Symbolize the eigenvalues of (2) in zero field by $E_0(S,M_S)$, where M_S are the eigenvalues of $\hat{S}^z$. The eigenvalues of (4) may now be written

$$E(S,M_S) = E_0(S,M_S) - g\beta HM_S - 2z'J'M_S\langle\hat{S}^z\rangle \quad (5)$$

The expectation value of the z component of total cluster spin is defined by

$$\langle\hat{S}^z\rangle = \sum_S\sum_{M_S} M_S e^{-E(S,M_S)/kT}/\mathrm{PF} \quad (6)$$

where PF is the partition function

$$\mathrm{PF} = \sum_S\sum_{M_S} e^{-E_0(S,M_S)/kT} \quad (7)$$

and the index S runs over all allowed values of total spin including any remaining degeneracy. By expanding the exponentials $e^{g\beta HM_S/kT}$ and $e^{2z'J'M_S\langle\hat{S}^z\rangle/kT}$, neglecting terms beyond the second, we obtain from (6) an implicit equation in $\langle\hat{S}^z\rangle$ which is easily solved to give

$$\langle\hat{S}^z\rangle = g\beta H\mathrm{F}(J,T)/[kT - 2z'J'\mathrm{F}(J,T)] \quad (8)$$

where

$$\mathrm{F}(J,T) = \sum_S\sum_{M_S} M_S{}^2 e^{-E_0(S,M_S)/kT}/\mathrm{PF} \quad (9)$$

The susceptibility equation follows as

$$\chi_A' = Ng^2\beta^2\mathrm{F}(J,T)/n[kT - 2z'J'\mathrm{F}(J,T)] \quad (10)$$

Comparison of eq 10 with the $T - \theta$ form of eq 1 shows that

$$\theta = 2z'J'k^{-1}\mathrm{F}(J,T) \quad (11)$$

The correction θ therefore has a temperature dependence determined by $\mathrm{F}(J,T)$ for the cluster. Numerical calculations with $\mathrm{F}(J,T)$ for several different clusters show that so long as $z'J' \ll J$, the approximation of taking θ to be a constant is satisfactory. To illustrate this we compare in Table I the least-squares best-fit parameters for the susceptibility *vs.* temperature (1.5–298°K) data of $[Ni_2(en)_4(SCN)_2]I_2$ and $[Ni_2(en)_4Cl_2]Cl_2$, obtained (A) on the assumption of constant θ[6] and (B) from eq 10.[7]

TABLE I

COMPARISON OF LEAST-SQUARES BEST-FIT PARAMETERS FOR SUSCEPTIBILITY *vs.* TEMPERATURE DATA[a]

	A			B		
Compound[6,7]	g	J, °K	θ, °K	g	J, °K	$Z'J'$, °K
$[Ni_2(en)_4(SCN)_2]I_2$	2.14[b]	7.6[b]	−2.0	2.14	7.2	−0.51
$[Ni_2(en)_4Cl_2]Cl_2$	2.15	13.3	−2.2	2.14	13.8	−0.54

[a] (A) Assuming constant θ and (B) from eq 10. [b] The value in ref 6 is slightly different because an error in the diamagnetic susceptibility correction gave χ_A' values uniformly low by 50×10^{-6} cm³ g-atom⁻¹; this has been corrected in ref 7.

---

(7) A. P. Ginsberg, R. L. Martin, R. W. Brookes, and R. C. Sherwood, *Inorg. Chem.*, in press.

BELL LABORATORIES A. P. GINSBERG*
MURRAY HILL, NEW JERSEY 07974 M. E. LINES

RECEIVED FEBRUARY 24, 1972

Pressure Effects on the Ligand-Field Spectra of Nickel(II) and Cobalt(II) Five-Coordinate Complexes of the Type ML_3X_2[1]

Sir:

Recently,[2] the effects of high external pressures on the ligand-field spectra of some five-coordinate Ni(II) complexes involving tetradentate, tridentate, and bidentate ligands were investigated. It was found that the spectra of the complexes with trigonal-bipyramidal (TBP) structures were much more sensitive to pressure than those having the square-pyramidal (SqPy) structures. For C_{3v} symmetry the low-energy band (ν_1), corresponding to the transition $^1A_1 \rightarrow a'E$, shifted toward higher energy, and in many cases the band became more symmetrical with increasing pressure. The technique was suggested as a means of distinguishing between TBP and SqPy structures.

Pressure effects of related five-coordinate complexes involving monodenate ligands have not been studied. This paper reports on such a study made with six Ni(II) and two Co(II) complexes. Table I summarizes the pressure dependences of several ML_3X_2 complexes, where M = Ni(II), Co(II); L = Me_3P, Ph_2PH, Ph_2PCH_3; and X = Cl, Br, I, CN. The results are compared with structural determinations made by X-ray measurements. For all pressure dependences which range from 8 to 29 cm⁻¹/kbar a distorted TBP–SqPy structure has been determined. The complex $Ni(Me_3P)_2I_2$ is observed to show a high pressure dependence of 35 cm⁻¹/kbar. The structure of this complex is unknown. Based on previous measurements,[2] we would suggest a TBP structure for the complex. Unpublished ambient pressure infrared data[3] appear to confirm this. This would preclude the possibility of conversion to a TBP structure occurring with pressure for this complex. Table II tabulates the dν/dp values for several five-coordinate nickel(II) complexes involving ligands varying from a tetradentate to a monodentate type. It may be observed that a general trend exists and that the highest pressure dependences are observed for a complex involving a TBP structure with

TABLE I

PRESSURE DEPENDENCE OF ML_3X_2 COMPOUNDS

Complex	Structure by X-ray data	dν/dp, cm⁻¹/kbar
$Ni(Me_3P)_3Br_2$	Distorted,[a] TBP–SqPy[b]	19
$Ni(Me_3P)_3I_2$	Undetermined[c]	35
$Ni(Ph_2PH)_3Cl_2$	Distorted, TBP–SqPy[d]	29
$Ni(Ph_2PH)_3Br_2$	Distorted, TBP–SqPy[d]	27,[e] 29[f]
$Ni(Ph_2PH)_3I_2$	Distorted, TBP–SqPy[d]	17,[e] 27[f]
$Ni(Ph_2PMe)_3(CN)_2$	Distorted, TBP–SqPy[g]	20
$Co(Ph_2PH)_3Br_2$	Distorted, TBP–SqPy[d]	8
$Co(Ph_2PH)_3I_2$	Distorted, TBP–SqPy[d]	23

[a] Determined from visible absorption studies. [b] B. B. Chastain, D. W. Meek, E. Billig, J. E. Hix, and H. B. Gray, *Inorg. Chem.*, **7**, 2412 (1968). [c] Unpublished infrared data supports TBP structure.[3] [d] J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **5**, 879 (1966). [e] High-frequency peak. [f] Low-frequency peak. [g] J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 1084 (1969).

---

(1) Based on work performed under auspices of U. S. Atomic Energy Commission.

(2) J. R. Ferraro, D. W. Meek, E. C. Siwiec, and A. Quattrochi, *J. Amer. Chem. Soc.*, **93**, 3862 (1971).

(3) K. Nakamoto, *et al.*, unpublished data.

TABLE II

COMPARISON OF PRESSURE DEPENDENCE FOR SEVERAL NICKEL(II) COMPLEXES WHERE THE LIGAND VARIES FROM A TETRADENTATE TO A MONODENTATE TYPE

Complex	Type of ligand	$d\nu/dp$, $cm^{-1}/kbar$	Structure
[NiLX]Y	Tetradentate	33–70	TBP
[NiLX$_2$]	Tridentate	9–32	Distorted, TBP–SqPy
[NiL$_2$X]Y	Bidentate	9–32[a]	Distorted, TBP–SqPy
[NiL$_3$X$_2$]	Monodentate	8–29	Distorted, TBP–SqPy

[a] [Ni(TEP)$_2$I]I shows a $d\nu/dp$ of 40 cm^{-1}/kbar but this complex may have been coverted to a TBP structure with pressure.[2] TEP = $(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2$.

tetradentate ligands and, as the ligand changes to a tri-, bi-, and monodentate, the pressure dependences decrease.

All of the observed five-coordinate complexes demonstrate limiting structures of either TBP or SqPy.[4–9] The energy of interconversion in solution is very small.[10] The factors determining which configuration will occur have been cited.[4–9] These include ligand–ligand repulsion, crystal-field stabilization energy, nature of the anion, shape of the ligand molecule, nature of the metal–ligand bond, and packing effects in the solid state. All of these factors play a role in determining which configuration will occur.

The effect of the tetradentate ligands in forming a maximum number of chelate rings increases the entropy and free energy of formation for the complex, and it is the complexes in the TBP structures which are more numerous and more stable. As the number of chelate rings are reduced, a decrease in stability occurs, and a tendency toward a distorted SqPy structure results. In the ultimate case, where no chelate rings are possible (L = monodentate), the complexes are unstable and dissociate in solution, and in the solid state tend toward a distorted TBP–SqPy structure.

The lifting of the degeneracy of the ν_1 transition at ambient pressure was ascribed to a ground-state distortion.[2] This can result in a different structure for the complex depending on the external pressure applied on the solid. With an increase in pressure, the ν_1 band becomes more symmetrical and reverses the effects occurring at ambient pressure. These pressure effects observed in the solid state may relate to the volume decrease occurring under pressure. The closer proximity of molecules could increase the interaction between bonded pairs of electrons and cause an increase in the covalency of the metal–ligand bond. The apical angle may also be affected, and changes in the crystal packing of the complex could occur. All of these changes with pressure tend to stabilize a regular TBP structure. The blue shifts with pressure have been attributed[2,11] to an increasing ligand-field interaction with the central metal ion. Apparently this occurs more effectively with complexes containing tetradentate ligands, which manifest the highest $d\nu/dp$ values.

The metal complexes studied in this examination have been previously prepared and reported elsewhere.[12–16] The pressure studies on the solids were made in a high-pressure diamond-anvil cell previously described[17,18] using type II diamonds, and the spectra were obtained with a Cary 14 spectrophotometer. The solid was loaded between the diamond anvils and the material cycled at various pressures to ensure an even distribution of the solid between the diamonds. The highest pressure observed was applied to the solid sample, and then pressure was lowered in increments to minimize the possibility of any sample extrusion effects. All pressure cycling was monitored with a microscope.

Acknowledgments.—The authors gratefully acknowledge Mr. Anthony Quattrochi for technical aid and Dr. A. Carty of the University of Waterloo, Waterloo, Ontario, Canada, for the supply of compounds; Professor D. W. Meek of the Ohio State University, Professor Luigi Sacconi of the University of Florence, Florence, Italy, and Professor Luigi Venanzi of the University of Delaware for the critical reading of this paper.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS 60439

JOHN R. FERRARO*[19]
K. NAKAMOTO

RECEIVED MARCH 16, 1972

---

[4] L. M. Venanzi, *Ric. Sci.*, **34**(7), 3 (1964).

[5] M. Ciampolini, *Struct. Bonding (Berlin)*, **6**, 52 (1968).

[6] L. Sacconi, *Pure Appl. Chem.*, **17**, 95 (1968).

[7] R. S. Nyholm, *Chem. Rev.*, **53**, 263 (1953).

[8] C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968).

[9] E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

[10] E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

[11] H. G. Drickamer, *Solid State Phys.*, **17**, 1 (1965).

[12] O. Dahl, *Acta Chem. Scand.*, **23**, 2342 (1969).

[13] C. A. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *J. Amer. Chem. Soc.*, **86**, 2958 (1964).

[14] R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963).

[15] G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).

[16] A. Carty, unpublished data.

[17] J. R. Ferraro, S. S. Mitra, and C. Postmus, *Inorg. Nucl. Chem. Lett.*, **2**, 269 (1966); **4**, 55 (1968).

[18] L. J. Basile, C. Postmus, and J. R. Ferraro, *Spectrosc. Lett.*, **1** (5), 189 (1968).

[19] To whom correspondence regarding this paper should be addressed.

A Caveat on Exchange Interactions

Sir:

It has been pointed out elsewhere[1,2] that magnetic susceptibility measurements should be made in a temperature region where magnetic exchange makes a significant contribution to the measured quantity if inferences regarding the character of the magnetic exchange are to be made. It appears that this point requires further emphasis.

For example, it was recently suggested[3] that intramolecular exchange interactions contributed to the susceptibility of some binuclear complexes containing tetrahedral cobalt(II). Measurements on powdered materials between 78 and 370°K were reported and antiferromagnetic interactions (J) of 2–5 cm^{-1} (*ca.* 3–8°K) were derived, but the zero-field splitting was ignored.

---

[1] E. Sinn, *Coord. Chem. Rev.*, **5**, 313 (1970).

[2] J. N. McElearney, D. B. Losee, S. Merchant, and R. L. Carlin, *J. Chem. Phys.*, **54**, 4585 (1971).

[3] A. B. P. Lever, L. K. Thompson, and W. M. Reiff, *Inorg. Chem.*, **11**, 104 (1972).