



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 $[\{H_2(PhCH_2)_2Cyclam\}Zn]Cl$, **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*-CH₂OMe 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 Cu²⁺ mediated process.

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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

macrocyclic 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'*-CH₂OMe 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 were 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.

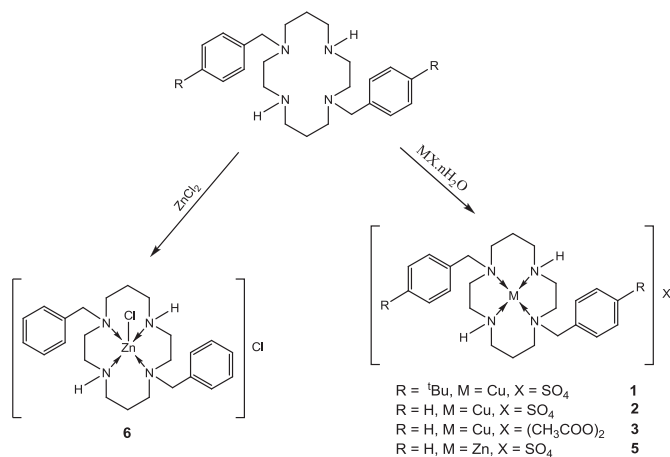
2. Results and discussion

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.



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 $H_2(PhCH_2)_2Cyclam$ 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 ($^\circ$) 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	–

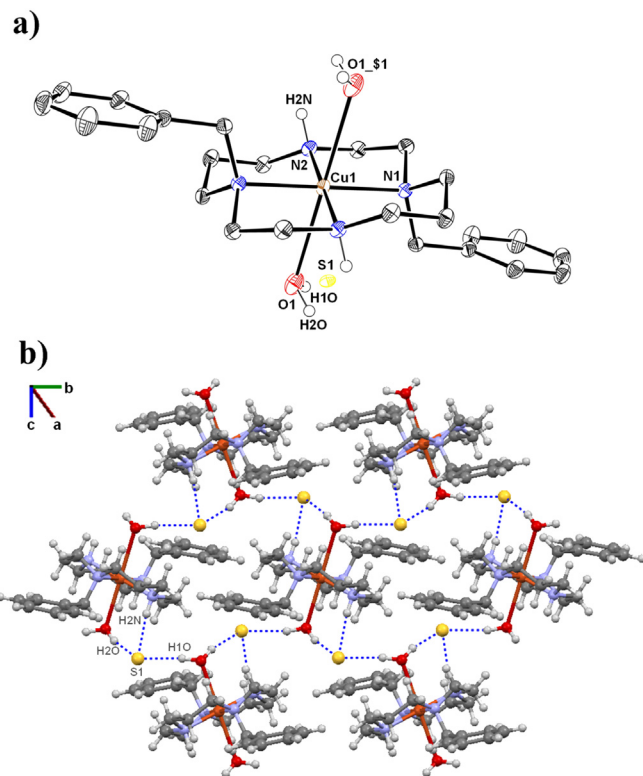


Fig. 1. a) ORTEP diagram of $[\{H_2(PhCH_2)_2Cyclam\}Cu(H_2O)_2]S$, **4**, showing thermal ellipsoids at 40% probability level. Half molecule is generated by symmetry. Selected hydrogen atoms are omitted for clarity; b) Best view of **4** revealing the hydrogen bonds between S(1) and H(10), H(20) and 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, $[H_2\{1,5,8,12\text{-tetramethyl-1,8,11-tetraazacyclo tetradecane}\}Cu(H_2O)_2]X$ ($X = NO_2, Br, Cl, I$) [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(10), H(20) 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 ($^\circ$) of the compounds **4**, **6**, **7** and **9**.

Compound	D–H...A	$d(D-H)$	$d(H...A)$	$d(D...A)$	(DHA)
4	O(1)–H(10)···S(1)	0.959	2.210	3.161	171.73
	O(1)–H(20)···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
	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

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