

ANALYSIS OF THE CRYSTAL FIELD INFLUENCE ON THE STRUCTURAL PARAMETERS OF THE LINDQVIST-TYPE HEXATUNGSTATE ANION

Popova A. V., Radio S. V.

Vasyľ Stus Donetsk National University, Vinnytsia, Ukraine
al.popova@donnu.edu.ua

The investigation and comparison of the structural parameters of polyoxometalates, specifically the Lindqvist-type hexatungstate anion $[\text{W}_6\text{O}_{19}]^{2-}$, as well as an analysis of the significant factors influencing them, require a multifaceted approach. Therefore, the following methods were applied in the present work:

1. Since X-ray diffraction data are obtained across a wide temperature range, accounting for the libration effect is critically important. It was established that during the transition from 100 K to 295 K, the shortening of W–O bonds can reach 0.01–0.03 Å, which is comparable to the magnitude of real structural changes. To minimize errors, a comparison of structural parameters for different compounds containing the $[\text{W}_6\text{O}_{19}]^{2-}$ anion was performed exclusively within the same temperature group (± 5 K).

2. For the quantitative assessment of anion geometry deviations from O_h symmetry, the Continuous Shape Measures method and the Shape 2.1 software were utilized. The analysis was conducted for three types of polyhedra: the tungsten framework, the overall geometry, and individual WO_6 octahedra within the $[\text{W}_6\text{O}_{19}]^{2-}$ anion. It was found that the tungsten framework and the overall anion shape are characterized by the high stability of their octahedral symmetry. In contrast, individual WO_6 polyhedra proved to be sensitive to the influence of external coordination.

3. The analysis of intermolecular interactions using Hirshfeld surfaces (d_{norm}) and 2D fingerprint plots with CrystalExplorer software allowed for the differentiation between the effects of weak contacts and strong coordination or hydrogen bonds in various compounds containing the $[\text{W}_6\text{O}_{19}]^{2-}$ anion.

4. The positions of maxima in the IR spectra of compounds with the $[\text{W}_6\text{O}_{19}]^{2-}$ anion, which are sensitive to changes in structural parameters, were compared with theoretically determined values obtained using the DFT method, followed by the calculation of corresponding scaling factors.

Thus, the application of the proposed integrated approach allows for the effective separation of the temperature factor influence from factual structural distortions caused by the specifics of the crystal field and the coordination interactions of the anion.

The proposed approach demonstrated that the tungsten framework of the Lindqvist-type hexatungstate anion exhibits high structural stability against external influences. In contrast, structural distortions are primarily observed at the local level of individual WO_6 octahedra under the influence of the crystal field of the cationic lattice or the solvate shell.

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