



Molecular Modeling Studies on Novel Open-chain and Cyclic Thia Compounds and their Ag(I) and Hg(II) Complexes

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Introduction

Selective and effective binding of metal ions by multi-functional structure units play an important role in biology, analytics and technique [1]. Therefore the design of novel macrocyclic and structure related open-chain ligands for cations is a main topic of investigations. Solvent extraction studies offer good possibilities to find structure-complexation relationships [2].

In this paper molecular modeling calculations of some novel sulfur containing compounds and their Ag(I) and Hg(II) complexes are demonstrated and used for the interpretation of the complexation and extraction behaviour of this ligands.

Computational Procedure

The structure of novel thia compounds (type 1 – 3) and their complexes has been determined by force field, semiempirical

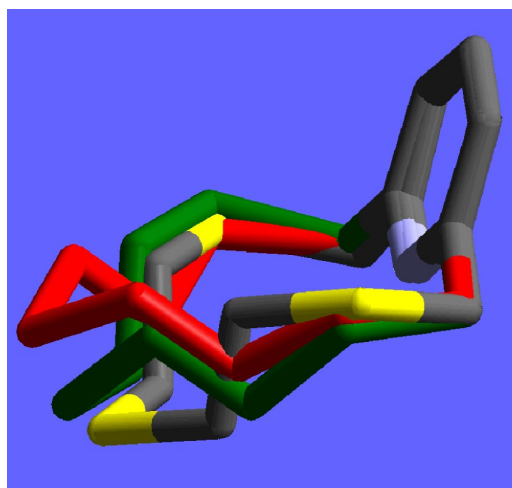


Figure 1. Ligand 3 (X=N): Three calculated minimum geometries (PM3) of the thermodynamic most stable chair conformation (the gray coloured lowest conformation is in very good agreement with the X-ray structure)

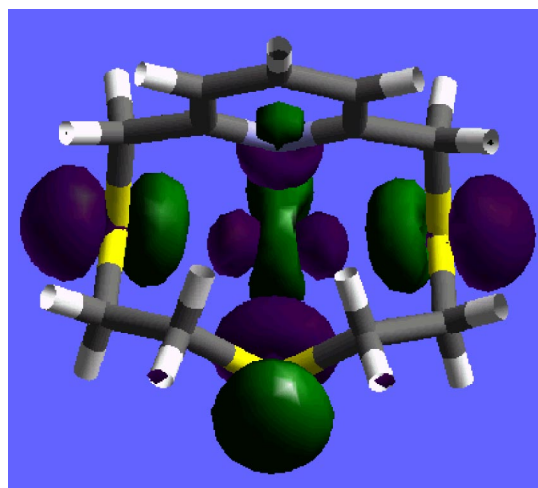
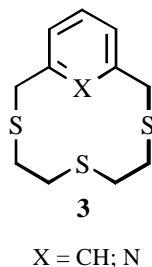
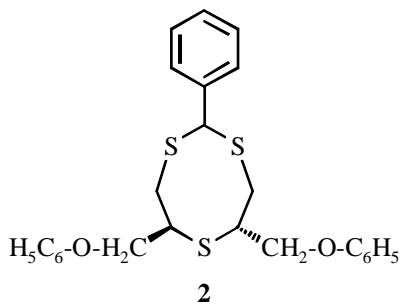
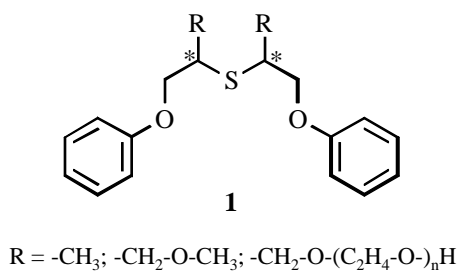


Figure 2. HOMO alpha orbitals of the 1:1 silver(I) complex with ligand 3 (X=N) using ADF

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Scheme 1 Investigated compounds.

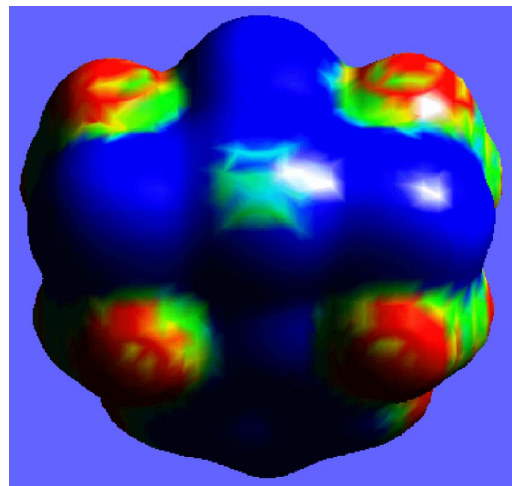


Figure 3. Electron density surface with electrostatic potential of the 1:1 silver(I) complex with ligand 3 (X=N) using ADF

and ab initio calculations and molecular dynamics simulations. The usefulness of the applied computer methods are proved by comparison of calculated and X-ray structure results [4, 5].

The initial model of the molecular structure were achieved using the UNIVERSAL FORCE FIELD of the CERIU² 1.6 (BIOSYM/MSI) software package. The semiempirical calculations were performed with MOPAC 6.0 [6] using the PM3 hamiltonian (ligands and Hg(II) complexes) and the HYPERCHEM 4.5 (HyperCube) program package using the ZINDO/1 method (Ag(I) complexes). The molecules under

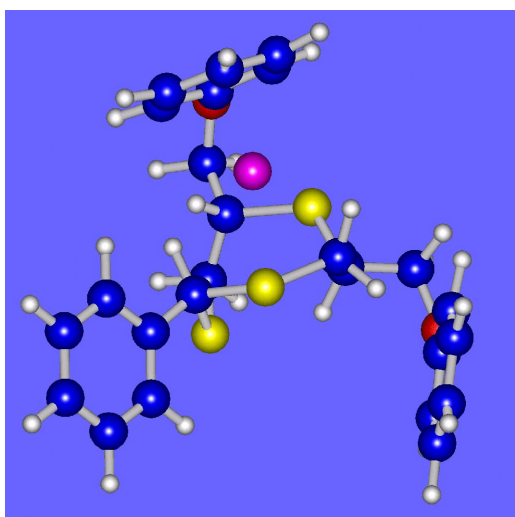
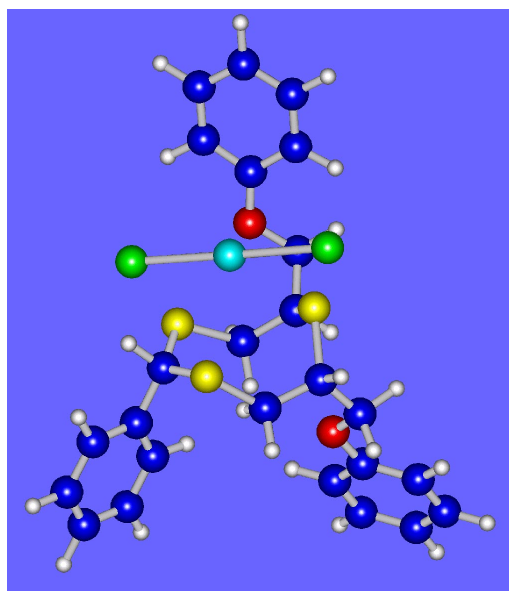


Figure 4. ZINDO/1 calculated structure of 1:1 Ag(I) complex with ligand 2

Figure 5. PM3 calculated structure of 1:1 HgCl₂ complex with ligand 2

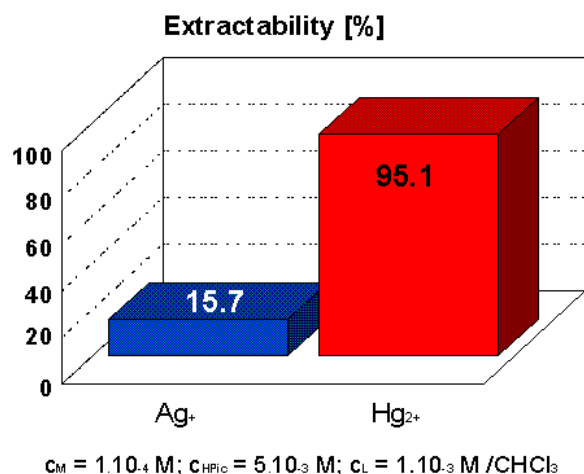


Figure 6. Solvent extraction studies of silver picrate and mercury chloride with ligand **2**

study were completely geometry optimized at the SCF level until a gradient norm less than $0.0001 \text{ kcal}\cdot\text{mol}^{-1}\cdot\text{\AA}^{-1}$. The ab initio calculations were carried out with GAUSSIAN 94 (Gaussian Inc.) using the 3-21G, 4-31G, 6-31G, 6-31G*, LanL2MB and LanL2DZ basis sets at the Hartree-Fock level. The DFT calculations were done with ADF (Amsterdam Density Functional) using the II(DZ) and IV(DZ) large core basis sets at the CGA method.

Discussion

The investigated thia compounds **1**–**3** give varying extractabilities towards Ag(I) and Hg(II) in dependence on the structure of the ligands. Compound **3** with X = CH gives a high

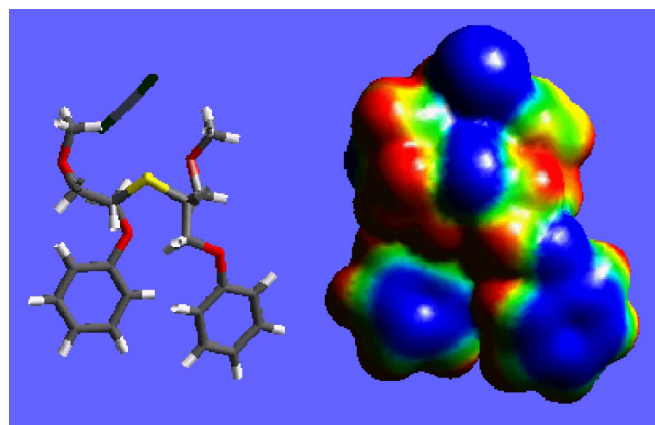


Figure 8. Electron density surface with electrostatic potential of the 1:1 HgCl_2 complex with ligand **1** ($R = \text{CH}_2\text{-O-CH}_3$) using PM3 (MOPAC 6.0)

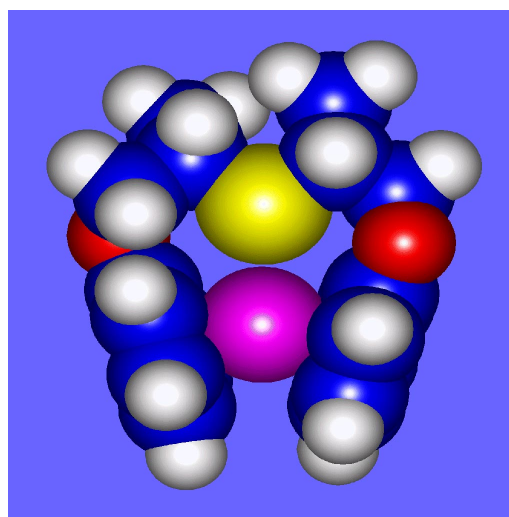


Figure 7. ZINDO/1 calculated structure of 1:1 silver(I) complex with ligand **1** ($R = \text{CH}_3$)

selectivity for Ag(I) over Hg(II), whereas **3** with X = N (structure see Fig. 1) extracts both Ag(I) and Hg(II) in a comparable order of magnitude.

These considerations are clearly confirmed by the calculated structures of Ag(I) and Hg(II) complexes. In case of **3** with X = N the structures of Ag(I) and Hg(II) complexes are very similar; the metal ions are coordinated by three S donor atoms and the pyridin nitrogen atom (see Figs. 2, 3). In contrast for **3** with X = CH only Ag(I) gives a bonding to all three sulfur atoms and, in addition, to the aromatic π -system. It is interesting that the order of selectivity is reversed in the case of **2** (Fig. 6). The HgCl_2 species extracted by **2** is best coordinated by all S atoms and one oxygen of the

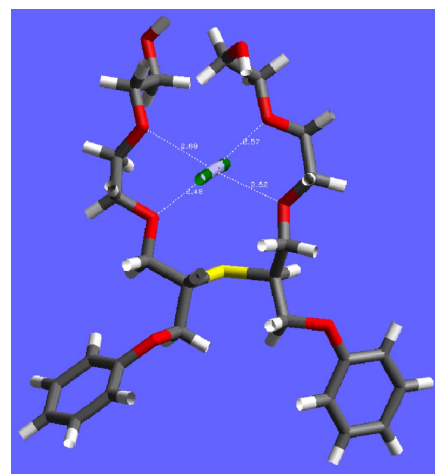


Figure 9. PM3 calculated structure of 1:1 HgCl_2 complex with ligand **1** ($R = \text{CH}_2\text{-O-(C}_2\text{H}_4\text{-O)}_2\text{H}$)

phenoxy substituent (Fig.5). In contrast Ag(I) is bonded by two sulfur and the aromatic π -system of the benzylic group only (Fig. 4). The extraction behaviour of type **1** compounds is characterized generally by a preference of Ag(I). So **1** with R = CH₃ can form a typical intramolecular sandwich structure of high hydrophobicity (Fig. 7). The highest extractability for Ag(I) is achieved using **1** with R = CH₂-O-(C₂H₄O)₂H and is obviously caused by a bonding pattern including sulfur and three ether oxygen atoms. In contrast the same ligand with HgCl₂ gives an interaction with four oxygen donor atoms only (Fig. 9). The best extractant of type **1** for HgCl₂ is given with R = CH₂-O-CH₃. According to our calculations the mercury is complexed by sulfur and the oxygens of two methoxy groups (Fig. 8). But also in this case the Ag(I) extraction is significantly better, because of the shorter bonding distances.

It can be shown that molecular modeling leads to a deeper insight in the phenomena of structure-property relations and stimulates the further development of efficient and selective complexing agents.

References

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