Supplementary materials

A Ketone Oximate Based Cyclic Cationic [Ni$^{II}_4$] Inverse Metallacrown from Simultaneous Chelation and Bridging of Two Ligands

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Materials and Physical Measurements. The chemicals used were obtained from the following sources: 2-amino ethanol from S.D. Fine Chem (India), butan-2,3-dionemonoxime from SRL (India). Nickel(II) perchlorate hexahydrate was prepared by treating nickel(II) carbonate with 1:1 HClO$_4$ and crystallized after concentration on a water-bath. *CAUTION!!Perchlorate-containing salts are potentially explosive and should be handled in very small quantities.* All other chemicals and solvents were reagent grade materials and were used as received without further purification. The elemental analyses (C, H, N) were performed with a Perkin-Elmer model 240 C elemental analyzer. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer. The solution electrical conductivity and electronic spectra were obtained using a Unitech type U131C digital conductivity meter with a solute concentration of about 10^{-3} *M* and a Shimadzu UV 3100 UV-vis-NIR spectrophotometer respectively. The room temperature magnetic susceptibilities in the solid state were measured using a home built Gouy balance fitted with a polytronic d.c. power supply. The experimental magnetic susceptibilities were corrected for the diamagnetic response using Pascal's constants. Magnetic measurements were carried out in the "Servei de Magnetoquímica (Universitat de Barcelona)" on polycrystalline samples (ca. 30 mg) using a Quantum Design MPMS XL-5 SQUID susceptometer operating at a constant magnetic field of 0.8 T between 2 and 300 K. The experimental magnetic moment was corrected for the diamagnetic contribution from the sample holder and the diamagnetic response from the sample, which was evaluated from Pascal's constants.

Crystallographic data of [(NHEt$_3$)·1·(ClO$_4$)$_3$]. C$_{30}$H$_{66}$N$_9$O$_{24}$Cl$_3$Ni$_4$, M$_r$ = 1278.11, monoclinic, space group C2/c, a = 14.9193(3)Å, b = 24.7954(6)Å, c = 14.0215(2) Å, β = 97.150(2)°, V = 5146.6(2) Å^3, ρ_{calcd} =1.650g /cm^3 and Z = 4. With the use of 6184 unique reflections from the 23241 measured reflections collected at 295 K with Mo Kα radiation (λ =0.71073 Å) out to θ range = 3.38 to 28.00 °. The crystal data of compound **[(NHEt$_3$)·1·(ClO$_4$)$_3$]** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo-Kα radiation. The data sets were integrated with the Denzo-SMN package[1] and corrected for Lorentz, polarization and absorption effects (SORTAV[2]). The structures were solved by direct methods (SIR97[3]) and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogens included on calculated positions, riding on their carrier atoms. The hydrogen positions of the triethylammonium cation could not be determined. The crystal contains tetranuclear metallacrown Ni(II) cation complexes (C$_{24}$H$_{20}$Ni$_4$N$_8$O$_{12}$)$^{++}$, ClO$_4^-$ anions and triethylammonium cations in the ratio 1:3:1. The Ni(II) complex lies about a two fold axis, one ClO$_4^-$ anion on a twofold axis and the triethylammonium cation is disordered around a centre of symmetry. The disordered hydrogen atoms linked to the oxygens O3 and O6 were refined in different ways. H6 was refined on the centre of symmetry in between the oxygens O3 and O3', while H6 was refined close to O6 oxygen with occupancy 0.5.
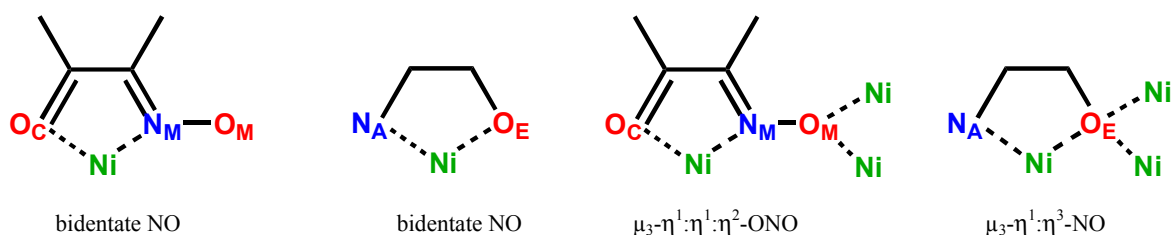
All calculations were performed using SHELXL-97[4] and PARST[5] implemented in WINGX[6] system of programs. The crystal data are given in Table 1. The refinement converged to final R1 = 0.0458, wR2 =0.1150; and GOF =1.022 with the largest difference peak and hole as 0.627 and -0.568 e Å^{-3} respectively.

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 294831. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or on application to CCDC, Union Road, Cambridge, CB2 1EZ, UK [fax: (+44)1223-336033, e-mail: deposit@ccdc.cam.ac.uk]

Table for selected bond lengths [Å] and bond angles [º] of [(NHEt₃)·1·(ClO₄)₃].

Bond lengths

Ni(1)-O(4´)	2.002(2)
Ni(1)-N(1)	2.012(3)
Ni(1)-O(2)	2.084(2)
Ni(1)-O(3)	2.091(2)
Ni(1)-N(2)	2.093(3)
Ni(1)-O(6´)	2.155(2)
Ni(2)-N(3)	2.025(2)
Ni(2)-O(1)	2.027(2)
Ni(2)-N(4)	2.079(3)
Ni(2)-O(6)	2.099(2)
Ni(2)-O(5)	2.110(2)
Ni(2)-O(3)	2.135(2)

Bond angles

O(2)-Ni(1)-N(2)	98.09(10)	O(1)-Ni(2)-N(4)	84.13(10)
O(4´)-Ni(1)-O(2)	94.20(9)	N(3)-Ni(2)-O(6)	90.77(9)
O(4´)-Ni(1)-O(6´)	91.82(8)	O(1)-Ni(2)-O(6)	96.36(9)
O(3)-Ni(1)-O(6´)	85.42(8)	N(3)-Ni(2)-O(1)	172.53(9)
N(3)-Ni(2)-N(4)	94.51(11)	N(4)-Ni(2)-O(6)	83.27(10)
N(2)-Ni(1)-O(6´)	167.46(10)	N(3)-Ni(2)-O(5)	77.68(9)
O(4´)-Ni(1)-N(1)	172.08(9)	O(6)-Ni(2)-O(3)	84.45(8)
O(2)-Ni(1)-O(6´)	94.16(8)	C(5)-O(3)-Ni(2)	119.93(19)
N(1)-Ni(1)-O(3)	91.83(9)	O(1)-Ni(2)-O(5)	95.07(9)
N(1)-Ni(1)-O(2)	78.27(10)	N(4)-Ni(2)-O(5)	94.53(11)
O(4´)-Ni(1)-O(3)	95.71(9)	C(2)-O(2)-Ni(1)	112.3(2)
C(5)-O(3)-Ni(1)	107.01(17)	N(1)-O(1)-Ni(2)	117.07(17)
N(1)-Ni(1)-N(2)	93.91(11)	O(6)-Ni(2)-O(5)	168.07(8)
O(2)-Ni(1)-O(3)	170.09(9)	Ni(1)-O(3)-Ni(2)	108.17(9)
O(4´)-Ni(1)-N(2)	84.63(10)	N(3)-Ni(2)-O(3)	91.46(9)
O(3)-Ni(1)-N(2)	82.98(10)	O(1)-Ni(2)-O(3)	91.46(8)
N(1)-Ni(1)-O(6´)	91.20(9)	N(4)-Ni(2)-O(3)	166.40(10)
N(3)-O(4)-Ni(1´)	118.58(17)	Ni(2)-O(6)-Ni(1´)	108.39(9)

bidentate NO   bidentate NO   μ₃-η¹:η¹:η²-ONO   μ₃-η¹:η³-NO

Scheme SI. Drawing of possible alternative chelating and bridging modes of bmo⁻ and ael⁻ ligands.

Experimental procedures

Synthesis of (NHEt₃)[Niᴵᴵ₄(bmo)₄(Hael)₂(ael)₂](ClO₄)₃ [(NHEt₃)·1·(ClO₄)₃]: A methanolic solution consisting of Ni(ClO₄)₂·6H₂O (0.59 g, 1.62 mmol), Hbmo (0.331g, 3.23 mmol) and a methanolic solution (20 ml) of

$Ni(ClO_4)_2.6H_2O$ (0.59 g, 1.62 mmol) , Hael (0.2g, 3.23 mmol) stirred under aerobic conditions at room temperature. $N(C_2H_5)_3$ (0.6626g, 6.54 mmol) in methanol (10 ml) added during stirring condition and continued for 1 h. The complex precipitates during a week as dark red-brown crystalline compound (~88 % yield) from the reaction mixture after solvent evaporation. The elemental analysis, solution electrical conductivity and room temperature magnetic susceptibility data are consistent with the formula $(NHEt_3)[Ni^{II}_4(bmo)_4(Hael)_2(ael)_2](ClO_4)_3$ for complex $[(NHEt_3) \cdot 1 \cdot (ClO_4)_3]$ (eq 1 of text). The single crystals suitable for X-ray analysis was obtained from 1:1(v/v) CH_3CN-CH_2Cl_2 during a week. Anal. calc. for $C_{30}H_{66}N_9O_{24}Cl_3Ni_4$ (1278.11): C, 28.19 ; H, 5.16 ; N, 9.86 ; Ni, 18.36 %. Found : C,28.09 ; H, 5.13 ; N, 9.61, Ni,18.25 %. Infrared spectrum (cm^{-1}, KBr disk): ν, 3437(b), 33356(s), 3294(s), 3100(m), 2926(m), 2875(m), 2476(m), 1617(m), 1474(s), 1382(s), 1331(s), 1248(m), 1095(m), 973(s), 881(s),656 (s), 615(s),533(s), 461(s). Molar conductance, Λ_M : (DMF solution) 158 ohm^{-1} cm^2 mol^{-1}. UV-vis spectra [λ_{max}, nm (ε, lmol^{-1}cm^{-1})]: (DMF) 526 (102), 382 (2690), 377 (4695), 310 (17545). Room temperature μ_{eff} (tot.): 5.727 BM ; μ_{eff} / Ni: 2.86 μ_B.

Caution!! Perchlorate-containing salts are potentially explosive and should be handled in very small quantities.
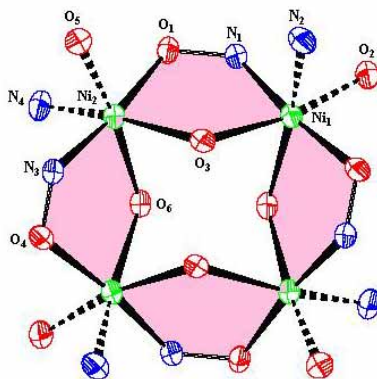
Figures S1 to S6 with captions

Figure S1. ORTEP representation of partial atom connectivity in $[Ni^{II}_4(bmo)_4(Hael)_2(ael)_2]^{2+}$ at 50% probability showing the superimposed Ni_4O_4 (eight membered) core within the 12-MC-4 metallacrown core and four fused five-membered rings.
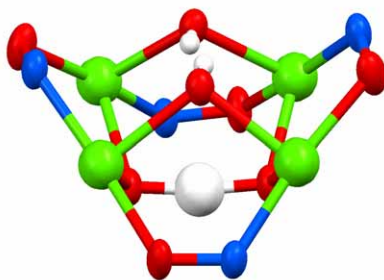

Figure S2. Partial ball and stick view of the central core in **1** showing the intramolecular hydrogen bonds above and below the Ni_4 plane.
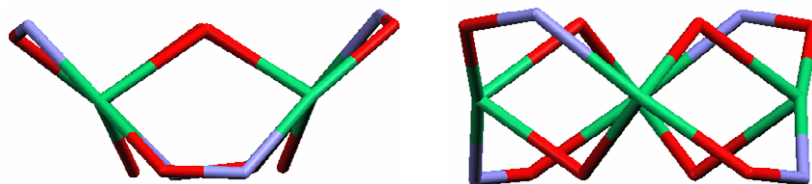
Figure S3. Capped sticks views of **1** in two different orientations.
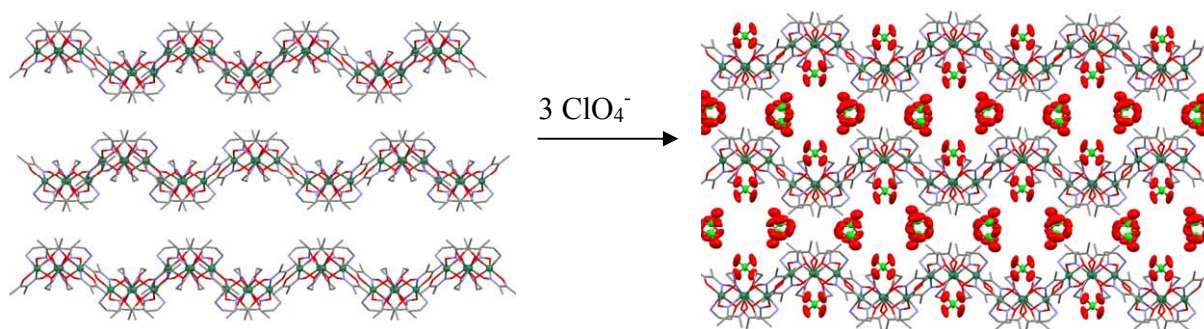

3 ClO$_4^-$

Figure S4. Packing diagram along 'c*' axis in **1** showing the arrangement of three perchlorate anions.
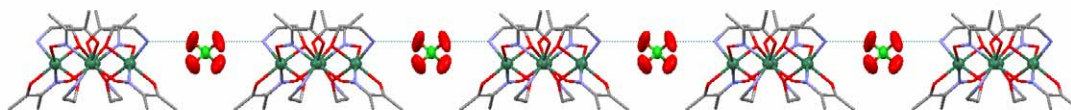

Figure S5. Perchlorate mediated hydrogen bonding network of **1** viewed along the crystallographic a-axis.

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