



Fig. 17. The cyanide stretching vibrational bands in $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5] \cdot 1.5 \text{H}_2\text{O}$: A, at 78 K and ambient pressure; B, at 78 K and ca. 7 kbar; C, at 78 K and ambient pressure after release of high pressure. Spectrum D is that of $[\text{Cr}(\text{en})_3][\text{Ni}(\text{CN})_5]$ at ambient temperature and pressure [249]. (Figure reproduced through the courtesy of the authors and the American Chemical Society, Washington, D.C.)

TABLE 25

Structural inferences from pressure effects for several Ni(II), Pd(II), Pt(II) and Co(II) complexes containing ligands varying from tetradentate to monodentate [223]

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

^a Numbers in parentheses indicate number of compounds studied.

Abbreviations: TBP = trigonal bipyramid; X = halide or pseudo-halide ion; SQP = square pyramid; Y = polyatomic anion.

[236]. This represents class 4 behavior with significant structural and electronic changes.

(3) 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 [215,216,246,247]. Table 22 summarizes some of these results. The initial conversion from the high-spin to the low-spin state has been explained [27,216] 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 [27].

(4) 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