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
$[NiL_2X]Y$	Bidentate	9–32[a]	Distorted, TBP–SqPy
$[NiL_3X_2]$	Monodentate	8–29	Distorted, TBP–SqPy

[a] $[Ni(TEP)_2I]I$ 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.

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RECEIVED MARCH 16, 1972

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.

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The zero-field splitting found with tetrahedral cobalt(II) can also exert a significant influence on the susceptibilities. Since this effect is usually of the same magnitude as the J's reported[3] (for example, it is about 9.4°K in $(Et_4N)_2CoCl_4$[4]), it is dangerous to omit this effect from such data analyses. Using a molecular-field approach similar to that reported for nickel salts[5] we have calculated exactly the energy levels and resulting susceptibility of tetrahedral cobalt(II) and used a least-squares procedure to fit the data reported earlier[3] for the representative compound Co_2(phthalazine)Cl_3. The parameters $\langle g \rangle = 2.25$, $D/k = 22.9$°K, $E/k = 12.5$°K, and $2Jz/k = 11.0$°K fit the measured susceptibilities within the stated accuracy of 1%, while the set of parameters $\langle g \rangle = 2.22$, $D/k = 107.4$°K, and $E/k = 2Jz/k = 0$°K fits the data almost as well.

Thus, we conclude along with Lever, Thompson, and Reiff[3] that exchange interaction may be present in this compound, although the experimental data presently available are not adequate to distinguish between intermolecular and intramolecular effects. Measurements at lower temperatures, particularly on single crystals, are required before one can conclude unambiguously that intramolecular interaction is present.

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Reply to "A Caveat on Exchange Interactions"

Sir:

The basic premise that, *under certain circumstances*, the magnetic effects of zero-field splitting may be confused with those due to an exchange interaction of comparable magnitude is, of course, correct.

In binuclear $S = 1/2$ complexes, for example (as cited by Carlin[1]), a small exchange interaction energy (J) may give rise to magnetic properties similar to those arising from a zero-field splitting of similar magnitude. In such cases the splitting of the ground-state spin manifold is $2J$ and D, respectively, and low-temperature (<80°K) and magnetic anisotropy studies would be needed to distinguish the source of such behavior.

However, in the systems we have studied,[2] with $S = 3/2$ ions, the overall splitting of the ground-state spin manifold is $|12J|$, and a value of D, much larger than J, is needed to simulate magnetic behavior.

To confirm this qualitative prediction the data for several of the binuclear cobalt(II) derivatives[2] (that with highest J, that with lowest J, and an intermediate case) were recalculated assuming that the magnetic behavior arises solely through the presence of a zero-field splitting of the $^4A_2$ (in T_d) ground state.

Using an appropriate set of equations[3,4] the following values of D and g will fit the observed data within the temperature limits of the experiment

	D, cm^{-1}	g	J, cm^{-1} [2]
(phthalazine)Co_2I_3	81	2.15	−5.5
(phthalazine)Co_2Cl_3	52	2.25	−3.4
(2-methylpyrazine)$_2Co_2Br_4$	34	2.35	−1.6

It is evident that a *very large D* value is needed to simulate the behavior of a relatively small exchange interaction (also quoted above).

The zero-field splitting arises from a spin–orbit interaction between the ground-state spinors and components of excited states whose degeneracy has been lifted by a noncubic crystal field. While D values are commonly very small (usually less than 10 cm^{-1}) tetrahedral cobalt(II) complexes might give rise to larger values since the first excited state ($^4T_2$) lies comparatively close (4000–4500 cm^{-1} in these cases) to the ground state. In axial systems a splitting of the excited state of ΔE, lying at $\sim 10Dq$ above the ground state, will lead[3] to an approximate D of $8\lambda^2 \Delta E/(10Dq)^2$. To obtain $D = 80$ cm^{-1}, for example, a splitting of the $^4T_2$ state of close to 10,000 cm^{-1} would be needed, while for $D = 34$, the splitting is close to 3500 cm^{-1}.

These derivatives have a CoN_2X_2 chromophore of approximately C_{2v} symmetry. While the validity of such a first-order evaluation of the magnitude of D may be questioned, it is evident that such a stereochemistry does *not* give rise to a very large zero-field splitting. This is exemplified by the observation that complexes such as the "tetrahedral" pyridinecobalt halides ($(py)_2CoX_2$) have magnetic moments, at least within the range 78–300°K, with little dependence on temperature.[5] For example the complexes $(3\text{-pic})_2CoI_2$ and $(3\text{-pic})_2CoBr_2$ can be fitted[5] with $D = 15$–20 cm^{-1}. The very high values of D necessary to fit most of the diazine complexes leave little doubt that the magnetic behavior of these binuclear cobalt(II) complexes[2] is indeed correctly interpreted in terms of a dominant exchange interaction. Certainly there will be some zero-field splitting, and when low-temperature (<80°K) studies of the magnetism of these complexes are carried out such splitting should be included in their analysis. There is little to gain, however, from including this parameter into the higher temperature analysis.

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(4) The equations employed apply to an axial perturbation which splits the $^4A_2$ term into two doubly degenerate spin states ($\pm 1/2$ and $\pm 3/2$) separated by D. While the calculation is only to first order, and an axial perturbation may not be entirely appropriate here, the calculation should serve to provide an order of magnitude value of D needed to solve the experimental data.

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