The kinetics of the solid state bond isomerization in \([\text{Co(NH}_3\text{)}_5\text{ONO}]\text{Br}_2\) is studied by quantitative IR spectroscopy in diamond anvils at pressures of 1.0, 2.0, 3.0, and 4.0 GPa and atmospheric pressure and at temperatures of 7, 16, 25, and 34°C. The pressure dependence of the reaction rate constant is adequately described by the equation \(\ln K = a + bP + cP^2\). Although solid state isomerization is accompanied by an increase in molar volume, the hydrostatic pressure accelerates the reaction. The reason for this unusual effect must be sought in the anisotropy of structure deformation in the course of bond isomerization; the total increment in volume is comparatively small (0.84%), but the structure is drastically compressed (by 3.4%) in a number of crystallographic directions, and the crystal structure is compressed under pressure in the same directions.

INTRODUCTION

Cobalt(III) nitritopentammoniates \([\text{Co(NH}_3\text{)}_5\text{ONO}]\text{X}_2\), in which the NO\(_2\) ligand is coordinated to cobalt via oxygen, are thermodynamically less stable than the corresponding nitro isomers, where the NO\(_2\) ligand is coordinated via nitrogen [1, 2]. As a result, nitrito-nitro bond isomerization takes place in solution and in the solid state [1-16]. Bond isomerization is intramolecular in solution [2, 4-6] and crystals [7], but the rate of this process is considerably affected by the environment of the complex cation: solvent, anions, protons, hydroxyl ions, acid and Lewis base microimpurities in solutions [8] and the crystalline surroundings in the solid state [3, 9-13]. The crystalline environment may be altered 1) by varying the outer-spheric anion, 2) by a transition to another polymorphic modification of the same compound, 3) by applying the hydrostatic pressure [3]. The third method is of special interest; the crystalline environment of the complex cation may be distorted continuously, whereas the chemical composition of the compound and the polymorphic modification remain constant as long as the pressure stays within the range of existence of the initial phase [3]. This method is especially prospective for studies of homogeneous reactions in crystals [14] among which is bond isomerization in cobalt(III) nitritopentammoniates [3, 7, 14-16].

As shown earlier, hydrostatic compression causes great shifts of absorption bands in the vibrational IR spectra of cobalt(III) nitritoammoniates [17]. Anisotropic compression of the crystal structures of these compounds under hydrostatic pressure was investigated [18]. It was shown that the quantum yield of nitro-nitrito bond isomerization decreases in the compressed regions of the nitro isomer crystals [19]. The effect of the hydrostatic pressure on the nitrito-nitro bond thermoisomerization was investigated in solution [6]. The aim of the present work is to study the effect of hydrostatic pressure on the nitrito-nitro bond thermoisomerization of solid \([\text{Co(NH}_3\text{)}_5\text{ONO}]\text{Br}_2\).
EXPERIMENTAL PROCEDURE

The kinetics of high-pressure isomerization was studied by quantitative IR spectroscopy [20] from variations of the integrated intensity of the band $\nu_2$(ONO), as done previously at normal pressures [10-13, 21, 22]. The measurements were performed on a Perkin-Elmer 180 spectrometer equipped with a focusing device for analyzing microsamples.

Quasihydrostatic pressure was exerted in diamond anvils of design described in [23]. CsBr was used as a pressure-transmitting medium and simultaneously as a diluent. The kinetics of isomerization was studied at pressures of 1.0, 2.0, 3.0, and 4.0 GPa. A shift of the fluorescence band of ruby was used for pressure monitoring [24]. Three ruby spheres were placed into different parts of the sample to monitor the nonhomogeneity of pressure distribution in the sample. The accuracy of pressure measurements was ±0.05 GPa; the maximal difference in pressure between the central and peripheral parts of the sample was 0.1 GPa at 1.0 GPa; 0.05 GPa at 2.0 GPa; 0.15 GPa at 3.0 GPa; 0.2 GPa at 4.0 GPa.

For each pressure, a series of experiments were accomplished at several temperatures. The diamond anvils were thermostatted using a HAAKE thermostat with an external contour. The temperature was monitored in the thermostat and on the anvil diamonds. The thermostat temperatures 5, 15, 25, and 35°C corresponded to the temperatures on the anvil diamonds 7, 16, 25, and 34°C. All temperatures used in this work correspond to the temperature on the anvil diamonds.

All experiments were run while constantly blowing a drying inert gas through the space of the IR spectrometer. To reduce the effect of sample layer thickness on the spectra, the experiments were performed "from high to low pressures;" a sample layer was initially formed at the maximal pressure (4.0 GPa), and the kinetics was studied at this pressure and four temperatures, then the pressure was reduced by partially discharging the anvils without changing the previously formed sample layer. Reproducibility of kinetic measurements was controlled at selected pressures and at the same temperature achieved after cooling and then after heating the sample. An analogous reproducibility control at the same pressure was difficult to perform because it was impossible to reach the same pressures twice without changing the state of the sample layer. The series of experiments ended with control measurements of the spectra and isomerization kinetics at atmospheric pressure. Good agreement was achieved with the data obtained previously at normal pressure for samples prepared as KBr macropellets or in oil [10-13]. Thus it was confirmed that sample preparation (thin layer squeezed between the anvil diamonds, dilution with CsBr) has little or no effect on the obtained kinetic parameters.

[Co(NH$_3$)$_5$ONO]Br$_2$ was synthesized photochemically in the solid state from the corresponding nitro isomer, by irradiating the sample with UV light directly in diamond anvils in the IR spectrometer. [Co(NH$_3$)$_5$NO$_2$]Br$_2$ was synthesized by the standard procedure [25].

The spectra were digitized manually. Subsequent quantitative treatment included determination of the integrated intensity of the band under analysis, analysis of its shape, and finding its maximum using the specially designed program SPECTRUM [26].

EXPERIMENTAL RESULTS

The IR spectra of the photochemically synthesized [Co(NH$_3$)$_5$ONO]Br$_2$ obtained in diamond anvils were in good agreement with the IR spectra measured previously for KBr pellets and oil preparations [10-13, 21, 22]. When hydrostatic pressure was increased, the pressure-induced bond isomerization did not occur, contrary to the case of Ni(II) complex compounds with the nitrito ligand [27, 28], but the maximum of $\nu_2$(ONO) was shifted to the blue region (Fig. 1). In the range of pressures up to 2.0 GPa, the dependence of $\nu_2$(ONO) on $P$ was qualitatively similar but differed quantitatively from the data obtained previously for the same pressure range [17]. The reason for these slight discrepancies may lie in the different methods of sample preparation and especially in using different methods of pressure measurement. In [17] a thin layer of undiluted [Co(NH$_3$)$_5$ONO]Br$_2$ was investigated and KBr was employed as a pressure-transmitting medium. The pressure was estimated according to the "polyethylene" rather than "ruby" scale, i.e., by the shift of the absorption band in the IR spectrum of polyethylene [23]. In this work, we observed pronounced deviations of the $P$ dependence of $\nu_2$(ONO) from linearity at pressures higher than those used in [17]. Variations of $\nu_2$(ONO) as a function of pressure were almost independent of temperature. The shift of $\nu_2$(ONO) with growth of $P$ may be explained by the