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Pressure-Induced Reversible Conversion of $Ni(CN)_5{}^{3-}$ from Trigonal-Bipyramidal to Square-Pyramidal Geometry[1]

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In an X-ray diffraction study of $[Cr(en)_3][Ni(CN)_5]\cdot1.5H_2O$,[3] it was found that the unit cell contained both trigonal-bipyramidal (TBP) and square-pyramidal (SQP) $[Ni(CN)_5]^{3-}$ ions. The water of crystallization participates in hydrogen bonding with these $[Ni(CN)_5]^{3-}$ ions, and dehydration of crystal water converts the TBP to SQP ions.[4] Vibrational spectroscopy has played an important role in characterizing the hydrated and anhydrous solids. The infrared and Raman spectra of these solids in the cyanide stretching region have been used to distinguish these two $[Ni(CN)_5]^{3-}$ ions.[4]

The energy difference between the TBP and SQP ions is known to be small.[3] This suggests a possibility that the TBP ion may be converted into the SQP ion under high pressure. Previous studies with five-coordinate complexes have demonstrated some changes in configuration with pressure.[5,6] It is, therefore, of particular interest to study the effect of pressure on $[Cr(en)_3][Ni(CN)_5]\cdot1.5H_2O$. This note reports the spectral change observed in the cyanide stretching region as a function of external pressure, which indicates the reversible pressure-induced conversion of the TBP to SQP $[Ni(CN)_5]^{3-}$ ion.

Experimental Section

Preparation of $[Cr(en)_3][Ni(CN)_5]\cdot1.5H_2O$. This compound was prepared using the method of Raymond and Basolo.[7] *Anal.* Calcd for $NiCrN_{11}C_{11}H_{24}\cdot1.5H_2O$: C, 29.45; H, 6.02; N, 34.40. Found: C, 29.26; H, 5.96; N, 34.44.

Spectroscopic Studies. The infrared spectra under pressure were obtained using sapphire windows on an opposed anvil cell (normally used with diamond windows) in a Beckman IR-12 interfaced with a 6X beam condenser. It was necessary to use sapphire windows because of the diamond absorption in the cyanide stretching region. The details of the technique and method of calibration of pressure have been previously reported.[8-10] Low-temperature studies were made using a cell with an inlet and outlet for circulating cold helium or liquid nitrogen.

Results and Discussion

It has been established[4] that for the $Ni(CN)_5{}^{3-}$ ion, in C_{4v} symmetry, four cyanide stretching vibrations are to be expected

$$\Gamma_{CN_{SQP}} = 2A_1(R, ir) + B_2(R) + E(R, ir)$$

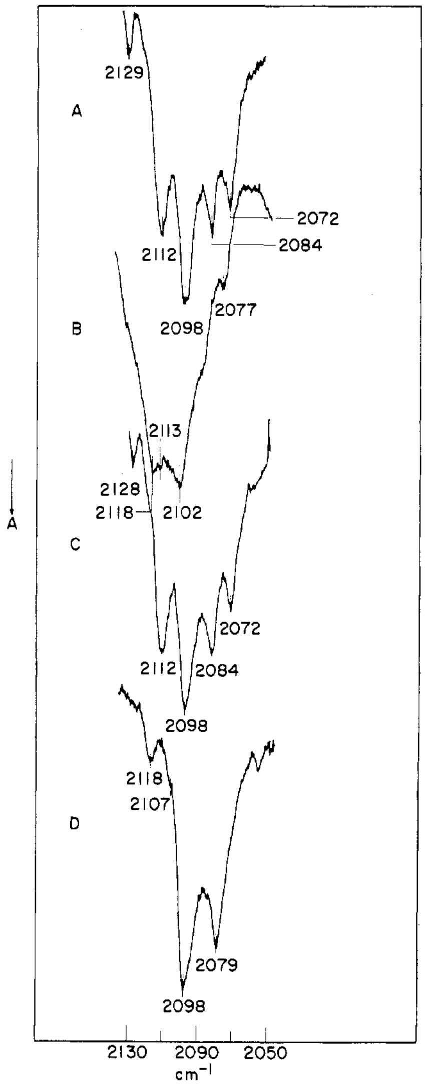

Figure 1. (A) Spectrum of $[Cr(en)_3][Ni(CN)_5]\cdot1.5H_2O$ at liquid nitrogen temperature and ambient pressure. (B) Spectrum of $[Cr(en)_3][Ni(CN)_5]\cdot1.5H_2O$ at liquid nitrogen temperature and ∿7 kbars pressure. (C) Spectrum of $[Cr(en)_3][Ni(CN)_5]\cdot1.5H_2O$ at liquid nitrogen temperature and ambient pressure, after release of pressure. (D) Spectrum of anhydrous $[Cr(en)_3][Ni(CN)_5]$ at ambient pressure and temperature.

In a distorted trigonal-bipyramidal (C_{2v}) environment, five cyanide stretching vibrations are expected

$$\Gamma_{CN_{TBP}} = 3A_1(R, ir) + B_1(R, ir) + B_2(R, ir)$$

The infrared spectrum of $[Cr(en)_3][Ni(CN)_5]\cdot1.5H_2O$ in the cyanide stretching region exhibits bands from both the TBP and SQP structures. Upon dehydration to $[Cr(en)_3][Ni(CN)_5]$, only those bands attributed to the SQP structure are apparent at 2116, 2105, 2096, and 2078 cm^{-1}.[4]

Figure 1 illustrates the ambient and nonambient temperature and pressure infrared spectra for $[Cr(en)_3][Ni(CN)_5]\cdot1.5H_2O$. It was found that dehydration of the compound resulted during the recording of spectra if some precautions were not taken. This, presumably, was a result of localized heating of the sample by the 6X beam condenser. This dehydration was prevented by cooling the sample prior to and during pressure application to nearly liquid nitrogen temperatures. No appreciable change occurred in the OH stretching region during our pressure experiments. The 3-μm region was recorded at ambient and nonambient pressures. It can be concluded from these results that the waters of crystalliza-

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tion remain in the molecule while the material is under pressure.

It may be observed that application of pressures up to a maximum of ~7 kbars causes a dramatic change in the cyanide stretching region (Figure 1). The spectrum is simplified from the spectrum occurring at ambient pressure, as only four absorptions remain at 2118, 2113, 2102, and 2077 cm^{-1}. The spectrum obtained at ambient pressure and at liquid nitrogen temperatures is identical with the room-temperature spectrum obtained in previous studies.[4] The spectrum measured at ~7 kbars is similar to the spectrum of the anhydrous material of $[Cr(en)_3][Ni(CN)_5]$, except that differences in frequency position and intensity are noted. These differences are to be expected, since the complex is under pressure and furthermore contains 1.5 mol of water.

The effect of pressure is reversible and upon release of pressure the spectrum in the cyanide region reverts to that of the starting material. The reversibility of the pressure effect is evidence that the waters of crystallization remain in the crystal during the pressure application, for if the material had become anhydrous the process would have been irreversible.

The results are interpreted in terms of a pressure conversion of the $Ni(CN)_5{}^{3-}$ ion from a mixture of SQP and TBP environments to one involving only SQP. The environment of the waters of crystallization during the pressure cycle is unknown. However, it is apparent that the hydrogen bonds must weaken to allow the conversion to the SQP structure. The conversion to the SQP structure is rather surprising, since previous studies on anhydrous five-coordinate complexes involving a structure or structures between a SQP and TBP symmetry indicated a tendency to shift the structure toward the TBP symmetry.[5] However, for the compound studied in this work, the water of crystallization plays an important role and may be the cause for the observed phenomenon. Additional factors may be the smaller molecular volume and better packing resulting for the SQP structure.

It should be noted that our starting material was a mixture of TBP and SQP structures and pressure has converted the TBP to SQP structure. One other example of this kind has recently been reported.[11] Four-coordinate nickel in the complex $Ni(BzP(C_6H_5)_2)_2Br_2$ exists at ambient temperature and pressure in a distorted symmetry (two tetrahedral and one square-planar molecules per unit cell). Pressure application converted the material to a square-planar symmetry. The latter conversion was also reversible.

Registry No. $[Cr(en)_3][Ni(CN)_5]$, 30207-43-3.

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