

Comparative charge density determination of potassium perchlorate

Malte Fugel¹, Simon Grabowsky¹¹University Of Bremen, Institute Of Inorganic Chemistry And Crystallography, Bremen, Germany

E-mail: m.fugel@uni-bremen.de

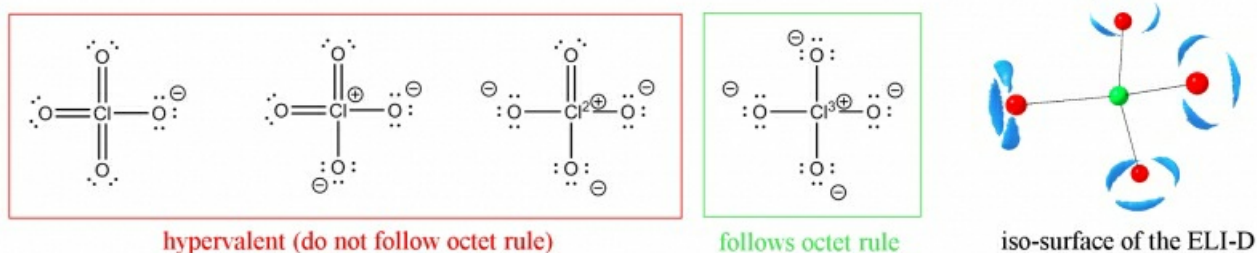
Potassium perchlorate may appear to be a simple salt at first glance, however, the bonding situation in the perchlorate anion is still a question of current research. One can draw a variety of different Lewis formulas, some of which exceed the octet rule at the chlorine center (Figure 1). These hypervalent formulas suggest that d-orbitals of the chlorine atom are involved in the bonding which is, however, energetically unfavorable and has been ruled out in the past. [1] Schmøkel et al. performed an experimental charge density study on the iso-electronic sulfate anion in potassium sulfate and found that hypervalent Lewis formulas are of no significance. [2] Instead they found four S-O single bonds and three lone pairs for each of the oxygen atoms.

In this study, we attempt to perform an experimental charge density study on potassium perchlorate crystals with the intention to analyze the bonding situation in the perchlorate anion. For that purpose, high quality single crystal X-ray diffraction experiments are required. While data sets of good quality were obtained from our home diffractometer (Bruker D8 Venture), synchrotron measurements (SPring8, Japan) failed due to severe radiation damage. However, the high primary intensity from synchrotron radiation is beneficial to properly model the potassium atom at which the highest residual density is located in our home data set. In order to obtain the "perfect" data set, we tested many different diffractometer set ups (both synchrotron radiation and home sources as well as image plate, pixel and CCD detectors) that will be presented. Multipolar and x-ray wavefunction refinements were performed for the data sets which are unaffected by radiation damage. We will present the experimental results from the "best" data set complemented by theoretical calculations on the bonding situation of the perchlorate anion.

It can be concluded that hypervalent Lewis formulas are of no significance for the perchlorate anion. Instead four Cl-O single bonds and three lone pairs for each of the oxygen atoms are implied by both experimental and theoretical studies (Figure 1 shows an iso-surface of the ELI-D). Though, one has to note that Lewis formulas are only a concept which represent a localized picture of the bonding situation. In the perchlorate anion, the oxygen lone pairs are highly delocalized. These delocalizations can be attributed to hyperconjugative interactions of LP(O)→σ*(Cl-O) type which are evident in both experimental and theoretical studies.

[1] Reed, A. E. & Schleyer, P. v. R. (1990). J. Am. Chem. Soc., 112, 1434-1445.

[2] Schmøkel, M. S. et al. (2012). Inorg. Chem., 51, 8607-8616.



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