Secondary Bonding. Part 3.[1] The Crystal and Molecular Structure of Tetramethylammonium μ-Dimethylamino-bis(chloroiodate)(1−): a Pseudopolyhalide

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The crystal structure of the title compound has been determined by the heavy-atom method at −60 °C from diffractometer data. The crystals are monoclinic, space group $P2/c$, with a = 11.233(3), b = 5.773 4(10), c = 11.087(2) Å, β = 98.24(2)°, Z = 4, and R = 0.063 for 1 056 reflections having $(\sin\theta)/\lambda > 0.5$. They contain $[NMe_4]^+$ and $[NMe_2(ICl)_2]^-$ ions. The latter can be considered as pseudopolyhalide ions, with $[NMe_2]^-$ as a pseudohalide. In the anion, the nitrogen atoms are tetrahedral and N–I–Cl is linear [N–I 2.220(7), I–Cl 2.672(3) Å].

DURING studies on the halogen-substituted ammonium cations, the reactions of chlorodimethylamine with a series of potential alkylating agents were investigated by workers at the University of Durham.[2] They found that powerful alkylating agents such as methyl fluorosulphate gave salts of the colourless chlorotrimethylammonium ion [equation (1)]. In contrast to this, when NMe_2Cl

$$NMe_2Cl + SFO_2(OMe) \longrightarrow [NMe_3Cl][SFO_3] \quad (1)$$

was dissolved in an excess of iodomethane at room temperature a fine yellow solid slowly precipitated. The elemental analysis showed this compound to have the empirical formula C_3H_9ClIN and the product was formed quantitatively on the chlorodimethylamine taken, as in equation (2).

$$2NMe_2Cl + 2MeI \longrightarrow [NMe_4][NMe_2(ICl)_2] \quad (2)$$

The compound represented an isomer of the known adduct of trimethylamine with iodine monochloride[3] but the i.r. spectrum clearly showed that it had a different structure.[2] Demonstration that C_3H_9ClIN was the ionic compound $[NMe_4][NMe_2(ICl)_2]$, as indicated in equation (2), only came with the results of X-ray analysis. A preliminary report has been published.[4] The bonding in the anion $[NMe_2(ICl)_2]^-$ can be compared to that in polyhalides and in iodine monochloride adducts; these have been described as charge-transfer adducts but can better be regarded as showing secondary bonds.[5]

EXPERIMENTAL

Crystals of the compound C_3H_9ClIN were obtained by its slow preparation in tetrahydrofuran at 243 K over a number of months.[2] They are pale yellow chunky plates or rhombs, generally with poorly defined faces, and they decompose in a few hours at 20 °C although they can be stored indefinitely at lower temperatures. Crystal selection, examination under polarised light, and mounting were performed in a minimal time and the mounted crystal was rapidly transferred to the diffractometer (within *ca.* 30 min). The photographic examination and data collections were performed at −60 °C on a Syntex $P2_1$ diffractometer, using the LT-1 attachment.

Crystal Data.—$C_6H_{18}Cl_2I_2N_2$, M = 442.92, Monoclinic, a = 11.233(3), b = 5.773 4(10), c = 11.087(2) Å, β = 98.24(2)°, U = 711.6(3) Å^3 at −60 °C, D_m = 2.08 g cm^{-3} (flotation), Z = 4, D_c = 2.607 g cm^{-3}, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 48.07 cm^{-1}, space group $P2/c$.

Several crystals showed signs of twinning, but that used for data collection appeared initially to be unaffected. Data were collected to $2\theta = 60°$ in several shells. Reflections were measured using θ—2θ scans over a scan range ($K_{\alpha1}$ −0.85) to ($K_{\alpha2}$ +0.85) and variable scan rate of 1.2—29.3° min^{-1} depending on the intensity of a preliminary 2-s count. Background counts were recorded at each end of the scan, each for one quarter of the scan time. The intensities of three standard reflections collected every 100 reflections showed a gradual loss of intensity, and collected data were rescaled according to the equation $F = F_0(1 + 0.000\,665\,5t)$, with t = time in h. The maximum rescale factor was 1.062 6. Of 2 363 collected data (excluding standards), 1 855 were considered observed $[I/\sigma(I) \geqslant 3.0]$. Lorentz and polarisation factors were applied, and absorption corrections were made at a later stage in the refinement, using the program ABSCOR.

Structure Solution and Refinement; Crystal Twinning.—There were no apparent systematic absences in the data, suggesting the monoclinic space groups Pm, $P2$, or $P2/m$. The Patterson synthesis could only be interpreted in terms of two independent iodine atoms in space group $P2$. Refinement in this space group enabled all the atoms to be located, and after several cycles gave R 0.067 with the iodine and chlorine atoms anisotropic. However, even with this low R factor there were several unsatisfactory features of the model. Notably, the temperature factors of the chemically similar atoms N(1) and N(2) had U = 0.014 and 0.098 8 respectively, the bond lengths and angles between the independent ions were markedly dissimilar, and the agreements for certain reflection classes ($h0l$ and $00l$) were very poor. It was discovered that, by a suitable origin shift, the co-ordinates could be transformed into $P2/c$, making independent ions equivalent. When this possibility was tested, the R factor improved slightly, but more importantly the refinement resulted in chemically more reasonable bond distances and angles. Space group $P2/c$ requires the systematic absence $h0l$, $l \neq 2n$ to which there are a significant number of exceptions. However, inspection showed that the groups of reflections $h0l$, $l0h$, $\bar{h}0l$, and $l0\bar{h}$ had intensities indicative of crystal twinning, with $a' \equiv c$, $b' \equiv -b$. The effect of this twinning is to bring $h0l$ and $l0h$ almost into coincidence (distorted only by the difference in length between a and c). By comparison between reflections absent from one set or the other, a twinning factor of *ca.* 0.4 was observed for several sets of reflections. The inconsistencies between equivalent pairs of reflections at higher angle showed that the twinning was not perfect, and that the reflections from the minor component did not contribute to the observed high-angle intensities.

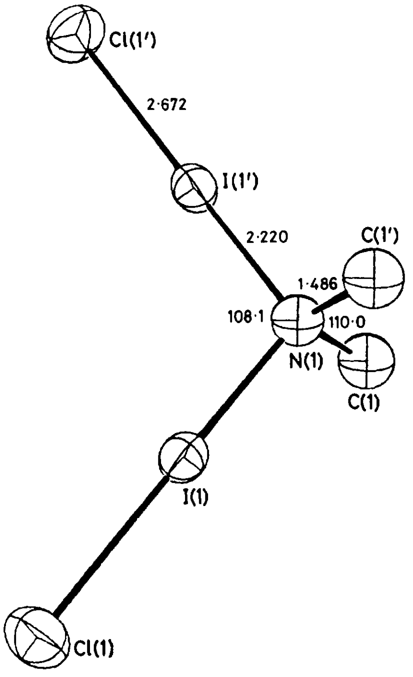

FIGURE 1 The $[NMe_2(ICl)_2]^-$ ion, with atomic numbering and principal dimensions

It therefore seems certain that space group *P*2/*c* is correct and that the unexpected *h*0*l* (*l* odd) reflections are due to twinning; this space group also gives more consistent bond lengths and angles. The success of the refinement in *P*2 is perhaps surprising. The effects of the crystal twinning were reduced by omitting all the reflections having $(\sin\theta)\lambda < 0.5$ from further refinement, leaving 1 056 observed reflections. Further, a weighting scheme was used which gives reflections with $0.41F_{\text{obs.}} \geqslant F_{\text{calc.}}$ zero weight. The weights for the other reflections were given by $w = XY$ where: (*i*) $X = 100.0/F$ if $F > 100.0$ or $X = F/20.0$ if $F < 20.0$, otherwise $X = 1.0$; and (*ii*) $Y = (\sin\theta)/0.42$ if $\sin\theta < 0.42$ otherwise $Y = 1.0$. Forty-seven reflections were given zero weight and the final least-squares refinement using anisotropic temperature factors for I and Cl converged to a final *R* of 0.066 and weighted *R′* of 0.057; in the final cycle no parameter shift was greater than 34% of its standard deviation. No contributions from hydrogen atoms were included. Scattering factors in the analytical form were from ref. 6. Calculations were made with the '*X*-RAY '76' system on a Burroughs B6700 computer.[7] Final positional parameters for all the atoms are listed in Table 1, bond lengths and angles in Table 2. The novel $[NMe_2(ICl)_2]^-$ anion is shown in Figure 1 and the molecular packing in Figure 2. Twinning, temperature, and final structure factors are listed in Supplementary Publication No. SUP 22389 (10 pp.).*

TABLE 1

Atomic co-ordinates for $[NMe_4][NMe_2(ICl)_2]$ with standard deviations in parentheses

Atom	*X*	*Y*	*Z*
I(1)	0.369 85(5)	0.119 52(9)	0.134 86(5)
Cl(1)	0.206 2(3)	−0.152 2(5)	0.005 7(3)
N(1)	0.500 0	0.345 2(19)	0.250 0
N(2)	0.000 0	−0.464 4(19)	0.250 0
C(1)	0.565 7(10)	0.492 8(18)	0.171 8(9)
C(2)	−0.073 7(9)	−0.611 4(21)	0.319 1(9)
C(3)	−0.080 7(11)	−0.312 7(20)	0.165 6(11)

TABLE 2

Bond lengths (Å) and bond angles (°) with standard deviations in parentheses

Bond lengths			
I(1)–Cl(1)	2.672(3)	N(2)–C(2)	1.475(13)
I(1)–N(1)	2.220(7)	N(2)–C(3)	1.491(13)
N(1)–C(1)	1.486(13)		
Bond angles			
N(1)–I(1)–Cl(1)	177.02(7)	C(2)–N(2)–C(2′)	109.7(9)
I(1)–N(1)–I(1′)	108.1(5)	C(2)–N(2)–C(3)	110.4(6)
I(1)–N(1)–C(1)	110.0(4)	C(2)–N(2)–C(3′)	109.1(6)
C(1)–N(1)–C(1′)	110.0(9)	C(3)–N(2)–C(3′)	108.0(9)
C(1)–N(1)–I(1′)	109.3(4)		

DISCUSSION

The crystal-structure analysis of the compound with empirical formula C_3H_9ClIN has shown that it consists of the ions $[NMe_4]^+$ and $[NMe_2(ICl)_2]^-$, each with crystallographic two-fold symmetry (Figure 1). The only possible analogues to the novel anion are the polyhalide anions, in particular $[I_5]^-$ which exists as a nearly planar V-shaped ion.[8] This latter can be regarded as I^- interacting with two iodine molecules with the distances shown in (B). In parallel with this, the present anion can be regarded as having the structure (A) with $[NMe_2]^-$ considered as a new pseudohalide. It is perhaps surpris-

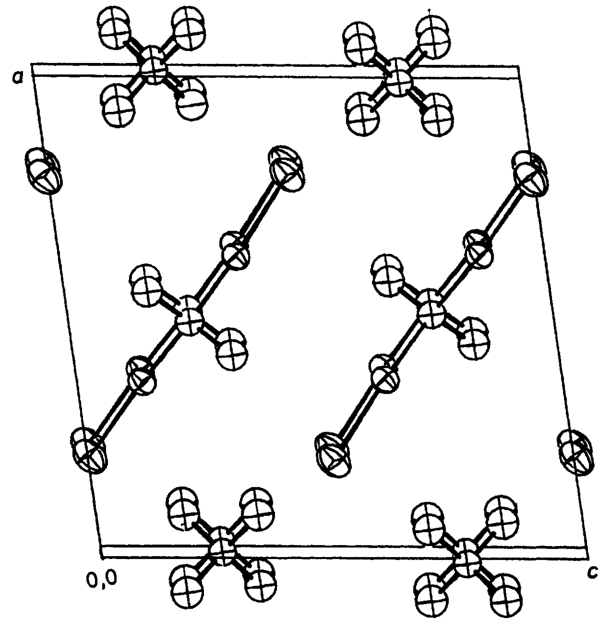

FIGURE 2 Packing in $[NMe_4][NMe_2(ICl)_2]$, viewed almost down *b*

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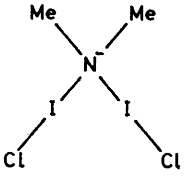
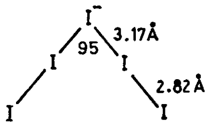
* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

ing to regard $[NMe_2]^-$ as acting as a pseudohalide in its interactions with iodine monochloride, although conventional pseudohalides have been found to form pseudopolyhalide anion analogues, for example in $[NCS{\cdot}I_2]^-$.[9]



(A)



(B)

In the anion, the N–I and I–Cl distances are 2.220(7) and 2.672(3) Å respectively, and the N–I–Cl system is very nearly linear [177.02(7)°]. The N–C(Me) distance is 1.486(13) Å compared to N–C distances of 1.475(13) and 1.491(13) Å in the cation. In the anion and cation the angles about nitrogen have values close to the tetrahedral value (Table 2).

The I–Cl bond length in the anion is considerably longer than that in gaseous ICl (2.321 Å) [10] or that found in the two polymorphic forms (α and β) of ICl in the solid state [2.44 and 2.37 (α), 2.440 and 2.351 Å (β)].[11] Iodine monochloride has also been characterised in several charge-transfer adducts with a variety of bases. The I–Cl distances in the adducts with pyridine,[12] 2-chloroquinoline,[13] and trimethylamine [2] are 2.510, 2.446, and 2.52 Å respectively. The I–Cl distance in the ICl adduct with 1-oxa-4-selenacyclohexane is even longer [2.73(1) Å] which, with the short Se–I distance [2.630(5) Å], suggests the formation of the selenonium salt $[C_4H_8OSeI]Cl$.[14] This behaviour is typical of adducts of iodine and the interhalogen compounds ICl and IBr. As the strength of the interaction with the Lewis base increases, the I–I, I–Cl, and I–Br bonds lengthen until they eventually result in centrosymmetric cations with a linear X–I–X (X = base) group being formed, as in bis(thiourea)iodine(I) iodide,[15] bis(hexamethylenetetramine)iodonium tri-iodide,[16] and other bis iodonium cations with pyridine [16] and 3-methylpyridine.[17]

The observed N–I distance [2.220(7) Å] is shorter than the N–I bond lengths in the pyridine, 2-chloroquinoline, and trimethylamine adducts (2.29, 2.43, and 2.30 Å respectively) and also that in $NMe_3{\cdot}I_2$ (2.27 Å) [18] and $NMe_3{\cdot}I(CF_3)$ (2.932 Å).[19]

An indication of the bond order can be obtained by comparison with the two centrosymmetric bis(pyridine)iodonium and bis(hexamethylenetetramine)iodonium cations. Considering these as having 3c–4e bonding between filled nitrogen sp^2 and sp^3 orbitals interacting with σ-symmetry (5*p*) orbitals on iodine, the resulting N–I bonds have bond orders ≈0.5 (although with the involvement of π orbitals on the ligands or *d* orbitals on the iodine, this bond order would increase).[6] The present N–I distance is intermediate between the distances [2.16(10) and 2.30(1) Å respectively] found in these two compounds: the value of 2.24(2) Å for N–I in the unpublished bis(3-methylpyridine)iodonium cation provides another value for N(sp^2)–I with bond order ≈0.5.[17]

Another measure of the strength of the bonding in each three-centre N–I–Cl system can be obtained by following Hassel and Rømming's method in calculating ' effective radii ' about the iodine atom by subtracting the covalent radii of the nitrogen (0.70 Å) and chlorine (0.99 Å) atoms from the evaluated N–I and I–Cl bond lengths.[20] The resulting values for the effective radii R_1 and R_2 in the present anion are 1.52 and 1.68 Å respectively which, when compared with Hassel and Rømming's graph of R_1 against R_2 values for a series of polyiodide and IX (X = Cl or Br) complexes, falls very close to their least-squares straight line. This confirms the validity of regarding the anion as a pseudopolyhalide, while the near equality of the two radii suggests that the bond orders of the N–I and I–Cl bonds are similar.

The bonding in the present anion and the majority of the complexes mentioned above has been described in terms of charge-transfer interactions.[20,21] However, these strong interactions are perhaps better described as secondary bonds in contrast to weak σ–π* interactions, or the dynamic charge-transfer effects observed spectroscopically. Two separate three-centre four-electron systems are formed in the present anion when the two lone pairs in sp^3 orbitals on the $[NMe_2]^-$ group interact with the σ* orbitals of both iodine monochloride molecules. The short N–I and long I–C distances indicate that the interactions in the present anion are among the strongest so far observed for iodine monochloride adducts. The strength of these interactions should give the two chlorine atoms in each anion an appreciable partial negative charge, and this may act to prevent any close interanion contacts. In any case, the packing is that of discrete ions, and this is somewhat surprising. A normal structural feature of the polyiodide ions and other complexes of the X·I–I (X = base) type (*e.g.* iodine adducts of 1-oxa-4-selenacyclohexane and 1,4-diselenacyclohexane) is that the compounds take up polymeric arrangements, *via* several weaker intermolecular contacts. Even iodine adducts of such compounds as the transition-metal complexes $[RuI(S_2CNEt_2)_3]$,[22] $[Pt(phen)I_6]$ and $[Pt_2(phen)_2I_{10}]$ (phen = 1,10-phenanthroline) [23] form zigzag or helical chains, with the iodine molecules bridging the directly bonded iodine atoms. For an adequate picture of their bonding it may be necessary to consider the use of semi-metallic bands of delocalised multi-centre orbitals, formed by the interaction of the *p* orbitals of each iodine along the polymeric chain of iodine atoms, giving rise to bands of semi-metallic character.

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