

(3) Ligand isomerism

Ligand isomerism is well characterized. Most of the studies have involved equilibria between the two forms in solution. Little is known of these equilibria in the solid state. In solid $\text{Ni(en)}_2(\text{NO}_2)_2$ at a pressure of 30 kbar, the violet form (obtained at ca. 120°C) was transformed to the red form [219]. The red isomer is the dinitro form, while the violet isomer is the dinitrito form. The 560 nm band was used to monitor the transformation.

(4) Pressure reduction

In a study at high pressure of $[(\text{CH}_3)_4\text{N}]_3[\text{Fe}(\text{NCS})_6]$ (ref. 220) it was observed that a pressure-dependent reduction of Fe(III) to Fe(II) occurred, confirming the Mössbauer studies of Fung and Drickamer [221]. The reduction was characterized by the appearance of a new band at 238 cm^{-1} at lower frequency than the 295, 270 cm^{-1} vibrations attributed to the $\nu_{\text{Fe}} + 3_{-\text{N}}$ mode. A similar reduction [222] was found with pressure for $[\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}$ and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ from a study of the ν_{CN} vibration in the $[\text{M}^{\text{III}}(\text{CN})_6]^{3-}$ species. No evidence was obtained, which could be attributed to any ligand isomerization occurring.

Other oxidation—reduction effects of pressure using Mössbauer techniques have been noted by Drickamer and Frank [27].

(5) Structural conversions with pressure

Most structural interconversions have been studied in solution. NMR spectroscopy has been an ideal tool for such studies because often the equilibrium established between labile structures can be shifted in favor of one structure by a change in temperature. Until recently, few high-pressure studies of solid-state structural interconversions of complexes have used vibrational and electronic spectroscopy. The Mössbauer effect has, however, been used extensively by Drickamer and Frank [27].

It is reasonable to assume that solid-state interconversions involve considerably larger energy effects than those observed in solution. For solid complexes, in addition to the symmetry effects discussed above, molecular packing, lattice forces, ligand flexibilities, metal—ligand bond distances, $d-d$ electronic transition energies, orbital overlap and orientation effects, and hydrogen bonding among other factors must also be considered. High pressure is known to affect many of these factors [27,223,224] and will favor the structure with a smaller packing volume. High-pressure effects are observed to shorten the metal—ligand bond distance and to increase the average ligand field strength [223–225]. In the cases involving high-spin complexes, this increase in ligand field energy may be sufficient to overcome the electron spin pairing energy and produce a low-spin complex.

Of particular interest is the effect of high pressure on the IR absorption bands of a solid complex. A reduction in the metal—ligand bond distance shifts the vibrational bands to higher energy. For bending modes, which might possibly transform one structure into another, the effects of pressure

may be smaller and conceivably the associated band may shift to a lower energy. It is also possible that, at high pressure, normally forbidden modes may become allowed (in a lower site symmetry), and if this mode yields a structural interconversion, the vibration may then become allowed. Thus, it is of interest to examine the solid-state rigidity of various molecules with differing stereochemical configurations at high pressure.

(iv) High-pressure studies of several solids in different symmetries

Solid-state structural transformations obtained for several representative solids at high pressure are presented in Table 23. From these results, it may be concluded that structural interconversions are possible for transition-metal complexes in the solid state. The interconversions are all reversible, with the exception of that for the $\text{Ni}(\text{Qnqn})\text{Cl}_2$ complex.

We have proposed a new scheme for the classification of the types of behavior observed in transition-metal compounds at high pressure (see Table 24) [226]. The four behavior classes are based primarily upon the presence or absence of a structural and/or electronic change in the complex between ambient and high pressure. Class 1 compounds exhibit neither large structural nor electronic changes, but they would include compounds which show small effects, such as slight unit cell contractions, minor crystallographic changes in space group, small changes in crystal-field parameters, and small shifts in charge-transfer bands. Class 2 compounds exhibit significant structural changes with, at most, minor electronic changes, whereas the reverse situation holds for class 3 compounds. Classes 2 and 3 may be further subdivided as shown in Table 24 depending upon the absence or presence of a coordination number change, etc. Class 4 includes compounds with both electronic structural changes at high pressure and, of course, could have many subdivisions if necessary based upon the presence or absence of each electronic and structural factor.

The behavior of various selected transition-metal complexes at high pressure will now be discussed in terms of their coordination number and behavior type.

(1) Four-coordinate complexes

The two complexes, dichloro- and dibromobis(benzylidiphenylphosphine)-nickel(II), $\text{Ni}(\text{BzPh}_2\text{P})_2\text{X}_2$, may each be prepared as both red and green isomers [237]. Both of the red complexes are the diamagnetic square-planar forms of the complex. However, there are substantial differences between the two green isomers. The green bromide isomer (with a reduced magnetic moment of $2.70 \mu\text{B}$ at room temperature) has been shown by single-crystal X-ray analysis [238] to contain one square planar and two tetrahedral nickel atoms per unit cell. The magnetic moment of the green chloride isomer ($3.23 \mu\text{B}$ at room temperature) and its spectroscopic properties reveal that it is fully tetrahedral in coordination geometry.