

## Molecular Dynamic and Conformational Study of an Unsaturated 12-crown-S<sub>2</sub>O<sub>2</sub> Ether and its Ag<sup>I</sup> Complexes<sup>§</sup>

Manuela Grotjahn<sup>1,\*</sup>, Hans-Joachim Drexler<sup>2</sup>, Norbert Jäger<sup>1</sup>, Erich Kleinpeter<sup>1</sup>, and Hans-Jürgen Holdt<sup>2</sup>

<sup>1</sup>Institut für Organische Chemie und Strukturanalytik, Universität Potsdam, Am Neuen Palais 10, D-14469 Potsdam, Germany (manuela@serv.chem.uni-potsdam.de)

<sup>2</sup>Fachbereich Chemie, Universität Rostock, Buchbinderstr. 9, D-18051 Rostock, Germany

Received: 9 June 1997 / Accepted: 21 June 1997 / Published: 14 August 1997

### Abstract

The preferred conformations and the complexional behaviour of mn-12S<sub>2</sub>O<sub>2</sub> were studied by means of both NMR spectroscopy and molecular modelling. Furthermore, the Ag<sup>I</sup> complexes of this ligand mn-12S<sub>2</sub>O<sub>2</sub> were also studied by molecular mechanical calculations.

**Keywords:** Thiocrown ether, NMR, Ag(I) complexes, Molecular Dynamic simulations

### Introduction

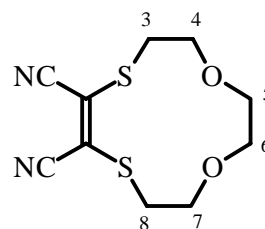
The maleonitrile-dithiocrown ethers are a suitable class of S/O-coronands in order to force on metal ions up to now unknown mixed ether / thioether coordination spheres.

The maleonitrile-dithiocrown ether (Figure 1) derives from the saturated parent compound 1,4-dithiocrown ether by substitution of the flexible ethylene sequence between the two S atoms by the rigid and voluminous maleonitril unit.

In contrast to the 1,4-dithiocrown ether, the sulfur atoms in the maleonitrile dithiocrown ether reveal a restricted exodentate conformation which was proved by X-ray investigation [1, 2]. This is caused by the strong affiliation of the

sulfur atoms to the rigid maleonitril subunit. The latter fact should be useful for the formation of endocyclic complexes.

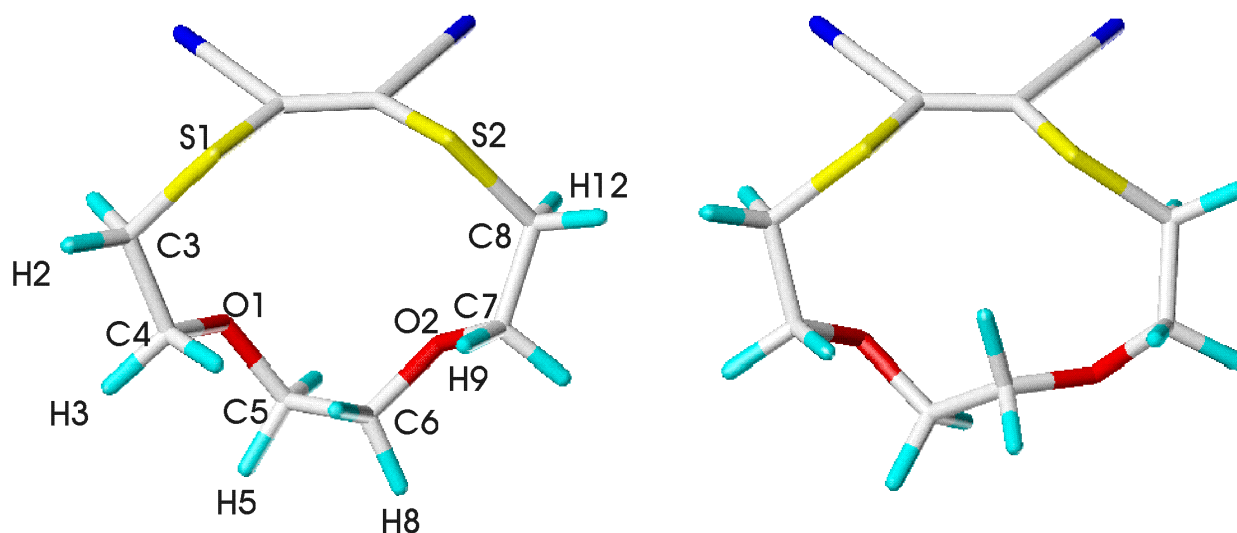
It is the major objective of this paper to examine the dynamics of both the ligand and its Ag<sup>I</sup> complexes.



**Figure 1.** mn-12S<sub>2</sub>O<sub>2</sub>

<sup>§</sup> Presented at the 11. Molecular Modeling Workshop, 6 -7 May 1997, Darmstadt, Germany

\* To whom correspondence should be addressed



**Figure 2.** The minimum energy conformations (calculated with PM3 and AM1)

software; the heats of formation were calculated using the program MOPAC (AM1, PM3).

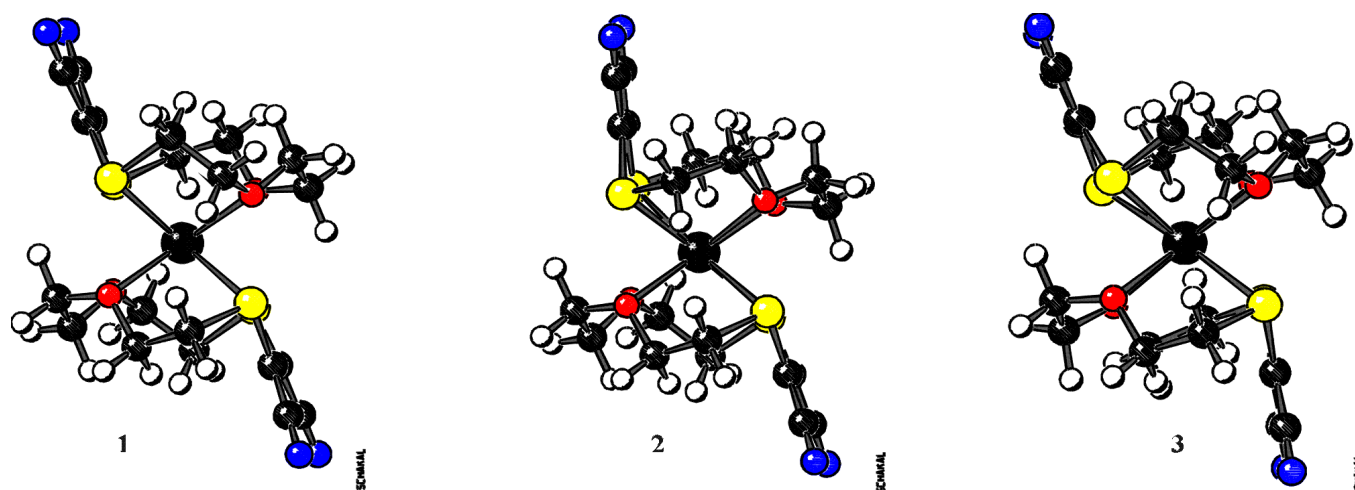
## Methods

- The structures of  $\text{mn-12S}_2\text{O}_2$ ,  $[\text{Ag}(\text{mn-12S}_2\text{O}_2)_2]\text{PF}_6$  and  $[\text{Ag}(\text{mn-12S}_2\text{O}_2)_2]\text{ClO}_4$  were investigated theoretically by empirical and semiempirical methods and experimentally by 1D and 2D NMR spectroscopy in solution ( $\text{CD}_3\text{NO}_2$ ,  $\text{CD}_2\text{Cl}_2$ ).
- The complex formation was studied by  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{109}\text{Ag}$  NMR titration experiments, respectively.
- The molecular dynamic simulations of the ligand and its  $\text{Ag}^{\text{I}}$  complexes were carried out using SYBYL (TRIPOS force field) and BIOSYM/DISCOVER95 (ESFF force field)

## Results

Molecular dynamic simulations were carried out using SYBYL in the TRIPOS force field at 250 K and 1000 K, respectively, to investigate the dynamic behaviour of the ligand  $\text{mn-12S}_2\text{O}_2$ . The coordinates of the X-ray analysis were used for the starting conformation /1/. The dihedral angles of the conformations obtained at 250 K proved to remain in the region of the X-ray crystal structure (Table 1).

The heats of formation of the (global) minimum were found to be 29,9 kcal/mol (PM3) and -6,7 kcal/mol (AM1), respectively (Figure 2).



**Figure 3.** The  $[\text{Ag}(\text{mn-12S}_2\text{O}_2)_2]\text{PF}_6$  conformations.

Table 1.

Bond	calculated [°]	X-ray analysis	AM1 minima	PM3 minima
H <sup>2</sup> -C <sup>3</sup> -C <sup>4</sup> -H <sup>3</sup>	30.50 - 82.60	48.4°, <i>sc</i>	52.4°	45.5°
H <sup>5</sup> -C <sup>5</sup> -C <sup>6</sup> -H <sup>8</sup>	34.42 - 88.63. <i>sc</i>	-61.3°, <i>ac</i>	7.5°, <i>sp</i>	39.2°, <i>sc</i>
H <sup>9</sup> -C <sup>7</sup> -C <sup>8</sup> -H <sup>12</sup>	-179.95 - -154.22	-175.0°, <i>ap</i>	-174.3°	-166.7°
S <sup>1</sup> -C <sup>3</sup> -C <sup>4</sup> -O <sup>1</sup>	-89.86 - -40.17	-71.5°, <i>ac</i>	-73.6°	-79.6°
O <sup>1</sup> -C <sup>5</sup> -C <sup>6</sup> -O <sup>2</sup>	-75.83 - -30.43	-58.3°, <i>ac</i>	-111.7°, <i>sc</i>	-78.3°
O <sup>2</sup> -C <sup>7</sup> -C <sup>8</sup> -S <sup>2</sup>	30.40 - 84.95	65.3°, <i>sc</i>	74.8°	84.0°

As expected, mn-12S<sub>2</sub>O<sub>2</sub> is completely flexible at 1000 K.

The <sup>1</sup>H NMR spectra of the ligand and its complexes show exchange phenomena at room temperature (broad signals). For mn-12S<sub>2</sub>O<sub>2</sub> the coalescence temperatures of three different signals of the molecule could be obtained by temperature-dependent NMR spectra. The free energy of activation for these processes were determined to be about 50 kJ/mol at 259 K [3].

Molecular dynamic simulations of the complexes [Ag(mn-12S<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub> were carried out using BIOSYM/DISCOVER95

in the ESFF force field to investigate the conformation of the ligand in the bounded state. Again, the X-ray analysis was used as the starting conformation (without the hexafluorophosphate anion) [2].

The X-ray analysis of the complexes [Ag(mn-12S<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub> and [Ag(mn-12S<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub> depicted the Ag<sup>I</sup> ion to be sandwiched between two mn-12S<sub>2</sub>O<sub>2</sub> molecules and coordinated to the S- and the O-atoms. <sup>13</sup>C NMR studies gave the same results for the mn-12S<sub>2</sub>O<sub>2</sub> complexes in nitromethane solutions [3].

Generally, in both the ligand and the complexes the ring system can interconverted. In order to differentiate the various ring inversions, the energy barriers were calculated. The calculated data were then compared with the results of the temperature-dependent NMR spectra.

At 500 K many conformations were obtained for [Ag(mn-12S<sub>2</sub>O<sub>2</sub>)<sub>2</sub>]PF<sub>6</sub>. Minimization of these conformations yielded 13 different structures. Three of these conformations (Figure 3) proved be different from the X-ray structure in only one of the S-C-C-O dihedral angles (Table 2) and were further investigated. Conformation 2 is the mirror image of conformation 3.

Table 2.

	X-ray	conf. 1	conf. 2	conf. 3
dihedral angle				
S-C-C-O [°]	74.37	70.79	-66.57	66.57
E <sub>pot</sub> [kcal/mol]	-	-13.6	-12.6	-12.6

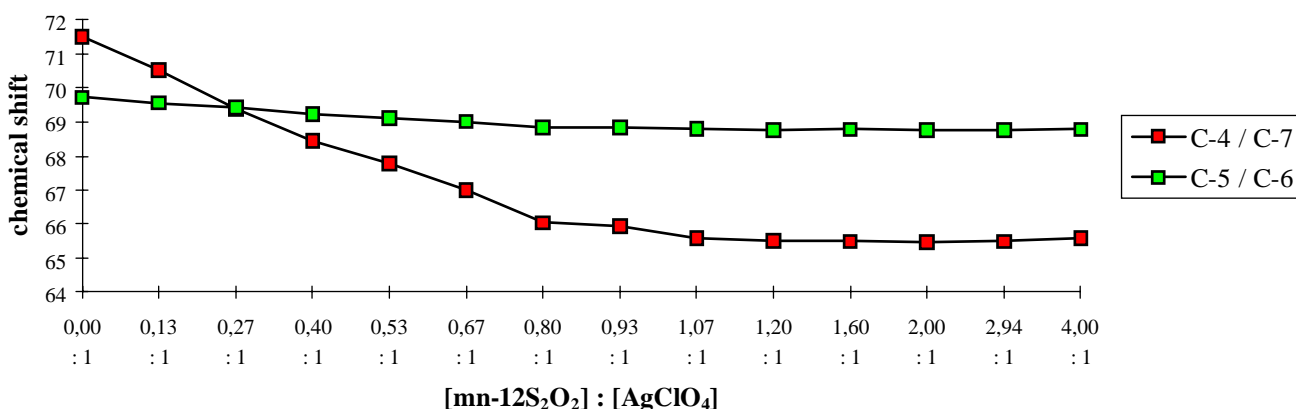
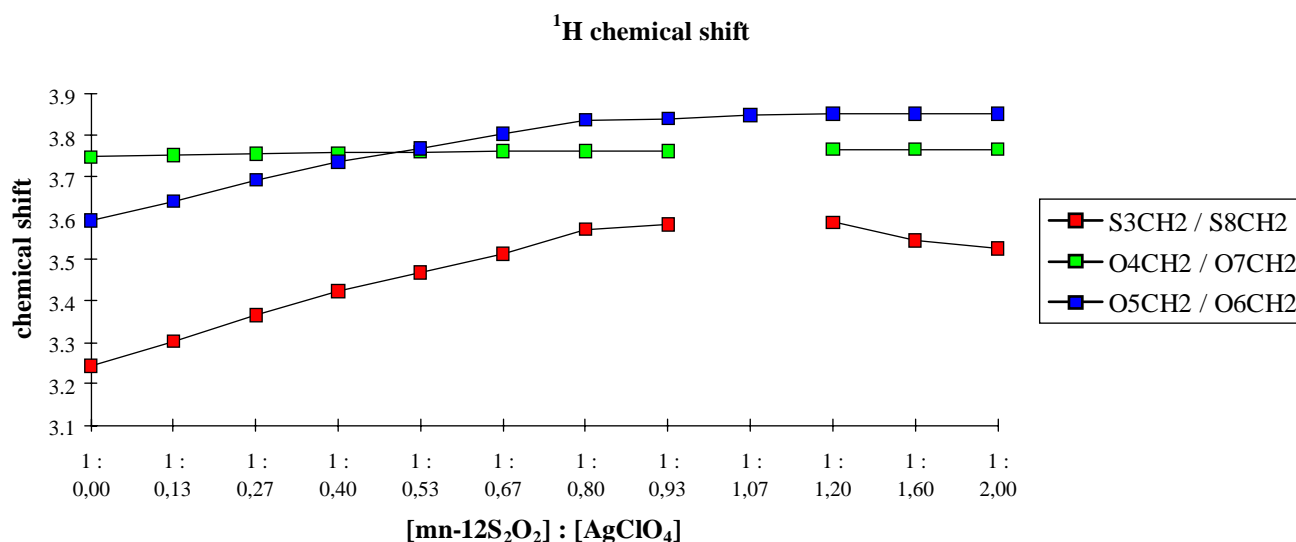
<sup>13</sup>C chemical shifts of C-4/C-7 and C-5/C-6

Figure 4a. The titration results



**Figure 4b.** The titration results

The determination of the energy barrier for the ring interconversion from 1 to 2 was also subject of the present study. The energy barrier of the ring S-C-C-O interconversion from 1 to 2 was calculated by molecular mechanical methods. The barrier was found to be -6,7 kcal/mol.

In order to study the corresponding complex formation,  $\text{AgClO}_4$  was added to the coronand solutions. The dependence of the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts on the [coronand]/[ $\text{AgClO}_4$ ] molar ratio was investigated (Figure 4). The exchange between the free and the complexed  $\text{mn-12S}_2\text{O}_2$  is generally fast on the NMR time scale; averaged shifts were obtained. The vs. molar ratio [coronand]/[salt] curves show a single sharp bend when the molar ratio is approximately 1:1. Accordingly, the formation of a 1:1 complex was concluded.

During  $^{109}\text{Ag}$  titration experiments of  $\text{AgClO}_4$  with  $\text{mn-12S}_2\text{O}_2$  in nitromethane solutions a yellow-coloured Ag com-

plex crystallized out at a molar ratio of 13.4 : 1. This complex has a 2 : 1 composition ( $\text{AgClO}_4$ :  $\text{mn-12S}_2\text{O}_2$ ). X-ray analysis of the complex revealed a polymeric structure with four Ag centres differing in the coordination sphere. The synthesis and the detailed structure of this and other oligonuclear  $\text{Ag}^{\text{I}}$  complexes of maleonitrile-dithiocrown ethers will be reported in a forthcoming report [5].

#### References

1. Holdt, H.-J. *Pure & Appl. Chem.* **1993**, 65(3), 477.
2. Drexler, H.-J.; Reinke, H.; Holdt, H.-J. *Chem. Ber.* **1996**, 129, 807.
3. Grotjahn, M.; Kleinpeter, E.; Drexler, H.-J.; Holdt, H.-J. GDCh-Fachgruppentagung Eichstätt (26. - 28. 09. 1996) (Poster)
4. Keller, E. *SCHAKAL 92/V256*. Freiburg, **1992**.
5. Drexler, H.-J.; Grotjahn, M.; Kleinpeter, E.; Holdt, H.-J. in preparation.