Pergamon

Bioorganic & Medicinal Chemistry Letters, Vol. 5, No. 17, pp. 1917-1918, 1995

0960-894X/95 $9.50+0.00

0960-894X(95)00323-1

SILVER SELECTIVE TRIDENTATE THIOETHER CORONANDS

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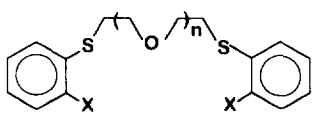
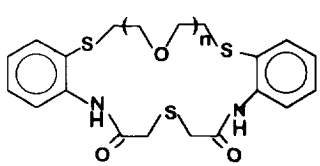
Abstract: The 18- and 21-membered tris thioether coronands show high binding selectivity towards silver(I).

The availability of two to four participative soft ligating sites i.e. thioether, amine etc., in an ionophore, constitutes a minimal structural feature for inducing Ag^+ selective character[1]. A rationally organised design of such a thioether ionophore should also incorporate structural features that facilitate formation of a spatial cavity[2]. In ^{13}C nmr monitored ionophore - metal cation interaction studies[1b], we found that podand **1(n=1)** binds Ag^+ through -S- and **2(n=1)** forms a pseudocavity by --NH_2 -- Ag^+--NH_2-- linkage where electrons on -S- are directed exodentate causing a decrease in interaction of -S- with Ag^+. Consequently, we have designed coronands **3** which in CPK models depict a symmetrical 3 x S cavity - optimum for Ag^+ binding. Here, the rigidity of the system induced by aromatic ring and amide bonds may not allow lonepair of -S- to move exodentate facilitating Ag^+ binding and amide and ether oxygens would not tend to participate in complexation with Ag^+.

The phase transfer catalysed (K_2CO_3 -DMF- TEBA Cl) nucleophilic displacement of appropriate dihalides with thiophenol and 2-aminothiophenol gave podands **1(n=1)** (77%), liquid, M+ m/z 290; and **2(n=1),** (85%), liquid, M+ m/z 320; **2(n=2)** (58%), liquid, M+ m/z 364; **2(n=3)** (80%), liquid, M+ m/z 408, respectively. The compounds **2 (n=1-3)** reacted with thiodiglycolyl chloride under phase transfer conditions (KF - dichloromethane - tetrabutylammonium hydrogen sulphate) to give macrocycles **3 (n=1)** (80%), m.p. 210°C, M^+ m/z 434; **3(n=2)** (75%), m.p. 205°C, M^+ m/z 478; **3(n=3)** (70%), m.p. 180°C, M^+ m/z 522, respectively.



1(X= H)
2 (X= NH_2)



3 (n=1-3)

Compound **1 (n=1)** extracts silver picrate nearly 7 times more than lead picrate (table -1) (entry 1). The presence of two NH_2 groups in **2(n=1)** though increases the extraction of both Ag^+ and Pb^{2+} picrates but the selectivity is not affected. However, **3 (n=1)** - a 18-membered coronand, shows only a small decrease in extraction of Ag^+ but that of Pb^{2+} is significantly decreased thus leading to nearly 280 times selective extraction of Ag^+ than Pb^{2+} (entry 3). The compound **3 (n=2)** - a 21-membered macrocycle also shows selective extraction of Ag^+ but of a lower order. Further, increase in ring size to 24 in **3(n=3)** causes total loss in Ag^+ selectivity which could be attributed to the enhanced adverse contribution of entropy factor toward binding. The alkali and alkaline earth and Tl^+ picrates are only marginally extracted by these ionophores. The absence of any change in carbonyl absorption positions of coronands **3** on their complexation with silver picrate rules out the participation of amide groups in complexation.

Table-1. Extraction (%) profile[#] of ionophores 1-3.

entry no.	Ionophore	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Pb^{2+}	Tl^+	Ag^+	$\frac{Ag^+}{Pb^{2+}}$	
1	1(n=1)	--*	---*	--*	--*	--*	3.15	8.97	0.14	66.8	7.4	
2	2(n=1)	0.34	0.55	0.40	0.17	0.39	3.80	10.10	0.54	79.6	7.8	
3	3(n=1)	0.15	0.29	0.23	0.12	0.39	0.17	0.25	0.21	70.37[@]	281	
4	3(n=2)	0.017	0.017	0.026	0.075	0.017	0.016	0.43	0.036	63.65[@]	146	
5	3(n=3)	0.025	0.024	0.026	0.025	0.019	0.008	28.00[@]	0.049	59.22[@]	2.1	

Extraction conditions[4]: Metal picrate (0.01 M) / 2ml, H_2O; ionophore (0.01M), 2ml, $CHCl_3$. The values are mean of three independent measurements which are consistent within + 2% error.
*not extracted. [@]solid metal picrate - ligand complex separates and values include the metal captured in precipitates.

Therefore, in thioether coronands **3**, the rigidity provided by the aryl ring and amide units contributes in creation of macrocyclic effect[5]. Further synthesis of coronands possessing three thioether and / or thioamides units in the relatively rigid cyclic systems and their role in silver selectivity is under investigation

Acknowledgements: We thank DST for research grant (SP / SI / 623 /92).

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(*Received in Japan* 14 *June* 1995; *accepted* 18 *July* 1995)