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# Synthetic Ionophores 16. Synthesis and Association Behaviour of Bis-Pyridine Tetramide Macrocycles : Role of Increased Preorganisation on $Ag^+$ Selectivity[1,2]

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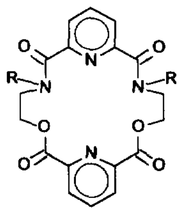
***Abstract:*** Pyridine based tetramide macrocycles (**6-9**) have been synthesized by nucleophilic displacement in pyridine-2,6-dicarbonyl dichloride with appropriate diamines. The 18-membered macrocycles **6** and **7** have well organized structures and 20-membered macrocycles **8** and **9** exist as mixtures of configurational isomers. The comparison of X-ray single crystal and energy minimized structures of previously reported diamide diester macrocycle(**1**) with those of macrocycles **6**, **7** and **1.AgNO$_3$** show that the macrocyles **6** and **7** possess type of preorganised structure attained by macrocycle **1** on complexation. This enhanced preorganisation in macrocycles **6** and **7** increases the $Ag^+$ extraction efficiency by >30% to 74 - 81% and $Ag^+$ / $Pb^{2+}$ selectivity by >300% to 245 - 283 times than in **1**. © 1997 Elsevier Science Ltd.

In designing of synthetic macrocyclic ionophores, the presence of amide group(s)[3] in their periphery, due to its dual ( O or N / NH) ligating character[4], higher negative charge on oxygen than ether and ester and incorporation of geometrical topology through partial carbon nitrogen double bond character induced steric control and hydrogen bonding, has acquired a special status. Recently, we have reported[5] that the in-built configurational rigidity induced by N-alkyl ($CH_3$ or benzyl) amide units present in the periphery of pyridine based diester - diamide macrocycles (**1**,**2**) invokes preorganisation conducive to $Ag^+$ binding and creates the steric bulk deterimental for the 2:1 (L:M) complexation desirable for soft metal cations other than $Ag^+$. We envisaged that if in these macrocycles, the two ester units are also replaced by the N-alkyl (R) amide units, the resulting tetramide macrocycles, which could conceptually acquire four configurational isomeric structures[6] (fig 1A-D), should show higher binding efficiencies and selectivities for $Ag^+$ than analogous diamide - diester macrocycles. Consequently, we have synthesized four macrocycles, 2 with two carbon (**6**, **7**) and 2 with three carbon (**8**, **9**) interceptions and have studied their extraction and transport behaviour towards alkali ($Li^+$, $Na^+$, $K^+$), alkaline earth($Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$), $Tl^+$, $Ag^+$ and $Pb^{2+}$ cations.



**1** R = Me; **2** R = $CH_2Ph$

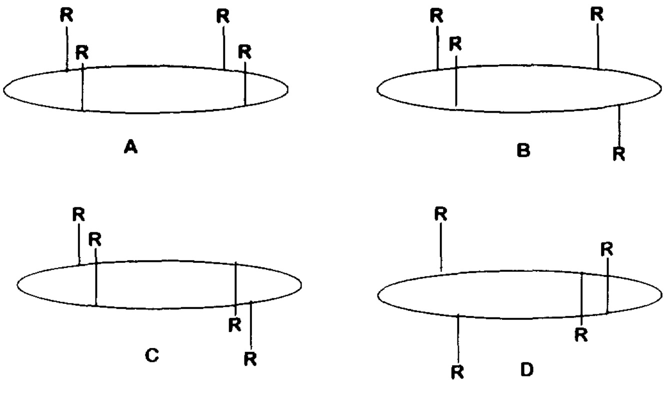
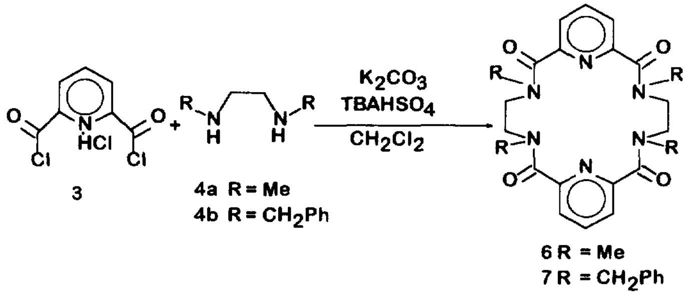


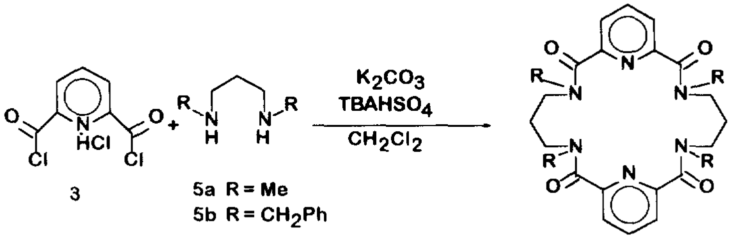
Fig 1

The nucleophilic displacement in pyridine - 2, 6 - dicarbonyl dichloride (**3**) with N, N' - dimethylethylenediamine (**4a**) under phase transfer catalytic conditions ($CH_2Cl_2$- $K_2CO_3$- TBAHSO$_4$) gives macrocycle **6** (26%), m.p. 272°C, M$^+$ m/z 438(35%). Its $^1$H nmr spectrum shows the presence of a singlet at δ 3.23 (12 H, 4 x $NCH_3$) and AB quartet due to $NCH_2$[δ 3.65, 4.28 (J = 9.0 Hz)] along with pyH multiplets at δ 7.81-7.85 and 7.95-8.03. Its $^{13}$C nmr spectrum shows one signal each due to $NCH_3$ (δ 41.66) and $NCH_2$(δ 47.64) along with pyridine carbon signals. These data point to a highly preorganised and a symmetrical structure for compound **6** in which four methyl groups are placed in a chemically equivalent environment.



The macrocycle 7, obtained by nucleophilic displacement in **3** with N,N' - dibenzylethylene diamine (**4b**), in its $^1$H nmr spectrum exhibits AB quartets due to both $NCH_{2\,(ring)}$ [δ 3.78, 4.05(J = 9.0 Hz)] and $NCH_{2(benzyl)}$ [δ 4.39, 5.94(J = 16Hz)] alongwith multiplets due to ArH and pyH, but in its $^{13}$C nmr spectrum shows normal $NCH_2$(δ 44.72), $NCH_2Ph$(δ 56.00), ArC and pyC signals. In the $^1$H nmr spectra, the appearance of NMe as singlet and $NCH_2$ and $OCH_2$ as broad signals in case of **1**; NMe as singlet and $NCH_2$ as AB quartet (Δ = 0.63 δ) in case of **6** and both $NCH_{2(ring)}$ (Δ = 0.27 δ) and $NCH_{2(benzyl)}$ (Δ = 1.55 δ) as AB quartets in case of 7, indicate an increase in organisation of the molecules while moving from macrocycles **1** to **6** to 7.

The macrocycles **8** and **9**, synthesized by phase transfer catalysed nucleophilic substitution in **3** with N,N'-dimethylpropylenediamine and N,N'-dibenzylpropylenediamine respectively, in their $^1H$ nmr show multiplets due to $NCH_2$(ring) and pyH / ArH protons and two singlets each due to NMe (**8**) / $NCH_2Ph$ (**9**) protons. $^{13}C$ nmr of **8** and **9** show multiple signals for each carbon. So, in macrocycles **8** and **9** the presence of more flexible spacers leads to the presence of a mixture of configurational isomers, which are responsible for the appearance of multiple signals in their $^1H$ as well as $^{13}C$ nmr spectra. However, the $^1H$ nmr data do not reflect on the extent of preorganisation in these macrocycles.



3

5a R = Me
5b R = $CH_2Ph$

8 R = Me
9 R = $CH_2Ph$

In order to ascertain the extent of preorganisation in macrocycles **6** and **7** in comparison with macrocycle **1**, the X-ray crystal structures of **7**, **1** and **1.AgNO₃** complex have been carried out and compared with that of **1**. Also, the force field energy minimizations[7] of the macrocycles **1**, **6** and **7** and hypothetical complexes of **1** and **6** with sodium nitrate presuming the complexation sites, as evident in X-ray crystal structure of **1. AgNO₃** complex, have been carried out.

The X-ray crystal structure of **1.AgNO₃** complex (fig 4b) shows that the macrocyclic ring co-ordinates with $Ag^+$ through two pyridine nitrogens N4 and N2. The geometry around $Ag^+$ is distorted tetrahedral, with other two positions being occupied by nitrate oxygens O7 and O8. The comparison between **1** and **1.AgNO₃** crystal structures reveals that complexation with $Ag^+$ does not significantly alter the bond distances, but leads to significant configurational and conformational changes. In free ligand **1** (fig. 2a), both the amide groups have cisoid configuration and two C=O units point in the same side of the plane of the ring and two methyl groups on the other side[5b]. On complexation with $AgNO_3$ one of the amide groups undergoes cisoid to transoid configurational change and the second one remains in cisoid configuration As a result, during complexation two methyl and one carbonyl of two amide groups remain on the same side and only one C=O moves to the other side of the mean plane of **1**. Further, in **1** the two pyridine rings are at a dihedral angle 17.2° which on complexation with $Ag^+$ attain a dihedral angle of 56.8° and macrocyclic ring attains a boat shaped structure.

The X-ray crystal structure of tetramide **7** (fig 2c) shows the orthognal placement of substituents of the four amide groups and alternate groups lie in opposite direction with respect to mean plane

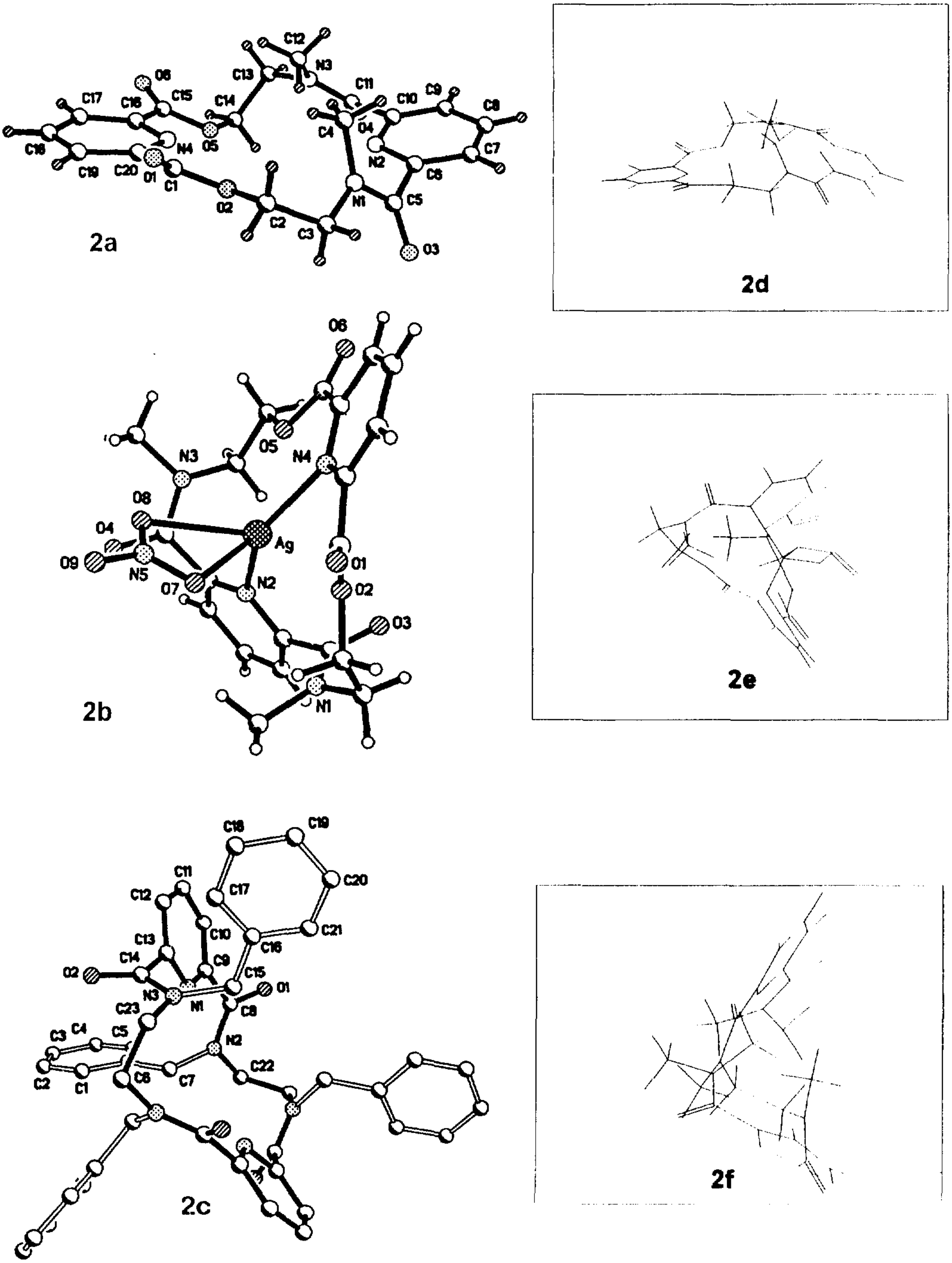


FIG 2. X-ray Crystal Structure of (a) macrocycle 1 (b) 1.Ag $NO_3$ Complex (c) macrocycle 7 and Energy minimized structures of (d) macrocycle 1 (e) 1.$NaNO_3$ complex and (f) macrocycle 6.

of pyridine rings. The macrocyclic ring thus possesses a crystallographic two fold axis of rotation at its centre and the cavity is protected by the two benzyl groups on each side. From the 8H of four $CH_2$ units 4H are directed into the cavity and the other 4H are placed outside the cavity, resulting in their non-equivalence and formation of AB quartets in the $^1H$ nmr spectrum. As a result of this organisation, two pyridine rings attain a dihedral angle of 32.8°. Thus we find that the tetramide macrocycle 7 as such possesses a boat shaped structure (fig 2c), which is quite similar to the one attained by ester amide macrocycle **1** on complexation with $AgNO_3$ (fig 2b).

The force field energy minimization of the macrocycle **1** (fig. 2d) shows that it attains a planar configuration in which both the N-Me groups lie on the one side and two amide carbonyl groups lie on the other side of the mean plane of the macrocyclic ring and the two pyridine rings lie in the plane of macrocyclic ring. The macrocycle **6** in its energy minimized configuration (fig 2f) shows the placement of alternate methyl groups of the four amide units in opposite direction and orthogonal with respect to the mean plane of the macrocyclic ring. Due to this arrangement, the two pyridine rings are tilted in the same direction. As a result the tetramide molecule **6** constitutes a boat shaped structure which is more organised than the planar structure of the diamide - diester macrocycle **1**. The macrocycle 7, in its energy minimized configuration again constitutes a boat configuration, like **6**, with sets of two alternate benzyl groups on the same side of the macrocyclic ring.

The energy minimization of **1.NaNO$_3$** complex[8] showing interaction between pyN and Na, as in the case of X-ray crystal structure of **1.AgNO$_3$**, shows that on complexation the two pyridine rings move out of the macrocyclic ring to attain boat shaped macrocyclic structure (fig 2e). However, in the formation of **6.NaNO$_3$** complex, the two pyridine rings in the macrocycle **6** have to move only slightly to give the energy minimized configuration of the complex. The comparison of structures of **1.NaNO$_3$** and **6.NaNO$_3$** complexes shows that both of them constitute quite similar boat shaped structures. Therefore, free diamide - diester **1** which has a planar structure, during complexation has to undergo considerable configurational / conformational changes to constitute boat shaped structure. But the tetramide macrocycle **6**, which in its free form already possesses the boat structure has to undergo only marginal conformational changes during complexation. Thus, both these approaches clearly define that the tetramide macrocycles **6** and 7 possess a preorganised configuration which is attained by **1** after complexation with $AgNO_3$. Hence, the macrocycles **6** and 7 are more compatible for complexation with $Ag^+$ than the macrocycle **1**.

## Association behaviour : extraction, transport and nmr titration studies

As the process of ligand facilitated transport of cations across a non-polar membrane has relevance to development of separation techniques for cations, the extraction[9] (complexation) and transport[10] (complexation/decomplexation) profiles of macrocycles **6-9** towards $Ag^+$, $Pb^{2+}$ , $Tl^+$, alkali metal cations ($Li^+$,

$Na^+$, $K^+$) and alkaline earth cations ($Mg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$) by using chloroform as apolar membrane have been determined.

**Table 1 :** Metal ion Extraction Profile (% Extraction) of Macrocycles

| Compd. No. | $Li^+$ | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Sr^{2+}$ | $Ba^{2+}$ | $Tl^+$ | $Pb^{2+}$ | $Ag^+$ | $\frac{Ag^+}{Pb^{2+}}$ | $\frac{Ag^+}{Tl^+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | ---- | ---- | ---- | ---- | ---- | 1.30 | ---- | 0.37 | 0.89 | 56.20 | 63.15 | 151.9 |
| **6** | 0.19 | 0.19 | 0.19 | 0.13 | 0.13 | 0.13 | 0.14 | 0.27 | 0.26 | 74.0* | 283.5 | 270 |
| **7** | ---- | ----- | ----- | ----- | ----- | ------ | ----- | ----- | 0.33 | 81.0* | 245 | ----- |
| **8** | ---- | ---- | 0.66 | 0.05 | 0.11 | 0.06 | 0.11 | 0.11 | 0.40 | 0.22 | 0.55 | 2.00 |
| **9** | ---- | ----- | 0.68 | ----- | 1.42 | 0.34 | ---- | 0.14 | 0.39 | 3.30 | 8.5 | 23.6 |

(---) not determined
*separation of solid silver - macrocycle complex

The macrocycle **6** extracts $Ag^+$ picrate (74%) nearly 283 times ( Table 1) than $Pb^{2+}$ (0.26%) whereas alkali and alkaline earth and $Tl^+$ cations are extracted by <0.27%. The macrocycle **7** shows further enhanced extraction of $Ag^+$ (81%) but $Ag^+$ vs. $Pb^{2+}$ selectivity is marginally lowered to 245. However, pyridine- diamide -diester **1** has been reported to show 56% $Ag^+$ extraction and $Ag^+$ vs. $Pb^{2+}$ selectivity is 63. Amongst all the pyridine or pyridine -thioether or thioether based macrocycles reported so far[5], the tetramide macrocycles **6** and **7** show highest order of extraction and $Ag^+$ / $Pb^{2+}$ selectivity.

In $^{13}C$ nmr titration studies, the macrocycle **6** on addition of one equivalent of silver picrate shows down field shifts for PyC-4 ( $\Delta\delta$ +2.84) and PyC-2 ($\Delta\delta$ +0.52) but coordination shift in other carbon signals is not seen. Therefore, macrocycle **6** complexes with silver picrate through two pyridine units and other constituents of the macrocycle are not affected during complexation. However, in its $^1H$ nmr, the addition of $Ag^+$ picrate causes collapse of the AB quartet ($\delta$ 3.97) due to $NCH_2$ protons to singlet ( $\delta$ 3.12) and shows that during complexation some conformational changes still occur in macrocycle **6**.

**Table 2 :** Metal Ion Transport Rafes Profiles ( x $10^7$ moles /24h ) of Macrocycles

| Compd. No. | $Li^+$ | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Sr^{2-}$ | $Ba^{2+}$ | $Tl^+$ | $Ag^+$ | $\frac{Ag^+}{Tl^+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1.2 | 2.7 | 2.2 | 3.0 | 2.0 | 0.0 | 1.5 | 11.5 | 543.0 | 47.2 |
| 6 | 3.4 | 5.9 | 6.8 | 2.9 | 2.1 | 3.5 | 2.2 | 232.3 | 4610* | 19.9 |
| 8 | ----- | ----- | ----- | ----- | ------ | 22.1 | ----- | 105.5 | 158.55 | 1.50 |
| 9 | 8.4 | 9.5 | 8.5 | 10.2 | 22.8 | 9.2 | 12.3 | 116.7 | 205.4 | 1.8 |

(----) not determined
*separation of solid silver - macrocycle complex

The macrocycles **8** and **9** containing three carbon spacers between two amide units, show poor extraction of all the cations including $Ag^+$ and $Pb^{2+}$. The macrocycle **8** extracts only 0.22% $Ag^+$ and 0.40% $Pb^{2+}$ whereas **9** extracts only 3.30% $Ag^+$ and 0.39% $Pb^{2+}$.

Macrocycle **6** shows transportation of $Ag^+$ 20 times than that of $Tl^+$ whereas it is 1317 times more than that of similar sized $Sr^{2+}$. The transport of cations has not been determined with macrocycle **7**, due to its low yield and hence non availability. Macrocycles **8** and **9**, due to their structural flexibility show poor transportation of $Ag^+$ and $Tl^+$ (table 2).

Evidently, the replacement of two ester units of **1** with two amide units in **6** and **7** remarkably enhances the rigidity and preorganisation of the macrocycles and as a result the extraction efficiency and selectivity towards $Ag^+$ over $Pb^{2+}$, $Tl^+$, alkali and alkaline earth cations is increased.

**Experimental :** For general experimental procedures see ref. 5b.

***Synthesis of macrocycles 6 - 9* : General Procedure :**

To a stirred mixture of anhydrous $K_2CO_3$ and tetrabutylammonium hydrogen sulphate (10 mg.) in dry dichloromethane (600 - 700 $cm^3$), a solution of diamine **4a** (1.0g., 11.3 mmol) in dry dichloromethane (60 - 70 $cm^3$) and a solution of pyridine-2,6-dicarbonyl dichloride (**3**) (2.73g., 11.3 mmol) in dry dichloromethane were simultaneously added dropwise and stirring was continued at room temperature. After completion of reaction (TLC, 7hrs.), the suspension was filtered off and the residue was washed with ethyl acetate. The combined filtrate and washings were distilled off and the crude reaction product was chromatographed over silica gel column using chloroform - ethyl acetate mixtures as eluents to isolate pure macrocycle **6**. Similarly, diamines **4a**, **5a** and **5b** were condensed with pyridine-2,6-dicarbonyl dichloride to give macrocycles **7**, **8** and **9**, respectively.

***Macrocycle 6*** : (26%); mp 272°C ($CH_2Cl_2$-ether); IR $\nu_{max}$(KBr) $cm^{-1}$ 1630(CONH); (Found : C, 60.98; H, 5.78; N, 19.12%. $C_{20}H_{22}N_6O_4$ requires C, 60.27, H, 5.94 and N, 19.18%); $^1H$ NMR ($CDCl_3$) δ(ppm): 3.23(12 H, s, 4 x $NCH_3$), 3.65, 4.28 (4 H, ABq, J 9, 4 x $NCH_2$), 7.81 - 7.85(2 H, m, PyH), 7.95 - 8.03(1 H, m, PyH); $^{13}C$ NMR ($CDCl_3$) δ(ppm): 41.66(+ve, $NCH_3$), 47.64(-ve, $NCH_2$), 125.32(+ve, PyCH), 138.44(+ve, PyCH), 152.39(PyC), 168.06(CONH); MS m/z 438($M^+$, 34.5).

***Macrocycle 7*** :( 2%); mp 210°C ($CH_2Cl_2$-ether); IR $\nu_{max}$(KBr) $cm^{-1}$ 1630(CONH); (Found C, 74.17; H, 5.37; N, 11.67%. $C_{46}H_{42}N_6O_4$ requires C, 74.39; H, 5.66 and N, 11.3%); $^1H$ NMR ($CDCl_3$) δ(ppm): 3.78, 4.06(8 H, ABq, J 9, 4 x $NCH_2$), 4.39, 5.94 (8 H, ABq, J 16, 4 x $NCH_2Ph$), 6.83 - 6.88, 7.14 - 7.26(20 H, m, ArH), 7.89-8.06(6 H, m, PyH); $^{13}C$ NMR ($CDCl_3$) δ(ppm): 44.72(-ve, $NCH_2$), 56.00(-ve, $NCH_2Ph$), 125.81(+ve, ArC), 126.88(+ve, ArC), 128.78(+ve, ArC) , 136.61(+ve, PyCH), 139.13(+ve, PyCH), 152.35(PyC), 168.81(CONH); MS m/z 742($M^+$, 76.5), 651($M^+$ - $CH_2Ph$, 15).

***Macrocycle 8*** : (10%); mp 208°C ($CH_2Cl_2$-ether); IR $\nu_{max}$(KBr) cm$^{-1}$ 1630(CONH); (Found : C, 61.37; H, 6.70; N, 20.50%. $C_{24}H_{30}N_6O_4$ requires C, 61.80, H, 6.44 and N, 20.60%); $^1$H NMR ($CDCl_3$) δ(ppm): 2.41(4 H, q, J 6, 2 x CH2), 2.99, 3.16(12 H, s, 4 x $NCH_3$), 3.17 - 3.27, 3.43 - 3.52(8 H, m, 4 x $NCH_2$), 7.64 - 7.96(6 H, m, PyH); $^{13}$C NMR ($CDCl_3$) δ(ppm): 26.84, 28.31 (-ve, $CH_2$), 33.59, 34.65, 37.01(+ve, $NCH_3$), 45.26, 48.95, 49.88(-ve, $NCH_2$), 124.00(+ve, PyCH), 124.62(+ve, PyCH), 124.71(+ve, PyCH), 138.11(+ve, PyCH), 138.24(+ve, PyCH), 152.60(PyC), 152.74(PyC), 167.75, 168.12, 168.68(CONH); MS m/z 466($M^+$, 39).

***Macrocycle 9*** : (13%); mp 216°C ($CH_2Cl_2$-ether); IR $\nu_{max}$(KBr) cm$^{-1}$ 1625(CONH); (Found C, 74.02; H, 5.12; N, 11.07%. $C_{48}H_{46}N_6O_4$ requires C, 74.81; H, 5.97 and N, 10.91%); $^1$H NMR ($CDCl_3$) δ(ppm): 3.19(4 H, q, J 8, 2 x $CH_2$), 3.00 - 3.45 (8 H, m, 4 x $NCH_2$), 4.56(4 H, s, 2 x $NCH_2Ph$), 4.72(4H, s, 2 x $NCH_2Ph$), 7.05 - 7.35 (20 H, m, ArH), 7.62 - 7.92(6 H, m, PyH); $^{13}$C NMR ($CDCl_3$) δ(ppm): 26.68(-ve, $CH_2$), 42.48(-ve, $NCH_2$), 46.78(-ve, $NCH_2$), 49.40(-ve, $NCH_2Ph$), 51.71(-ve, $NCH_2Ph$), 124.10, 124.89, 126.97, 127.70, 128.10, 128.68, 128.76(+ve, ArC) , 136.62(+ve, PyCH), 138.43(+ve, PyCH), 152.89(PyC), 168.78(CONH); MS m/z 770($M^+$, 73), 679($M^+$ -$CH_2Ph$, 12).

### *Synthesis of 1.AgNO$_3$ complex*

To a solution of **1**(100mg, 0.00024 mmol) in acetonitrile (25 ml), $AgNO_3$ (0.041g, 0.00024 mmol) was added and reaction mixture was refluxed for 2hrs. Acetonitrile was distilled off and the resulting product was crystallised from methanol (90%), m.p. 220°C, IR $\nu_{max}$(KBr) cm$^{-1}$ 1724(COO), 1645(CONH); Found C, 41.88; H, 3.57; N, 12.28%. $C_{20}H_{20}N_6O_4.AgNO_3$ requires C, 41.24, H, 3.43 and N, 12.03%; $^1$H NMR [$CDCl_3$ + $(CD_3)_2SO$] δ(ppm): 3.28(6 H, s, 2 x $NCH_3$), 3.74(4 H, bs, 2 x $NCH_2$), 4.77(4 H, bs, $OCH_2$), 7.79 - 7.82(2 H, m, PyH), 7.92 - 8.33(2 H, m, PyH), 8.36 - 8.40(2 H, m, PyH); $^{13}$C NMR [$CDCl_3$ + $(CD_3)_2SO$] δ(ppm): 32.45(+ve, $NCH_3$), 44.54(-ve, $NCH_2$), 63.99(-ve, $OCH_2$), 122.02(+ve, PyCH), 129.97(+ve, PyCH), 140.63 (+ve, PyCH), 142.23(PyCH), 149.56(PyC), 163.24(CONH), 166.74(COO).

### *Crystal Structure Determinations*

Data for the crystals of 7 were measured at room temperature using Seifert XRD 3000S diffractometer with graphite monochromatized CuKα radiation to a maximum θ value of 65°. Two standard reflections were measured after every 100 reflections. Cell constants were refined using LSCUCRE[11] programme with 52 reflections for crystals of 7. The data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct method with SIR92 and SHELXS86[12]. All the known hydrogen atoms were refined anisotropically using full matrix least squares method[13,14].

Data for the crystals of **1.AgNO$_3$** was measured at room temperature using Siemens P4 diffractometer with graphite monochromatized MoKα radiation using a θ - 2θ scan mode. Of the 4447 measured reflections 43 were unique [I > 2 σ (I)]. Data were corrected for Lorentz and polarisation effects and an empirical absorption correction was applied.

**Table 3** : Crystal Data and Data collection parameters

| Compound | **1.$AgNO_3$** | 7 |
|---|---|---|
| Formula | $C_{20}H_{20}N_5O_9Ag$ | $C_{46}H_{42}N_6O_4$ |
| Mol Wt | 582.82 | 742.86 |
| lattice group | monoclinic | monoclinic |
| space group | $P2_1/c$ | Ic or I2/c |
| cell dimensions | | |
| a (Å ) | 8.904(1) | 19.425(5) |
| b (Å ) | 11.473(1) | 9.904(2) |
| c (Å) | 22.434(1) | 20.300(5) |
| β (deg) | 100.9(1) | 97.03(2) |
| V ($Å^3$) | 2250.4(3) | 3876.1 |
| Z | 4 | 4 |
| Dc ($g/cm^3$) | 1.719 | 1.273 |
| μ (Cu $K_\alpha$) ($cm^{-1}$) | 0.959(MoKα) | 0.66 |
| No. of reflections: | | |
| measured | 4447 | 3292 |
| independent | 2943 | 3080 |
| obsd. [I >2σ(I)] | 2429 | 1473 |
| no. of variables | 316 | 254 |
| R (%) | 0.049 | 0.04 |
| Rw (%) | 0.06 | 0.05 |

The structure was solved by heavy - atom Patterson methods and expanded using Fourier methods. All the non-hydrogen atoms were refined anisotropically. Refinement was by full - matrix least squares R = 0.049 and Rw = 0.06 [ $R = \Sigma ( |F_o| - |F_c| / \Sigma |F_o| )$ and $Rw = [\Sigma w( |F_o| - |F_c| )^2 / \Sigma(wF_o^2)]^{1/2}$. The maximum and minimum electron densities in the difference Fourier map are 0.62 and -0.56 $Å^3$. All crystallographic calculations were performed using SHELXTL crystallographic package.

***Extraction Measurements :***

An aqueous solution (2 $cm^3$) of metal picrate (0.01 mol $dm^{-3}$) and a chloroform solution (2 $cm^3$) of the macrocycle (0.01 mol $dm^{-3}$) were shaken in a cylindrical tube closed with a septum for 5 minutes and kept at 27± 1°C for 3 - 4 h. An aliquot of chloroform layer (1 $cm^{-3}$) was withdrawn with a syringe and diluted with acetonitrile to 10 $cm^{-3}$. The UV absorption of this solution was measured against $CHCl_3$ - $CH_3CN$(1:9) solution at 374 nm. Extraction of metal picrates has been calculated as the percentage of metal picrate extracted in chloroform layer and the values are the mean of three independent measurements which were within ± 2% error (Table 1).

***Transport Measurements:***

Transport experiments were carried out in a cylindrical glass cell consisting of outer and inner jackets by using (i) metal picrate (0.01 mol $dm^{-3}$) in water (3 $cm^3$) in the inner phase; (ii) water (10 $cm^3$) in the outer phase; (iii) ligand (10 mmol $dm^{-3}$) in the chloroform layer (15 $cm^3$) with stirring (150±5 r.p.m.) at 27 ±

0.05 °C. After stirring for 8h, the concentrations of the picrates transported in the aqueous receiving phase were determined from the UV absorptions at 355 nm. Each value is a mean of three experiments which are consistent within ± 10% (Table 2). Before determining the transport rates, blank experiments were performed in the absence of the carrier macrocycle in the chloroform layer to check the leakage of metal picrates. Only a significant leakage was observed in case of $Pb^{2+}$ and so, transport of $Pb^{2+}$ was not determined. (Table 2)

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