Chirality Inversion Process in Cobaloxime Complex Crystals by Photoirradiation

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It was found that the racemic crystal of (1-cyanoethyl)-(piperidine)cobaloxime complex was transformed to a chiral one on exposure to visible light with retention of the single crystal form [1]. Although the crystal showed the optical rotation after photoirradiation, the molecule in the crystal was racemized. Recently we found that the chirality of the molecule was inverted to the opposite configuration when the crystal was irradiated with visible light.

The first example is the crystal of ((*S*)-1-ethoxycarbonylethyl) ((*S*)-cyclohexylamine)cobaloxime. The (*S*)-1-ethoxycarbonylethyl group of the complex was inverted to the opposite configuration. The R:S ratio of the chiral group was changed from 0:100 to 76:24. The second example is the crystal of ((*S*)-chlorocyanomethyl)(pyridine)-cobaloxime. The R:S ratio was changed from 0:100 to 80:20. The third one, which did not show the chirality inversion, is ((*R*)-*tert*-butoxycarbonylethyl)(phenylethylamine)cobaloxime. The R:S ratio of the chiral group became from 100:0 to 60:40 and was not changed to 50:50.

Such chirality changes were well explained by the cavity shape of the chiral group in the original crystals.

[1] a) Osano Y.T., et al., *Nature*, 1991, **352** 510; b) Nemoto T., et al., *Bull Chem Soc. Jpn*., 1999, **72**, 1971.

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