

## Thiacrown compounds with 1,2-dicyano-1,2-dithioethene units

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**Abstract** –  $S_2O_{n+1}$ -Coronands containing one 1,2-dicyano-1,2-dithioethene unit ((*Z*)-**2**( $n=1$ ), **3**( $n=2$ ), **4**( $n=3$ )) and macrocyclic tetrathioethers containing two 1,2-dicyano-1,2-dithioethene units bridged by propylene(**6**), butylene(**8**), pentylene(**9**) or hexylene(**10**) were synthesized by the reaction of (*Z*)-disodium-1,2-dicyanoethene-1,2-dithiolate with oligoethylene glycol dichlorides and  $\omega,\omega'$ -dibromoalkanes, respectively. The (*E*)-isomer of macrocycle **2** is the first example of an *S/O*-coronand with planar chirality. The enantiomers were separated by capillary gas chromatography with modified  $\beta$ -cyclodextrin as stationary phase. Unsaturated dithia[12]crown-4 (*Z*)-**2** is a selective extracting agent for  $PdCl_2$ . In the solid state the unsaturated tetrathia[14]crown-4 **6** and tetrathia[16]crown-4 **8** adopt "chair-like" conformations. Each of four sulfur atoms of both macrocyclic tetrathiaethers direct one lone electron pair toward the hole of the macrocycle.

### INTRODUCTION

The crown thioether 1,4,8,11-tetrathiacyclotetradecane ([14]ane $S_4$ ) adopts an "inside-out" conformation in his  $\alpha$ -form in which the electron densities of the sulfur atoms point out of the ring (ref. 1). Exodentate sulfur atoms necessitate extensive conformational rearrangement before chelation can occur, the ligand must turn "right-side in" with a corresponding enthalpic cost (ref. 2).

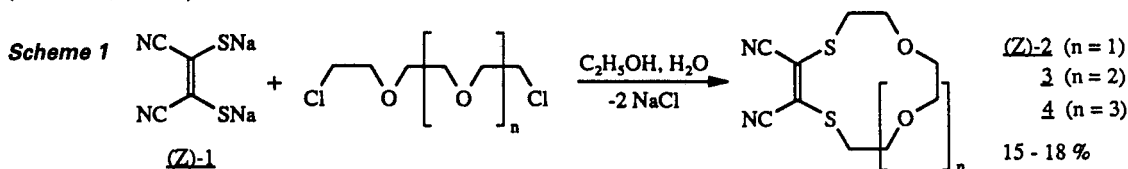
Unlike other crown thioethers in 1,4,7-trithiacyclononane all sulfur atoms point towards the central cavity (ref. 3). The resulting endodentate conformation closely resembles that required for chelation of a metal ion (ref. 4).

Peripheral modifications of macrocyclic tetrathioethers by introduction of geminal dimethyl groups change the conformations of the parent ligands to such conformers resembling those of oxa analogues. The introduction of two geminal dimethyl groups in [14]ane $S_4$  induces a macrocyclic conformation that is preorganized to receive  $Ni^{2+}$  (ref. 5). With 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane as auxiliary ligand a molybdenum(0)-dinitrogen complex was synthesized (ref. 6).

In contrast to crown thioether ligands containing only aliphatic chains crown thioethers with rigid 1,2-dithioethene units adopt only a limited number of possible ring conformations and the effective ring size are reduced (ref. 7-10). These properties provide a measure of steric control and predictability in ligand design. Of course, the  $\sigma$ -donor ability of the sulfur atoms in the 1,2-dithioethene units is decreased relative to common thioethers, but the chelate effect should increase the complexation strength which will be tunable by selecting the substituents at the carbon-carbon double bonds. Disubstituted unsaturated crown ethers are key substances for the synthesis of polymacrocyclic ligands (ref. 11).

## RESULTS AND DISCUSSION

A synthon for the synthesis of unsaturated crown thioethers is BAHR and SCHLEITZER's (Z)-disodium-1,2-dicyanoethene-1,2-dithiolate (ref. 12). The dithiacrown compounds (Z)-2, 3 and 4 were synthesized by high dilution reactions of the dithiolate (Z)-1 with oligoethylene glycol dichlorides in aqueous ethanol (scheme 1, ref. 13).



In (Z)-2 and 3 the exodentate orientation of the sulfur atoms and the endodentate orientation of the oxygen atoms (Fig. 1) are in agreement with the hitherto existing data for common O/S-coronands (ref. 14). Nevertheless, the exodentate orientation of the sulfur atoms is restricted since the sulfur atoms are an integral part of the rigid 1,2-dicyano-1,2-dithioethene unit (ref. 15).

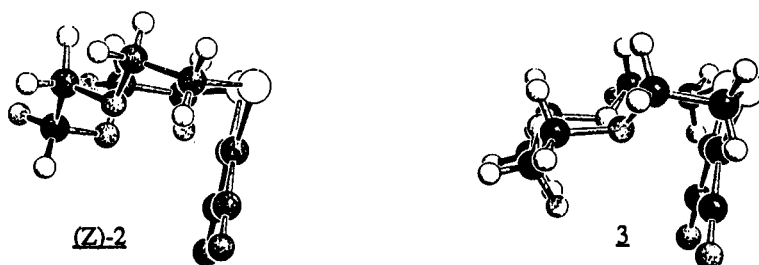
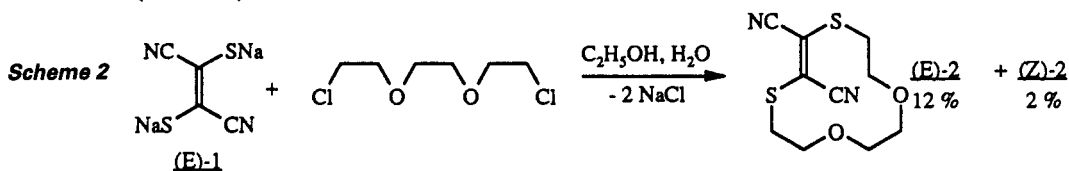


Fig. 1: Crystal structure of unsaturated dithiacrown compounds (Z)-2 and 3

## (E)-1,4-DIOXA-7,10-DITHIACYCLODODEC-8-EN-8,9-DICARBONITRILE (E)-2

The (E)-isomer of macrocycle 2 was synthesized by reaction of dithiolate (E)-1 with 1,8-dichloro-3,6-dioxaoctane (scheme 2).



In solution the macrocycle (E)-2 can be completely converted to its geometrical isomer by irradiation with uv-light, as shown by SIMMONS et al. in the case of bis(methylmercapto)fumaronitrile (ref. 16). Photoisomerization of (Z)-2 to (E)-2 is not possible. This observation should be similar to the case of the isomers bis(methylmercapto)fumaro- and bis(methylmercapto)maleonitrile, where the (Z)-isomer is thermodynamically more stable than the (E)-isomer. Due to the steric hindrance of the cyano functionalities a rotation of dicyanoethene groups around the axis along the C-S-bonds is not possible (Fig. 2).

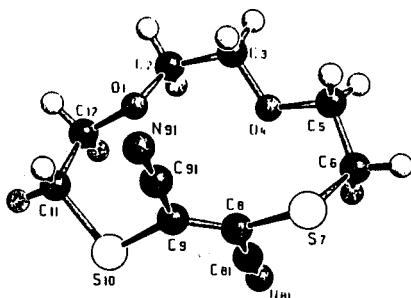


Fig. 2: Crystal structure of (E)-2

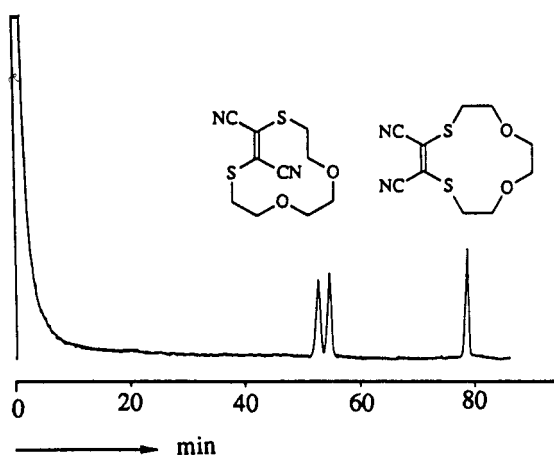
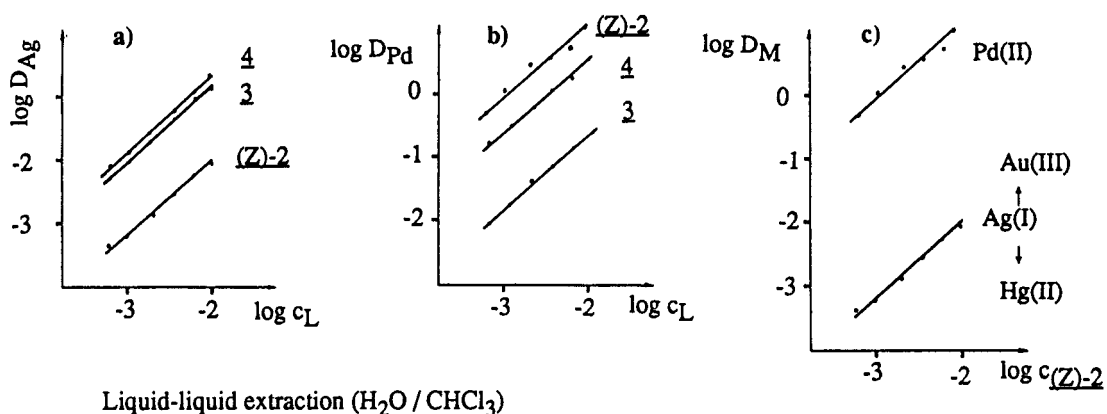


Fig. 3: Enantiomer separation of (E)-2. 25 m fused silica capillary coated with heptakis(2,6-di-O-methyl-3-O-pentyl)- $\beta$ -cyclodextrin at 180 °C

(E)-2 is the first example of an S/O-coronand with planar chirality. The enantiomers were separated by capillary gas chromatography with modified  $\beta$ -cyclodextrin as stationary phase (Fig. 3). The investigations of complexing capabilities in methanol and liquid/liquid extraction experiments revealed a very small tendency for (E)-2 to complex thiophilic metal ions (ref. 17).

#### COMPLEXING CAPABILITIES OF UNSATURATED DITHIACROWN COMPOUNDS

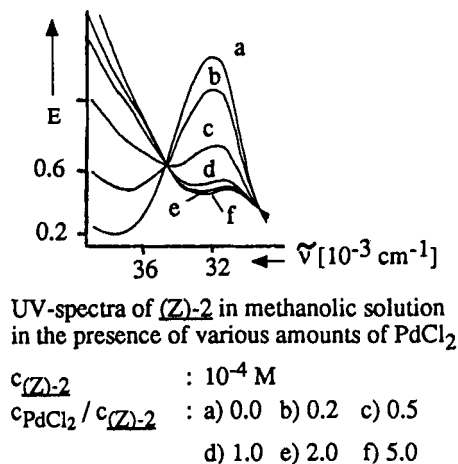
The results of the extracting capabilities of the unsaturated dithiacrown compounds (Z)-2, 3 and 4 for Ag(I) and PdCl<sub>2</sub> are pictured in Fig. 4. The distribution ratios for Ag(I) are small (Fig. 4a). With the ligand (Z)-2 they lie already within the range of the blind dates. These unsaturated dithiacrown compounds extract no detectable amounts of Cu(II) and Au(III). Better extracting results were obtained for PdCl<sub>2</sub> where the highest distributions ratios were reached with (Z)-2 (Fig. 4b). This macrocyclic ligand is a selective extracting agent for PdCl<sub>2</sub>. Under the chosen experimental conditions (Z)-2 extract PdCl<sub>2</sub> thousandfold better than Ag(I), Au(III), and Hg(II) (Fig. 4c, ref. 18).



$c_{M(NO_3)_n}$  :  $1 \cdot 10^{-4}$  M(Ag, Hg) / 1 H<sub>2</sub>O  
 $c_{MCl_n}$  :  $1 \cdot 10^{-4}$  M(Pd, Au) / 1 H<sub>2</sub>O  
 $c_{HPic}$  :  $5 \cdot 10^{-3}$  M / 1 H<sub>2</sub>O  
 $c_L$  :  $5 \cdot 10^{-4} - 1 \cdot 10^{-2}$  M / 1 CHCl<sub>3</sub>

Fig. 4a-c: Selective extraction of PdCl<sub>2</sub> by dithiacrown compound (Z)-2

Besides liquid/liquid extraction we investigated spectrophotometrically the interactions of (Z)-2, 3 and 4 with Pd(II) and Ag(I) in methanolic solutions (Fig. 5). We observed a direct proportionality between extraction constants and related complex stability constants. The good extracting capability of the ligand (Z)-2 for PdCl<sub>2</sub> should be caused by the relatively high complex formation constant. The crystal structure of the extracted complex PdCl<sub>2</sub>((Z)-2) is shown in Fig. 6. As can be seen, the ligand (Z)-2 has the correct geometrical coordination requirements for chelation of PdCl<sub>2</sub>. Comparison of the structures of the free ligand (Z)-2 and its PdCl<sub>2</sub>-complex suggest, that hardly any change of the ligand conformation occurs due to complexation of PdCl<sub>2</sub>.



| log $K_a(\text{CH}_3\text{OH})$ and log $\bar{K}_{\text{Ex}}(\text{CHCl}_3 / \text{H}_2\text{O})$ |                |                                      |                           |
|---|----------------|--------------------------------------|---------------------------|
| complex   | log $K_a$      | complex                              | log $\bar{K}_{\text{Ex}}$ |
| [PdCl <sub>2</sub> ( <u>(Z)</u> -2)]  | $6.2 \pm 0.3$  | [PdCl <sub>2</sub> ( <u>(Z)</u> -2)] | $7.8 \pm 0.2$             |
| [PdCl <sub>2</sub> (4)]   | $4.7 \pm 0.1$  | [PdCl <sub>2</sub> (4)]              | $7.2 \pm 0.2$             |
| [PdCl <sub>2</sub> (3)]   | $3.9 \pm 0.1$  | [PdCl <sub>2</sub> (3)]              | $5.9 \pm 0.1$             |
| [Ag(4)] <sup>+</sup>  | $3.1 \pm 0.03$ | [Ag(4)]Pic                           | $3.6 \pm 0.2$             |
| [Ag(3)] <sup>+</sup>  | $2.5 \pm 0.1$  | [Ag(3)]Pic                           | $3.4 \pm 0.1$             |
|   |                | [Ag( <u>(Z)</u> -2)]Pic              | $2.2 \pm 0.3$             |

Fig. 5: Interactions in methanolic solution of dithiacrown compounds with Pd(II) and Ag(I) at 25 °C

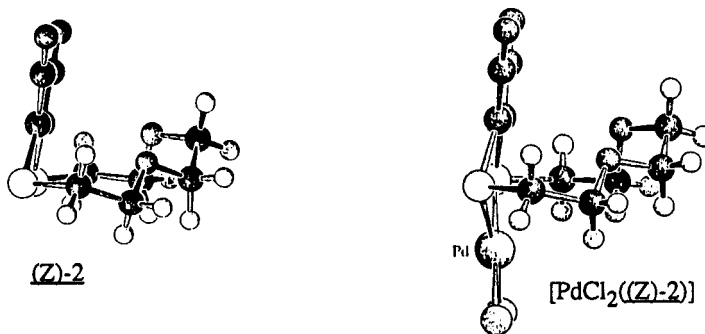


Fig. 6: Crystal structures of macrocycle (Z)-2 and its PdCl<sub>2</sub>-complex

The relatively small and constraint unsaturated dithia[12]crown-4 (Z)-2 can form only the *syn*-isomer with PdCl<sub>2</sub> (Fig. 7). In contrast the larger unsaturated dithia[18]crown-6 4 forms the *anti*-isomer with PdBr<sub>2</sub> (ref. 19).

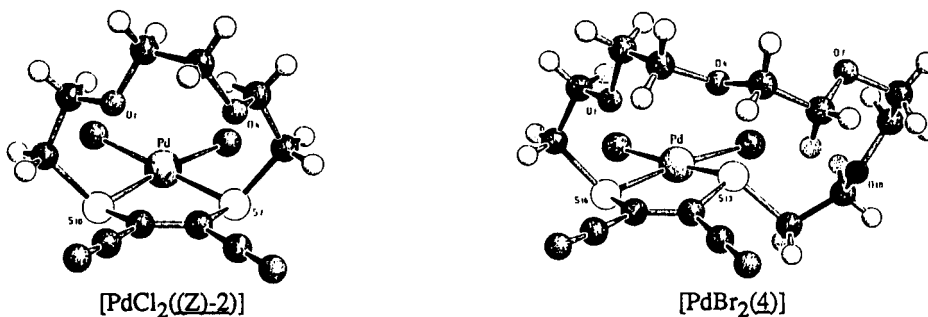


Fig. 7: Crystal structures of the complexes [PdCl<sub>2</sub>((Z)-2)] and [PdBr<sub>2</sub>(4)]

## TETRATHIACROWN COMPOUNDS WITH TWO DITHIOETHENE UNITS

On the basis of the previously discussed results we intended to investigate whether more than one dithioethene unit in polymacrocyclic ligands are compatible for the construction of preorganized coordination geometries. At first, we synthesized macrocycles with two 1,2-dicyano-1,2-dithioethene units.

## Scheme 3

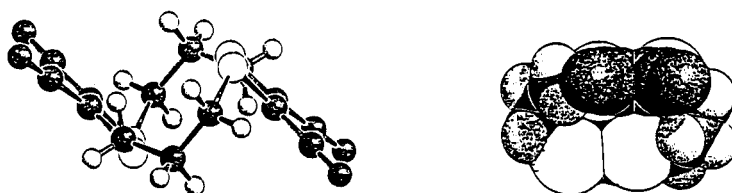
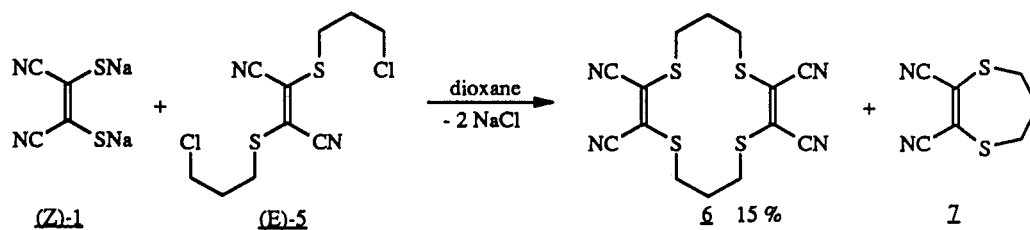


Fig. 8: Crystal structure of 2,3,9,10-tetracyano-2,3,9,10-tetradehydro-1,4,8,11-tetrathia[14]crown-4 **6**

The unsaturated tetrathia[14]crown-4 **6** was obtained by reaction of the dithiolate **(Z)-1** with bis( $\gamma$ -chloropropylthio)fumaronitrile **(E)-5** in dioxane (scheme 3). In the solid state the ring geometry of **6** can be described as "double chair" conformation (Fig. 8). Each of the sulfur atoms direct one lone electron pair towards the center of the ring. In this conformation **6** has practically no cavity (ref. 20). Unsaturated tetrathiacrown compounds with larger bridges than propylene can be synthesized by reaction of  $\omega,\omega'$ -dibromoalkanes with dithiolate **(Z)-1** in dioxane in yields of about 10-14 % (scheme 4) In the solid state the unsaturated tetrathia[16]crown-4 **8** adopt a "chair-like" conformation. As in the case of the tetrathia[14]crown-4 **6** all four sulfur atoms direct a lone electron pair toward the hole of the macrocycle (Fig. 9, ref. 21).

The investigations of the metal complexing ability, the electronic properties and the photochemical behaviour of these novel macrocycles and related systems are the subject of forthcoming reports.

## Scheme 4

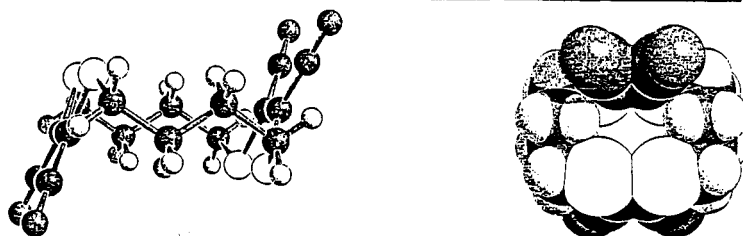
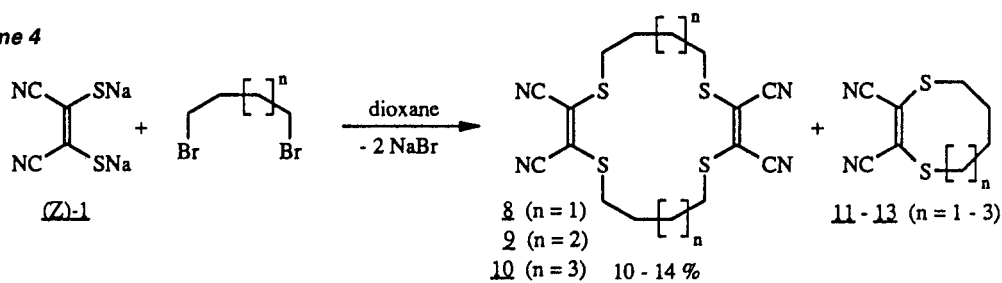


Fig. 9: Crystal structure of 2,3,10,11-tetracyano-2,3,10,11-tetradehydro-1,4,9,12-tetrathia[16]crown-4 **8**

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