

Solid-State Pressure Effects on Stereochemically Nonrigid Structures

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The geometric structure of a molecule depends upon the magnitude of the energy barrier which prevents conversion into any of its geometric isomers.

In an extensive and impressive group of papers,^{1,2} Pearson has presented a series of symmetry rules which may be used to predict the most stable structure of a molecule,¹ its structural rigidity, and its mode of reaction.² The rules, which are an extension of the work of Bader,³ are based upon the use of perturbation theory and group theory to evaluate the effect of a vibrational distortion on the ground-state geometric configuration of a molecule. The theory supporting these symmetry rules has been extensively developed during the past few years.¹⁻⁴

However, in general, experimental verification of the rules has been based upon molecular interconversions or reactions which occur either in solution or in the isolated gaseous state. The reliability of these orbital symmetry rules in predicting a stereochemically rigid or flexible geometric structure in the solid state has not as yet been experimentally confirmed.

This Account presents evidence which indicates that these symmetry rules are useful for predicting

solid-state structural interconversions between geometric isomers at high pressure. Due to space limitation, an extension of the ideas on this topic will be presented elsewhere.⁵ Furthermore, this Account provides a new approach to the classification of the various effects which are observed in coordination compounds under high pressure.

In the approach developed by Pearson,¹ it is first assumed that all first-order structural distortions of the molecular geometry have occurred. These distortions include any first-order Jahn-Teller distortions required to produce a nondegenerate electronic ground state, and any vibrational distortions which can occur along the totally symmetric normal vibrational modes. On the basis of this assumption, the energy of an initial molecular configuration in the presence of a distortion may be expressed as

$$E = E_0 + \frac{1}{2} Q^2 \int \psi_0 \left| \frac{\partial^2 v}{\partial Q^2} \right| \psi_0 d\tau + \sum_k \frac{\left[Q \int \psi_0 \left| \frac{\partial v}{\partial Q} \right| \psi_k d\tau \right]^2}{E_0 - E_k} \quad (1)$$

$$E = E_0 + f_{00} Q^2 + f_{0k} Q^2 \quad (2)$$

where Q is a measure of the magnitude of the displacement of the initial molecular configuration along a normal coordinate which is then designated

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as the Q coordinate, and V is the nuclear-nuclear and nuclear-electronic potential energy. The remaining symbols have their usual meanings and are discussed below. The reader should consult ref 1 and 2 for further details on the derivation and use of this expression.

In eq 1 and 2, the first term, E_0 , is the minimized energy of the initial undistorted molecular configuration. The term $f_{00}Q^2$ represents the distortion-induced change in the energy of the initial electronic configuration and is always positive because the initial energy is minimized for the undistorted initial molecular configuration. This term provides a restoring force which would tend to remove the distortion and return the molecule to its initial configuration. The term $f_{0k}Q^2$ is always negative because it in effect changes the initial wave function, ψ_0 , to fit the nuclear coordinates of the distorted molecular configuration. The sum of the second and third terms is the experimental force constant for the normal coordinate Q .

Three cases are possible, depending upon the relative magnitudes of the values of f_{00} and f_{0k} . If $f_{00} \gg f_{0k}$, the initially chosen molecular configuration is stable and no distortion is expected. If $f_{00} \cong f_{0k}$, the initial molecular configuration is potentially unstable and may spontaneously distort along the normal coordinate Q to a new molecular configuration. Finally, if $f_{00} \ll f_{0k}$, the initial molecular configuration is unstable and will spontaneously change *via* normal coordinate Q to a relatively more stable configuration. From these results, we can see that a knowledge of the magnitude of f_{0k} can provide us with some information about the relative stability of the initial molecular configuration.

At this point, as discussed in detail by Pearson,² some rather extensive approximations must be made in order to evaluate the probable magnitude of f_{0k} . The first of these approximations involves limiting the summation in the f_{0k} term to only the one or two lowest excited electronic states (represented by ψ_k) available to the molecular configuration. This approximation will only be good if the energy of the remaining terms is much greater than E_0 . The second approximation involves replacing the total ground-state electronic wave function, ψ_0 , with the highest occupied molecular orbital, ψ_{HOMO} , for the configuration. Similarly, the total first excited state wave function, ψ_k , is replaced by the lowest unoccupied molecular orbital, ψ_{LUMO} , for the configuration, etc.

We may now determine whether the integrals in the f_{0k} terms are zero or nonzero by making use of the symmetry of the wave functions and the symmetry of the operator, $\partial v / \partial Q$, which will be the same as that of the normal coordinate, Q .¹ The integral will be nonzero only if the direct symmetry product

$$\Gamma_{\psi_{\text{HOMO}}} \times \Gamma_Q \times \Gamma_{\psi_{\text{LUMO}}}$$

contains the totally symmetric irreducible representation. In Pearson's papers, this requirement is stated in terms of the transition density, ρ_{0k} , which is the product, $\psi_0\psi_k$, of the two wave functions and represents the amount of electronic charge transferred within the molecule as a result of nuclear motion. In terms of the transition density the integral will be nonzero only if the symmetry of the transition

density is the same as that of Q , i.e.,

$$\Gamma_{\rho_{0k}} = \Gamma_{\psi_0} \times \Gamma_{\psi_k} = \Gamma_{\psi_{\text{HOMO}}} \times \Gamma_{\psi_{\text{LUMO}}} = \Gamma_Q$$

Apart from the symmetry requirement, the value of f_{0k} will depend upon the energy difference, $E_0 - E_k$. Pearson¹ has suggested that an energy gap of the order of 4 eV between the HOMO and the LUMO is sufficiently small enough to indicate the possibility of a structural instability. Hence, with the proper symmetry, and with a small enough energy gap, a change in molecular configuration may occur. However, there is an additional requirement for the occurrence of a molecular interconversion, namely, that distortion along the normal coordinate, Q , must, if continued, lead to an alternative structure.

In summary, there are three basic requirements which, if satisfied, would lead to a possible structural interconversion. First, the symmetry product must be correct, i.e., the symmetry of the transition density, ρ_{0k} , must be the same as that of a normal coordinate, Q . Second, the energy gap between the HOMO and one or more of the excited-state molecular orbitals must be of the order of 4 eV or less. Finally, the normal coordinate, Q , must lead to a viable alternative structure.

We believe that these ideas, as developed by Pearson, may be useful in predicting whether or not a structural interconversion will occur in a solid which is subjected to high pressures.⁵ It should be noted that, in general, bending force constants are much smaller than stretching force constants, and as a result, for normal modes involving vibrations, f_{0k} is more likely to be larger than f_{00} , which in this case should be small. Thus, molecular rearrangements involving bending modes and hence changes in bond angles are more likely to occur than those involving stretching modes.

On the basis of the above arguments, a solid complex is more likely to show a structural interconversion along a normal coordinate at high pressure if the symmetry of that coordinate is the same as that of the transition density, ρ_{0k} , as determined for the HOMO and LUMO of the complex. The lack of such agreement may not prevent such an interconversion, but it might make an alternative structural change more likely. One must also, at this point, consider the changes in the energy gap between the HOMO and the excited-state molecular orbitals at high pressure. In general, these energies are expected to shift with the application of pressure.

Structural Interconversion in the Solid State

As emphasized above, most structural interconversions have been studied in solution. Nuclear magnetic resonance 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 his coworkers.⁶

(6) H. G. Drickamer and C. W. Frank in "Electronic Transitions and the High Pressure Chemistry and Physics of Solids," Chapman and Hall, London, 1973.

Table I
Solid-State Pressure-Induced Structural Transformations

Compound ^a	Coordination No.	Approximate local symmetry, ambient pressure	Structural transformation	Approximate transformation pressure, kbar	Spectroscopic probe	Remarks
Ni(BzPh ₂ P) ₂ Cl ₂	4	T _d	No change		Electronic Far-ir	
Ni(BzPh ₂ P) ₂ Br ₂	4	1/3 square planar 2/3 T _d	Square planar	20	Electronic Far-ir	Reversible
Ni(Qnqn)Cl ₂	4	T _d	Dimeric	2	Electronic Far-ir	Irreversible Dimerization
CuCl ₄ ²⁻ ^b	4	Flattened T _d	Square planar	20	Far-ir	Reversible
Ni(CN) ₅ ³⁻ ^c	5	SQP + TBP	SQP	7	Ir(2100-cm ⁻¹ region)	Reversible
[NiLX] ⁺ , NiLX ₂ , [NiL ₂ X] ⁺ , NiL ₃ X ₂	5	SQP + TBP	TBP	Onset of P	Electronic	Reversible

^a Abbreviations: Bz, benzyl; Ph, phenyl; Qnqn, *trans*-2-(2'-quinolyl)methylene-3-quinuclidinone; L, organic ligand; X, halide or pseudohalide; SQP, square pyramidal; TBP, trigonal bipyramidal. ^b With Cs⁺ and (CH₃)₂CHNH₃⁺. ^c In [Cr(en)₃][Ni(CN)₅]·1.5H₂O.

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 effect many of these factors⁶⁻⁸ 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, 10Dq.⁷⁻⁹ In the cases involving high-spin complexes, this increase in 10Dq 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 infrared 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 conversion 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.

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 I. 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 Ni(Qnqn)Cl₂ complex.

We now propose a new scheme for the classification of the types of behavior observed in transition-metal compounds at high pressure (see Table II).^{6,9-22} 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 II 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

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Table II
Behavior Classes for Pressure-Induced Solid-State Changes

Behavior class	Structural change		Electronic change		Examples ^a	Ref
	Geometric change	CN change	Spin-state change	Oxidation-state change		
1	No	No	No	No	Green Ni(BzPh ₂ P) ₂ Cl ₂ [Ni(Qnqn)Cl ₂] ₂ Co(Qnqn)Cl ₂ FeS ₂	10 11 9 12
2A	Yes	No	No	No	Red Ni(BzPh ₂ P) ₂ Br ₂ Several CuCl ₄ ²⁻ Ni(CN) ₅ ³⁻	10 13-14 15
2B	Yes	Yes	No	No	Ni(Qnqn)Cl ₂	11
3A	No	No	Yes	No	Mn(Fe)S ₂ Fe(phen) ₂ (N ₃) ₂ Fe(phen) ₂ (NCS) ₂	16 17 17-19
3B	No	No	No	Yes	Fe(acac) ₃ Cu(OXin) ₂ Hemin	20 21 6
4	Yes		Yes		Co(NO)(Ph ₂ CH ₃ P) ₂ Cl ₂	22

^a Abbreviations: see Table I; also phen, phenanthroline; acac, acetylacetonate; OXin, 8-hydroxyquinoline.

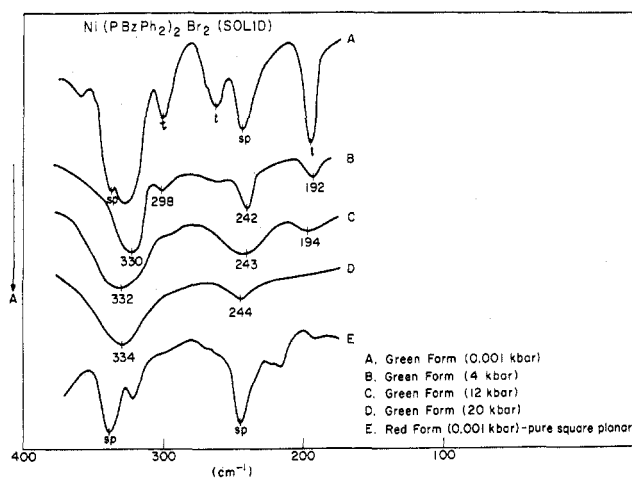


Figure 1. Skeletal vibrations in the green and red isomers of Ni(BzPh₂P)₂Br₂ at ambient and high pressure; t = tetrahedral; sp = square planar. Green isomer: A, ambient pressure; B, 4 kbar; C, 12 kbar; D, 20 kbar. Red isomer: E, ambient pressure (pure sp isomer).

terms of their coordination number and behavior type. Later, we will publish a more extensive evaluation, classification, and review of all such high-pressure studies.

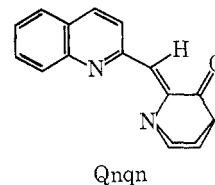
Four-Coordinate Complexes

The two complexes, dichloro- and dibromobis(benzylidiphenylphosphine)nickel(II), Ni(BzPh₂P)₂X₂, may each be prepared as both red and green isomers.²³ 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 μ_B at room temperature) has been shown by single-crystal X-ray analysis²⁴ to contain one square planar and two tetrahedral nickel atoms per unit cell. The magnetic mo-

ment of the green chloride isomer (3.23 μ_B at room temperature) and its spectroscopic properties reveal that it is fully tetrahedral in coordination geometry.²³

Both the electronic and infrared absorption spectra of the two paramagnetic green isomers were studied as a function of pressure.¹⁰ The results for the ν_{Ni-N} and ν_{Ni-X} vibrational bands are presented in Figure 1. The green Ni(BzPh₂P)₂Cl₂ isomer retains its tetrahedral coordination geometry at all pressures and shows no indication of any conversion to a square-planar geometry at high pressure. However, the green Ni(BzPh₂P)₂Br₂ isomer is transformed from the above-mentioned mixture of tetrahedral and square-planar coordination geometries at ambient pressure, to the purely square-planar red isomer at high pressure.¹⁰ This reversible pressure-induced structural transformation is essentially complete at ca. 20 kbar and represents class 2A behavior. In this instance, the change in the spin state of the nickel ion occurs as a result of the geometric structural change and not directly as a consequence of the high pressure.

In another high-pressure study,¹¹ it was possible to irreversibly convert the paramagnetic violet pseudo-tetrahedral nickel complex, Ni(Qnqn)Cl₂, into its yellow paramagnetic binuclear [Ni(Qnqn)Cl₂]₂ isomer. In these complexes, the Qnqn ligand is



trans-2-(2'-quinolyl)methylene-3-quinuclidinone. Both the yellow and violet isomers have been pre-

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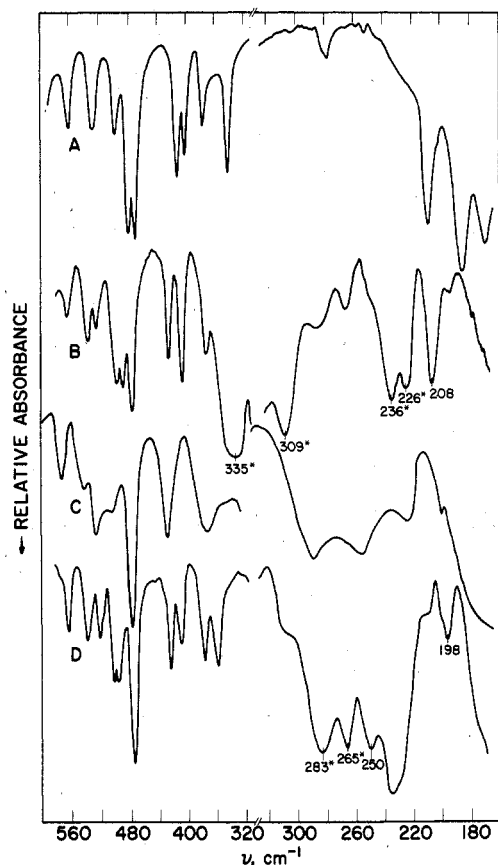


Figure 2. The low-frequency infrared spectrum of the ligand, Qnqn, A; violet $\text{Ni}(\text{Qnqn})\text{Cl}_2$ at ambient pressure, B; at ca. 20 kbar, C; and at ambient pressure after the release of pressure, D. * indicates an isotope-sensitive band.

pared directly,¹¹ and the X-ray structure²⁵ 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 low-frequency infrared spectra of the ligand and the violet complex are presented in Figure 2. The spectrum of the complex clearly reveals the irreversible changes in both the $\nu_{\text{Ni-Cl}}$ and $\nu_{\text{Ni-N}}$ 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 1.¹¹

The room-temperature preparation of $[(\text{CH}_3)_2\text{CHNH}_3]_2\text{CuCl}_4$ has been found²⁶ from X-ray studies to contain one copper ion in a square-planar

Table III
Structural Inferences from Pressure Effects on Several Five-Coordinate Complexes

Complex ^a	Type of ligand	$d\nu/dp$, $\text{cm}^{-1}/\text{kbar}$	Structure
$[\text{NiLX}]Y$ (24) ^b	Tetradentate	33-70	TBP
$[\text{PdLX}]Y$ (2)	Tetradentate	33-81	TBP
$[\text{PtLX}]Y$ (1)	Tetradentate	27	TBP
$[\text{CoLX}]Y$ (1)	Tetradentate	7	SQP
$[\text{NiLX}_2]$ (3)	Tridentate	9-32	Intermediate
$[\text{NiL}_2\text{X}]Y$ (5)	Bidentate	9-32	Intermediate
$[\text{CoL}_2\text{X}]$ (2)	Bidentate	Very slight shift	SQP
$[\text{NiL}_3\text{X}_2]$ (6)	Monodentate	8-29	Intermediate
$[\text{CoL}_3\text{X}_2]$ (2)	Monodentate	8-23	Intermediate

^a Abbreviations: see Table I; also, Y, polyatomic anion. ^b Number of compounds studied.

configuration and two copper ions in tetrahedrally distorted square-planar 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.¹³ The conversion is observed as a change in the $\nu_{\text{Cu-Cl}}$ and δ_{ClCuCl} vibrational bands. Confirmation for the conversion was also found in the change occurring in the electronic region.^{13,14} A similar structural conversion is also found¹⁴ 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.

Five-Coordinate Complexes

An X-ray diffraction study²⁷ of the $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 1.5\text{H}_2\text{O}$ complex 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.²⁷ 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.¹⁵ The infrared spectrum of this compound at ambient and high pressure is presented in Figure 3. 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.⁷ The results for several metal ions are presented in Table III 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

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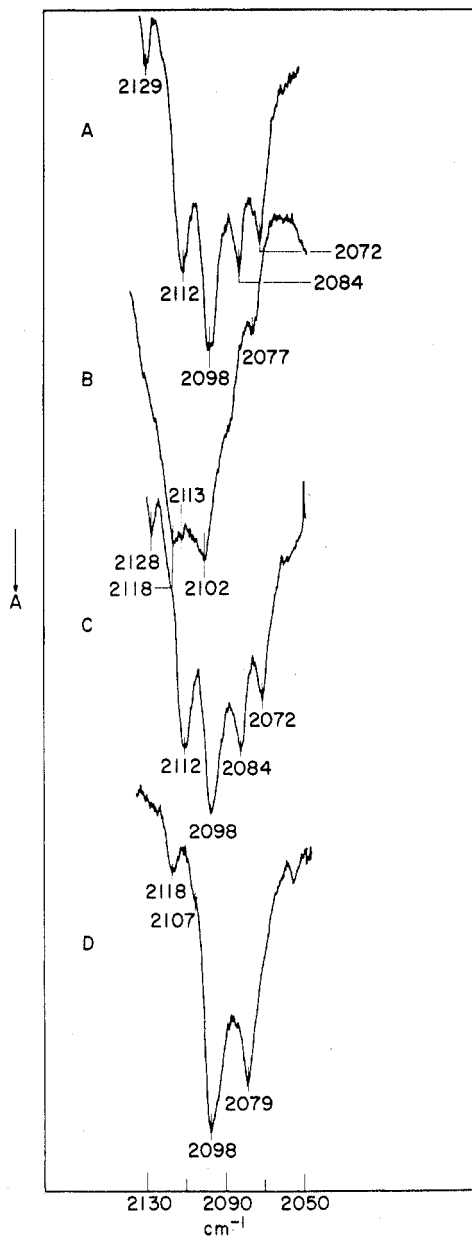


Figure 3. The cyanide stretching vibrational bands in $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 1.5\text{H}_2\text{O}$ at 78 K and ambient pressure, A; at 78 K and ca. 7-kbar, B; and at 78 K and ambient pressure after release of high pressure, C. Spectrum D is that of $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5]$ at ambient temperature and pressure.

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.²⁸ NiL_3X_2 complexes with no chelate rings are unstable and dissociate in solution, whereas, the application of high pressure 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 $\text{Fe}(\text{NO})(\text{salen})$ ($\text{salen} = N,N'$ -ethylenebis(salicylideneimine)) has been shown to contain iron in an intermediate spin state ($S = 3/2$) and to exhibit spin equilibrium at low temperature.²⁹ 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.³⁰ These results appear to be consistent with a change in spin state for the iron ion which may be accompanied by a change in NO oxidation state. 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 $\text{Co}(\text{NO})(\text{Ph}_2\text{CH}_3\text{P})_2\text{Cl}_2$ are known.³¹ One of these isomers is trigonal bipyramidal and contains $\text{Co}(\text{I})$ and NO^+ ions—most likely with a linear Co-N-O bond. The second isomer is square pyramidal and contains $\text{Co}(\text{III})$ and NO^- with a bent Co-N-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.²² This represents class 4 behavior with significant structural and electronic changes.

Six-Coordinate Complexes

To date we have not been successful in changing the coordination number or geometry of an octahedral (or close to octahedral) complex at high pressure. However, several octahedral high-spin complexes have been reversibly converted—at least in part—to the analogous low-spin octahedral complexes at high pressure.^{17,18,32} Table IV summarizes some of these results. The effect of pressure on the skeletal vibrations in $\text{Fe}(\text{phen})_2(\text{NCS})_2$ is shown in Figure 4. The initial conversion from the high-spin to the low-spin state has been explained^{6,17} by the increase in ligand-field potential with pressure until it exceeds the electron pairing energy. This initial effect is accompanied by the back-donation of the metal t_{2g} electrons into the π^* orbitals of the ligand. With a further increase in pressure this back donation is reduced by the accessibility of π electrons from the ligand.⁶

In an extensive series of papers,^{12,16,17,20,33-36} Drickamer and his coworkers have studied the change in spin state with pressure of a wide variety of iron compounds by utilizing Mössbauer effect spectroscopy. In one of these studies,¹² the Mössbauer effect spectrum of FeS_2 as a function of pressure gave changes in the chemical isomer shift and quadrupole splitting which indicated small and continuous changes with increasing pressure. This be-

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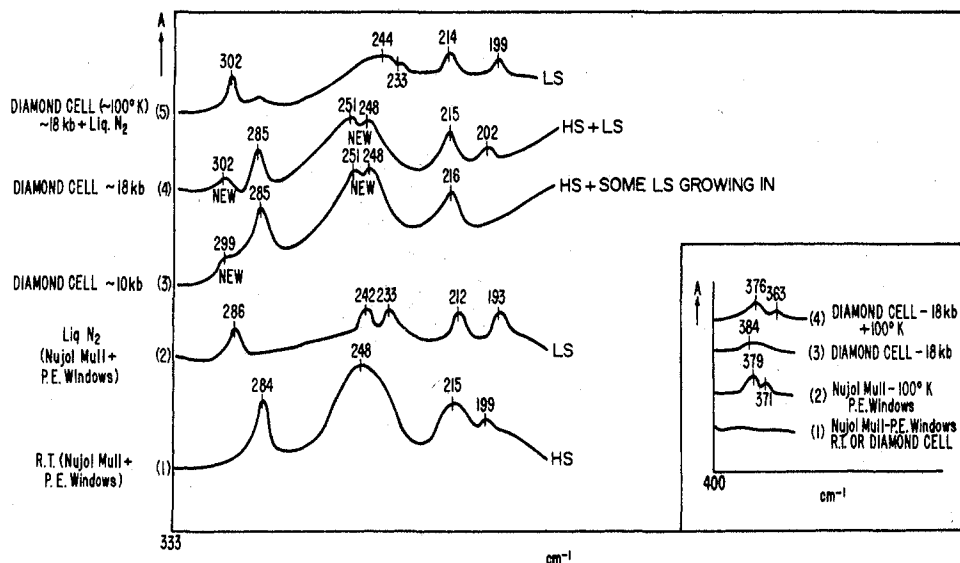


Figure 4. The skeletal vibrations in $\text{Fe}(\text{phen})_2(\text{NCS})_2$ as a function of pressure and temperature.

Table IV
High-Pressure Spin-State Interconversions

Compound ^a	Central atom coordination no.	No. of unpaired electrons	Pressure effect	Conversion pressure, kbar	Experimental probe
$\text{Fe}(\text{NO})(\text{salen})(d^5)$	5	3	High spin \rightarrow low spin	21	NO stretching region
$\text{Fe}(\text{phen})_2(\text{NCS})_2(d^6)$	6	2	High spin \rightarrow low spin	18	Skeletal far-ir and Mössbauer effect.
$\text{Fe}(\text{phen})_2(\text{NCSe})_2(d^6)$	6	2	High spin \rightarrow low spin	8–10	Skeletal far-ir
$\text{Fe}(\text{bipy})_2(\text{NCS})_2(d^6)$	6	2	High spin \rightarrow low spin	15	Skeletal far-ir
$\text{Co}(\text{nnp})(\text{NCS})_2(d^7)^b$	5	3	High spin \rightarrow low spin	4	Skeletal far-ir

^a Abbreviations: see Tables I and II; also bipy, bipyridyl; salen, *N,N'*-ethylenebis(salicylideneimine); nnp is $(\text{C}_2\text{H}_5)_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{P}(\text{Ph})_2$. ^b L. Sacconi and J. R. Ferraro, *Inorg. Chim. Acta*, 9, 49 (1974).

havior would indicate class 1 behavior for FeS_2 . However, a related Mössbauer effect study¹⁶ of ^{57}Fe as a substitutional impurity in MnS_2 , which has the same cubic structure as FeS_2 with a larger lattice parameter, revealed a distinct change in the electronic spin state of the $\text{Fe}(\text{II})$ ion as a function of pressure. The Mössbauer spectrum of this material is shown in Figure 5. The substitutional $\text{Fe}(\text{II})$ ion, which exists predominately in the high-spin state at ambient pressure, is gradually converted to low-spin $\text{Fe}(\text{II})$ as the pressure is increased. The change is rapid from ca. 50 to 120 kbar, and above 120 kbar the iron(II) is essentially all in the low-spin state. The change in spin state at high pressure has been attributed¹⁶ to an increase in the ligand-field strength at high pressure with the resulting spin pairing of the six d electrons in the t_{2g} orbitals of the iron(II) ion. This provides additional evidence for the pressure dependence of the ligand field.⁷⁻⁹ This compound exhibits class 3A behavior with a change in spin state from high spin to low spin with increasing pressure.

In a related study of the high-pressure Mössbauer spectra of a series of metal ferrocyanides, Fung and Drickamer³³ observed evidence for the conversion of low-spin iron(II) to its high-spin state at very high pressure and high temperature. This surprising observation was explained on the basis of a reduced

amount of metal-to-ligand back-bonding at the higher pressures. Associated with this decrease in back-bonding would be a weakening of the π bonding between the filled t_{2g} orbitals of the iron(II) and the orbitals of the cyanide ligands. This would result in an increase in the energy of the low-spin state relative to the high-spin state, and an increased population—especially at high temperature—of the high-spin state.

The preceding argument indicating a decreased amount of back-bonding at high pressure is further supported by the work of Fisher and Drickamer¹⁷ on iron(II)—phenanthroline complexes, and by Barger and Drickamer¹⁹ on similar substituted phenanthroline complexes. For these ligands, all of the tris complexes are low spin at ambient pressure, but a small amount of conversion to the high-spin complex was observed at high pressure. The bis(phenanthroline)iron(II) halide and pseudohalide complexes are high spin at ambient pressure and tend to convert to the low-spin state with increasing pressure. However, at very high pressures, the rate of conversion either slows or reverses with increasing pressure, depending upon the back-bonding ability of the halide or pseudohalide ligand. Specifically, for $\text{Fe}(\text{phenanthroline})_2(\text{N}_3)_2$, the amount of the low-spin complex is at a maximum at ca. 40 kbar¹⁷ and decreases at higher

pressures, presumably because of the decreasing amount of back-bonding. All of these complexes exhibit class 3A behavior.

A study of the high-pressure Mössbauer spectra of several related ferricyanide complexes^{33,36} revealed the reduction of the Fe(III) ion to the expected low-spin iron(II) state at intermediate pressures. This was confirmed in Prussian Blue which had been prepared with selectively labeled ⁵⁷Fe sites. At higher pressures, once again the low-spin iron(II) ion was converted to the high-spin iron(II) ion. These materials exhibit class 3B behavior at lower pressures, and class 3A behavior at higher pressures. In a related study²⁰ of 12 ferric β -diketone complexes, Frank and Drickamer have observed a reversible reduction of iron(III) to iron(II) at high pressure. The degree of reduction is related to the change in the Mössbauer isomer shift with pressure and the nature of the ligands. An additional agreement between the intensity of the charge-transfer absorption band and the extent of reduction was also observed. These compounds exhibit class 3B behavior at all pressures studied.

To date, as would be predicted by the Bader and Pearson model,¹⁻³ no octahedral complexes have been converted at high pressure to complexes with a different coordination number or coordination geometry. However, because such successful structural interconversions have occurred with distorted four-coordinate complexes, it is planned to study a series of highly distorted octahedral complexes at high pressure.

There has been, as of this writing, no detailed study of any seven- or eight-coordinate complexes as a function of pressure.

Discussion of the Nonrigidity of Solids at High Pressure

It may be concluded that solid-state high-pressure structural transformations are possible in transition-metal complexes. All of the transformations examined thus far have been reversible, with the exception of that in Ni(Qnqn)Cl₂, in which a dimer is formed at high pressure. In this complex, two additional bonds are formed on dimerization, and they contribute to the stability of the high-pressure phase.

The probability of producing structural interconversions with pure or nearly pure tetrahedral and octahedral complexes is predicted, on the basis of the theoretical considerations discussed above, to be small. For undistorted tetrahedral complexes, this prediction is borne out by experiment. Attempts³⁷ 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).

It is possible that distorted six-coordinate complexes may also behave similarly.³⁸⁻⁴⁰ The results

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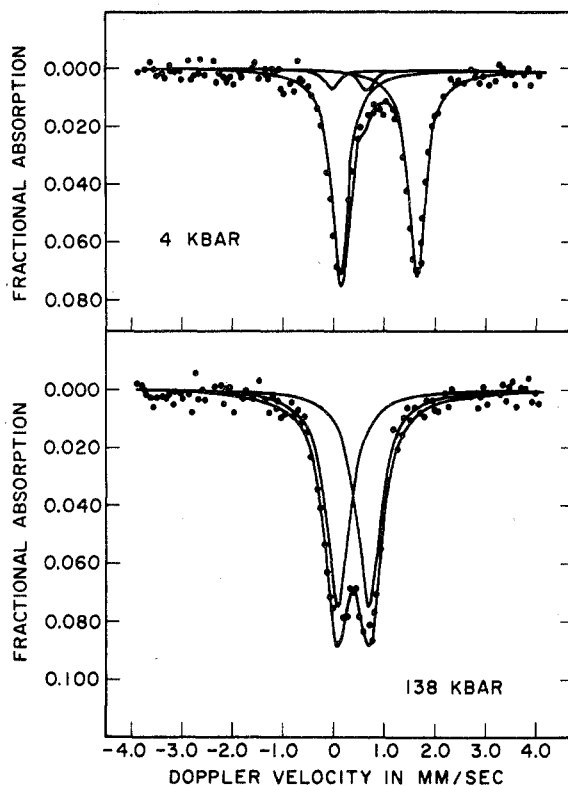


Figure 5. The Mössbauer effect spectrum of Mn(⁵⁷Fe)S₂ at 4 and 138 kbar.

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 Ni(BzPh₂P)₂Br₂ 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.^{32,41-45} 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 Ni(CN)₅³⁻ 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.⁴⁶⁻⁵⁷ However, no solid-state high-pres-

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vestigations are presently under way in our laboratories.

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Mean Square Force in Simple Liquids and Solids from Isotope Effect Studies

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Although a difference in vapor pressures of isotopic substances was predicted and demonstrated about a decade before chemical equilibrium and kinetic isotope effects, vapor pressure isotope effects have not been as significant in the development of chemical and related sciences as either of the latter two.

Like the chemical equilibrium and kinetic isotope effects, the vapor pressure isotope effect has its physical origin in the fact that the zero-point energy of a light molecule is larger than that of a heavy molecule. This leads to a smaller energy of vaporization and a higher vapor pressure for light isotopic species compared with heavy isotopic species of simple molecules (e.g., $P_{\text{H}_2} > P_{\text{D}_2}$). Yet it was demonstrated early in the thirties that deuteriocarbons usually have higher vapor pressures than their related hydrocarbons.

In the case of methane, vapor pressures are in the sequence $P_{^{12}\text{CH}_3\text{D}} > P_{^{12}\text{CH}_4} > P_{^{13}\text{CH}_4}$ at 93 K. At 80 K the sequence is $P_{^{12}\text{CH}_4} > P_{^{13}\text{CH}_4} > P_{^{12}\text{CH}_3\text{D}}$. Clearly there is an interplay of isotope effects on the enthalpy and entropy changes in vaporization as well as on details of molecular structure which play an important role in the vapor pressure isotope effect.

The vapor pressure isotope effect is typically one to two orders of magnitude smaller than chemical equilibrium or kinetic isotope effects. The determination of such a quantity, of order between a few hundredths and a few tenths of a percent, and equally important of its temperature coefficient, clearly requires careful quantitative work. The requisite ex-

perimental techniques were developed during the last 15 years simultaneously with significant advances in the statistical mechanical theory of the phenomenon. The latter took into account the structure of a molecule, which the methane experiments among many others showed to be of major significance in determining even the qualitative aspects of vapor pressure isotope chemistry.

Systematic pursuit of vapor pressure isotope studies on polyatomic molecules has led to important information about translation, hindered rotation, the perturbation of molecular vibrations in solids and liquids, and the coupling of molecular translation, rotation, and internal vibration in the condensed state.¹

In the development of the condensed phase isotope chemistry of polyatomic molecules, it became evident that it would be necessary to understand in as complete detail as possible the differences in vapor pressures of the simple rare gases—neon, argon, and krypton. The statistical mechanical theory of this phenomenon revealed that such measurements could supply complementary and even unique information about anharmonic forces in solids, liquid structure, and their relationship to intermolecular forces.

In the case of a monatomic substance, the vapor pressure ratio or the separation factor, α , is directly related to properties of the intermolecular potential. Other thermodynamic properties which may be used to obtain useful information about the intermolecular potential, $U(r)$, are the internal energy, E

$$\beta E/N = \frac{3}{2} + 2\pi n \int_0^\infty r^2 \beta U(r) g(r) dr \quad (1)$$

and the virial pressure, P .

$$\beta P/n = 1 - \frac{2\pi n}{3} \int_0^\infty r^3 \beta \frac{dU(r)}{dr} g(r) dr \quad (2)$$

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Additions and Corrections

Volume 8, 1975

John R. Ferraro and Gary J. Long: Solid-State Pressure Effects on Stereochemically Nonrigid Structures.

Page 174. In Table II, on line for behavior class 2A, under Examples: Red $\text{Ni}(\text{BzPh}_2\text{P})_2\text{Br}_2$ should read Green $\text{Ni}(\text{BzPh}_2\text{P})_2\text{Br}_2$.