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The synthesis and crystal structure of a new diprotonated Schiff base cryptand

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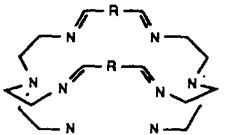
The synthesis and crystal structure of the diprotonated cryptand derived from the reaction of tren and 2,6-diacetyl pyridine is reported. The imino nitrogens of the Schiff base linkages are directed so that the dicarbimine functions are in *trans,trans* geometry relative to the pyridine C–N bond. This configuration has not previously been reported in related pyridine-derived Schiff base macrocycles.

The [2 + 3] Schiff base cyclocondensation of triamines with dicarbonyls has generated a range of hexa-imino cryptands either as free ligands by direct synthesis[1-8] or as metal complexes by use of metal-template procedures involving alkali metals,[9,10] alkaline earth metals[11,12] and silver.[2,3,7,13] Further metal complexes incorporating alkaline earth metals, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{I}, Cu^{II} and Zn^{II} have been synthesised by direct synthesis from the free ligands[1,4,6-8] or by transmetallation reactions with kinetically labile precursor complexes.[9-13] In particular a series of compounds, **1** (**2**–**9**), has been synthesised from tris(2-aminoethyl)amine (tren); a notable absence from this collection is the anticipated cryptand derived from the reaction of tren and 2,6-diacetyl pyridine and attempts to form this compound, particularly by template procedures involving Ag^+, have led only to the recovery of homodinuclear metal complexes of the bibracchial [2 + 2] Schiff base macrocycle (**10**).[14,15] In this paper we report the synthesis and characterisation of the diprotonated Schiff base cryptand [(**11**)] which is derived from tren and 2,6-diacetylpyridine under various sets of reaction conditions. The X-ray crystal structure of $[(\mathbf{11})][BF_4]_2.CH_3CN$ is also reported.



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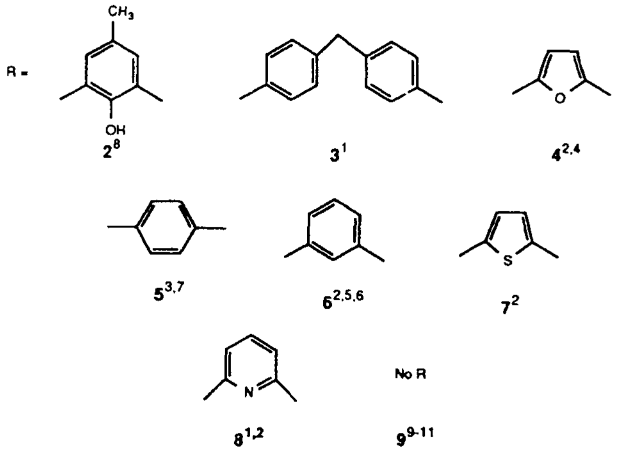

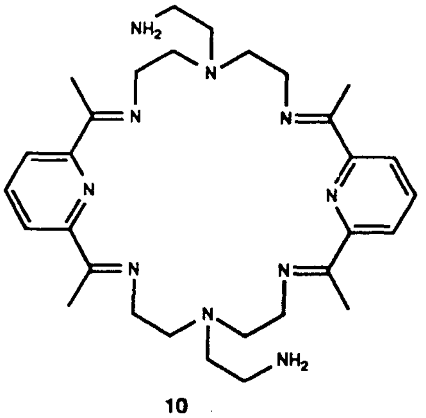

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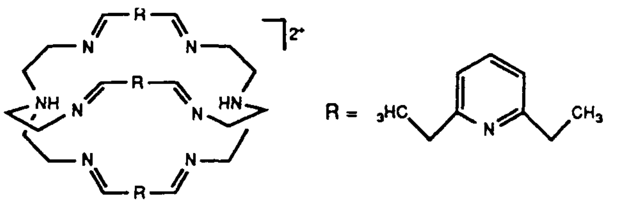

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EXPERIMENTAL

The microanalytical and spectroscopic data were obtained as previously reported.[14] The complexes $Ag_2(\mathbf{10})(BF_4)_2$ and $Ba(\mathbf{10})(ClO_4)_2$ were prepared by cyclocondensation of tris(2-aminoethyl)amine (tren) and 2,6-diacetyl pyridine using literature methods.[14,15]

The reaction of $Ag_2(\mathbf{10})(BF_4)_2$ with H_2/Pd(5%)-C in methanol

A stream of dihydrogen was bubbled into a suspension of $Ag_2(\mathbf{10})(BF_4)_2$ (1.085 g; 1.16 mmol) and Pd(5%)-charcoal (0.2 g) in methanol (70 cm^3) at room temperature and atmospheric pressure for 4 hours. The resulting suspension was removed by filtration and the colourless filtrate reduced *in vacuo* to *c.a.* 10 cm^3 facilitating a white crystalline precipitate. This product was washed with diethyl ether and dried *in vacuo* for 1 hour. Yield = 59.3%; decomposes 116–120°. Found, C, 54.50; H, 6.24, N, 17.92; calculated for $[(\mathbf{11})][BF_4]_2$, $0.5H_2O$, C, 54.56; H, 6.34, N, 17.95; i.r. (KBr disc) $\nu_{C=N}$ 1650, ν_{B-F} 1200–1000 (broad) cm^{-1}; FAB m.s. 762 ($\{[(11)][BF_4]\}^+$); ^{1}H nmr (CD_3CN) 2.48 (t, 6H, CH_3), 3.72 (m, 8H; CH_2), 7.18 (d; 2H; pyr), 7.60 ppm (s; 1H; pyr); ^{13}C nmr (CD_3CN) 15.7, 46.1, 58.5, 121.4, 138.6, 155.6, 171.3 ppm. Recrystallisation from methanol/acetonitrile (10/1) gave clear, elongated crystals.

The reaction of $Ag_2(\mathbf{10})(BF_4)_2$ with phthaloyl chloride in methanol

A solution of phthaloyl chloride (0.203 g; 1 mmol) in methanol (4 cm^3) was added to a hot methanolic solution (50 cm^3) of $Ag_2(\mathbf{10})(BF_4)_2$ (0.936 g; 1 mmol), refuxed for 5 min and filtered hot. A white crystalline product was obtained on cooling. This was identified as $[(\mathbf{11})][BF_4]_2$ on spectroscopic comparison with the above sample. Yield = 36.9%.

The reaction of tris(2-aminoethyl)amine and 2,6-diacetyl pyridine in methanol in the presence of hydrochloric acid

(a) To prepare $[(\mathbf{11})][BF_4]_2$:

A solution of hydrochloric acid (4 mmol) in methanol (8 cm^3) was added to a methanolic solution (30 cm^3) of 2,6-diacetyl pyridine (0.979 g; 6 mmol). A methanolic solution (5 cm^3) of tris(2-aminoethyl)amine (0.585 g; 4 mmol) was then added and the resulting solution stirred at room temperature for 10 mins. The solution was filtered into a solution of sodium tetrafluoroborate (4 mmol) in methanol (20 cm^3). A white crystalline product was obtained on cooling. This was identified as $[(\mathbf{11})][BF_4]_2$ on spectroscopic comparison with the above authentic sample. Yield = 40%.

(a) To prepare $[(\mathbf{11})][ClO_4]_2$:

The preceding method was followed except that the solution was filtered into a solution of sodium perchlorate (4 mmol) in methanol (20 cm^3). A white crystalline product was obtained on cooling. Yield = 46.8%. Found, C, 51.41; H, 6.30, N, 16.64, Cl, 8.20; calculated for $[(\mathbf{11})][ClO_4]_2$, $2H_2O$, C, 51.43; H, 6.31, N, 16.92, Cl, 7.78; i.r. (KBr disc) $\nu_{C=N}$ 1650, ν_{Cl-O} 1200–1000 (broad) cm^{-1}; FAB m.s. 775 ($\{[(11)][ClO_4]\}^+$); ^{1}H nmr (CD_3CN) 2.48 (t, 6H, CH_3), 3.74 (m, 8H; CH_2), 7.18 (d; 2H; pyr), 7.60 ppm (s; 1H; pyr); ^{13}C nmr (CD_3CN) 15.7, 46.1, 58.5, 121.4, 138.7; 155.6, 171.4 ppm.

The reaction of $Ba(\mathbf{10})(ClO_4)_2$ with phthaloyl chloride in methanol

A solution of phthaloyl chloride (0.203 g; 1 mmol) in methanol (4 cm^3) was added to a hot methanolic solution (50 cm^3) of $Ba(\mathbf{10})(ClO_4)_2$ (0.883 g; 1 mmol), refuxed for 5 mins and filtered hot. A white crystalline product was obtained on cooling. This was confirmed as $[(\mathbf{11})][ClO_4]_2$ on spectroscopic comparison with the above authentic sample. Yield = 26.7%.

The reaction of $Ba(\mathbf{10})(ClO_4)_2$ with hydrochloric acid in methanol

A solution of hydrochloric acid (2 mmol) in methanol (4 cm^3) was added to a hot methanolic solution (60 cm^3) of $Ba(\mathbf{10})(ClO_4)_2$ (0.883 g; 1 mmol), refuxed for 5 mins and filtered hot. A white crystalline product was obtained on cooling. This was confirmed as $[(\mathbf{11})][ClO_4]_2$ on spectroscopic comparison with the above authentic sample. Yield = 33.2%.

Structure determination

Crystal data for $[(\mathbf{11})][BF_4]_2.CH_3CN$, $C_{41}H_{56}B_2F_8N_{12}$; M = 890.59 crystallises from methanol/acetonitrile as clear elongated blocks; crystal dimensions 0.75 × 0.40 × 0.25 mm. Monoclinic, $a = 9.883(13)$, $b = 27.713(24)$, $c = 16.738(9)$Å, $\beta = 90.74(8)°$, $U = 4584(8)$Å^3, $Z = 4$, $D_c = 1.29$ g cm^{-3}, space group $P2_1/n$, Mo-K_α radiation ($\lambda = 0.71069$ Å), μ(Mo-K_α) = 0.96 cm^{-1}, F(000) = 1871.57.

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 40°$ on a Nicolet R3 diffractometer by the omega scan method. The 2653 independent reflections (of 6503 measured) for

Table 1. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	*Ueq*
N(1)	2992(4)	1106(2)	5337(2)	59(2)
N(2)	3005(4)	2348(2)	5703(2)	52(2)
N(3)	3536(5)	3573(2)	5277(2)	68(2)
N(4)	814(5)	1144(2)	3526(2)	69(2)
N(5)	557(4)	2382(1)	3181(2)	50(2)
N(6)	1236(5)	3608(2)	3502(2)	61(2)
N(7)	4524(5)	1050(2)	3340(2)	64(2)
N(8)	5508(4)	2257(2)	3174(2)	54(2)
N(9)	4991(4)	3498(2)	3256(2)	61(2)
N(10)	2646(4)	438(2)	4108(2)	62(2)
N(11)	3378(4)	4227(2)	3976(2)	59(2)
C(1)	2801(6)	283(2)	4968(3)	72(3)
C(2)	2237(6)	664(2)	5507(3)	69(3)
C(3)	1664(6)	1527(2)	6351(3)	72(3)
C(4)	2720(6)	1487(2)	5733(3)	53(2)
C(5)	3574(8)	1917(2)	5547(3)	53(3)
C(6)	4868(8)	1868(2)	5245(3)	57(3)
C(7)	5600(7)	2276(3)	5101(3)	64(3)
C(8)	5033(6)	2720(2)	5243(3)	55(3)
C(9)	3725(5)	2738(2)	5531(3)	48(2)
C(10)	3070(6)	3220(2)	5674(3)	58(3)
C(11)	1946(6)	3241(2)	6249(3)	71(3)
C(12)	2951(7)	4056(2)	5392(3)	85(3)
C(13)	3634(7)	4386(2)	4820(3)	78(3)
C(14)	1280(6)	313(2)	3770(3)	83(3)
C(15)	877(7)	672(2)	3145(3)	85(3)
C(16)	144(6)	1526(2)	2267(3)	78(3)
C(17)	486(6)	1516(2)	3138(3)	58(3)
C(18)	372(5)	1971(2)	3595(3)	52(2)
C(19)	127(6)	1967(2)	4399(3)	59(3)
C(20)	73(6)	2395(3)	4803(3)	67(3)
C(21)	333(6)	2818(2)	4389(3)	57(3)
C(22)	551(5)	2796(2)	3592(3)	51(3)
C(23)	778(6)	3247(2)	3132(3)	57(3)
C(24)	458(6)	3239(2)	2240(3)	69(3)
C(25)	1479(6)	4059(2)	3073(3)	73(3)
C(26)	2064(6)	4418(2)	3658(3)	71(3)
C(27)	3757(6)	249(2)	3610(3)	77(3)
C(28)	4965(6)	583(2)	3667(4)	83(3)
C(29)	6869(5)	1359(2)	3528(3)	76(3)
C(30)	5400(5)	1392(2)	3295(3)	58(3)
C(31)	4857(7)	1856(2)	2947(3)	55(3)
C(32)	3761(7)	1866(3)	2421(4)	69(3)
C(33)	3332(7)	2298(2)	2126(3)	68(3)
C(34)	3944(6)	2721(2)	2376(3)	62(3)
C(35)	5026(6)	2678(2)	2918(3)	53(3)
C(36)	5703(8)	3125(2)	3239(3)	62(3)
C(37)	7169(8)	3077(2)	3489(4)	82(4)
C(38)	5620(7)	3961(2)	3521(4)	84(3)
C(39)	4528(6)	4338(2)	3446(3)	73(3)
B(1)	3034(8)	3989(2)	767(4)	70(3)
F(1)	3059(4)	3499(1)	742(2)	94(2)
F(2)	3758(4)	4180(1)	178(2)	99(2)
F(3)	1722(4)	4156(1)	697(2)	109(2)
F(4)	3557(4)	4147(1)	1480(2)	116(2)
B(2)	1816(4)	5021(2)	6838(2)	160
F(5)	1932	5404	7352	263(6)
F(6)	2389	5138	6123	126(3)
F(7)	476	4913	6719	224(6)
F(8)	2469	4629	7159	201(5)
B(2A)	1639(6)	5036(3)	6765(4)	160
F(5A)	1399	5331	7404	111(5)
F(6A)	1326	5275	6071	312(16)
F(7A)	2977	4907	6765	157(7)
F(8A)	854	4630	6821	113(6)
C(40)	3936(10)	863(4)	377(6)	252(8)
C(41)	2885(11)	733(4)	711(8)	214(7)
N(12)	1840(7)	643(3)	917(4)	167(4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods and refined by blocked cascade least squares methods. One tetrafluoroborate anion was found to be disordered (0.66:0.34) with approximately coincident boron sites, the two components were refined with constrained T_d symmetry (B-F 1.37 Å). An acetonitrile of solvation was permitted full occupancy, but had rather high thermal vibration parameters. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.072$ ($R_w = 0.072$, 586 parameters, mean and maximum δ/σ 0.018, 0.091), with allowance for the thermal anisotropy of all non-hydrogen atoms, with the exception of the partial occupancy boron atoms. Minimum and maximum final electron density, -0.21 and $0.26\ e\ Å^{-3}$. A weighting scheme $w^{-1} = \sigma^2(F) + 0.00041\ (F)^2$ was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXTL[16] as implemented on the Data General DG30 computer. Atomic coordinates and temperature factors for $[(\mathbf{11})][BF_4]_2$, CH_3CN are listed in Table 1; the bond lengths and angles, with estimated standard deviations, for (**11**) are listed in Table 2. Anisotropic thermal vibrational parameters with e.s.d.s, hydrogen atom position parameters, observed structure amplitudes and calculated structure factors are deposited as supplementary material together with the bond lengths and angles, with estimated standard deviations, for the tetrafluoroborate anions and the acetonitrile of solvation.

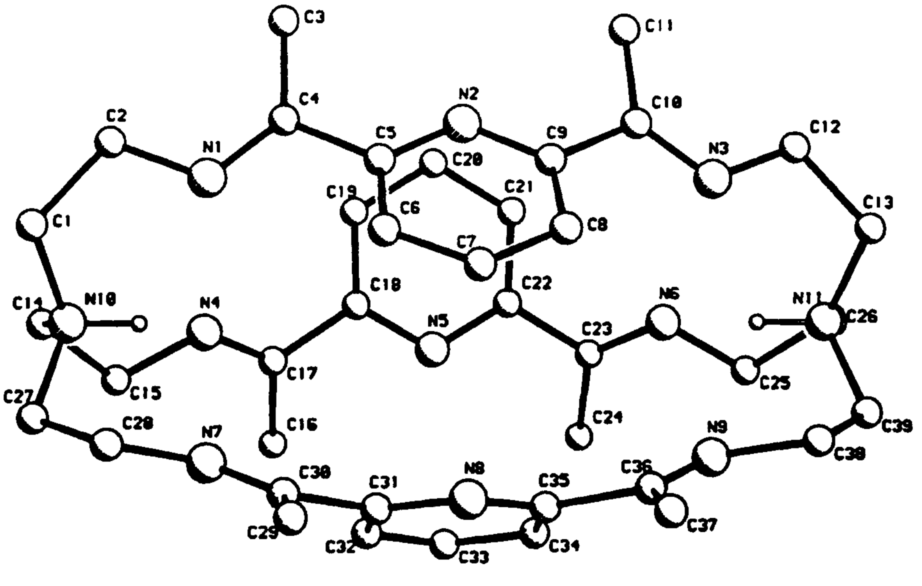
RESULTS AND DISCUSSION

During an investigation into the reaction of the disilver complex $Ag_2(\mathbf{10})(BF_4)_2$ it was noted that reaction with $H_2/Pd/C$ in MeOH and reaction with phthaloyl dichloride in MeOH gave an identical product. Furthermore the reactions of $Ba(\mathbf{10})(ClO_4)_2$ with phthaloyl dichloride in MeOH and with hydrochloric acid in MeOH also gave identical products. The

Table 2 Bond lengths (Å) and angles (°)

N(1)–C(2)	1.464(7)	N(1)–C(4)	1.279(7)
N(2)–C(5)	1.347(7)	N(2)–C(9)	1.327(7)
N(3)–C(10)	1.272(7)	N(3)–C(12)	1.471(7)
N(4)–C(15)	1.455(7)	N(4)–C(17)	1.258(7)
N(5)–C(18)	1.345(6)	N(5)–C(22)	1.340(7)
N(6)–C(23)	1.257(7)	N(6)–C(25)	1.463(7)
N(7)–C(28)	1.469(7)	N(7)–C(30)	1.286(7)
N(8)–C(31)	1.337(7)	N(8)–C(35)	1.327(7)
N(9)–C(36)	1.252(8)	N(9)–C(38)	1.491(8)
N(10)–C(1)	1.508(6)	N(10)–C(14)	1.497(8)
N(10)–C(27)	1.482(7)	N(11)–C(13)	1.498(6)
N(11)–C(26)	1.494(7)	N(11)–C(39)	1.483(8)
C(1)–C(2)	1.500(8)	C(3)–C(4)	1.483(8)
C(4)–C(5)	1.494(8)	C(5)–C(6)	1.387(11)
C(6)–C(7)	1.364(10)	C(7)–C(8)	1.375(10)
C(8)–C(9)	1.387(8)	C(9)–C(10)	1.505(8)
C(10)–C(11)	1.481(8)	C(12)–C(13)	1.494(8)
C(14)–C(15)	1.495(8)	C(16)–C(17)	1.493(7)
C(17)–C(18)	1.480(7)	C(18)–C(19)	1.371(7)
C(19)–C(20)	1.366(9)	C(20)–C(21)	1.387(9)
C(21)–C(22)	1.356(8)	C(22)–C(23)	1.486(8)
C(23)–C(24)	1.523(7)	C(25)–C(26)	1.507(8)
C(27)–C(28)	1.512(8)	C(29)–C(30)	1.502(8)
C(30)–C(31)	1.507(8)	C(31)–C(32)	1.388(9)
C(32)–C(33)	1.360(9)	C(33)–C(34)	1.382(9)
C(34)–C(35)	1.399(8)	C(35)–C(36)	1.503(9)
C(36)–C(37)	1.509(11)	C(38)–C(39)	1.506(9)
B(1)–F(1)	1.357(7)	B(1)–F(2)	1.336(8)
B(1)–F(3)	1.381(9)	B(1)–F(4)	1.366(7)
B(2)–F	1.370	B(2A)–F	1.370
C(40)–C(41)	1.239(15)	N(41)–N(12)	1.122(13)
C(2)–N(1)–C(4)	118.7(4)	C(5)–N(2)–C(9)	117.0(5)
C(10)–N(3)–C(12)	119.0(5)	C(15)–N(4)–C(17)	121.5(4)
C(18)–N(5)–C(22)	117.4(4)	C(23)–N(6)–C(25)	119.8(4)
C(28)–N(7)–C(30)	118.3(5)	C(31)–N(8)–C(35)	118.0(5)
C(36)–N(9)–C(38)	119.0(5)	C(1)–N(10)–C(14)	112.0(4)
C(1)–N(10)–C(27)	111.7(4)	C(14)–N(10)–C(27)	112.2(4)
C(13)–N(11)–C(26)	111.5(4)	C(13)–N(11)–C(39)	112.5(4)
C(26)–N(11)–C(39)	112.5(4)	N(10)–C(1)–C(2)	109.9(4)
N(1)–C(2)–C(1)	106.1(4)	N(1)–C(4)–C(3)	125.3(5)
N(1)–C(4)–C(5)	115.3(5)	C(3)–C(4)–C(5)	119.4(5)
N(2)–C(5)–C(4)	115.3(6)	N(2)–C(5)–C(6)	123.1(6)
C(4)–C(5)–C(6)	121.6(5)	C(5)–C(6)–C(7)	118.5(6)
C(6)–C(7)–C(8)	119.5(6)	C(7)–C(8)–C(9)	118.4(6)
N(2)–C(9)–C(8)	123.4(5)	N(2)–C(9)–C(10)	117.1(5)
C(8)–C(9)–C(10)	119.4(5)	N(3)–C(10)–C(9)	116.1(5)
N(3)–C(10)–C(11)	126.1(5)	C(9)–C(10)–C(11)	117.8(5)
N(3)–C(12)–C(13)	107.0(5)	N(11)–C(13)–C(12)	110.6(5)
N(10)–C(14)–C(15)	110.0(5)	N(4)–C(15)–C(14)	107.7(4)
N(4)–C(17)–C(16)	124.9(5)	N(4)–C(17)–C(18)	117.0(4)
C(16)–C(17)–C(18)	118.1(5)	N(5)–C(18)–C(17)	116.3(4)
N(5)–C(18)–C(19)	122.6(5)	C(17)–C(19)–C(19)	121.0(5)
C(18)–C(19)–C(20)	119.2(5)	C(19)–C(20)–C(21)	118.5(5)
C(20)–C(21)–C(22)	119.1(5)	N(5)–C(22)–C(21)	123.0(5)
N(5)–C(22)–C(23)	117.0(4)	C(21)–C(22)–C(23)	120.0(5)
N(6)–C(23)–C(22)	118.0(4)	N(6)–C(23)–C(24)	124.4(5)
C(22)–C(23)–C(24)	117.7(5)	N(6)–C(25)–C(26)	108.0(4)
N(11)–C(26)–C(25)	108.8(4)	N(10)–C(27)–C(28)	109.9(4)
N(7)–C(28)–C(27)	106.5(5)	N(7)–C(30)–C(29)	126.1(5)
N(7)–C(30)–C(31)	114.5(5)	C(29)–C(30)–C(31)	119.3(5)
N(8)–C(31)–C(30)	115.6(5)	N(8)–C(31)–C(32)	122.1(5)
C(30)–C(31)–C(32)	122.2(5)	C(31)–C(32)–C(33)	119.1(6)
C(32)–C(33)–C(34)	120.2(6)	C(33)–C(34)–C(35)	116.9(5)
N(8)–C(35)–C(34)	123.5(5)	N(8)–C(35)–C(36)	116.9(5)

C(34)-C(35)-C(36)	119.6(5)	N(9)-C(36)-C(35)	116.2(7)
N(9)-C(36)-C(37)	127.2(6)	C(35)-C(36)-C(37)	116.6(5)
N(9)-C(38)-C(39)	106.1(5)	N(11)-C(39)-C(38)	111.1(5)
F(1)-B(1)-F(2)	111.4(5)	F(1)-B(1)-F(3)	110.5(6)
F(2)-B(1)-F(3)	108.4(5)	F(1)-B(1)-F(4)	109.9(5)
F(2)-B(1)-F(4)	108.5(6)	F(3)-B(1)-F(4)	108.1(5)
F-B(2)-F	109.5	F-B(2A)-F	109.5
C(40)-C(41)-N(12)	169.8(13)		



The structure of the diprotonated cryptand.

infra-red spectra of the compounds formed were similar save for the bands ascribable to the inorganic counterions and gave bands ascribable to $\nu_{C=N}$ but not for $\nu_{C=O}$ or ν_{NH_2}. The FAB mass spectra gave parent peaks at 763 amu for the first pair of products and at 775 amu for the second pair of products. The ^{13}C nmr spectra, run in CD_3CN, of all four products were identical and consisted only of seven lines deriving from three aliphatic, three aromatic and one imino-carbon environments. The ^1H nmr spectra, run in CD_3CN, were also very similar and could be assigned to the presence of methyl, methylene and pyridinyl protons. The simplicity of the spectra suggested that the compounds were very symmetric and from the above information it was proposed that the compounds formed were the diprotonated cryptand salts $[(11)][BF_4]_2$ and $[(11)][ClO_4]_2$. Crystals of $[(11)][BF_4]_2$ grown from $MeOH:CH_3CN$ (10:1) and the X-ray crystal structure solved.

The structure of the di-cation, with atom labelling, is shown in the Figure. The asymmetric unit contains a di-protonated cryptand di-cation comprising three bis(ethylcarbimine)pyridyl chains linked at each end to a tertiary ammonium nitrogen atom, two tetrafluoroborate anions, and an acetonitrile of crystallization: the dication possesses almost precise, but not crystallographically imposed C_{3h} symmetry. The pyridyl fragments are planar (r.m.s. deviations 0.010, 0.015, 0.018 Å) and are mutually inclined at 58.2, 60.8 and 61.0°. The imino nitrogens are directed so that the dicarbimine functions are in *trans,trans* geometry relative to the pyridine C–N bond. This configuration has not been found in related pyridine-derived Schiff base macrocycles for which it was noted that there was generally a requirement for a metal template ion to induce cyclocondensation.[17,18] It was commented that this may have as its origin the conformer distribution in solution of the requisite pyridine-2,6-dicarbonyl – for example the dipole moments, measured in benzene, of both pyridine-2,6-dicarboxaldehyde and 2,6-diacetylpyridine have been interpreted as arising from a high *trans,trans-* conformer content with ca. 5% *cis,trans-* and negligible *cis,cis*-presence.[19] If it is the *cis,cis*-conformer that leads to macrocyclisation then the metal template could redirect the conformer distribution from the *trans,trans*-form on coordinating with the pyridine-2,6-dicarbonyl.

The hydrogen atoms on the tertiary ammonium nitrogens are necessarily directed into the cryptand cavity, permitting no hydrogen bonding to the anion or solvent. There is, however, one short contact between the methyl carbon (and its associated hydrogens) of the acetonitrile molecule and a fluorine of the low occupancy component of the second tetrafluoroborate anion (C...F 2.930, H...F 2.02 Å).

The common denominator in the experiments starting from $M_n(\mathbf{10})X_m$ appears to be the generation of an acidic medium which facilitates a full or partial retro-Schiff base reaction to dissemble the macrocycle before allowing reassembly as the protonated cryptand. This hypothesis is supported by the direct synthesis of $[(\mathbf{11})][X]_2$ from tren and 2,6-diacetylpyridine in the presence of the corresponding acid.

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