Electronic Supplementary Material (ESI) for Dalton Transactions.

Multinuclear Ni(II) and Cu(II) complexes of *meso* 6+6 macrocyclic amine derived from *trans*-1,2-diaminocyclopentane and 2,6-diformylpyridine

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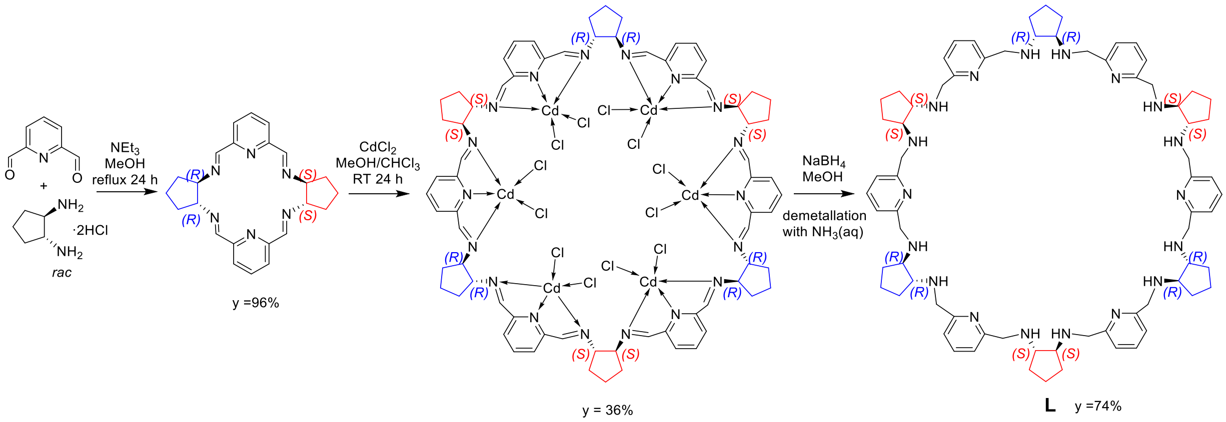
1. Synthesis of *meso* 6+6 amine ligand L



Supporting figure 1. Synthesis of *meso* 6+6 amine ligand **L** via hexanucler Cd(II) dodecaiminie complex.[8a,c]

2. Crystal structures

Crystallizations of $[Ni_6\mathbf{L}Cl_{10}(CH_3CN)_2(H_2O)_6]Cl_2\cdot0.25NiCl_2(H_2O)_4\cdot4CH_3CN\cdot5H_2O$ (**1’**), $[Ni_6\mathbf{L}(SO_4)_6(H_2O)_{12}]$·solvent (**2’**), $[Cu_4\mathbf{L}(CH_3OH)_2](NO_3)_8\cdot2CH_3OH\cdot2H_2O$ (**3’**), $[Cu_4\mathbf{L}(H_2O)_2](NO_3)_8\cdot4H_2O$ (**3”**), $[Cu_6\mathbf{L}Cl_8]Cl_4\cdot19H_2O$ (**4’**) and $[Cu_6\mathbf{L}(SO_4)_4(H_2O)_2](SO_4)_2\cdot36.5H_2O$ (**5’**) is described in the main text of the paper.

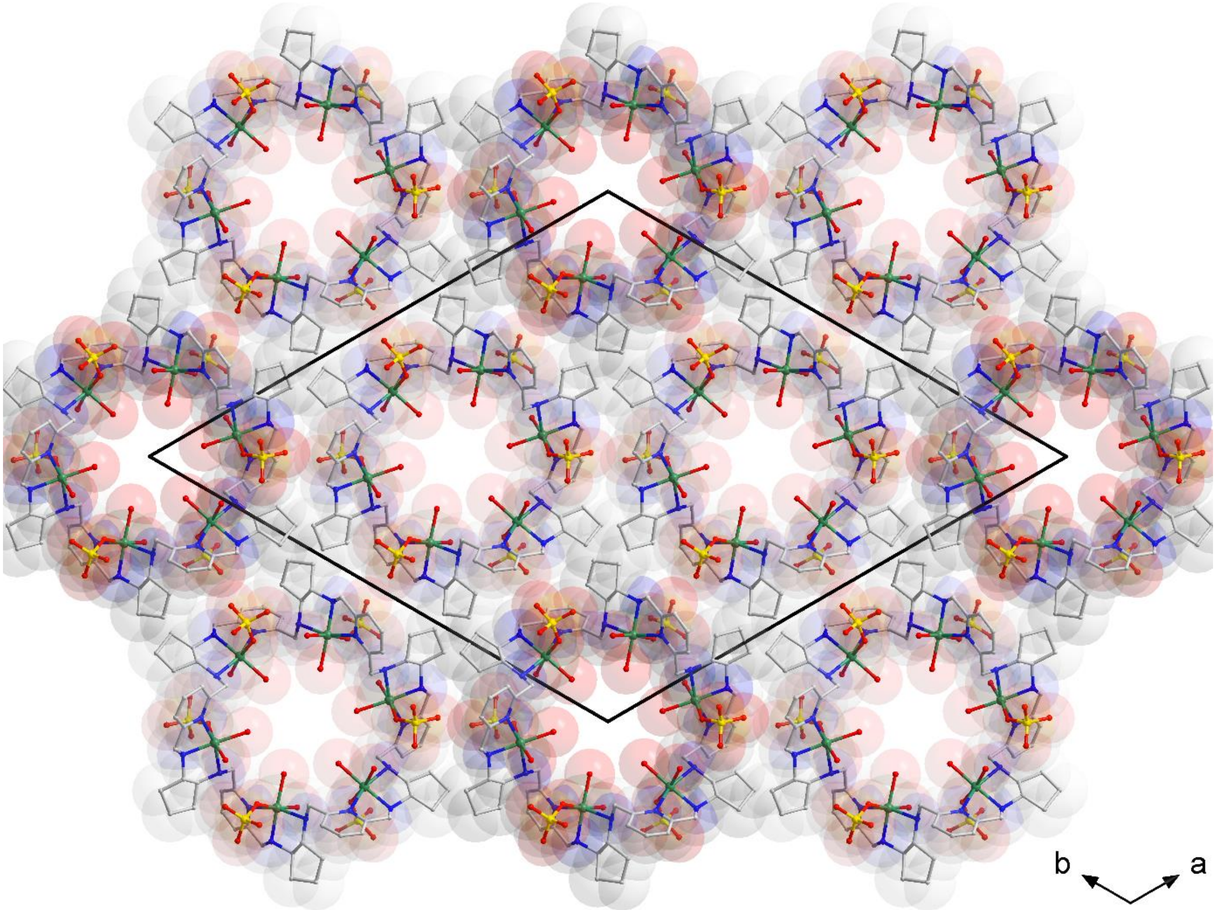
Single-crystal X-ray diffraction data for **1’**-**5’** were collected at 80 or 100 K on Agilent Technologies Xcalibur R (Ruby CCD detector) *κ*-geometry diffractometer using Mo *Kα* radiation (for details see **supporting table S1a**). Data collections, cell refinements, data reductions and analyses, including analytical or empirical (multi-scan) absorption corrections, were carried out with CrysAlis*PR*[13a].

Crystal structures were solved using a dual-space algorithm with SHELXT-2014 program[13b], and refined on F^2 by a full-matrix least-squares method using the SHELXL-2014/7 program[13c]. All non-H atoms in **3’** and **3”**, and most of them in the remaining structures, i.e. fully occupied and those with site occupation factors (SOFs) > 0.5 were refined with anisotropic atomic displacement parameters (exceptions are Cl7 and Cl8 atoms in **4’**, which were refined anisotropically despite their SOF < 0.5, as well as O6*W*, O7*W*, O8*W* in **4’** and O17*W* in **5’** which, despite the SOF > 0.5, were refined isotropically).

All coordination cations in **1’**, **3’**, **3”**, **4’** and **5’** and molecule in **2’** are centrosymmetric. Thus, there is a half of the cation (lying on $\bar{1}$) in the asymmetric unit of **1’**, **3’**, **3”**, **4’** and **5’** ($Z' = 0.5$), and 1/6 of the molecule (lying on $\bar{3}$) in **2’** ($Z' = 1/6$).

Due to very low quality of diffraction pattern of **2’** (all tested crystals diffracted to low resolution, about 1.2 Å) only a model of its crystal structure is presented here. (Crystal is trigonal, $R\bar{3}$ space group, $a = 31.304(6)$, $c = 14.801(6)$ Å, $V = 12561(7)$ Å^3, $T = 80$ K, $Z = 3$). In the crystal structure of **2’** highly disordered solvent molecules were detected (ions should not be excluded). They were not modelled, and their electron density was taken into account using the SQUEEZE procedure[13d] in *PLATON* program.[13e] Disordered solvent molecules are located mainly in the channels running down the **c** axis (**supporting figure S1a**). The volume of the solvent accessible voids is 6311 Å^3 (and 2398 electrons) per unit cell, i.e. about 2104 Å^3 (and 799 electrons) per molecule of **2’**.

One of the inorganic (Cl^-/H_2O) ligands coordinated to Ni2 and Ni3 in the crystal of **1’** was found to be substitutionally disordered. Both positions were finally refined as occupied by Cl^-anions or H_2O molecules (with SOFs = 0.670(12)/0.330(12) for O3*W*/Cl3 coordinated to Ni2, and Cl4/O4*W* coordinated to Ni3). Therefore, the formula of the complex cation is $[Ni_6\mathbf{L}Cl_{10}(CH_3CN)_2(H_2O)_6]^{2+}$, but the coordination environments of the respective metal centers are as follows: $NiN_3Cl(H_2O)_2$ for Ni1, $NiN_3Cl(CH_3CN)(H_2O)$ (67%) or $NiN_3Cl_2(CH_3CN)$ (33%) for Ni2, and NiN_3Cl_3 (67%) or $NiN_3Cl_2(H_2O)$ (33%) for Ni3. It means that the presence of two different isomers of the complex cation with the same formula should be considered in the crystal of **1’**. Additionally, disordered and partially occupied $NiCl_2(H_2O)_4$ molecules (sharing its position with the disordered water molecules; SOFs = 0.75, 0.5, 0.25, 0.125) have been identified in the crystal. However, their amount should be treated as a rough approximation.



Supporting figure S2a. Packing of the [Ni_6**L**$(SO_4)_6(H_2O)_{12}$] molecules in the crystal of [Ni_6**L**$(SO_4)_6(H_2O)_{12}$]·solvent (**2'**), showing solvent accessible channels running down the **c** axis.

One of the *trans*-1,2-diaminocyclopentane rings in **5'** is slightly disordered and was refined with two atoms in two positions each (SOFs = 0.570(10) and 0.430(10)). To get acceptable and appropriate model of this disordered fragment, some geometrical restraints (SADI and SAME instructions in SHELXL) and constraints on the coordinates and displacement parameters (EXYZ and EADP instructions) were applied in the refinement procedure.

Many of the non-coordinated anions and water molecules in **4'** and **5'** are disordered or partially occupied. Chloride/water positions in **4'**, i.e. Cl6/O6*W*, Cl7/O7*W* and Cl8/O8*W* were refined with SOFs = 0.371(7)/0.629(7), 0.301(7)/0.699(7) and 0.329(8)/0.671(8), respectively. Restraint on the sum of SOFs of Cl6, Cl7 and Cl8 (1.00(1); SUMP instruction) was applied. Remaining 30 water positions in **4'** were refined with SOFs = 0.5, 0.375, 0.25 and 0.125. For the details, see the CIF file. Non-coordinated SO_4^{2-} anion in **5'** was found to be disordered and was refined with and SOFs = 0.629(5)/0.371(5) and SAME restraint applied. 17 water molecules in the asymmetric unit of **5'** are fully occupied. However, two of them were refined with oxygen atoms in two positions and SOFs = 0.75/0.25 for O13*W*/O13*X*, and 0.531(17)/0.469(17) for O17*W*/O17*X*. Remaining 6 water positions in **5'** were refined with SOFs = 0.5 and 0.25. For the details, see the CIF file.

H atoms in **1’-5’** were included using geometrical considerations or were found in difference Fourier maps. In the final refinement cycles, C- and N-bound H atoms, as well as those from CH_3OH hydroxyl groups were repositioned in their calculated positions and refined using a riding model (or as riding rotating groups), with N–H = 1.00 Å, C–H = 0.95–1.00 Å and O–H = 0.84 Å, and with $U_{iso}(H) = 1.2U_{eq}(N,C)$ for NH_2, CH and CH_2 or $1.5U_{eq}(O,C)$ for OH and CH_3.

Water H atoms in **3’** and **3”**, O1*W* and O2*W* in **1’**, and O1*W*–O17*W* in **5’** were refined with the O–H bond lengths restrained to 0.840(2) Å, H···H distances restrained to 1.360(2) Å and then a rigid group or riding model constraints were applied (AFIX 6 or AFIX 7 instructions in SHELXL). Positions of the remaining water H atoms in **1’** and **5’**, and all of the water H atoms in **4’** were not found in difference Fourier maps.

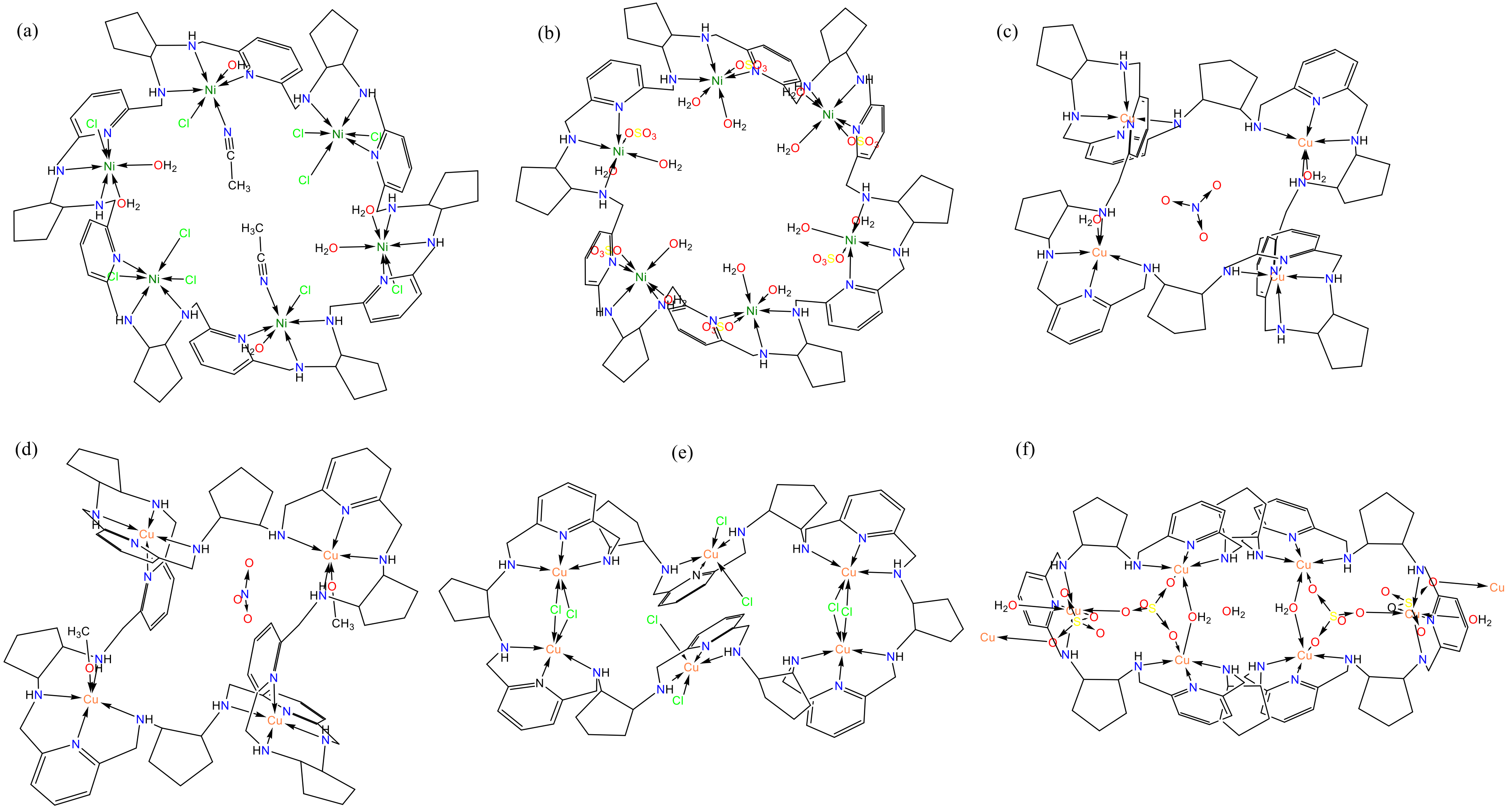
The finally accepted formulas for the crystals are as given above and in **supporting table S1a**, but the amount of water molecules in **1’**, **4’** and **5’** should be treated as a rough approximation.

Figures presenting X-ray structures were made using the Mercury[13f] and DIAMOND[13g] programs. The coordination geometries around the hexacoordinate metal centers[13h,i] were analysed for compounds **1’**, **2’** and **5’** using SHAPE program.[13j] The Continuous Shape Measurements (CShMs) are listed in **supporting table S1b**.

The details of structures refinements are given in **supporting table S1a**. The crystallographic information files (CIFs) have been deposited at the Cambridge Crystallographic Data Centre (CCDC Nos. 2168650–2168654) and provided as Supporting Information.

References:

See the main text.



Supporting figure S2b. ChemDraw representations of multinuclear complexes present in: **1’** (a), **2’** (b), **3’** (c), **3”** (d), **4’** (e), and **5’** (f). Most solvent molecules and some anions as well as disorder in **1’** omitted for clarity.

Supporting table S1a. Crystallographic data for the crystals.

	$[Ni_6\mathbf{L}Cl_{10}(CH_3CN)_2(H_2O)_6]Cl_2 \cdot 0.25NiCl_2(H_2O)_4 \cdot 4CH_3CN \cdot 5H_2O$ (**1’**)	$[Cu_4\mathbf{L}(CH_3OH)_2](NO_3)_8 \cdot 2CH_3OH \cdot 2H_2O$ (**3’**)	$[Cu_4\mathbf{L}(H_2O)_2](NO_3)_8 \cdot 4H_2O$ (**3”**)	$[Cu_6\mathbf{L}Cl_8]Cl_4 \cdot 19H_2O$ (**4’**)	$[Cu_6\mathbf{L}(SO_4)_4(H_2O)_2](SO_4)_2 \cdot 36.5H_2O$ (**5’**)
CCDC No.	2168650	2168651	2168652	2168653	2168654
Chemical formula	$C_{84}H_{144}Cl_{12.5}N_{24}Ni_{6.25}O_{12}$	$C_{76}H_{122}Cu_4N_{26}O_{30}$	$C_{72}H_{114}Cu_4N_{26}O_{30}$	$C_{72}H_{140}Cl_{12}Cu_6N_{18}O_{19}$	$C_{72}H_{179}Cu_6N_{18}O_{62.5}S_6$
M_r	2492.29	2134.15	2078.05	2368.65	2870.92
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	80	100	80	100	100
a, b, c (Å)	11.665(3), 14.436(4), 17.691(4)	11.371(2), 24.469(4), 16.157(2)	13.257(3), 24.388(3), 14.846(3)	13.566(3), 14.710(3), 16.733(4)	12.697(2), 15.022(3), 17.907(2)
α, β, γ (°)	71.42(2), 78.55(2), 75.98(2)	90, 90.98(2), 90	90, 116.22(3), 90	74.04(2), 70.91(2), 76.91(2)	98.93(2), 100.75(2), 114.39(2)
V (Å^3)	2715.8(13)	4494.8(12)	4306.0(17)	2999.4(13)	2951.3(10)
Z	1	2	2	1	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.43	1.03	1.07	1.37	1.27
Crystal size (mm)	0.20 × 0.16 × 0.06	0.32 × 0.20 × 0.13	0.21 × 0.15 × 0.06	0.14 × 0.05 × 0.04	0.16 × 0.11 × 0.08
Diffractometer	Agilent Technologies Xcalibur with Ruby CCD detector (κ-geometry, omega-scan)				
Absorption correction	Multi-scan	Analytical	Analytical	Analytical	Multi-scan
T_{min}, T_{max}	0.945, 1.000	0.787, 0.888	0.826, 0.938	0.873, 0.945	0.971, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25540, 10312, 6122	53792, 8533, 6650	11804, 7374, 5655	20914, 11619, 6114	22499, 11638, 9410
R_{int}	0.052	0.041	0.035	0.059	0.026
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.610	0.610	0.610	0.617	0.617
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.077, 0.250, 1.05	0.060, 0.171, 1.09	0.039, 0.093, 1.01	0.076, 0.224, 0.97	0.042, 0.106, 1.04
No. of reflections	10312	8533	7374	11619	11638
No. of parameters	684	620	602	637	818
No. of restraints	6	3	9	1	80
H-atom treatment	H-atom parameters constrained				
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.65, −0.96	1.66, −0.42	0.51, −0.37	0.85, −0.58	0.93, −0.69

Computer programs: *CrysAlisPRO* (Rigaku OD, 2015, 2018, 2020), SHELXT-2014/7 (Sheldrick, 2015), SHELXL2014/7 (Sheldrick, 2015).

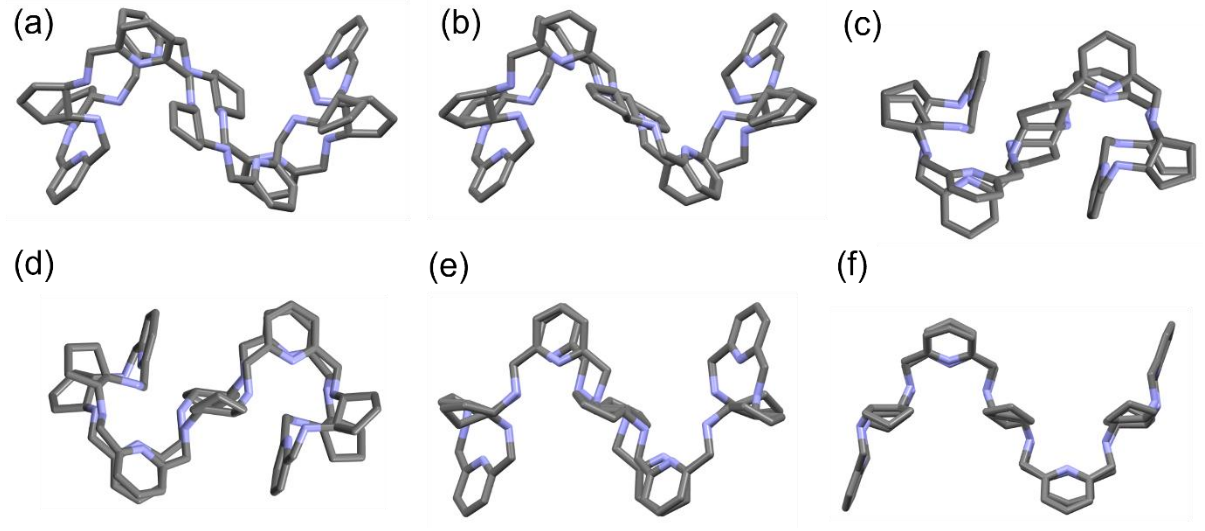
Supporting table S1b. Continuous Shape Measurements (CShMs) for Ni^{II} and Cu^{II} ions in ML$_6$ polyhedra in crystals **1'**, **2'** and **5'**.

ML$_6$	JPPY (C_{5v})[(a)]	TPR (D_{3h})	OC (O_h)	PPY (C_{5v})	HP (D_{6h})
Crystal **1'**					
Ni1	29.755	14.071	0.850	26.004	31.827
Ni2[(b)]	28.544	11.787	1.309	24.617	32.546
Ni3[(c)]	26.228	13.102	1.465	23.048	30.710
Crystal **2'**					
Ni1	29.09	13.22	0.95	25.10	32.61
Crystal **5'**					
Cu3	27.01	16.11	3.08	25.44	28.78

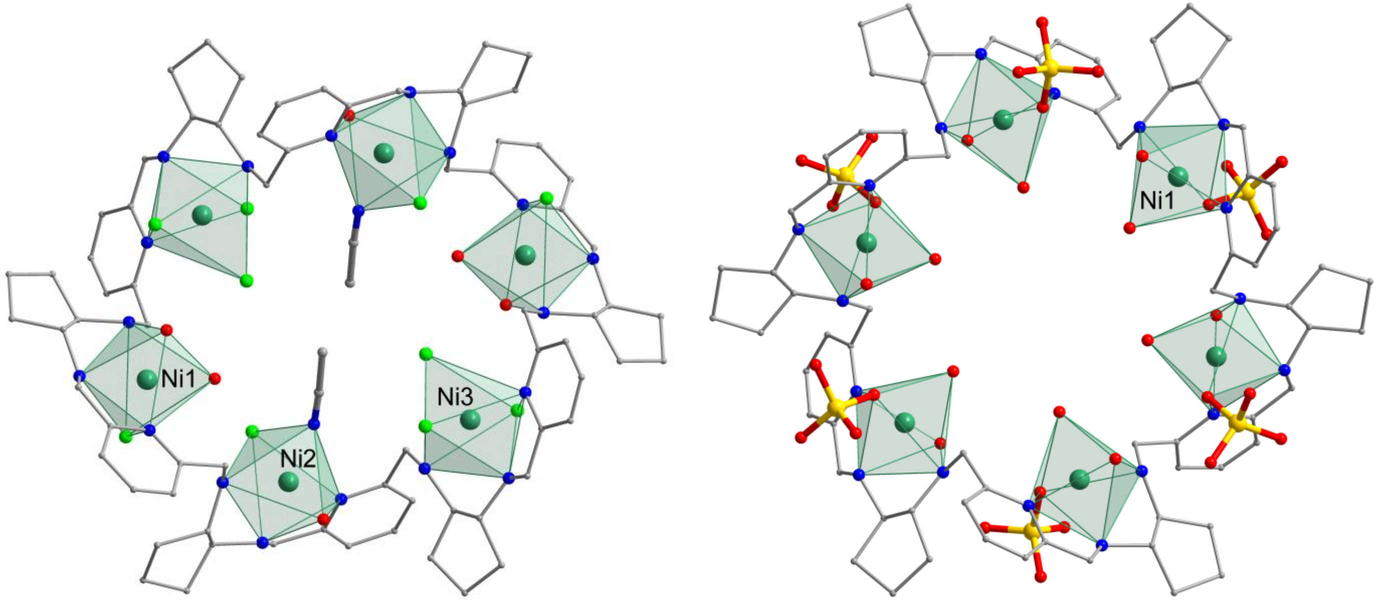
[(a)] Ideal structures for ML$_6$: JPPY – Johnson pentagonal pyramid J2; TPR – trigonal prism; OC – octahedron; PPY – pentagonal pyramid; HP – hexagon

[(b)] H_2O as a ligand in disordered coordination sphere; [$NiN_3Cl(CH_3CN)(H_2O)$], s.o.f. = 0.67

[(c)] Cl^- as a ligand in disordered coordination sphere; [NiN_3Cl_3], s.o.f. = 0.67



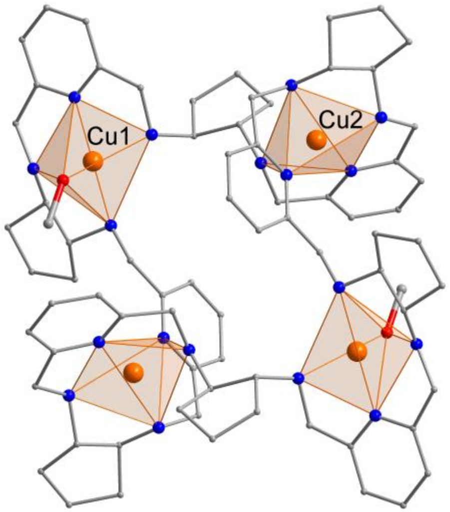
Supporting figure S2c. Side views. Comparison of the macrocycle conformation in its multinuclear Ni(II) and Cu(II) complexes: **1'** (a), **2'** (b), **3'** (c), **3"** (d), **4'** (e), and **5'** (f), respectively.



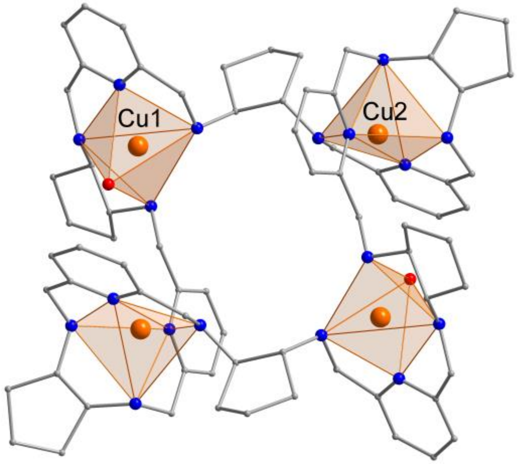
$[Ni_6\mathbf{L}Cl_{10}(CH_3CN)_2(H_2O)_6]^{2+}$ in **1’**

$[Ni_6\mathbf{L}(SO_4)_6(H_2O)_{12}]$ in **2’**

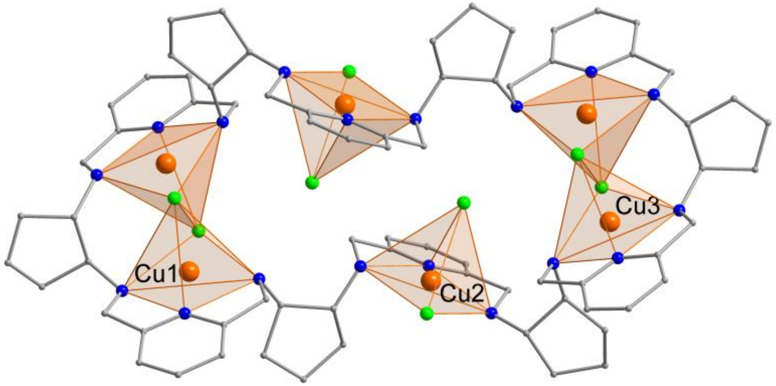
Supporting figure S2d. Coordination cation in **1’** or molecule in **2’** with the coordination polyhedra of the Ni^{II} ions shown. Hydrogen atoms and Cl^-/H_2O disorder in **1’** omitted for clarity. Colour code: Ni, green; N, blue, Cl, light green, O, red, S, yellow.



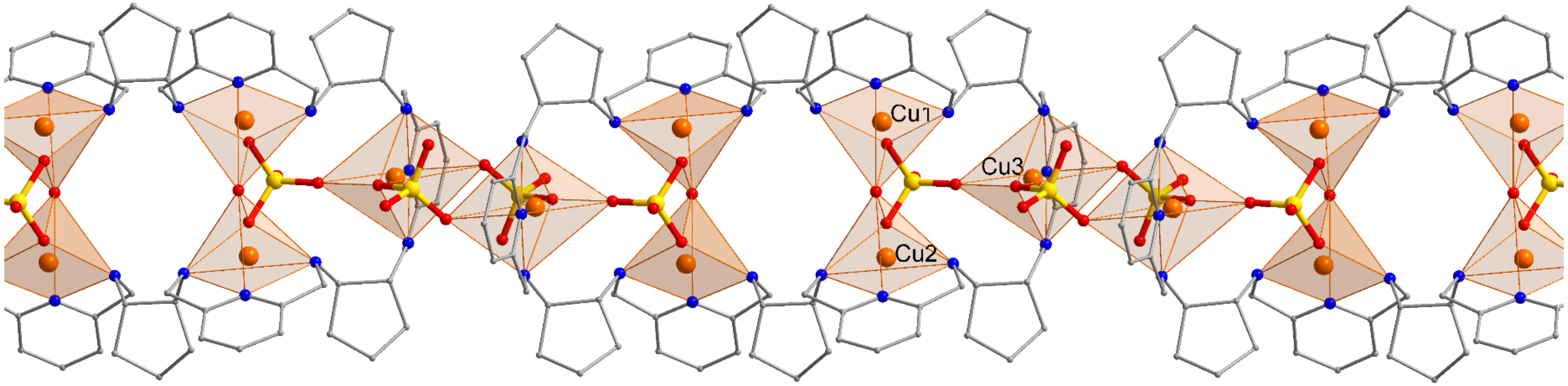
$[\mathrm{Cu_4}\mathbf{L}(\mathrm{CH_3OH})_2]^{8+}$ in **3’**



$[\mathrm{Cu_4}\mathbf{L}(\mathrm{H_2O})_2]^{8+}$ in **3”**



$[\mathrm{Cu_6}\mathbf{L}\mathrm{Cl_8}]^{4+}$ in **4’**



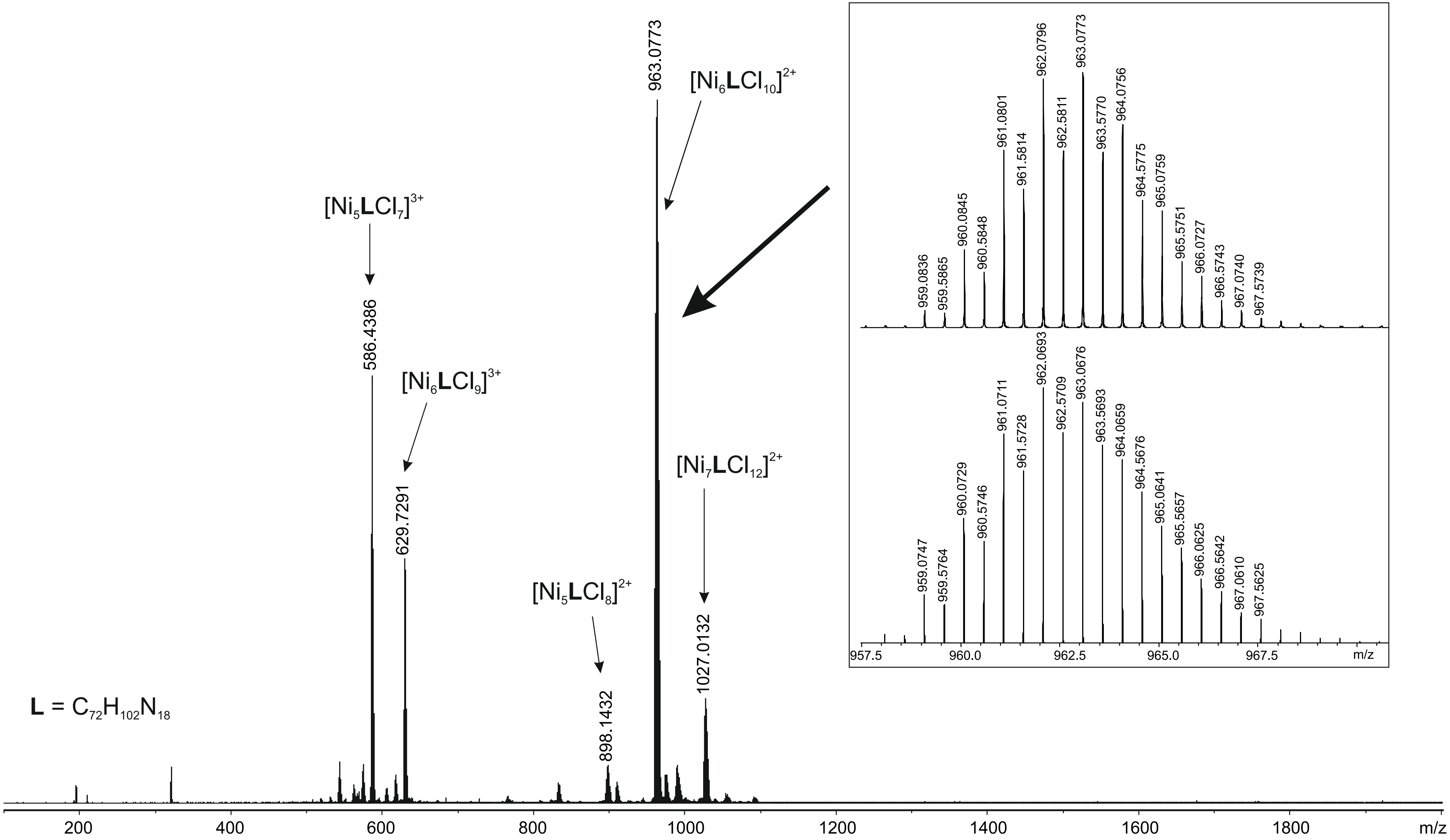
fragment of $[\mathrm{Cu_6}\mathbf{L}(\mathrm{SO_4})_4(\mathrm{H_2O})_2]_n^{(4n)+}$ in **5’**

Supporting figure S2e. Coordination cations in **3’**, **3”**, **4’** and **5’** with the coordination polyhedra of the Cu$^{\mathrm{II}}$ ions shown. Hydrogen atoms and disorder of the organic ligand in **5’** omitted for clarity. Colour code: Cu, orange; N, blue, Cl, light green, O, red, S, yellow.

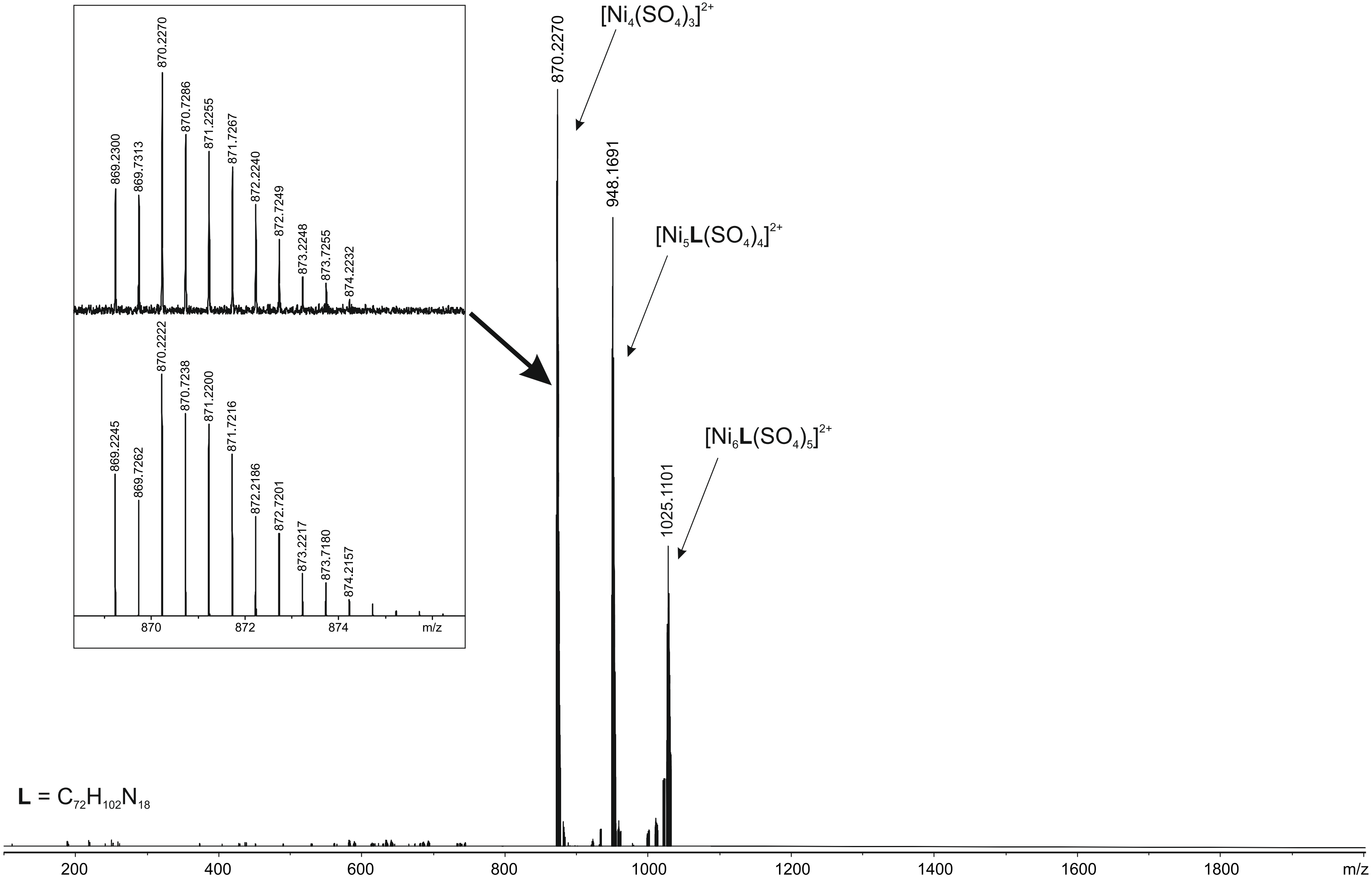
Supporting table S1c. Summary of the main features of multinuclear complexes with ligand **L**.

crystal structure (ref. or No.)	No. and kind of metal cations	counter anion(s)	type of structure	void occupation
$[Zn_6(\mathbf{L})Cl_{12}]\cdot 3.2CH_3CN$ [8c]	6 Zn^{2+}	Cl^-	widely open, loose conformation	coordinated solvents
$\{[Zn_3(\mathbf{L})]\cdot(NO_3)_5Cl\}\cdot 9H_2O$ [8c]	3 Zn^{2+}	NO_3^-, Cl^-	triply twisted, compact conformation	uncoordinated anion
$\{[Ni_6(\mathbf{L})(NO_3)_{11}(CH_3CN)(H_2O)]NO_3\}$ $\cdot 6CH_3CN\cdot 6.5H_2O$ [8c]	6 Ni^{2+}	NO_3^-	widely open, loose conformation	coordinated solvents
$[Ni_6\mathbf{L}Cl_{10}(CH_3CN)_2(H_2O)_6]Cl_2$ $\cdot 0.25NiCl_2(H_2O)_4\cdot 4CH_3CN\cdot 5H_2O$ (**1'**)	6 Ni^{2+}	Cl^-	widely open, loose conformation	coordinated solvents
$[Ni_6\mathbf{L}(SO_4)_6(H_2O)_{12}]\cdot$solvent (**2'**)	6 Ni^{2+}	SO_4^{2-}	widely open, loose conformation	coordinated solvents
$[Cu_4\mathbf{L}(CH_3OH)_2](NO_3)_8\cdot 2CH_3OH\cdot 2H_2O$ (**3'**)	4 Cu^{2+}	NO_3^-	four times twisted, compact conformation	uncoordinated anion
$[Cu_4\mathbf{L}(H_2O)_2](NO_3)_8\cdot 4H_2O$ (**3"**)	4 Cu^{2+}	NO_3^-	four times twisted, compact conformation	uncoordinated anion
$[Cu_6\mathbf{L}Cl_8]Cl_4\cdot 19H_2O$ (**4'**)	6 Cu^{2+}	Cl^-	elongated, loose conformation	-
$[Cu_6\mathbf{L}(SO_4)_4(H_2O)_2](SO_4)_2\cdot 36.5H_2O$ (**5'**)	6 Cu^{2+}	SO_4^{2-}	elongated, loose conformation, squeezed in the middle, coordination polymer	uncoordinated solvent

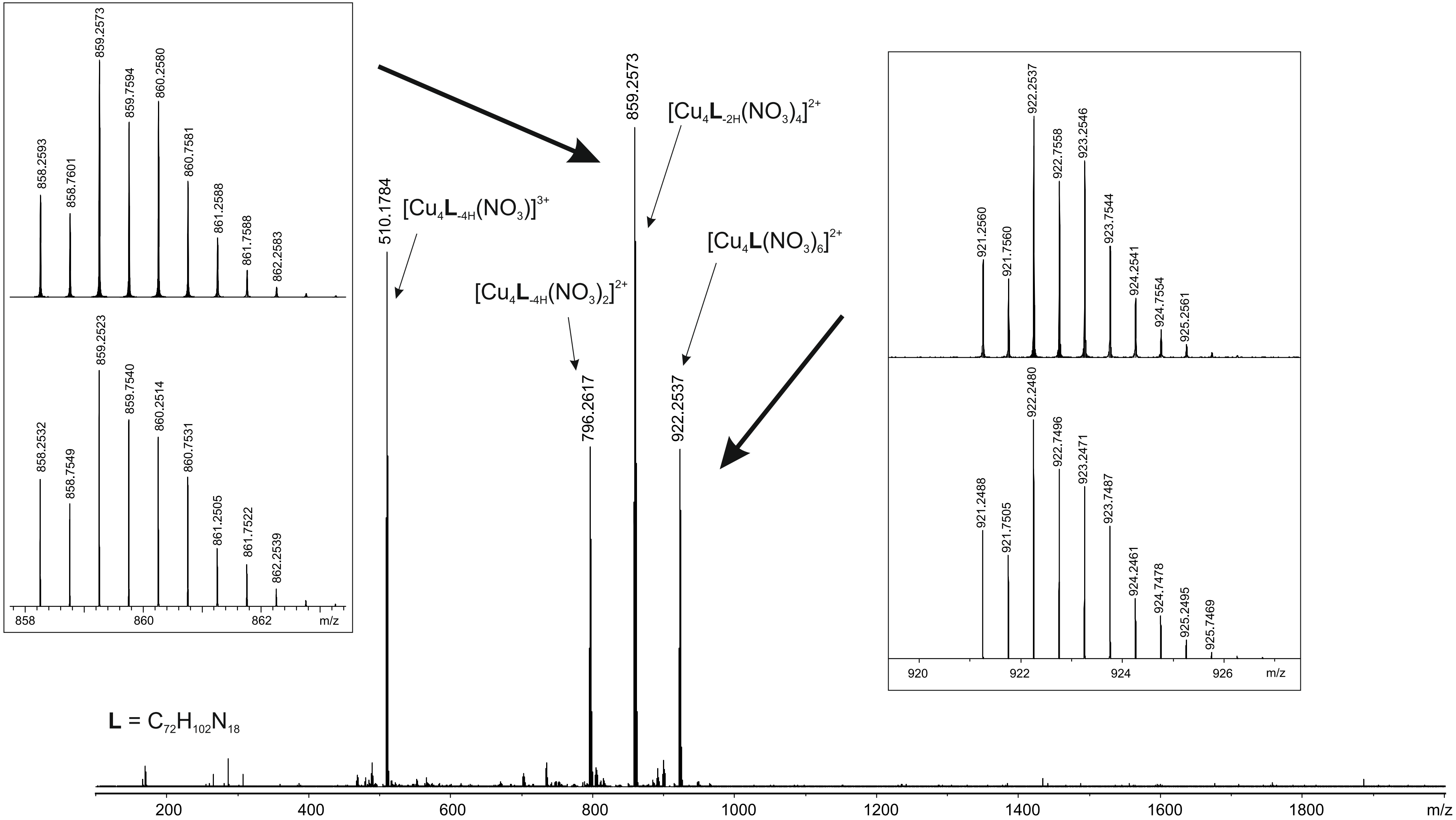
3. ESI MS spectra



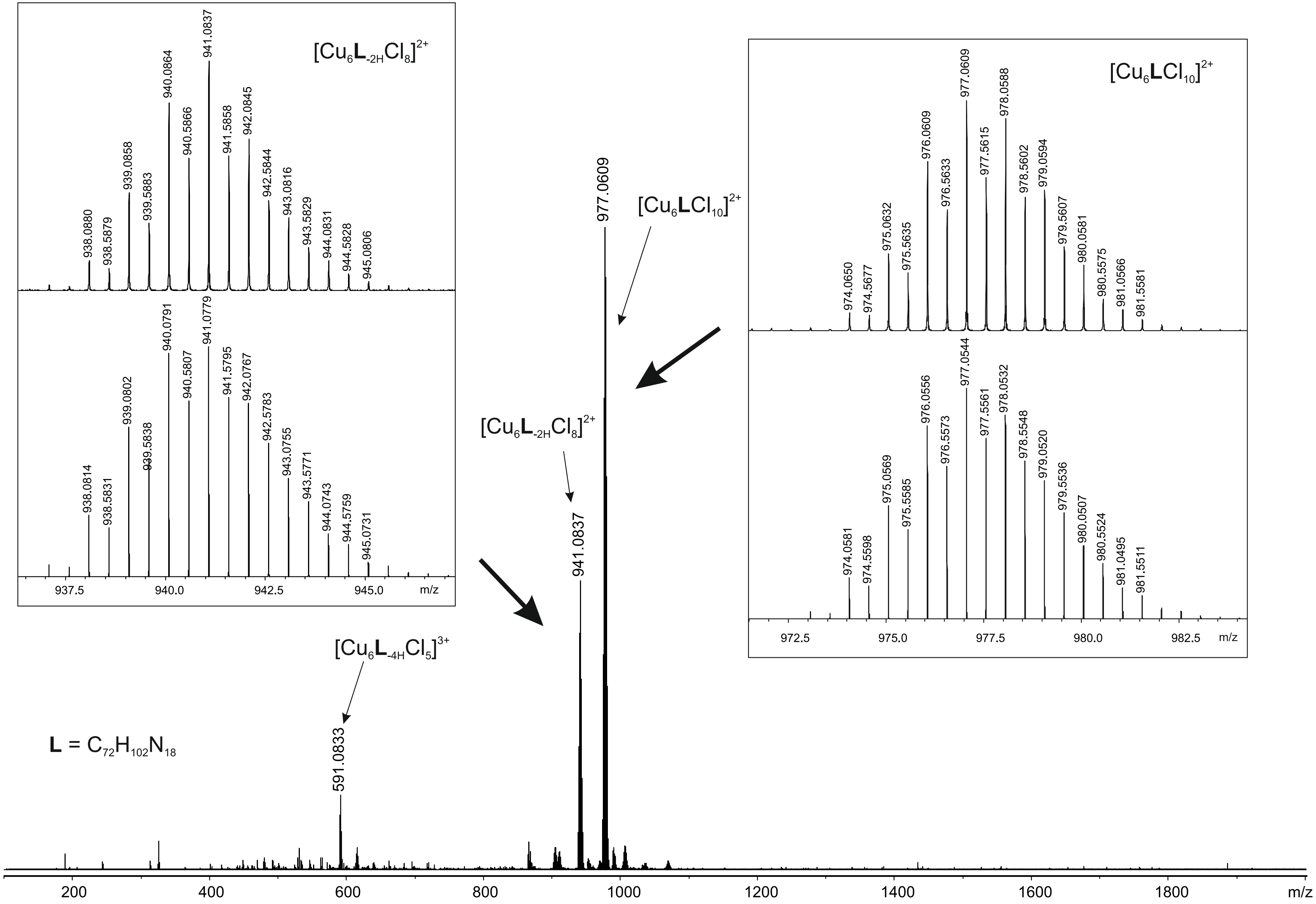
Supporting figure S3a. ESI MS spectrum of $[Ni_6\mathbf{L}Cl_{12}]$ complex. Spectral pattern of the main peak in the frame.



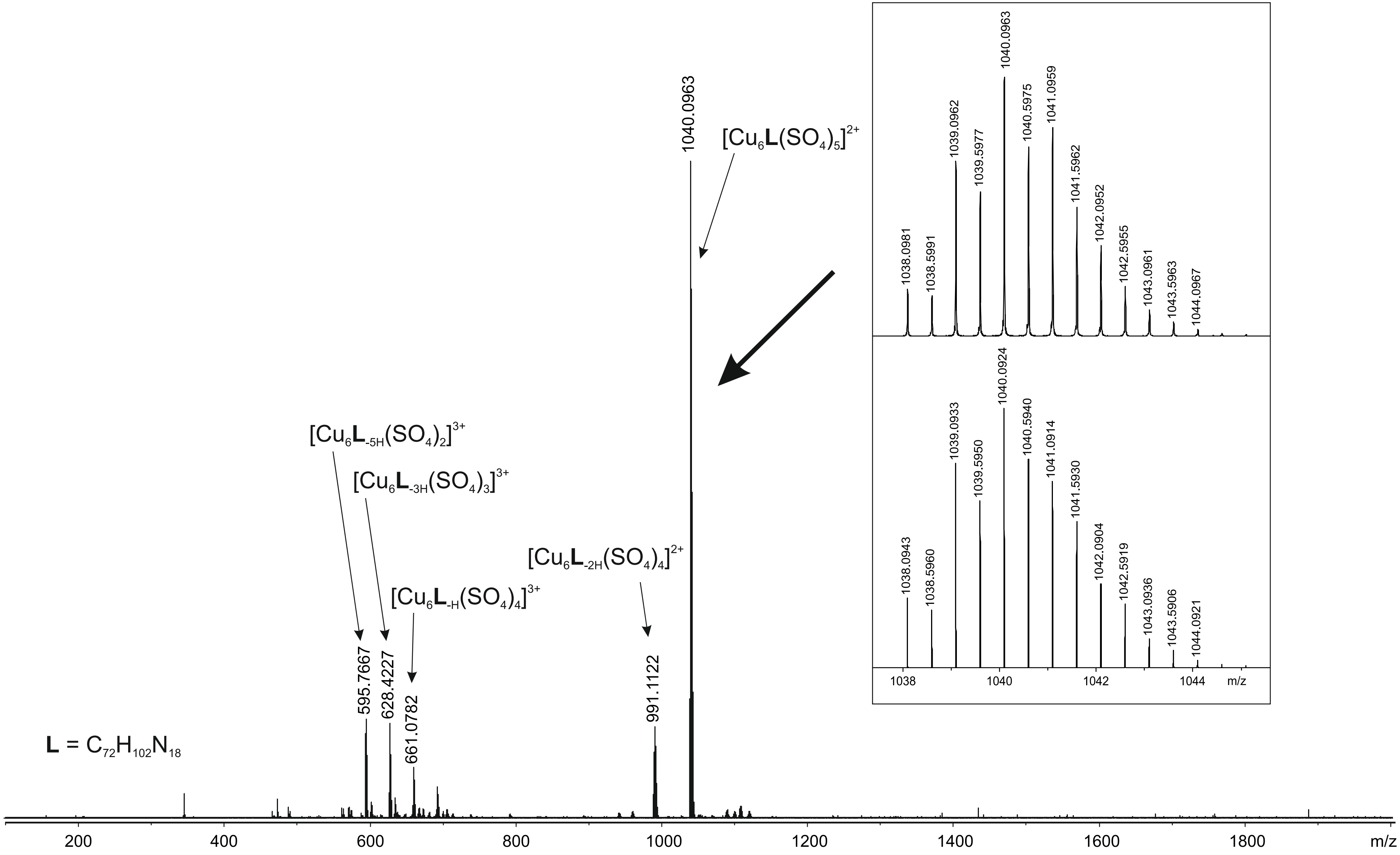
Supporting figure S3b. ESI MS spectrum of $[Ni_6\mathbf{L}(SO_4)_6]$ complex. Spectral pattern of the main peak in the frame.



Supporting figure S3c. ESI MS spectrum of [Cu$_4$**L**(NO$_3$)$_8$] complex. Spectral patterns of two main peaks in frames.

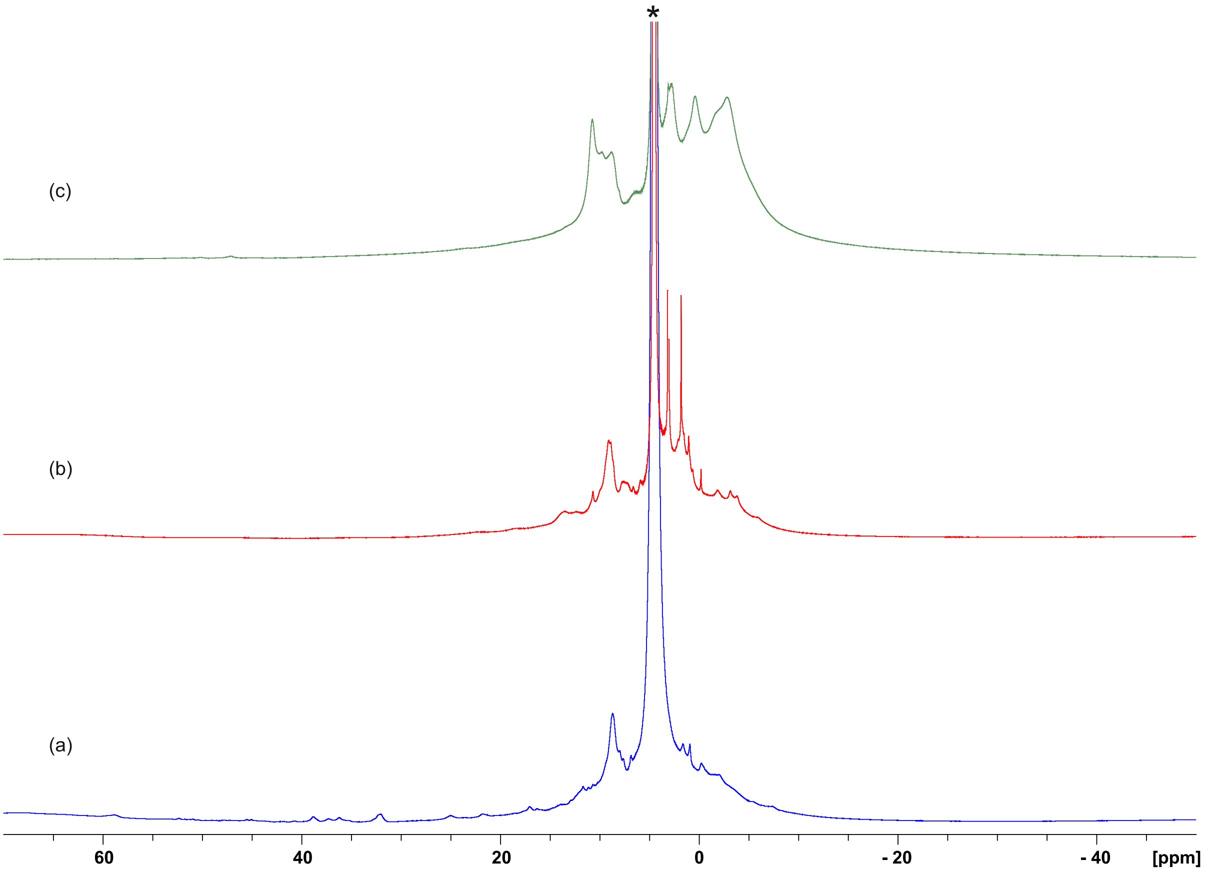


Supporting figure S3d. ESI MS spectrum of [Cu$_6$**L**Cl$_{12}$] complex. Spectral patterns of two main peaks in frames.

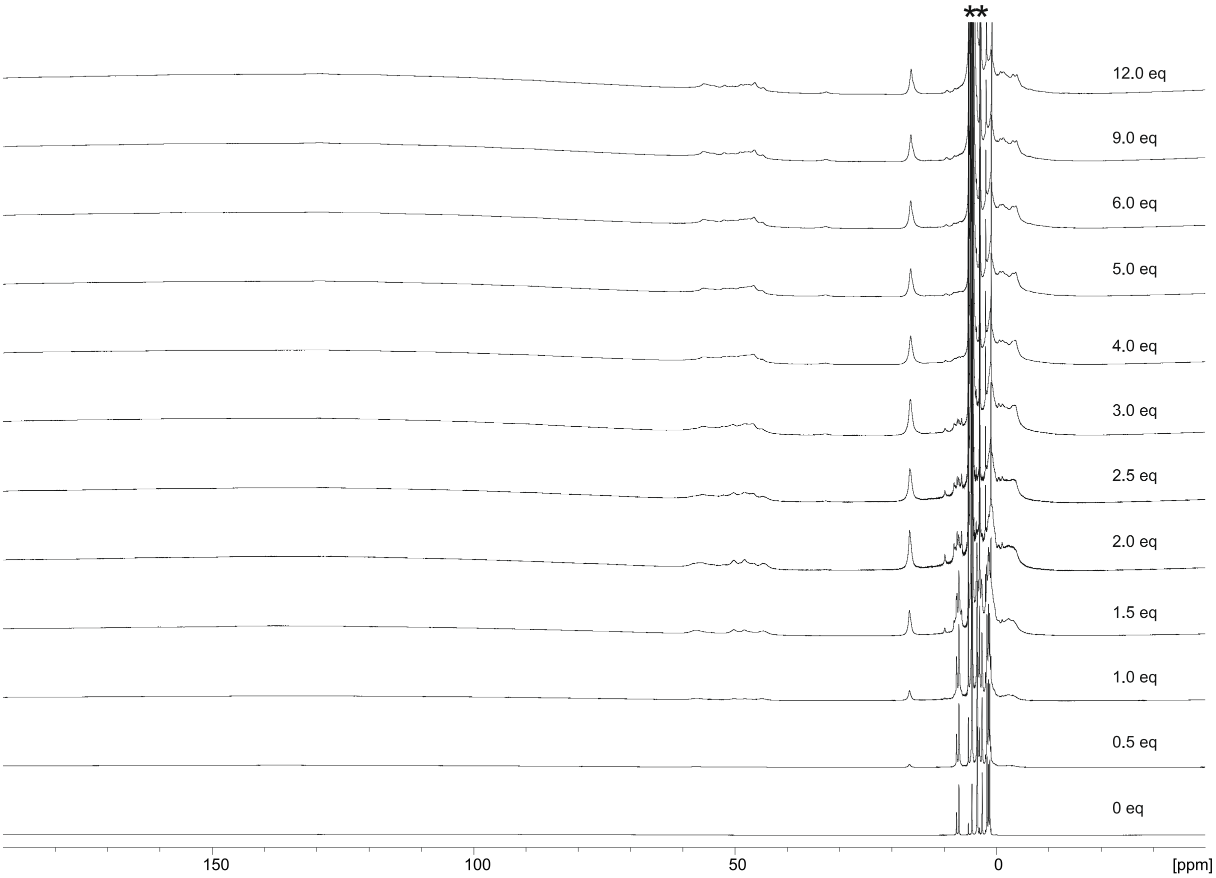


Supporting figure S3e. ESI MS spectrum of [Cu$_6$**L(**SO$_4$)$_6$] complex. Spectral patterns of the main peak in the frame.

4. NMR spectra

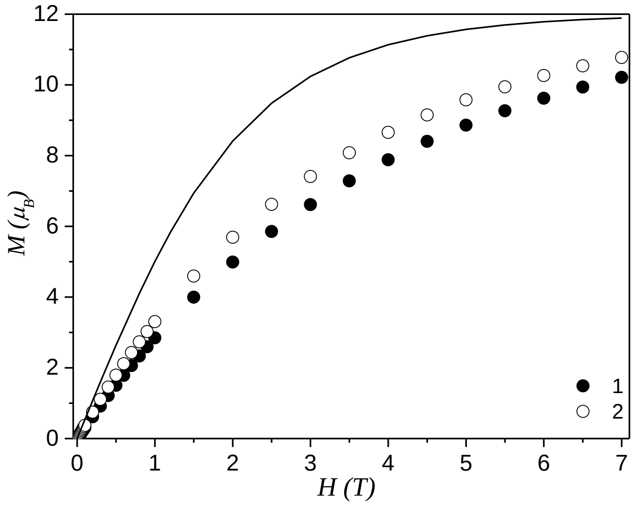


Supporting figure S4a. ^{1}H NMR spectra (D_2O, 500 MHZ) of [$Cu_6(SO_4)_6$(**L**) (a), [Cu_6Cl_{12}(**L**)] (b) and [$Cu_4(NO_3)_8$(**L**)] (c) complexes. Asterisk denotes a residual solvent signal.

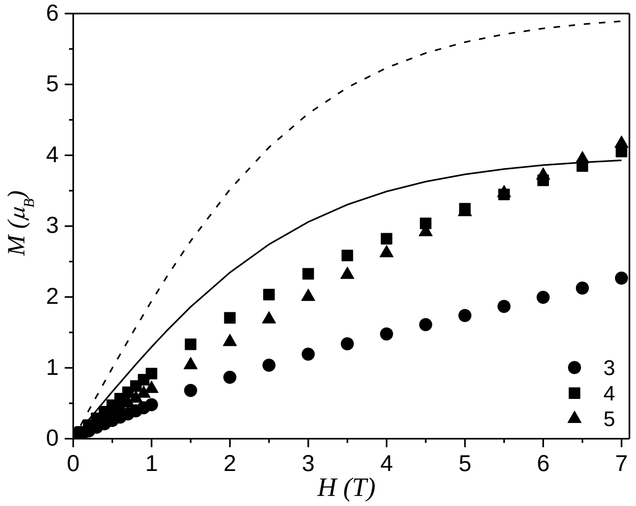


Supporting figure S4b. ^{1}H NMR spectra (500 MHZ, D_2O/CD_3OD (v/v 1/1)) corresponding to the titration of the macrocycle **L** with the solution of $NiSO_4{\cdot}6H_2O$. Asterisk denotes the residual solvent signals.

5. Magnetic properties



Supporting figure S5a. Field dependence of the magnetization for **1** (●) and **2** (○) (*M* per Ni_6 entities) at 2 K. The solid line is the Brillouin function curve for the system of six uncoupled spins with $S = 1$ and $g = 2.0$ in the absence of zero-field splitting.



Supporting figure S5b. Field dependence of the magnetization for 3 (●), **4** (■) and 5(▲) (*M* per Cu_4 and Cu_6 units, respectively) at 2 K. The solid line is the Brillouin function curve for the system of four uncoupled spins with $S = {}^1/_2$ and $g = 2.0$; dashed line is the Brillouin function for six noninteracting $S = {}^1/_2$ systems.