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
$Ni(Bz\phi_2P)_2Cl_2$	4	Pure T_d	No change		Electronic FIR	
$Ni(Bz\phi_2P)_2Br_2$ [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
$[NiLX]^+$, $NiLX_2$, $[NiL_2X]^+$ NiL_3X_2	5	SQP + TBP	TBP	Onset of press.	Electronic	Reversible

[a] Local symmetry around central metal atom considered. [b] $Ni(Bz\phi_2P)_2I_2$ inferred to be similar $Ni(Bz\phi_2P)_2Br_2$ from magnetic moment. [c] Cation is $(CH_3)_2CHNH_3^+$ or Cs^+. [d] Cation is $Cr(en)_3^{3+}$; compound is $[Cr(en)_3Ni(CN)_5]$ 1.5 H_2O.
Abbreviations: Bz = benzyl; ϕ = phenyl; Qnqn = *trans*-2-(2′-quinolyl)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.
	Geometric change	C.N. change	Spin-state change	Oxidation state change		
1	No	No	No	No	Green $Ni(BzPh_2P)_2Cl_2$	213
					$[Ni(Qnqn(Cl_2]_2$	227
					$Co(Qnqn)Cl_2$	225
					FeS_2	228
2A	Yes	No	No	No	Several $CuCl_4^{2-}$	229, 230
					$Ni(CN)_5^{3-}$	231
2B	Yes	Yes	No	No	$Ni(Qnqn)Cl_2$, $Co(py)_2Cl_2$	204, 227
2C	Yes	No	Yes	No	Green $Ni(BzPh_2)_2Br_2$	213
3A	No	No	Yes	No	$Mn(Fe)S_2$	232
					$Fe(phen)_2(N_3)_2$	216
					$Fe(phen)_2(NCS)_2$	215, 216, 233
3B	No	No	No	Yes	$Fe(acac)_3$	234
					$Cu(OXin)_2$	235
					Hemin	27
4	Yes		Yes		$Co(NO)(Ph_2CH_3P)_2Cl_2$	236

[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 = $(H_2N)_2CNH(CH_2)_3CHNH_2COO^-$; 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 $Ni(BzPh_2P)_2Cl_2$ 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 $Ni(BzPh_2P)_2Br_2$ 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.