Conversion of Distorted Tetrahedral Bis(benzyldiphenylphosphine)dibromonickel(II) into a Pure Planar Complex by High Pressure[†]

By JOHN R. FERRARO*
(*Argonne National Laboratory, Argonne, Illinois* 60439)

K. NAKAMOTO
(*Marquette University, Milwaukee, Wisconsin* 53233)

and JIN TSAI WANG and LINDA LAUER
(*Duquesne University, Pittsburgh, Pennsylvania* 15219)

Summary Electronic and far-i.r. spectral evidence for a structural change occurring in the solid state between the distorted tetrahedral and planar forms of $Ni(Ph_2PCH_2Ph)_2Br_2$, produced by high external pressure, has been obtained; this is the first reported spin-pairing occurring for solid nickel complexes, and conversion from a distorted tetrahedral into a planar structure with an increase in pressure.

THE green form of bis(benzyldiphenylphosphine)dibromonickel(II) has been reported to consist of a paramagnetic molecular compound of $Ni(Ph_2PCH_2Ph)_2Br_2$ (planar) and $2Ni(Ph_2PCH_2Ph)_2Br_2$ (tetrahedral).[1,2] The diamagnetic, red form is the pure planar compound. However, the pure tetrahedral (paramagnetic) compound has not yet been isolated. The compounds can be prepared by the method of Venanzi *et al.*[1] There is evidence for an equilibrium

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in solution between the paramagnetic and diamagnetic forms.[3] We have now obtained electronic and far-i.r. spectral evidence for a spin-state change occurring in the solid state between the green and red forms, and produced by high external pressures.

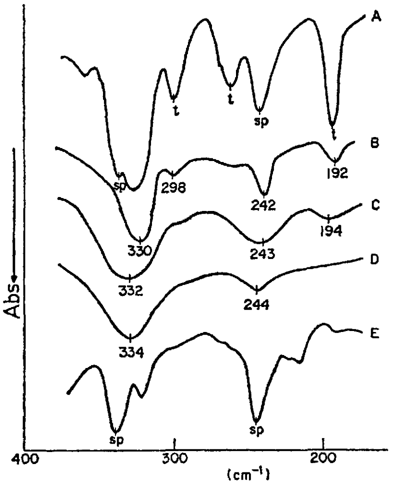

FIGURE. *Skeletal vibrations in the green and red forms of* Ni-$(Ph_2PCH_2Ph)_2Br_2$ *at ambient and high pressure. t = tetrahedral form; sp = square-planar form.*
Green form: A, *ambient pressure;* B, 4 kbar; C, 12 kbar; D, 20 kbar. *Red form:* E, *ambient pressure* (*pure sp form*).

The Figure illustrates the i.r. spectrum of the green form which contains the planar (red) and tetrahedral (green) forms in a 1:2 molar ratio. As discussed previously,[4] the tetrahedral form of the $Ni(PRPh_2)_2Br_2$ type compound exhibits Ni–Br stretching bands in the 270—230 cm^{-1} region and Ni–P stretching bands in the 200—160 cm^{-1} region, whereas the square-planar form exhibits a Ni–Br stretching band near 330 cm^{-1} and a Ni–P stretching band near 260 cm^{-1}. The spectrum of the green form at ambient pressure can therefore be assigned as follows: 335—325 cm^{-1} (Ni–Br str., planar form), 296 and 260 cm^{-1} (Ni–Br str., tetrahedral form), 240 cm^{-1} (Ni–P str., planar form), and 196 cm^{-1} (Ni–P str., tetrahedral form). Three bands at 296, 260, and 196 cm^{-1} which are characteristic of the tetrahedral form disappear with external pressures up to 20 kbar (Figure), and the spectrum becomes almost identical with that of the pure red form, indicating that the green form has been predominantly converted into the pure red form (planar form) under high external pressure, and any possible equilibrium existing in the solid state has been substantially shifted toward the planar form.

Confirmatory evidence comes from the ligand-field spectra of these complexes. Both forms give a red solution in benzene, λ_{max} 4000s, 5250m, and 8800m Å. The green solid has a very intense absorption at $<$ 4500 Å, an intense absorption at 5500 Å, and a shoulder at 8800 Å. With pressure, the intense absorption at 5500 Å shifts toward higher energy and at 25 kbar is at 5200 Å. The shoulder shifts to 8250 Å, weakens considerably in intensity, and is barely visible at 25 kbar. The very intense absorption at $<$ 4500 Å shifts into the extremely intense charge-transfer region at high frequencies. The red solid shows intense bands at $<$ 4200 and 5250 Å (ambient pressure) and with pressure these absorptions are shifted to higher frequencies and lost in the charge-transfer region. The conversion is reversible, and with the removal of pressure, the stable green form is again obtained. Low temperature effects (*ca.* 77 K), although expected to act somewhat in the same direction as pressure, do not cause the conversion. It is therefore assumed that if a critical temperature exists, it is below liquid-nitrogen temperatures.

As far as we know, this is the first reported spin-pairing occurring for solid nickel complexes and conversion of a distorted tetrahedral structure into a planar structure with an increase in external pressures. Our previous attempts at this conversion in the solid state starting with a pure tetrahedral complex have failed. Pearson[5] stated that the pure tetrahedral structure would not be expected to exhibit structural conversion into a planar form for any possible electronic configurations involving orbitally non-degenerate ground states. However, an accessible distorted structure is apparently a requirement for such a conversion, and the green form of $Ni(Ph_2PCH_2Ph)_2Br_2$ fulfills this requirement.

The pressure experiments were conducted with an opposed anvil diamond cell and a 6X beam condenser interfaced with a Beckman IR-11 far-i.r. instrument and a Cary 14 u.v.-visible spectrophotometer.[6]

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