Determination of bond length and some crystal structures of compounds containing the dioxygenyl cation \([O_2]^+\)

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The dioxygenyl cation, \([O_2]^+\), is a peculiar species, which can be regarded as an oxidized molecule of oxygen. The first dioxygenyl salt, O:PtF\(_6\), was synthesized by Bartlett and coworkers in 1962 [1]. Approximately 30 compounds of dioxygenyl have been reported by the time of writing this abstract [2]. Some examples include O:SbF\(_6\) [3], (O:Ti:F\(_{30}\) [4], O:H:Pt:Fe [5], O:RhF\(_8\) [6], and more.

The experimental oxygen-oxygen bond length in the \([O_2]^+\) cation is an important data value, which provides better understanding of the fundamental chemistry of elements. It may play, for example, an important role in quantum chemistry allowing the quantum chemists to refine computational models so that they correspond better to the experimental data. However, the values of the oxygen-oxygen bond length in the \([O_2]^+\) cation found in different compounds vary considerably from 0.89 to 1.12 with big standard uncertainties [2]. There are two main reasons for that: First, with only a few exceptions all \([O_2]^+\) containing compounds have a disordered dioxygenyl cation, which results in an underestimated interatomic distance. And second, high electron density between the oxygen nuclei (in accord with the bond order of 2.5) may also be responsible for some “shortening” of the atom distance in X-ray diffraction, similar to what is found in the compounds with C–C or C–N triple bonds.

Here we will present our results on the crystal structure determination of some compounds containing the dioxygenyl cation \([O_2]^+\) (O:AsF\(_6\), O:SbF\(_6\) and likely a few more) by means of single crystal and powder X-ray and neutron diffraction using home lab X-ray data as well as data obtained the synchrotron beamline at DESY and neutron beamline at ILL, including some some insights into the \([O_2]^+\) bond length using X-ray and neutron pair distribution functions.


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