

TABLE 23

Solid state structural transformations induced by high pressure [226]

Compound	C.N.	Symmetry ^a ambient pressure	Structural transformation with pressure	Transformation press. (kbar)	Spectroscopic probe	Remarks
Ni(Bzφ ₂ P) ₂ Cl ₂	4	Pure T _d	No change		Electronic FIR	
Ni(Bzφ ₂ P) ₂ Br ₂ ^b	4	1/3 Planar (Square) 2/3 T _d	Planar (square)	20	Electronic FIR	Reversible
Ni(Qnqn)Cl ₂	4	Distorted T _d	Binuclear, SQP [Ni(Qnqn)Cl ₂] ₂	2	Electronic FIR	Irreversible
CuCl ₄ ²⁻ ^c	4	Flattened T _d	Planar (square)	20	FIR	Reversible
Ni(CN) ₅ ³⁻ ^d	5	SQP + TBP	SQP	7	IR in 4 μm	Reversible
[NiLX] ⁺ , NiLX ₂ , [NiL ₂ X] ⁺ NiL ₃ X ₂	5	SQP + TBP	TBP	Onset of press.	Electronic	Reversible

^a Local symmetry around central metal atom considered. ^b Ni(Bzφ₂P)₂I₂ inferred to be similar Ni(Bzφ₂P)₂Br₂ from magnetic moment.

^c Cation is (CH₃)₂CHNH₃⁺ or Cs⁺. ^d Cation is Cr(en)₃³⁺; compound is [Cr(en)₃Ni(CN)₅] 1.5 H₂O.

Abbreviations: Bz = benzyl; φ = phenyl; Qnqn = *trans*-2-(2'-quinoly)methylene-3-quinuclidione; L = organic ligand; X = halogen or pseudo halogen; T_d = tetrahedral; SQP = square pyramidal; TBP = trigonal bipyramid.

TABLE 24

Behavior classes for pressure-induced solid-state changes [226] ^a

Behavior class	Structural change		Electronic change		Examples	Ref.
	Geo-metric change	C.N. 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 Several CuCl ₄ ²⁻	213 227 225 228 229, 230
2A	Yes	No	No	No	Ni(CN) ₅ ³⁻ Ni(Qnqn)Cl ₂ , Co(py) ₂ Cl ₂	231 204, 227
2B	Yes	Yes	No	No	Green Ni(BzPh ₂) ₂ Br ₂	213
2C	Yes	No	Yes	No	Mn(Fe)S ₂ Fe(phen) ₂ (N ₃) ₂ Fe(phen) ₂ (NCS) ₂	232 216 215, 216, 233
3A	No	No	Yes	No	Fe(acac) ₃ Cu(OXin) ₂ Hemin	234 235 27
3B	No	No	No	Yes	Co(NO)(Ph ₂ CH ₃ P) ₂ Cl ₂	236
4	Yes			Yes		

^a A modified version of that in ref. 226 appears above.

Abbreviations: C.N. = coordination number; Bz = benzyl; Qnqn = *trans*-2-(2'-quinolyl)methylene-3-quinuclidione; py = pyridine; ArgH = (H₂N)₂CNH(CH₂)₃CHNH₂COO⁻; aca = acetylacetonate; OXin = 8-hydroxyquinoline.

Both the electronic and IR absorption spectra of the two paramagnetic green isomers were studied as a function of pressure [213]. 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 [213]. This reversible pressure-induced structural transformation is essentially complete at ca. 20 kbar and represents class 2C 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.