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CRYSTAL LATTICE ENERGY OF AMMONIUM AND METHANAMINIUM CHLORIDES

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The fraction of crystal lattice energy of ammonium and methanaminium chlorides caused by electrostatic interactions has been evaluated on the basis of modified Coulomb equation for infinite number of interacting charges using available crystallographic information and estimating charge distribution for cations by MNDO and INDO methods. The evaluated characteristics compare well with experimentally derived crystal lattice energies particularly with respect to the observed trends of both quantities on the degree of substitution.

Crystal lattice energy (U) is one of the most important thermochemical characteristics for solid substances. The values of this quantity can be derived on the basis of the Hess law and knowledge of pertinent thermochemical data. Values of U can also be evaluated theoretically. For ionic substances the crystal lattice energy at 0 K is defined by the equation

$$U = E_{\mathrm{elec}} + E_D + E_R + E_{\mathrm{o}} \tag{1}$$

where E_{elec} - electrostatic interactions (the Madelung term), E_D -the Van der Waals interactions, E_R-the repulsion term and E_{o}-the zero point energy.

So far crystal lattice energies have been determined theoretically for numerous inorganic but only a few simple organic ionic systems [1, 2]. The main problem occurring during such calculations is the need for a knowledge of charge distribution and distances between atoms in the lattice. The latter characteristics are, in some cases, available from the crystallographic data. The theoretical procedures are relatively simple for compounds containing ions of spherical symmetry of charge distribution (e.g. Na^+, Cl^-). The calculations are also feasible for substances composed of symmetrical complex ions (e.g. $(CH_3)_4N^+$ MX_6^{2-}), for which charge distribution is relatively easy to predict. To our knowledge no general procedure for the determination of lattice energy of crystals containing highly

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asymmetrical ions, e.g. cations of nitrogen organic bases has, so far, been reported. This subject is of a great importance since such cations occur in numerous biological systems. In this note we present a preliminary attempt to determine the electrostatic part of the lattice energy in crystals of ammonium and methanaminium chlorides.

The principles of the method

The main contribution to the crystal lattice energy is in the Madelung term (E_{elec} term in Eq. (1)). The remaining terms of the right band side of Eq. (1) describe short-range interactions, which are essential only on distances comparable to intermolecular distances in crystals. E_D and E_R terms in ionic crystals admit opposite signs and the sum $E_D + E_R + E_o$ never exceed 0.1 of E_{elec} [1, 2]. In the first approximation therefore, E_{elec} best describes the lattice energy of ionic substances. This term can be expressed by the equation

$$E_{\mathrm{elec}} = \frac{1}{4 * \pi * \varepsilon_o} M * N_o * \frac{e^2}{a_o} \tag{2}$$

where N_o is the Avogadro number, e is the electron charge, ε_o is the permittivity of free space, M denotes the Madelung constant and a_o expresses the shortest equilibrum distance in the lattice between cation and anion. Equation (2) is a simple form of the Coulomb law for infinite number of charges located periodically in atoms forming crystals of a given substance. The Madelung constant in Eq. (2) is defined by the equation

$$M = \frac{a_o}{2} \sum_i \sum_{i \neq j} \frac{q_i * q_j}{|\bar{r}_i - \bar{r}_j|} \tag{3}$$

where $\bar{r}_i$ and $\bar{r}_j$ are the vectors characterising the positions of q_i and q_j charges or positions of centres of charge distribution in the lattice (q_i and q_j actually characterize the fraction of the charge of the electron). The Madelung constant is, first of all, defined by the symmetry of the crystal lattice. However, as mentioned above, it depends also on fractional charges on individual atoms. The problem of calculating the electrostatic part of the lattice energy is, therefore, identical with the problem of evaluation of the Madelung constant for the compound.

The use of Eq. (3) requires a knowledge of both charge distribution and location of charged centres in the lattice. The charge of chloride ion was always assumed to be –1. The distribution of the positive charge in polyatomic ammonium or alkanaminium ions is not a priori known. Thus, we applied quantum chemistry methods, namely MNDO [3] and INDO [4] to resolve the latter problem. The necessary structural information has been taken directly from known crystallographic data for N-methyl-methanaminium [7] and N,N-dimethyl-methanaminium [8] chlorides. The possibility of thermal rotation of NH_4^+ and $CH_3NH_3^+$ in the lattice results in the crystallographic data for appropriate chlorides [5, 6] being insufficient to afford all necessary structural information. In the case of NH_4Cl we adopted the approach proposed by Narayan *et al.* [9]. For methanaminium chloride it has been assumed that one H atom of $CH_3NH_3^+$ is situated along $\geqslant N-H\cdots Cl$ line and that the latter N–H distance is equal to 0.103 nm [7, 8]. The location of the remaining six atoms was found by the application of standard DFP optimization procedure together with MNDO method and lowest energy criterion.

The Madelung constants for the compounds studied were calculated by Ewald's double series method [10]. The original program for monoatomic ions has been modified so as to enable computations for asymmetrical complex cations.

Result and discussion

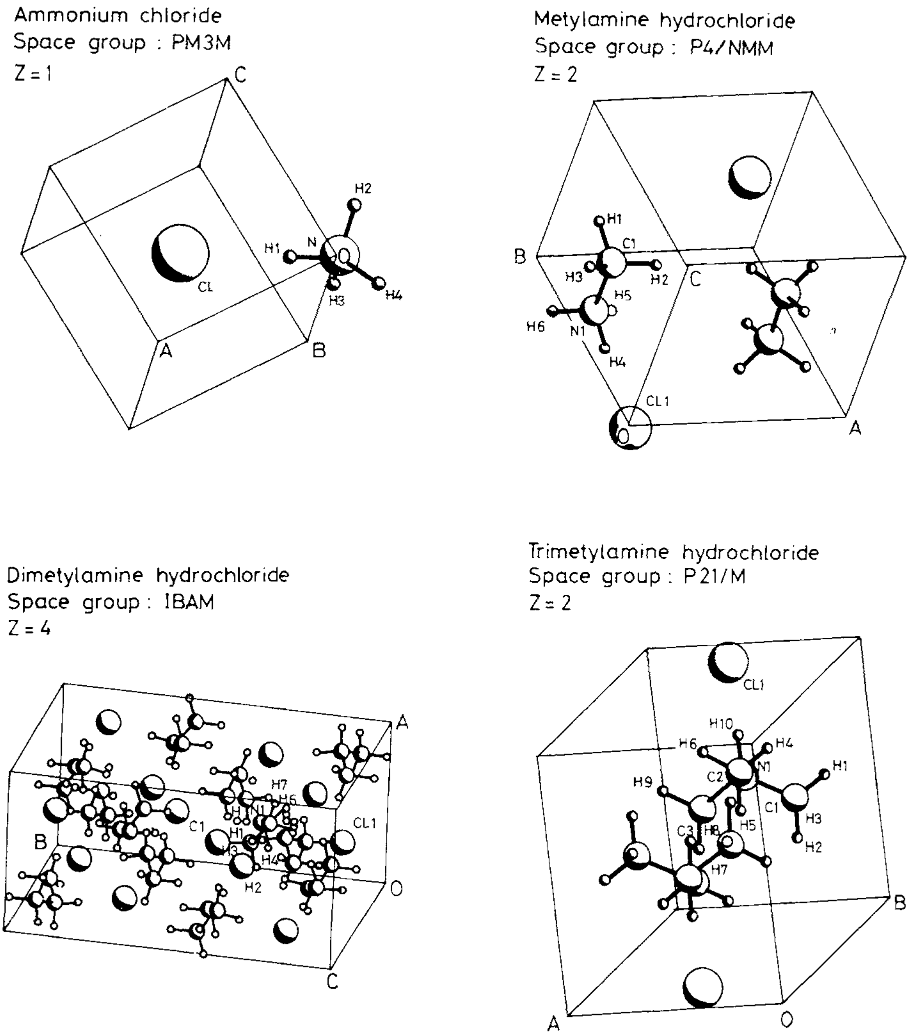
To give some insight into the structure of the compounds examined the orientation of ions in the elementary cell is presented schematically in Fig. 1. Table 1 compiles the evaluated theoretically crystal lattice energies together with the selected information from the literature.

Table 1 Crystal lattice energy (in kJ.mol^{-1}) of ammonium and methanaminium clorides

Compound	E_{elec} from Eq. (2)		U_{exp} from literature	
	a	b	Ref. [11, 12]	Ref. [13]
$(NH_4)Cl$	741.7	795.5	697.4	692
$(MeNH_3)Cl$	688.2	688.7	638.8	656
$(Me_2NH_2)Cl$	634.9	625.2	624.0	627
$(Me_3NH)Cl$	625.9	593.5	596.0	596

a charge distribution in cation calculated by MNDO method,

b charge distribution in cation calculated by INDO method



Ammonium chloride
Space group : PM3M
Z = 1

Metylamine hydrochloride
Space group : P4/NMM
Z = 2

Dimetylamine hydrochloride
Space group : IBAM
Z = 4

Trimetylamine hydrochloride
Space group : P21/M
Z = 2

Fig. 1 Crystallographic structures of ammonium and methanaminium chlorides

Despite the approximate character of the approach applied which neglects other than electrostatic interactions, assumes that charge distribution in cations can be calculated by semi-empirical quantum chemistry methods and neglects the influence of the environment on charge distribution in the lattice, the derived crystal lattice energies best compare with those determined experimentally (U_{exp}). This particularly concerns the compounds whose structures are exactly known from crystallographic studies (i.e. $(Me_2NH_2)Cl$ and $(Me_3NH)Cl$). In the case of $(NH)_4Cl$ and $(MeNH_3)Cl$ some structural parameters had to be admitted arbitrarily and thus the agreement between E_{elec} and U_{exp} is not so good. Nevertheless, both theoretical and experimental values show very similar dependency on the degree of substitution and thus size of the cation. Present data also imply that electrostatic interactions play the most important role in the bonding forces of crystals of nitrogen organic bases.

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Zusammenfassung — Unter Verwendung zugänglicher kristallographischer Informationen und einer Schätzung des Ladungsbeitrages von Kationen (MNDO, INDO) wurde auf der Basis einer modifizierten Coulomb-Gleichung für eine unendliche Zahl von beteiligten Ladungen derjenige Anteil der Kristallgitterenergie von Ammonium- und Methanaminiumchloriden geschätzt, der auf elektrostatischen Wechselbeziehungen beruht. Die geschätzten Angaben stimmen gut mit experimentell ermittelten Kristallgitterenergien überein, besonders im Hinblick auf die beobachtete Tendenz beider Größen in Abhängigkeit vom Substitutionsgrad.