

of the theoretical considerations discussed [197,198], to be small. For undistorted tetrahedral complexes, this prediction is borne out by experiment. Attempts [248] to convert complexes of nearly tetrahedral symmetry have been unsuccessful. The results of our work, however, indicate that the pressure-induced conversions of tetragonally distorted tetrahedral complexes are possible, in particular where an asymmetric ligand field is observed by the central atom (e.g., a complex involving several types of ligands). The importance of a distorted structure appears to be a necessity in a solid-state pressure conversion [249].

It is possible that distorted six-coordinate complexes may also behave similarly [250–252]. The results observed to date for four- and six-coordinate complexes are not surprising because the energy barrier to rearrangement for true tetrahedral and octahedral structures is certainly high. For the $\text{Ni}(\text{BzPh}_2\text{P})_2\text{Br}_2$ complex, the unpaired electrons may contribute to the lowering of the energy difference between the distorted tetrahedral and the square-planar configurations. This effect would be superimposed upon the beneficial effect of a starting structure which is distorted toward the square-planar geometry.

For five-coordinate complexes the energy barrier for structural interconversion is small, and many examples have been reported in which the trigonal-bipyramidal and square-pyramidal isomers both exist [246,253–257]. This is apparently also true in the solid state, because our high-pressure studies indicate that interconversion is readily obtained. In systems containing a tripod-like tetradentate ligand, the ligand flexibility favors the trigonal-bipyramidal structure. For the $\text{Ni}(\text{CN})_5^{3-}$ ion, a structure which is distorted in the direction of the pressure-stable square-pyramidal phase, the monodentate cyanide ion permits the rearrangement to occur.

Nonrigid configurations for seven- and eight-coordinate complexes have been demonstrated in solution studies [258–269]. However, no solid-state high-pressure studies have been reported to date.

Recent studies have disclosed pressure effects on solids which are interesting and surprising [270,271]. Copper(II) and nickel(II) complexes of *N,N*-diethylethylenediamine, *N,N*-dimethylethylenediamine and *C,C*-dimethylethylenediamine of the type $\text{M}(\text{L})_2\text{X}_2$ where X = anion, have been found to be reversibly thermochromic [271a]. The Lever effect has been advocated as the mechanism for the thermochromism, axial interactions between the anions and the $\text{M}-\text{N}_4$ plane increase with temperature and metal–nitrogen distances are expanded. Axial interaction causes an increase in coordination number from 4 to 6, accompanied by a color change. The reverse occurs with an increase in pressure, and axial interactions are at a minimum, maintaining the four-coordinate state.

A pressure study involving MCl_4^{2-} ions was made using counter ions which were capable of hydrogen bonding and those which were incapable [272]. It was found that hydrogen bonding stabilizes an octahedral geometry for Mn^{2+} and Fe^{2+} . With Ni^{2+} , preparations in solution gave RNiCl_3 complexes which

TABLE 26

Summary of pressure effects on R_2MCl_4 complexes [272]

Counterion ^b	Mn(II) d^5	Fe(II) d^6	Co(II) d^7	Ni(II) d^8	Cu(II) d^9
R_4N^+	T_d	T_d	T_d	T_d	D_{2d}
R_3NH^+	Increasing internal pressure				
$R_2NH_2^+$					
RNH_3^+	O_h	O_h	D_{2d}	O_h^a	D_2 and D_{2h}
R_3NH^+	Increasing internal pressure				
$R_2NH_2^+$					
RNH_3^+			D_{2d}		D_{2h}

^a Stoichiometry involves $NiCl_3^-$ from solution; from melt [272] polymeric octahedral structures are obtained with a stoichiometry of $[R_2NiCl_4]_x$. ^b R = alkyl group.

contain $NiCl_6$ octahedra, and polymeric octahedral complexes with the stoichiometry $(R_2NiCl_4)_x$ from melts. Table 26 summarizes the results of pressure effects on R_2MCl_4 complexes.

F. GEOLOGICAL APPLICATIONS

The interior of the earth is at high temperature and under megabar pressures. In our discussions heretofore we have stressed changes in molecules created at kbar pressures. It is of the utmost importance to be able to know what major physical and chemical changes occur to matter at megabar pressures. Since the composition of the core and the mantle involve, besides silicates, transition metal minerals, mostly iron and nickel, effects of Mbar pressures and high temperatures on these substances is of obvious interest. It would be expected that transition chemistry under these conditions would be different than under ambient conditions. Changes in oxidation state, spin state, coordination numbers, and absorption properties with pressure and temperatures affect the density, magnetic, electrical and thermal properties of the earth's interior. It is of interest to geochemists and to geophysicists to simulate conditions in the laboratory to make *p* and *t* studies on minerals. New concepts of the earth's constitution, evolution and properties depend on these studies, and the interpretation of the results. This research would serve to answer many questions which still remain unanswered concerning our own planet, and could serve as an aid in explaining the behavior of other planets. Studies at high temperature and Mbar pressures are now possible, and have commenced. The necessary experimental tools to accomplish this are now available (see Section B). X-ray, Mössbauer and visible measurements have been made with the Mbar cell of Mao and Bell [289,297,303]. Vibrational spectroscopy may play a role in these applications in the future. However, the present construction of the cell may restrict its use in the IR region, because