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Silver Selective Pyridine Based Diamide-Diester 18-Membered Macrocycle- Synthesis and Ionophore Character

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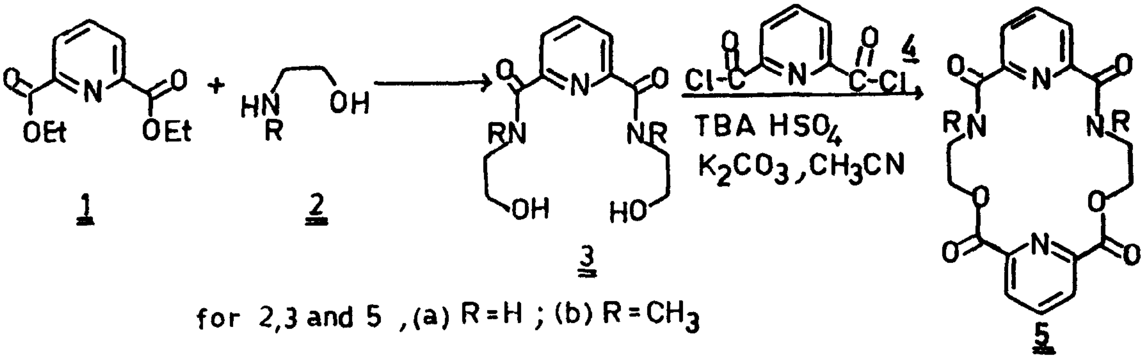
Abstract: The macrocycle **5b** transports and extracts ($CHCl_3$) silver picrate with remarkably high selectivity over alkali, alkaline earth, Tl^+ and Pb^{2+} picrates.

A periodic distribution of ester-amide combination in valinomycin and enniatins directs their binding specificity towards K^+ cation[1], but the amide group in many hosts through N-C=O··metal interactions has been found to direct the specificity of the host towards relatively soft alkaline earth cations[2]. The CPK models of 18-membered macrocycles **5** depict that in **5a** either the amide O or N can direct itself into the cavity whereas in **5b**, the steric restriction for inward transposition of Me group, directs only the amide O inwards.

1 condenses with 2-aminoethanol/2-methylaminoethanol to give diols **3a** and **3b**, which cyclize with pyridine-2,6-dicarbonyl dichloride (**4**) to form the macrocycles **5a** (35%) and **5b** (45%), respectively. Macrocycle **5a** extracts Pb^{2+} picrate more efficiently than the alkali, alkaline earth, Ag^+ and Tl^+ picrates, but selectivity factor is only of the order of 2-4 (table-1). The macrocycle **5b** is so selective in binding Ag^+ that it extracts Ag^+ nearly 40 and 50 times than similar sized Sr^{2+} and Pb^{2+}



for 2,3 and 5 ,(a) R=H ; (b) R=CH_3

Table-1 Cation extraction and Transport properties of macrocycles **5**

Ligand	Li^+	Na^+	K^+	Tl^+	Ag^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Pb^{2+}
Extraction[a] ($x10^2$, R values)[4]										
5a	3.08	3.37	3.34	3.43	7.07	2.43	3.72	3.84	3.36	18.65
5b	0	0	0	0.37	56.2	0	0	1.30	0	0.89
Transport rates[b] ($x10^8$ mol/ 24h)[4]										
5a	3.7	4.4	3.1	5.7	7.0	3.1	4.0	---	3.1	---
5b	1.2	2.7	2.2	11.5	543	3.0	2.0	---	1.5	---

[a] Extraction conditions: Metal picrate (0.01M)/2ml,H_2O; macrocycle (0.01M) 2ml,$CHCl_3$; [b] Transport conditions: Aq.I, metal picrate (0,01M),3ml,H_2O; membrane, macrocycle (0.01M),15ml,$CHCl_3$; Aq.II, 10ml,H_2O. Stirred for 6-8h at 27±0.1°C.

picrates, respectively and alkali and alkaline earth cations are hardly extracted. Similarly, **5b** transports Ag^+ picrate across $CHCl_3$ membrane nearly 50 times faster than Tl^+ picrate whereas other cations are hardly transported. Again, **5a** transports all the cations with same efficiency.

I.R. spectra of both **5a** and **5b** (KBr pellets) show two absorption bands at 1720(ester) and 1670(amide) cm^{-1} . However, in the complexes of Ag^+ picrate with **5a** and **5b**, the ester absorption band is shifted to 1735 cm^{-1} and the amide C=O band shifts to 1680 and 1610 cm^{-1} , respectively. Therefore, **5a** binds with Ag^+ picrate through amide nitrogen and **5b** does so through amide O. In the ^{13}C NMR spectra of the solutions of 1:1, **5a**:Ag^+ picrate and **5b**:Ag^+ picrate in $CDCl_3$-DMF, the downfield shifts of the pyridine carbon signals ($\Delta\delta$ ~2.0) as compared to those in free ligands, show the strong participation of pyridine nitrogen in complexation.

Thus, in **5b**, three dimensional arrangement of ligating sites (2xpy N, 2x N-C=O) determined by a minor structural variation caused by incorporation of a Me group in **5a**, perpetuates both qualitative and quantitative difference in their binding behaviour. Further investigations to determine the role of structural variations in invoking the binding selectivity in these macrocycles are being carried out.

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