

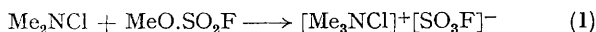
## Preparation and X-Ray Structure of a Novel Pseudo-polyhalide Anion $[\text{Me}_2\text{N}(\text{ICl})_2]^-$

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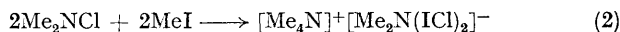
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**Summary** The reaction of dimethylchloramine with an excess of iodomethane at room temperature gives a yellow crystalline material which has been shown by low temperature X-ray analysis to contain the  $[\text{Me}_4\text{N}]^+$  cation and the novel anion  $[\text{Me}_2\text{N}(\text{ICl})_2]^-$  which can be regarded as having the structure (A), analogous to  $[\text{I}_5]^-$ , with  $[\text{NMe}_2]^-$  as a pseudo-halide ion.

DURING the study of the halogen-substituted ammonium cations, the reactions of dimethylchloramine with a series of potential alkylating agents were investigated and it was found that powerful alkylating agents such as methyl fluorosulphate gave salts of the colourless trimethylchloroammonium ion [equation (1)].

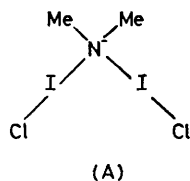


In contrast to this, when dimethylchloramine was dissolved in an excess of iodomethane at room temperature, a fine yellow solid slowly precipitated. The elemental analysis showed the compound to have the empirical formula  $\text{C}_3\text{H}_9\text{ClIN}$ . The product was formed quantitatively on the dimethylchloramine taken, with respect to equation (2).



The compound represented an isomer of the known adduct of trimethylamine with iodine monochloride,<sup>1</sup> but the i.r. spectrum clearly showed that the compound was of a different structure. Crystals of the compound were obtained by its slow preparation in tetrahydrofuran at 243 K over a number of months.

**Crystal data:**  $\text{C}_6\text{H}_{18}\text{Cl}_2\text{I}_2\text{N}_2$ ,  $M$  442.92, monoclinic,  $a = 11.233(3)$ ,  $b = 5.773(1)$ ,  $c = 11.087(2)$  Å,  $\beta = 98.24(2)^\circ$ ,  $U = 711.6(3)$  Å<sup>3</sup>,  $D_c = 2.067$  for  $Z = 4$ ,  $D_m = 2.08$  g cm<sup>-3</sup>, Mo- $K_\alpha$  radiation,  $\lambda = 0.7169$  Å, space group  $P2_1/c$ .



The crystals decompose in a few hours at 20 °C, so all X-ray work was performed at -60 °C using a Syntex  $P2_1$  diffractometer with an LT-1 low temperature device. Three-dimensional data were collected to a maximum  $2\theta$  of 60° and reduced to 1855 observed reflections [ $I/\sigma(I) \geq 3.0$ ]. The structure was solved by Patterson methods. The crystals are invariably twinned ( $a' \equiv c$ ) but the effects

of this were removed by excluding all data with  $\sin \theta/\lambda < 0.5$  from the final refinement. Least-squares refinement using the remaining 1045 reflections resulted in an  $R$  factor of 0.066 (I and Cl with anisotropic temperature factors).†

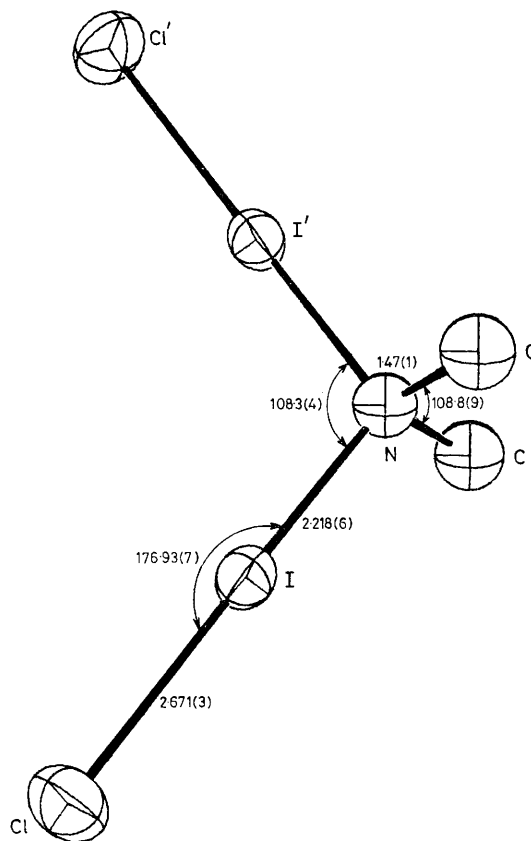


FIGURE. Structure of the  $[\text{Me}_2\text{N}(\text{ICl})_2]^-$  ion. Primed atoms are related to unprimed ones by the crystallographic 2-fold axis. Bond distances are in Å.

The crystal has been found to consist of  $[\text{NMe}_4]^+$  and  $[\text{Me}_2\text{N}(\text{ICl})_2]^-$  ions, each with crystallographic two-fold symmetry (Figure). The only possible analogues to the novel anion are the polyhalide anions, in particular  $[\text{I}_5]^-$  which exists as a nearly planar V-shaped ion.<sup>2</sup> In parallel with this, the present anion can be regarded as having the structure (A) with  $[\text{Me}_2\text{N}]^-$  considered as a new pseudo-halide. The N-I and I-Cl distances in the anion are 2.218(6) and 2.671(3) Å, respectively, and the N-I-Cl system is very nearly linear [ $\angle \text{N-I-Cl} = 176.9(1)^\circ$ ].

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Other angles around nitrogen have values close to those for a tetrahedron. The I-Cl bond length is considerably longer than in gaseous ICl (2.321 Å)<sup>3</sup> or in the adducts of iodine monochloride with pyridine (2.510 Å),<sup>4</sup> 2-chloroquinoline (2.446 Å),<sup>5</sup> and trimethylamine (2.52 Å).<sup>1</sup> The observed N-I distance is shorter than the N-I bond lengths in the same adducts (2.29, 2.43, and 2.30 Å, respectively). However, the N-I distance is longer than the single N-I bond lengths of 2.09 and 2.14 Å observed in the adducts NI<sub>3</sub>·C<sub>5</sub>H<sub>5</sub>N and NI<sub>3</sub>·I<sub>2</sub>C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>,<sup>6</sup> though the former also has a longer N-I bond of 2.36 Å to a further iodine linking NI<sub>4</sub> tetrahedra together.

If the bonding in the present anion is described in terms of charge transfer interactions between lone pairs of electrons on the nitrogen atom and two iodine monochloride molecules, the short N-I and long I-Cl distances

indicate that these interactions are the strongest so far observed for iodine monochloride adducts.

The study of this and similar compounds is continuing. When dimethylbromamine is treated with methyl iodide, the corresponding bromo-compound is produced, formulated as [Me<sub>4</sub>N]<sup>+</sup>[Me<sub>2</sub>N(IBr)<sub>2</sub>]<sup>-</sup>, but the interaction of dimethylchloramine with methyl bromide gives the compound Me<sub>3</sub>NBrCl. When methyl chloride is used as the alkylating agent, only decomposition products of the chloramine are obtained.

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<sup>1</sup> O. Hassel and H. Hope, *Acta Chem. Scand.*, 1960, **14**, 391

<sup>2</sup> E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 148.

<sup>3</sup> E. Hulthen, N. Johansson, and U. Pilsäter, *Arkiv Fysik*, 1959, **14**, 31.

<sup>4</sup> C. Rømming, *Acta Chem. Scand.*, 1972, **26**, 1555; G. Eia and O. Hassel, *ibid.*, 1956, **10**, 139.

<sup>5</sup> G. Bernardinelli and R. Gerdil, *Acta Cryst.*, 1976, **B32**, 1906.

<sup>6</sup> H. Hartl and D. Ullrich, *Z. anorg. Chem.*, 1974, **409**, 228; H. Pritzkow, *ibid.*, 1974, **409**, 237.