Spiral Growth on the Metal Complex Crystal

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Synopsis. Spiral growth patterns were found on the crystals of $(+)_D$- and $(-)_D$-$[Co(ox)(en)_2]Cl \cdot 4H_2O$. The handedness of the spirals was statistically counted on each enantiomeric complex crystal. No stereoselectivity of the handedness suggests that the visible spirals do not arise from the molecular or crystal structural origin, but more macroscopic one.

Crystal growth from solutions has been extensively carried out for both inorganic salts[1] and organic compounds.[2] However there are very few studies on crystal growth of metal coordination compounds. In the preceding paper,[3] we reported the spectrophotometric study on crystal growth of some cobalt (III) complexes, where the supersaturated aqueous solutions were seeded with the complex crystals. It was suggested that the crystal growth of a few cobalt(III) complexes proceeds by a spiral growth mechanism.

In the present study we found the spiral growth by in situ observation on the crystal surface, (001) face of the optically-active oxalatobis(ethylenediamine)cobalt(III) chloride tetrahydrate, $[Co(ox)(en)_2]Cl \cdot 4H_2O$, which is spontaneously resolved in aqueous solutions,[4] and statistically counted the frequencies of occurrence of right- or left-handed spiral on each enantiomeric complex crystal in order to search the cause of occurrence of spirals.

Experimental

All the complexes used were prepared following the literature methods. A transmission type differential-interference microscope (Nikon DIAPHOT-TMD) was used for in situ observation of the crystal surfaces. SEM observations were carried out with an Akashi ALPHA-30 scanning electron microscope.

Results and Discussion

Figure 1 shows typical spirals observed on the (001) faces of the crystal of $(+)_D$- or $(-)_D$-$[Co(ox)(en)_2]Cl \cdot 4H_2O$ in supersaturated aqueous solution (about 0.13 mol dm^{-3}; supersaturation ratio, 0.15) at 25 °C. The results for the counted occurrence-frequencies of the handedness of spirals (under the aforementioned condition) are shown in Table 1. There is no correlation between the chirality of complex crystals and the handedness of spirals. It can be considered that the handedness of the large spiral as observed does not reflect the chirality of the molecular and/or crystal structures of the optically-active complexes, but it may be caused by something macroscopic which can be often observed in the center of the spirals (Fig. 1). Possibly, these are foreign crystallites of the same

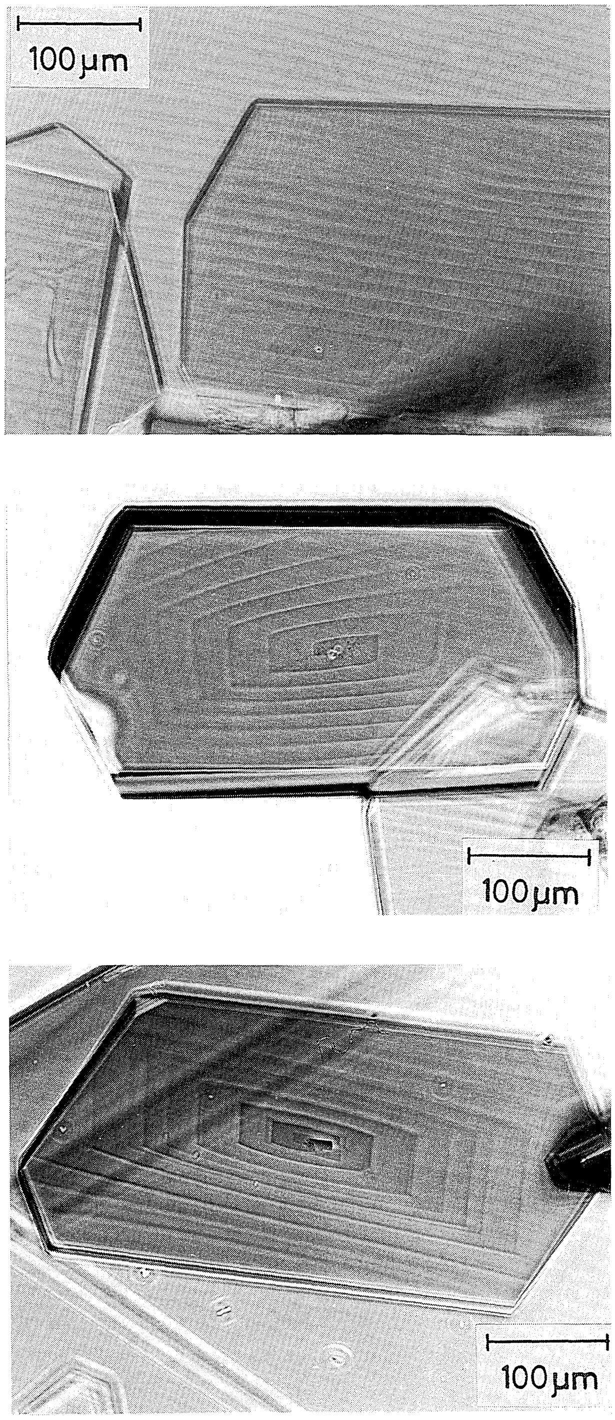

Fig. 1. Typical spirals observed on the (001) faces of $[Co(ox)(en)_2]Cl \cdot 4H_2O$ crystals.

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Table 1. The Counted Occurrence-Frequencies of the Handedness of Spirals on the (001) Faces of the $[Co(ox)(en)_2]Cl\cdot 4H_2O$ Crystal

Handedness	$(-)_D$-Complex	$(+)_D$-Complex
Right	35[a]	34[a]
Left	34[a]	34[a]
Right	72[b]	
Left	69[b]	

a) On the individual complex crystals spontaneously resolved from the racemic aqueous solution. b) On the resolved complex crystals.

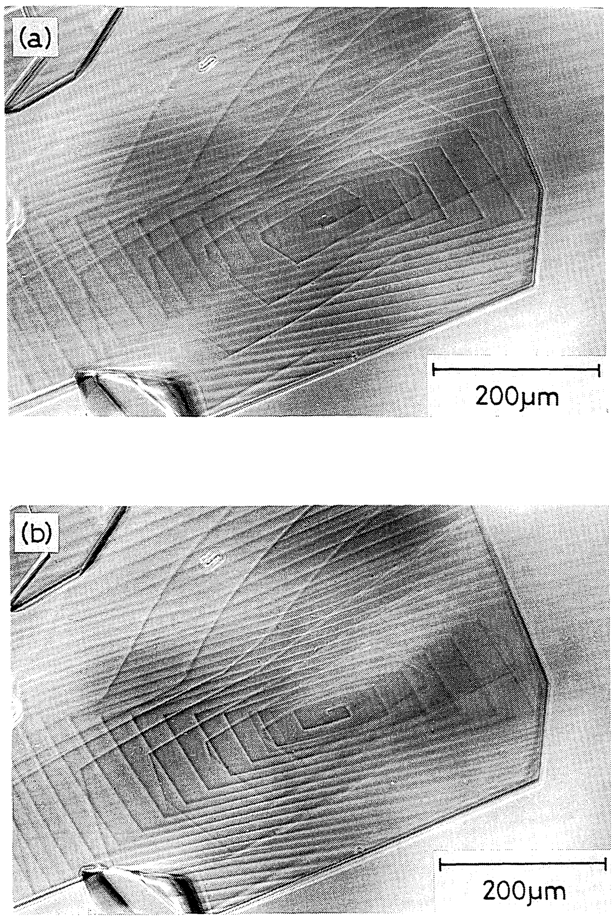

Fig. 2. Double spirals on the (001) faces of $[Co(ox)(en)_2]Cl\cdot 4H_2O$ crystals. (a) Focussed on the top surface and (b) focussed on the bottom surface.

complex compound or insoluble impurities. Furthermore we also found a few double spirals which can be regarded as being simultaneously generated on both the top and bottom surfaces of the thin plate from the same macroscopic origin as shown in Fig. 2.

For the same complex bromide, the crossed ridgeline was found (Fig. 3), but the spirals could not be observed even with the aid of the scanning electron microscope.

Although we also tried to find spirals for the other cobalt(III) complexes, i.e., *trans*-$[Co(NO_2)_2(en)_2]NO_3$, *cis*-$[Co(NO_2)_2(en)_2]X$ (X=Cl, NO_2), $[Co(ox)(en)_2]I$, $[Co(en)_3]X_3$ (X=Cl, I), $[Co(NH_3)_6]X_3$ (X=Cl, I), *trans*-$[Co(NCS)_2(en)_2]SCN$, *cis*-$[Co(NCS)_2(en)_2]Cl$, $[Co(CO_3)(en)_2]X$ (X=Cl, NO_3), *cis*-$[Co(N_3)_2(en)_2]X$ (X=Br, I, NO_3), *cis*-$Na[Co(SO_3)_2(en)_2]$, K[Co(edta)], *trans*-$NH_4[Co(NO_2)_4(NH_3)_2]$, no spirals were found on the crystals of all the used complexes.

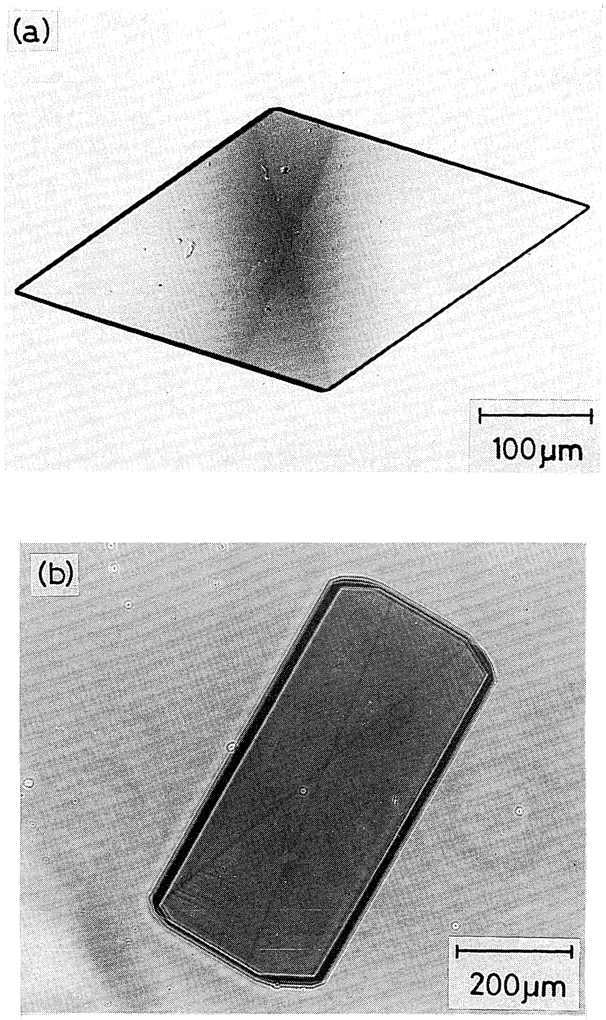

Fig. 3. The examples of the crossed ridgelines on (a) $[Co(ox)(en)_2]Br\cdot H_2O$ and (b) $[Co(ox)(en)_2]Cl\cdot 4H_2O$ crystals.

The linear crystal growth rate, R can be expressed by

$$R = k\,\sigma^n,$$

where k is the rate constant for crystal growth, σ the superaturation ratio, and n the effective order of reaction which can be empirically determined. In the present in situ observation, the crystal growth rate of the (1 1 1) face was measured at 25 °C, which gave about 1.6 for the effective order, n. In can be considered that the crystal growth on the (1 1 1) face also proceeds by a spiral growth.

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