evaporation as
168 orange bricks. Anal. calcd for dried C₇₀H₉₆N₂₄Na₂Ni₁₃O₆₀S₈ (1): C, 25.48; H, 2.94; N,
169 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),
170 2226(w), 1603(m), 1468(s), 1432(w), 1303(w), 1266(w), 1224(m), 1142(s), 1107(s), 1037(m),

171 781(w), 712(w), 632(w). Reaction performed with CsOH instead NaOH yields the equivalent
172 compound as tin needles (not adequate for X-ray determination) with the same IR spectra.
173 Infrared spectra (4000–400 cm⁻¹) were recorded from KBr pellets on a Bruker IFS-125 FT-IR
174 spectrophotometer.

175 [13] Data for compound 1 was measured from orange crystals at 273 K and $\lambda = 0.71073 \text{ \AA}$ using a
176 Bruker APEX-II CCD diffractometer with graphite monochromator. Crystal data and structural
177 parameters for 1: [C₇₀H₉₆N₂₄Na₂Ni₁₃O₆₀S₈], MW: 3299.39, triclinic space group P-1, a =
178 14.0686(18) Å, b = 22.314(3) Å, c = 29.223(4) Å, $\alpha = 93.991(2)^\circ$, $\beta = 103.354(2)^\circ$, $\gamma =$
179 108.295(2)°, V = 8373.6(2.18) Å³, Z = 2, D_c = 1.306 g·cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.605 \text{ mm}^{-1}$, T =
180 273(2) K, 34,029 reflections measured, 17,825 independent reflections (R_{int} = 0.0782), final
181 R₁[I₂ σ(I)] = 0.0622 and final wR₂ = 0.1569. Program SQUEEZE, part of the PLATON
182 package of crystallographic software, was used to calculate the solvent disorder area and remove
183 its contribution to the overall intensity data; as consequence methanol and water molecules
184 around Na(2) were not determined. CCDC 972518.

185 [14] Harris notation, referred as X.Y₁Y₂Y₃...Y_n, where X is the overall number of metals bound by
186 the whole ligand and each value of Y refers to the number of metal ions attached to the different
187 donor atoms. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules, hence here O
188 before N. R.A. Coxall, S.G. Harris, D.K. Henderson, S. Parsons, P.A. Tasker, R.E.P. Winpenny,
189 Chem. Soc. Dalton Trans. (2000) 2349–2356.

190 [15] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez, SHAPE version 2.0, 2010.
191 (Barcelona) The program can be obtained free of charge by request to the authors.

192 [16] Magnetic susceptibility measurements were carried out on polycrystalline samples using a
193 Quantum Design MPMS-5 SQUID susceptometer working in the range 2–300 K under magnetic
194 fields of 0.3 T (300–30 K) and 0.03 T (30–2 K) to avoid saturation effects. Diamagnetic
195 corrections were estimated from Pascal tables

196

197 .

198 **Legends to figures**

199

200 **Scheme 1.** Left, pyC{CN}NOHligand and the coordination mode for pyC{CN}NO—present in this
201 communication, in Harris notation [14]. Right, sulfate coordination modes presented in this work. Color
202 code: NiII, green; O, red, N, blue; S, orange; Na⁺ purple.

203

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

206

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

209

210 **Figure 3.** View of the {–Ni₁₂Na₂–Ni–}_n chain showing the bridging Ni(13) ion and the position of
211 Na(2) linked to one of the 4.1111 sulfates.

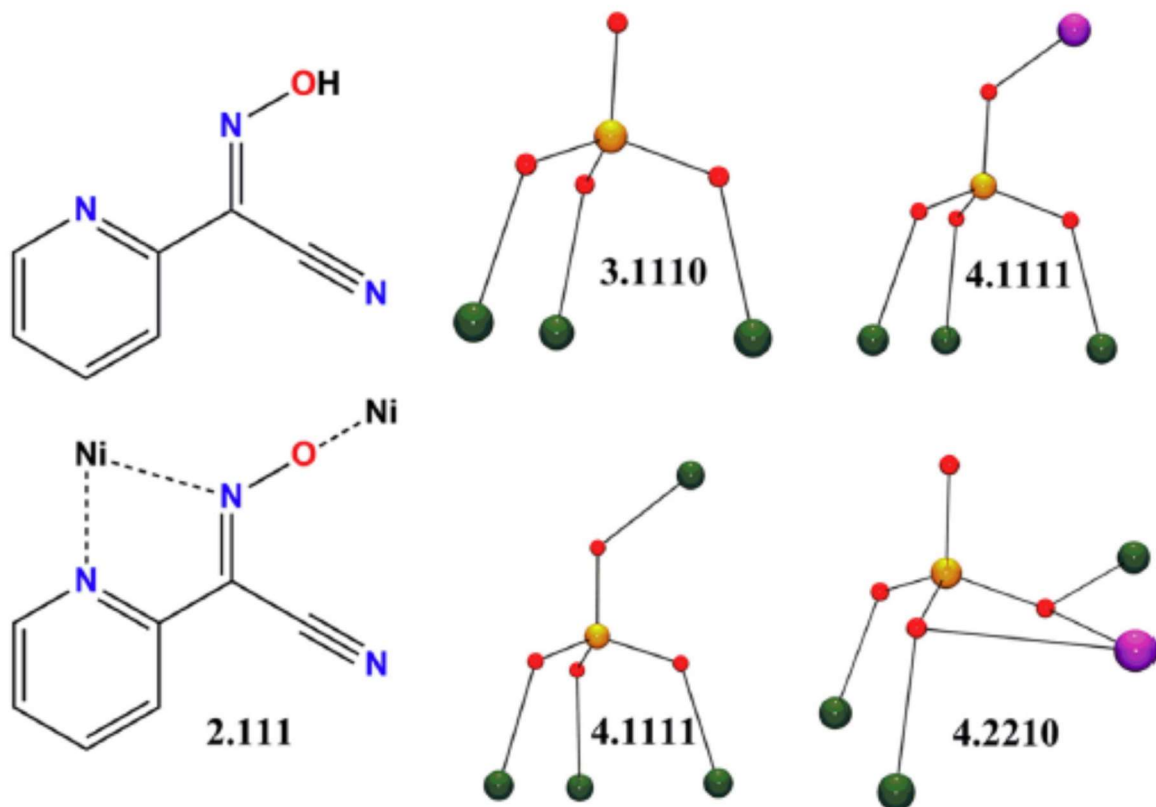
212

213 **Figure 4.** χ^2_{MT} product vs. T for compound 1. Solid line shows the best obtained fit. Inset: coupling
214 scheme for each of the triangles (see text).

215

216
217
218

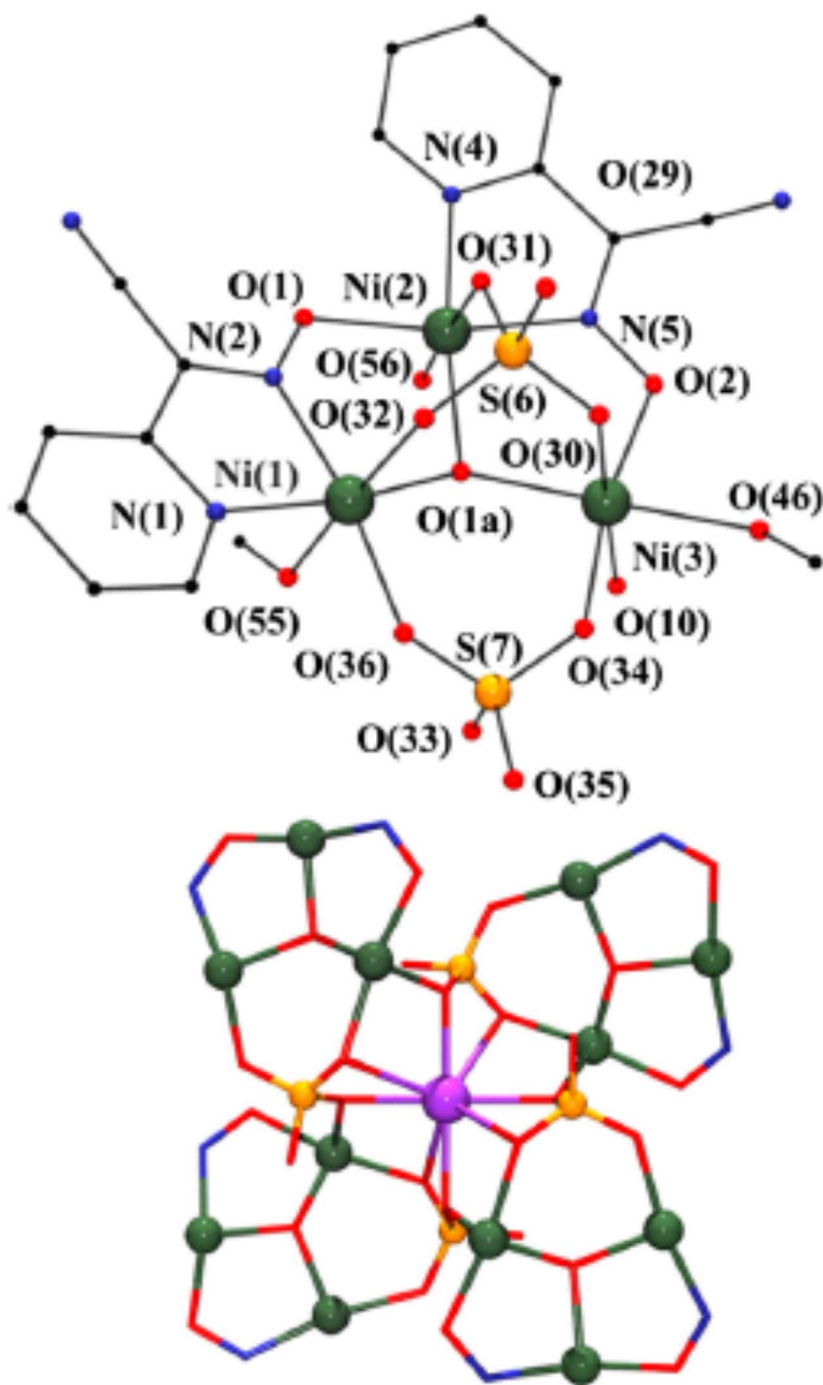
SCHEME 1



219
220
221

222
223
224

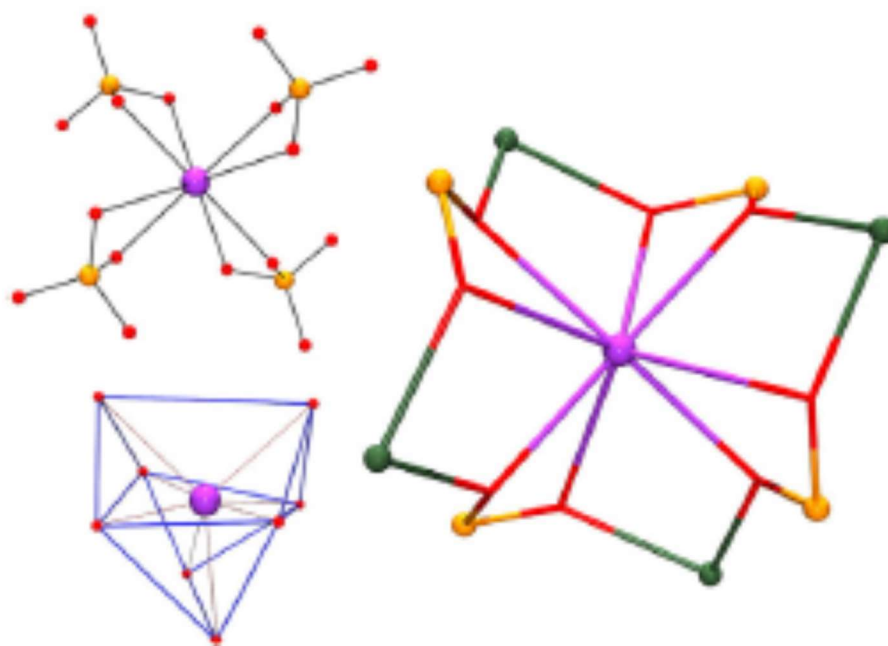
FIGURE 1



225
226

227
228
229

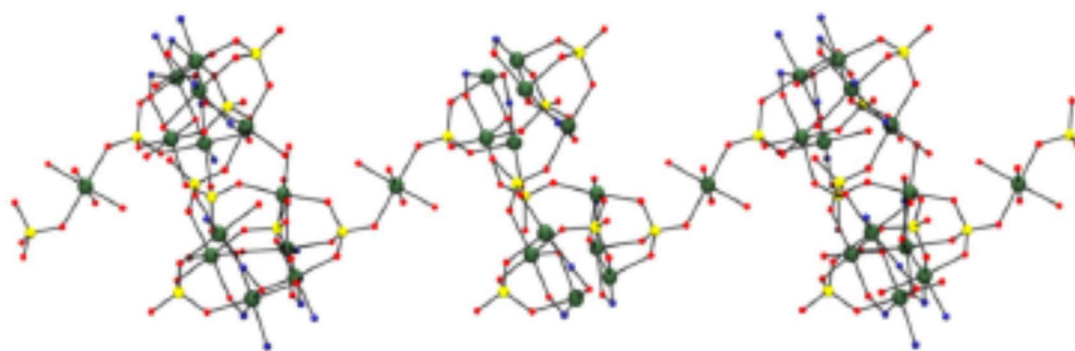
FIGURE 2



230
231
232

233
234
235

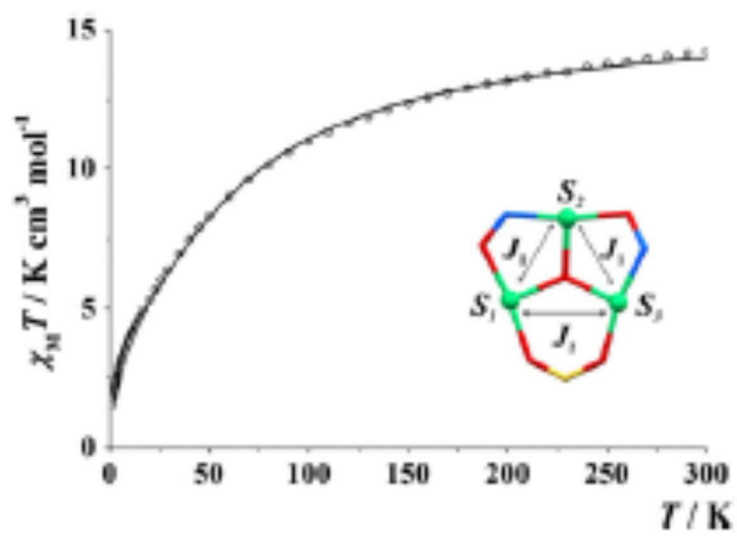
FIGURE 3



236
237

238
239
240

FIGURE 4



241
242