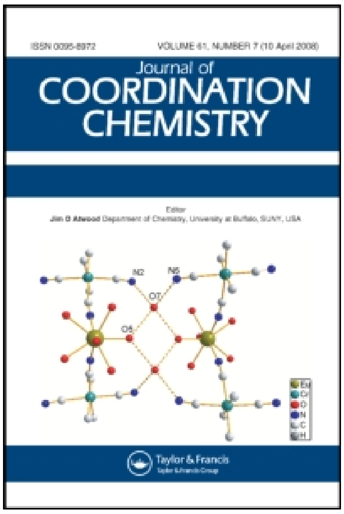

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A NEW EXPANDED SCHIFF-BASE CRYPTAND

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A new expanded Schiff-base cryptand derived from the direct '2+3' cyclocondensation of tris(2-aminoethyl)amine (tren) and 2,6-bis[formylphenoxymethyl]-pyridine (bfpp) is reported with its dinuclear copper (II) perchlorate complex. Reaction of tren and bfpp in the same ratio and in the presence of metal templates gave metal complexes of '1+1' and '2+2' macrocycles bearing one and two aminoethyl pendant arms, respectively.

Keywords: Schiff base; Cryptand; Cu(II); Macrocyclic ligand

INTRODUCTION

Schiff-base condensation reactions have been used to produce a large number of macrocyclic ligands and metal complexes [1]. Whereas '1+2' condensations of the appropriate dicarbonyl precursor with the required monoamine give acyclic ligands, '1+' and '2+2' cyclo-condensations of dicarbonyls with diamines generate mononucleating or binucleating macrocycles and these products can arise as a result of direct synthesis or *via* metal-templated reactions [2]. If a Schiff-base cyclo-condensation occurs between a dicarbonyl and triamine in a 3:2 ratio (Scheme 1) then the result is a cryptand [3]. For example, hexaimino-cryptands may be obtained by '2+3' condensation of tris-(2-aminoethyl)amine (tren) with dialdehydes OHC—R—CHO, in some cases without the aid of a template ion [4]. It has

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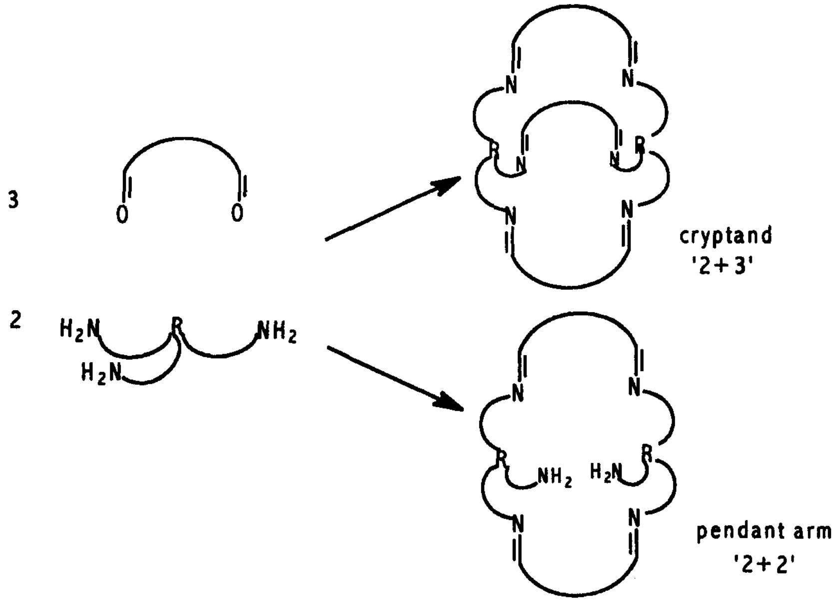


SCHEME 1 Pathways for Schiff-base condensation to yield either a cryptand or a pendant arm macrocycle.

also been reported that when the reaction of tren with 2,6-diacetylpyridine (in the presence of either barium or silver(I) cations) is carried out in a '2+3' ratio a 24-membered pendant-arm Schiff-base macrocycle results (Scheme 1) and the anticipated cryptand is not obtained [5,6]. The '2+2' macrocyclic products are isolated in higher yield when a '2+2' macrocycle was subsequently found to undergo readjustment in the presence of an acidic medium to produce the analogous cryptand as its diprotonated salt [8].

The goal in this work was to introduce a larger spacer unit incorporating an aromatic moiety to ensure the generation of a new cryptand bearing an enlarged central cavity. The precursors chosen for this type of cryptand were tren and 2,6-bis[formylphenoxymethyl]pyridine (bfpp). The synthesis was attempted using both direct '2+3' Schiff-base condensation of tren and bfpp and template procedures in the presence of either barium or silver(I) ions.

EXPERIMENTAL

2,6-bis[formylphenoxymethyl]pyridine was prepared by literature methods [9].

Cryptand $L^1 \cdot H_2O$

A solution of tris(2-aminoethyl)amine (tren) (4 mmol) in methanol (20 mL) was added to a warm solution of 2,6-bis[formylphenoxymethyl]pyridine (bfpp) (6 mmol) in methanol (300 mL) and refluxed for 2 h. The hot solution was filtered and left to stand in a refrigerator overnight. The resulting suspension was filtered to leave a pale yellow solid in 54% yield.

Microanalysis

Anal. Calcd. for $C_{75}H_{77}N_{11}O_7$ (%): C, 72.38; H, 6.24; N, 12.3. Found: C, 72.18; H, 6.02; N, 11.93. IR (KBr disc): 1636υ_{CN} cm^{-1}; MS(FAB; matrix, NOBA): 1226[L^1+H]$^+$.

[$BaL^2(SCN)_2$]

To a refluxing solution of bfpp (3 mmol) in acetonitrile (150 mL), a solution of barium thiocyanate (3 mmol) in acetonitrile (45 mL) was added. Tren (2 mmol) in methanol (20 mL) was then added dropwise and the resulting solution was refluxed for about 15 minutes before being filtered hot and allowed to cool to room temperature. The volume was reduced by rotary evaporation to obtain [$BaL^2(SCN)_2$], (**1**), as a yellow solid in 74% yield. Microanalysis: Anal. Calcd. for $C_{29}H_{31}N_7O_2S_2Ba$ (%): C, 48.99; H, 4.39; N, 13.62. Found: C, 48.64; H, 4.00; N, 13.79. IR(KBr disc): 3385 and 3325 υNH_2, 2054υSCN, 1636υCN cm^{-1}; MS(FAB; matrix, NOBA): 653 [BaL^2SCN]$^+$, 458[L^2+H]$^+$.

[$Ag_2L^3(NO_3)_2$]

By applying the procedure described and using $AgNO_3$ as the template the mixture was refluxed for 5 h under nitrogen and protected from the light. After refluxing, the solution was filtered hot, then cooled to room temperature. The volume was reduced by rotary evaporation to obtain [$Ag_2L^3(NO_3)_2$] as a cream solid in 64%. Microanalysis: Anal. Calcd. for $C_{54}H_{62}N_{12}O_{10}Ag_2$ (%): C, 51.75; H, 4.95; N, 13.41. Found: C, 51.47; H, 4.63; N, 13.24. IR (KBr disc): 3380 and 3323υNH_2, 1635υCN, 1383υNO_3 cm^{-1}; MS (FAB; matrix, NOBA): 1021 [AgL^3]$^+$, 915 [L^3+H]$^+$.

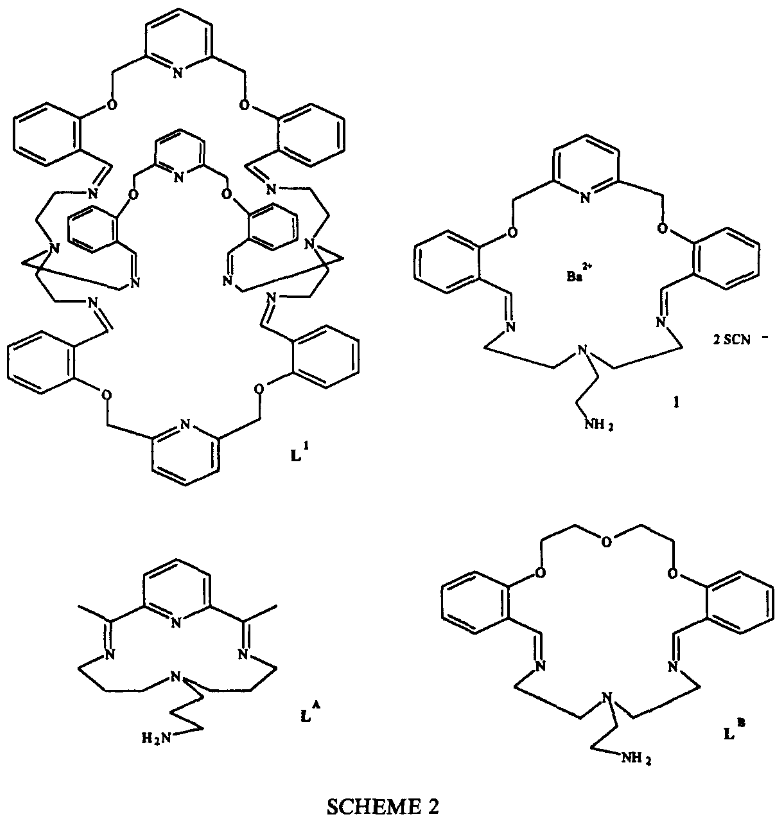
[$Cu_2L^1(ClO_4)_4$]

The cryptand L^1 (05 mmol) was dissolved in hot ethanol-acetonitrile (1 : 1, 50 mL) and added to $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol) in acetonitrile (20 mL).

On mixing, a blue solution was produced from which small blue crystals of $[Cu_2L^1(ClO_4)_4]$ were isolated after letting the solution stand for 18 h. Yield, 53%. Microanalysis: Anal. Calcd. for $C_{75}H_{75}N_{11}O_{22}Cl_4Cu_2$ (%): C, 51.4; H, 4.28; N, 8.80. Found: C, 50.9; H, 4.10; N, 9.02. IR (KBr disc): 1630υCN, 1084υClO$_4$, cm^{-1}; MS (FAB; matrix, NOBA): 1551 $[Cu_2L^1(ClO_4)_2]^+$, 1452 $[Cu_2L^1ClO_4]^+$, 1389 $[CuL^1ClO_4]^+$ a.m.u.; '2+3'.

RESULTS AND DISCUSSION

The synthesis of L^1 was first attempted by both direct and template '2+3' Schiff-base condensation of tris(2-aminoethyl)amine (tren) with 2,6-bis[formylphenoxymethyl]pyridine (bfpp) by using barium or silver(I) ions as templating agents.



SCHEME 2

In the presence of barium the anticipated cryptand was not obtained and a barium complex, $[BaL^2](SCN)_2$ (**1**), arising from a 1 : 1 macrocyclic condensation was recovered. That an incomplete condensation to give the cryptand had occurred was evidenced in the IR spectrum where bands at 3385 and 3325 cm^{-1} indicated the presence of unreacted amine groups with further bands at 2054 cm^{-1} (υSCN) and 1636 cm^{-1} (υC=N). The FAB mass spectrum of the product showed a parent peak at $m/e = 653$ corresponding to $[BaL^2SCN]^+$, arising from the loss of one anion, and a second peak at $m/e = 458$ corresponding to protonated metal-free L^2. It has not been possible to grow crystals suitable for structural analysis. But, by analogy [6, 10], it can be suggested that the barium is coordinated to all of the donor atoms from the macrocycle and to at least one, if not both, of the N-bonded anions [11].

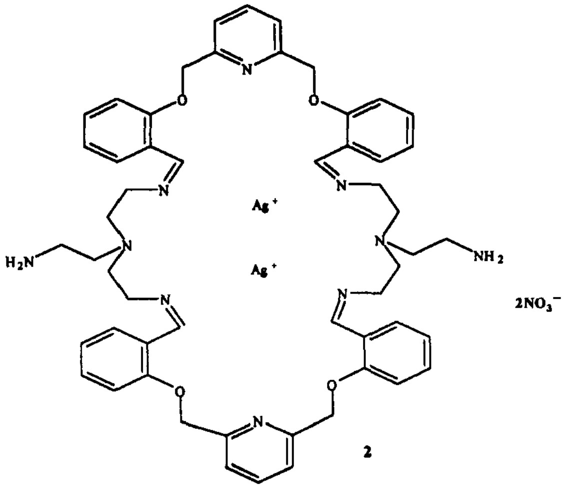
Macrocycle L^2 is a rare example of a 1+1 cyclocondensation leading directly to a product having an amino-pendant arm. Complexes of the analogous Schiff base L^A, derived from template condensation of 2,6-diacetylpyridine and tris(3-aminopropyl)amine were first suggested [12] in 1979 and have recently been confirmed through the X-ray crystal structure of $[NiL^A](ClO_4)_2$ which shows the metal to be coordinated by the annular and pendant donor atoms [13]. Macrocycle L^B has been prepared by reaction of tren with 1,7-bis(2′-formylphenyl)-1,4,7-trioxaheptane both directly and by metal-template procedures [14]. The structure of the cadmium complex $[CdL^B](ClO_4)_2$ shows that the macrocycle folds into a cleft-like conformation to accommodate the metal which is hepta-coordinated by all of the ligand donors [14].

Lanthanides have been successfully used in the preparation of cryptates, particularly with phenol-derived head units [15, 16]. Preliminary results [17] show that the use of $La(NO_3)_3$ as the template in the reaction of tren and bfpp leads to a '1+1' cyclocondensation as evidenced by the formation of $[LaL^2](NO_3)_3$. The IR again showed free amine bands and the FAB mass spectrum gave a parent peak at $m/e = 720$ corresponding to $[LaL^2(NO_3)_2]^+$.

When silver(I) was used as the metal ion template the '2+2' silver complex of L^3, $Ag_2L^3(NO_3)_2$, (**2**), was formed. Again the IR spectrum showed evidence of incomplete cyclization with NH_2-stretches arising at 3380 and 3323 cm^{-1} and with further bands at 1383 cm^{-1} (υNO_3) and 1635 cm^{-1} (υC=N). The FAB mass spectrum showed a parent peak at $m/e = 915$. It was again not possible to obtain crystals suitable for structural analysis but it is proposed, by analogy with related dinuclear silver(I) complexes [5, 7], that the macrocycle would be folded into a cleft-like conformation with the silver atoms bound by the nitrogen atoms of the ligand. Intriguingly, expansion of the mass spectra of the described macrocyclic products indicated the presence of trace amounts of L^1 as evidenced by very small peaks at $m/e = 1226$ $[L^1+H]^+$. This suggested that a direct synthesis should be attempted in order to try and synthesize the metal-free cryptand.

The ligand L^1 was then obtained in good yield (54%) by direct reaction of tren and bfpp in a 2:3 ratio in methanol at room temperature with stirring [9]. The white product was characterized by IR, a band at $1636\,cm^{-1}$ was attributed to the imine bond and there was no amine signal indicating that cyclocondensation had fully occurred to obtain the cryptand. The FAB mass spectrum showed a main peak at $m/e = 1226$ corresponding to $[L^1+H]^+$. ^1H NMR and studies of the cryptand were not possible because of the limited solubility of the cryptand. A broad IR signal *ca.* $3400\,cm^{-1}$ and the microanalytical data suggest the presence of a water molecule and it is likely that this is encapsulated within the cryptand.

The cryptand L^1 was expected to function as a dinucleating host. Treatment of L^1 with copper(II) perchlorate in ethanol-acetonitrile solution generated blue crystals which, unfortunately, were too small for an X-ray crystallographic structure determination, as was also the case for the barium, lanthanum and silver complexes described above. The IR spectrum showed peaks at 1630 and $1084\,cm^{-1}$ assigned to $\nu C{=}N$ and the presence of ionic perchlorate, respectively. The FAB mass spectrum showed peaks at $m/e = 1551$ $[Cu_2L^1(ClO_4)]^+$ and 1389 $[CuL^1(ClO_4)]^+$ and this information



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SCHEME 3

together with the microanalytical results lead to the formulation of the product as $[Cu_2L^1](ClO_4)_4$.

CONCLUSIONS

The direct, non-template synthetic route from tris(2-aminoethyl)amine and 2,6-bis[formylphenoxymethyl]pyridine gave the '2+3' cryptand (L^1). However when barium was used as metal template only a '1+1' pendant-armed macrocyclic product (L^2) resulted as the corresponding mononuclear complex. Similar results are reported for La(III) as metal [17], in contrast to silver(I) as the metal template then a '2+2' bibracchial macrocyclic product (L^3) resulted which was recovered as the corresponding dinuclear silver(I) complex. It is not obvious why different products arise from La^{3+} and Ag^+ since they have similar ionic radii for the anticipated coordination numbers of eight and six ($r_{cat} = 130$ and 129 pm respectively); Ba^{2+} is larger and has $r_{cat} = 156$ pm for eight coordination and gives a '1+1' product as does La^{3+}. The ionic potentials (Z^+/r_{cat}) are higher for La^{3+} and Ba^{2+} and this may have an influence on the ready formation of the '1+1' macrocycle in the presence of these ions.

The opportunity to explore this area further has been restricted due to solubility problems and the generation of poor quality crystals. Nevertheless, it has been possible to show the potential of the cryptand to form oligonuclear complexes in a complexation experiment with copper(II) which produced a dinuclear copper(II) species.

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