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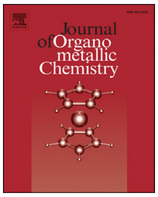

Syntheses and solid state structures of cyclam-based copper and zinc compounds

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ABSTRACT

Copper(II) and zinc(II) complexes of general formula $[\{H_2(4-{}^tBuPhCH_2)_2Cyclam\}Cu]SO_4$, **1**, $[\{H_2(PhCH_2)_2Cyclam\}Cu]X$, ($X = SO_4$, **2**; $X = (CH_3COO)_2$, **3**), $[\{H_2(PhCH_2)_2Cyclam\}Zn]SO_4$, **5**, and $[\{H_2(PhCH_2)_2Cyclam)\}ZnCl]Cl$, **6**, were prepared by reaction of $H_2Bn_2Cyclam$ ($Bn = PhCH_2$ or $4-{}^tBuPhCH_2$) with one equiv. of the appropriate Cu(II) or Zn(II) salt.

The preparation of Cu(II) complexes of general formula $[\{H_2(MeOCH_2)_2Cyclam\}Cu]X$ ($X = SO_4$, **7**, $(CH_3COO)_2$, **8**, and $CuCl_4$, **9**) displaying a modified cyclam ligand with two *N*-CH_2OMe pending arms was achieved by nucleophilic attack of methanol to the bridging methylene groups of 1,4,8,11-tetraazatricyclo[9.3.1.1^{4,8}]hexadecane in a Cu^{2+} mediated process.

1. Introduction

The field of macrocyclic complexes is extremely wide due to the diverse uses found for that kind of compounds in catalysis [1], selective metal recovery and recycling [2], sensors [3] and therapy and diagnosis [4]. Among other macrocyclic ligands, cyclens and cyclams were extensively studied because they are able to accommodate and stabilize a large variety of metal cations in several oxidation states [5]. Copper(II) complexes based on such ligands display high thermodynamic stability with respect to metal dissociation as well as interesting electrochemical properties. The properties of tetra-*N*-functionalized cyclams are quite different from those of the unsubstituted parent macrocyclic compounds [6]. Moreover, coordinative pendant arms on the nitrogen atoms allow the tuning of the properties and the selectivity for particular metal ions [7]. The establishment of selective synthetic procedures for tetrazamacrocyclic compounds is thus an important topic. *Trans-N,N′*-disubstituted cyclams may be obtained by reactions of the bisaminal cyclam 1,4,8,11-tetraazatricyclo[9.3.1.1^{4,8}]hexadecane with electrophiles [8]. Those reactions are highly selective because the stereochemical conformation imposed by the methylene cross-bridges forces *trans*-nitrogen atoms lone pairs to point out of the macrocycle backbone, making them the less sterically hindered and simultaneously the most negative atoms [8]. The reactions of 3,14-dimethyl-2,6,13,17-tetraazapentacyclo[16.4.1$^{2.17}$.1$^{6.13}$.0.0$^{7.12}$]tetracosane or 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazatricyclo[9.3.1.1^{4,8}]hexadecane with $Cu(ClO_4)_2 \cdot 6H_2O$ in methanol were reported to give metal complexes displaying *trans-N,N′*-CH_2OMe cyclam ligands [9].

In recent years we have been using dianionic *trans-N,N′*-disubstituted cyclams as supporting ligands for early metals, namely block-s metals (Mg) [10], lanthanides (Ln) [11] and particularly, early transition metals ((Zr, Hf)) [12]. The results obtained allowed us establishing structure/reactivity relations that where explored in catalytic applications such as polymerization [13] and hydroamination [14]. A new method for cyclams functionalization was attained using $(Bn_2Cyclam)ZrX_2$ complexes and several heteroallenes [15]. An extension of this work to the chemistry of late transition metals is presented here where the synthesis and characterization of new copper(II) and zinc(II) complexes anchored by *trans-N,N′*-disubstituted cyclams are described.

2. Results and discussion

Trans-N,N′-disubstituted cyclams of the type $H_2Bn_2Cyclam$ ($Bn = PhCH_2$ or $4-{}^tBuPhCH_2$) react with one equiv. of zinc(II) or copper(II) salts to afford $[\{H_2(4-{}^tBuPhCH_2)_2Cyclam\}Cu]SO_4$, **1**,

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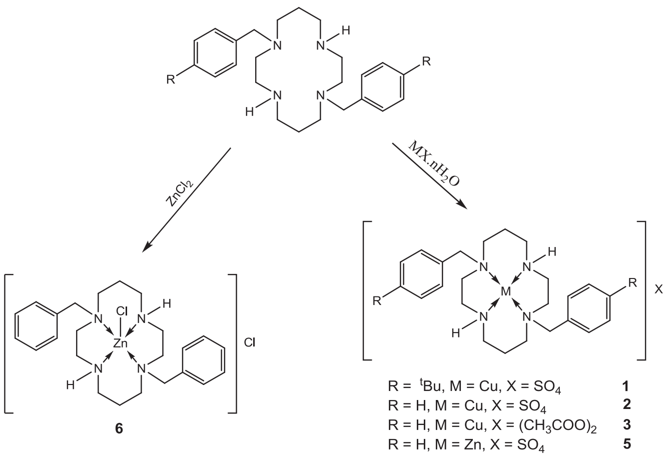
[$\{H_2(PhCH_2)_2Cyclam\}Cu$]X, (X = SO_4, **2**; X = $(CH_3COO)_2$, **3**), [$\{H_2(PhCH_2)_2Cyclam\}Zn$]$SO_4$, **5**, and [$\{H_2(PhCH_2)_2Cyclam\}ZnCl$]Cl, **6**, as shown in Scheme 1.



Scheme 1.

The IR spectra of complexes **1**–**3**, **5** and **6** show that the ligand frame bands are sensitive to metal complexation and deviate to higher wavenumbers in comparison with the values obtained for the free ligands. In the spectra of complexes **1**, **2** and **5** strong bands due to the sulphate ion are observed in the ranges 1103–1020 cm^{-1} and 632–619 cm^{-1} for the anti-symmetric stretching and bending vibration modes, respectively. In complex **3**, the $\nu_{C=O}$ band corresponding to the acetate ion shows up at 1560 cm^{-1}. Complexes **1**–**3** are paramagnetic having magnetic moments of 1.6 MB, 1.8 MB and 1.9 MB, respectively, in agreement with the presence of a Cu(II) metal center.

The reaction of $H_2(PhCH_2)_2$Cyclam with $CuSO_4 \cdot 5H_2O$ depends on the solvent. If performed in methanol [$\{H_2(PhCH_2)_2Cyclam\}Cu$]$SO_4$, **2**, is the unique product obtained. When a mixture of CH_3CN/H_2O is used as solvent, along with the formation of **2**, few pink crystals of [$\{H_2(PhCH_2)_2Cyclam\}Cu(H_2O)_2$]S, **4**, were also obtained. The formation of **4** attests the reduction of SO_4^{2-} to S^{2-} and is reminiscent of the biological role of enzymes in the $SO_4^{2-}/SO_3^{2-}/S^{2-}$ reducing chain [16]. Complex **4** was identified by mass spectrometry and single crystal X-ray diffraction. Its molecular structure is shown in Fig. 1a and relevant distances and angles are shown in Table 1. Crystallographic and experimental details of data collection and crystal structure determination are presented in Table 4.

Table 1
Selected distances (Å) and angles (°) of the compounds **4**, **6**, **7** and **9**.

	Ligand set				Substituents	
	M–N(1)	M–N(2)	M–N(3)	M–N(4)	M–O	M–Cl
4	2.094(2)	1.992(2)	–	–	2.670(4)	–
6a	2.283(3)	2.063(3)	2.313(3)	2.056(3)	–	2.247(1)
6b	2.333(4)	2.052(4)	2.295(3)	2.065(3)	–	2.235(1)
7a	2.108(3)	1.995(2)	–	–	2.440(2)	–
7b	2.113(2)	2.000(3)	–	–	2.395(2)	–
9	2.025(3)	2.009(3)	2.040(3)	2.006(3)	2.444(3)	2.846(3)

	N_{eq}–M–N'_{eq}		N_{eq}–M–Cl_{eq}	N_{eq}–M–Cl_{eq}	X_{ax}–M–X'_{ax}
4	86.58(7)	93.42(7)			180.00
6a	120.9(1)		118.6(1)	120.5(1)	159.6(1)
6b	107.9(2)		128.3(2)	123.8(1)	165.0(1)
7a	86.6(1)	93.4(1)	–	–	180.00(8)
7b	86.3(1)	93.7(1)	–	–	180.0
9	85.6(1)	86.8(1)	–	–	151.27

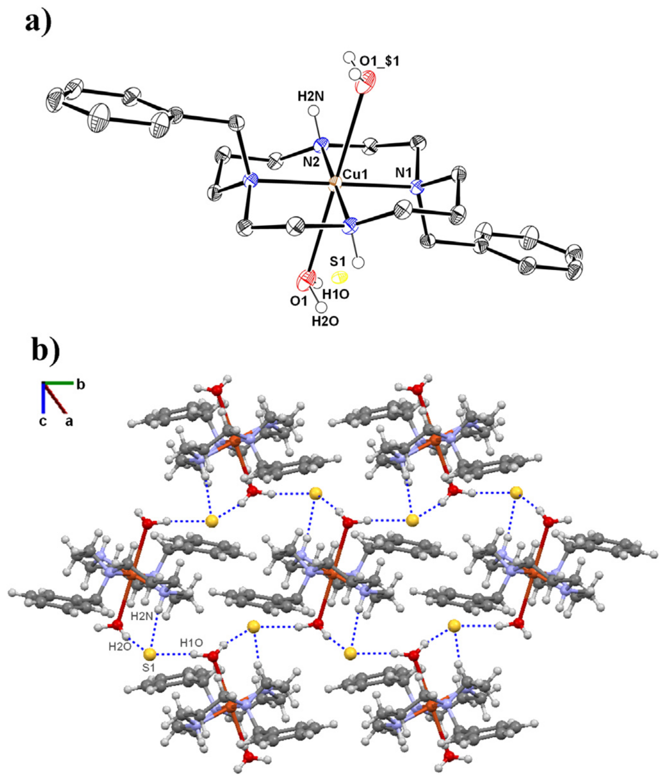


Fig. 1. a) ORTEP diagram of [$\{H_2(PhCH_2)_2Cyclam\}Cu(H_2O)_2$]S, **4**, showing thermal ellipsoids at 40% probability level. Half molecule is generated by symmetry. Selected hydrogen atoms are omitted for clarity; b) Best view of **4** revealing the hydrogen bonds between S(1) and H(1O), H(2O) and H(2N) atoms (*dashed lines*).

The coordination geometry of copper is octahedral. The equatorial plane is defined by the four nitrogen atoms of the cyclam ring with internal N–Cu–N angles close to 90° and the axial positions are occupied by two water molecules. The data obtained for complex **4** are similar to those reported for other octahedral Cu(II) complexes displaying cyclams and two axial water molecules [17], in particular, [H_2\{1,5,8,12-tetramethyl-1,8,11-tetraazacyclotetradecane\}$Cu(H_2O)_2$]X (X = NO_2, Br, Cl, I) [17a]. The two benzyl substituents are located at opposite sides of the cyclam ring defining a *trans*-III configuration that corresponds to the most stable diastereomer in octahedral cyclam complexes [18]. Hydrogen bonds are established between S(1) and the hydrogen atoms H(1O), H(2O) and H(2N) with distances of 2.210, 2.315 and 2.323 Å, respectively, as shown in Fig. 1b (see Table 2 for details).

Table 2
Hydrogen bond distances (Å) and angles (°) of the compounds **4**, **6**, **7** and **9**.

Compound	D–H···A	d (D–H)	d (H···A)	d (D···A)	(DĤA)
4	O(1)–H(1O)···S(1)	0.959	2.210	3.161	171.73
	O(1)–H(2O)···S(1)	0.911	2.315	3.196	162.56
	N(2)–H(2N)···S(1)	0.916	2.323	3.231	171.61
6a	N(4)–H(4N)···Cl(2)	0.889	2.341	3.186	158.70
6b	N(8)–H(8N)···Cl(4)	0.843	2.593	3.354	150.70
7a	N(2)–H(2N)···O(5)	0.825	2.078	2.892	168.52
7b	N(4)–H(4N)···O(6)	0.783	2.145	2.918	169.42
9	N(2)–H(2N)···Cl(1)	0.855	2.445	3.282	166.14

The ^1H NMR spectra of compounds [$\{H_2(PhCH_2)_2Cyclam\}Zn$]$SO_4$, **5**, and [$\{H_2(PhCH_2)_2Cyclam\}ZnCl$]Cl, **6**, display ten chemically non-equivalent resonances corresponding to the macrocyclic protons of the [C2] and [C3] cyclam chains in agreement with average C_2 symmetry. The benzyl protons are diastereotopic and appear as AB systems exhibiting coupling constants

${}^{2}J_{H-H}$ of 19 and 15 Hz for **5** and **6**, respectively. The $^{13}C\{^{1}H\}$ NMR spectra are in conformity with the proton data showing six resonances for the ligand methylene carbons and one set of aromatic signals.

Crystals of complex **6** suitable for X-ray diffraction were obtained from slow evaporation of an aqueous solution (crystallographic and experimental details are presented in Table 4). Compound **6** crystallized in the triclinic space group P-1 with two molecules in the asymmetric unit (**6a** and **6b**). An ORTEP depiction of the molecular structure of **6a** is shown in Fig. 2 and relevant distances and angles are presented in Table 1.

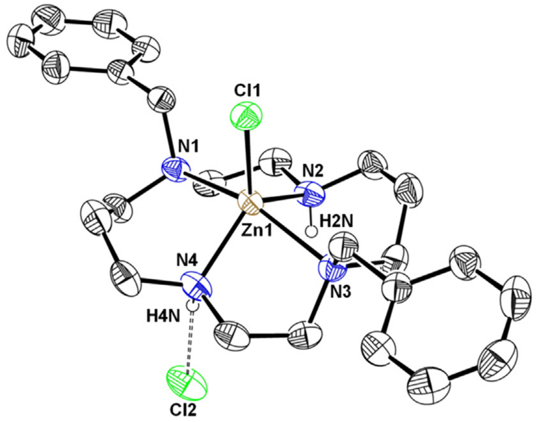
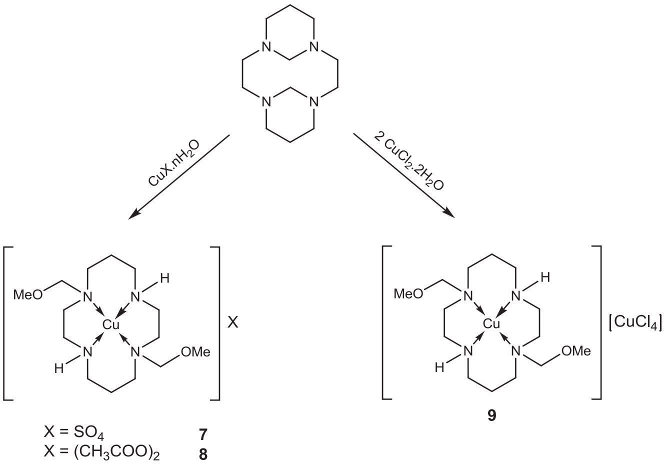


Fig. 2. ORTEP diagram of $[\{H_2(PhCH_2)_2Cyclam\}ZnCl]Cl$, **6a**, showing thermal ellipsoids at 35% probability level. Selected hydrogen atoms are omitted for clarity. Hydrogen bond is represented by dashed line.

The coordination geometry around the zinc is trigonal bipyramidal as observed in other pentacoordinated zinc cyclam complexes [19]. The equatorial plane is defined by N(2), N(4) and Cl(1) atoms. The axial positions are occupied by the other two nitrogen atoms of the macrocycle with N(1)–Zn(1)–N(3) angle of 159.6(1)° in **6a** and 165.0(1)° in **6b**. In general, the distances and angles determined for **6a** and **6b** are in agreement with values reported [20]. The counter-ion is in the proximity of one NH group of the cyclam ring with which it forms a Cl···H···N bridge (see Table 2 for details).

The compounds presented in Scheme 2, with general formula $[\{H_2(MeOCH_2)_2Cyclam\}Cu]X$ ($X = SO_4$, **7**, $(CH_3COO)_2$, **8**, and $[CuCl_4]$, **9**) were obtained from reactions of 1,4,8,11-tetraazatricyclo[9.3.1.1^{4,8}]hexadecane with the corresponding Cu(II) salts in methanol. A comparable procedure was reported for the preparation of other copper cyclam derivatives using $Cu(ClO_4)_2 \cdot 6H_2O$ [9]. Complex **9** is obtained independently of the reaction being performed with one or two equiv. of $CuCl_2 \cdot 2H_2O$.



Scheme 2.

The role of Cu^{2+} is critical for the outcome of the reactions once it is only in the presence of copper that the bridging methylene carbons are activated for nucleophilic attack by methanol.

In the IR spectra of complexes **7**–**9** the ν_{N-H} bands are observed in the range 3159–2946 cm^{-1}. The $\nu_{S=O}$ bonds in **7** give rise to a broad band at 1108–1020 cm^{-1} and one sharp band at 620 cm^{-1} and the $\nu_{C=O}$ bands in **8** show up at 1622 and 1569 cm^{-1}.

The magnetic moments of compounds **7**–**9** are 1.6 MB, 1.7 MB and 2.1 Bohr magnetons, respectively, in agreement with their formulations. The EPR spectra are shown in Fig. 3 and the experimental spin Hamiltonian parameters are presented in Table 3.

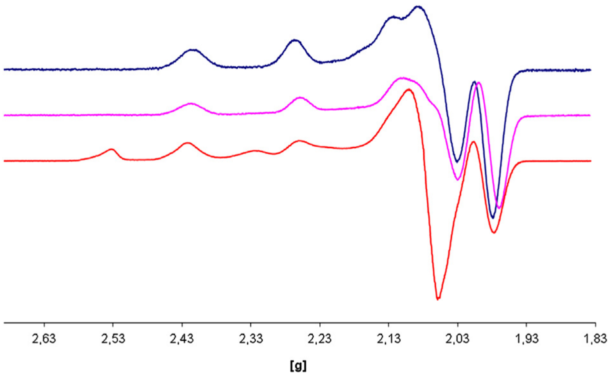


Fig. 3. First derivative X-band EPR spectra of compounds **7** (*top*), **8** (*middle*) and **9** (*bottom*) recorded at 77 K in ethyleneglycol.

In general, the spectra are typical of essentially tetragonal Cu(II) complexes with a d_{x2-y2} ground state ($g_z > g_x, g_y > g_e$) [21], which means that in solution the copper is coordinated to the four nitrogen atoms of the cyclam ring and no bonding to either the pending arms or the anions are observed.

Table 3
Experimental spin Hamiltonian parameters for compounds **7**–**9**.[a]

	g_x, g_y (or $g_\perp$)	A_x, A_y (or $A_\perp$) $\times 10^{-4}$ cm^{-1}	g_z (or $g_{\|}$)	A_z (or $A_{\|}$) $\times 10^{-4}$ cm^{-1}	g_z/A_z cm
7	2.045	15.3	2.190	193.9	112
8	2.067	16.9	2.187	200.2	109
	2.013	21.7			
9	2.094	1.9	2.190	200.0	109
	2.060	1.1			
$[CuCl_4]^{2-}$			2.385	139.0	171

[a] EPR spectra measured at 77 K in ethyleneglycol.

The values of g_z and A_z for complexes **7**–**9** were plotted in a Peisach–Blumberg [22] representation and are consistent with a $[CuN_4]$ core in solution with g_z/A_z ratios of 112 cm for **7** and 109 cm for **8** and **9** revealing that the geometry around the metal center is square-planar for all complexes. In the case of **9**, it is possible to observe the hyperfine signals that are assigned to the $[CuCl_4]^{2-}$ counter-anion. The significantly higher g_z/A_z ratio found for the $[CuCl_4]^{2-}$ species is indicative of its tetrahedral geometry. Moreover, there is no observable indication of spin–spin coupling between $[CuN_4]$ and $[CuCl_4]^{2-}$ cores.

Crystals of **7** and **9** were obtained from slow evaporation of methanol solutions at room temperature. Compounds **7** and **9** crystallized in the monoclinic $P2_1/n$ space group. The asymmetric unit of **7** displays two molecules (**7a** and **7b**). Relevant distances and angles are shown in Table 1 and crystallographic and experimental details of data collection and crystal structure determinations are presented in Table 4.

Table 4
Crystal data and structure refinement for complexes **4**, **6**, **7** and **9**.

Compound	**4**	**6**	**7**·$(CH_3OH)_2$	**9**
Empirical formula	$C_{24}H_{40}CuN_4O_2S2$	$C_{24}H_{36}C_{l2}N_4Zn$	$C_{16}H_{40}CuN_4O_8S$	$C_{14}H_{32}C_{l4}Cu_2N_4O_2$
Formula weight	544.29	516.86	512.14	557.34
Temperature (K)	150	302	150	150
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_1/n$	$P2_1/n$
Unit cell dimensions:				
a (Å)	9.8760(4)	9.584(1)	11.291(1)	10.026(3)
b (Å)	9.8668(5)	12.661(1)	13.327(1)	15.934(2)
c (Å)	13.2932(6)	23.035(3)	17.455(2)	14.438(2)
α(°)	90	88.848(4)	90	90
β(°)	94.243(2)	82.146(4)	98.260(4)	95.93(1)
γ(°)	90	68.358(4)	90	90
Volume (Å^3)	1291.8(1)	2572.3(5)	2599.3(4)	2294.2(8)
Z	2	4	4	4
Calculated density (g m^{-3})	1.399	1.335	1.309	1.613
Absorption coefficient (mm^{-1})	1.036	1.181	0.963	2.336
F (000)	578	1088	1092	1144
Crystal size (mm)	0.08 × 0.10 × 0.20	0.20 × 0.20 × 0.20	0.30 × 0.30 × 0.30	0.02 × 0.06 × 0.10
Theta range for data collection (°)	2.57–29.60	2.32–25.38	1.93–27.21	1.91–25.77
Limiting indices	$-13 \le h \le 13$, $-13 \le k \le 13$, $-18 \le l \le 18$	$-11 \le h \le 11$, $-15 \le k \le 15$, $-27 \le l \le 27$	$-14 \le h \le 14$, $-15 \le k \le 17$, $-22 \le l \le 22$	$-12 \le h \le 12$, $-19 \le k \le 19$, $-17 \le l \le 17$
Reflections collected/unique [R_{int}]	23,227/3631 [0.0497]	80,203/9444 [0.0373]	39,447/5756 [0.0352]	28,985/4365 [0.0695]
Completeness to θ (%)	99.9 ($\theta = 29.60$)	99.5 ($\theta = 25.38$)	99.1 ($\theta = 27.21$)	99.1 ($\theta = 25.77$)
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	3631/0/163	9444/0/569	5756/0/288	4365/0/244
Goodness-of-fit on F^2	1.087	1.047	1.055	1.058
Final *R* indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0390$, $wR_2 = 0.1158$	$R_1 = 0.0596$, $wR_2 = 0.1580$	$R_1 = 0.0472$, $wR_2 = 0.1246$	$R_1 = 0.0409$, $wR_2 = 0.0815$
R indices (all data)[a]	$R_1 = 0.0507$, $wR_2 = 0.1211$	$R_1 = 0.0695$, $wR_2 = 0.1656$	$R_1 = 0.0648$, $wR_2 = 0.1326$	$R_1 = 0.0645$, $wR_2 = 0.0877$
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Largest diff. peak/hole (e Å^{-3})	1.182 and −0.609	1.669 and −1.390	0.931 and −0.676	0.711 and −0.422

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

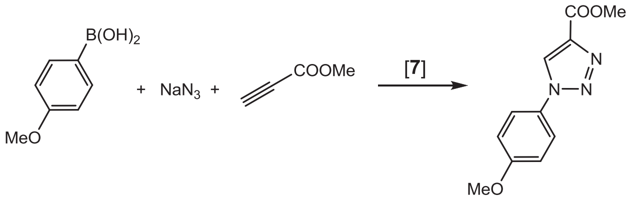
The molecular structures of complexes **7** and **9** show that the SO_4^{2-} anions and $[CuCl_4]^{2-}$ have a determining role in the solid state conformations of the macrocycle ring as well as in the supramolecular structures adopted by the complexes, as discussed below.

Compound **7** reveals a linear polymeric structure growing in the *b* direction as shown in Fig. 4a. The average planes defined by two consecutive cyclam rings of molecules **7a** and **7b** define dihedral angles of 31.30°, leading to a zigzag arrangement (Fig. 4b). This supramolecular architecture is maintained by hydrogen bonds between the oxygen atoms of the sulphate anion and NH groups of the macrocyclic rings (see details in Table 2).

The coordination of copper is octahedral with four nitrogen atoms of the macrocycle defining the equatorial plane and two oxygen atoms of sulphate ions at the axial positions (Fig. 4c). The Cu—N and Cu—O bond distances are within the ranges observed for other compounds [20]. The *N*-CH_2OMe pending arms attached to the *trans*-nitrogen atoms of the cyclam ring point in opposite directions in relation to the average [N4] plane resulting in *trans*-II conformation of the complex [18].

The supramolecular arrangement in **9** is shown in Fig. 5a and an ORTEP view of the molecular structure is presented in Fig. 5b. The complex shows a *trans*-III conformation with the two *N*-CH_2OMe pending arms directed to the same side of the average nitrogen plane of cyclam [18]. The coordination geometry of copper is distorted octahedral in the cation and tetrahedral in the anion. The equatorial plane of the cation is defined by the four nitrogen atoms of the cyclam ring and presents very regular Cu—N bond lengths and N—Cu—N angles, in agreement with other copper cyclam complexes [6b,17a,23]. The two axial positions are occupied by the oxygen atom of one CH_2OMe group and by a chlorine atom that bridges the metal centers of the cation and the anion. The angle O(2)—Cu(1)—(Cl3_$1) deviates from linearity with a value of 151.27°. The $[CuCl_4]^{2-}$ anions are responsible for the polymeric arrangement observed in the crystal. One hydrogen bond between a NH group of cyclam and the Cl(1) atom of $[CuCl_4]^{2-}$ and a chlorine bridge between the cation and another $[CuCl_4]^{2-}$ anion originate a chain with alternating cations and anions. The Cu(1)—Cl(3_$1)—Cu(2_$1) bridge is very asymmetric with the Cu(1)—Cl(3_$1) bond much longer than Cu(2_$1)—Cl(3_$1). The latter bond distance is also longer than the terminal Cu—Cl bonds in the anion, in agreement with its bridging position between the two copper centers.

Copper compounds have been used as catalyst for the click reaction between aryl halides, sodium azide and terminal alkynes leading to the synthesis of triazoles [24]. An alternative procedure for click reactions was described using aryl boronic acids, sodium azide and terminal alkynes [25]. Using the latter procedure, preliminary tests revealed that complex $[\{H_2(MeOCH_2)_2Cyclam\}Cu]SO_4$, **7**, is an efficient catalyst for the preparation of methyl 1-(4-methoxyphenyl)-1*H*-1,2,3-triazole-4-carboxylate according to Equation (1). The reaction led to the quantitative and selective formation of the 1,4-isomer in 24 h at 55 °C.



(1)

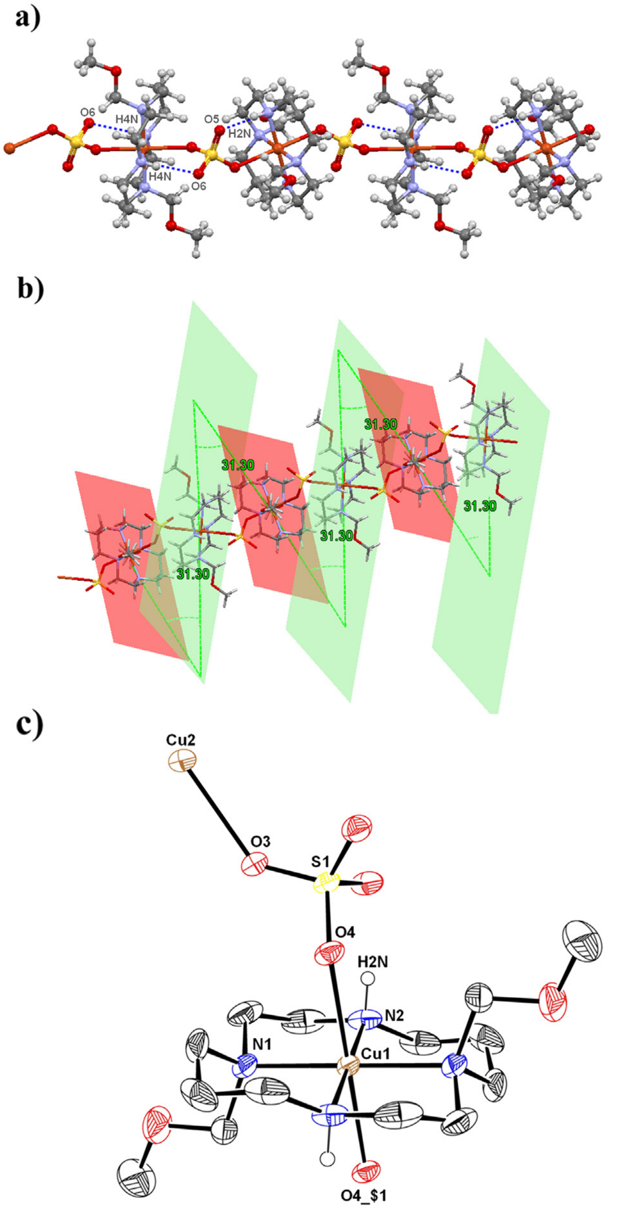


Fig. 4. a) View along *a* of the supramolecular arrangement in compound **7**: the chain grows in the *b* direction. Hydrogen bonds are shown by dashed lines; b) View of dihedral angles between the average [N4] planes of **7a** and **7b** creating a zigzag arrangement; c) ORTEP diagram of [{$H_2(MeOCH_2)_2$Cyclam}Cu]SO_4, **7a**, showing thermal ellipsoids at 40% probability level. Half molecule is generated by symmetry. Selected hydrogen atoms are omitted for clarity.

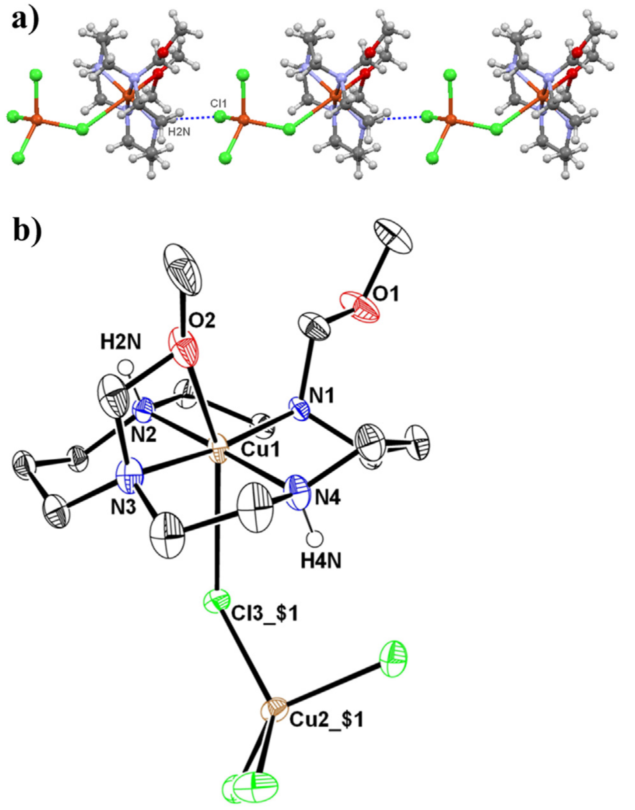


Fig. 5. a) View along *c* of the supramolecular arrangement in compound **9**: the chain grows in the *a* direction. Hydrogen bonds are shown as dashed lines; b) ORTEP diagram of [{$H_2(MeOCH_2)_2$Cyclam}Cu][$CuCl_4$], **9**, showing thermal ellipsoids at 40% probability level. Selected hydrogen atoms are omitted for clarity.

3. Experimental section

3.1. General considerations

$H_2(PhCH_2)_2$Cyclam, $H_2(4-{}^tBuPhCH_2)_2$Cyclam and 1,4,8,11-tetraazatricyclo[9.3.1.14,8]hexadecane were prepared according to described procedures [8,13a]. All other reagents were commercial grade and used without further purification. NMR spectra were recorded in a Bruker AVANCE II 400 MHz spectrometer, at 296 K unless stated otherwise, referenced internally to residual proton-solvent (^{1}H) or solvent (^{13}C) resonances, and reported relative to tetramethylsilane (0 ppm). $^1H-^{13}C\{^1H\}$ HSQC NMR experiments were performed in order to make all the assignments. Elemental analyses were obtained from Laboratório de Análises do IST. FT-IR spectra were recorded on a Jasco FT/IR-4100 spectrometer at IST. EPR spectra were recorded at 77 K (on glasses made by freezing solutions in liquid nitrogen) in a Bruker ESP 300E X-band spectrometer at IST. The measured spectra (1st derivative X-band EPR) were simulated with the EPR simulation software developed by Rockenbauer and Korecz [26]. Magnetic Susceptibility was measured at 298 K on a Magway MSB Mk1 Magnetic Susceptibility Balance at IST.

3.2. Synthetic procedures

3.2.1. Synthesis of [{$H_2(4-{}^tBuPhCH_2)_2$Cyclam}Cu]SO_4 (**1**)

$H_2(4-{}^tBuPhCH_2)_2$Cyclam (0.50 g, 1.01 mmol) was dissolved in 50 mL of MeOH and one equiv. of $CuSO_4\cdot 5H_2O$ (0.25 g, 1.01 mmol) was added at room temperature. The blue solution turned violet and it was left stirring for 4 h. After filtration and evaporation of the solvent to dryness, the compound was obtained as a violet solid in 81% yield (0.58 g, 0.82 mmol). Anal. calcd for $C_{32}H_{52}CuN_4O_4S\cdot 3H_2O$: C, 54.41; H, 8.28; N, 7.93; S, 4.54. Found: C, 54.93; H, 8.17; N, 7.62; S, 4.64. FT-IR (KBr, cm^{-1}): 3127 (ν_{NH}), 1119, 1078 and 620 (ν_{SO4}). $\chi_m = 1.0 \times 10^{-3}$ cgs ($\mu = 1.6$ Bohr magnetons).

3.2.2. Synthesis of [{$H_2(PhCH_2)_2$Cyclam}Cu]SO_4 (**2**) and [{$H_2(PhCH_2)_2$Cyclam}$Cu(H_2O)_2$]S (**4**)

Method A: $H_2(PhCH_2)_2$Cyclam (0.50 g, 1.32 mmol) was dissolved in 50 ml of CH_3CN/H_2O (3:1) and one equiv. of $CuSO_4.5H_2O$ (0.33 g, 1.32 mmol) was added at room temperature. The blue solution turned dark violet and it was left stirring for 4 h. After filtration, the solution was concentrated until a minimal volume and stored at room temperature. Compound **2** was obtained as a dark violet powder from slow evaporation of the solvent in 72% yield (0.53 g, 0.95 mmol). Few pink crystals of $[\{H_2(PhCH_2)_2Cyclam\}Cu(H_2O)_2]S$, **4**, were also obtained.

Method B: $H_2(PhCH_2)_2$Cyclam (0.50 g, 1.32 mmol) was dissolved in 50 ml of MeOH and one equiv. of $CuSO_4 \cdot 5H_2O$ (0.33 g, 1.32 mmol) was added at room temperature. The blue solution turned dark violet and it was left stirring for 4 h. After filtration, the solution was evaporated to dryness affording compound **2** as a dark violet powder in 82% yield (0.61 g, 1.09 mmol). Anal. calcd for $C_{24}H_{36}CuN_4O_4S \cdot H_2O$: C, 51.64; H, 6.86; N, 10.04; S, 5.74. Found: C, 51.51; H, 6.84; N, 10.09; S, 5.69. FT-IR (KBr, cm^{-1}): 3091 (ν_{NH}), 1119, 1094, 1067 and 619 (ν_{SO4}). $\chi_m = 1.3 \times 10^{-3}$ cgs ($\mu = 1.8$ Bohr magnetons).

3.2.3. Synthesis of $[\{H_2(PhCH_2)_2Cyclam\}Cu](CH_3COO)_2$ (3)

$H_2(PhCH_2)_2$Cyclam (0.50 g, 1.32 mmol) was dissolved in 50 ml of CH_3CN/H_2O (3:1) and one equiv. of $Cu(CH_3COO)_2 \cdot H_2O$ (0.26 g, 1.32 mmol) was added at room temperature. The blue solution turned violet and it was left stirring for 4 h. After filtration, the solution was concentrated until a minimal volume and stored at room temperature. A violet powder was obtained from slow evaporation of the solvent in 85% yield (0.67 g, 1.12 mmol). Anal. calcd for $C_{28}H_{42}CuN_4O_4.2H_2O$: C, 56.22; H, 7.75; N, 9.37. Found: C, 56.79; H, 7.42; N, 9.31. FT-IR (KBr, cm^{-1}): 3141, 3064 (ν_{NH}), 1560 (ν_{CO}). $\chi_m = 1.5 \times 10^{-3}$ cgs ($\mu = 1.9$ Bohr magnetons).

3.2.4. Synthesis of $[\{H_2(PhCH_2)_2Cyclam\}Zn]SO_4$ (5)

$H_2(PhCH_2)_2$Cyclam (0.50 g, 1.32 mmol) was dissolved in 50 ml of CH_3CN/H_2O (3:1) and one equiv. of $ZnSO_4 \cdot 7H_2O$ (0.33 g, 1.32 mmol) was added at room temperature. A white powder was obtained after filtration in 62% yield (0.38 g, 0.70 mmol). Anal. calcd for $C_{24}H_{36}N_4O_4SZn$: C, 53.18; H, 6.69; N, 10.34; S, 5.92. Found: C, 55.23; H, 7.41; N, 10.65; S, 4.62. FT-IR (KBr, cm^{-1}): 3192 (ν_{NH}), 1103, 632 (ν_{SO}). ^1H NMR (DMSO-d_6/D_2O, 400.1 MHz, 296 K): δ (ppm) 7.44–7.31 (overlapping, 10H total, $PhCH_2N$), 4.33 (d, 2H, $^2J_{H-H} = 19$ Hz, $PhCH_2N$), 4.20 (d, 2H, $^2J_{H-H} = 19$ Hz, $PhCH_2N$), 3.34 (m, 2H, CH_2N), 3.23 (m, 2H, CH_2N), 3.15–3.03 (overlapping, 4H total, CH_2N), 2.91 (m, 2H, CH_2N), 2.78 (m, 2H, CH_2N), 2.56 (m, 2H, CH_2N), 2.43 (m, 2H, CH_2N), 1.92–1.81 (overlapping, 4H total, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (DMSO-d_6/D_2O, 100.6 MHz, 296 K): δ (ppm) 132.8 ($PhCH_2N$), 131.2 ($PhCH_2N$), 129.7 ($PhCH_2N$), 129.3 ($PhCH_2N$), 55.6 ($PhCH_2N$), 53.7 (CH_2N), 53.5 (CH_2N), 50.8 (CH_2N), 46.4 (CH_2N), 24.0 ($CH_2CH_2CH_2$).

3.2.5. Synthesis of $[\{H_2(PhCH_2)_2Cyclam\}ZnCl]Cl$ (6)

An aqueous solution of $ZnCl_2$ (0.18 g, 1.32 mmol) was added to a solution of $H_2(PhCH_2)_2$Cyclam (0.50 g, 1.32 mmol) in 50 ml of CH_3CN. A white powder was obtained after filtration in 61% yield (0.12 g, 0.16 mmol). Anal. calcd for $C_{24}H_{36}Cl_2N_4Zn$: C, 55.77; H, 7.02; N, 10.84. Found: C, 54.91; H, 7.42; N, 10.70. FT-IR (KBr, cm^{-1}): 3132, 3028 (ν_{NH}). ^1H NMR (DMSO-d_6/D_2O, 400.1 MHz, 296 K): δ (ppm) 7.69–7.55 (overlapping, 10H total, $PhCH_2N$), 4.41 (d, 2H, $^2J_{H-H} = 15$ Hz, $PhCH_2N$), 4.35 (d, 2H, $^2J_{H-H} = 15$ Hz, $PhCH_2N$), 3.45–3.36 (overlapping, 4H total, CH_2N), 3.18–2.94 (overlapping, 8H total, CH_2N), 2.75 (m, 2H, CH_2N), 2.63–2.53 (overlapping, 4H total, CH_2N and $CH_2CH_2CH_2$), 1.99 (m, 2H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (DMSO-d_6/D_2O, 100.6 MHz, 296 K): δ (ppm) 134.0 ($2 \times PhCH_2N$), 130.8 ($2 \times PhCH_2N$), 57.2 ($PhCH_2N$), 54.7 ($2 \times CH_2N$), 52.2 (CH_2N), 47.5 (CH_2N), 25.5 ($CH_2CH_2CH_2$).

3.2.6. Synthesis of $[\{H_2(MeOCH_2)_2Cyclam\}Cu](SO_4)$ (7)

1,4,8,11-tetraazatricyclo[9.3.1.14,8]hexadecane (1.00 g, 4.46 mmol) was dissolved in 80 mL of MeOH and two equiv. of $CuSO_4 \cdot 5H_2O$ (1.14 g, 4.56 mmol) was added. The mixture was stirred for five days at room temperature. After filtration and evaporation of the solvent to dryness, the compound was obtained as a dark blue semi-crystalline solid in 52% yield (1.08 g, 2.32 mmol). Anal. calcd for $C_{14}H_{32}CuN_4O_6S \cdot H_2O$: C, 36.08; H, 7.35; N, 12.02. Found: C, 35.68; H, 7.56; N, 12.96. FT-IR (KBr, cm^{-1}): 3227 (ν_{N-H}), 1120 (ν_{SO4}). $\chi_m = 1.1 \times 10^{-3}$ cgs ($\mu = 1.6$ Bohr magnetons).

3.2.7. Synthesis of $[\{H_2(MeOCH_2)_2Cyclam\}Cu](CH_3COO)_2$ (8)

1,4,8,11-tetraazatricyclo[9.3.1.14,8]hexadecane (1.00 g, 4.46 mmol) was dissolved in 75 mL of MeOH and two equiv. of $Cu(CH_3COO)_2 \cdot H_2O$ (0.82 g, 4.11 mmol) was added. The mixture was stirred for three days at room temperature. After filtration and evaporation of the solvent to dryness, the compound was obtained as a blue solid in 58% yield (1.30 g, 2.57 mmol). Anal. calcd for $C_{18}H_{38}CuN_4O_6 \cdot 2H_2O$: C, 42.72; H, 8.36; N, 11.07. Found: C, 42.95; H, 7.01; N, 11.05. FT-IR (KBr, cm^{-1}): 3163 (ν_{N-H}). $\chi_m = 1.2 \times 10^{-3}$ cgs ($\mu = 1.7$ Bohr magnetons).

3.2.8. Synthesis of $[\{H_2(MeOCH_2)_2Cyclam\}Cu][CuCl_4]$ (9)

1,4,8,11-tetraazatricyclo[9.3.1.14,8]hexadecane (1.00 g, 4.46 mmol) was dissolved in 80 mL of MeOH and two equiv. of $CuCl_2 \cdot 2H_2O$ (1.56 g, 9.15 mmol) was added. The mixture was stirred for five days at room temperature. After filtration and evaporation of the solvent to dryness, the compound was obtained as a brown semi-crystalline solid in 69% yield (1.72 g, 3.09 mmol). Anal. calcd for $C_{14}H_{32}Cl_4Cu_2N_4O_2$: C, 30.17; H, 5.79; N, 10.05. Found: C, 29.91; H, 5.90; N, 9.81. FT-IR (KBr, cm^{-1}): 3159 (ν_{N-H}). $\chi_m = 1.8 \times 10^{-3}$ cgs ($\mu = 2.1$ Bohr magnetons).

3.2.9. Catalytic procedure for the synthesis of methyl 1-(4-methoxyphenyl)-1H-1,2,3-triazole-4-carboxylate

4-methoxyboronic acid (75 mg, 0.49 mmol) and sodium azide (48 mg, 0.74 mmol) were dissolved in methanol and compound **7** (10%) was added. The mixture was stirred for 2.5 h at 55 °C. Methyl propiolate (0.13 mL, 1.46 mmol) and sodium ascorbate (10 mg, 0.05 mmol) were added. The mixture was stirred overnight at 55 °C. The crude was chromatographed by silica gel using an ethylacetate/hexanes (1:3) mixture as eluent. The product was obtained as a white solid (107 mg, 0.46 mmol) after evaporation of the solvent to dryness and characterized by NMR spectroscopy. ^1H NMR ($CDCl_3$, 300 MHz, 296 K): δ (ppm) 8.40 (s, 1H, CH), 7.60 (d, $J = 8$ Hz, 2H, *o-Ph*), 6.99 (d, $J = 8$ Hz, 2H, *m-Ph*), 3.94 (s, 3H, CH_3), 3.82 (s, 3H, CH_3); ^1H NMR (CD_3OD, 500 MHz, 296 K): δ (ppm) 9.01 (s, 1H, CH), 7.78 (d, 2H, *o-Ph*), 7.12 (d, 2H, *m-Ph*), 3.95 (s, 3H, CH_3), 3.88 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (CD_3OD, 125 MHz, 296 K): δ (ppm) 162.3 ($COOCH_3$), 162.0 ($NCCOOCH_3$), 141.1 (*Ph*), 131.1 (*Ph*), 127.7 (NCH), 123.5 (*Ph*), 116.6 (*Ph*), 56.2 (OCH_3), 52.6 ($COOCH_3$).

3.3. General procedures for X-ray crystallography

Crystallographic and experimental details of data collection and crystal structure determinations for the four compounds are available in Table 3. Suitable crystals of compounds **4**, **6**, **7** and **9** were coated and selected in Fomblin® oil. Data were collected using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Bruker AXS-KAPPA APEX II diffractometer. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections [27]. Absorption corrections were applied using SADABS [28]. The structures were solved by direct methods using SIR92 [29], SIR97 [30] or SIR2004 [31]. Structure refinement was done using SHELXL-97 [32]. These programs are part of the WinGX software package version 1.80.05 [33]. The hydrogen atoms of the NH groups were located in the electron density map. The other hydrogen atoms were inserted in calculated positions and allowed to refine in the parent atoms. Torsion angles, mean square planes and other geometrical parameters were calculated using SHELX [32]. Illustrations of the molecular structures were made with Mercury 3.0 [34] or ORTEP-3 [35] for Windows.

Compounds **6**, **7** and **9** crystallized with disordered molecules of solvent. As all attempts to model the disorder did not lead to acceptable solutions, the Squeeze/PLATON [36] sequence was applied.

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Appendix A. Supplementary material

CCDC 965244–965247 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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