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EXTRACTION OF METAL CATIONS WITH POROUS OXO-AZA MACROCYCLIC COMPOUNDS

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Introduction: Removal of highly toxic air, water and soil pollutants from the environment is a major scientific topic. Macrocycles are organic compounds that can bind toxic species and be designed for the extraction of specific metal cations [1, 2]. Macrocycles containing oxygen and nitrogen donor atoms in the inner macrocyclic ring (*oxa-aza* macrocycles) have been studied for that purpose [1]. The affinity of an *oxa-aza* macrocycle towards specific cations can be designed by changing several factors: ring size (cavity size), HSAB principle, donor atom properties, planarity of the system (puckering) and orientation of donor atoms (*exodentate* or *endodentate*) [1, 2]. In this work we have synthesized a novel N_4O_4 -donor macrocycle (**2**) by reduction of previously prepared [2] porous macrocyclic Schiff base (**1**).

Experimental:
Compound **1** (1,6,20,25 – tetraaza – 2,5:8,9:17,18:21,24:27,28:36,37 – heksabenzo – 10,16,29,35-tetraoksa-ciklooktatriakonta-1,6,20,25 – tetraen) was prepared by a [2+2] cyclocondensation reaction of the corresponding dialdehyde and diamine. The crystal and molecular structure of **1** were previously determined [2]. Reduced Schiff base **2** (1,6,20,25 – tetraaza – 2,5:8,9:17,18:21,24:27,28:36,37 – heksabenzo – 10,16,29,35-tetraoksa-ciklooktatriakonta) was prepared by a reduction of **1xCLF** with $NaBH_4$ (**Figure 1.**). Compound **2** was characterized by elemental analysis, FT-IR, and NMR spectroscopy. Picrate extraction studies were performed following modified Pedersen's procedure [3] for Ni^{2+}, Cd^{2+}, Zn^{2+}, Ag^{+}, Co^{2+}, Hg^{2+}, Cu^{2+}, Fe^{3+}, Mn^{3+}, Au^{3+}, and Cr^{3+}. The composition of extracted species and extraction constant (K_{ex}) were calculated using the dependence of the distribution ratio (D) on macrocycle concentration (log$D$-log$L$ plot) for Cu^{2+}, Au^{3+} and Ag^{+}.

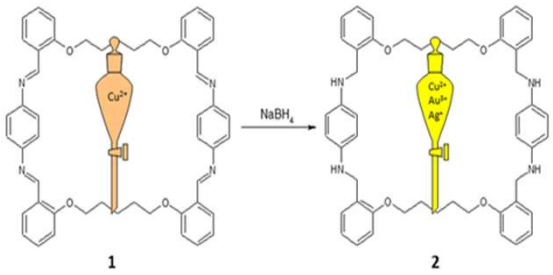

Figure 1. Molecular structure of compounds 1 and 2, the synthetic pathway for the preparation of 2 and metal cations with the highest extractability

Results and discussion:
Compound **1** crystallizes in the monoclinic crystal system, space group $P\,2_1/c$. The host molecule is square-shaped and planar. Minor deviations from the planarity are observable for C2-C7 and C13-C18 benzene rings (3.85(8)° and 7.29(8)°, respectively). The calculated diagonal distances between the nitrogen and oxygen donor atoms are 13.48 Å ($d_{N\text{-}N}$) and 11.20 Å ($d_{O\text{-}O}$). The open tubular structure in the host compound is formed by stacking molecules into columns along *a* axis, *via* weak C-H···N and C-H···π interactions (**Figure 2.**). In the FT-IR spectrum of newly synthesized compound 2, several maxima indicate a successful reduction of **1** (**Figure 3a.**). Maximum close to 3400 cm^{-1} is due to N-H vibration of the secondary amine group. Maxima typical for C=N stretching vibration in **1** [2], close to 1620 cm^{-1} is not present in the spectrum of **2**. In the NMR spectrum of **2**, the maximum at 4.95 ppm is due to the resonance of amine hydrogen atoms (**Figure 3b.**). Resonance at 8.5 ppm, observed in imine analog is not present in the spectrum, thus confirming the successful reduction of imine macrocycle. Metal extraction experiments indicate that highest extraction is achieved for Cu^{2+} (87 %) in the case of compound **1** and for Au^{3+} (100 %), Cu^{2+} (100 %) and Fe^{3+} (100 %) in the case of compound **2** (**Table 1.**). The composition of extracted species in case of **1** and Cu^{2+} is 1:1 (ligand:metal ratio, K_{ex} = 11.062), and 1:1 ratio for **2** and Ag^{+} and Au^{3+} (K_{ex} = 8.7107 and 17.667, respectively).

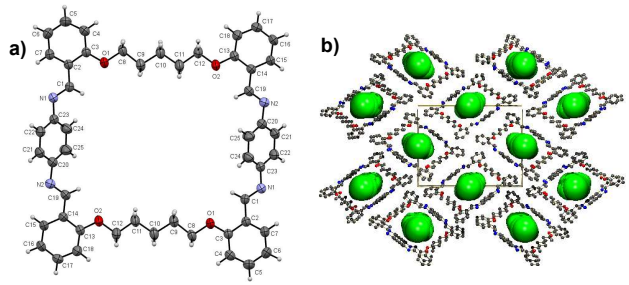

Figure. 2. a) Crystal structure of compound 1. b) Crystal packing of 1 along a axis. Green-colored surfaces represent voids in the crystal.

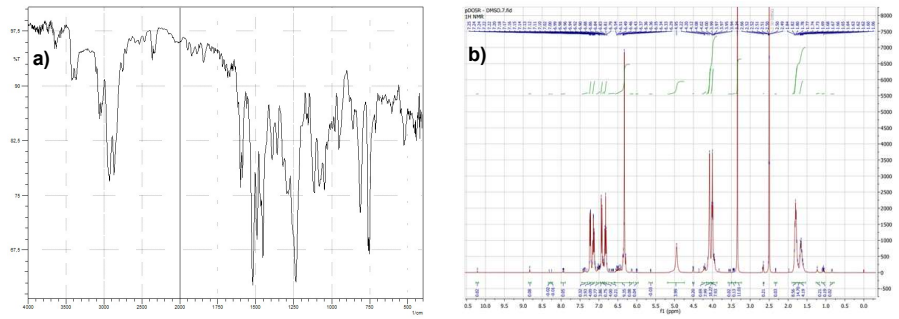

Figure. 3. FTIR (a) and ^{1}H NMR (b) spectrum of 2

Table 1. The extractability of various metal cations for 1 and 2.

Metal ion	Extractability (%) #	
	1	2
Fe^{3+}	0	100
Hg^{2+}	19,40	83,28
Ag^{+}	4,94	91,01
Cr^{3+}	5,85	73,21
Cu^{2+}	86,97	100
Ni^{2+}	7,12	49,94
Cd^{2+}	0	29,05
Zn^{2+}	0	63,67
Co^{2+}	11,88	90,61
Mn^{2+}	5,67	52,07
AuPIK	0	93,1
$HAuCl_4$	52,70	100

#The extractability was calculated using equation: E (%) = $[(A_0\text{-}A)/A_0] \times 100$. A_0 and A is absorbance in absence and presence of the ligand, respectively

Conclusions: A novel N4O4-donor macrocyclic compound **2** was prepared by simple reduction of imine analog (**1**) using $NaBH_4$. The compound was characterized by spectroscopic methods (FT-IR and NMR). The extraction experiments were performed using an aqueous solution of the metal picrates and organic solutions of the ligands (newly synthesized compound **2** and imine macrocyclic analog, **1**). Results of the extraction experiments indicate that the extractability of metal cations by the investigated macrocycles is quite different. The best extractability achieved for the imine macrocycle was observed for the Cu^{2+} ion (87 %), and in the case of the reduced form (**2**), excellent results were obtained for almost all metal cations. This enhanced ability of **2** can be attributed to the increase of basicity in comparison to imine analog. The synthesized compounds have a potential application for the extraction of copper and cations of precious metals (gold (III) and silver (I)).

References:

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