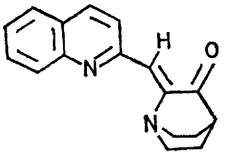
A Study of the Pressure Induced Irreversible Conversion of Distorted Tetrahedral Dichloro-*trans*-2-(2′-quinolyl)methylene-3-quinuclidinonenickel(II), [Ni(qnqn)Cl_2], into Binuclear Square Pyramidal [Ni(qnqn)Cl_2]$_2$

By GARY J. LONG*
(*Department of Chemistry, University of Missouri-Rolla, Rolla, Missouri* 65401)
and JOHN R. FERRARO
(*Argonne National Laboratory, Argonne, Illinois* 60439)

Summary Low-frequency i.r. spectral evidence has been obtained which indicates that the violet distorted tetrahedral complex, Ni(qnqn)Cl_2, is irreversibly converted under pressure into its yellow, binuclear, square pyramidal isomer, [Ni(qnqn)Cl_2]$_2$; we believe this to be the first irreversible pressure induced solid state structural transformation reported for a transition-metal complex.

SEVERAL papers have described co-ordination complexes with reversible pressure induced structural transformations in the solid state [1] and in solution.[2] However, to date, we know of no reported instance of an irreversible pressure induced structural transformation.[3] This communication reports the first such irreversible transformation—a transformation involving both a change in co-ordination number and co-ordination geometry.



qnqn

Coffen and McEntee reported[4] on the preparation of both a yellow and a violet isomer of nickel chloride with *trans*-2-(2′-quinolyl)methylene-3-quinuclidinone, (qnqn). Subsequent spectral and magnetic studies[5] have shown that violet Ni(qnqn)Cl_2 contains nickel in a distorted tetrahedral environment bonded to two nitrogen atoms and two chlorine atoms. A single-crystal *X*-ray study[6] has shown that the yellow [Ni(qnqn)Cl_2]$_2$ isomer is binuclear, containing two nickel(II) ions with square pyramidal co-ordination geometry. The two nickel atoms are linked by two bridging chlorine atoms with slightly asymmetric bridging bond distances.

The Figure presents the low-frequency i.r. spectrum of the ligand, qnqn. It is apparent that the i.r. spectrum of violet Ni(qnqn)Cl_2 undergoes a distinct change with increasing pressure; the major bands at 335 and 309 cm^{-1}, and 208 cm^{-1} either undergo large shifts or large decreases in intensity. After the release of the pressure, a spectrum quite different from that of violet Ni(qnqn)Cl_2, but essentially identical to that of yellow [Ni(qnqn)Cl_2]$_2$ is obtained, and strong bands are found at 283, 265, 250, and 198 cm^{-1}. Visual microscopic examination of the sample indicates that it has changed irreversibly from violet to yellow during the course of the experiment.

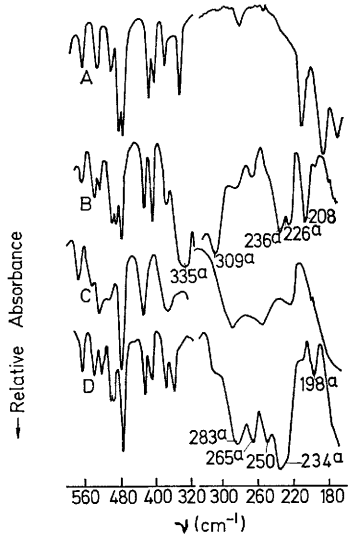


FIGURE. The low-frequency i.r. spectrum of the ligand, qnqn, A; violet Ni(qnqn)Cl_2 at ambient pressure, B; at *ca.* 20 kbar, C; and at ambient pressure after release of the pressure, D; a indicates an isotope-sensitive band. Only *ca.* 2 kbar are required for the structural transformation; but *ca.* 20 kbar are required to overcome the pressure gradients inherent in the diamond anvil cell.

A pure nickel isotope study[7] of both complexes has revealed that the 335, 309, 236, and 226 cm^{-1} bands in violet Ni(qnqn)Cl_2 are isotope sensitive; the first two bands are assigned to the nickel–chlorine stretch and the second two bands to the nickel–nitrogen stretch. The relative pressure dependence[8] of the first two bands indicate that the 309 cm^{-1} band is the symmetric nickel–chlorine stretching vibration. In yellow $[Ni(qnqn)Cl_2]_2$ the bands at 283, 265, 234, and 198 cm^{-1} are isotope sensitive and are assigned[7] to nickel–ligand skeletal vibrations.

The authors believe that this unique irreversible structural change is a direct result of the compression of the unit cell. Under pressure, the two nickel–chlorine non-bonded distances decrease with the eventual formation of the two bridging chlorine atoms found[6] in yellow $[Ni(qnqn)Cl_2]_2$. Simultaneously, the remaining co-ordinated atoms undergo a twist to, in part, relieve the pressure and to produce the square pyramidal geometry about each nickel atom. The thermodynamically unfavourable reverse transformation[5] does not occur on release of the pressure. It is interesting to note that $Co(qnqn)Cl_2$[9] also undergoes a reversible high pressure structural change.[7]

This work was performed under the auspices of the U.S. Atomic Energy Commission. G.J.L. would like to thank Argonne National Laboratory for a Faculty Research Participation Award.

(*Received*, 12*th July* 1973; *Com.* 992.)

---

[1] E. R. Lippincott, C. E. Weir, A. Van Valkenburg, and E. N. Bunting, *Spectrochim. Acta*, 1960, **16**, 58; J. R. Ferraro, *J. Chem. Phys.*, 1970, **53**, 117; K. Nakamoto, C. Udovich, J. R. Ferraro, and A. Quattrochi, *Appl. Spectroscopy*, 1970, **24**, 606; J. R. Ferraro, D. W. Meek, E. C. Siwiec, and A. Quattrochi, *J. Amer. Chem. Soc.*, 1971, **93**, 3862; J. R. Ferraro, and K. Nakamoto, *Inorg. Chem.*, 1972, **11**, 2290; W. T. Carnall, S. Siegel, J. R. Ferraro, B. Tani, and E. Gebert, *Inorg. Chem.*, 1973, **12**, 560; J. R. Ferraro, K. Nakamoto J. T. Wang, and L. Lauer, *J.C.S. Chem. Comm.*, 1973, 266.

[2] H. D. Ludemann and E. U. Franck, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 455; 1968, **72**, 514; C. A. Angell and M. L. Abkemeier, *Inorg. Chem.*, 1973, **12**, 1462.

[3] J. R. Ferraro in 'Spectroscopy in Inorganic Chemistry,' vol. 2, eds. C. N. R. Rao and J. R. Ferraro, Academic Press, New York, 1971, p. 57.

[4] D. L. Coffen and T. E. McEntee, *J. Org. Chem.*, 1970, **35**, 503.

[5] G. J. Long and D. L. Coffen, *Inorg. Chem.*, in the press.

[6] G. J. Long and E. O. Schlemper, *Inorg. Chem.*, in the press.

[7] G. J. Long and J. R. Ferraro, *Inorg. Chem.*, in preparation.

[8] C. Postmus, K. Nakamoto, and J. R. Ferraro, *Inorg. Chem.*, 1967, **6**, 2194.

[9] G. J. Long and E. O. Schlemper, *J.C.S. Dalton*, in preparation.

[10] J. R. Ferraro, S. S. Mitra, and C. Postmus, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 269.