Inorganic Chemistry
Article
pubs.acs.org/IC

Collapsed Cu(II)-Hydroxamate Metallacrowns

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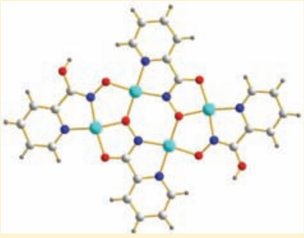
Ⓢ *Supporting Information*

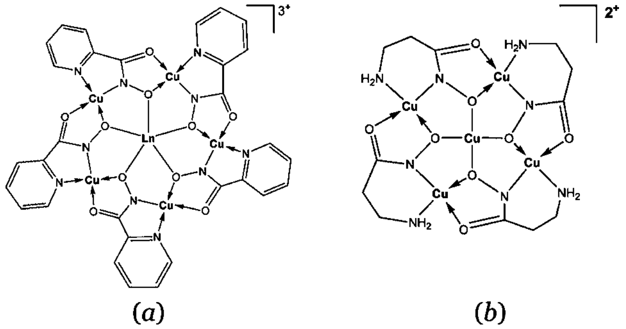
ABSTRACT: Degradation of a strained, thermodynamically destabilized pentanuclear copper(II) 12-metallacrown-4 complex based on a picoline hydroxamic acid resulted in the formation of the tetranuclear compounds which are the first examples of solely hydroxamate-based Cu(II) metallacrown complexes with a collapse of the metallamacrocyclic cavity.



Metallacrowns (MCs) are one of the types of metallamacrocyles which can be regarded as inorganic analogues of crown ethers in which the carbon atoms in the $\{C-C-O\}_n$ sequence are replaced by metal ions and heteroatoms.[1] MCs have received considerable attention as attractive functional materials for various applications (e.g., as luminescent materials,[1b,2] selective recognition agents for cations and anions,[1a,b] building blocks for mesoporous solids,[1b,3] single molecule magnets,[1a,b,4] and potential MRI contrast agents) because of their metal-rich nature and chemical tunability, high thermodynamic stability, and possibility of straightforward preparation as a result of reproducible facile one-step synthetic procedures. Although several hundred papers dedicated to metallacrowns have been published since their discovery in 1989, their structural diversity and reactivity still remain insufficiently explored. For example, metallacrown complexes having zinc ions in the metallamacrocylic frame have been obtained for the first time only in 2011.[2] These zinc-containing metallacrowns are the first examples of MC complexes that can be really considered as perspective luminescent materials, as the Zn(II) d^{10} electronic configuration precludes quenching through a d−d transition.[2] Recently, it has been shown that the ability to control molecular topology afforded by metallacrowns allows for orientation of single ion anisotropy that enhances SMM properties of lower total spin systems.[4] Also, systematic study of sorption properties of porous MOFs based on MCs has been started only during the past two years.[3]

Most of the reported MCs were synthesized using aminohydroxamic acids as ligands.[1] While α-aminohydroxamic acids are preferable ligands to obtain 15-metallacrwons-5 (15-MC-5) containing cavity suitable for incorporation of large metal ions (e.g., lanthanides, Ca^{2+}, UO_2^{2+}, Scheme 1a), β-aminohydroxamic analogs are more suitable for synthesis of 12-metallacrwons-4 (12-MC-4) with a cavity appropriate for binding of cations with smaller ionic radius, such as 3d-metals (Scheme 1b).[1,5a] Also α-aminohydroxamic acids are able to form 12-MC-4 with 3d-metal ions in the central cavity (Scheme 2a); such complexes are however much less stable than those formed with β-aminohydroxamic acids and, on reaction with metal ions with larger ionic radius, easily rearrange into 15-MC-5.[1] Indeed, comparison of the stability constants reported for $[Cu_5(L-H)_4]^{2+}$ species of α- and β-alanine hydroxamic acids (HL) shows 9 orders of magnitude difference in favor of the β-derivative (40.16 vs 49.39).[1c,5a,b]

Scheme 1. General Schematic of the Ln[15-$MC_{Cu\alpha\text{-aminohydroxamic acid}}$-5]$^{3+}$ and Cu[12-$MC_{Cu\beta\text{-aminohydroxamic acid}}$-4]$^{2+}$ Complexes

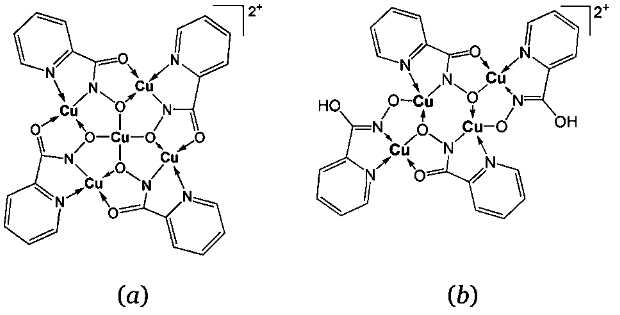


One of the most intriguing problems in metallacrown chemistry is a failure of isolation of pentanuclear 12-MC-4 complexes based on α-aminohydroxamates (Scheme 1a) in a single crystalline state.[1c] Although such species were many times detected in solution,[5] the corresponding complexes have never been structurally characterized. Even if the DFT calculations revealed that the 12-MC-4 can exist as nonplanar, cap-shaped complexes,[5b,e] they should be quite strained, as they

Received: February 21, 2012
Published: May 18, 2012

dx.doi.org/10.1021/ic300387e | *Inorg. Chem.* 2012, 51, 6221−6227

Scheme 2. General Schematic of the Cu[12-$\mathrm{MC_{Cu\alpha\text{-}aminohydroxamic\ acid}}$-4]$^{2+}$ and Collapsed [12-$\mathrm{MC_{Cu\alpha\text{-}aminohydroxamic\ acid}}$-4]$^{2+}$ Complexes



contain 12 fused five-membered chelate rings, and it is not evident that they can retain the structure upon transfer from solution to crystalline state. Herein we report the results of our study on pathways of degradation of copper(II) pentanuclear 12-MC-4 complexes that appeared to be rearranged into collapsed metallacrown structure (Scheme 2b) which is likely the principal structure motif in both hydroxamate and metallacrown chemistry.

EXPERIMENTAL SECTION

Materials and Methods. All the reagents used in this work were of analytical grade and used without further purification. Elemental analysis was conducted by the Microanalytical Service of the University of Wroclaw. IR spectra (KBr pellets) were recorded on a Perkin-Elmer 180 Spectrometer in the range of 200–4000 cm^{-1}. EPR spectra were recorded at room temperature and 77 K on a Bruker ESP 300 spectrometer operating at X-band equipped with an ER 035 M Bruker NMR gaussmeter and HP 5350B Hewlett–Packard microwave frequency counter. Electrospray (ESI) mass spectra were collected on Finigan TSQ 700 or Bruker APEX IV (HRMS, ESI) mass spectrometers. Complexes were dissolved in methanol, methanol/water (1:1) or methanol/DMSO (1:3) solutions with concentrations of 10^{-4}–10^{-6} M. Variable-temperature magnetic measurements of polycrystalline samples were carried out with a Quantum Design SQUID magnetometer (MPMSXL-5-type) at a magnetic field of 0.5 T over the temperature range 1.8–300 K. Each raw data file for the measured magnetic moment was corrected by subtracting the sample holder signal. The molar susceptibility data were corrected for the diamagnetic contribution χ_{Dia} estimated from Pascal's constants. The effective magnetic moment was calculated from the equation: $\mu_{\mathrm{eff}} = 2.83(\chi_{\mathrm{M}}T)^{1/2}$ (B.M.).

Magnetization versus magnetic field measurements were carried out at 2 K in the magnetic field range 0–5 T.

Synthesis of Ligand. The ligand picoline hydroxamic acid (**PicHA**) was prepared as described elsewhere.[6]

Synthesis of the Coordination Compounds. *$Cu_5(PicHA\text{-}2H)_4(ClO_4)_2{\cdot}6H_2O$ (1).* A solution of $Cu(ClO_4)_2{\cdot}6H_2O$ in methanol (0.1 M, 1.25 mL, 0.125 mmol) was added to a solution of **PicHA** in

Table 1. Summary of Crystal Data and Experimental Details for 2, 3, and 4

complex	2	3	4
molecular formula	$C_{30}H_{32}Cl_2Cu_4N_{10}O_{18}$	$C_{60}H_{72}Cl_4Cu_8N_{16}O_{38}S_6$	$C_{72}H_{60}Cl_6Cu_{12}N_{24}O_{51}$
formula weight [g mol^{-1}]	1145.72	2467.82	3052.62
temperature [K]	120(2)	120(2)	100(2)
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	6.5310(2)	10.0116(4)	12.3345(3)
b [Å]	15.2000(5)	11.6271(5)	14.2873(5)
c [Å]	20.4857(8)	18.9536(7)	14.7552(4)
α [deg]	105.214(2)	93.695(2)	72.154(2)
β [deg]	91.607(2)	95.822(2)	75.096(2)
γ [deg]	96.118(2)	98.124(2)	79.062(2)
volume [Å^3]	1947.86(12)	2165.94(15)	2374.42(12)
Z	2	1	1
density (calculated), ρ [Mg m^{-3}]	1.953	1.892	2.135
absorption coefficient, μ [mm^{-1}]	2.384	2.291	2.915
$F(000)$	1152	1244	1518
crystal size [mm^3]	0.29 × 0.15 × 0.08	0.10 × 0.10 × 0.05	0.22 × 0.22 × 0.17
θ range for data collection [deg]	3.85–26.08	2.17–27.53	2.12–28.50
index ranges	$-8 \le h \le 8$ $-18 \le k \le 18$ $-12 \le l \le 25$	$-12 \le h \le 13$ $-15 \le k \le 15$ $-24 \le l \le 24$	$-16 \le h \le 16$ $-19 \le k \le 19$ $-19 \le l \le 19$
reflections collected	7357	39254	50039
independent reflections	7357 [R(int) = 0.0000]	9898 [R(int) = 0.0824]	22438 [R(int) = 0.0388]
completeness to θ	(26.08°) 95.2%	(27.53°) 99.4%	(28.50°) 99.7%
absorption correction	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
max and min transmission	0.8228 and 0.5290	0.8940 and 0.7966	0.6105 and 0.5456
refinement method	full-matrix least-squares on F2	full-matrix least-squares on F2	full-matrix least-squares on F2
data/restraints/parameters	7357/0/584	9898/0/602	22438/3/1522
goodness-of-fit on F^2	1.156	1.064	1.035
final R indices [$I > 2\rho(I)$]	R_1 = 0.0706, wR^2 = 0.1732	R_1 = 0.0486, wR^2 = 0.0912	R_1 = 0.0402, wR^2 = 0.0808
R indices (all data)	R_1 = 0.0866, wR^2 = 0.1816	R_1 = 0.1057, wR^2 = 0.1083	R_1 = 0.0618, wR^2 = 0.0889
largest diff. peak and hole [e Å^{-3}]	0.970 and −0.986	0.589 and −0.656	0.876 and −0.856

methanol (0.1 M, 1 mL, 0.1 mmol), afterward the obtained transparent green solution was left for evaporation in the air at ambient temperature. Over 12 h the green polycrystalline product was precipitated from the solution. It was filtered off, washed with cold water, and dried in the air. Yield: 85%. Analysis for $Cu_5C_{24}H_{28}N_8O_{22}Cl_2$ (1169.16) calcd: C 24.66, H 2.41, N 9.58. Found: C 24.52, H 2.51, N 9.70. IR (cm^{-1}): 626 ν(Cl−O), 1050 ν(N−O), 1092 ν(Cl−O), 1400, 1555, 1580, 1604, 1629, 3073, 3405w. ESI-MS (in methanol), *m/z* (%): 430.4 (100) [Cu$_5$(**PicHA**-2H)$_4$]$^{2+}$, 798.9 (<1) [Cu$_4$(**PicHA**-H)$_2$ (**PicHA**-2H)$_2$ − H$^+$]$^+$, 961.6 (21) [Cu$_5$(**PicHA**-2H)$_4$$^{2+}$ + ClO$_4$$^-$]$^+$. UV−vis (refl.): 685 nm. Addition of an excess of sodium perchlorate solution in methanol (1 M, 0.3 mL, 0.3 mmol) forced the precipitation of the same compound (**1**) within few minutes.

*[Cu$_4$(PicHA-H)$_2$(PicHA-2H)$_2$](ClO$_4$)$_2$·2DMF (**2**). Method A.* Solution of Cu(ClO$_4$)$_2$·6H$_2$O in methanol (1 M, 0.125 mL, 0.125 mmol) was added to solution of **PicHA** in methanol (1 M, 0.1 mL, 0.1 mmol), afterward the obtained transparent green solution left for evaporation in the air at ambient temperature. The obtained dry solid residue was dissolved in 5 mL DMF at room temperature, and the obtained solution was filtered. Brown single crystals suitable for X-ray analysis were grown by slow diffusion of vapors of diethyl ether into the filtrate at room temperature. Yield: 67%. Analysis for $Cu_4C_{30}H_{32}N_{10}O_{18}Cl_2$ (1145.73) calcd: C 31.45, H 2.82, N 12.23. Found: C 31.49, H 2.86, N 12.02. ESI-MS (in methanol), *m/z* (%): 430.4 (100) [Cu$_5$(**PicHA**-2H)$_4$]$^{2+}$, 798.9 (18) [Cu$_4$(**PicHA**-H)$_2$ (**PicHA**-2H)$_2$ − H$^+$]$^+$, 961.6 (15) [Cu$_5$(**PicHA**-2H)$_4$$^{2+}$ + ClO$_4$$^-$]$^+$. UV−vis (refl.): 586 nm.

Method B. Aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O in methanol (1 M, 0.1 mL, 0.1 mmol) was diluted with DMF (1 mL) and added to solution of **PicHA** in DMF (0.1 M, 1 mL, 0.1 mmol), afterward the obtained transparent green solution was left for crystallization. Brown single crystals suitable for X-ray analysis were grown by slow diffusion of vapors of diethyl ether into the filtrate at room temperature. Yield: 73%.

*[Cu$_8$(PicHA-H)$_4$(PicHA2H)$_4$(DMSO)$_4$(ClO$_4$)$_2$](ClO$_4$)$_2$·2DMSO (**3**). Method A.* Solution of Cu(ClO$_4$)$_2$·6H$_2$O in methanol (1 M, 0.125 mL, 0.125 mmol) was added to solution of **PicHA** in methanol (1 M, 0.1 mL, 0.1 mmol), afterward the obtained transparent green solution left for evaporation in the air at ambient temperature. The obtained dry solid residue was dissolved in 5 mL DMSO at room temperature, and the obtained solution was filtered. Brown single crystals suitable for X-ray analysis were grown by slow diffusion of vapors of isopropanol into the filtrate at room temperature. Yield: 79%. Analysis for $Cu_8C_{60}H_{72}N_{16}O_{38}Cl_4S_6$ (2467.86) calcd: C 29.20, H 2.94, N 9.08. Found: C 29.43, H 3.16, N 8.77. IR (cm^{-1}): 624 ν(Cl−O), 1043 ν(N−O), 1092 ν(Cl−O), 1404, 1555, 1580, 1603, 1630, 3491w. ESI-MS (in methanol), *m/z* (%): 430.4 (100) [Cu$_5$(**PicHA**-2H)$_4$]$^{2+}$, 798.9 (12) [Cu$_4$(**PicHA**-H)$_2$ (**PicHA**-2H)$_2$ − H$^+$]$^+$, 961.6 (15) [Cu$_5$(**PicHA**-2H)$_4$$^{2+}$ + ClO$_4$$^-$]$^+$.

Method B. An aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O in methanol (1 M, 0.1 mL, 0.1 mmol) was diluted with DMSO (1 mL) and added to solution of **PicHA** in DMSO (0.1 M, 1 mL, 0.1 mmol), afterward the obtained transparent green solution left for crystallization. Brown single crystals suitable for X-ray analysis were grown by slow diffusion of vapors of isopropanol into the filtrate at room temperature. Yield: 74%.

*{[Cu$_{12}$(PicHA-H)$_6$(PicHA-H)$_6$(ClO$_4$)$_4$]}$_n$(ClO$_4$)$_{2n}$·3nH$_2$O (**4**).* Solution of Cu(ClO$_4$)$_2$·6H$_2$O in methanol (0.1 M, 1.25 mL, 0.125 mmol) was added to solution of **PicHA** in methanol (0.1 M, 1 mL, 0.1 mmol). To the obtained mixture, an aqueous solution of lithium hydroxide (0.1 M, 1 mL, 0.1 mmol) was added. The obtained solution was placed to the fridge and kept at 4 °C. In 3 weeks, the formed brown single crystals were picked from solution, soaked with filter paper, and dried in the air. Yield: 73%. Analysis for $C_{72}H_{60}Cl_6Cu_{12}N_{24}O_{51}$ (3052.67) calcd: C 28.33, H 1.98, N 11.01. Found: C 29.52, H 2.06, N 10.87. IR (cm^{-1}): 626 ν(Cl−O), 959 ν(N−O), 1092 ν(Cl−O), 1390, 1556, 1587, 1607, 3074, 3447w. ESI-MS (in methanol), *m/z* (%): 430.4 (100) [Cu$_5$(**PicHA**-2H)$_4$]$^{2+}$, 798.9 (<1) [Cu$_4$(**PicHA**-H)$_2$ (**PicHA**-2H)$_2$ − H$^+$]$^+$, 961.7 (15) [Cu$_5$(**PicHA**-2H)$_4$$^{2+}$ + ClO$_4$$^-$]$^+$.

Single Crystal X-ray Analysis. Crystallographic and experimental details of **2**, **3**, and **4** crystal structures determinations are given in Table 1. Measurements were carried out on a Nonius Kappa CCD diffractometer at 120 K with horizontally mounted graphite crystal as a monochromator and Mo−K$_\alpha$ radiation (λ = 0.71073 Å). Data was collected and processed using *Denzo-Scalepack*[7] or *Collect*.[8] A semiempirical absorption correction (*SADABS*[9]) was applied to all data. The structures were solved by direct methods (*SIR2004*[10] or SHELXS-97[11]) and refined by full-matrix least-squares on all F_o^2 (SHELXL-97)[11] anisotropically for all non-hydrogen atoms. Specific refinement details for the structures **2**, **3**, and **4** are given below.

2. The crystal was refined as a twinned structure with twin law [-1 0 0 0 −1 0 0.335 0.724 1], and BASF refined to 0.2177. The OH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.2−1.5U_{eq} (parent atom). Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms, with C−H = 0.95−0.98 Å and U_{iso} = 1.2−1.5U_{eq} (parent atom).

The highest peak is located 0.62 Å from atom H1, and the deepest hole is located 1.03 Å from atom Cu1B.

3. The OH hydrogens were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5U_{eq} (parent atom). Other hydrogens were positioned geometrically and were also constrained to ride on their parent atoms, with C−H = 0.95−0.98 Å, and U_{iso} = 1.2−1.5U_{eq} (parent atom). The highest peak is located 1.16 Å from atom N8 and the deepest hole is located 0.99 Å from atom Cu2.

4. The structure was refined as a racemic twin. The BASF value was refined to 0.27. The H$_2$O hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5U_{eq} (parent atom) or with fixed U_{iso} = 0.1000. Other hydrogen atoms were positioned geometrically and were constrained to ride on their parent atoms, with C−H = 0.95 Å, O−H = 0.84 Å, and U_{iso} = 1.2−1.5U_{eq} (parent atom). Water oxygen O27 as well as ClO$_4$ oxygens O19 and O20 were disordered over two sites with occupancies 0.38/0.62 and 43/57, respectively. Due to the disorder, U_{eq}(max)/U_{eq}(min) remained high. The highest peak is located 0.88 Å from atom O24, and the deepest hole is located 0.76 Å from atom Cu2C.

Bond lengths and angles for structures **2**, **3**, and **4** are given in Supporting Information Tables S1, S3, and S5, respectively. Hydrogen bonds parameters for structures **2**, **3**, and **4** are given in Supporting Information Tables S2, S4, and S6, respectively.

■ RESULTS AND DISCUSSION

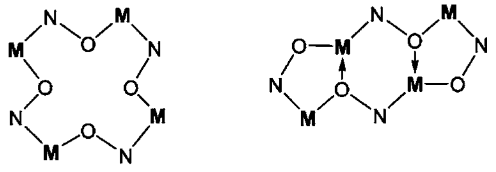
We have performed a series of attempts with the aim of obtaining single crystals of the target pentanuclear 12-MC-4 complexes as products of reaction of copper(II) salts with several α-functionalized hydroxamic acids. In the case of the picoline hydroxamic acid (**PicHA**) we succeeded to isolate single crystals of three compounds grown under different experimental conditions.

The reaction of **PicHA** with copper(II) perchlorate, taken in 1:1.5 to 1.5:1 molar ratio in methanol, results in formation of pentanuclear 12-MC-4 species (Scheme 1a), as the only detectable complex. This is clearly evidenced by the presence of the characteristic isotopic patterns with *m/z* = 430.4 ([Cu$_5$(**PicHA**-2H)$_4$]$^{2+}$) and 961.7 ([Cu$_5$(**PicHA**-2H)$_4$$^{2+}$ + ClO$_4$$^-$]$^+$) in ESI-MS spectra of the reaction mixtures (Supporting Information Figure S1). When the ligand was taken in excess (1:3 metal-to-ligand molar ratio), the ESI mass-spectrum indicated only two signals corresponding to the mononuclear [Cu(**PicHA**-H)$_2$ + H$^+$]$^+$ (*m/z* = 338.0) and binuclear [Cu$_2$(**PicHA**-H)$_2$]$^{2+}$ (*m/z* = 200.0) species. All our efforts to isolate the product corresponding to the pentanuclear species in the form of single crystals suitable for X-ray analysis failed. Instead, the polycrystalline green solid material was obtained, for which the elemental analysis suggested 5:4 metal-to-ligand molar ratio and corroborated the molecular formulas Cu$_5$(**PicHA**-2H)$_4$(ClO$_4$)$_2$·6H$_2$O (**1**). It is evident that **1** is similar to the analogous nitrate and hydrosulfate-containing 12-MC-4 complexes with **PicHA** reported by Lisowski et al.[12] and not characterized crystallographically.

In further attempts to obtain single crystals of the target pentanuclear 12-MC-4 complex, we have performed recrystallization of **1** from various solvents. Upon redissolving the polycrystalline solid **1** in DMF and DMSO, followed by few days of slow diffusion of diethyl ether or isopropanol vapors at room temperature, single crystals of [Cu$_4$(**PicHA**-H)$_2$(**PicHA**-2H)$_2$](ClO$_4$)$_2$·2DMF (**2**) and [Cu$_8$(**PicHA**-H)$_4$(**PicHA**-2H)$_4$(DMSO)$_4$(ClO$_4$)$_2$] (ClO$_4$)$_2$·2DMSO (**3**), respectively, were obtained and characterized crystallographically. The same compounds were obtained when the reactions between copper(II) perchlorate and **PicHA** were conducted in DMF or DMSO, with consequent crystallization of the products from the obtained solutions. Both **2** and **3** contain the tetranuclear collapsed 12-MC-4 molecules[1a] (Scheme 1b). Moreover, by slight change of synthetic conditions (addition of 1 equiv LiOH, keeping at 4 °C for 3 weeks), we succeed to isolate from methanol solution {[Cu$_{12}$(**PicHA**-H)$_6$(**PicHA**-2H)$_6$(ClO$_4$)$_4$]}$_n$(ClO$_4$)$_{2n}$3nH$_2$O (**4**), X-ray analysis of which also confirmed the presence of the collapsed MC structure.

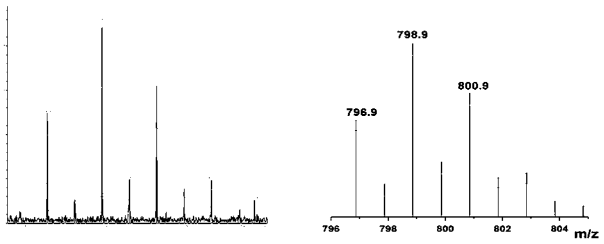
The collapsed MCs do not contain the central guest cations and formally retain the central cavity; however, unlike normal MCs with vacant cavity (Scheme 3a), the ring metal ions are oriented toward the center of the cavity thus forming coordinative bonds with the ring oxygen atoms situated on the opposite side of the metal- lamacrocylic ring (Scheme 3b).[1a] Note that the collapsed 12-MC-4 motif is quite rare, and only few complexes with collapsed MC structure have been reported up to date.[13] All of them are based on the oximate ligands, and only in one reported case the heterometallic Ni^{II}/Mn^{III} tetranuclear complex with collapsed MC structure contained both the oxime and the hydroxamate ligands.[13a] The only reported solely hydroxamate-based compound containing collapsed 12-MC-4 motifs, is a 28-nuclear helicate composed of copper(II) ions and 20 nornvaline-hydroxamates, in which the collapsed MC fragments are united into the helicate macrostructure by additional coordination bonds.[14]

Scheme 3. Normal (a) and Collapsed (b) 12-MC-4 Rings



(*a*) (*b*)

Interestingly, on dissolving **2**−**3** in methanol, the tetranuclear collapsed MC complex molecules undergo nearly complete rearrangement into pentanuclear 12-MC-4 complexes: the ESI-MS spectra of the obtained solutions contain signals corresponding to both the tetranuclear (m/z = 798.9, [Cu$_4$(**PicHA**-H)$_2$ (**PicHA**-2H)$_2$ − H$^+$]$^+$) (Figure 1) and pentanuclear species (Supporting Information Figure S2). The intensity of the signals corresponding to the tetranuclear species is less than 5%, and it is likely that it is minor species while the pentanuclear one is dominating. On the other hand, ESI-MS spectra of **2**−**4** taken in the DMSO−methanol (3:1) mixture reveal both types of patterns with relatively equal intensity (Supporting Information Figure S4). It means that the processes of rearrangement of the tetranuclear species into the pentanuclear complexes is likely to be solvent-dependent, and in aprotic solvents as DMSO and DMF, an equilibrium between these two types of species favors formation of the collapsed MC species in a relatively large extent, while in methanol nearly complete rearrangement into pentanuclear 12-MC-4 complexes occurs. What is more, **4** was crystallized from methanol, although after keeping at decreased temperature for a long period of time. These observations suggest existence of not only complicated solvent-dependent equilibria in solution between the tetra- and pentanuclear species but probably also between the solution and solid phase of growing crystals (i.e., transfer to crystalline phase may favor lost of the fifth copper ion which would result in conversion of significantly tensioned, destabilized pentanuclear structure into stable, planar molecule).



(*a*) (*b*)

Figure 1. Experimental (a) and calculated (b) isotopic patterns for the [Cu$_4$(**PicHA**-H)$_2$(**PicHA**-2H)$_2$$^{2+}$ − H$^+$]$^+$ (m/z = 798.9) species in ESI-MS spectra of **2** in methanol.

The structures of **2**, **3**, and **4** are ionic and consist of the double-charged tetranuclear single-decked [Cu$_4$(**PicHA**-H)$_2$(**PicHA**-2H)$_2$]$^{2+}$ (**2**), octanuclear double-decked [Cu$_8$(**PicHA**-H)$_4$(**PicHA**-2H)$_4$(DMSO)$_4$(ClO$_4$)$_2$]$^{2+}$ (**3**), and dodecanuclear triple-decked [Cu$_{12}$(**PicHA**-H)$_6$(**PicHA**-2H)$_6$(ClO$_4$)$_4$]$^{2+}$ (**4**) complex cations, perchorate anions, and solvent molecules. The complex cations of **4** are united into 1D coordination polymer. As the structures **2**−**4** are essentially similar within the tetranuclear core, we focus our discussion on **2** containing isolated collapsed 12-MC-4 cations.

There are two crystallographically independent centrosymmetric tetranuclear complex cations in **2**, which slightly differ in their geometrical parameters. The complex cations (Figure 2) adopt a nearly planar configuration, with a maximum deviation of the non-hydrogen atoms from their mean plane of 0.256(6) Å and consist of four copper(II) ions and four hydroxamate ligands, organized in such a way that they form the collapsed 12-MC-4 structural motif. The central part of the complex cation contains the six-membered bimetallic ring, with the Cu(2)···Cu(2A) separation of 3.909(2) Å. Six five-membered chelate rings, two of which are bimetallic, are attached to the sides of the central hexagon. In the five-membered bimetallic chelates, the two copper(II) ions are linked by two bridges: the monatomic (—O−) and the diatomic (−N−O−), leading to the Cu(1)···Cu(2) separation = 3.333(1) Å. The other intermetallic distances in the complex cation are the following: Cu(1)···Cu(2A) = 4.693(1), Cu(1)···Cu(1A) = 7.141(2) Å. The coordination number of each copper ion is 4 (distorted

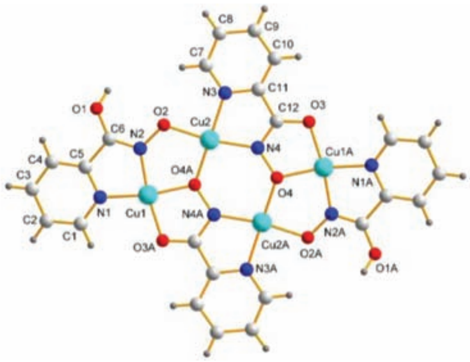


Figure 2. Molecular structure of tetranuclear complex cation (conformer A) $[Cu_4(\mathbf{PicHA}\text{-H})_2(\mathbf{PicHA}\text{-2H})_2]^{2+}$ in **2**. Symmetry code for A: 1 − *x*, 1 − *y*, 1 − *z*.

square-planar environment), as in the crystal packing the closest Cu···O intermolecular contacts are longer than 3 Å.

Two of the ligands' residues in the collapsed 12-MC-4 fragments in **2**−**4** are doubly (N,O)-deprotonated, while two other are monodeprotonated. Noteworthy, the latter hydroxamate functions exist not in the hydroxamic but in the oximic form, as is evidenced by the corresponding C−O, N−O, and C−N bond lengths and also by localization of the hydrogen atom on the C−O (not N−O) oxygen atom (Table 2). Thus, the C−O bond lengths in the monodeprotonated ligands in **2** (1.322(11) and 1.326(7) Å) are noticeably longer when compared with those in the doubly deprotonated ligands (1.295(10) and 1.287(1) Å), even though the oxygen atoms of the later are coordinated. The difference in the N−O bond lengths is even more pronounced: 1.340(5)−1.371(9) Å in the monodeprotonated ligands, against 1.395(6)−1.418(9) Å in the doubly deprotonated ones in **2**−**4**. The former value is typical for the bridging coordinated oxime group, and the latter is typical for the hydroxamic group. The C−N bond lengths are also noticeably different for the two pairs of ligands and are shorter for the monodeprotonated ones (Table 2). Note, that mono- and doubly deprotonated ligands are coordinated in different modes. While (**PicHA**-H) residue chelates Cu(1) ions with two nitrogen atoms and forms the hydroxamate (−N,O−) bridge between Cu(1) and Cu(2), in (**PicHA**-2H) the formation of the (−N,O−) bridge between Cu ions is supported by chelation with the help of the carbonyl oxygen atom O(3). Also, the hydroxamate oxygen O(4) exhibits μ_2-bridging function, forming the Cu(2A)−O(4) coordination bond, so that (**PicHA**-2H) bridges 3 copper ions. Interestingly, the (μ_1-N, μ_1-O) coordination mode of the hydroxamate groups found in (**PicHA**-H) has never been observed before in the hydroxamate complexes.

Table 2. Important Bond Lengths (Å) in the Structures 2, 3, and 4[a]

bond	2	3	4
Cu1—N2	1.894(7), 1.906(7)	1.935(4), 1.946(4)	1.872(4), 1.876(4), 1.891(4), 1.890(4), 1.879(4), 1.879(4)
Cu1—O3[b]	1.913(6), 1.912(6)	1.923(3), 1.926(3)	1.893(4), 1.908(3), 1.910(4), 1.892(4), 1.893(4), 1.884(4)
Cu1—O4[b]	1.917(6), 1.908(6)	1.914(3), 1.895(3)	1.918(4), 1.921(4), 1.922(4), 1.911(5), 1.900(4), 1.922(4)
Cu1—N1	1.950(7), 1.947(7)	1.974(4), 1.989(4)	1.943(5), 1.955(5), 1.946(5), 1.948(5), 1.947(5), 1.934(5)
Cu2—O4[b]	1.909(5), 1.924(6)	1.944(3), 1.936(3)	1.916(4), 1.915(4), 1.915(4), 1.926(4), 1.924(4), 1.920(4)
Cu2—O2	1.925(6), 1.919(6)	1.946(3), 1.966(3)	1.933(4), 1.963(4), 1.955(4), 1.932(4), 1.943(4), 1.934(4)
Cu2—N4	1.951(7), 1.945(7)	1.953(4), 1.963(4)	1.954(5), 1.944(4), 1.948(5), 1.957(5), 1.945(5), 1.945(5)
Cu2—N3	1.984(7), 1.992(6)	2.002(4), 2.015(4)	1.984(4), 1.980(4), 1.978(4), 1.992(5), 1.980(4), 2.001(5)
O2—N2 (protonated)	1.371(9), 1.361(9)	1.346(5), 1.355(5)	1.353(6), 1.340(5), 1.360(6), 1.360(6), 1.366(6), 1.358(6)
O4—N4 (deprotonated)	1.418(9), 1.407(8)	1.407(4), 1.390(4)	1.409(5), 1.408(5), 1.396(6), 1.395(6), 1.398(6), 1.411(5)
O1—C6 (protonated)	1.322(11), 1.326(7)	1.328(5), 1.324(5)	1.340(6), 1.301(6), 1.326(7), 1.288(7), 1.304(6), 1.332(7)
O3—C12 deprotonated)	1.295(10), 1.287(10)	1.285(5), 1.303(5)	1.290(6), 1.282(7), 1.277(7), 1.294(6), 1.280(7), 1.277(6)
N2—C6 (protonated)	1.296(11), 1.296(10)	1.293(5), 1.281(6)	1.269(7), 1.289(7), 1.266(7), 1.290(7), 1.296(7), 1.274(7)
N4—C12 deprotonated)	1.317(11), 1.314(10)	1.316(6), 1.301(6)	1.286(7), 1.309(7), 1.302(7), 1.306(7), 1.318(7), 1.302(7)

[a] The numbering schemes for **3** and **4** used in this table are in accordance with this used for **2** for the sake of convenience. The original numbering schemes for **3** and **4** present in CIF files are different, as the tetranuclear units in **3** and **4** do not have crystallographic centers of symmetry (as in **2**), so that it is impossible to use the same numbering schemes for **2**, **3**, and **4**. [b] Symmetry codes: (i) −*x* + 1, −*y* + 1, −*z* + 1.

In **3**, the equatorial Cu−N and Cu−O distances are somewhat longer (in some cases by ca. 0.04 Å) as compare to the corresponding values found in **2** and **4**. This is probably due to the involvement into dimeric structure, which causes noticeable deviation of Cu atoms from the equatorial donor plane toward the coordinated DMSO molecules. Another consequence of this is more puckered structure of the tetranuclear moiety in **3** (the maximal deviation from the mean plane defined by the non-hydrogen atoms is 0.452(3) Å for O4).

While in **2** the tetranuclear collapsed MC units can be regarded as isolated, in **3** they are dimerized into the double-decked associates, and in **4** they exist in 1D-polymeric chains comprising the triple-decked complex cations. In **3**, two tetranuclear collapsed MC fragments are united in the double-decked octanuclear cation on account of two long Jahn−Teller axial contacts formed between copper(II) ions and the carbonyl oxygen atoms of the neighboring tetranuclear fragment, Cu(1)···O(7) (2 − *x*, −*y*, 2 − *z*) = 2.627(3) Å. The "interdecked" Cu(1)···Cu(1) (2 − *x*, −*y*, 2 − *z*) separation is 3.441(1) Å (Figure 3). The octanuclear cations additionally contain axially coordinated DMSO molecules and perchlorate anions. In **4**, three planar tetranuclear fragments are organized

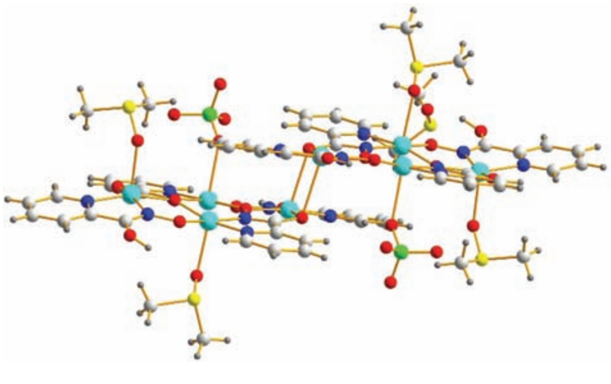


Figure 3. Structure of octanuclear complex cation $[Cu_8(\mathbf{PicHA}\text{-H})_4(\mathbf{PicHA}\text{-2H})_4(DMSO)_4(ClO_4)_2]^{2+}$ in **3**.

into the triple-decked aggregate due to long (2.628(4)−2.777(4) Å) axial Cu···O interdecked contacts (Figure 4). Additional Cu···O axial contacts (2.864(4) and 2.989(4) Å) further join the formed dodecanuclear complex cations into 1D-polymeric chain.

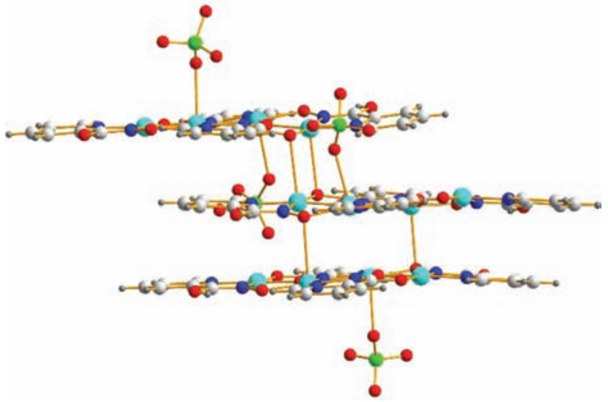


Figure 4. Structure of dodecanuclear fragment $[Cu_{12}$(**PicHA**-H)$_6$(**PicHA**-2H)$_6$ $(ClO_4)_4]^{2+}$ in **4**.

It should be noted that each tetranuclear collapsed MC unit in **2**−**4** structures contains two vacant hydroxyl oxygen atoms situated in close proximity to the potentially μ_3-bridging hydroxamate oxygen atoms, so that they both form a vacant chelating compartment. In the case of the present **PicHA**-containing complexes, this bidentate pocket is shielded by the pyridine rings which hinder in-plane coordination of extra metal ions. In the case of α-aminohydroxamic acids in which the α-nitrogen is not included in the ring, such coordination is possible. For example, in 28-nuclear helicate reported by Pecoraro et al., the tetranuclear collapsed MC fragments are united by copper(II) ions coordinated to two such bindentate (O,O′)-chelating units of the neighboring fragments.[14]

Magnetic susceptibility measurements of **2**, performed in the temperature range 1.8−300 K, show the occurrence of strong antiferromagnetic interactions within the tetranuclar copper(II) core resulting in complete spin coupling at 200 K and indicating realization of the singlet ground state (μ_{eff} value at 300 K is only 0.752 μ_B per 4 copper ions). Such behavior is expected for planar tetranuclear copper(II) complexes with a quadrilateral topology. Magnetization measurements at 2 K in the field range 100−50000 Oe revealed typical saturation behavior caused by mononuclear paramagnetic impurities with $M/N\beta$ value 0.044 at 50000 Oe with corresponds approximately to 0.5% of such impurities with $g = 2.15$. As expected, **2**−**4** are EPR-silent.

■ CONCLUSIONS

In summary, we report the first examples of the exclusively hydroxamate-based Cu(II) 12-MC-4 complexes with a collapse of the metallamacrocyclic cavity. We demonstrate that the collapsed 12-MC-4 species is formed as a result of complex processes of degradation of significantly strained, thermodynamically destabilized pentanuclear 12-MC-4 complex of the picoline hydroxamic acid, being a good representative of α-aminohydroxamic acids in spite of the structural and electronic differences. The question if the pentanuclear 12-MC-4 complexes containing 12 fused five-membered chelating rings could be indeed isolated from solution in the single crystalline state still remains open. The findings depicted here demonstrate that the collapsed 12-MC-4 complexes represent a regular, stable structural motif which can be formed under various conditions. We believe that our results will prompt future studies on the reactivity of collapsed MCs which offer several interesting directions: (i) the possibility of axial coordination to the metal ions, which in the present work resulted in the formation of oligonuclear aggregates and coordination polymers; (ii) the variety of rearrangement processes, in particular induced by reagents able to "open" the collapsed cavity (e.g., lanthanides); (iii) the use of the collapsed 12-MC-4 as building blocks for the preparation of discrete higher nuclearity assemblies via coordination of the vacant peripheral oxygen atoms, as it was observed in the 28-nuclear helicate complex.[14] Such studies are underway in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

ESI-MS spectra of **1**, **2**, and **4**; single crystal X-ray diffraction data and CIF files for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The financial support from the State Fund for Fundamental Researches of Ukraine (grant No. F40.3/041), the Polish Ministry of Science and Higher Education (N N204 308137), and the Swedish Institute (Visby Program) is gratefully acknowledged.

■ REFERENCES

(1) (a) Pecoraro, V. L.; Stemmler, A. J.; Gibney, B. R.; Bodwin, J. J.; Wang, H.; Kampf, J. W.; Barwinski, A. *Prog. Inorg. Chem.* **1997**, *45*, 83. (b) Mezei, G.; Zaleski, C. M.; Pecoraro, V. L. *Chem. Rev.* **2007**, *107*, 4933. (c) Tegoni, M.; Remelli, M. *Coord. Chem. Rev.* **2012**, *256*, 289.

(2) Jankolovits, J.; Andolina, C. M.; Kampf, J. W.; Raymond, K. N.; Pecoraro, V. L. *Angew. Chem. Intl. Ed.* **2011**, *50*, 9660.

(3) (a) Pavlishchuk, A. V.; Kolotilov, S. V.; Fritsky, I. O.; Zeller, M.; Addison, A. W.; Hunter, A. D. *Acta Cryst. C* **2011**, *67*, m255. (b) Pavlishchuk, A. V.; Kolotilov, S. V.; Zeller, M.; Shvets, O. V.; Fritsky, I. O.; Lofland, S. E.; Addison, A. W.; Hunter, A. D. *Eur. J. Inorg. Chem.* **2011**, 4826. (c) Pavlishchuk, A. V.; Kolotilov, S. V.; Zeller, M.; Thompson, L. K.; Fritsky, I. O.; Addison, A. W.; Hunter, A. D. *Eur. J. Inorg. Chem.* **2010**, 4851.

(4) Boron, T. T., III; Kampf, J. W.; Pecoraro, V. L. *Inorg. Chem.* **2010**, *49*, 9104.

(5) (a) Kurzak, B.; Farkas, E.; Glowiak, T.; Kozlowski, H. *J. Chem. Soc., Dalton Trans.* **1991**, 163. (b) Tegoni, M.; Remelli, M.; Bacco, D.; Marchio, L.; Dallavalle, F. *Dalton Trans.* **2008**, 2693. (c) Dallavalle, F.; Tegoni, M. *Polyhedron* **2001**, *20*, 2697. (d) Careri, M.; Dallavalle, F.; Tegoni, M.; Zagnoni, I. *J. Inorg. Biochem.* **2003**, *93*, 174. (e) Pacco, A.; Parac-Vogt, T. N.; van Besien, E.; Pierloot, K.; Gorller-Walrand, C.; Binnemans, K. *Eur. J. Inorg. Chem.* **2005**, 3303. (f) Parac-Vogt, T. N.; Pacco, A.; Gorller-Walrand, C.; Binnemans, K. *J. Inorg. Biochem.* **2005**, *99*, 497.

(6) Hynes, J. B. *J. Med. Chem.* **1970**, *13*, 1235.

(7) Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode*; Academic Press: New York, 1997.

(8) *COLLECT*; Nonius BV, Delft, The Netherlands, 2000.

(9) Sheldrick, G. M. *SADABS*, v 2.10 ed.; Bruker AXS, Inc.: Madison, WI, 2003.

(10) Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **2005**, *38*, 381.

(11) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.

(12) Seda, S. H.; Janczak, J.; Lisowski, J. *Inorg. Chim. Acta* **2006**, *359*, 1055.

(13) (a) Psomas, G.; Stemmler, A. J.; Dendrinou-Samara, C.; Bodwin, J. J.; Schneider, M.; Alexiou, M.; Kampf, J. W.; Kessissoglou, D. P.; Pecoraro, V. L. *Inorg. Chem.* **2001**, *40*, 1562. (b) Bertrand, J. A.; Smith, J. H.; Vanderveer, D. G. *Inorg. Chem.* **1977**, *16*, 1477. (c) Saarinen, H.; Orama, M.; Korvenranta, J. *Acta Chem. Scand.* **1989**, *43*, 834. (d) Orama, M.; Saarinen, H.; Korvenranta, J. *J. Coord. Chem.* **1990**, *22*, 183. (e) Orama, M.; Saarinen, H.; Korvenranta, J. *Acta Chem. Scand.* **1994**, *48*, 127. (f) Papatriantafyllopoulou, C.; Jones, L. F.; Nguyen, T. D.; Matamoros-Salvador, N.; Cunha-Silva, L.; Almeida Paz, F. A.; Rocha, J.; Evangelisti, M.; Brechin, E. K.; Perlepes, S. P. *Dalton Trans.* **2008**, 3153−3155. (g) Ji, C. M.; Yang, H. J.; Zhao, C. C.; Tangoulis, V.; Cui, A. L.; Kou, H. Z. *Cryst. Growth Des.* **2009**, *9*, 4607−4609. (h) Kou, H. Z.; An, G. Y.; Ji, C. M.; Wang, B. W.; Cui, A. L. *Dalton Trans.* **2010**, *39*, 9604. (i) Afrati, T.; Zaleski, C. M.; Dendrinou-Samara, C.; Mezei, G.; Kampf, J. W.; Pecoraro, V. L.; Kessissoglou, D. P. *Dalton Trans.* **1997**, 2658.

(14) Johnson, J. A.; Kampf, J. W.; Pecoraro, V. L. *Angew. Chem. Intl. Ed.* **2003**, *42*, 546.