four aryl rings of TPE^{2-}, we are drawn to the conclusion that TPE^{2-} must actually exist in a nearly planar state (III) with the antibonding electrons highly delocalized. It is therefore unlikely that rehybridization at C_1 and C_2 of the ethylenic portion (structures I or II) occurs to any great extent, since the π-bonding electrons are only slightly countered.

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Effect of Pressure on the Ligand-Field Spectra of Some Five-Coordinate Nickel(II) Complexes[1]

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Abstract: The pressure effects on the ligand-field spectra of several five-coordinate Ni(II) complexes are reported. The spectra of trigonal-bipyramidal structures are extremely pressure sensitive and shift to higher energies; those of square-pyramidal structures are less sensitive to pressure. The method may be used to distinguish between a trigonal-bipyramidal and a square-pyramidal structure in lieu of, or in complementation with, X-ray crystallography.

In recent years many complexes of five-coordinate transition metals involving mono-, bi-, tri-, and tetradentate ligands have been reported. Several reviews on the subject have been written.[2-5] Of particular interest to the discussion of this paper are the complexes involving tetradentate "tripod-like" ligands.[6-19] Characterization and, in some cases, X-ray structural determinations have been made on complexes of the type [MLX]Y, where L is a tetradentate ligand, X is a halide or pseudohalide, Y is usually a large polyatomic anion, and M = Ni(II), Co(II), Pd(II), or Pt(II).[6-25] The X-ray structural studies have shown that the five-coordinate MLX^+ ions may approximate either a trigonal-bipyramidal or a square-pyramidal structure.

Most of the ligand-field spectra measured for these complexes have been limited to ambient temperatures. These materials had never been studied under pressure, and it was of interest to examine the effects of pressure on their ligand-field spectra. Pressure effects on the electronic spectra of several transition metal complexes have been previously studied by Drickamer and coworkers[26] and others.[27,28] While this work was in progress, Gray, Venanzi, and coworkers[29] measured the electronic spectra of some of these complexes at 77°K. This paper reports the effects of high pressure on the ligand-field spectra of five-coordinate Ni(II) complexes where the ligand may be mono-, bi-, tri-, and tetradentate. For comparison, Ni(II) complexes of other coordination numbers were also studied, as well as several Co(II), two Pd(II), and one Pt(II) five-coordinate complexes.

Experimental Section

The metal complexes studied in this paper have been prepared, analyzed, and reported elsewhere.[7-11,16,17] Table I lists the sym-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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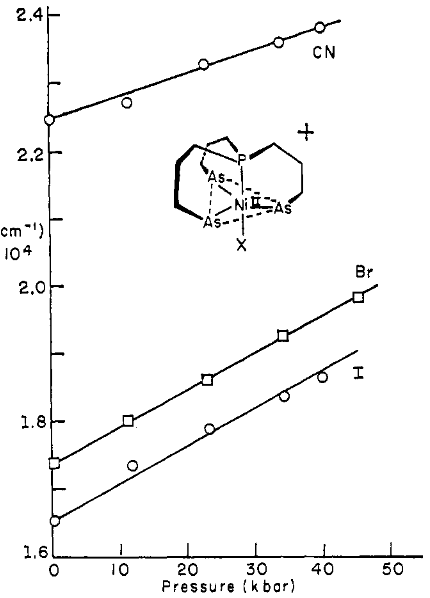

Figure 1. A plot of ν_1 against pressure for three trigonal-bipyramidal [NiLX]ClO$_4$ complexes of tris(3-dimethylarsinopropyl)phosphine. Characteristic features of all the five-coordinate complexes of the "tripod-like" ligands studied are the linear pressure dependence and the similar slopes for the different complexes of a given ligand.

bolism for the ligands used in this study. The pressure studies on the solids were made in a high-pressure diamond-anvil cell, previously described,[30,31] using type II diamonds and a Cary 14 spectrophotometer. Diamond absorption at frequencies greater than 29,000 cm^{-1} prevented any measurement of pressure effects on the charge-transfer spectra of these complexes. The highest pressure desired was applied to the solid sample. Then pressure was removed in increments to minimize the possibility of any sample extrusion effects. A preliminary publication outlining the use of these trigonal-bipyramidal complexes as internal pressure calibrants for the pressure optical cell has appeared previously.[32]

Table I. Types of Ligands Used

Ligand	Symbolism	Ref
	Tetradentate	
P[*o*-C_6H_4S(or Se)CH_3]$_3$	TSP	7
	TSeP	8
P[$(CH_2)_3$As$(CH_3)_2$]$_3$	TAP	6
As[$(CH_2)_3$As$(CH_3)_2$]$_3$	TTA	10
Sb[$(CH_2)_3$As$(CH_3)_2$]$_3$	TASb	*a*
As[*o*-C_6H_4AsPh$_2$]$_3$	QAS	3
[*o*-C_6H_4AsPh$_2$]$_2$As-*o*-$C_6H_4SCH_3$	SAs$_3$	*b*
N$(CH_2CH_2PPh_2)_3$	NP$_3$	17
$(Ph_2PCH_2CH_2)_2NCH_2CH_2OCH_3$	NOP$_2$	*c*
	Tridentate	
PhP[*o*-$C_6H_4SCH_3$]$_2$	DSP	9
CH_3As[$(CH_2)_3$As$(CH_3)_2$]$_2$	TAS	*d*
$CH_3C(CH_2PPh_2)_3$	TPP	*e*
HN$(CH_2CH_2PPh_2)_2$	PNP	16
	Bidentate	
$(C_2H_5)_2P(CH_2)_2P(C_2H_5)_2$	TEP	*f*
$Ph_2As(CH_2)_2AsPh_2$	diarsine	*e*
cis-$Ph_2PCH{=}CHPPh_2$	VPP	11
$Ph_2P(CH_2)_2PPh_2$	diphos	*e*

[a] G. A. McAuliffe and D. W. Meek, *Inorg. Chim. Acta*, **5** (2) (1971). [b] G. Dyer and D. W. Meek, manuscript in preparation. [c] D. Dapporto, R. Morassi, and L. Sacconi, *J. Chem. Soc. A*, 1298 (1970). [d] G. A. Barclay and R. S. Nyholm, *Chem. Ind. (London)*, 378 (1953). [e] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962). [f] C. E. Wymore and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **14**, 42 (1960).

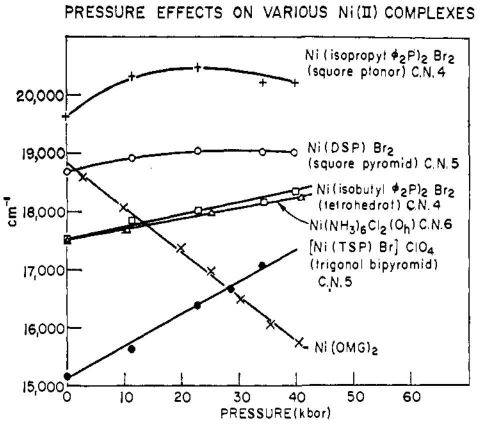

Figure 2. The effect of pressure on the absorption maximum of nickel(II) complexes with coordination numbers 4, 5, and 6 and having tetrahedral, planar, square-pyramidal, trigonal-bipyramidal, and octahedral structures. The ligand abbreviations are given in Table I; DMG is the anion of dimethylglyoxime.

Results

The pressure effects obtained for the five-coordinate Ni(II) complexes of trigonal-bipyramidal structure are dramatic. In C_{3v} symmetry, the low-energy band (ν_1) corresponding to the transition $^1A_1 \rightarrow a^1E$ ($d_{x^2-y^2}$, $d_{xy} \rightarrow d_{z^2}$) shifts linearly toward higher energy (blue shift) in all cases (Figure 1). For those complexes where the higher energy, weaker intensity band (ν_2) appears, only small shifts are observed. This band has been assigned as the $^1A_1 \rightarrow b^1E$ transition (d_{xz},$d_{yz} \rightarrow d_{z^2}$) in C_{3v} symmetry. The peak intensities of the ν_1 band show only minor variations, and in general remain relatively unaffected with pressure. Table II summarizes the pressure data for several trigonal-bipyramidal, square-pyramidal, tetrahedral, square-planar, and octahedral Ni(II) complexes, as well as two trigonal-bipyramidal Pd(II) and one Pt(II) and several square-pyramidal Co(II) complexes. The pressure dependency data are presented in terms of dν/dp ratios. It may be observed that for five-coordinate Ni(II) complexes, which have been characterized as trigonal bipyramidal (either from the electronic spectra or an X-ray structural determination), dν/dp values ranging from 33 to 71 cm^{-1}/kbar are obtained. This ratio is considerably greater than that obtained for square-pyramidal, five-coordinate Ni(II) complexes. Table III makes a comparison of the structures, which are presently available from X-ray data and the pressure data. Except for [Ni(TEP)$_2$I]I, the pressure dependence on the trigonal-bipyramidal complexes is clearly larger than for the square-pyramidal ones.

The band shapes also appear to be affected by pressure. In general, whenever a band can be followed with pressure, the asymmetric ν_1 band at ambient pressure becomes more symmetrical at high pressure.

Figure 2 shows a plot of the frequency (in reciprocal centimeters) against pressure (in kilobars) for several complexes of Ni(II) in various stereochemistries and for nickel dimethylglyoxime (Ni(DMG)$_2$). The trigonal-

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Table II. Electronic Spectra of Solid Ni(II), Co(II), and Pd(II) Complexes at High Pressures (Ligand-Field Bands)

Complex	Bands at ambient pressure	$d\nu/dp$, cm^{-1}/kbar	Effect of pressure on band shape
[Ni(TSP)NCS]ClO$_4$	21,300, 16,400	0, 65	Asym, broadens with pressure
[Ni(TSP)Cl]ClO$_4$	15,150	0, 33	Asym, broadens with pressure
[Ni(TSP)Br]ClO$_4$	21,400, 15,150	11, 57	Asym, broadens with pressure
[Ni(TSP)I]ClO$_4$	20,000, 15,050	0, 57	Asym, broadens with pressure
[Ni(TSeP)Cl]ClO$_4$	21,050, 15,150	0,[a] 47	Asym, broadens with pressure
[Ni(TSeP)Br]ClO$_4$	20,600, 15,150	0,[a] 45	Asym, broadens with pressure
[Ni(TSeP)I]ClO$_4$	14,700	52	Asym, broadens with pressure
[Ni(TSeP)NCS]ClO$_4$	20,850, 16,150	0,[a] 36	Asym, broadens with pressure
[Ni(TAP)Br]ClO$_4$	17,100	47	Slightly asym, becomes more sym
[Ni(TAP)Br]BPh$_4$	17,400	54	Slightly asym, becomes more sym
[Ni(TAP)I]BPh$_4$	16,500	51	Slightly asym, becomes more sym
[Ni(TAP)CN]ClO$_4$	22,500	33	Slightly asym, becomes more sym
[Ni(TTA)Cl]ClO$_4$	16,300	49	Asym, becomes more sym
[Ni(TTA)Br]ClO$_4$	15,400	46	Asym, becomes more sym
[Ni(TTA)CN]ClO$_4$	20,900	55	Asym, becomes more sym
[Ni(TASb)Cl]BPh$_4$	18,500	51	Asym, difficult to follow as the band goes into the charge-transfer band
[Ni(TASb)Br]BPh$_4$	16,800	71	Asym, difficult to follow as the band goes into the charge-transfer band
[Ni(TASb)I]BPh$_4$	16,400	40	Asym, difficult to follow as the band goes into the charge-transfer band
[Ni(TASb)CN]BPh$_4$	21,650	61	Asym, becomes more sym
[Ni(TASb)NCS]BPh$_4$	18,500	64	Asym, becomes more sym
[Ni(SAs$_3$)Br]ClO$_4$	15,900	40	Asym, becomes more sym
[Ni(SAs$_3$)I]ClO$_4$	15,400	41	Asym, becomes more sym
[Ni(NP$_3$)I]I	18,500	35	Little change in band shape
[Ni(NOP$_2$)I]I	18,700	12	Little change in band shape
Ni(DSP)Br$_2$	18,700	9	Little change in band shape with pressure
Ni(DSP)I$_2$	16,800	12	Little change in band shape with pressure
Ni(TAS)Br$_2$	21,050	18	Asym, becomes more sym
[Ni(TPP)NO]BPh$_4$	20,000	0	
Ni(PNP)Br$_2$	20,600	8	Little change in band shape
[Ni(TEP)$_2$I]I	23,800	40	Asym, becomes more sym
[Ni(TEP)$_2$Br]BF$_4$	22,700	29	Asym, becomes more sym
[Ni(TEP)$_2$Br]BPh$_4$	24,400	31	Asym, becomes more sym
[Ni(TEP)$_2$I]BPh$_4$	23,900	32	Asym, becomes more sym
Ni(TEP)I$_2$	20,900	13	Asym, becomes more sym
[Ni(diarsine)$_2$I]I	19,400	9	Asym, becomes more sym
Ni(isopropyl PPh$_2$)$_2$Br$_2$ (planar)	19,700	13	Shifts into the charge-transfer band
Ni(isobutyl PPh$_2$)$_2$Br$_2$ (tetrahedral)	17,550	20	Broadens with pressure
Ni(PPh$_3$)$_2$Br$_2$ (tetrahedral)	17,240	7	
Ni(NH$_3$)$_6$Cl$_2$[b] (O_h)	17,500	20	
Ni(DMG)$_2$[c]	18,000	−80	Broadens with pressure
[Co(NP$_3$)Cl]PF$_6$	18,450	7	Little change with pressure
[Co(VPP)$_2$NCS]BPh$_4$	22,850	Very slight shift	Band disappears with pressure
[Co(VPP)$_2$Br]BPh$_4$	22,000 (sh)	Very slight shift	Band disappears with pressure
[Co(diphos)$_2$Br]SnBr$_3$	22,750 (sh)	No shift	Band disappears with pressure
[Co(diphos)$_2$Cl]SnCl$_3$	22,750 (sh)	No shift	Band disappears with pressure
[Pd(QAS)Cl]Cl	22,000	81	Asym, becomes more sym
[Pd(QAS)I]ClO$_4$	18,900	33	Asym, becomes more sym
[Pt(QAS)I]ClO$_4$	22,500	27	Asym, becomes more sym
[Ni(QAS)I]ClO$_4$	21,050, 14,900	16, 33	Little change with pressure

[a] Peak disappears with pressure. [b] R. W. Parsons and H. G. Drickamer, *J. Chem. Phys.*, **29**, 930 (1958). [c] J. C. Zahner and H. G. Drickamer, *ibid.*, **33**, 1625 (1960); red shift with pressure.

bipyramidal complex manifests the steepest positive slope.

Discussion

There are two possible idealized structures that may exist for five-coordinate complexes of Ni(II), Pd(II), and Pt(II). The energy needed to interconvert these trigonal-bipyramidal and square-pyramidal structures is quite small in solution.[33] In the [MLX]Y complexes, where L is a "tripod-like" tetradentate ligand, the structure of the [MLX]$^+$ cation may be trigonal bipyramidal or square pyramidal, depending on the metal ion and the nature of donor atoms in the tetradentate ligand (Table III). Since solvent or crystal lattice forces apparently affect which structure is favored, we were interested if high pressure could interconvert the two forms in the solid state. To date, we have observed only one possible interconversion; however, dramatic linear blue shifts in the electronic absorption bands are observed in the trigonal-bipyramidal complexes.

In complexes involving a "tripod-like" tetradentate ligand, the coordination sphere around the metal may be considered to approximate D_{3h} symmetry if the axial atoms are equivalent, and C_{3v} if they differ. For a D_{3h} symmetry, the $^1A_1' \rightarrow a^1E'$ electronic transition (d_{xy}, $d_{x^2-y^2} \rightarrow d_{z^2}$), ν_1, is allowed, whereas the $^1A_1' \rightarrow {}^1E''$ transition (d_{xz}, $d_{yz} \rightarrow d_{z^2}$), ν_2, is forbidden by selection

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(33) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

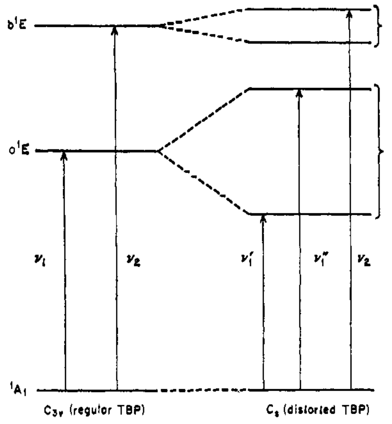

Figure 3. A schematic illustration of the energy levels and the "d-d" transitions in a low-spin, trigonal-bipyramidal d^8 metal complex in C_{3v} (regular TBP) and C_s (distorted TBP) symmetries.

rules. If the symmetry of the complex is lowered to C_{3v}, the latter transition becomes allowed. If the symmetry is lowered further to C_{2v} or C_s, both bands may split as they involve degenerate E levels (Figure 3). In most of the complexes studied here, only the ν_1 band seems to be asymmetric, perhaps indicative of a slight structural distortion from C_{3v} symmetry. Also, even though the $^1A_1 \rightarrow b^1E$ transition is allowed in C_{3v} symmetry, it is usually weaker by a factor of 5–10 than the $^1A_1 \rightarrow a^1E$ transition, which occurs as a very strong "d-d" band.

Table III. Comparison of X-Ray and Pressure Data

Complex	Structure, by X-ray	dν/dp	Ref
$[Ni(TAP)CN]ClO_4$	Trigonal bipyramidal	33	*a*
$[Ni(TSP)Cl]ClO_4$	Trigonal bipyramidal	33	*b*
$[Ni(NP_3)I]I$	Trigonal bipyramidal	35	*c*
$[Ni(SAs_3)Br]ClO_4$	Trigonal bipyramidal	40	*l*
$Ni(TAS)Br_2$	Square pyramidal (distorted)	18	*d*
$Ni(DSP)I_2$	Square pyramidal (distorted)	12	*e*
$Ni(PNP)Br_2$	Square pyramidal (distorted)	8	*f*
$[Ni(TEP)_2I]I$	Square pyramidal (distorted)	40	*g*
$[Ni(NOP)_2I]I$	Square pyramidal (distorted)	12	*h*
$[Co(NP_3)Cl]PF_6$	Capped tetrahedron	7	*i*
$[Ni(TPP)NO]BPh_4$	Tetrahedral	0	*j*
$Ni(PPh_3)_2Br_2$	Tetrahedral	7	*k*

[a] D. L. Stevenson and L. F. Dahl, *J. Amer. Chem. Soc.*, **89,** 3424 (1967). [b] L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, **8,** 1072 (1969). [c] D. Dapporto and L. Sacconi, *Chem. Commun.*, 1091 (1969); *J. Chem. Soc. A*, 1804 (1970). [d] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc., London*, 415 (1960). [e] D. W. Meek and J. A. Ibers, *Inorg. Chem.*, **8,** 1915 (1969). [f] P. L. Orioli and L. Sacconi, *Chem. Commun.*, 1310 (1968). [g] G. J. Palenik, personal communication, 1970. [h] P. Dapporto, R. Morassi, and L. Sacconi, *J. Chem. Soc. A*, 1298 (1970). [i] L. Sacconi, M. DiVaira, and A. Bianchi, *J. Amer. Chem. Soc.*, **92,** 4465 (1970). [j] P. G. Eller and P. W. R. Corfield, personal communication, 1970. [k] G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 3625 (1963). [l] These data were received after this paper had gone to press: G. J. Palenik, personal communication, June 1971.

Application of high pressure to the trigonal-bipyramidal complexes at ~300°K causes the ν_1 band to shift significantly to higher energies with little change in intensity. In many cases, the band becomes more symmetrical with pressure. The ν_2 band, whenever it is observed, shifts only slightly to higher energy. Figure 4 shows the effect of pressure on $[Ni(TSeP)NCS]ClO_4$ at 319°K. At 319°K and at ambient pressure, the ν_1 transition has split. This splitting disappears when pressure is applied and a single band is observed at higher frequency. The ν_2 transition shows little change under these conditions.

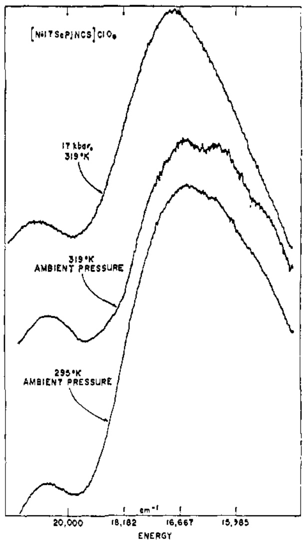

Figure 4. The effect of pressure and temperature on the ν_1 and ν_2 transitions for $[Ni(TSeP)NCS]ClO_4$.

If these same complexes are measured in a glass at 77°K and ambient pressure, the $^1A_1 \rightarrow a^1E$ band does not shift significantly to higher energy. However, it becomes much sharper and is more symmetrical. At first glance, the effects of the glass matrix and high pressure appear to coincide. However, we believe that a different behavior is being observed in the high-pressure experiment at 300°K as compared to the glass matrix at 77°K. This is illustrated by the fact that the band shapes of the *pure solids* (as opposed to the glasses) at 77°K and ambient pressure do not become markedly sharper or more symmetrical than at 300°K, even though the bands shift slightly to higher energy.[29]

The spectral changes in the glass at 77°K have been interpreted in terms of a dynamic Jahn–Teller effect involving the excited states and/or of temperature dependent distortions of the ground state.[29] The dynamic Jahn–Teller effect can lift the degeneracy of the E levels, giving rise to a more complicated spectrum at room temperature. Such effects would be less prominent at lower temperatures and could account for the spectral results observed in the glass at 77°K. Alternatively, the degeneracy of the E states may be lifted by a ground-state distortion, which results in a different structure for a complex at 77° as compared to 300°K. The temperature dependence in the spectrum may be analyzed in terms of an equilibrium between two discrete structures, *i.e.*

$$C_{3v}\ (D_{3h}) \rightleftharpoons C_s\ (C_{2v})$$

It may also be possible that at a given intermediate temperature, one species that is an intermediate geometry between C_{3v} and C_s symmetries exists. In such a case, a large number of structures, representing the different degrees of distortion from C_{3v} symmetry, would be possible, and the precise structure would depend on the temperature. Thus, the splitting of the a^1E level (ν_1 band in C_{3v} symmetry) would then be taken to reflect the amount of distortion present, as shown by Figure 3.

Of the two possible explanations of the low-temperature effects in the glass, the distorted ground state at 300°K is a more satisfying explanation for our pressure effects. For example, the degree of asymmetry in the ν_1 bands of the $[NiLX]^+$ complexes generally increases in the order $Cl^- < Br^- < I^-$, consistent with increasing steric effects of the halide.

The shift of the ν_1 band to higher energy with increasing pressure implies an increasing ligand-field interaction with the central metal ion. A similar explanation has been given by Drickamer for high-pressure effects on the d–d transitions of other transition metal complexes.[26]

It may be observed from Table II that the $d\nu/dp$ values are 33–71 cm^{-1}/kbar for trigonal-bipyramidal Ni(II) complexes involving tetradentate ligands. For complexes involving bidentate or tridentate ligands, the $d\nu/dp$ values are generally lower. However, with the possible exception of the TEP ligand, these tridentate and bidentate ligands give square-pyramidal complexes (Table III). The pressure dependence is also lower for four- and six-coordinate nickel(II) complexes, as compared with trigonal-bipyramidal cases.

The $d\nu/dp$ change for a trigonal-bipyramidal Pd(II) complex is about double the value observed for the Ni(II) complexes (Table II), in agreement with predictions based on the larger splitting of the a^1E level in Pd(II) complexes.[14]

The utility of the pressure technique is to differentiate between trigonal-bipyramidal and square-pyramidal complexes. The $d\nu/dp$ values (Table II) for 23 trigonal-bipyramidal complexes fall within the range 33–71 cm^{-1}/kbar, whereas the values for 6 square-pyramidal Ni(II) complexes are 6–18 cm^{-1}/kbar. The method may also be useful in assigning a structural type to a group of pentacoordinate complexes if the structure of one member of a series, or a complex of a similar ligand, has been determined by X-ray crystallography. Thus, square-pyramidal structures are confirmed for all of the complexes, $[Ni(DSP)X_2]$ and $[Ni(SP)_2X]^+$ (X = Cl, Br, I),[9,34] by relating the pressure dependencies in Table II with the square-pyramidal structure of $Ni(DSP)I_2$.[25]

The TEP complexes give $d\nu/dp$ values of 29–40 cm^{-1}/kbar, in the lower part of the range for trigonal-bipyramidal Ni(II) complexes. However, an X-ray structural determination at ambient pressure and temperature shows a five-coordinate cation that is markedly twisted from a square-pyramidal toward a trigonal-bipyramidal structure.[35] Perhaps the high pressure used in this study transforms the $[Ni(TEP)_2X]^+$ complexes to trigonal bipyramids; if that occurs, it is the only series of complexes that has been observed to rearrange in the solid state to a different structure under 45 kbar of pressure. These complexes and similar ones are being investigated further.

Conclusions

The trigonal-bipyramidal Ni(II) and Pd(II) complexes give a dramatic and linear shift of the ν_1 electronic band ($^1A_1 \rightarrow a^1E$ transition) to higher energy. The magnitude of the shift per kilobar of pressure is greater by a factor of 2–4 than for any other coordination geometry examined to date. Several different series of square-pyramidal Ni(II) and Co(II) complexes exhibited only small band shifts ($d\nu/dp$ = 6–18 cm^{-1}/kbar) on application of pressure. Thus, taking electronic absorption spectra with a high-pressure cell offers the possibility of being able to differentiate definitively between a trigonal-bipyramidal and a square-pyramidal Ni(II) complex without requiring an X-ray structure determination. Moreover, it may be possible to recognize intermediate structures by their $d\nu/dp$ ratios (see Table II). The pressure measurements are made easily on micro quantities of powdered samples, and require only a small amount of time, in contrast to an X-ray structure determination.

Of the group of compounds studied in this paper, 18 contained ionic perchlorate outside the coordination sphere of the central atom. This had been determined from other experiments such as conductivity and X-ray. The compounds were stable at the pressures used in this work, and the results were indicative that the perchlorate remained ionic even in the compressed solid. However, extreme caution must be exercised whenever pressure is applied to any solid containing perchlorate even when micro quantities are used.

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(34) SP is the bidentate ligand analogous to DSP, *i.e.*, diphenyl(*o*-thiomethylphenyl)phosphine.

(35) G. J. Palenik, personal communication, 1970; manuscript in preparation.