

STUDY OF STRUCTURE-SOLID STATE PHOTOREACTIVITY CORRELATION IN 4-CYANO BUTYL COBALOXIME COMPLEXES USING X-RAY POWDER DIFFRACTION

K.R. PAHALAGEDARA, D.M.U.K. SOMISARA AND C. VITHANA*

Department of Chemistry, Faculty of Science, University of Peradeniya

The 4-cyanobutyl group (δ -cyanobutyl group) bonded to the Co atom in cobaloxime complex is found to be isomerized to α -cyanobutyl isomer though γ and β cyanobutyl groups upon irradiation with visible light in the solid state. Generally, in solid state reactions, the reactivity depends on microscopic structures present in the solid state in different ways.

Hence, in order to identify the structural factors controlling the photoisomerization taking place in 4-cyanobutyl complexes, a series of closely related compounds with known molecular and crystal structures were used to investigate the solid state reactivity. Single crystal X-ray diffraction studies done previously revealed that among six complexes used here, C-C-N groups of 4-cyanobutyl chains of (4-cyanobutyl)(4-sopropylpyridine)bis(dimethylglyoximate)cobalt(III) (4cb4ippy), (4-cyanobutyl)(3-methylpyridine)bis(dimethylglyoximate)cobalt(III) (4cb3mpy), and (4-cyanobutyl)(3-chloropyridine)bis(dimethylglyoximate)cobalt(III) (4cb3clpy) take parallel conformations with respect to the cobaloxime planes, whereas those of (4-cyanobutyl)(isonicotonic acid)bis(dimethylglyoximate)cobalt(III) (4cbisonic), (4-cyanobutyl)(4-cyanopyridine)bis(dimethylglyoximate)cobalt(III) (4cb4cpy), and (4-cyanobutyl)(aniline)bis(dimethylglyoximate)cobalt(III)(4cbani), have perpendicular conformations to the cobaloxime planes.

The reactivity was estimated quantitatively for each complex as a percent conversion of the reactant to products, taking the change in the intensity of the strongest peak in each X-ray powder diffraction (XRPD) pattern recorded before and after irradiation of samples for 120 hrs, into account.

The percent conversion calculated according to the XRPD data revealed that the photoreactivity of complexes having similar alkyl conformations is governed by the size of the void space around the reactive group (reaction cavity volume). Because when there is more space in the cavity, atomic movements are more feasible in the solid state. However, the comparison of the reactivity of complexes with different conformers indicated that the C-C-N groups of 4-cyanobutyl chains with parallel conformations to the cobaloxime planes are topochemically more favorable here, as they have shown high isomerization activity.