Table VI. Comparison of Calculated and Experimental Radii of Gyration of Ethyl-Branched Polyethylenes

No. of ethyl branches per 100 backbone carbons	$g = \langle S^2 \rangle_{o.B}/\langle S^2 \rangle_{o.L}$	
	Exptl[a]	Calcd[b]
5	0.94	0.95–0.97
10	0.89	0.91–0.95
20	0.80	0.86–0.91

[a] Determined from viscosity and light scattering measurements and compared to linear polyethylene with the same degree of polymerization as the backbone of the branched polymer. [b] Branches were assumed to be of zero length and $\Delta\varphi = 10°$, $\sigma = 0.61$, $\omega = 0.11$ with τ^* and τ between 0.1 and 0.5.

that any backbone bond in a branched polyethylene is in the trans conformation. The Flory–Jernigan matrix methods[26] were employed to obtain the calculated results given in Table VII. It is clear that the backbones of even these heavily branched polyethylenes

Table VII. *A Priori* Bond Rotational State Probabilities

Polymer	$P_t{}^a$	$(P_{g^+} + P_{g^-})^a$
No branches ($\sigma = 0.54$, $\omega = 0.088$)	0.598	0.402
No branches ($\sigma = 0.61$, $\omega = 0.11$)	0.572	0.428
Trifunctional branch every 5 bonds ($\sigma = 0.54$, $\omega = 0.088$)	0.609–0.654 (0.653–0.684)[b]	0.391–0.346 (0.347–0.316)[b]
Trifunctional branch every 5 bonds ($\sigma = 0.61$, $\omega = 0.11$)	0.594–0.644 (0.639–0.669)[b]	0.406–0.356 (0.361–0.331)[b]
Tetrafunctional branch every 5 bonds ($\sigma = 0.54$, $\omega = 0.5$–0.088)	0.624–0.634 (0.661)[c]	0.376–0.366 (0.339)[c]
Tetrafunctional branch every 5 bonds ($\sigma = 0.61$, $\omega = 0.11$)	0.615–0.625 (0.652)[c]	0.385–0.375 (0.348)[c]

[a] τ and τ^* are between 0.1 and 0.5. [b] $\tau^* = 1.0$, $0.1 \leq \tau \leq 0.5$. [c] $\tau^* = 1.0$.

have calculated conformational characteristics and flexibilities very similar to linear polyethylene.

Solution and Solid-State Electronic Spectra of Low-Spin Trigonal-Bipyramidal Complexes Containing Nickel(II), Palladium(II), and Platinum(II). Temperature Dependence of the Lowest Energy Ligand-Field Band

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Abstract: Solution and solid-state electronic spectral measurements at 295° and at low temperatures (77° or 100°K) have been carried out on the low-spin trigonal-bipyramidal complexes [Ni(CN)₂(PhPR₂)₃] (R = Me, OEt) and [MX(L′L₃)]Y, where M = Ni(II), Pd(II), Pt(II), X = Cl, Br, I, CN, Y = X, ClO₄, BPh₄, and L′L₃ represents a potentially quadridentate "tripod-like" ligand (Me₂AsCH₂CH₂CH₂)₃L′ (L′ = P, As), (o-MeL·C₆H₄)₃P (L = S, Se) or (o-Ph₂L·C₆H₄)₃L′ (L′ = L = P, As). The lowest energy band ν_1 is usually asymmetric and even may be split into a double peak at 295°K; on cooling *solutions* of the complexes, band ν_1 exhibits a dramatic increase in extinction coefficient and becomes more symmetrical. This unusual effect is discussed in terms of a Jahn–Teller distortion of the doubly degenerate excited state and a temperature-dependent static distortion of the ground state. By contrast, the two transitions contributing to band ν_1 of the *solid* complexes do not approach one another on cooling but instead become somewhat better resolved, indicating that the asymmetry or splitting of ν_1 is due primarily to a permanent ground-state distortion. The band ν_1 in the solution spectra of the complexes [MCl(P·As₂P)]Cl, where M = Pd, Pt and P·As₂P = (o-Ph₂As·C₆H₄)₂(o-Ph₂P·C₆H₄)P, shows two well-resolved peaks at 100°K, as the three equatorial atoms are no longer the same and the complexes have C_s rather than C_{3v} micro-symmetry.

Since the preparation of the first complexes of quadridentate "tripod-like" ligands,[3–5] much work has

been carried out on the characterization of this class of complex.[6,7] Structural determinations on certain of the [MX(L′L₃)]⁺ complexes have shown them to be trigonal-bipyramidal, with the unidentate anion X occupying an axial position trans to the central atom, L′,

(1) State University of New York at Albany.
(2) (a) California Institute of Technology; (b) National Science Foundation Predoctoral Fellow, 1966–1969.
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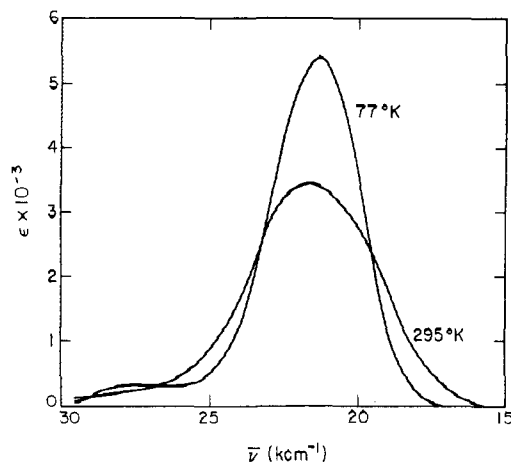(7) G. S. Benner and D. W. Meek, *Inorg. Chem.*, 6, 1399 (1967), and references therein.

Figure 1. Temperature dependence of the ligand-field spectrum of [Ni(CN)(TAA)]ClO₄ in 2-methyltetrahydrofuran–ethanol.
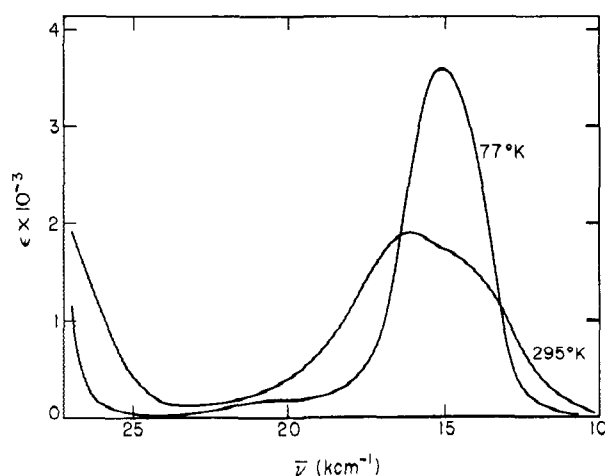

Figure 2. Temperature dependence of the ligand-field spectrum of [NiBr(TAA)]ClO₄ in 2-methyltetrahydrofuran–ethanol.

of the quadridentate ligand.[8–11] Study of the ligand-field portion of the electronic spectra of low-spin d^8 complexes of the above type (M = nickel(II), palladium(II), platinum(II)) had led to the conclusion that all their structures are trigonal-bipyramidal.[12–14] Five coordinate complexes of low-spin d^8 ions containing only unidentate ligands are also known with basically trigonal-bipyramidal structures, which are somewhat distorted in the solid state.[15–17]

We have carried out detailed spectral measurements in rigid glasses at 77°K (or in some cases at 100°K) on complexes [Ni(CN)₂(PhPR₂)₃] (R = Me, OEt) and a number of compounds of the type [MX(L'L₃)]Y, where M = Ni(II), Pd(II), Pt(II); X = a unidentate

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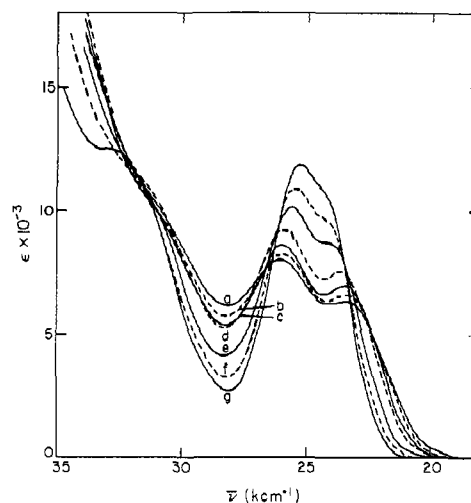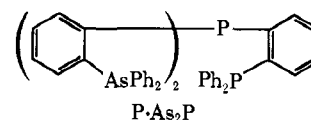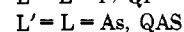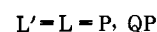
Figure 3. Ligand-field spectrum of [PtCl(QP)]Cl in 2-methyltetra-hydrofuran–dichloromethane as a function of temperature (°K): (a) 295°, (b) 258°, (c) 207°, (d) 156°, (e) 132°, (f) 119°, (g) 100°.

anion; Y = X, ClO₄, BPh₄; and the ligands L'L₃ are listed below.

(Me₂AsCH₂CH₂CH₂)₃L'

L' = P, TAP
L' = As, TAA

L = S, TSP
L = Se, TSeP

L' = L = P, QP
L' = L = As, QAS

P·As₂P
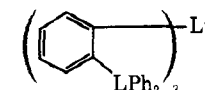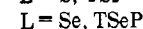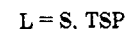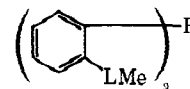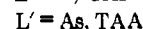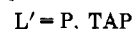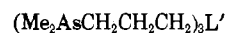
On the basis of these results, the asymmetry at room temperature of one of the two ligand-field bands in the electronic spectra of these complexes is discussed.

Experimental Section

The metal complexes [Ni(CN)₂{PhP(OEt)₂}₃],[18] [Ni(CN)₂(Ph-PMe₂)₃],[19] and those of the ligands QP[20] and QAS[3,4,6,21] were prepared as described previously. Compounds of the ligand P·As₂-P[22] were prepared in an analogous fashion to those of the latter two ligands. Professor D. W. Meek of the Ohio State University kindly furnished analyzed complexes (prepared by Drs. G. S. Benner and G. Dyer) of the ligands TAP, TAA, TSP, and TSeP.

Solutions for spectral measurements on most of the nickel complexes were made using a 2:1 mixture by volume of 2-methyltetra-

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(22) J. W. Dawson and L. M. Venanzi, *ibid., A,* 2897 (1971).

hydrofuran (2-MeTHF) and ethanol. The 2-methyltetrahydrofuran was chromatoquality reagent (Matheson Coleman and Bell) and was distilled from lithium aluminum hydride to remove peroxides and residual water; the ethanol was anhydrous USP-NF grade (U. S. Industrial Chemicals Co.). The two dicyanonickel compounds were studied in a 5:5:2 mixture of diethyl ether, isopentane, and ethanol (EPA solvent; Matheson Coleman and Bell). Spectral measurements with these solvent mixtures were carried out as described previously.[23] Molar extinction coefficients at 77°K have been corrected for solvent contraction using the fact that 1.00 ml (at 295°K) of 2:1 2-MeTHF–ethanol and EPA solvent contracts to 0.79 ± 0.02 and 0.77 (1) ml, respectively, at 77°K.

The palladium and platinum complexes and [NiCl(L'L₃)]Cl (L'L₃ = QP, P·As₂P) were studied using a 9:1 2-MeTHF–dichloromethane mixture; the dichloromethane was "Instra-Analyzed" (Baker). Electronic spectra were obtained using a Cary 14 spectrophotometer together with a Beckman Research and Industrial Instrument Co. variable-temperature unit, VLT-2, fitted with silica windows. The lowest temperature obtainable with this apparatus was 100 ± 1°K, with 1.00 ml (at 295°K) of 2-MeTHF–dichloromethane contracting to 0.83 (2) ml. The temperatures of solutions in the VLT-2 cell were measured by use of a copper–constantan thermocouple, which was attached to a Sargent Model SR recorder, modified to read 0–10 mV. Gaussian analyses were performed on the variable-temperature spectra of [PtCl(QP)]Cl with a Du Pont Model 310 curve analyzer. The spectra of solid complexes were examined using a thin-film technique,[24] in which a solution of the [MX(L'L₃)]Y complex (ca. 2 mg in 0.2 ml of dichloromethane) was added dropwise onto one of the silica windows of the VLT-2 cell, each drop being allowed to evaporate before another was added. The resultant thin film of complex was nearly transparent, and the silica window was mounted in the variable-temperature cell.

Results

Complexes [MX(L'L₃)]Y. The visible absorption spectra of the complexes [Ni(CN)(TAA)]ClO₄, [NiBr(TAA)]ClO₄ and [PtCl(QP)]Cl are shown in Figures 1–3. The first is an example of a complex with a fairly symmetrical lowest energy band at room temperature, the second shows intermediate behavior, and in the third the splitting of this band is clearly seen at higher temperatures. In all cases, at low temperature, this broad asymmetric band exhibits a dramatic increase in extinction coefficient and becomes more symmetrical. A much less intense band at somewhat higher energy is usually better resolved at low temperature. These results confirm the Gaussian analyses performed earlier on some of these spectra,[7,12] and are presented in Table I. The charge-transfer spectra of these complexes have also been studied and will be reported elsewhere.[25]

The assignment of ligand-field spectra presented here agrees with that given earlier by Venanzi, Meek, Ciampolini, and others for this type of complex.[7,12–14] Assuming C_{3v} symmetry, the d-level ordering is xz, $yz < xy$, $x^2 - y^2 < z^2$. The lowest energy band (ν_1), which is asymmetric or even split at room temperature, and which narrows and becomes more symmetrical at low temperature, is due to the transition $^1A_1 \rightarrow a^1E$ (xy, $x^2 - y^2 \rightarrow z^2$). The band at higher energy (ν_2), which is considerably less intense, is assigned as $^1A_1 \rightarrow b^1E$ (xz, $yz \rightarrow z^2$). This intensity pattern has been observed for a large number of trigonal-bipyramidal complexes of both C_{3v} and D_{3h} symmetries.[26] In a D_{3h} system ν_1 is symmetry allowed and ν_2 is forbidden.[12]

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Table I. Temperature Dependence of the $^1A_1 \rightarrow a^1E$ Transition of the Complexes [MX(L'L₃)]Y in Solution

Complex	$\bar{\nu}_{max}$, kcm⁻¹	ϵ_{max}, l. mol⁻¹ cm⁻¹	$\bar{\nu}_{max}$, kcm⁻¹	ϵ_{max}, l. mol⁻¹ cm⁻¹
	295°K		77°K	
[NiCl(TAP)]ClO₄	15.9 (sh)ᵃ	1900ᵇ		
			16.9	3,800
	17.9	2300		
			22.5ᶜ (sh)	85ᵇ
[NiBr(TAP)]ClO₄	15.3 (sh)	1800ᵇ		
			16.2	4,300
	17.3	2100		
			22.2ᶜ (sh)	140ᵇ
[NiI(TAP)]ClO₄	15.0 (sh)	1500ᵇ	15.6	2,000
	16.8	1800	17.1 (sh)	1,700ᵇ
			21.7ᶜ (sh)	250ᵇ
[Ni(CN)(TAP)]ClO₄	22.9	4500	22.9	6,900
			29.4ᶜ (sh)	210ᵇ
[NiCl(TAA)]ClO₄	14.6 (sh)	1600ᵇ		
			15.6	3,900
	16.6	1950		
			20.8ᶜ (sh)	120ᵇ
[NiBr(TAA)]ClO₄	14.3 (sh)	1600ᵇ		
			15.1	3,700
	16.2	1900		
			19.8ᶜ (sh)	170ᵇ
[Ni(CN)(TAA)]ClO₄	21.6	3000	21.2	4,700
			27.6ᶜ	310
[NiBr(TSP)]ClO₄	15.1	840	14.7	1,300
	20.7ᶜ	220	21.5ᶜ	230
[NiI(TSP)]ClO₄	14.0 (sh)	1200ᵇ	14.0	1,750
	15.4	1300	15.4 (sh)	1,500ᵇ
			20.6ᶜ	420
[NiCl(TSeP)]ClO₄	15.5	1900	14.65	3,200
	20.5ᶜ (sh)	220ᵇ	21.7ᶜ	320
[NiBr(TSeP)]ClO₄	15.4	1700	14.5	3,400
	20.6ᶜ (sh)	200ᵇ	21.2ᶜ (sh)	480ᵇ
[NiI(TSeP)]ClO₄	13.7 (sh)	1400ᵇ	14.3	2,500
	15.0	1500	15.4 (sh)	2,100ᵇ
	19.5ᶜ	300	20.2ᶜ	380
	295°K		100°K	
[NiCl(QP)]Cl	17.7	4550	17.6	5,700
[PdCl(QP)]Cl	20.5 (sh)	6800ᵇ		
			21.65	13,000
	22.3	8000		
[PdBr(QP)]Br	20.1 (sh)	6800ᵇ		
			21.0	12,800
	21.5	7600		
[PdI(QP)]I	19.8	6500	20.0	10,400
[PtCl(QP)]Cl	23.4	6300	24.4 (sh)	10,800ᵇ
	26.0	8000	25.3	11,900
[PtBr(QP)]Br	22.9	5800	23.8 (sh)	9,800ᵇ
	25.25	6800	24.6	10,500
[PtI(QP)]I	22.5 (sh)	5000ᵇ		
			23.4	8,400
	23.4	5200		
[PdCl(QAS)]Cl	20.0 (sh)	7900ᵇ		
			21.05	15,800
	21.5	9500		
[PtCl(QAS)]Cl	23.7 (sh)	6900ᵇ	24.2 (sh)	13,000ᵇ
	25.2	8200	24.7	13,600
[NiCl(P·As₂P)]Cl	17.3	4600	17.15	6,200
	23.3ᶜ (sh)	470ᵇ	23.7	480
[PdCl(P·As₂P)]Cl	21.3 (sh)	6600ᵇ	21.2	11,700
	23.3	7900	22.4	12,500
[PtCl(P·As₂P)]Cl	23.7	6900	24.3	11,600
	26.35	7800	25.6	11,550

ᵃ sh = shoulder. ᵇ Band height at point of inflection. ᶜ $^1A_1 \rightarrow$ b¹E transition.

Although the band ν_2 becomes formally allowed on lowering the symmetry from D_{3h} to C_{3v}, the intensity of ν_2 is not affected markedly.[26]

The asymmetry of ν_1 at room temperature is strongly dependent on the metal ion (Pt > Pd > Ni), on the

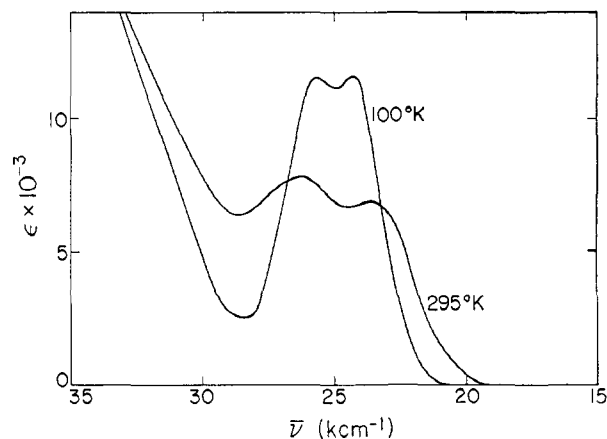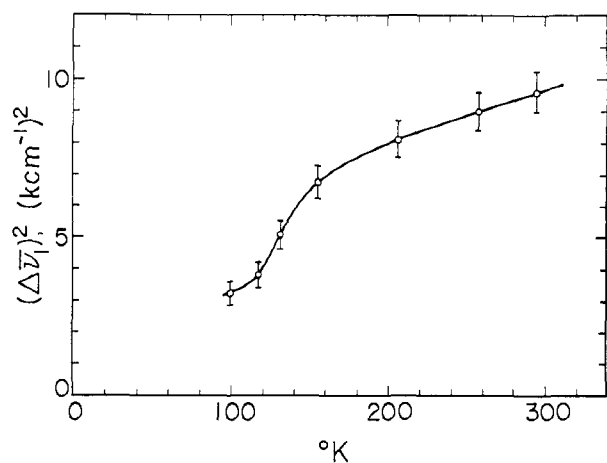Figure 4. Temperature dependence of the ligand-field spectrum of [PtCl(P·As₂P)]Cl in 2-methyltetrahydrofuran-dichloromethane.

Figure 5. Variation of $(\Delta\bar{\nu}_1)^2$ with temperature for the two-component $^1A_1 \rightarrow a^1E$ transition of [PtCl(QP)]Cl in 2-methyltetrahydrofuran-dichloromethane.

organic ligand (TAP $\sim$ TAA > TSeP > TSP > QP $\sim$ QAS), and on the anionic ligand X (for Ni, I > Br > Cl > CN; for Pd and Pt, Cl > Br > I). The most asymmetric bands still retain some asymmetry at low temperature. It would be desirable to measure these spectra at liquid helium temperature to determine whether ν_1 becomes equally symmetric in every case, given sufficiently low temperatures.

The spectra of [MCl(P·As₂P)]Cl (M = Ni, Pd, Pt) are of interest because the three equatorial donor atoms are no longer the same and the complex has C_s rather than C_{3v} symmetry. The band ν_1 of the palladium and platinum complexes increases in extinction coefficient on lowering the temperature, but at 100°K shows two well-resolved peaks (Table I and Figure 4) rather than a single asymmetric peak as was found in the spectra of the QP and QAS analogs. In the low-temperature spectrum of [NiCl(P·As₂P]Cl, the corresponding two peaks are not resolved.

As observed in Figure 3, the splitting of band ν_1 for [PtCl(QP)]Cl is well defined at room temperature and the asymmetry is pronounced at 100°K. Gaussian analyses were performed on the spectra to elucidate the energies, extinction coefficients, and half-widths (i.e., widths at half-height) of the bands contributing to ν_1. A satisfactory fit to the shapes of ν_1 was obtained using
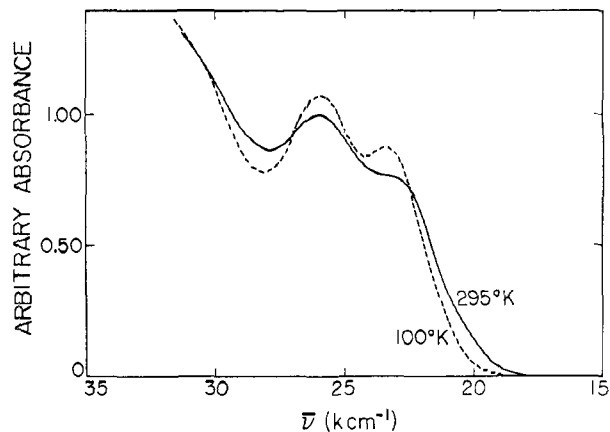

Figure 6. Temperature dependence of the ligand-field spectrum of [PtCl(QP)]Cl in the solid state.

two bands ν_1' and ν_1'' (ν_1' is at lower energy) and the tails of higher energy bands. As the temperature is lowered, the two bands ν_1' and ν_1'' approach each other, resulting in a decrease in $\Delta\bar{\nu}_1$ ($= \bar{\nu}_1'' - \bar{\nu}_1'$) and therefore $(\Delta\bar{\nu}_1)^2$, as shown in Figure 5.

The oscillator strength f of the transition ν_1 is proportional to the area of the two bands that contribute to it, and is related to the extinction coefficients ϵ_{max} and half-widths H_1 (in kcm⁻¹) by[27]

$$f \cong \sum^{''}(4.6 \times 10^{-6})\epsilon_{max}H_1$$

For [PtCl(QP)]Cl, the oscillator strength was found to be approximately independent of temperature ($f = 0.177 \pm 0.006$) as expected for the electronically allowed $^1A_1 \rightarrow a^1E$ transition.[28]

The spectral measurements on [MX(L'L₃)]Y were all carried out using solutions containing 2-methyltetrahydrofuran. Room-temperature spectra were measured for [PtCl(QP)]Cl in several other solvents: dichloromethane, chloroform, chlorobenzene, acetone, ethanol, ethyl acetate, acetonitrile, and N,N-dimethylformamide. The band shape and splitting of ν_1 remain almost constant and in no way approach the more symmetrical form found at low temperatures in 2-MeTHF-CH₂Cl₂. The lowest energy peak is in the range 25.8–26.1 kcm⁻¹, while the higher peak (corresponding to ν_1'') is invariant in the limits of experimental error (± 0.1 kcm⁻¹).

In order to determine whether the spectra of the solid complexes behave in a similar fashion to those in solution, measurements at 295° and 77° or 100°K were made on the complexes [MX(QP)]X (M = Pd, Pt; X = Cl, Br, I), [MCl(P·As₂P)]Cl (M = Pd, Pt), [PtI-(QAS)]BPh₄, [Ni(CN)(TAP)]ClO₄, and [NiCl(TSP)]-ClO₄. The last three complexes were included as X-ray structural determinations are available.[8-10] As observed in Table II and Figure 6, the behavior with change in temperature is very different from that found for the solution spectra. The two bands contributing to ν_1 do not approach one another, but instead become somewhat better resolved due to band narrowing at lower temperature. In case a phase change in the

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Table II. Temperature Dependence of the $^1A_1 \rightarrow a^1E$ Transition of Some Complexes [MX(L'L₃)]Y in the Solid State

Complex	$\bar{\nu}_{max}$, kcm^{-1}	Absorbance[a]	$\bar{\nu}_{max}$, kcm^{-1}	Absorbance
		295°K		77°K
[Ni(CN)(TAP)]ClO₄	21.7	1.00	21.9	1.20
[NiCl(TSP)]ClO₄	14.5	1.00	14.2	1.08
			15.4 (sh)[b]	1.02[c]
		295°K		100°K
[PdCl(QP)]Cl	20.4 (sh)	0.88[c]	20.4	0.87
	22.2	1.00	22.3	0.99
[PdBr(QP)]Br	20.0 (sh)	0.91[c]	19.8	0.99
	21.4	1.00	21.5	1.09
[PdI(QP)]I	19.8	1.00	19.9	1.08
[PtCl(QP)]Cl	23.5 (sh)	0.77[c]	23.4	0.87
	25.9	1.00	25.9	1.08
[PtBr(QP)]Br	22.8	0.89	22.8	0.93
	25.0	1.00	25.1	1.02
[PtI(QP)]I	22.3 (sh)	0.96[c]	22.2 (sh)	1.04[c]
	23.15	1.00	23.4	1.08
[PtI(QAS)]BBh₄			21.7 (sh)	1.11[c]
	22.1	1.00	22.6	1.07
[PdCl(P·As₂Cl)]Cl	21.3 (sh)	0.91[c]	21.05 (sh)	0.87[c]
	22.7	1.00	23.4	0.97
[PtCl(P·As₂P)]Cl	24.1 (sh)	0.86[c]	23.6	0.90
	26.3	1.00	26.25	1.00

[a] Absorbances are normalized so that the maximum due to the component ν_1'' has a value of 1.00 at 295°K. [b] sh = shoulder. [c] Band height at point of inflection.

solid structure occurred after extended periods at low temperature, the [PtCl(QP)]Cl sample was cooled in liquid nitrogen for 75 hr. After this time, the low-temperature spectrum was remeasured, but no difference was found from the spectrum obtained after only 30 min of cooling.

Complexes [Ni(CN)₂(PhPR₂)₃]. The electronic spectra of [Ni(CN)₂{PhP(OEt)₂}₃] have been measured at 295° and 77°K, and the lowest energy ligand-field band has a very strong temperature dependence; the ligand-field spectrum as a function of temperature is shown in Figure 7. The two room-temperature bands (at 24.0 and 27.5 kcm^{-1}) appear to merge as the temperature is decreased, and a single symmetrical band is observed at 77°K. At this temperature the band position is 25.7 kcm^{-1}, nearly equidistant between the two room-temperature bands. A weak shoulder also appears in the low-temperature spectrum at *ca.* 30.0 kcm^{-1}.

The assignment of the ligand-field spectrum of [Ni(CN)₂{PhP(OEt)₂}₃], which possesses approximately D_{3h} symmetry,[15] is analogous to that given for the [MX(L'L₃)]⁺ complexes. The band which exhibits two components at room temperature and becomes symmetrical at 77°K (ν_1) is assigned as $^1A_1' \rightarrow {}^1E'$ (xy, $x^2 - y^2 \rightarrow z^2$). The weak shoulder ($\nu_2$) which is observed at 77°K is assigned to the symmetry-forbidden transition $^1A_1' \rightarrow {}^1E''$ (xz, $yz \rightarrow z^2$).

The similar compound [Ni(CN)₂(PhPMe₂)₃] also exhibits an asymmetric ν_1 at room temperature, with two components at 21.7 and 24.1 kcm^{-1}. This splitting of 2.4 kcm^{-1} is less than the 3.5 kcm^{-1} found for [Ni(CN)₂{PhP(OEt)₂}₃].

Discussion

The spectral results reported here are in agreement with the original studies of these compounds at room temperature,[7,12,14] and the spectrochemical series order-
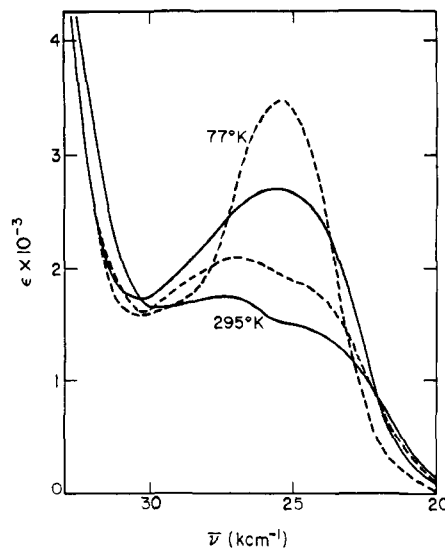

Figure 7. Ligand-field spectrum of [Ni(CN)₂{PhP(OEt)₂}₃] in EPA solvent as a function of temperature (°K).

ing is maintained in the low-temperature spectra. Both ligand-field bands exhibit the energy ordering CN > Cl > Br > I. Upon changing the tripod ligand, the ordering is QP > TAP > QAS > TAA > TSP > TSeP.

The position of the ligand-field bands is strongly dependent on the anionic ligand X in trigonal-bipyramidal complexes [NiX(L'L₃)]⁺, but not in square-pyramidal compounds [NiX(diars)₂]⁺ (diars = *o*-phenylenebis-dimethylarsine, X = halide or cyanide).[23] The crucial factor is thought to be the degree of occupancy of the d_{z^2} orbital in the complex. In the trigonal-bipyramidal complexes, the lowest energy ligand-field transition (ν_1) is from a ($d_{x^2-y^2}$, d_{xy}) level which is approximately independent of X, to a d_{z^2} level, the energy of which is strongly dependent on the σ-donor ability of the X group.

Theoretical treatments[12,18] of trigonal-bipyramidal complexes of low-spin d⁸ metal ions predict a single band ν_1, and the splitting of this band, which is observed in a number of complexes, has been attributed to a static distortion involving the equatorial ligand atoms.[6] This distortion would destroy the threefold rotation axis of the molecule and thus lift the degeneracy of all electronic levels that were degenerate under C_{3v} symmetry. The observation that the asymmetric or split band becomes more narrow when solutions are cooled to liquid nitrogen temperature prompted us to reexamine the above conclusion. Possible explanations[29] for this unusual spectroscopic behavior in solution could involve (1) a Jahn-Teller distortion of the doubly degenerate excited state or (2) a temperature-dependent static distortion of the ground state.

Dynamic Jahn-Teller Effect. The dynamic Jahn-Teller effect could account for both the splitting of the low energy band ν_1 and its temperature dependence in solution. We consider, therefore, how electronic levels

(29) The a¹E and ¹E′ levels, in C_{3v} and D_{3h} symmetry, respectively, will be unaffected in terms of degeneracy by first-order spin-orbit coupling, whereas the a³E levels will split into $\Gamma_1 + \Gamma_2 + 2\Gamma_3$ (*i.e.* A₁ + A₂ + 2E) and ³E′ will give $\Gamma_3 + \Gamma_4 + \Gamma_5 + \Gamma_6$ (*i.e.*, E′ + A₁″ + A₂″ + E″). Thus the split low-energy band might arise from transitions to levels derived from both a¹E (or ¹E′) and a³E (or ³E′) levels. The observed temperature dependence precludes this explanation, as the spin-orbit coupling Hamiltonian is not affected by temperature changes.

Table III. Electronic and Vibrational States for Trigonal-Bipyramidal Molecules

Point group	Electronic function[a]	Symmetric direct products	Normal, vibrational modes
D_{3h}	A_1'	$(A_1')^2 = A_1'$	$2\alpha_1'$, $2\alpha_2''$,
	E'	$(E')^2 = A_1' + A_2' + E'$	$3\epsilon'$, ϵ''
	E''	$(E'')^2 = A_1' + A_2' + E'$	
C_{3v}	A_1	$(A_1)^2 = A_1$	$4\alpha_1$, 4ϵ
	E	$(E)^2 = A_1 + A_2 + E$	

[a] Only electronic states appropriate to low-spin d^8 complexes are considered.

Jahn–Teller active vibrations are $2\alpha_1'$ and $3\epsilon'$, and interaction with the ϵ' vibrations will result in a splitting of both E$'$ and E$''$ levels. In C_{3v} complexes, all eight normal vibrations, $4\alpha_1$ and 4ϵ will interact to first order with excited E states, and the ϵ distortions will lift the degeneracy of the E levels.

The interaction of an $\epsilon('$) vibrational mode with an E electronic state has been treated previously in detail,[30,31] and it leads to a double-valued potential energy surface given in terms of polar coordinates (ρ, θ) by

$$V(\rho, \theta) = (^1/_2)\mu\omega_\epsilon{}^2\rho^2 \pm A\rho \qquad (1)$$

Table IV. Molecular Structure Data Indicating Distortions from C_{3v} or D_{3h} Symmetry for Some Complexes [MX(L'L$_3$)]Y and [Ni(CN)$_2$(PhPR$_2$)$_3$]

Complex[a]	Angles L'–M–X, deg		Angles L–M–L, deg		Bond lengths M–L, Å	
[Ni(CN)(TAP)]ClO$_4$[9]	P–Ni–C	178.4 (8)	As$_1$–Ni–As$_2$	119.6 (2)	Ni–As$_1$	2.317 (6)
			As$_1$–Ni–As$_3$	120.3 (2)	Ni–As$_2$	2.313 (5)
			As$_2$–Ni–As$_3$	118.1 (3)	Ni–As$_3$	2.338 (6)
[NiCl(TSP)]ClO$_4$[10]	P–Ni–Cl	178.5 (3)	S$_1$–Ni–S$_2$	120.6 (2)	Ni–S$_1$	2.269 (6)
			S$_1$–Ni–S$_3$	112.1 (3)	Ni–S$_2$	2.242 (8)
			S$_2$–Ni–S$_3$	127.1 (3)	Ni–S$_3$	2.290 (7)
[PtI(QAS)]BPh$_4$[8]	As$_1$–Pt–I	177.8 (1)	As$_2$–Pt–As$_3$	119.3 (1)	Pt–As$_2$	2.488 (3)
			As$_2$–Pt–As$_4$	117.0 (1)	Pt–As$_3$	2.450 (3)
			As$_3$–Pt–As$_4$	122.1 (1)	Pt–As$_4$	2.428 (4)
[Ni(CN)$_2${PhP(OEt)$_2$}$_3$][15]	C$_1$–Ni–C$_2$[b]	170.8 (8)	P$_1$–Ni–P$_2$	113.0 (2)	Ni–P$_1$	2.289 (5)
			P$_1$–Ni–P$_3$	113.5 (2)	Ni–P$_2$	2.205 (6)
			P$_2$–Ni–P$_3$	133.5 (2)	Ni–P$_3$	2.189 (6)
[Ni(CN)$_2$(PhPMe$_2$)$_3$][16]	C$_1$–Ni–C$_2$[b]	176.5 (4)	P$_1$–Ni–P$_2$	116.75 (11)	Ni–P$_1$	2.223 (3)
			P$_1$–Ni–P$_3$	127.01 (11)	Ni–P$_2$	2.261 (3)
			P$_2$–Ni–P$_3$	116.21 (11)	Ni–P$_3$	2.223 (3)

[a] References to full structural details are given as superscripts. [b] For [Ni(CN)$_2$(PhPR$_2$)$_3$], L' refers to an axial cyano carbon.

of the trigonal-bipyramidal complexes are affected by distortions of the nuclear framework, with special reference to doubly degenerate excited states. The electrons of these complexes can be regarded as moving in a potential $V(r, Q)$ which is a function of electron coordinates r_i and nuclear displacement coordinates Q_i. The total Hamiltonian in C_{3v} or D_{3h} symmetry is given by

$$\mathcal{H} = \mathcal{H}_e + \mathcal{H}_v + \mathcal{H}_{ev}$$

Where $\mathcal{H}_e$ and $\mathcal{H}_v$ are the electronic and vibrational Hamiltonians, respectively. The electronic-vibrational (vibronic) interaction Hamiltonian $\mathcal{H}_{ev}$ is given to first order in Q_i by

$$\mathcal{H}_{ev} = \sum_i \left(\frac{\partial \mathcal{H}}{\partial Q_i}\right)_0 Q_i$$

Those vibrations which are Jahn–Teller active have nonvanishing matrix elements of the form $\langle k|\sum_i (\partial\mathcal{H}/\partial Q_i)_0|k\rangle$, where k represents an electronic state.[30] If Q_i (and consequently $(\partial\mathcal{H}/\partial Q_i)_0$) and $|k\rangle$ transform as components of the irreducible representations Γ' and Γ, respectively, then for the matrix element to be nonzero, Γ' must be contained in the symmetric direct product $[\Gamma]^2$. Some relevant symmetric products and the irreducible representations spanned by normal vibrational modes are given in Table III. The totally symmetric ground states of both the C_{3v} and D_{3h} complexes can only suffer a totally symmetric distortion which will not lower the symmetry of the systems. For the E$'$ and E$''$ excited states in a D_{3h} compound, the

(30) M. D. Sturge, *Solid State Phys.*, **20**, 91 (1967).

where $V(\rho, \theta)$ is the potential energy, μ is the reduced mass of the vibrating atoms, ω_ϵ is the frequency the $\epsilon('$) normal mode, and A is a measure of the strength of the electron–lattice coupling (as the E term will be split by $2A$ on unit distortion). This potential surface has a Jahn–Teller energy of $-\delta E = -A^2/2\mu\omega_\epsilon{}^2$ at a coordinate position $\rho_0 = |A|/\mu\omega_\epsilon{}^2$. Slonczewski[32] has shown that when an E electronic level interacts with several doubly degenerate vibrational modes, such a system behaves in a similar fashion to one involving a single pair of ϵ modes. This result is fortunate as, for example, the interaction of the four ϵ modes in C_{3v} complexes with E electronic levels involves Jahn–Teller movements in eight-dimensional space.

The above discussion of Jahn–Teller interaction of electronic and vibrational levels applies to molecules of rigorous C_{3v} or D_{3h} symmetry. Structural determinations are now available for several of the trigonal-bipyramidal compounds considered here, and in Table IV are given relevant bond angles and lengths that show deviations in structure from C_{3v} or D_{3h} microsymmetry. These complexes all have A ground states, and distortions in the solid state could be caused by packing interactions in the lattice and the conformations of the multidentate ligands, or else by the energy-favorable mixing of the ground and excited states arising from the second-order Jahn–Teller effect.[33] In contrast, low-spin d^7 ions in a trigonal-bipyramidal environment have doubly degenerate ground states, and the large distor-

(31) A. D. Liehr, *Progr. Inorg. Chem.*, **3**, 281 (1962); **4**, 455 (1962); **5**, 385 (1963).

(32) J. C. Slonczewski, *Phys. Rev.*, **131**, 1596 (1963).

(33) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

tions observed in compounds such as [CoCl(QP)]-BPh$_4$[34] and [NiBr$_3$(PhPMe$_2$)$_2$][35] have been attributed to a static Jahn–Teller effect.

From Table IV it is seen that the two complex cations [Ni(CN)(TAP)]$^+$ and [PtI(QAS)]$^+$ are only slightly distorted, while [NiCl(TSP)]$^+$ is less regular owing to the relative orientation of two of the S-bonded methyl groups. These three cations are not as distorted as [Ni(CN)$_2${PhP(OEt)$_2$}$_3$] and [Ni(CN)$_2$(PhPMe$_2$)$_3$], which contain unidentate ligands, presumably owing to the steric requirements of the multidentate ligands. The distortions found in the solid state are not necessarily present in solution, where lattice restraints are removed, nor in a glass matrix at low temperature, where the complexes have solvent molecules as near neighbors rather than other large complex cations. The possibility of the splitting of ν_1 being due to static distortion in solution at room temperature is considered later, but provided that the excited levels that are orbitally degenerate in rigorous C_{3v} or D_{3h} microsymmetry are nearly degenerate in the complexes considered here, the Jahn–Teller approach to a discussion of the ligand-field spectra will be valid.

Transitions ν_1 and ν_2 are from A ground states to E excited states suffering from dynamic Jahn–Teller distortions. When the doubly degenerate excited level is coupled to a single ϵ vibration, then the A $\rightarrow$ E transition can be represented schematically as in Figure 8. Although at 0°K all transitions arise from the ground-state vibrational level, the most probable transition is not at $\rho = 0$ but at a higher value of $\rho = (\hbar/4\mu\omega_\epsilon)^{1/4}$ where there is more phase space.[30,36] An A $\rightarrow$ E transition is therefore expected to consist of two bands, and the separation $\Delta\bar{\nu}^0$ at 0°K will be $A(2\hbar/\mu\omega_\epsilon)^{1/2} = 2 \cdot (\hbar\omega_\epsilon\delta E)^{1/2}$. For compounds of C_{3v} or D_{3h} microsymmetry, a sum over all the Jahn–Teller-active ϵ or ϵ' vibrations, respectively, is taken, and $(\Delta\bar{\nu}^0)^2 = 2A^2 \cdot \hbar/\mu\omega_\epsilon$ is replaced by

$$\sum_{i=1}^{n} (2A_i{}^2\hbar/\mu_i\omega_{\epsilon i})$$

At higher temperatures, excited vibrational levels in the electronic ground state become occupied and the mean value of ρ increases.[30,36] The equation for the splitting of the two bands now contains a temperature factor and is given by

$$(\Delta\bar{\nu})^2 = \sum_{i=1}^{n} (2A_i{}^2\hbar/\mu_i\omega_{\epsilon i}) \coth (\hbar\omega_{\epsilon i}/2kT) \qquad (2)$$

If a "pseudo-centrifugal" term[32] is included in the Jahn–Teller treatment to correct for nuclear kinetic energy, then the higher energy peak should be somewhat sharper than the lower, but the overlap of the two bands ν_1' and ν_1'' contributing to ν_1 is such that accurate width measurements by Gaussian analysis are difficult to obtain.

The magnitude of the splitting of the ligand-field band ν_1 depends on the metal, the multidentate or unidentate organic ligand, the anion X, and the temperature. From eq 2, the splitting $\Delta\bar{\nu}_1$ is expected to increase as the values of A_i and T increase and as $\omega_{\epsilon i}$ and μ_i decrease. The summation in eq 2 involves three

(34) T. L. Blundell, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 763 (1967).

(35) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, 9, 453 (1970).

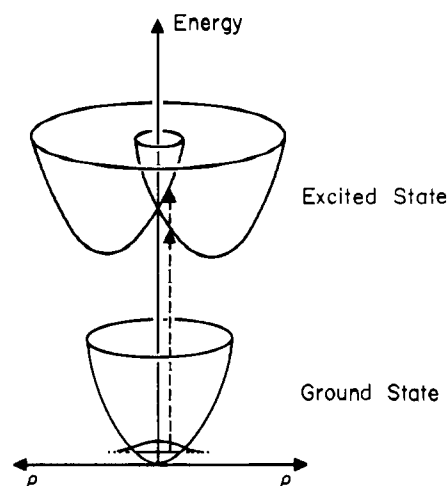(36) M. C. M. O'Brien, *Proc. Phys. Soc.*, 86, 847 (1965).

Figure 8. Potential energy surfaces for an A ground state and E excited state, the latter suffering a Jahn–Teller distortion owing to interaction with a single ϵ vibration; ρ represents the radial polar coordinate. The most probable transition is shown as a vertical dotted line which can end on either of the two potential sheets of the excited state.

(for D_{3h} species) or four (C_{3v}) vibrations for which the values of A_i and $\omega_{\epsilon i}$ are unknown, the latter because vibrations of excited rather than ground electronic states are being considered. As only one parameter, *viz.*, $\Delta\bar{\nu}_1$, is measured experimentally, only a qualitative discussion of the factors affecting the magnitude of this splitting is possible.

Let us assume that eq 2 can be simplified so that at temperature T

$$(\Delta\bar{\nu})^2 = [\sum_{i=1}^{n} (2A_i{}^2\hbar/\mu_i\omega_{\epsilon i})] \coth (\hbar\bar{\omega}_\epsilon/2kT)$$

$$= (\Delta\bar{\nu}^0)^2 \coth (\hbar\bar{\omega}_\epsilon/2kT) \qquad (3)$$

where $\bar{\omega}_\epsilon$ must be regarded as a pseudovibrational frequency that could equalize the right-hand sides of eq 2 and 3. As $T \rightarrow 0$, $\coth (\hbar\bar{\omega}_\epsilon/2kT) \rightarrow 1$ and $(\Delta\bar{\nu})^2 \rightarrow (\Delta\bar{\nu}^0)^2$, but as $T \rightarrow \infty$, $\coth (\hbar\bar{\omega}_\epsilon/2kT) \rightarrow \infty$. The shape of the curve relating $(\Delta\bar{\nu}_1)^2$ to temperature for [PtCl(QP)]Cl (Figure 5) is different from that expected[37] for the simple coth function, eq 3. The deviation in direction of the curve at higher temperatures could well indicate that if a Jahn–Teller approach is appropriate here, eq 3 is only valid when *one* vibration is involved in eq 2, but is invalid when a summation over four vibrations (for C_{3v} symmetry) is necessary; *i.e.*, the pseudovibrational frequency $\bar{\omega}_\epsilon$ is temperature dependent.

The dependence of $\Delta\bar{\nu}_1$ on the metal M, organic ligand, or anion X is readily seen at room temperature. The most important terms at constant temperature in eq 2 are the electronic-vibrational coupling parameters A_i and the vibrational frequencies $\omega_{\epsilon i}$, while values of μ_i should not vary by more than *ca.* 10% between various compounds. For complexes of the ligands QP and QAS with a given anion X, $\Delta\bar{\nu}_1$ increases Ni < Pd < Pt as expected for decreasing values of $\omega_{\epsilon i}$. The relative importance of the $\omega_{\epsilon i}$ terms is, however, difficult to evaluate, as there is a decrease in splitting Cl > Br > I for palladium and platinum compounds, even
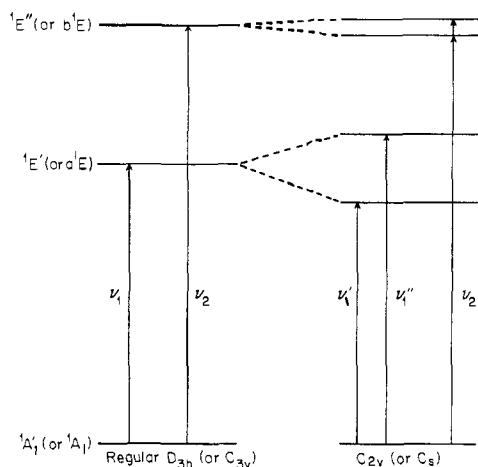
(37) P. Day and E. A. Grant, *Chem. Commun.*, 123 (1969).

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Figure 9. Effect of distortion on the ligand-field levels of D_{3h} and C_{3v} complexes.

though ω_{ei} values are becoming smaller, but a general increase CN < Cl < Br < I for the nickel complexes of the multidentate ligands; presumably changes in A_i terms are dominant.

The separation $\Delta\bar{\nu}_1$ at room temperature is much larger for the complexes [Ni(CN)$_2$(PhPR$_2$)$_3$] than for the other nickel complexes containing multidentate ligands. The former compounds must possess ϵ' vibrations in the excited E' state of relatively low frequency and/or large coupling parameters A_i.

The ν_2 band in the solution spectra of the various trigonal-bipyramidal complexes does not show a double peak, even when it is well resolved from charge-transfer transitions. The excited strong-field configuration for the ν_1 transition is $(e'')^4(e')^3(a_1')^1$ and for ν_2 is $(e'')^3(e')^4(a_1')^1$ in D_{3h} symmetry; in a C_{3v} environment, a_1', e', and e'' are replaced by a_1, e_a, and e_b, respectively. In D_{3h} and C_{3v}, both of these excited configurations will couple with the same vibrations (see Table III), and consequently the relative splittings of the bands ν_1 and ν_2 will depend on the coupling parameters A_i. The antibonding character of the e' or e_a (xy, $x^2 - y^2$) orbital depends on the σ- and π-overlap characteristics of the surrounding ligands, whereas the e'' or e_b (xz, yz) orbital only participates in π overlap and is less antibonding. Electrons in orbitals that participate in σ bonding are expected to be more sensitive to distorting ϵ' or ϵ vibrations than those in π-bonding only orbitals,[30] and ν_1 should be more asymmetric than ν_2. There is some experimental evidence for this conjecture in terms of Jahn–Teller distortions of trigonal-bipyramidal complexes with doubly degenerate *ground* states. Thus, the complex [TiBr$_3$(NMe$_3$)$_2$] has a singly occupied e'' orbital and Br–Ti–Br angles[38] of 121.3, 117.5, and 117.5°, whereas [CrCl$_3$(NMe$_3$)$_2$] has a singly occupied e' orbital with Cl–Cr–Cl angles[39] of 124.2, 111.6, and 111.6°; *i.e.*, the distortion from D_{3h} toward C_{2v} symmetry is more pronounced in the latter case.

There are a few other examples of transitions to doubly degenerate levels where the splitting of bands has been ascribed to a dynamic Jahn–Teller effect, and most of these involve the $T_{2g} \rightarrow E_g$ transitions of Ti^{3+} (d^1) or Fe^{2+} (high-spin d^6) ions in an octahedral en-

vironment.[30,35,40] As the ground T_{2g} term is subject to spin–orbit coupling and it only interacts weakly with vibrational motions, the spectra obtained approximate to those expected for A $\rightarrow$ E transitions. When the Ti^{3+} or Fe^{2+} ion is in a cubic (or trigonal) lattice site, the degeneracy of the excited E_g term will not be lifted by site-symmetry effects and the splitting of the $T_{2g} \rightarrow E_g$ band decreases with temperature as predicted for a Jahn–Teller interaction. The A $\rightarrow$ E transitions found in D_{4h} square-planar complexes[41] are not strictly comparable with those considered in this paper, unless couplings to the nondegenerate β_{1g} and β_{2g} distortions are of the same magnitude.

Ground-State Distortion. If a molecule of D_{3h} (or C_{3v}) symmetry suffers a ground-state distortion, the degeneracy of electronic excited states would be lifted as shown schematically in Figure 9. The splitting of the $^1E'$ (or a^{1}E) level is expected to be larger than that of the $^1E''$ (or b^{1}E) level as the d$_{z^2-y^2}$ and d$_{xy}$ orbitals are more sensitive to distortion than the d$_{zz}$ and d$_{yz}$ orbitals.

There are only small changes in the shapes of band ν_1 in the thin-film spectra of a variety of complexes [MX(L′L$_3$)]Y, some of which are known to be slightly distorted in the solid state, after cooling from 295 to 77 or 100°K. The asymmetry or splitting of ν_1 in the solid-state spectra thus appears to be due primarily to a ground-state distortion. The small effect of temperature on the spectra indicates that the Jahn–Teller description is not appropriate for these complexes in the *solid* state. A similar lack of sensitivity to temperature was found[10b] for the splitting of the $^5T_{2g}$ (^{5}D) $\rightarrow$ ^5E_g (^{5}D) transition in the spectrum of solid FeF$_2$, where the iron atoms are in a low-symmetry orthorhombic site. On the other hand, the analogous band in the spectra of MgO:Fe^{2+} and FeSiF$_6$·6H$_2$O shows a reduction in splitting with temperature as the iron atoms are in cubic and trigonal environments, respectively, and the Jahn–Teller approach is valid.

The complex [Ni(CN)$_2$\{PhP(OEt)$_2$\}$_3$] is more distorted towards C_{2v} symmetry than its PhPMe$_2$ analog in the solid state, and it is found that in solution $\Delta\bar{\nu}_1$ is greater for the former complex. These separations are larger than those found in the spectra of the other nickel complexes, which are less distorted in the solid state. The irregularity found in the molecular structure of [NiCl(TSP)]$^+$ does not give rise,[42] however, to a large $\Delta\bar{\nu}_1$ in solution compared with the other [NiX(L′L$_3$)]$^+$ complexes.

If the structures remain distorted in solution at low temperature, the two components ν_1' and ν_1'' should be better resolved. The band ν_1, however, becomes more symmetrical, and thus if ground-state distortion is to be used to provide an explanation for the asymmetry at room temperature, then there must be a difference in structure between the complex at 295 and at 77°K (or 100°K).

The energy difference between the idealized trigonal-bipyramidal and square-pyramidal structures of five-

(38) B. J. Russ and J. S. Wood, *Chem. Commun.*, 745 (1966).
(39) G. W. A. Fowles, P. T. Greene, and J. S. Wood, *ibid.*, 971 (1967).

(40) (a) H. D. Koswig, V. Petter, and W. Ulrici, *Phys. Status Solidi*, 24, 605 (1967); (b) G. D. Jones, *Phys. Rev.*, 155, 259 (1967); (c) G. Winter, *Aust. J. Chem.*, 21, 2859 (1968).
(41) C. J. Ballhausen, *Theor. Chim. Acta*, 3, 368 (1965).
(42) G. Dyer and D. W. Meek, *Inorg. Chem.*, 4, 1398 (1965); the solution spectrum of [NiCl(TSP)]ClO$_4$ could not be measured at low temperature owing to insolubility or decomposition in the appropriate solvents.

coordinate molecules, particularly those containing unidentate ligands, is usually small.[43] As the potential energy surface connecting these two forms is irregular,[43] molecules of intermediate structure could be favored under certain solvent and temperature conditions. The temperature dependence of band ν_1 using the ground-state distortion description could be analyzed in terms of an equilibrium between the two forms: regular trigonal-bipyramid (D_{3h} or C_{3v}) $\rightleftarrows$ distorted trigonal-bipyramid (C_{2v} or C_s). At temperatures between 295 and 77° (or 100°K), an equilibrium mixture would be obtained and three spectral bands in the region of ν_1 would be predicted. In no case, however, have more than two bands been observed.

A more satisfactory explanation of the temperature dependence of ν_1 involving the ground-state distortion model is to consider the possibility that species of intermediate geometry are present at intermediate temperatures. It is likely that the energy differences between the two "limiting"structures, D_{3h} (or C_{3v}) and C_{2v} (or C_s), are rather small and that solvent–solute interactions, for example, could alter significantly the shape and the equilibrium position of the ground-state potential function. Thus a variety of stable structures with differing degrees of distortion could exist, and the precise structure would be a function of temperature. The appearance of ν_1 would then reflect the amount of distortion in this intermediate structure, rather than simply being the superposition of bands due to the two "limiting" structures.

Comparison of Dynamic Jahn–Teller and Ground-State Distortion Models. The interpretations involving Jahn–Teller distortions of excited states and variable ground-state distortions of complexes in solution are not necessarily mutually exclusive, because even if there is a ground-state distortion that lifts the degeneracy of excited E(') levels, the separation of these levels may be sufficiently small for Jahn–Teller effects to operate. If, however, the ground state distortion is large, the splitting of E(') levels might be such that a Jahn–Teller approach is invalid; it is difficult to estimate how large these distortions must be.

To explain the temperature dependence of $\Delta\bar{\nu}_1$, the ground-state distortion approach requires a progressive change in solvent–solute interactions, resulting in more symmetrical complexes at low temperature, whereas the Jahn–Teller effect predicts a reduction in $\Delta\bar{\nu}_1$ due to the coth ($\hbar\omega_{ei}/2kT$) term in eq 2. The curve in Figure 5 is not a simple coth function of the type given in eq 3, but the experimental result may

just reflect the complexity of a system requiring a summation over four (rather than one) vibrations. Liquid helium data are necessary for conclusive discussions on the validity of eq 2 and 3.

A disadvantage of the ground-state distortion interpretation is that $\Delta\bar{\nu}_1$ at room temperature would be expected to vary greatly with the nature of the solvent if solvent–solute interactions were important in causing a deviation from D_{3h} or C_{3v} microsymmetry. Experiments on [PtCl(QP)]Cl, however, indicate that $\Delta\bar{\nu}_1$ is insensitive to the nature of several solvents with varying dielectric constants. One might also expect $\Delta\bar{\nu}_1$ to increase for some complexes as the temperature is lowered because the nature of the solute–solvent interactions would be complex dependent, but this result was not found experimentally.

The complexes [MCl(P·As$_2$P)]Cl (M = Ni, Pd, Pt) have C_s rather than C_{3v} microsymmetry, as a C_3 axis is no longer present. The shapes of transitions ν_1 at 100°K for the palladium and platinum complexes are distinctly different from those of the analogous QP and QAS complexes in solution. It is interesting to note that none of the band shapes of [PtCl(QP)]Cl shown in Figure 3 closely resembles the low-temperature spectrum of [PtCl(P·As$_2$P)]Cl, which is known to have a C_s structure.

Summary

The asymmetry of band ν_1 in the *solid-state* electronic spectra of complexes [MX(L'L$_3$)]Y is primarily due to a ground-state distortion of the complexes, presumably because of lattice packing interactions and the effect of ligand conformations or because of the second-order Jahn–Teller effect. Both the dynamic Jahn–Teller and the temperature-dependent ground-state distortion models provide reasonable interpretations of the asymmetry or splitting of band ν_1 in the *solution* spectra of complexes [MX(L'L$_3$)]Y and [Ni(CN)$_2$(PhPR$_2$)$_3$].[44]

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

(44) The electronic spectra of several other trigonal-bipyramidal complexes, such as [NiBr{(Ph$_2$LCH$_2$CH$_2$)$_3$N}]BPh$_4$ (L = P, As)[45] and [Ni(CN)$_2${(MeO)$_3$P}$_3$],[46] show asymmetric bands ν_1. It is most probable that these band envelopes will also become more symmetrical at low temperature in solution.

(45) L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 89, 2235 (1967); 90, 5443 (1968).

(46) K. J. Coskran, J. M. Jenkins, and J. G. Verkade, *ibid.*, 90, 5437 (1968).