

Photo-reversibility and wavelength dependence of excited intermediates in nitro-nitrito linkage isomerization of [Co(NH₃)₅NO₂]Cl(NO₃) crystals unveiled by photomechanical response

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The phenomenon of linkage isomerization in [Co(NH₃)₅NO₂]²⁺ complex, allowing two variants of NO₂ coordination to the metal ion, Co-NO₂ (nitro) and Co-ONO (nitrito), has attracted considerable attention for more than a hundred years [1]. The thermally stable nitro isomer can be isomerized to the nitrite by UV and visible light with $\lambda < 530$ nm; the reverse nitrito-nitro transformation proceeds as a monomolecular reaction with an activation energy of ~ 100 kJ/mol. One of the open questions is related to the maximum achievable degree of photoisomerization, i.e., with the possibility of reverse ONO- \rightarrow NO₂ isomerization under the light. Determination of the photostationary state upon irradiation of solutions is impossible due to the parallel photolysis of the complex. It is believed that almost complete transformation is achievable in crystals. However, exact photostationary nitrito/nitro ratio is unknown due to the insufficient accuracy of spectroscopic and X-ray diffraction methods, including due to deformation and cracking of crystals caused by the difference in the crystal parameters.

At the same time, the mechanical effects caused by the transformation in crystals can be used for a highly sensitive method for studying such reactions. A methodology has been developed that makes it possible to measure the kinetics of the transformation by the mechanical response it causes (bending and elongation of acicular crystals) with a sensitivity inaccessible to traditional methods [2]. The kinetics of photoisomerization has been studied in the wavelength range 350 – 523 nm. Evidence of the photoreversibility of photoisomerization was found: the corresponding dependence of the photostationary nitrito/nitro ratio was determined from the dependence of the stationary deformation of crystals on the wavelength; the fraction of the nitrito form reaches a maximum of $>10\%$ near 400 nm. In addition, analysis of the effect of crystal deformation on the transformation rate makes it possible to establish the wave-length dependence of intermediate excited states.

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[1] S. M. Jørgensen, Z. Anorg. Chem., 1894, 5, pp. 147-196.

[2] E. Ahmed, S. Chizhik, A. Sidelnikov, E. Boldyreva and P. Naumov, Inorg. Chem., 2022, 61, pp. 3573-3585.