Anion coordination by metallamacrocycles: a cryptand-like cavity

SUPPORTING INFORMATION

S1 - SYNTHESES

Compound 1 was obtained in good yield by reaction in methanolic medium of 1 mmol (199 mg) of py_2CNOH ligand, 1 mmol (576 mg) of $[Ni_2(Medpt)_2(N_3)_4]$ and 2 mmols (202 mg) of triethylamine. The resulting solution was left to slow evaporation and prismatic dark crystals appeared after a week. Anal. Calcd for $C_{37}H_{58}N_{24}Ni_3O_3$ (**1·MeOH**): C, 41.80; H, 5.50 %; N, 31.62. Found: C, 40.9; H, 5.3; N, 31.5 %.

Compound 2 was initially synthesized by reaction of 1 mmol (198 mg) of (py)C(ph)NOH, 1 mmol (547 mg) of $[Ni_2(dpt)_2(N_3)_4]$ and 2 mmols (202 mg) of triethylamine in the presence of small amounts of $Ni(NO_3)_2$.

The optimized direct reaction was performed mixing 1 mmol (198 mg) of (py)C(ph)NOH, 2 mmols (580 mg) of $Ni(NO_3)_2$, 2 mmols (162 mg) of dipropylene triamine, 4 mmols (260 mg) of NaN_3 and 2 mmols (202 mg) of NEt_3 in 20 mL of acetonitrile. Both solutions were left to slow evaporation and brown prisms were obtained after a week. Calcd for $C_{108}H_{156}N_{62}Ni_9O_{12}$ (**2**): C, 42.63; H, 5.17 %; N, 28.54. Found: C, 42.4; H, 5.2; N, 29.0 %.

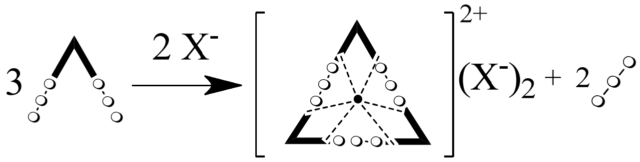
Finally, **compounds 3**, **4 and 5** following the same procedure than for compound **2**, starting from the corresponding nickel salt and in methanolic solution. Dark rhombus crystallized one week later. Calcd for $C_{108}H_{158}Cl_2N_{60}Ni_9O_7$ (**2·H$_2$O**): C, 43.12; H, 5.29 %; N, 27.94. Found: C, 42.31; H, 5.11; N, 28.14 %.Calcd for $C_{108}H_{158}Br_3N_{57}Ni_9O_7$ (**4·H$_2$O**): C, 41.38; H, 5.08 %; N, 25.47. Found: C, 41.49; H, 5.17; N, 25.76 %. Calcd for $C_{108}H_{160}I_3N_{57}Ni_9O_8$ (**5·2H$_2$O**): C, 39.38; H, 4.90 %; N, 24.24. Found: C, 39.78; H, 5.03; N, 24.06 %.

Comments to the syntheses

Our initial synthetic strategy was to employ as nickel source one neutral dinuclear complex, $[Ni_2(Medpt)_2(N_3)_4]$ previously reported by us (*Inorg. Chem.* 1995, 34, 1793), which contains the aminated ligand Medpt and preformed end-on azido bridges. Our target was to avoid the presence of other counteranions than azido in order to reach the syntheses of ferromagnetic clusters containing end-on azido bridges and effectively, compound **1** was obtained.

In light of the structural data we realize that the nuclearity of **1** is limited by the terminal azido ligands. Bridging ligation of these azido ligands implies the need of additional negative anionic charges and then, the same reaction was performed from $[Ni_2(dpt)_2(N_3)_4]$ adding small amounts of nitrate anion resulting the enneanuclear complex **2**.

Both structures show an evident relationship and in spite that do not corresponds to the real interconversion (the ligands on the corners are not the same), the following scheme offers the "*stechiometric*" correlation between them. Azido ion becomes crucial to obtain **2**, being a template synthesis in which the host-guest interactions are determinant for its stability and topology:



Characterization of **2** gave us additional information about the size of the anion binding cavity and becomes evident its ability to coordinate spherical anions and thus, reactions starting from nickel halides were tried. It is interesting to point out that the synthesis of **3 - 5** were made in competitive 1:1 azido:halide solution.

Characterization

Conventional measurements as IR or powder X-ray spectrum are identical for the isostructural **2-4** compounds as can be expected. Identity of the guest anion can't be stablished from these measures and thus, unambiguous characterization requires single crystal X-ray determination. As example, two IR and porder X-ray spectra are shown:

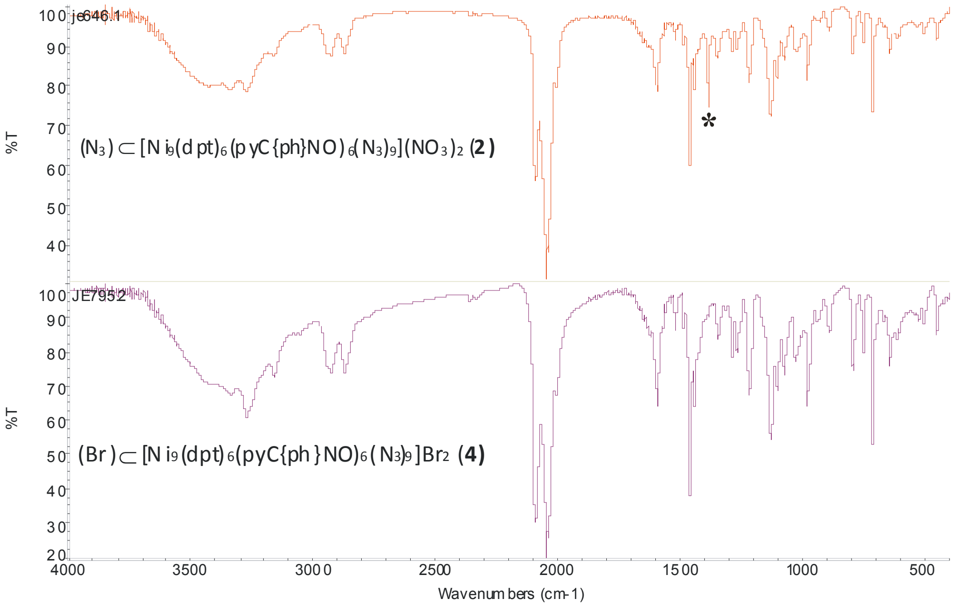


Figure S1. IR data for the reported complexes $(N_3)\subset[Ni_9(dpt)_6(pyC\{ph\}NO)_6(N_3)_9](NO_3^-)_2$ **(2)**, and $(Br)\subset[Ni_9(dpt)_6(pyC\{ph\}NO)_6(N_3)_9]Br_2$ **(4)**. As can be seen, the IR spectra do not differentiate the anionic guest. The only difference among these spectra is the anionic nitrate peak (*).

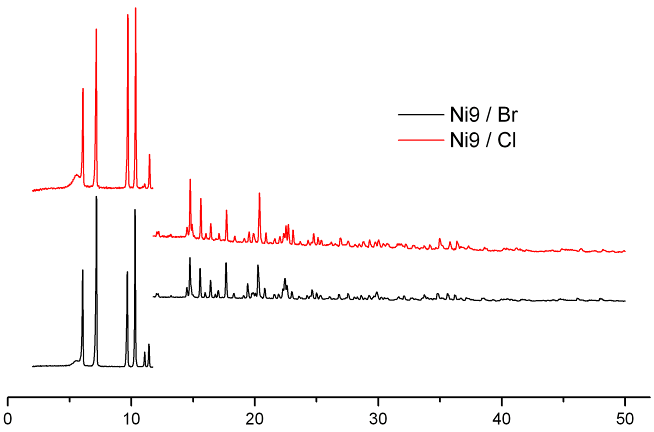


Figure S2. X ray powder diffraction for the Cl (**3**) and Br (**4**) complexes. The spectra confirm that isostructurality of both compounds but newly, they cannot differentiate the anionic guest.

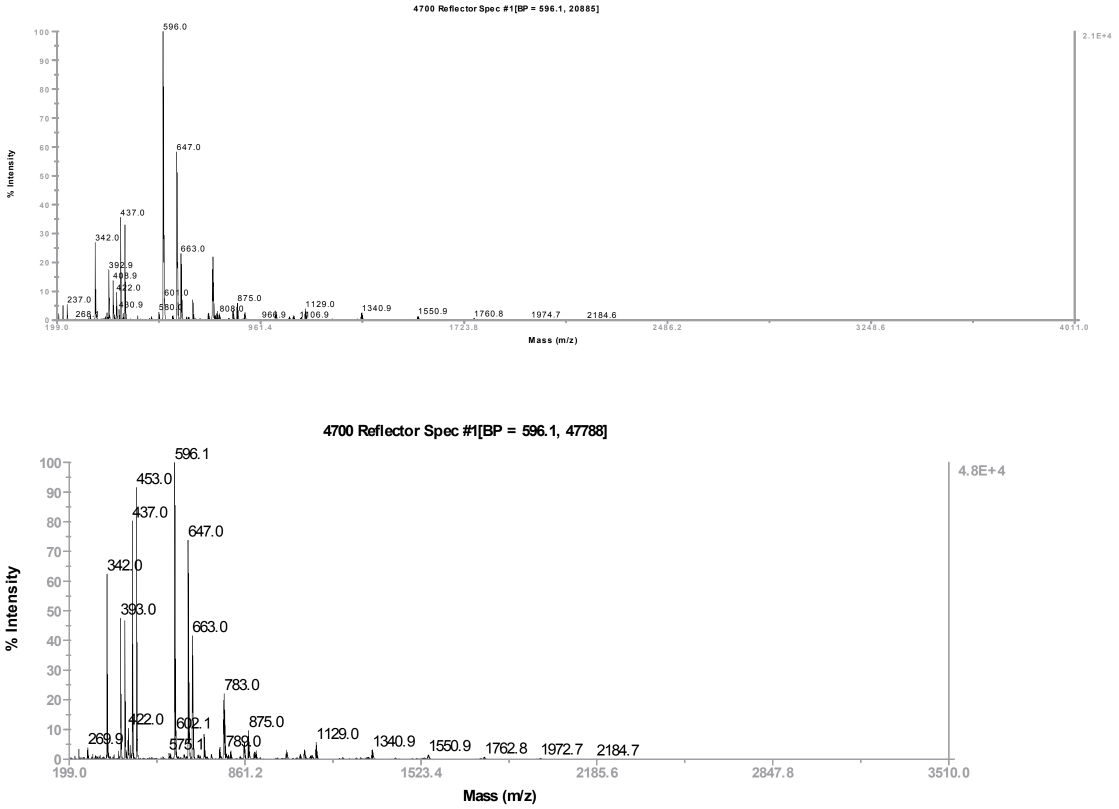


Figure S3. MALDI-TOFmass spectra for compounds **2** and **4**, pointing out their similar high degree of fragmentation in low molecular weight species in solution.

S2 - CRYSTALLOGRAPHIC INFORMATION

Crystal data, data collection and structure refinement details for the X-ray structure determination of compounds **1**-**3**.

	($1\cdot$MeOH)	**($2\cdot$MeCN)**	**($3\cdot H_2O$)**	**($4\cdot H_2O$)**	**($5\cdot 2H_2O$)**
formula	$C_{37}H_{58}N_{24}Ni_3O_3$	$C_{110}H_{159}N_{63}Ni_9O_{12}$	$C_{108}H_{158}Cl_2N_{60}Ni_9O_7$	$C_{108}H_{158}Br_3N_{57}Ni_9O_7$	$C_{108}H_{160}I_3N_{57}Ni_9O_8$
M [gmol^{-1}]	1063.20	3084.39	3006.22	3133.02	3294.02
Space group	Triclinic	Trigonal	Trigonal	Trigonal	Trigonal
Crystal system	P-1	R-3c	R-3c	R-3c	R-3c
a [Å]	12.183(5)	17.8824(3)	18.0085(9)	18.0774(8)	17.911(1)
b [Å]	12.582(4)	17.8824(3)	18.0085(9)	18.0774(8)	17.911(1)
c [Å]	16.689(5)	72.966(1)	73.205(5)	72.889(4)	72.574(5)
α□ [º]	93.84(2)	90	90	90	90
β [º]	91.81(2)	90	90	90	90
γ [º]	107.65(2)	120	120	120	120
V [Å^3]	2429(2)	20207.1(6)	20560(2)	20628(2)	20164(2)
Z	2	6	6	6	6
T [K]	105(2)	100(2)	100(2)	100(2)	100(2)
Dc [gcm^{-3}]	1.454	1.521	1.457	1. 513	1.628
F(000)	1112	9648	9422	9703	10092
μ(Mo-Kα) [mm^{-1}]	1.214	1.310	1.320	2.147	1.995
Measured reflections	20649	69558	4756	4716	4598
Unique reflections	12039	4621	4756	4698	4598
Rint	0.0520	0.0453	0.0557	0.0000	0.0000
θmin/θmax [°]	1.70-32.36	1.43-26.45	1.42-26.60	1. 71-26.42	1.68/26.38
$R(F^2)$	0.0530	0.0267	0.0375	0. 0501	0.0545
w$R(F^2)$	0.1313	0.0715	0.1231	0. 1676	0.1883
No. variables	598	298	297	277	280
Δρmax; Δρmin [eÅ^{-3}]	0.983/-0.618	0.599/-0.488	0.632/-0.262	1. 55/-2.09	1.153/-2.239

Isostructural complexes with azido as guest have been obtained following the same experimental procedure for anions which do not fit into the cavity, as for example:

$(N_3)\subset[Ni_9(dpt)_6(pyC\{ph\}NO)_6(N_3)_9](BF_4)_2$ [R-3c, a 17.918(5) b 17.918(5) c 73.01(2), α 90º β 90º γ 120º]

$(N_3)\subset[Ni_9(dpt)_6(py_2NO)_6(N_3)_9](ClO_4)_2$ [R-3c, a 17.7920(5) b 17.7920(5) c 72.826(3), α 90º β 90 γ 120º]

$(N_3)\subset[Ni_9(dpt)_6(pyC\{ph\}NO)_6(N_3)_9]F_2$, [R-3c, a 17.9145(8) b 17.9145(8) c 72.917(5), α 90º β 90 γ 120º]

Unambiguous characterization of the trapped anion has been made in all cases by single crystal X-ray determination of the full structure.

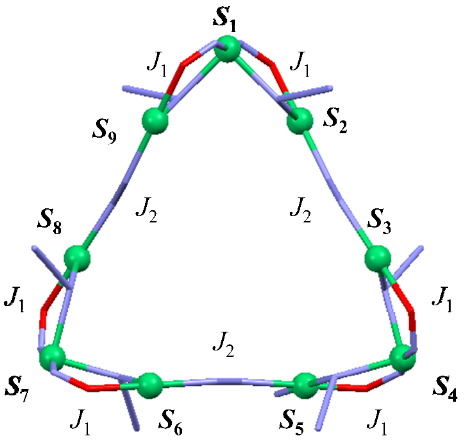
S3 - Magnetic data for compound 4

AC magnetic susceptibility was measured on powdered samples under external fields of 0.7 T in the 300-30 K range of temperature and 0.04 T in the 30-2 K range to avoid saturation effects at the Magnetochemistry Service of the University of Barcelona.

Fit of the nonanuclear rings were performed applying the Hamiltonian:

$$\mathrm{H} = -J_1(S_9{\cdot}S_1 + S_1{\cdot}S_2 + S_3{\cdot}S_4 + S_4{\cdot}S_5 + S_6{\cdot}S_7 + S_7{\cdot}S_8\,) - J_2(S_2{\cdot}S_3 + S_5{\cdot}S_6 + S_8{\cdot}S_9)$$

based on the coupling scheme:



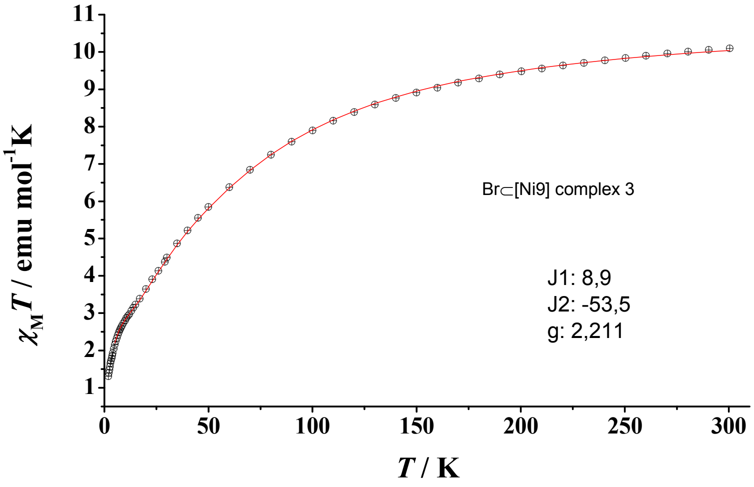


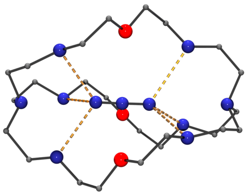
Figure S4. $\chi_M T$ plot vs T for complex (Br)⊂[$Ni_9(dpt)_6(pyC\{ph\}NO)_6(N_3)_9]Br_2$ (**4**). Shape and $\chi_M T$ values are practically identical to compound **2** and it has not been included in Figure 5 for clarity. As can be expected from the ring structural data, the guest anion does not modify the magnetic properties.

S4 – Tuning of the cavity size

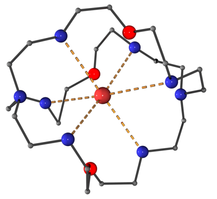
In the case of the (X)$\subset$[BT-6H$^+$] bis-trend cryptand anionic complexes, the tuning of the cavity size is performed by means of the rotation of both moieties of the molecule.

The elongated conformation shows a distance between the apical N atoms of 8.841 Å and its cavity is close to a trigonal prism for (N$_3$)$\subset$[BT-6H$^+$].

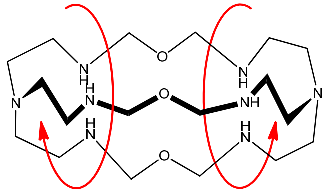
Rotation in opposite sense of both moieties of the cryptand reduces the distance between the apical N atoms (7.528 Å in the case of the Br derivative) and places the NH$_2^+$ groups in an octahedral arrangement.



Azido: D$_3$h cavity[*]

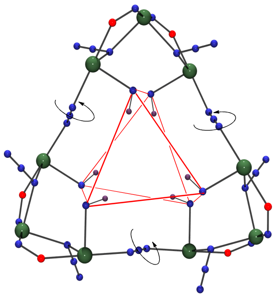


Halides: Oh cavity[*]



In the case of the {Ni$_9$} metallacycle, the corners are rigid due to the double oximato/azido bridges. The freedom to change the torsion and Ni-N-N bond angles involving the end-to-end azido bridges is also limited by steric hyndrance.

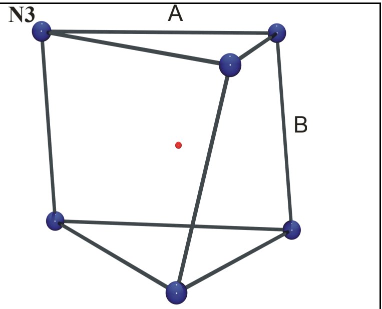
Small symmetrical changes of these bond parameters can slightly tune the size of the cavity, always keeping the prismatic shape, (Table S1).



Always D$_3$h cavity[*]

[*] D$_3$h and Oh ideal symmetry. Real compounds show small deviation from the regular polyhedra.

Table S1. Geometrical parameters of the prismatic cavity defined from the N3 and symmetry related nitrogen atoms. N···Ct distance is practically constant for all of them. Lateral edge and height of the prism is minimum for the bromide guest whereas the base edge is maximum for the iodine guest.

Compound	Prism height	A	B	N···Ct	 (Red point: cavity centroid, Ct)
(2)	3.933	5.122	4.013	3.552	
(3)	3.879	5.134	3.951	3.535	
(4)	3.786	5.176	3.861	3.537	
(5)	3.922	5.207	4.013	3.589	