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$ClO_3^-\cdots ClO_3^-$ interactions in crystalline sodium chlorate

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The chemical bonding between chlorate anions, its energy and role in the crystal packing formation of the title compound were examined within topological analysis of electron density function.

The astonishing feature of crystalline ionic materials is bonding between species with the same sign of charge. The most convenient approach to the description of such interactions on both qualitative and quantitative levels is the charge density analysis within Bader's 'Atoms in Molecule' theory.[1] The latter makes it possible to determine whether or not the interatomic contacts expected on the basis of the 'geometrical' criteria correspond to attractive (bonding) interactions, as well as to estimate their energy.[2] A number of investigations revealed the presence of anion–anion interactions in high-symmetric inorganic systems with point-charge ions such as halogen···halogen in alkaline halides[3(a)] or molecular chlorine[3(b)] and O···O in danburite[4(a)] or dinitrogen tetraoxide.[4(b)] Moreover, it was reported that such contacts occasionally occur in the crystals of organic salts, for instance, in hydroxylammonium chloride[5] and urea nitrate,[6] with bulky cations participating in the formation of numerous H-bonds. Accordingly, to check if the tendency of anions to interact with each other is their characteristic feature, we have extended our investigation for other systems. As such anion in the current communication we have chosen the chlorate one due to the presence of $ClO_3^-\cdots ClO_3^-$ bonds in the majority of corresponding salts. Indeed, in agreement with the statistical analysis of ISCD, the occurrence of shortened Cl···O contacts (the interatomic separations are less than the sum of van der Waals radii[7] of 3.13 Å) is common for chlorate-containing inorganic compounds. In particular, the Cl···O distance varies in the range 2.868–3.064 Å with the smallest value in hexagonal potassium chlorate[8] and the biggest one in $TlClO_3$.[9] In addition to the shortened Cl···O distance, these contacts are characterised by the pronounced directionality with O···Cl–O angle gaining to 157.2°. The latter can be interpreted as possible sign of electron transfer from the oxygen electron lone pair to the antibonding Cl–O orbital. Furthermore, the analysis of CSD has shown that the same type of contacts occurs in two structures (refcodes WASQEM and AYUXOH) among 10 available chlorates with bulky cations. Although their distances (3.258 and 3.417 Å) are slightly elongated, as compared with those in inorganic salts, the above directionality of O···Cl–O contacts persists (O–Cl···O angles are 130.8 and 133.4°). In order to analyse the chlorate–chlorate interactions, we carried out a high-resolution X-ray diffraction (XRD)[†] study of crystalline sodium chlorate **1**, which is of particular interest in the context of spontaneous resolution[10] and nonlinear optic materials.[11]

According to the XRD data, the ions in **1** are assembled into a 3D framework by cation–anion [Na–O distance is equal to 2.4024(5) and 2.4690(4) Å] and anion–anion [Cl···O is 3.0474(5) Å] interactions (Figure 1) in a manner that each Na/Cl atom is surrounded by six oxygens. The Cl···O contacts are characterised by a certain degree of directionality with the O–Cl···O angle of 148.6°.

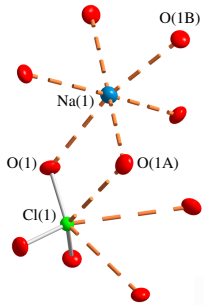

Figure 1 General view of **1** in representation of atoms by thermal ellipsoids at $p = 80\%$. The interatomic distances (Å) for given bonds and contacts are Cl(1)–O(1) 1.4909(4), Cl(1)–O(1A) 3.0441(3), Na(1)–O(1) and Na(1)–O(1A) 2.4691(4), Na(1)–O(1B) 2.4027(4). The O(1A) and O(1B) atoms are obtained from the basic one by the symmetry operations $-x + 0.5$, $-y + 1$, $z - 0.5$ and x, y, z.

In contrast to the $Cl^-\cdots Cl^-$ and $NO_3^-\cdots {}^-O_3N$ interactions, the anion–anion contacts in **1** occur between atoms with opposite sign of charge as it is observed in the case of the $C(=O)O–H\cdots {}^-O_2C$

[†] *Crystallographic data.* Crystals of **1** ($NaClO_3$, $M = 106.44$) are cubic, space group $P2_13$, at 100 K: $a = 6.5303(1)$ Å, $V = 278.483(4)$ Å^3, $Z = 4$ ($Z' = 1/3$), $d_{calc} = 2.539$ g cm^{-3}, (MoKα) = 12.81 cm^{-1}, $F(000) = 208$. Intensities of 34183 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 115°$] and 1293 independent reflections [$R_{int} = 0.0382$] were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. For **1** the refinement converged to $wR_2 = 0.0422$ and GOF = 1.002 for all independent reflections [$R_1 = 0.0172$ was calculated against F for 1286 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

The multipole refinement was carried out within the Hansen-Coppens formalism[13] using the XD program package[14] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac–Fock solution.[15] The level of multipole expansion was hexadecapole for chlorine and sodium and octupole for oxygen atoms. The refinement was carried out against F and converged to $R = 0.0109$, $wR = 0.0121$ and GOF = 1.08 for 515 merged reflections with $I > 3\sigma(I)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria. The residual electron density was not more that 0.21 eÅ^{-3}. Analysis of topology of the $\rho(r)$ function was carried out using the WinXPRO program package.[16]

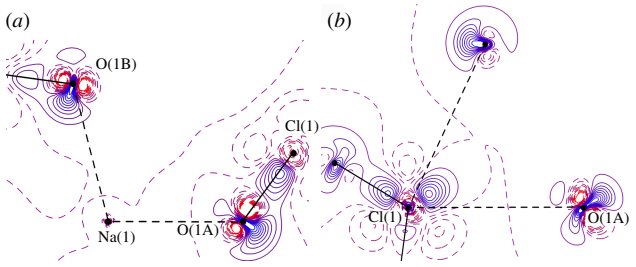

Figure 2 Sections of the static deformation electron density (*a*) in the plane O(1A)Na(1)O(1B) and (*b*) in the region of the Cl(1)···O contacts of **1**. Contours are drawn with 0.1 eÅ^{-3} interval, the non-positive contours are dashed.

bonds in deprotonated dicarboxylic acids.[12] Therefore, they can be considerably stronger in comparison with those, *e.g.*, in hydroxylammonium chloride[5] and urea nitrate.[6] To evaluate the energy of the above contacts and to estimate their role in the crystal packing formation on the quantitative level, we have performed a topological analysis of the electron density distribution $\rho(r)$ in the crystal of **1**.

The search for bond critical points CPs (3, –1) performed in the interatomic area revealed the presence of the above Na–O and Cl···O contacts in **1**. In agreement with the static deformation electron density (DED) distribution in the plane of Na(1), O(1A) and O(1B) atoms, the Na–O electrostatic interactions can be described in terms of a 'peak-to-hole' formalism [Figure 2(*a*)]. One of the DED maxima observed in the vicinity of each oxygen and attributed to LPs is directed toward the region of the DED depletion near the sodium atom. Note that the strength of M–O (M is an alkali metal) contacts depends on the directionality of the oxygen lone pair.[17] The disposition of LPs for O(1A) and O(1B) relative to the Na–O lines in **1** is different, and the degree of directionality correlates well with the shortening of the Na–O(1B) distance. Accordingly, we can assume that the latter is slightly stronger than the Na–O(1A) one.

The Cl…O interactions also appear to be of 'peak-to-hole' type, but from the current or any other section it is impossible to establish the direction of charge transfer, *i.e.*, from chlorine to the O–Cl antibonding orbital or *vice versa* [Figure 2(*b*)]. The interesting feature is that the DED distribution in the region of the O(1A) atom is characterised by three maxima corresponding to three LPs of oxygen. In addition, the analysis of the $-\nabla^2\rho(r)$ function topology has revealed three critical points (3, –3) in the vicinity of O atoms, that unambiguously indicates the presence of three LPs in the oxygen valence shell (see Online Supplementary Materials). Moreover, the same trend was found for the 3D distribution of DED in the Cl···O area in the crystal of **1** (Figure 3). The close examination of LPs mutual disposition shows that the Cl···O interaction can be described as the transfer of O atom's LP to the antibonding orbital of the Cl–O bond. On the other hand, the presence of three LPs for oxygen atom apparently indicates the significant contribution of resonant form $^{-}$Cl(–O)$_3$ with formal single character of Cl–O bonds formed by a donor–acceptor mechanism. The latter agrees well with the

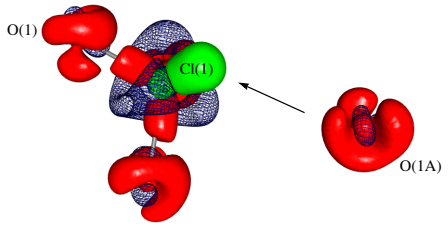

Figure 3 The 3D distribution of DED in the section of the Cl(1)···O(1A) contact in **1**. Isosurface of DED equal to 0.4 eÅ^{-3} is shown by solid; the negative isosurface (DED is –0.2 eÅ^3) is shown by wireframe.

ellipticity (ε) in the corresponding CPs (3, –1) showing that Cl–O bonds (ε = 0.067) in crystalline **1** are almost single ones. Thus, the character of the chemical bonding for the chlorate anion in the crystal of **1** does not coincide with the commonly presumed resonant form O=Cl(O$^-$)=O and is similar to those for P–O in diphenylphosphonic acid.[18]

In order to investigate the charge distribution in the crystal of **1**, we determined the atomic basins (Ω) surrounded by zero-flux surface [the integrated values of $-1/4\nabla^2\rho(r)$ for atoms were no greater than 2.0×10^{-4} a.u.][1] and integrated $\rho(r)$ over Ω. The charges obtained according to this procedure lead to +1.36 for Cl(1) atom, –0.76 for oxygens and +0.91e in the case of Na(1) cation. The value of charge transfer accompanying the formation of the interionic contacts is equal to 0.09e that is apparently the consequence of the relative weakness of electrostatic Na–O interactions. In addition to the atomic charges in **1**, we also estimated atomic volumes according to an analogous procedure.[1] The corresponding values were found to be 11.8, 16.3 and 9.0 Å^3 for chlorine, oxygen and sodium atoms, respectively. Their sum in the crystal (69.61 Å^3) reproduces well the unit cell volume per $NaClO_3$ (69.62 Å^3) with a relative error of 0.01%.

According to the topological parameters in the above CPs (3, –1), both the Na–O and Cl···O interactions correspond to closed-shell type with positive $\nabla^2\rho(r)$ (1.87/2.5 and 1.01 eÅ^{-5}) and electron energy densities [$h_e(r)$ is 0.004264/0.007386 and 0.002146 a.u. for Na–O and Cl···O, respectively]. In contrast, the Cl–O bonds in the ClO_3^- anion are of a shared type [$\rho(r)$ = = 2.401 eÅ^{-3}, $\nabla^2\rho(r)$ = –3.80 eÅ^{-5}]. The values of $\rho(r)$ function in the case of the cation–anion and anion–anion contacts are equal to 0.07/0.09 and 0.07 eÅ^{-3}, respectively. Taking into account the similarity of these characteristics for two types of interactions, one can expect their energies to be roughly comparable.

The energy of the interionic contacts (E_{cont}) in crystalline **1** was estimated by means of the Espinosa correlation between the values of E_{cont} and potential energy density function $v(r)$ in the corresponding CP (3, –1).[2] Thus, the E_{cont} for Na–O interactions is 3.4 or 3.5 kcal mol^{-1} with the smallest one in the case of the longer Na–O(1A) contact as it was expected on the basis of LP directionality and interatomic distance. At the same time, the energy of Cl···O interaction in **1** amounts to 2.0 kcal mol^{-1} that is somewhat smaller than the cation–anion ones, but of the same order of magnitude. For comparison, the value of E_{cont} in the case of interactions between like-charged moieties such as halide–halide[3,5,19] and nitrate–nitrate[6] ones in the corresponding salts is no higher than 1.3 kcal mol^{-1}. The energy of the ClO_3^-···ClO_3^- contacts formed by the chlorate ion in **1** results in the total value of 6.0 kcal mol^{-1}, while the summation of the E_{cont} for six Na–O interactions leads to 20.7 kcal mol^{-1}. Accordingly, the overall energy per formula unit was found to be 26.7 kcal mol^{-1} with the substantial contribution of the cation–anion contacts. However, the total E_{cont} for the anion–anion interactions in **1** averages out 23% of the latter.

Thus, we may conclude that the interionic contacts between species having net charges of the same sign are stabilising ones despite their formally repulsive character. Furthermore, the anion–anion interactions observed in the majority of ClO_3^--containing materials are highly competitive with cation–anion bonds by strength and influence on the crystal structure and, as a result, the physical-chemical properties of inorganic and organic chlorates as well.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2008.01.012.

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