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2,8,14-Trithio[15] *m*- / *p*- phenylene crownophanes: Ag^+ Selective Receptors

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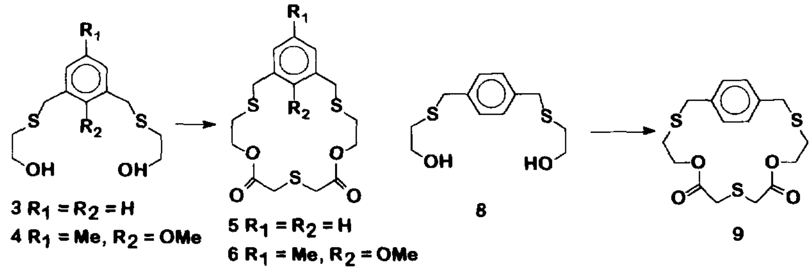
Abstract: Stereochemical restriction of *m*- and *p*- phenylene rings in phenylenethio crownophanes for sandwich type complexation with Pb^{2+} leads to their high Ag^+ selectivity. Copyright © 1996 Elsevier Science Ltd

In sulphur based organic receptors, for inducing Ag^+ selectivity from amongst soft metal cations, the optimum requirement of 2-4 ligating sites[1] preorganised in a three dimensional system[2] has been emphasized. We argued that any stereochemical or structural inhibition in such ionophores for sandwich complexation requiring > 1:1 stoichiometric host - guest interactions with most of the soft cations could further enhance their Ag^+ selectivity even against similar sized Pb^{2+} cation. Thus it has been found that macrocyclic designs **5**, **6** and **9** which can resort an edge -on disposition of *m*- and *p*- phenylene rings with respect to the plane of the macrocyclic ring, as evident from CPK models and solution nmr studies, are highly Ag^+ selective.



3 $R_1 = R_2 = H$
4 $R_1 = Me$, $R_2 = OMe$

5 $R_1 = R_2 = H$
6 $R_1 = Me$, $R_2 = OMe$

8

9

The phase transfer catalysed (K_2CO_3 - DMF - tetrabutylammonium hydrogensulphate) nucleophilic displacement of dibromides 1,3-bis(bromomethylene)benzene (**1**), 1,3-bis(bromomethylene)-2-methoxy-5-methylbenzene (**2**) and 1,4-bis(bromemethylene)benzene (**7**) with 2-mercaptoethanol give the diols **3** (80%), liquid, M^+ m/z 258; **4** (80%), liquid, M^+ m/z 286 and **8** (85%), m.p. 58°C, M^+ m/z 258, respectively. **3**, **4** and **8** react with thiodiglycolyl chloride under PTC conditions (KF - CH_2Cl_2-TBA HSO_4) to give macrocycles **5** (40%), liquid, M^+ m/z 372; **6** (35%), m.p. 100°C, M^+ m/z 416 and **9** (10%), m.p. 62°C, M^+ m/z 372, respectively. In the ^1H nmr spectra, the upfield shifts of $S\underline{CH_2}CH_2$ (-0.10), $S\underline{CH_2}CO$ (-0.20) and OCH_2 (-0.42) signals of **9**, in comparison with those of **5** and **6**, clearly show that in **9** the *p*-phenylene ring is oriented perpendicular to the plane of macrocycle, whereas *m*-phenylene ring of **5** and **6** is in its plane. The planar *p*-

phenylene ring of **8** does not show such an affect. The enhancement of OMe signal of **6** on saturation of OCH_2 signal in an n.o.e. experiment also favours its planar structure. However, saturation of OCH_2 in **9** enhances both ArH and SCH_2CO signals and saturation of ArH enhances OCH_2 and SCH_2 signals, indicating their proximities and edge-on structure for *p*-phenylene ring.

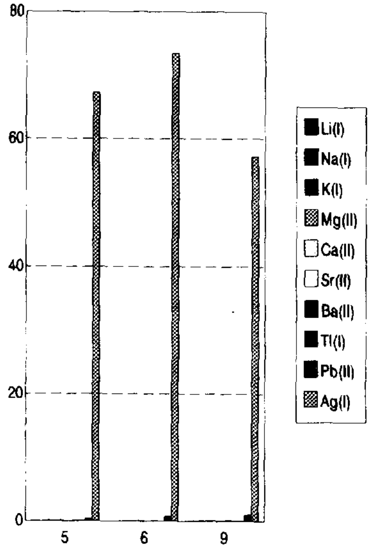


Fig 1. Extraction (%) profile[3] of macrocycles 5, 6 and 9.

The macrocycle **5** extracts[3] silver picrate (67.30 %) nearly 172 times than Pb^{2+} (0.39%) and **6** shows further enhanced extraction of Ag^+ (73.3%) but Ag^+ vs. Pb^{2+} selectivity is lowered due to increased extraction of Pb^{2+} (0.75%). The alkali, alkaline earth and Tl^+ cations are extracted only marginally. The lack of enhancement of OMe signal in solution of **6** and Ag^+ picrate (1:1) indicates that during complexation, rotation of phenylene ring places the OMe group out of the cavity and creates a steric inhibition for sandwich binding with metal ions other than Ag^+. However, in case of crownophane **9**, its smaller effective cavity size might be responsible for decreased extraction of Ag^+ (57.2%). In the ^{13}C nmr spectra of 1:1 solutions of **5**:Ag^+, **6**:Ag^+ and **9**:Ag^+ in $CDCl_3$ - DMF (1:1), the downfield shifts of all the three SCH_2 signals ($\Delta\delta$ 0.9 - 2.2) and in the ^1H nmr spectrum of **6**:Ag^+ ($CDCl_3$ - DMSO-d_6), the downfield shifts of $S\mathit{CH_2}$ ($\Delta\delta$ 0.29), $S\mathit{CH_2}Ar$ ($\Delta\delta$ 0.18) and $S\mathit{CH_2}CO$ ($\Delta\delta$ 0.15) signals as compared to those in macrocycles clearly show the participation of only -S- units in complexation with Ag^+.

Thus, the inability of macrocycles **5**, **6** , **9** to form sandwich complexes with other soft metal cations, invokes in them, the binding selectivity towards Ag^+.

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3. Conditions: 2 ml Metal picrate(0.01M)/ 2ml, H_2O; Ionophore (0.01M), 2ml $CHCl_3$.The values are in terms of % extraction. Each value is the mean of three independent measurements which are consistent within ± 1% error. Moore, S.S.; Tarnowski, T.L.; Newcomb, M.; Cram, D.J. J.Am.Chem.Soc., **1977**, 99, 6398.

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