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# Synthesis, crystal structure and magnetic properties of new molecular, macrocyclic building blocks of Ni(II) and Cu(II)

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ABSTRACT

New macrocyclic building blocks $[NiL_1Cl_2]$ (**1**) ($L_1$ = N-dl-2,9-dimethyl-1,5,8,12-tetraazacyclotetradecan) and $[CuL_2(ClO_4)_2]$ (**2**) ($L_2$ = N-d-2,3,9,10 tetramethyl-1,5,8,12-tetraazacyclotetradeka-1,8 diene) were synthesized and the crystal structure of both compounds were determined. Complexes **1** and **2** crystallizes in monoclinic, space group P 21/c. Their magnetic properties were studied over the temperature range 1.8–300 K using a Quantum Design SQUID magnetometer (MPMSXL-5-type). The results indicate that both compounds behave as weakly interacting paramagnetic centers in the crystal lattice. The effects of hydrogen bond mediating the magnetic exchange interactions on the spin density have been evidenced by DFT calculations.

## 1. Introduction

The field of building new molecular species and addressing their architectures in order to control their physical properties, has been a topic for many research groups dealing, for example, with supramolecular chemistry [1] and molecular magnetism [2]. One of the strategies to design these systems based on metal and organic building block. The employment of capped molecular entities $[ML]^{2+}$ (M – paramagnetic metal ions; L – tetraazamacrocyclic ligand) is appropriate because the precursors with macrocyclic ligand can control the structural evolution in constrained directions. Square – planar macrocyclic complexes of $Cu^{II}$ and $Ni^{II}$ with two free coordination sites at the metal atom can play the role of the "building block" for multidimensional compounds. The building principle can be exemplified by various possible arrangements of the $ML_n$ macrocyclic complexes and M′ (high-spin $d^5$) ions connected by bridging ligands (e.g. $SCN^-$, $CN^-$, $CX^-$). Depending on the nature of $ML_n$, one-, two- or three-dimensional frameworks can emerge, as function of the geometrical proximity of available coordination sites on M and M′, the coordination number of M and M′, of the steric hindrance the macrocyclic ligand experiences around M and of the oxidation state of the metal ions [3]. In this respect, much attention has been paid to the planar tetraaza copper(II) and nickel(II) complexes containing two free coordinating sites at the axial positions. The access to the metal ion is very easy when there are no substituents in the macrocyclic ring [4,5]. This situation changes with the size and character of substituents, which may form a steric hindrance, preventing any coordination to the metal ion. The position of the substituents around the equatorial nitrogen atoms of the ligands and also N-configuration of the macrocyclic ring influences on the coordination mode of polymetallic complexes from simple dimeric form, through the trimeric unit $[NiL]_2[Mn(NCS)_4]\,(ClO_4)_2\cdot H_2O$ [6] to chain structure $[CuL_\beta][ReCl_4(ox)]\cdots DMF$ [3]. In this reason it seems interesting to synthesized next macrocyclic "building block" with additional bridging ligand in metal coordination sphere [Scheme 1]. Concerning the magnetic properties of this kind of system, the chloride or perchlorate ligand may act an efficient mediator for the magnetic interaction between the paramagnetic centers. The analysis of geometry of both, macrocyclic compound together with theoretical calculations of atomic spin densities and magnetic properties allows us to project new heterometallic system with interesting magnetic properties. In the present paper, further results concerning that issue are presented.

## 2. Experimental section

Materials: All materials used in this work were of reagent grade purity and were used as commercially obtained.

### 2.1. Synthesis of the complex

#### 2.1.1. $[NiL_1Cl_2]$

N-dl-2,9-dimethyl-1,5,8,12-tetraazacyclotetradecan dihydrogenperchlorate (325 mg, 0.68 mmol) was slowly added to a boiling solution of nickel acetate tetrahydrate (174 mg, 0.7 mmol) in

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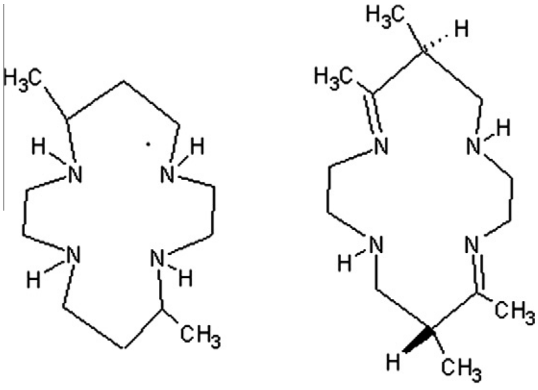

1. 2.

**Scheme 1.** Schematic view of ligands **1** and **2**.

methanol (40 $cm^3$). The mixture was refluxed for 2 h following which time sodium chloride was added (438 mg, 0.75 mmol). The resulting solid was dissolved by addition of water (8 $cm^3$) and the solution was filtered and left for crystallization. Orange crystals (21.5 g) of [$NiL_1Cl_2$] were filtered off and dried under reduced pressure.

> Anal. Calcd. for $C_{12}H_{28}Cl_2N_4Ni$ (358): C, 40.2; H, 7.82; N, 15.6; Cl, 19.8%.
> Found: C, 40.6; H, 7.56; N, 15.4; Cl, 19.7%.

The nickel content was determined by ICP method. Ni (calcd.): 16.4%; Ni (found): 16.1%.

#### 2.1.2. [$CuL_2(ClO_4)_2$]

N-d-2,3,9,10 tetramethylo-1,5,8,12-tetraazacyclotetradeca-1,8 diene dihydrogenperchlorate (325 mg, 0.68 mmol) was slowly added to a solution of copper acetate monohydrate (140 mg, 0.7 mmol) in methanol (20 $cm^3$). The resultant deep orange solution was stirred under nitrogen for 1 h. Red solid was dissolved by addition of water (8 $cm^3$) and the solution was filtered and left for crystallization. Red precipitate (22.9 g) of [$CuL_2(ClO_4)_2$] were filtered off and dried under reduced pressure.

> Anal. Calcd. for $C_{14}H_{28}Cl_2CuN_4O_8$ (514.8): C, 32.6; H, 5.44; N, 10.9; Cl, 13.8%.
> Found: C, 32.6; H, 5.76; N, 10.4; Cl, 13.9%.

The copper content was determined by ICP method. Cu (calcd.): 12.3%; Cu (found):12.5%.

### 2.2. Crystal structure determination

The violet prism crystals of compounds 1 and 2 were mounted in turn on a KM-4-CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at temperature 291.0(3) K, with ω scan mode. 12 and 8 s exposure times were used respectively for 1 and 2, and reflections inside Ewald sphere were collected up to $2\theta = 50°$. The unit cell parameters were determined from 8802 and 5971 strongest reflections respectively for **1** and **2**. Details concerning crystal data and refinement are given in Table 1. Examination of reflections on two reference frames monitored after each 20 frames measured showed no loss of the intensity for both compounds. During the data reduction Lorentz, polarization, and numerical absorption [7] corrections were applied. The structures were solved by partial structure expansion procedure. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F2. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent atom with geometric idealization after each cycle of refinement and individual isotropic displacement factors equal 1.2 times the value of equivalent displacement factor of the parent non-methyl carbon or nitrogen atom and 1.5 times of parent methyl group carbon atom. The methyl groups were allowed to rotate about their local threefold axis. The SHELXS97 [8], SHELXL97 [9] and SHELXTL [10] programs were used for all the calculations. Atomic scattering factors were

**Table 1**
Crystal data and structure refinement.

| Compound | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{12}H_{28}Cl_2N_4Ni$ | $C_{14}H_{28}Cl_2CuN_4O_8$ |
| Formula weight | 357.99 | 514.84 |
| Temperature (K) | 291.0(3) K | |
| Wavelength (Å) | $\lambda$ (Mo Kα) = 0.71073 | |
| Crystal system, space group | Monoclinic, $P\ 2_1/c$ | |
| Unit cell dimensions (Å, °) | $a = 8.3498(3)$<br>$b = 6.6269(2)$<br>$c = 14.9670(11)$<br>$\beta = 95.462(3)$ | $a = 7.3677(4)$<br>$b = 8.0980(5)$<br>$c = 18.0915(9)$<br>$\beta = 97.209(5)$ |
| Volume (Å$^3$) | 824.41(7) | 1070.87(10) |
| Z, Calculated density (Mg/m$^3$) | 2, 1.442 | 2, 1.597 |
| Absorption coefficient (mm$^{-1}$) | 1.494 | 1.317 |
| F(000) | 380 | 534 |
| Crystal size (mm) | 0.153 × 0.150 × 0.137 | 0.149 × 0.144 × 0.126 |
| $\theta$ range for data collection (°) | 2.45–5.01 | 2.27–5.00 |
| Index ranges | $-9 \leqslant h \leqslant 9, -7 \leqslant k \leqslant 7, -17 \leqslant l \leqslant 17$ | $-8 \leqslant h \leqslant 7, -9 \leqslant k \leqslant 9, -21 \leqslant l \leqslant 21$ |
| Reflections collected/unique | 10419/1441 [$R_{(int)} = 0.0447$] | 9892/1882 [$R_{(int)} = 0.0439$] |
| Completeness to 2 $\theta = 50°$ (%) | 99.7 | 100.0 |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Min. and max. transmission | 0.800 and 0.817 | 0.819 and 0.850 |
| Data/restraints/parameters | 1441/0/89 | 1882/0/135 |
| Goodness-of-fit on $F^2$ | 1.199 | 1.346 |
| Final $R$ indices ($I > 2\sigma(I)$) | $R1 = 0.0757$, $wR2 = 0.2477$ | $R1 = 0.0548$, $wR2 = 0.1261$ |
| R indices (all data) | $R1 = 0.0803$, $wR2 = 0.2477$ | $R1 = 0.0584$, $wR2 = 0.1274$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.716 and −0.647 | 0.504 and −0.440 |