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KINETIC-MORPHOLOGICAL PECULIARITIES OF SOLID-STATE ISOMERIZATION OF COMPLEXES

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The thermal solid-state isomerizations of $Copy_2Cl_2$ (py = pyridine), $Nien_2(NO_2)_2$ and $Nien_2(NCS)_2$ (en = ethylenediamine) were studied by thermal analysis, thermomicroscopy, X-ray diffraction and IR-spectroscopy. It was shown that the reactions proceed by nuclear formation and growth. The kinetic-morphological peculiarities of the processes suggest that the process-determining stage is a phase stage, i. e. structural transformation. The topography and kinetics of processes are therefore determined by the crystal structures of the initial material and the reaction product, and by the contact conditions at the interface. The stress relaxation processes affect the morphology of the products and the kinetics of the transformation.

In recent years an increasingly large number of investigations involving solid-state isomerizations of coordination compounds have been reported. On the basis of kinetic and structural studies, the mechanisms of these processes have been proposed in some cases. However, little has been accomplished as regards the topochemistry of these reactions.

This report presents a brief summary of research on the topochemical peculiarities (topography, kinetics and product morphology) of the thermal solid-state isomerizations of certain Co(II) and Ni(II) complexes: $Copy_2Cl_2$ (py = pyridine), $Nien_2(NO_2)_2$ (en = ethylenediamine).

Configurational isomerization of $Copy_2Cl_2$

Upon heating to 373 K, $Copy_2Cl_2$ single-crystals undergo a sharp, reversible change from the polymeric octahedrally coordinated α-form to the monomeric tetrahedrally coordinated β-form [1]. Microscopic observations have shown [2] that the reaction starts from the edges or surface imperfections and can be observed moving through the entire crystal (Fig. 1a). The front motion is highly anisotropic and is accompanied by cracking of the initial crystal in the [001] and [010]

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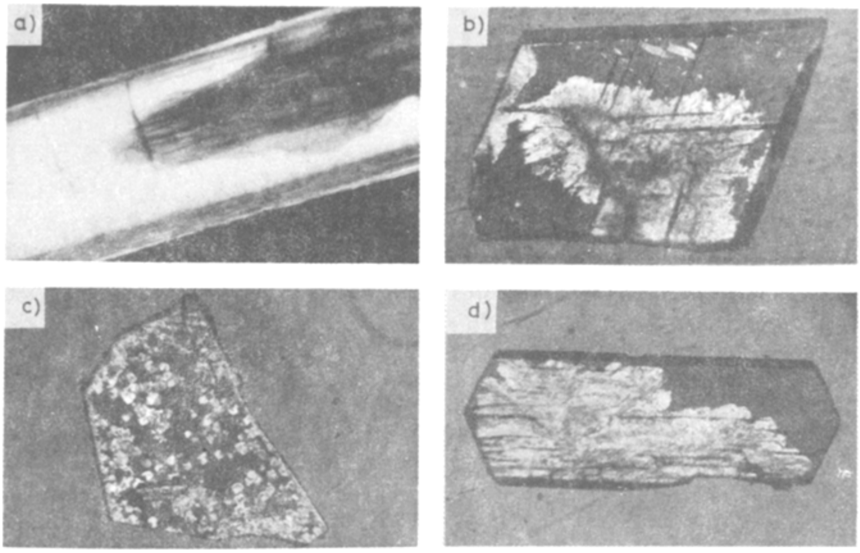

Fig. 1 Micrographs of isomerization processes in single crystals of $Copy_2Cl_2$ (a), $Nien_2(NO_2)_2$ (b), $Nien_2(NCS)_2$ (c, d). Polarized light, ×40

directions. A detailed analysis of the kinetics of the interface advance by filming proved its irregular character.

The reaction is topotactic: [001]||[001]. The pseudomorphous product is polycrystalline and has a texture, as determined by diffraction techniques.

When previously deformed crystals of α-$Copy_2Cl_2$ were used, the number of nucleation centers increased, whereas for deformed crystals the interface advance rate was lower than for undeformed ones.

Linkage isomerization in $Nien_2(NO_2)_2$

The reversible change from the low-temperature red form to the high-temperature blue form of $Nien_2(NO_2)_2$ occurs at 383–423 K. According to Hitchman [3], the blue isomer contains one chelating and one ionic nitrite per metal. Microscopic observations showed that a very distinct reaction front moves across the crystal, parallel to the crystal edges [4] (Fig. 1b). The advance of the interface is accompanied by cracking of the initial crystal in these directions. In thin (30–50 μm) plates of crystals, cracking was not observed. These crystals reacted more slowly than those with a thickness of 100–200 μm.

It has been found that the reaction is localized at distinct sites not only in a single-crystals but in powder-pressed pellets too. Deformation of crystals adjacent to transformed ones is possibly the reason why the localization is observed for polycrystalline samples.

Conformational isomerization of $Nien_2(NCS)_2$

It appears that the phase transition in $Nien_2(NCS)_2$ at 403–453 K [4] is associated with a conformational change in this complex from the KK′ to the KK conformation [5]. Depending on the reaction conditions, the process may occur in two ways [4]: through the slow growth of monocrystalline nuclei on thin crystals (30–50 μm) (Fig. 1c), and through the rapid advance of an interface in thicker crystals (100–300 μm) (Fig. 1d). In the latter case, the orientation relation between the structures of the initial material and the reaction product has been established: $[010)_i \| [010]_p$. In this case too anisotropic front motion is observed, which is accompanied by cracking, except in thin crystals. The process rate for thin crystals is lower than that for thick ones.

It seems that the two kinetic-morphological types observed are due to two transformation mechanisms, well-known for phase transitions [6], per-atomic and cooperative.

Discussion

The obtained results indicate that the solid-state isomerizations investigated are in many cases characterized by: a) nucleus formation and growth, b) anisotropic interface advance, c) crystal cracking, d) irregular advance of an interface, and e) dependence of the process rate on the crystal thickness.

The isomerization processes investigated are accompanied by changes in crystal structure, as evidenced by the X-ray diffraction data (Fig. 2). The changes in molecular volume $\Delta V/V$ are equal to ~14, 8, and 2% for the $Copy_2Cl_2$, $Nien_2(NO_2)_2$ and $Nien_2(NCS)_2$ transformations, respectively. Thus the formation of nuclei produces stresses at the interface. It seems that this is a reason why nucleus formation proceeds at the edges and surface defects of crystals and not in their volumes.

The observed effects, including anisotropic front motion, crystal cracking, and the dependence of the rate of motion on the crystal thickness, are associated with stress relaxation processes, as discussed in [4].

The irregular character of the interface advance was observed earlier in phase transitions [7–9]. Interface propagation is assumed to be accompained by the

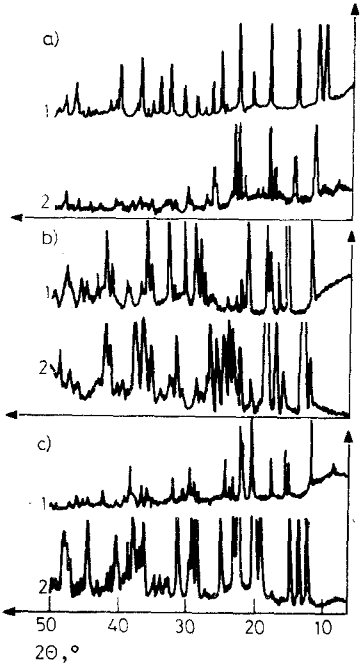

Fig. 2 X-ray diffraction patterns of the initial materials (1) and reaction products (2) in $Copy_2Cl_2$ (a), $Nien_2(NO_2)_2$ (b), $Nien_2(NCS)_2$ (c) transformations

motion of interphase dislocations. As a consequence, the interface advance can be modulated by imperfections in the initial crystal. For this reason, there was probably a slower rate of reaction front motion in deformed $Copy_2Cl_2$ crystals. An investigation of the defect structure of $Nien_2(NCS)_2$ crystals by synchrotron radiation topography [10] showed that there are many imperfections, such as bundles of dislocations and inclusions in the crystals. This is likely to effect the kinetics of interface advance.

The analysis of the kinetic-morphological peculiarities of the investigated isomerizations shows that they proceed a large extent in a similar way as polymorphic transformations. Indeed, since isomerizations of complex molecules are accompanied by changes in the crystal structures of the compounds, it seems possible (similarly as in many other solid-state reactions [11]) to detect two stages in these processes: chemical and phase. Due to the available phase stages, the topography and kinetics of the processes studied are determined by the crystal structures of the initial material and the reaction product, and mainly by the contact conditions at the interface.

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Zusammenfassung — Thermische Isomerisierungsreaktionen in fester Phase wurden durch thermische Analyse, Thermomikroskopie, Röntgenbeugung und IR-Spektroskopie an $CoPy_2Cl_2$ (Py = Pyridin), $Nien_2(NO_2)_2$ und $Nien_2(NCS)_2$ (en = Ethylendiamin) untersucht. Es wird gezeigt, dass die Reaktionen durch Keimbildung und Wachstum ablaufen. Die kinetischen und morphologischen Charakteristika der Prozesse weisen darauf hin, dass der geschwindigkeitsbestimmende Schritt ein Phasenschritt, d. h. eine Strukturumwandlung ist. Deshalb sind Topographie und Kinetik der Vorgänge durch die Kristallstrukturen des Ausgangsstoffe und des Reaktionsprodukts und durch die Kontaktbedingungen an der Grenfläche bestimmt. Die Spannungsrelaxationsprozesse beeinflussen die Morphologie der Produkte und die Umwandlungskinetik.

Резюме — Методом термического анализа, термомикроскопии, рентгенофазового анализа и ИК спектроскопии изучены термические реакции твердотельной изомеризации комплексов $CoPy_2Cl_2$, $Nien_2(NO_2)_2$ и $Nien_2(NCS)_2$, где en = этилендиамин, а Py = пиридин. Показано, что эти реакции протекают по механизму образования и роста центров кристаллизации. Кинетически-морфологические особенности процессов предполагают, что определяющим процессом явпяется образование фазы и ее структурно превращение. В связи с этим, топография и кинетика процесса определяется кристаллическими структурами исходного вещества и продукта реакции и условиями соприкосновения на границе раздела поверхности. Релаксационные процессы напряжения затрагивают морфологию соединений и кинетику их превращений.