Structure of the Complex of Sodium Chloride with '*p,p'*-Methylene Dianiline'

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Summary In the complex [(mda)$_3$NaCl], (mda = *p,p'*-diaminodiphenylmethane) each amino-group is hydrogen-bonded to one Cl^- and co-ordinated to one Na^+; the co-ordination round Na^+ is nearly octahedral (Na–N 2·52 Å) and that round Cl^- nearly trigonal prismatic (Cl–N 3·44 Å).

MOST organic molecules which form complexes with alkali or alkaline earth metal ions interact with the cation through oxygen atoms in ether, oxo-, or carboxy-groups;[1,2] where the anion is incorporated in the crystal it is usually non-specifically held in a cavity. Co-ordination through both oxygen and nitrogen atoms has been noted in one case.[3] Of all the amino-compounds examined only *p,p'*-diaminodiphenylmethane ('methylene dianiline', mda) and *p,p'*-diamino-2,3-diphenylbutane (dadp) have given crystalline complexes, and these only with NaCl and NaBr.[4–7] We have determined the crystal structure of [(mda)$_3$NaCl] to elucidate the nature of the bonding and the reasons for the unusual specificity of these ligands. The corresponding NaBr complex is isomorphous.

Crystal data: $C_{39}H_{42}ClN_6Na$, $M = 653{\cdot}2$; rhombohedral, referred to hexagonal axes, $a = 18{\cdot}425(3)$, $c = 17{\cdot}424(4)$ Å; $U = 5123$ Å^3; D_m (by flotation) 1·29, $D_c = 1{\cdot}27$, $Z = 6$; space group $R\bar{3}c$ (D^6_{3d}, no. 167); niobium filtered Mo-K_α radiation; Picker automatic four-circle diffractometer. 689 independent reflections with $|F| \geqslant 10\sigma(F)$ were used in the structure analysis. The Na^+ and Cl^- ions lie on special positions, and the positions of the light atoms were found by standard Fourier methods. Refinement, using anisotropic thermal parameters for the Na^+ and Cl^- ions, and isotropic ones for all other atoms including hydrogen, gave R 0·052.

The principal interactions in the crystal are shown in Figure 1; Na^+ and Cl^- ions lie alternately in columns along the crystal *c*-axes ($\bar{3}$), separated from each other by planes each containing three amino groups. As indicated by the i.r. and n.m.r. spectra,[8] one hydrogen atom of each NH_2 group takes part in a weak hydrogen bond between nitrogen and chlorine [N–Cl 3·442(4) Å, Cl–H 2·65(3) Å]; the second hydrogen atom is not involved in any specific interaction. Each chloride ion is thus hydrogen-bonded to six equivalent amino-groups from six different mda molecules, the symmetry of the co-ordination polyhedron being 32 (D_3), and nearly trigonal prismatic.

Each sodium ion is surrounded by six equivalent nitrogen atoms from six different mda molecules (Na–N 2·520(3) Å). The hydrogen atoms, which are clearly visible in an electron density difference map, play no part in the Na–N interactions. The co-ordination is nearly octahedral; [it is strictly trigonal anti-prismatic, $\bar{3}(S_6)$, with the angles N–Na–N 93·6(1) and 86·3(1)° which are close to the value

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of 90° required for exact octahedral symmetry]. The four atoms nearest to nitrogen (C, Na, and two H atoms) are approximately tetrahedrally disposed, so that the lone pair of each nitrogen atom is directed towards the sodium ion.

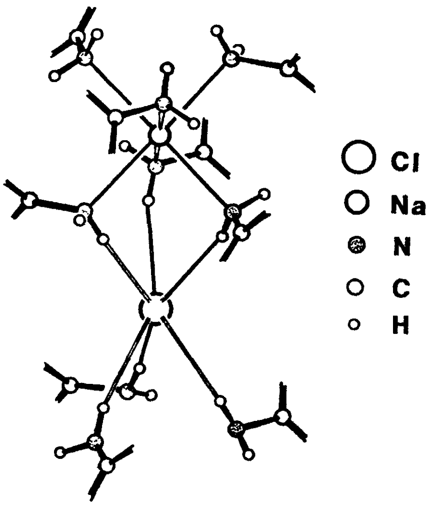

FIGURE 1. *The immediate environment of a pair of neighbouring* $\mathrm{Na^+}$ *and* $\mathrm{Cl^-}$ *ions.*

The geometrical arrangement thus suggests that this is an octahedral co-ordination complex of $\mathrm{Na^+}$ with six amino-groups acting as donors. A similar co-ordination, with Na–N 2·62 Å is found[9] for one of the sodium ions in $\mathrm{NaCl},5\frac{1}{7}\mathrm{NH_3}$; the other sodium ion is five-co-ordinated with Na–N 2·48—2·55 Å.

The Na–N distances (2·52 Å) are rather shorter than predicted from Pauling's crystal radii for ionic interactions (0·95 + 1·71 = 2·66 Å). They fall within the range of Na–N distances in $\mathrm{NaCl},5\frac{1}{7}\mathrm{NH_3}$. They also fall within the range of the Na–O distances reported in refs. 1 and 2 (2·3—2·8 Å) and the Na–N bonds are probably of similar strength to the Na–O bonds in those compounds.

Each amino-group is co-ordinated to an $\mathrm{Na^+}$ ion, and hydrogen bonded to the $\mathrm{Cl^-}$ immediately above or below the $\mathrm{Na^+}$. Each mda molecule is linked to two columns of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions, and the space between all the columns is entirely occupied by organic groups (Figure 2). The planes defined by the $\mathrm{NH_2}$ and $\mathrm{CH_2}$ groups of each molecule are approximately perpendicular to the *c*-axes, and the $\mathrm{CH_2}$ groups lie on the diad crystal axes. The phenyl groups are closely packed, and their planes are inclined at 50° to the N–C–N planes. The structure thus has some of the characteristics of an organic matrix with channels lined with amino-groups, in which the $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ ions are held. The Na–Cl distance (4·32 Å) is much larger than in NaCl (2·82 Å). These channels are in a hexagonal array, but are completely independent of each other. The stability of the complex is attributable to the ability of the ligands to pack together efficiently and in such a way as to allow hydrogen-bonding to the anion and co-ordination to the cation to occur simultaneously.

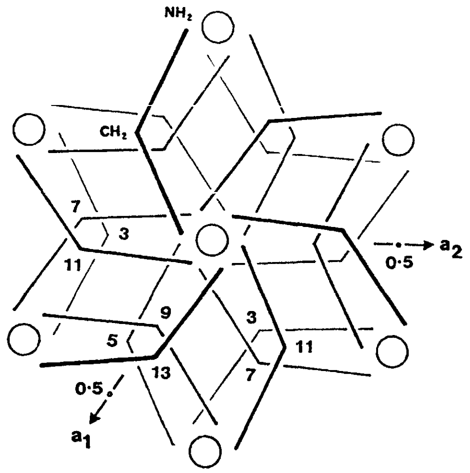

FIGURE 2. *A diagrammatic view of the structure, projected down the* c-*axis. Each organic molecule is represented by a* **V**-*shaped pair of lines joining the* ($\mathrm{NH_2}$) and ($\mathrm{CH_2}$) *groups, and its height above the plane* c = 0 *is given by the number* (3, 5, 7, etc.) *in units of* (1/12) × 17·42 Å. *The circles represent the columns of alternate* $\mathrm{Na^+}$ *and* $\mathrm{Cl^-}$ *ions; the* $\mathrm{Na^+}$ *ions are at heights* 0 *and* 6 *on the central column, and at* 4 *and* 10 *or* 2 *and* 8 *on the outer columns shown.*

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