# Co-ordination Chemistry of Iodine(I) with Tetraazamacrocycles or Monodentate Ligands. Comparisons with Bromine(I) and with Some d-Block Metals†

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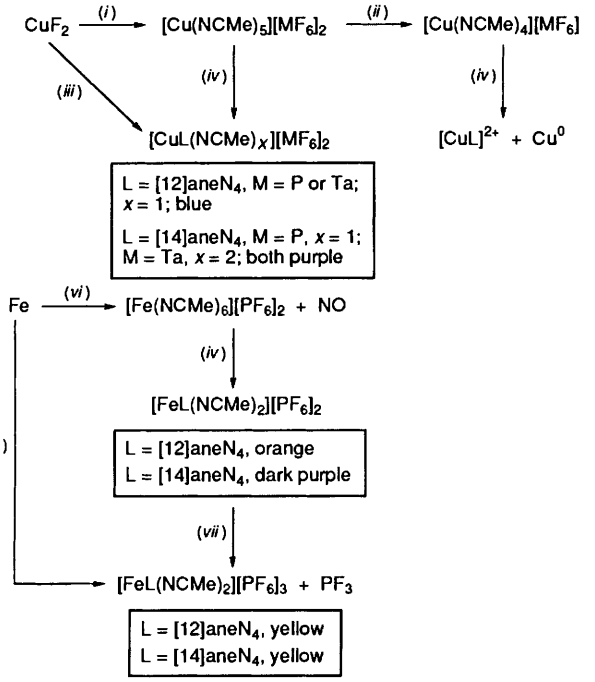
Co-ordination compounds of iodine(I), including those with tetraazamacrocyclic ligands, have been prepared either by direct reaction with the $[I(NCMe)_2]^+$ cation or by the previously reported ligand-induced disproportionation reaction of $I_2$. The syntheses and the properties of the iodine complexes so prepared are compared with analogous work involving bromine, iron(II) or copper(II).

The formation of linear, centrosymmetric $[IL_2]^+$, for example L = pyridine (py),[1] thiourea,[2] hexamethylenetetramine,[3] quinuclidine[4] or MeCN,[5] is a characteristic feature of iodine(I) chemistry. Bromine(I) has been studied less thoroughly but at least two examples of $[BrL_2]^+$ cations, L = quinoline[6] or quinuclidine,[7] have been characterized structurally. The cations $[IL_2]^+$, L = py or 2,4,6-trimethylpyridine, have attracted attention as selective iodinating and/or cyclization agents for a variety of aromatics and olefins;[8] in contrast $[BrL_2]^+$, L = quinuclidine, behaves as a mild oxidant rather than a source of electrophilic bromine.[9] In many cases the reactions are acid-catalysed suggesting that the active reagent may be $[IL]^+$ or $[BrL]^+$ (*cf.* ref. 9) and, consistent with this, several $[IL]^+$, L = MeCN, $NH_3$, py or ICN, monoligated complexes have been prepared from reactions of $[I_3][AsF_6]$ and L in $SO_2$.[10]

We are currently investigating the behaviour of these types of complex cations as alternatives to $I_2$ and $Br_2$ for the selective etching of semiconductor materials in solution and for this reason have become interested in the possibility of preparing complexes of $I^I$ or $Br^I$ with other co-ordination geometries. Tetraazamacrocycles were obvious candidates for ligands and the results of our synthetic work are now reported. In order to test the general applicability of one of our proposed synthetic routes, starting from the $[I(NCMe)_2]^+$ cation,[5] we have also examined the behaviour of the macrocycles 1,4,7,10-tetraazacyclododecane, [12]ane$N_4$, and 1,4,8,11-tetraazacyclotetradecane, [14]ane$N_4$, towards acetonitrile-solvated iron(II) and copper(II) cations.



**Scheme 1** Preparation of copper(II), iron-(II) and -(III) tetraazamacrocycle complexes in MeCN. (*i*) $MF_5$; (*ii*) $Cu^0$; (*iii*) $MF_5$ + L; (*iv*) L; (*v*) $PF_5$ + L; (*vi*) $NOPF_6$; (*vii*) $PF_5$

## Results and Discussion

*Iron and Copper Complexes.*—Solvated iron(II) or copper(II) hexafluorophosphate or hexafluorotantalate(V) salts react smoothly with [12]ane$N_4$ or [14]ane$N_4$ in MeCN at room temperature to give the corresponding macrocyclemetal(II) cations which are additionally co-ordinated by two or one MeCN ligands (Scheme 1). The macrocyclemetal(II) salts are freely soluble in MeCN whereas the free macrocycles are insoluble, hence solid products are easily isolated. The compound *trans*-$[Fe([14]aneN_4)(NCMe)_2][PF_6]_2$ has been reported previously from the reaction between $[Fe(NCMe)_6][CF_3SO_3]_2$ and [14]ane$N_4$ in MeCN followed by anion exchange, although attempts to isolate the corresponding 1,4,8,11-tetraazacyclotridecane, [13]ane$N_4$, salt were unsuccessful.[11] The well known ability of $N_4$ macrocycles in stabilizing higher oxidation states of d-block elements is further illustrated by the oxidation of $[FeL(NCMe)_2]^{2+}$, L = [12]ane$N_4$ or [14]ane$N_4$, to the corresponding iron(III) cations by phosphorus pentafluoride, a weak oxidizing agent in MeCN. Consistent with this, $E_{\frac{1}{2}}$ for $Fe^{III}$–$Fe^{II}$ was determined by cyclic voltammetry to be +0.325 V *vs.* $Ag^+$–$Ag^0$.

Oxidation of iron metal by $PF_5$, in MeCN and in the presence of the macrocycles, yields iron(III) cations; in their absence only $Fe^{II}$ is accessible in MeCN even when strong oxidizing agents are used.[12] Pre-formation of the iron(II) complexes is necessary to obtain analytically pure solids however, since $PF_5$ reacts slowly with the free macrocycles to give HF as one product. In contrast, the reaction between $[Fe(OH_2)_6]^{2+}$ and [14]ane$N_4$ in oxygenated MeCN results in a bimetallic iron(II) complex in which two *trans*-$[Fe(N_4)(NCMe)_2]$ units are bridged by a conjugated $C_6$ moiety.[13] Reactions between the macrocycles

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J $T^{-1}$.

**Table 1** Characteristic IR bands (cm$^{-1}$) for solid tetraazamacrocycle complexes of Cu$^{II}$, Fe$^{II}$, Fe$^{III}$ and I$^{I}$ band

| Complex | ν(NH) | ν(C≡N) + comb. | δ(NH) | $\nu_3(MF_6^-)$ | $\nu_4(MF_6^-)$ |
|---|---|---|---|---|---|
| $[Cu([12]aneN_4)(NCMe)][PF_6]_2$ | 3470m | | 1730m | | |
| | 3400m | 2300w | 1675s | 840vs | 558vs |
| | 3320m | | | | |
| | 3250m | 2260m | 1610s | | |
| $[Cu([12]aneN_4)(NCMe)][TaF_6]_2$ | 3520m | | 1685m | | |
| | 3355m | 2300w | | 590s | |
| | 3300m | | 1620m | | |
| | 3130m | 2260m | 1585m | | |
| $[Cu([14]aneN_4)(NCMe)][PF_6]_2$ | 3270m | 2300w | 1675m | 840vs | 558vs |
| | | 2260m | | | |
| $[Cu([14]aneN_4)(NCMe)_2][TaF_6]_2$ | 3270m | 2300w | 1675m | 590s | |
| | | 2260m | | | |
| $[Fe([12]aneN_4)(NCMe)_2][PF_6]_2$ | 3480m | | 1700m | | |
| | 3400m | 2295w | 1650m | 840vs | 558vs |
| | 3270m | 2260m | 1620m | | |
| $[Fe([14]aneN_4)(NCMe)_2][PF_6]_2$ | 3290m | 2300w | 1730m | 840vs | 558vs |
| | | 2260m | | | |
| $[Fe([12]aneN_4)(NCMe)_2][PF_6]_3$ | 3480m | | 1675s | | |
| | 3400m | 2290w | 1650s | 840vs | 558vs |
| | 3260m | 2260m | 1610s | | |
| $[Fe([14]aneN_4)(NCMe)_2][PF_6]_3$ | 3240m | 2300w | 1590s | 840vs | 558vs |
| | | 2260m | | | |
| $[I([12]aneN_4)][I_3]^a$ | 3300s (br) | | 1600m (br) | | |
| $[I([14]aneN_4)][I_3]^b$ | 3240m | | 1620m | | |
| | 3100m | | 1570m | | |
| $[I([14]aneN_4)(NCMe)][UF_6]^c$ | 3310m | 2300w | 1730m | 520vs | |
| | 3260m | 2260m | 1610m | | |
| $[I([14]aneN_4)(NCMe)][PF_6]^c$ | 3310m | 2300w | 1730w | 845vs | 558vs |
| | 3250m | 2260m | 1610s | | |

[a] Electronic spectrum (MeCN): $\lambda_{max}$ = 360, 290, 255 and 220 nm. [b] $\lambda_{max}$ 360 and 290 nm. [c] $\lambda_{max}$ 290 nm.

**Table 2** Analytical * and electronic spectral data for tetraazamacrocycle complexes of Cu$^{II}$, Fe$^{II}$ and Fe$^{III}$

| | Analysis (%) | | | | |
|---|---|---|---|---|---|
| Complex | C | H | N | $\tilde{\nu}_{max}$/cm$^{-1}$ | ε/dm$^3$ mol$^{-1}$ cm$^{-1}$ |
| $[Cu([12]aneN_4)(NCMe)][PF_6]_2$ | 21.0 (21.2) | 3.9 (4.1) | 12.4 (12.3) | 17 000 | 85 |
| | | | | 33 200 | 1360 |
| $[Cu([12]aneN_4)(NCMe)][TaF_6]_2$ | 14.3 (13.9) | 2.75 (2.65) | 8.2 (8.1) | 16 900 | 135 |
| | | | | 36 000 | 1210 |
| $[Cu([14]aneN_4)(NCMe)][PF_6]_2$ | 24.2 (24.2) | 4.7 (4.6) | 11.9 (11.7) | 18 900 | 85 |
| | | | | 33 800 | 2250 |
| $[Cu([14]aneN_4)(NCMe)_2][TaF_6]_2$ | 17.9 (17.9) | 3.2 (3.2) | 8.8 (8.9) | 19 700 | 145 |
| | | | | 35 300 | 2250 |
| $[Fe([12]aneN_4)(NCMe)_2][PF_6]_2$ | 24.3 (24.0) | 4.4 (4.3) | 14.2 (14.0) | 20 000 | 40 |
| | | | | 26 700 | 80 |
| $[Fe([14]aneN_4)(NCMe)_2][PF_6]_2$ | 26.7 (26.7) | 4.85 (4.8) | 13.8 (13.4) | 18 500 | 50 |
| | | | | 27 000 | 95 |
| $[Fe([12]aneN_4)(NCMe)_2][PF_6]_3$ | 19.8 (19.3) | 3.6 (3.5) | 11.4 (11.3) | 27 900 | 115 |
| | | | | 38 500 | 300 |
| $[Fe([14]aneN_4)(NCMe)_2][PF_6]_3$ | 22.9 (22.7) | 4.3 (4.0) | 10.6 (10.9) | 27 700 | 115 |
| | | | | 32 300 | 295 |

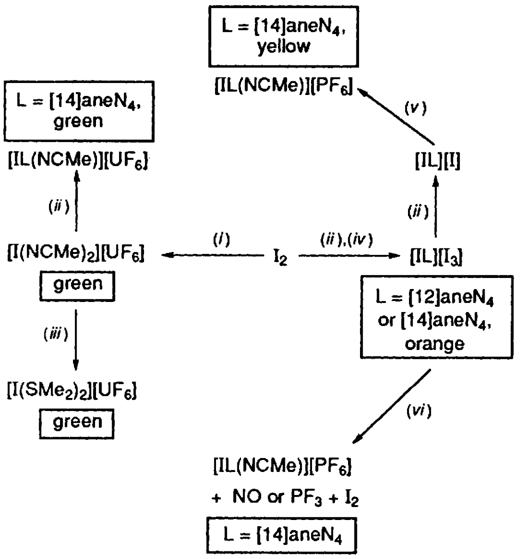
* Required values are given in parentheses.

and solvated Cu$^{I}$ in MeCN result in ligand-induced disproportionation; similar behaviour has been encountered for silver(I) in MeCN, particularly if trace water or other impurities are present.[14]

Characteristic spectroscopic data for the compounds contained in Scheme 1 are in Tables 1 and 2. Comparisons with previous studies of complexes of Fe$^{II}$ (ref. 11) and Cu$^{II}$ [15,16] indicate consistency where similar ligands are compared. There is little doubt from previous spectroscopic and magnetic work[11] that low-spin $[Fe([14]aneN_4)(NCMe)_2]^{2+}$ has a *trans* octahedral $FeN_6$ configuration and it is reasonable to infer that the low-spin iron(III) and the copper(II) analogues are similar, at least in solution. Structures of the $[12]aneN_4$ complexes are more problematic. The crystal structure of $[Cu(Me_4[12]aneN_4)(H_2O)]^{2+}$ ($Me_4[12]aneN_4$ = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclodecane) indicates that Cu$^{II}$ is in a square-pyramidal environment and located 0.5 Å above the macrocycle $N_4$ plane.[16] A similar environment is possible for the MeCN solvates of $[Cu([12]aneN_4)]^{2+}$ prepared here but the multiple ν(N–H) bands observed in their IR spectra suggest, by analogy with previous spectroscopic work on related complexes of Cu$^{II}$ and Ni$^{II}$,[15,17] that $[12]aneN_4$ has a folded conformation.

*Iodine and Bromine Complexes.*—Oxidation of elemental iodine by the strong one-electron oxidizing agent $UF_6$ in MeCN below room temperature gives pale green $[I(NCMe)_2][UF_6]$ in quantitative yield from which the pale green solid $[I(SMe_2)_2][UF_6]$ or $[I([14]aneN_4)(NCMe)][UF_6]$ are readily accessible by room-temperature ligand-exchange reactions in

MeCN. Alternatively $I_2$ in EtOH, $CH_2Cl_2$, MeOH or $CHCl_3$, under anhydrous conditions, undergoes disproportionation in the presence of [12]ane$N_4$ or [14]ane$N_4$ at room temperature to give orange, sparingly soluble solids formulated from their analyses as [IL][$I_3$], L = [12]ane$N_4$ or [14]ane$N_4$. In the presence of an excess of $I_2$ dark brown solids are obtained. The [12]ane$N_4$ complex decomposes readily at room temperature but the $[I_3]^-$ anion in the [14]ane$N_4$ complex can be replaced either by oxidation with $NOPF_6$ or $PF_5$ or by conversion with an additional equivalent of [14]ane$N_4$ then $[Ag(NCMe)_2][PF_6]$ to give yellow [I([14]ane$N_4$)(NCMe)][$PF_6$], which is soluble in MeCN. These reactions are summarized in Scheme 2 and characteristic spectroscopic data and analytical data presented in Tables 1, 3 and 4.



**Scheme 2** Preparation of iodine(I) complexes in MeCN (except where indicated). (*i*) $UF_6$; (*ii*) L; (*iii*) $Me_2S$; (*iv*) EtOH; (*v*) $[Ag(NCMe)_2][PF_6]$; (*vi*) $NOPF_6$ or $PF_5$

**Table 3** Proton and $^{13}C$ NMR chemical shifts (δ)[a]

| [I([14]ane$N_4$)(NCMe)][$PF_6$][b] | [I([14]ane$N_4$)][$I_3$][b] | [14]ane$N_4$[c] |
|---|---|---|
| $^1H$ | | |
| 1.79 | 1.83 | 1.62 β-$CH_2$ |
| 5.64 | 5.78 | 2.10 NH |
| 2.93 | 2.99 | 2.59 α-$CH_2$ |
| 3.00 | 3.00 | 2.86 α′-$CH_2$ |
| $^{13}C$ | | |
| 25.7 | 25.7 | 29.5 β-C |
| 47.5 | 47.5 | 49.4 } α,α′-C |
| 50.4 | 50.7 | 50.7 } α,α′-C |

[a] Chemical shifts are positive to high frequency of $SiMe_4$. Spectra recorded at 200 ($^1H$) or 503 MHz ($^{13}C$). [b] Measured in $CD_3CN$. [c] Measured in $CD_2Cl_2$.

Displacement of MeCN from $[I(NCMe)_2]^+$ by other ligands appears to be a general route to co-ordination compounds of $I^I$. Several salts were prepared by this means, from $[I(NCMe)_2][MoF_6]$[5] and $Me_2S$, tetramethylthiourea (tmtu), 2,2′-bipyridyl (bipy), [14]ane$N_4$ and 1,4,8,12-tetraazacyclopentadecane ([15]ane$N_4$). Co-ordinated MeCN was never apparent in the cations, unlike the reaction between $[I(NCMe)_2][UF_6]$ with [14]ane$N_4$ (Scheme 2). The stabilization of $I^I$ by these ligands compared with the effect of MeCN is apparent from cyclic voltammetry measurements in this solvent. A quasi-reversible wave assigned to $I^I$–$I^0$ is observed in all cases but $E_{\frac{1}{2}}$ values with respect to $Ag^+$–$Ag^0$ vary from +0.32 and +0.28 V in $[IL_2]^+$, L = $Me_2S$ and tmtu respectively, through +0.25 V in $[I(bipy)_2]^+$ to +0.12 V for $[IL]^+$, L = [14]ane$N_4$ or [15]ane$N_4$. In contrast, $E_{\frac{1}{2}}$ for $I^I$–$I^0$ in $[I(NCMe)_2]^+$ has been estimated as *ca.* 1.1 V *vs.* $Ag^+$–$Ag^0$.[18] Although there have been a number of reports describing complex formation between $I_2$ and macrocylic ligands such as crown ethers[19] or cryptands[20] in solution, solid complexes do not appear to have been isolated in previous work. The species in solution have been usually formulated on the basis of their spectra, as $[IL]^+$ cations with $I^-$ or $[I_3]^-$ counter anions. The optimum cavity diameter for cryptand ligands appears to be *ca.* 2.8 Å.[20]

In the present work a value for the radius of $I^+$ was calculated using a double-zeta basis set[21a] and the ATOMORB program[21b] to construct contour diagrams, and three-dimensional plots of both the Slater wavefunction and electronic charge density for the outermost occupied orbital (5p). This approach, with the covalent radius of I set at 1.33 Å, gave a value for the radius of $I^+$ of 1.30 Å. The macrocycle [14]ane$N_4$ in its complexes with $Hg^{2+}$ and $Pb^{2+}$ (ionic radii = 1.1 and 1.2 Å respectively) adopts a folded conformation with the metal cations located above the $N_4$ plane.[22] It is likely that a similar arrangement is obtained in the iodine(I) complexes. Their IR spectra are not inconsistent with this suggestion, however crystals suitable for X-ray structural determinations could not be obtained. The $^1H$ and $^{13}C$-{$^1H$} NMR spectra of [I([14]ane$N_4$)(NCMe)]$^+$ in $CD_3CN$ are very similar to those of the free macrocycle, although co-ordination is indicated by variation in the NH and, to a lesser extent, the α-$CH_2$ $^1H$ chemical shifts (Table 3). Spectra of the $Fe^{II}$([14]ane$N_4$) complex were almost identical. In all cases the spectra were invariant down to −50 °C.

Solvated $Br^+$ is apparently too electrophilic to exist in MeCN,[23] but an orange-yellow solid, sparingly soluble in organic solvents and of stoichiometry *ca.* [14]ane$N_4$·2$Br_2$, can be isolated from the components mixed in dry $CH_2Cl_2$ at room temperature. In contrast to the product obtained from the corresponding reaction with $I_2$ (Scheme 2), there was no unambiguous evidence that a $Br^I$-containing cation was formed. The adduct loses $Br_2$ in solution and is very susceptible to trace hydrolysis yielding a protonated [14]ane$N_4$ derivative as one product. On the evidence obtained we prefer to formulate it as a weakly bound molecular adduct of $Br_2$.

**Table 4** Analytical[a] data for iodine(I) complexes

| | Analysis (%) | | | |
|---|---|---|---|---|
| Compound | C | H | I | N |
| [I([12]ane$N_4$)][$I_3$] | 14.4 (14.1) | 3.0 (2.9) | 74.2 (74.7) | 8.2 (8.2) |
| [I([14]ane$N_4$)][$I_3$] | 16.7 (16.9) | 3.2 (3.4) | 71.7 (71.7) | 7.7 (7.9) |
| $[I(SMe_2)_2][UF_6]$ | 7.9 (7.9) | 1.9 (1.9) | 20.9 (21.0) | *b* |
| [I([14]ane$N_4$)(NCMe)][$UF_6$] | 19.7 (20.0) | 3.7 (3.7) | 17.4 (17.6) | 9.7 (9.7) |
| [I([14]ane$N_4$)(NCMe)][$PF_6$] | 28.3 (28.1) | 5.0 (5.3) | 24.4 (24.8) | 13.5 (13.6) |
| [14]ane$N_4$ | 59.2 (60.2) | 12.1 (12.0) | | 27.3 (28.0) |
| [12]ane$N_4$ | 55.7 (55.8) | 11.4 (11.6) | | 32.3 (32.6) |

[a] Required values are given in parentheses. [b] F, 18.7 (18.9); S, 10.4 (10.5); U, 39.6 (37.5)%.

Nevertheless the adduct does show promise as a modified-bromine reagent for chemomechanical polishing of semiconductor wafers and the results of these studies will be reported elsewhere.

## Experimental

Standard Pyrex vacuum-line and glove-box techniques were used throughout. All reactions were carried out in Pyrex double-limb reaction vessels fitted with Pyrex–poly(tetrafluoroethylene) stopcocks (J. Young) and, in those cases where filtration was required, sintered-glass pads. The methods used for preparation of starting materials, for reagent and solvent purification and for spectroscopic measurements have been reported previously.[5,12,23–25] Tetraazamacrocycles were prepared according to literature methods.[26]

*Preparation of Macrocyclic Ligand Complexes.*—(*a*) *From solvated cation, fluoroanion salts.* A pale green solution of [I(NCMe)$_2$][UF$_6$] (1 mmol) in dry MeCN (5 cm$^3$) was prepared *in vacuo* in one limb of a flamed-out double-limb Pyrex reaction vessel and was added slowly to solid [14]aneN$_4$ (1 mmol) contained in the other limb at room temperature. Reaction appeared to be instantaneous and the solution became dark green. Removal of material volatile at room temperature left a green solid identified on the basis of its analysis (Table 4), IR (Table 1) and NIR/VIS spectrum, the latter containing bands characteristic of [UF$_6$]$^-$,[27] as [I([14]aneN$_4$)(NCMe)][UF$_6$]. The complexes of Fe$^{II}$ and Cu$^{II}$ listed in Tables 1 and 2 were prepared and characterised in an identical manner from iron(II) or copper(II) salts of [PF$_6$]$^-$ or [TaF$_6$]$^-$. Addition of PF$_5$ to solutions of [Fe([12]aneN$_4$)][PF$_6$]$_2$ (orange) or [Fe([14]aneN$_4$)][PF$_6$]$_2$ (purple) in MeCN *in vacuo* led to pale yellow solutions and the evolution of PF$_3$. Yellow solids, identified as the corresponding iron(III) complexes (Tables 1 and 2), were isolated after removal of volatile material. Room-temperature $\mu_{eff}$ values were 2.2 and 2.1 $\mu_B$ respectively for the [12]aneN$_4$ and the [14]aneN$_4$ complexes. Corresponding values for the iron(II) complexes were 4.0 and 0.3 $\mu_B$ (*cf.* ref. 11).

A similar method was used to prepare bis(dimethyl sulfide)iodine(I) hexafluorouranate(V) (Table 4), in this case the sulfide being added by direct distillation, and for a series of iodine(I) hexafluoromolybdate(V) complexes for cyclic voltammetry (CV) measurements. Voltammograms were referenced internally to the MoF$_6$–[MoF$_6$]$^-$ and [MoF$_6$]$^-$–Mo$^{IV}$ couples[25] and the solid complexes were characterized by their spectra. The CV data have been discussed above.

(*b*) *By direct reaction between halogen and macrocycle.* In a glove box [14]aneN$_4$ (1.0 mmol) was transferred to one limb of a flamed-out, double-limbed Pyrex vessel and resublimed I$_2$ (2.0 mmol) to the other. The vessel was evacuated and dry ethanol (5 cm$^3$) distilled into each arm. The [14]aneN$_4$ solution was added slowly to the I$_2$ solution through a glass sinter pad and a brown-yellow solid was obtained on concentrating the solution. This was washed *in vacuo* with portions of dry EtOH then dry Et$_2$O to remove traces of I$_2$; the orange solid was then pumped for several hours. It was characterized as [I([14]aneN$_4$)][I$_3$] on the basis of its analysis (Table 4) and IR spectrum (Table 1). The [12]aneN$_4$ analogue was prepared in an identical fashion. Portions of [I([14]aneN$_4$)][I$_3$] (1.25 mmol) and NOPF$_6$ (1.25 mmol) contained in separate limbs of a reaction vessel reacted rapidly when they were mixed in the presence of MeCN (5 cm$^3$) *in vacuo* at room temperature. Nitric oxide and I$_2$ were evolved and a pale yellow solid, identified as [I([14]aneN$_4$)(NCMe)][PF$_6$] (Tables 1 and 4), isolated on removal of the volatile material. A spectroscopically identical solid was isolated when [I([14]aneN$_4$)][I$_3$] (1.0 mmol) in the presence of MeCN (5 cm$^3$) reacted with solid [14]aneN$_4$ (1.0 mmol) followed by the addition of a solution of [Ag(NCMe)$_2$][PF$_6$] (2.0 mmol) in MeCN (5 cm$^3$) and separation of AgI.

(*c*) *Reaction between dibromine and* [14]aneN$_4$. The reaction between [14]aneN$_4$ (1.0 mmol) and Br$_2$ (2.0 mmol) in CH$_2$Cl$_2$ (5 cm$^3$) was carried out by the procedure described in (*b*) except that Br$_2$ was added to the vessel by distillation *in vacuo*. The yellow-orange solid product was sparingly soluble in CH$_2$Cl$_2$ and was recrystallized from this solvent by multiple extractions with aliquots of CH$_2$Cl$_2$ *in vacuo* (Found: C, 21.9; H, 5.0; Br, 57.5; N, 9.4. C$_{10}$H$_{24}$Br$_4$N$_4$ requires C, 23.1; H, 4.7; Br, 61.5; N, 10.8%). The IR spectrum of the solid contained bands attributable to [14]aneN$_4$, notably 3252 [$\nu$(NH)] and 1684, 1622 cm$^{-1}$ [$\delta$(NH)]. Its electronic spectrum in CH$_2$Cl$_2$ comprised bands at $\lambda_{max}$ = 269 and 312 nm; the presence of [Br$_3$]$^-$ in solution could not be established unambiguously as Br$_2$ was liberated slowly on standing. Single crystals grown from Me$_2$SO solution proved on preliminary X-ray crystallographic examination to be a hydrolysis product containing protonated [14]aneN$_4$. The solid reacted with NOPF$_6$ in MeCN with the liberation of NO and Br$_2$. The $^1$H NMR spectrum was similar to that obtained for [I([14]aneN$_4$)(NCMe)][PF$_6$] but contained additional complex signals; the $^{19}$F and $^{31}$P spectra contained multiplets attributable to [PF$_6$]$^-$ and [PO$_3$F]$^{2-}$, the latter indicating that some HF elimination, and therefore subsequent hydrolysis, had occurred.

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