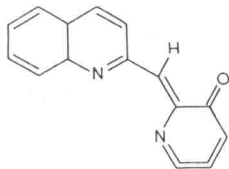


In another high-pressure study [227], it was possible to irreversibly convert the paramagnetic violet pseudotetrahedral nickel complex, $\text{Ni}(\text{Qnqn})\text{Cl}_2$, into its yellow paramagnetic binuclear $[\text{Ni}(\text{Qnqn})\text{Cl}_2]_2$ isomer. In these complexes, the Qnqn ligand is *trans*-2-(2'-quinoly)methylene-3-quinuclidinone.



Qnqn

Both the yellow and violet isomers have been prepared directly [227], and the X-ray structure [239] of the yellow binuclear isomer has revealed two bridging and two terminal chlorine ligands and bidentate coordination for Qnqn. The application of pressure to the violet monomeric complex causes the two nickel-chloride nonbonded distances to decrease to a point where the two additional bridging chlorine bonds are formed, and the yellow binuclear complex results. The spectrum of the complex clearly reveals the irreversible changes in both the $\nu_{\text{Ni}-\text{Cl}}$ and $\nu_{\text{Ni}-\text{N}}$ vibrational bands as a function of pressure. The electronic absorption spectrum of the violet isomer also reveals the expected changes in the *d-d* bands at high pressure.

This is the first example of such an irreversible pressure-induced structural transformation known to us. The irreversibility of this transformation may result from the bond energy of the two additional chlorine bridging bonds, which would make the reverse transformation thermodynamically unfavorable. This transformation involves both a change in coordination number and a change in coordination geometry and represents class 2B behavior. The yellow dimeric $[\text{Ni}(\text{Qnqn})\text{Cl}_2]_2$ exhibits only minor changes at high pressure and is in class 1 [226,227].

The room-temperature preparation of $[(\text{CH}_3)_2\text{CHNH}_3]_2\text{CuCl}_4$ has been found [240] from X-ray studies to contain one copper ion in a square-planar configuration and two copper ions arranged in tetrahedrally distorted configurations. The crystal is held together by hydrogen bonding from the isopropylammonium ions. At high pressures the coordination geometry of the two tetrahedrally distorted copper ions is reversibly converted to a square-planar geometry [229]. The conversion is observed as a change in the $\nu_{\text{Cu}-\text{Cl}}$ and δ_{ClCuCl} vibrational bands. Confirmation for the conversion was also found in the change occurring in the electronic region [229,230]. A similar structural conversion is also found [230] in Cs_2CuCl_4 and Cs_2CuBr_4 . These compounds exhibit a geometric structural change with no change in coordination number or spin-state and belong to class 2A.

(2) Five-coordinate complexes

An X-ray diffraction study [241] of the $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 1.5 \text{H}_2\text{O}$ com-

plex has shown that its unit cell contains two crystallographically independent $[\text{Ni}(\text{CN})_5]^{3-}$ ions, one with a regular square-pyramidal geometry, and one with a distorted trigonal-bipyramidal geometry. Dehydration of the complex converts all of the $[\text{Ni}(\text{CN})_5]^{3-}$ ions to the square-pyramidal geometry [241]. When this compound was subjected to pressures of ca. 7 kbar at 78 K, the coordination geometry of the trigonal-bipyramidal $[\text{Ni}(\text{CN})_5]^{3-}$ ion was converted reversibly to the square-pyramidal geometry [231]. The IR spectrum of this compound at ambient and high pressure is presented in Fig. 17. In order to prevent the dehydration of the complex at high pressure (presumably a result of localized heating produced by the 6X beam condenser used with the pressure cell) these studies were made at 78 K. In this complex, the reversible transformation represents behavior class 2A in a five-coordinate complex.

An extensive high-pressure study of many five-coordinate nickel(II) complexes with ligands ranging from monodentate to tetradentate has revealed several nonrigid structures in the solid state [223]. The results for several metal ions are presented in Table 25 and reveal that "tripod-like" tetradentate ligands prefer the trigonal-bipyramidal structure. The importance of the larger number of chelate rings, and the increased entropy and free energy of formation for tetradentate ligand complexes of the type $[\text{NiLX}] \text{Y}$, are indicated by the more numerous trigonal-bipyramidal structures. As the number of chelate rings is reduced, stability decreases, and the tendency to form intermediate five-coordinate complexes results [242]. NiL_3X_2 complexes with no chelate rings are unstable and dissociate in solution, whereas the application of high pressures tends to distort these solids toward the distorted intermediate five-coordinate geometry. In these five-coordinate complexes, a gradual change from class 1 behavior (with small values of $d\nu/dp$) to class 2A behavior is observed.

The five-coordinate square-pyramidal complex $\text{Fe}(\text{NO})(\text{salen})$ ($\text{salen} = \text{N},\text{N}'$ -ethylenebis(salicylideneimine)) has been shown to contain iron in an intermediate spin state ($S = \frac{3}{2}$) and to exhibit spin equilibrium at low temperature [243]. Mössbauer spectral results indicate that the complex most likely contains $\text{Fe}(\text{III})$ and NO^- , although this formulation is still open to question. A recent study of the NO vibrational absorption band as a function of pressure has revealed a shift to lower frequency at high pressure [244]. These results appear to be consistent with a change in spin state for the iron ion. This compound would appear to fit into class 3, but additional studies will be required to confirm and refine this classification because structural changes may also be significant.

Two isomers of $\text{Co}(\text{NO})(\text{Ph}_2\text{CH}_2\text{P})_2\text{Cl}_2$ are known [245]. One of these isomers is trigonal bipyramidal and contains $\text{Co}(\text{I})$ and NO^+ ions, most probably with a linear $\text{Co}-\text{N}-\text{O}$ bond. The second isomer is square pyramidal and contains $\text{Co}(\text{III})$ and NO^- with a bent $\text{Co}-\text{N}-\text{O}$ bond. The NO vibrational absorption band occurs at ca. 1750 cm^{-1} in the first isomer and at ca. 1650 cm^{-1} in the second. A preliminary study indicates the structural conversion of the trigonal-bipyramidal isomer to the square-pyramidal isomer at high pressure