ELECTRONIC SUPPORTING INFORMATION

Rare nuclearities in Ni(II) cluster chemistry: A Ni₁₁ cage from the first use of N-salicylidene-2-amino-5-chlorobenzoic acid in metal cluster chemistry

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Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using materials as received. The organic ligand sacbH₂ (yellow crystalline solid) was synthesized by following a well-known synthetic protocol for the synthesis of Schiff base ligands. This includes the condensation in refluxing absolute methanol of 2-amino-5-chlorobenzoic acid with salicylaldehyde, in accordance with literature methods for the similar ligand saphH₂.¹ *Caution! Although no such behavior was observed during the present work, perchlorate salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.*

[Ni₁₁(OH)₄(O₂CCH₂Bu^t)₈(sacb)₅(MeCN)₃(H₂O)]·4.5MeCN·1.5H₂O

(1•4.5MeCN•1.5H₂O): To a stirred, yellow solution of sacbH₂ (0.06 g, 0.2 mmol) and NEt₃ (0.17 mL, 1.2 mmol) in MeCN (20 mL) were added Ni(ClO₄)₂·6H₂O (0.15 g, 0.4 mmol) and Bu^tCH₂CO₂H (0.05 mL, 0.4 mmol). The resulting green-yellow solution was stirred for 20 min, during which time all the solids dissolved and the color of the solution changed to dark green. The solution was filtered, and the filtrate was left to evaporate slowly at room temperature. After ten days, X-ray quality dark-green plate-like crystals of 1·4.5MeCN·1.5H₂O had appeared and were collected by filtration, washed with cold MeCN (2 x 2 mL) and dried in air. Note that the crystalline product 1 is extremely soluble in Et₂O and thus avoidance of washing with such solvent is strongly recommended. The yield was 65 %. Selected IR data (ATR): v= 2949 (mb), 1587 (vs), 1536 (vs), 1460 (m), 1440 (s), 1407 (s), 1360 (s), 1300 (m), 1229 (w), 1177 (m), 1150 (m), 1119 (m), 1038 (w), 899 (w), 850 (m), 820 (m), 792 (s), 740 (m), 553 (m), 460 (mb).

¹ A. Kagkelari, G. S. Papaefstathiou, C. P. Raptopoulou and T. F. Zafiropoulos, *Polyhedron*, 2009, 28, 3279.

X-ray structure determination. A green crystal $(0.03 \times 0.19 \times 0.21 \text{ mm})$ was taken from the mother liquor and immediately cooled to -123 °C. Diffraction measurements were made on a Bruker X8 Kappa APEX II Charge-Coupled Device (CCD) area-detector diffractometer controlled by the APEX2 software package² using graphite monochromated Mo Kα radiation. Images were processed with the software SAINT+,³ and absorption was corrected using the multi-scan semi-empirical method implemented in SADABS.⁴ Important crystallographic data are listed in Table S1. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on F² with SHELXL-97.⁵ Further experimental crystallographic details for 1.4.5MeCN.1.5H₂O: $2\theta_{max} = 50^{\circ}$; reflections collected/unique/used, 466517/27654 [R_{int} = 0.0744]/27654; 1814 parameters refined; $(\Delta/\sigma)_{max} = 0.002; (\Delta\rho)_{max}/(\Delta\rho)_{min} = 1.637/-$ 0.765 e/Å³; R1/wR2 (for all data), 0.0775/0.1325. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms, except of those on hydroxido ions and aqua molecules which we located by difference maps and were refined with U equal 1.3 time the U(eq) of their riding atom. All non-hydrogen atoms were refined anisotropically. There are five MeCN and two H₂O solvate molecules per Nill cluster. One of the MeCN and one of the H₂O solvates were refined with partial occupancy fixed at 0.50; no Hatoms for these molecules were included in the refinement.

² APEX2, Data Collection Software Version 2.1-RC13, Bruker AXS, Delft, The Netherlands 2006.

³ SAINT+, Data Integration Engine v. 7.23a [©] 1997-2005, Bruker AXS.

⁴ G. M. Sheldrick, *SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program* 1998, Bruker AXS.

⁵ G. M. Sheldrick, Acta Crystallogr., 2008, A64, 112-122.

	$1.4.5$ MeCN $\cdot 1.5$ H ₂ O		
Formula	$C_{133}H_{159.5}Cl_5N_{12.5}Ni_{11}O_{37.5}$		
Fw	3356.29		
Space group	$P2_{1}/c$		
<i>a</i> (Å)	27.090(3)		
<i>b</i> (Å)	22.251(2)		
<i>c</i> (Å)	28.725(3)		
α (°)	90		
β (°)	114.718(4)		
γ (°)	90		
$V(Å^3)$	15728(3)		
Ζ	4		
<i>T</i> (°C)	-123		
Radiation	Μο Κα		
$\rho_{\text{calcd}}(\text{g cm}^{-3})$	1.417		
μ (mm ⁻¹)	1.443		
Reflections with $I > 2\sigma(I)$	22644		
R_1^{a}	0.0594		
wR_2^a	0.1240		

Table S1. Crystallographic data for complex 1.4.5 MeCN $\cdot 1.5$ H2O.

 $\overline{a} w = 1/[\sigma^2(F_o^2) + (\alpha P)^2 + bP]$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$,

 $R_1 = \Sigma(|F_0| - |F_c|) / \Sigma(|F_0|)$ and $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]\}^{1/2}$.

2			
Nil-Ol	2.063(3)	Ni8-O5	2.064(3)
Ni1-O4	2.194(3)	Ni8-O41	1.991(3)
Ni1-O11	2.090(3)	Ni8-O42	2.041(3)
Ni1-O51	2.009(4)	Ni8-O62	2.071(3)
Ni1-O55	2.020(4)	Ni8-O63	2.108(3)
Ni1-N71	2.073(5)	Ni8-N41	1.998(4)
Ni2-O4	2.096(3)	Ni9-07	2.026(3)
Ni2-O11	1.981(3)	Ni9-O21	2.094(3)
Ni2-O12	2.006(3)	Ni9-O33	2.098(3)
Ni2-O52	2.039(3)	Ni9-O64	2.138(3)
Ni2-O53	2.098(3)	Ni9-O66	2.030(3)
Ni2-N11	2.003(4)	Ni9-N72	2.103(5)
Ni3-O2	2.081(3)	Ni10-O6	2.070(3)
Ni3-O4	2.144(3)	Ni10-O13	2.096(3)
Ni3-O6	2.004(3)	Ni10-O21	2.025(3)
Ni3-O12	2.091(3)	Ni10-O22	2.045(3)
Ni3-O22	2.031(3)	Ni10-O65	2.102(3)
Ni3-O54	2.044(3)	Ni10-N21	2.037(4)
Ni4-O1	1.993(3)	Ni11-O1W	2.052(4)
Ni4-O2	2.057(3)	Ni11-O3	2.087(3)
Ni4-O4	2.079(3)	Ni11-O6	2.034(3)
Ni4-O23	2.101(3)	Ni11-07	2.045(3)
Ni4-O56	2.053(3)	Ni11-O43	2.053(3)
Ni4-N1	1.999(4)	Ni11-O65	2.110(3)
Ni5-O5	2.197(3)	Ni1Ni2	3.002(1)
Ni5-O31	2.117(3)	Ni1Ni3	4.311(1)
Ni5-O41	2.079(3)	Ni1Ni4	2.970(1)
Ni5-O57	2.012(4)	Ni2Ni3	2.963(1)
Ni5-O61	2.054(3)	Ni2Ni4	4.159(1)

Table S2. Selected Interatomic Distances (Å) and Angles (°) for Complex $1.4.5MeCN.1.5H_2O$

Ni5-N73	2.076(4)	Ni3Ni4	3.048(1)
Ni6-O5	2.079(3)	Ni3Ni10	3.058(1)
Ni6-O31	1.987(3)	Ni3Ni11	3.589(1)
Ni6-O32	1.995(3)	Ni5Ni6	2.999(1)
Ni6-O58	2.040(3)	Ni5Ni7	4.368(1)
Ni6-O60	2.127(3)	Ni5Ni8	3.027(1)
Ni6-N31	1.990(4)	Ni6Ni7	2.983(1)
Ni7-O5	2.185(3)	Ni6Ni8	4.110(1)
Ni7-07	2.015(3)	Ni7Ni8	2.992(1)
Ni7-O32	2.053(3)	Ni7Ni9	3.060(1)
Ni7-O42	2.074(3)	Ni7Ni11	3.476(1)
Ni7-O59	2.037(3)	Ni9Ni10	3.558(1)
Ni7-O64	2.038(3)	Ni9Ni11	3.544(1)
		Ni10Ni11	3.072(1)
Ni1-O11-Ni2	95.0(1)	Ni5-O5-Ni8	90.5(1)
Ni1-O1-Ni4	94.1(2)	Ni5-O41-Ni8	96.1(1)
Ni1-O4-Ni2	88.8(1)	Ni5-O31-Ni6	93.9(1)
Ni1-O4-Ni3	167.1(2)	Ni6-O5-Ni7	88.8(1)
Ni1-O4-Ni4	88.0(1)	Ni6-O5-Ni8	164.4(2)
Ni2-O4-Ni3	88.6(1)	Ni6-O32-Ni7	94.9(1)
Ni2-O4-Ni4	169.7(2)	Ni7-O5-Ni8	89.5(1)
Ni2-O12-Ni3	92.6(1)	Ni7-07-Ni9	98.4(1)
			,(-)
Ni3-O4-Ni4	92.4(1)	Ni7-O7-Ni11	117.7(2)
Ni3-O4-Ni4 Ni3-O2-Ni4	92.4(1) 94.9(1)	Ni7-O7-Ni11 Ni7-O64-Ni9	117.7(2) 94.2(1)
Ni3-O4-Ni4 Ni3-O2-Ni4 Ni3-O22-Ni10	92.4(1) 94.9(1) 97.2(1)	Ni7-O7-Ni11 Ni7-O64-Ni9 Ni7-O42-Ni8	117.7(2) 94.2(1) 93.3(1)
Ni3-O4-Ni4 Ni3-O2-Ni4 Ni3-O22-Ni10 Ni3-O6-Ni10	92.4(1) 94.9(1) 97.2(1) 97.3(1)	Ni7-O7-Ni11 Ni7-O64-Ni9 Ni7-O42-Ni8 Ni9-O21-Ni10	117.7(2) 94.2(1) 93.3(1) 119.5(2)
Ni3-O4-Ni4 Ni3-O2-Ni4 Ni3-O22-Ni10 Ni3-O6-Ni10 Ni3-O6-Ni11	92.4(1) 94.9(1) 97.2(1) 97.3(1) 125.5(2)	Ni7-O7-Ni11 Ni7-O64-Ni9 Ni7-O42-Ni8 Ni9-O21-Ni10 Ni9-O7-Ni11	117.7(2) 94.2(1) 93.3(1) 119.5(2) 121.0(2)
Ni3-O4-Ni4 Ni3-O2-Ni4 Ni3-O22-Ni10 Ni3-O6-Ni10 Ni3-O6-Ni11 Ni5-O5-Ni6	92.4(1) 94.9(1) 97.2(1) 97.3(1) 125.5(2) 89.0(1)	Ni7-O7-Ni11 Ni7-O64-Ni9 Ni7-O42-Ni8 Ni9-O21-Ni10 Ni9-O7-Ni11 Ni10-O6-Ni11	117.7(2) 94.2(1) 93.3(1) 119.5(2) 121.0(2) 96.9(1)



Fig. S1 Hydrogen bonding interactions in the structure of **1** (intra- and inter-molecular H-bonds are shown as yellow and orange dashed lines, respectively).

Interaction	D…A (Å)	H…A (Å)	D-H…A (°)	symmetry operation
O(4)-H(4O)···O(53)	2.846	2.355	123.8	<i>x</i> , <i>y</i> , <i>z</i>
O(5)-H(5O)···O(61)	2.920	2.462	114.5	<i>x</i> , <i>y</i> , <i>z</i>
O(6)-H(6O)…N(81)	3.068	2.365	157.3	<i>x</i> , <i>y</i> , <i>z</i>
O(7)-H(7O)…N(81)	3.170	2.436	164.8	<i>x</i> , <i>y</i> , <i>z</i>
O(1w)-H(1wA)…O(2w)	2.695	1.888	170.8	<i>x</i> , <i>y</i> , <i>z</i>
O(1w)-H(1wB)…O(59)	2.634	1.868	156.6	<i>x</i> , <i>y</i> , <i>z</i>
O(2w)-H(2wB)…O(54)	2.748	2.191	123.0	<i>x</i> , <i>y</i> , <i>z</i>

Table S3. Hydrogen bonds in 1.4.5 MeCN $\cdot 1.5$ H₂O.



Fig. S2 UV-vis spectrum of 1 in MeCN (10⁻⁵ M).



Fig. S3 Plot of magnetization (*M*) versus field (*H*) for $1.3H_2O$ at 2 K.



Fig. S4 Excitation (at 397 nm, blue line) and emission (at 423 nm, red line) spectra of 10^{-5} M sacbH₂ in MeCN.