

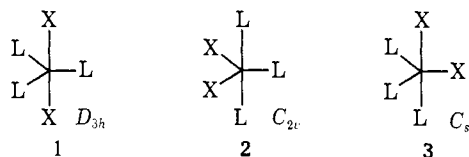
Crystal and Molecular Structure of Dibromotris(trimethylphosphine)nickel(II). Electronic Structures and Stereochemistries of the Complexes $[\text{NiX}_2(\text{PMe}_3)_3]$

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Abstract: The crystal and molecular structure of dibromotris(trimethylphosphine)nickel(II) has been determined from three-dimensional X-ray data collected by counter methods. Full-matrix least-squares refinement of the structure has led to a final conventional R factor on F of 7.3%. The crystals have monoclinic symmetry, space group $P2_1/c$, with eight molecules in a unit cell of dimensions $a = 16.519(2) \text{ \AA}$, $b = 12.956(1) \text{ \AA}$, $c = 17.482(2) \text{ \AA}$, and $\beta = 102.17(2)^\circ$. The crystallographically derived density is $1.62(1) \text{ g cm}^{-3}$. The crystal chemical unit consists of two well-separated monomeric molecules. In each of these five-coordinate molecules the nickel atoms are at the center of cis trigonal bipyramids in approximate C_{2v} site symmetries. One nickel, one phosphorus, and two bromine atoms lie in the equatorial plane with the remaining two phosphorus atoms occupying apical positions, equidistant from the nickel atom. Solid state and solution electronic spectra of $[\text{NiX}_2(\text{PMe}_3)_3]$ ($X = \text{Cl}, \text{Br}, \text{I}$) have been measured at 295 and 77°K. Similarities between these spectra indicate that all three compounds have a C_{2v} structure in the solid state and also in solution (at 295°K) provided an excess of PMe_3 is present to prevent dissociation to $\text{trans}[\text{NiX}_2(\text{PMe}_3)_2]$. On cooling solutions of the bromo and iodo compounds containing excess PMe_3 to 77°K, the predominant nickel species appears to be the $[\text{Ni}(\text{PMe}_3)_3]^{2+}$ cation. The difference in stereochemistry between $[\text{NiX}_2(\text{PMe}_3)_3]$ ($X = \text{Cl}, \text{Br}, \text{I}$) and the corresponding dicyano compound, which has a distorted D_{3h} symmetry, is discussed in terms of the second-order Jahn–Teller effect.

Investigations of diamagnetic five-coordinate nickel complexes $[\text{NiX}_2\text{L}_3]$ ($X = \text{halogen or CN}$; $L = \text{phosphine, phosphite, or phosphonite}$) have shown that the stability and stereochemistry of these compounds depend on a subtle blend of electronic and steric effects.⁴ Complexes of trimethylphosphine with nickel halides^{5,6} and cyanide^{7,8} are particularly intriguing as five-coordinate structures have been found for $X = \text{Cl}, \text{Br}, \text{I}$, and CN , and yet the geometries of these compounds are not all similar. Spectroscopic and dipole moment studies⁸ indicate that $[\text{Ni}(\text{CN})_2(\text{PMe}_3)_3]$ has a distorted version of the trans trigonal bipyramidal (TBP) isomer **1**. From similar experiments with



complexes $[\text{NiX}_2(\text{PMe}_3)_3]$ ($X = \text{Cl}, \text{Br}, \text{I}$), however, Dahl concluded that the halogeno derivatives had cis TBP structures, although the isomers **2** and **3** could not be differentiated from electronic spectra.⁶ Chastain,

et al.,⁵ were able to interpret the electronic spectrum of $[\text{NiBr}_2(\text{PMe}_3)_3]$ in terms of the TBP structure **1**, but the possibility of the ground state having a cis rather than trans configuration of the bromine atoms was not ruled out.

In order to obtain more pertinent information about the ground state of the compounds $[\text{NiX}_2(\text{PMe}_3)_3]$, we have examined the crystal and molecular structure of $[\text{NiBr}_2(\text{PMe}_3)_3]$. Dahl⁶ has previously measured the room temperature solution and solid state spectra of complexes $[\text{NiX}_2(\text{PMe}_3)_3]$; in addition we have determined the low-temperature (77°K) spectra of these complexes to see if their lowest energy ligand field bands have the unusual temperature dependence found for other TBP complexes containing uni- and multidentate ligands.⁹

Experimental Section

Preparation of the Compounds. Trimethylphosphine was prepared by the method of Jensen, *et al.*,¹⁰ and stored as its silver iodide complex in the dark and in a cold room. The phosphine was regenerated on heating this complex under nitrogen.

Dibromotris(trimethylphosphine)nickel(II), $[\text{NiBr}_2(\text{PMe}_3)_3]$, and Diiodotris(trimethylphosphine)nickel(II), $[\text{NiI}_2(\text{PMe}_3)_3]$. These complexes were prepared by the methods of Dahl.⁶ The sample of $[\text{NiBr}_2(\text{PMe}_3)_3]$ used for the X-ray crystallographic investigation was prepared according to Chastain, *et al.*⁵ Suitable crystals were obtained by dissolving the complex in the minimum amount of dichloromethane, adding petroleum ether (50–115°), and allowing the solution to reduce in volume on standing over concentrated sul-

- (1) California Institute of Technology.
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- (4) E. C. Alyea and D. W. Meek, *J. Amer. Chem. Soc.*, **91**, 5761 (1969), and references therein.
- (5) B. B. Chastain, D. W. Meek, E. Billig, J. E. Hix, Jr., and H. B. Gray, *Inorg. Chem.*, **7**, 2412 (1968).
- (6) O. Dahl, *Acta Chem. Scand.*, **23**, 2342 (1969).
- (7) K. A. Jensen and O. Dahl, *Acta Chem. Scand.*, **22**, 1044 (1968).
- (8) A. Merle, M. Dartiguenave, Y. Dartiguenave, J. W. Dawson, and H. B. Gray, *J. Coord. Chem.*, in press.

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Table I. General Physical Data and Analyses of Complexes $[\text{NiX}_2(\text{PMe}_3)_3]$ ($X = \text{Br}, \text{I}$)

Complex	Color	Dec pt, ^a °C	Mol wt		Dipole moment (D)	μ_{eff} (295°K), BM	% C		% H		% X	
			Calcd	Found			Calcd	Found	Calcd	Found	Calcd	Found
$[\text{NiBr}_2(\text{PMe}_3)_3]$	Blue-black	145–150	443	421	6.3	0.65	24.19	24.10	6.09	6.19	35.8	36.0
$[\text{NiI}_2(\text{PMe}_3)_3]$	Green-black	165–170	541	525	4.7	0.58	19.99	19.48	5.03	5.09	46.9	47.6

^a In a sealed capillary tube.

furic acid in a closed vessel. As the crystals slowly decompose with loss of PMe_3 , they were sealed in Lindermann glass capillaries for crystallographic purposes.

Dichlorotris(trimethylphosphine)nickel(II), $[\text{NiCl}_2(\text{PMe}_3)_3]$. On adding a large excess of trimethylphosphine to a solution of $[\text{NiCl}_2(\text{PMe}_3)_2]$ (ref 6) in dichloromethane a blue solution was obtained, from which a dark blue powder (mp 119–121° dec) was isolated on cooling. The $[\text{NiCl}_2(\text{PMe}_3)_3]$ so produced loses trimethylphosphine readily at room temperature, and consequently we have not been able to obtain satisfactory analyses.

Physical Measurements. Electronic spectra were measured on a Cary 14 spectrophotometer using EPA (5:5:2 mixture of diethyl ether, isopentane, and ethanol; Fluka spectroquality) solutions in 1-cm silica cells were held in a low-temperature dewar. The spectra of solid complexes were examined by using a thin film of Rhodopas (polyvinyl acetate) as a support.

Magnetic susceptibilities of the solid complexes were determined by the Faraday method using a Sétaram MTB 10-8 microbalance coupled with an Alpha electromagnet. Experimental values are the mean of three determinations at 295°K.

Dipole moments were measured using a DM 01 dipolemeter, a DFL 2 measuring cell, and benzene as the solvent. Molecular weights were determined cryoscopically in diphenyl or camphor.

Some general properties and analyses of the bromo and iodo five-coordinate compounds are given in Table I.

Results

Collection and Reduction of the X-Ray Intensity Data. Two Lindemann glass capillaries containing crystals of $[\text{NiBr}_2(\text{PMe}_3)_3]$ were examined by precession photography and they showed systematic absences uniquely consistent with space group $P2_1/c$ (no. 14). Unit cell dimensions $a = 16.519$ (2) Å, $b = 12.956$ (1) Å, $c = 17.482$ (2) Å, and $\beta = 102.17$ (2)° were obtained by least-squares refinement of the setting angles of 12 reflections accurately centered in a 3.5 mm diameter circular receiving aperture, on an Hilger and Watts four-circle, computer-controlled diffractometer ($\lambda(\text{Mo K}\alpha) 0.7107$ Å; $T = 26^\circ$). Here and elsewhere in this paper, digits in parentheses are estimated standard deviations in the least significant figures quoted and were usually derived from the inverse matrix in the course of normal least-squares refinement calculations.

Diffraction data were collected from a well-formed, dark dodecahedral crystal mounted in a random orientation on a eucentric goniometer head. Its 12 bounding faces were identified and their distances from an arbitrary crystal were measured using a calibrated graticule in a binocular microscope. The maximum crystal dimension was 0.650 mm and its volume was 0.1003 mm³. Its mosaicity was examined by means of open-counter ω -scans at a takeoff angle of 3°. Typical widths at half-height, for strong low angle reflections, ranged from 0.14 to 0.18°. Zirconium-filtered Mo $\text{K}\alpha$ X-radiation and the θ - 2θ scan technique were used to record the intensities of two equivalent members of the form for those reflections for which $0 > 2\theta \leq 46^\circ$. A symmetric scan range of 1.20° in 2θ , centered on the calculated peak position ($\lambda(\text{Mo K}\alpha) 0.7107$ Å), was

(11) T. C. Furnas, Single Crystal Orienter Instruction Manual, General Electric Co., Milwaukee, Wis.

composed of 60 steps of 1-sec duration. Stationary-crystal, stationary-counter background counts of 15 sec were measured at each end of the scan range. Reflections for which counts were greater than 10,000 per second were re-collected using nickel foil attenuators to bring them within the linear response range of the scintillation counter. The counter was located with its 5 mm diameter receiving aperture 250 mm from the crystal. During data collection the intensities of three standard reflections, monitored at regular intervals, dropped to 91% of their starting values. These observations were used to place all intensities on the same relative scale.¹² Data were corrected for Lorentz and polarization (Lp)¹³ factors and then for absorption¹⁴ ($\mu(\text{Mo K}\alpha) = 59.25 \text{ cm}^{-1}$) using Gaussian integration. Maximum and minimum values of transmission coefficients were 0.2044 and 0.1059, respectively. After averaging reflections recorded more than twice, and also those equivalent by symmetry, the data reduced to 2857 reflections of which 1586 had $F^2 > 3\sigma(F^2)$, where $\sigma(F^2)$ is defined below.¹⁵ These were the data used in final refinements of the structure parameters.

Solution and Refinement of the Structure

Full-matrix least-squares refinements¹⁶ were based on F and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $4F_o/\sigma^2(F_o^2)$ where $|F_o|$ and $|F_c|$ are observed and calculated structure amplitudes and

$$\sigma(F^2) = (c + 1/4(t_c/t_b)^2(B_1 + B_2) + pF^2)^{1/2}$$

where p is a factor introduced to avoid overweighting strong reflections, in this case = 1.15, c is the scan count, B_1 and B_2 are the first and second background counts, and t_c and t_b are scan and background counting times. The atomic scattering factors for Ni, Br, P, and C were taken from a standard tabulation.¹⁷ The effects of anomalous dispersion for nickel, bromine, and phosphorus were included in F_c ¹⁸ using Cromer's¹⁹

(12) Calculations were performed at the University of Canterbury using an IBM 360/44 computer with 32K words of core storage and twin disk drives.

(13) The data processing program HILGOUT is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens).

(14) Numerical absorption corrections were applied using program DABS which is a modified version of DATAPH (C. P. Coppens). Mathematical methods are fully described in "Crystallographic Computing," Munksgaard, Copenhagen, 1970.

(15) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(16) Structure factor calculations and least-squares refinements were carried out using program CUCLS and Fourier summations using program FOURIER. These are highly modified versions of well-known programs ORFELS (W. R. Busing, K. O. Martin, and H. A. Levy) and FORDAP (A. Zalkin), respectively.

(17) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

(18) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(19) D. J. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

Table II. Final Positional and Thermal Parameters for $[\text{NiBr}_2(\text{PMe}_3)_2]^a$

Atom	X	Y	Z	B		
Ni(1)	0.1353 (2)	0.2449 (2)	0.4068 (2)	3.12 (7)		
Br(11)	0.1196 (2)	0.4361 (2)	0.3654 (2)			
Br(12)	0.2209 (2)	0.2058 (2)	0.5342 (2)			
P(11)	0.0626 (5)	0.1464 (6)	0.3145 (5)	4.4 (2)		
P(12)	0.2508 (5)	0.2421 (6)	0.3622 (4)	3.8 (2)		
P(13)	0.0347 (4)	0.2735 (5)	0.4694 (4)	3.6 (2)		
Ni(2)	0.6581 (2)	0.2391 (2)	0.8632 (2)	3.10 (7)		
Br(21)	0.5029 (2)	0.2465 (2)	0.8051 (2)			
Br(22)	0.7415 (2)	0.2057 (2)	0.7652 (2)			
P(21)	0.6865 (5)	0.2665 (6)	0.9899 (5)	4.4 (2)		
P(22)	0.6438 (4)	0.0705 (5)	0.8716 (4)	3.6 (2)		
P(23)	0.6628 (5)	0.4039 (6)	0.8312 (5)	4.6 (2)		
C(21)	0.593 (2)	0.292 (3)	1.028 (2)	8.0 (9)		
C(22)	0.754 (2)	0.126 (2)	0.533 (2)	5.9 (8)		
C(23)	0.735 (2)	0.160 (2)	1.058 (2)	5.2 (7)		
C(24)	0.573 (2)	0.020 (2)	0.932 (2)	4.7 (6)		
C(25)	0.736 (2)	-0.004 (2)	0.902 (2)	4.6 (7)		
C(26)	0.599 (2)	0.011 (2)	0.774 (2)	5.0 (7)		
C(27)	0.766 (2)	0.460 (2)	0.842 (2)	5.8 (8)		
C(28)	0.621 (2)	0.427 (2)	0.726 (2)	5.9 (8)		
C(29)	0.603 (2)	0.494 (2)	0.880 (2)	5.7 (7)		
C(11)	0.002 (2)	0.228 (2)	0.235 (2)	5.5 (7)		
C(12)	-0.016 (2)	0.063 (3)	0.340 (2)	7.1 (9)		
C(13)	0.117 (2)	0.051 (2)	0.264 (2)	5.8 (8)		
C(14)	0.242 (2)	0.274 (2)	0.257 (2)	5.7 (7)		
C(15)	0.311 (2)	0.125 (2)	0.381 (2)	4.7 (7)		
C(16)	0.324 (2)	0.340 (2)	0.410 (2)	3.5 (6)		
C(17)	0.008 (2)	0.165 (2)	0.530 (2)	5.1 (7)		
C(18)	0.060 (2)	0.374 (2)	0.541 (2)	4.1 (6)		
C(19)	-0.066 (2)	0.321 (2)	0.416 (2)	5.2 (7)		
Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br(11)	0.0060 (2)	0.0047 (2)	0.0039 (1)	0.0003 (1)	-0.0001 (1)	0.0016 (1)
Br(12)	0.0048 (2)	0.0085 (3)	0.0024 (1)	0.0011 (2)	-0.0008 (1)	0.0008 (1)
Br(21)	0.0033 (1)	0.0085 (3)	0.0056 (2)	0.0007 (2)	-0.0003 (1)	0.0012 (2)
Br(22)	0.0040 (1)	0.0087 (3)	0.0029 (1)	0.0007 (2)	0.0004 (1)	0.0007 (1)

^a The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

values for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

and

$$R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$$

The data were used to obtain a set of normalized structure factors^{20,21} (E 's). The 398 largest E 's were chosen for sign determination by the symbolic addition procedure.²² A unique consistent set of signs was obtained for 388 reflections. The resultant E map clearly revealed the positions of the four bromine and two nickel atoms. Refinement of these coordinates with isotropic temperature factors gave values for R_1 and R_2 of 0.319 and 0.448. From this point three difference Fourier syntheses with intermediate least-squares refinements enabled the development of a model including all 30 non-hydrogen atoms of the structure. Using isotropic temperature factors, refinement of this model gave $R_1 = 0.113$ and $R_2 = 0.136$. At this stage examination of electron density maps and the isotropic temperature factors suggested that the bromine atoms might be better described by anisotropic temperature factors. Refinement of this model ultimately converged

(20) H. Hauptmann and J. Karle, "Solution of the Phase Problem. I The Centrosymmetric Crystal," American Crystallographic Association Monograph, No. 3, Pittsburgh, Pa., 1953.

(21) SHNORM is a program derived from NRC-4 (S. R. Hall and F. R. Ahmed) to calculate normalized structure factors.

(22) Symbolic addition was carried out using SAP, a program emanating from NRC-4 (S. R. Hall and F. R. Ahmed).

with $R_1 = 0.074$ and $R_2 = 0.095$. However, the strong low angle reflections showed some evidence of secondary extinction and so an isotropic extinction parameter was refined until convergence was achieved with $R_1 = 0.073$ and $R_2 = 0.094$. Shifts in the last cycle of refinement were all less than 1/100th of their estimated standard deviations. The relative weighting scheme appeared satisfactory in that the average values of the minimized function appear to be independent of $|F_o|$. The error in an observation of unit weight is 1.377. Structure factor calculations for the 1271 reflections having $F_o^2 > 3\sigma(F_o^2)$ show only one reflection for which $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$.

The top peaks of a final difference Fourier suggested that the thermal motions of the nickel atoms might be better described by anisotropic temperature factors, but it was not considered that such expensive refinements would reveal any further points of significant chemical interest. None of the remaining peaks exceeded 25% of the value at which the last carbon atom was located. Hydrogen atom positions were not established nor were their contributions included in any structure factor calculations.

The positional and vibrational parameters obtained from the final cycle of the least-squares refinement are listed in Table II. Derived root-mean-square amplitudes of vibration for the anisotropic atoms are listed in Table III, and Table IV contains final values of $|F_o|$ and $|F_c|$ for the 1586 reflections used in the refinement. (See paragraph at end of paper regarding supplementary material.)

Table III. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Br(11)	0.181 (5)	0.242 (4)	0.303 (4)
Br(12)	0.155 (5)	0.268 (4)	0.290 (4)
Br(21)	0.191 (4)	0.266 (4)	0.312 (4)
Br(22)	0.198 (4)	0.235 (4)	0.277 (4)

Description of the Structure

The crystal structure consists of well-separated molecules of $[\text{NiBr}_2(\text{PMe}_3)_3]$. There are two independent molecules in the crystal chemical unit. The closest nonbonded intermolecular distance between non-hydrogen atoms ($\text{C}(27)\cdots\text{C}(12)$) is 3.62 Å. Since bromine atoms are not involved, this eliminates the remote possibility of weak hydrogen bonding between the molecules.

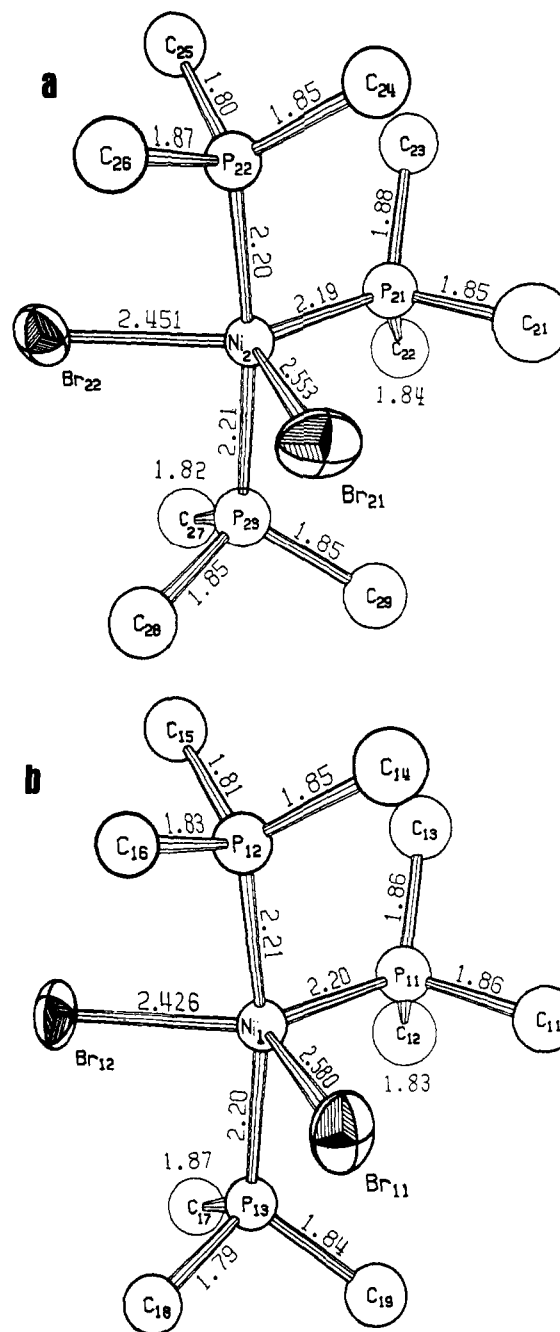
Perspective views of the independent molecules are shown in Figure 1(a) and (b) which define the atom numbering scheme used throughout the text. Bond lengths are shown and their standard deviations range from 0.004 Å for the $\text{Ni}(1)\text{--Br}(12)$ bond to 0.04 Å for the $\text{P}(21)\text{--C}(21)$ bond. Selected bond angles are given in Table V. Each nickel atom has a distorted trigonal

Table V. Bond Angles (deg) for $[\text{NiBr}_2(\text{PMe}_3)_3]$

Angles around Ni(1)		Angles around Ni(2)	
$\text{P}(11)\text{--Ni}(1)\text{--P}(12)$	96.3 (3)	$\text{P}(21)\text{--Ni}(2)\text{--P}(22)$	95.5 (3)
$\text{P}(11)\text{--Ni}(1)\text{--P}(13)$	96.3 (3)	$\text{P}(21)\text{--Ni}(2)\text{--P}(23)$	95.0 (3)
$\text{P}(11)\text{--Ni}(1)\text{--Br}(11)$	110.1 (2)	$\text{P}(21)\text{--Ni}(2)\text{--Br}(21)$	112.2 (3)
$\text{P}(11)\text{--Ni}(1)\text{--Br}(12)$	132.3 (3)	$\text{P}(21)\text{--Ni}(2)\text{--Br}(22)$	134.5 (3)
$\text{P}(12)\text{--Ni}(1)\text{--P}(13)$	167.3 (3)	$\text{P}(22)\text{--Ni}(2)\text{--P}(23)$	169.3 (3)
$\text{P}(12)\text{--Ni}(1)\text{--Br}(11)$	87.7 (2)	$\text{P}(22)\text{--Ni}(2)\text{--Br}(21)$	87.2 (2)
$\text{P}(12)\text{--Ni}(1)\text{--Br}(12)$	86.6 (2)	$\text{P}(22)\text{--Ni}(2)\text{--Br}(22)$	87.5 (2)
$\text{P}(13)\text{--Ni}(1)\text{--Br}(11)$	86.3 (2)	$\text{P}(23)\text{--Ni}(2)\text{--Br}(21)$	87.1 (2)
$\text{P}(13)\text{--Ni}(1)\text{--Br}(12)$	86.3 (2)	$\text{P}(23)\text{--Ni}(2)\text{--Br}(22)$	86.5 (2)
$\text{Br}(11)\text{--Ni}(1)\text{--Br}(12)$	117.6 (2)	$\text{Br}(21)\text{--Ni}(2)\text{--Br}(22)$	113.2 (2)
Angles around P(11)		Angles around P(21)	
$\text{C}(11)\text{--P}(11)\text{--C}(12)$	103 (1)	$\text{C}(21)\text{--P}(21)\text{--C}(22)$	101 (1)
$\text{C}(11)\text{--P}(11)\text{--C}(13)$	105 (1)	$\text{C}(31)\text{--P}(21)\text{--C}(23)$	100 (1)
$\text{C}(11)\text{--P}(11)\text{--Ni}(1)$	110 (1)	$\text{C}(21)\text{--P}(21)\text{--Ni}(2)$	112 (1)
$\text{C}(12)\text{--P}(11)\text{--C}(13)$	99 (1)	$\text{C}(22)\text{--P}(21)\text{--C}(23)$	99 (1)
$\text{C}(12)\text{--P}(11)\text{--Ni}(1)$	118 (1)	$\text{C}(22)\text{--P}(21)\text{--Ni}(2)$	121 (1)
$\text{C}(13)\text{--P}(11)\text{--Ni}(1)$	120 (1)	$\text{C}(23)\text{--P}(21)\text{--Ni}(2)$	119 (1)
Angles around P(12)		Angles around P(22)	
$\text{C}(14)\text{--P}(12)\text{--C}(15)$	106 (1)	$\text{C}(24)\text{--P}(22)\text{--C}(25)$	104 (1)
$\text{C}(14)\text{--P}(12)\text{--C}(16)$	102 (1)	$\text{C}(24)\text{--P}(22)\text{--C}(26)$	101 (1)
$\text{C}(14)\text{--P}(12)\text{--Ni}(1)$	117 (1)	$\text{C}(24)\text{--P}(22)\text{--Ni}(2)$	119 (1)
$\text{C}(15)\text{--P}(12)\text{--C}(16)$	103 (1)	$\text{C}(25)\text{--P}(22)\text{--C}(26)$	101 (1)
$\text{C}(15)\text{--P}(12)\text{--Ni}(1)$	116 (1)	$\text{C}(25)\text{--P}(22)\text{--Ni}(2)$	117 (1)
$\text{C}(16)\text{--P}(12)\text{--Ni}(1)$	111 (1)	$\text{C}(26)\text{--P}(22)\text{--Ni}(2)$	112 (1)
Angles around P(13)		Angles around P(23)	
$\text{C}(17)\text{--P}(13)\text{--C}(18)$	101 (1)	$\text{C}(27)\text{--P}(23)\text{--C}(28)$	100 (1)
$\text{C}(17)\text{--P}(13)\text{--C}(19)$	104 (1)	$\text{C}(27)\text{--P}(23)\text{--C}(29)$	106 (1)
$\text{C}(17)\text{--P}(13)\text{--Ni}(1)$	117 (1)	$\text{C}(27)\text{--P}(23)\text{--Ni}(2)$	116 (1)
$\text{C}(18)\text{--P}(13)\text{--C}(19)$	99 (1)	$\text{C}(28)\text{--P}(23)\text{--C}(29)$	103 (1)
$\text{C}(18)\text{--P}(13)\text{--Ni}(1)$	113 (1)	$\text{C}(28)\text{--P}(23)\text{--Ni}(2)$	113 (1)
$\text{C}(19)\text{--P}(13)\text{--Ni}(1)$	120 (1)	$\text{C}(29)\text{--P}(23)\text{--Ni}(2)$	116 (1)

bipyramidal coordination environment with *cis* bromine atoms in the equatorial plane. Thus the nickel sites have approximate C_{2v} symmetry and not D_{3h} as had been considered more likely. There are, however, statistically significant deviations from this implied idealized molecular shape and, furthermore, these are observed in each of two independent molecules.

The range of Ni–P bond lengths (2.19–2.21 Å) is smaller than those found in other five-coordinate com-

**Figure 1.** Perspective drawings of the two independent molecules of $[\text{NiBr}_2(\text{PMe}_3)_3]$.

plexes, such as 2.13–2.22 in $[\text{NiI}_2(\text{PPh}_2)_3]$,²³ 2.22 in $[\text{Ni}(\text{C}\equiv\text{CPh}_2)(\text{PEt}_3)_3]$,²⁴ 2.19–2.29 in $[\text{Ni}(\text{CN})_2\{\text{PPh}(\text{OEt})_2\}_3]$,²⁵ and 2.22–2.26 Å in $[\text{Ni}(\text{CN})_2(\text{PPhMe}_2)_3]$.²⁶

It is apparent from the diagrams, and from Table V, that the nickel atoms do not lie on a straight line joining the apical phosphorus atoms. This is certainly due to the apical groups experiencing greater repulsion from the nonbonded equatorial PMe_3 groups than from the equatorial bromine ligands.

Deviations from ideal trigonal equatorial plane geometry are difficult to explain without detailed knowledge of hydrogen atom positions. Shortest nonbonded

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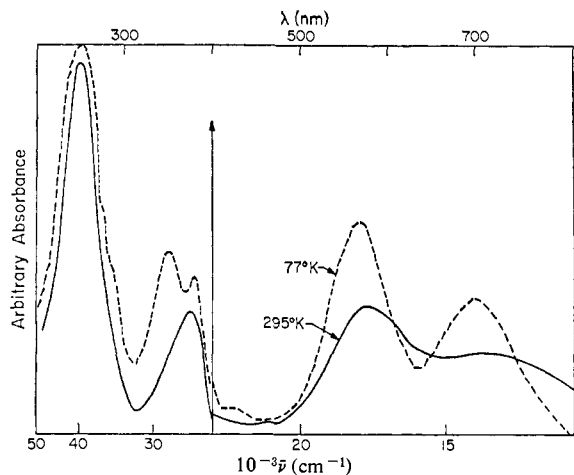


Figure 2. Temperature dependence of the solid state electronic spectrum of $[\text{NiBr}_2(\text{PMe}_3)_3]$.

intramolecular carbon-carbon distances range from 3.5 to 4.0 Å, while all apical phosphorus-bromine distances range from 3.169 to 3.328 Å. Doubtless, if hydrogen atom positions were known, hydrogen-hydrogen contacts would confirm the indication, obtained from the carbon-carbon range, that the most stable orientation of the apical PMe_3 groups is simply related to the orientation of the equatorial PMe_3 group. Given these relative orientations for the PMe_3 groups, all Ni-Br bond lengths are consistent with the equalization of all equivalent $\text{P}\cdots\text{Br}$ nonbonded interatomic repulsions as evidenced in the $\text{P}\cdots\text{Br}$ distances.

The resultant configuration has both apical groups staggered with respect to the equatorial plane ligands and eclipsed with respect to each other. Thus, for each molecule, the plane which contains the nickel, bromine, and the equatorial phosphorus atoms is an approximate mirror plane. (The nickel atoms lie within 0.01 Å of the exact plane defined by these three ligand atoms.) It is important that the same deviations from idealized trigonal bipyramidal structures are observed in both molecules.

There are statistically significant differences between the two molecular geometries (e.g., Br-Ni-Br bond angles) which must be due to different intermolecular interactions and consequently have no chemical significance, particularly in the liquid and vapor phases. In fact analyses involving two, crystallographically independent, neutral, chemically identical molecules such as these should give a good indication of the degree of distortion which can be imposed on free molecules when they are crystallized.

Electronic Absorption Spectra. The solid state spectra of the complexes $[\text{NiX}_2(\text{PMe}_3)_3]$ are presented in Table VI. The solution spectral data are given in Table VII, together with results obtained when an excess of the ligand PMe_3 was added to the EPA solutions of the nickel complexes.

The solid state spectrum of $[\text{NiBr}_2(\text{PMe}_3)_3]$ is shown in Figure 2; at 77°K, the resolution is significantly improved owing to band narrowing. The room temperature spectrum of a blue solution of $[\text{NiBr}_2(\text{PMe}_3)_3]$ containing excess PMe_3 is similar to the equivalent solid state spectrum. On lowering the temperature to 77°K, however, there are drastic changes in band positions and intensities as indicated in Figure 3. If

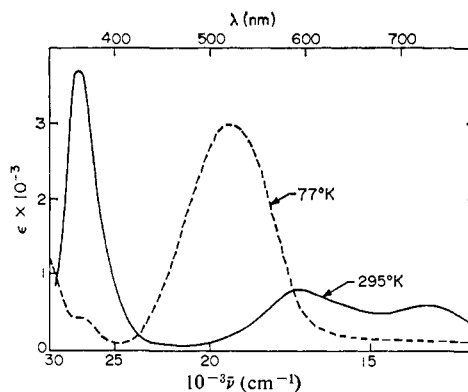


Figure 3. Temperature dependence of the electronic spectrum of $[\text{NiBr}_2(\text{PMe}_3)_3]$ in EPA solvent containing excess PMe_3 .

Table VI. Solid State Electronic Absorption Spectra of the Complexes $[\text{NiX}_2(\text{PMe}_3)_3]$

Compound	$\bar{\nu}_{\text{max}}, \text{cm}^{-1}$	
	295°K	77°K
$[\text{NiCl}_2(\text{PMe}_3)_3]$	15,100 sh ^a	15,100
	17,200	18,500
	23,200	24,500 sh
	30,300	32,300
	34,500 sh	36,400
	40,100	40,000
$[\text{NiBr}_2(\text{PMe}_3)_3]$	13,700	13,900
	17,200	17,700
	21,600	23,500
	28,000	26,400
	34,000 sh	28,500
	39,400	34,000 sh
	36,600 sh	
	39,400	
$[\text{NiI}_2(\text{PMe}_3)_3]$	13,700	13,900
	16,700	17,200
	23,800 sh	23,700
	29,500	25,400
	35,100 sh	29,700
	37,500	34,500
	39,300	

^a sh = shoulder.

the blue complex is dissolved in EPA without the benefit of excess PMe_3 , a red solution is obtained with an electronic spectrum reminiscent of that found for *trans*- $[\text{NiBr}_2(\text{PMe}_3)_2]$.⁶

The spectra (295 and 77°K) of $[\text{NiI}_2(\text{PMe}_3)_3]$ have similar features to those of the bromo analog in the solid state and in EPA solution and in EPA with excess trimethylphosphine. If the iodo complex is dissolved in PMe_3 , the 13,700- and 16,700- cm^{-1} bands disappear completely and a new band appears at 25,000 cm^{-1} in the spectrum of the resulting yellow solution; the spectrum is similar at 77°K.

When examined in the solid state in a polyvinyl acetate film, the chloro complex $[\text{NiCl}_2(\text{PMe}_3)_3]$ loses PMe_3 to give the spectrum found for *trans*- $[\text{NiCl}_2(\text{PMe}_3)_2]$.⁶ A spectrum typical of five-coordinate complexes is only obtained when excess PMe_3 is present in the polyvinyl acetate support.

Discussion

$[\text{NiBr}_2(\text{PMe}_3)_3]$. The X-ray structural results presented here show that the two independent molecules of $[\text{NiBr}_2(\text{PMe}_3)_3]$ found in the unit cell of this complex both have geometries which are somewhat distorted

Table VII. Solution Electronic Absorption Spectra of the Complexes $[\text{NiX}_2(\text{PMe}_3)_3]$

Compound	EPA only		EPA containing excess PMe_3	
	295°K	77°K	295°K	77°K
$[\text{NiBr}_2(\text{PMe}_3)_3]$	18,500 (500)	14,300 (300)	13,800 (650)	19,200 (3000)
	21,700 (450)	18,500 (900)	17,100 (950)	27,800 sh ^b (300)
	26,400 (2600)	21,700 (650)	27,800 (3700)	32,000
	29,000 (1100)	26,400 (3000)	39,200 (20,000)	38,000
	36,400 (3000)	33,300 (2400)		
	40,800 (>3000)	36,400 (5200)		
$[\text{NiI}_2(\text{PMe}_3)_3]$		40,800 (>5500)		
	13,700 (1300)	13,900 (3550)	13,700 (1200)	18,700 (4000)
	17,200 (2400)	17,200 (4400)	16,700 (2300)	29,500 sh (2200)
	18,100 (3200)	19,500 (6600)	23,800 sh (1650)	
	23,300 (2250)	23,300 (3550)	29,500 (4400)	
	26,000 (3000)	26,000 (4750)	30,800 (>30,000)	
	27,500 (3700)	29,400 (6200)		
	34,000 (~8000)			
	38,200 (~6650)			

^a Extinction coefficients ($\text{l. mol}^{-1} \text{cm}^{-1}$) in parentheses. ^b sh = shoulder.

versions of the cis TBP isomer **2**. These stereochemistries are similar to that of the complex $^{23}[\text{NiI}_2(\text{PPh}_2)_3]$ rather than the distorted trans TBP compounds $[\text{Ni}(\text{CN})_2(\text{PPhR}_2)_3]$ ($\text{R} = \text{Me}, \text{OEt}$).^{25, 26}

If a low-spin TBP complex $[\text{NiX}_2\text{L}_3]$ has the trans structure shown in **1**, the two lowest energy ligand-field bands found in its electronic spectrum should correspond to the $^1\text{A}_1' \rightarrow ^1\text{E}'$ (e' ; $d_{x^2-y^2}, d_{xy} \rightarrow a_1'$; d_{z^2}) and $^1\text{A}_1' \rightarrow ^1\text{E}''$ (e'' ; $d_{xz}, d_{yz} \rightarrow a_1'$; d_{z^2}) transitions,^{27, 28} with the latter being orbitally forbidden in D_{3h} symmetry. If the symmetry of a TBP molecule is reduced from D_{3h} to C_{2v} , then the $^1\text{E}'$ and $^1\text{E}''$ energy levels split into ($^1\text{A}_1 + ^1\text{B}_1$) and ($^1\text{B}_2 + ^1\text{A}_2$), respectively, as shown in Figure 4. It is possible, therefore, to make the following assignments in the solid state spectrum (295°K) of $[\text{NiBr}_2(\text{PMe}_3)_3]$, which has approximate C_{2v} symmetry: 13,700 cm^{-1} , $^1\text{A}_1 \rightarrow ^1\text{A}_1$ (a_1 ; $d_{x^2-y^2} \rightarrow a_1$; d_{z^2}); 17,200 cm^{-1} , $^1\text{A}_1 \rightarrow ^1\text{B}_1$ (b_1 ; $d_{xy} \rightarrow a_1$; d_{z^2}); 21,600 cm^{-1} , $^1\text{A}_1 \rightarrow ^1\text{B}_2$ (b_2 ; $d_{xy} \rightarrow a_1$; d_{z^2}). Although these transitions are all allowed in C_{2v} symmetry, the $^1\text{A}_1 \rightarrow ^1\text{B}_2$ band is weak and can only be readily observed in the spectrum obtained at 77°K. The small extinction coefficient for this band is not surprising as the $^1\text{A}_1 \rightarrow ^1\text{B}_2$ transition is derived from the orbitally forbidden $^1\text{A}_1 \rightarrow ^1\text{E}''$ in D_{3h} symmetry.

For $[\text{NiBr}_2(\text{PMe}_3)_3]$ with C_{2v} symmetry a maximum of eight ligand $\rightarrow \text{Ni}(d_z)$ transitions is allowed, *viz.*, three $\text{Br}(p\pi) \rightarrow \text{Ni}$, two $\text{Br}(p\sigma) \rightarrow \text{Ni}$, and three $\text{PMe}_3(p\sigma) \rightarrow \text{Ni}$ bands. In the solid state not all of these charge transfer transitions are resolved even at low temperature. Assignment is aided, however, by comparison with electronic spectra obtained using chloro and iodo analogs as the ligand orbital energies increase according to $\text{Cl} < \text{Br} < \text{I}$. Thus the band at 28,000 cm^{-1} (26,400 and 28,500 cm^{-1} at 77°K) can be ascribed to $\text{Br}(p\pi) \rightarrow \text{Ni}$, the corresponding transitions for $\text{X} = \text{Cl}$ and I being at 30,300 and 23,800 cm^{-1} , respectively. Similarly the 34,000 cm^{-1} shoulder is assigned to $\text{Br}(p\sigma) \rightarrow \text{Ni}$, as there are analogous bands for $\text{X} = \text{Cl}$ (34,500 cm^{-1}) and I (29,500 cm^{-1}). Finally for all of these halogenophosphines $[\text{NiX}_2(\text{PMe}_3)_3]$ there is an intense band between 39,000 and 41,000

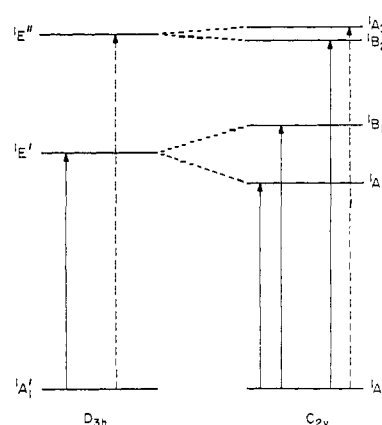
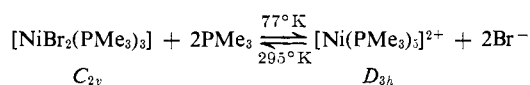


Figure 4. Effect of site symmetry on the ligand field levels of trigonal bipyramidal complexes. Orbitally allowed (—) and forbidden (---) transitions are shown.

cm^{-1} and it is reasonable to assign this to the common transition $\text{PMe}_3(p\sigma) \rightarrow \text{Ni}$.

On dissolving blue $[\text{NiBr}_2(\text{PMe}_3)_3]$ in solvents such as EPA or methylene chloride, a red solution is obtained owing to dissociation to *trans*- $[\text{NiBr}_2(\text{PMe}_3)_2]$. Addition of excess PMe_3 restores the blue color and at room temperature the similarity between solution and solid state electronic spectra indicates that the C_{2v} structure **2** is retained in solution. The presence of this cis TBP stereochemistry explains the high dipole moment of 6.3 D.

On lowering the temperature of an EPA solution of $[\text{NiBr}_2(\text{PMe}_3)_3]$ containing excess PMe_3 (20:1 $\text{PMe}_3:\text{Ni}$ ratio), a remarkable change in spectral shape occurs; see Figure 3. The spectrum at 77°K which contains a symmetrical peak at 19,200 cm^{-1} indicates that a non-distorted trigonal bipyramid species is predominant. This lowest frequency band is still at higher energy than those found in the spectra of the halogeno complexes $[\text{NiX}_2(\text{PMe}_3)_3]$. In addition, no $\text{Br}(p\pi) \rightarrow \text{Ni}$ transition is observed. These observations suggest that the D_{3h} cation $[\text{Ni}(\text{PMe}_3)_3]^{2+}$ is present according to the equilibrium



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With this in mind we make the following assignments: 19,200 cm^{-1} , ${}^1A_1' \rightarrow {}^1E'$ (e' ; $d_{x^2-y^2}$, $d_{xy} \rightarrow a_1'$; d_{z^2}) and 27,800 cm^{-1} , ${}^1A_1' \rightarrow {}^1E''$ (e'' ; d_{xz} , $d_{yz} \rightarrow a_1''$; d_{z^2}) the latter weak transition being forbidden. The intense charge transfer transition at 38,000 cm^{-1} is presumably due to $\text{PMe}_3(p\sigma) \rightarrow \text{Ni}$.

[NiI₂(PMe₃)₃]. There are several similarities in the physical and chemical properties of [NiI₂(PMe₃)₃] and its bromo analog. (1) Both solid compounds show small magnetic moments (see Table I) consistent with low-spin d⁸ five-coordinate structures having a small temperature-independent paramagnetism. (2) Without excess PMe₃, both compounds dissociate in solvents such as EPA giving the trans isomers of [NiX₂(PMe₃)₂]. The pure iododiphosphine complex cannot be isolated from the resultant violet solution. (3) The electronic spectra of the two compounds have similar features in the solid state and in solution (with or without excess PMe₃). (4) In solution with excess PMe₃ both complexes display a substantial dipole moment.

The correspondence between the properties of [NiX₂(PMe₃)₃] (X = Br, I) indicates that they possess the same stereochemistry in the solid state and in solution (with excess PMe₃), *i.e.*, the cis TBP structure 2. In C_{2v} the solid state 13,700 cm^{-1} transition can be assigned to ${}^1A_1 \rightarrow {}^1A_1$ (a_1 ; $d_{x^2-y^2} \rightarrow a_1$; d_{z^2}) and the 16,700 cm^{-1} peak to ${}^1A_1 \rightarrow {}^1B_1$ (b_1 ; $d_{xy} \rightarrow a_1$; d_{z^2}); the $d_{xz} \rightarrow d_{z^2}$ band is apparently obscured by the I($p\pi$) \rightarrow Ni shoulder at 23,800 cm^{-1} . This and higher energy charge transfer bands have been discussed in the previous section.

The complex [NiI₂(PMe₃)₃] further resembles its bromo analog in that on cooling a solution in EPA containing excess PMe₃ to 77°K a purple solution is obtained presumably due to the presence of the [Ni(PMe₃)₃]²⁺ cation.

On addition of a very large excess of PMe₃ to a solution of [NiI₂(PMe₃)₃] at room temperature, a yellow solution is obtained with its lowest energy transition at *ca.* 25,000 cm^{-1} . There is little change in this spectrum at 77°K. Work is still in progress concerning the nature of the molecular species present in this mixture.

[NiCl₂(PMe₃)₃]. This complex can be obtained as a dark blue powder which readily loses trimethylphosphine at room temperature to give [NiCl₂(PMe₃)₂]. It has been possible, however, to obtain a solid state spectrum using a polyvinyl acetate film containing excess PMe₃. Once more the electronic spectrum can be assigned on the basis of a cis TBP structure such as 2. The separation of the two lowest energy bands at 15,100 and 17,200 cm^{-1} (15,100 and 18,500 cm^{-1} at 77°K) is too large for the spectrum to be consistent with a distorted version of the D_{3h} structure 1. As before, the lowest frequency transitions at 15,100, 17,200, and 23,200 cm^{-1} can be assigned to nickel(II) $d_{x^2-y^2} \rightarrow d_{z^2}$, $d_{xy} \rightarrow d_{z^2}$, and $d_{xz} \rightarrow d_{z^2}$, respectively. The charge transfer bands have already been discussed above with reference to the corresponding bromophosphine.

Stereochemistries of Complexes [NiX₂(PMe₃)₃]. The structural chemistry of complexes [NiX₂(PMe₃)₃] is complicated by the fact that three trigonal bipyramidal (1-3) and three square pyramidal idealized forms are theoretically possible.²⁹ The energy differences between

these geometries should be small,³⁰ and, as the potential energy surfaces involved are irregular, it is possible for molecules of intermediate structure to exist under the influence of appropriate lattice or solvent interactions. Here we shall address ourselves to the problem of deciding why the C_{2v} TBP structure 2 is favored when X = Cl, Br, and I and yet a somewhat distorted version of the D_{3h} species 1 is predominant when X = CN.

The empirical observation that for many closed shell molecules MX₂Y₃ the more electronegative ligands lie in the axial positions²⁹ is of little help here as this suggests that both X atoms of [NiX₂(PMe₃)₃] should always be axial. The second-order Jahn-Teller effect,^{31,32} however, can account for this dichotomy of structures. If the ground state wave function of a complex is degenerate, the molecule may be unstable relative to symmetric displacements but its symmetry cannot be lowered by these first-order changes. Assuming these changes have already occurred, and the molecule is distorted by one of its normal vibrational modes, the energy of the ground electronic state is given by³¹

$$E = E_0 + f_{00}Q_i^2 + f_{0k}Q_i^2 \quad (1)$$

where E_0 is the energy of the unperturbed wave function ψ_0 , Q_i is the normal vibrational coordinate, and f_{00} and f_{0k} contribute to the force constant of the normal mode Q_i . The constant f_{00} consists of matrix elements involving ψ_0 only, but f_{0k} relates to matrix elements of the form and is therefore negative. If Q_i (and con-

$$\sum_k [(\psi_0 | \partial U / \partial Q_i | \psi_k)]^2 / (E_0 - E_k)$$

sequently $(\partial U / \partial Q_i)$, ψ_0 , and ψ_k transform as components of the irreducible representations Γ_Q , Γ_0 , and Γ_k , respectively, then for the latter matrix elements to be nonzero, Γ_Q must be contained in the direct product $\Gamma_0\Gamma_k$. If this condition is fulfilled, a molecule of given symmetry may be unstable with respect to that structure provided that the energy gap $E_0 - E_k$ is reasonably small (say < 30,000 cm^{-1}) for at least one pair of states.

For a molecule [NiX₂(PMe₃)₃] with a D_{3h} structure 1 the ground and first excited states have ${}^1A_1'$ and ${}^1E'$ symmetries, respectively. Such a complex should therefore be unstable with respect to e' vibrations which could convert it to a square pyramidal structure. This in turn would be unstable with respect to vibrations which could return the geometry to one of the TBP isomers 1-3. The idealized D_{3h} stereochemistry will be most stable relative to e' vibrations when the value $|E({}^1A_1') - E({}^1E')|$ is greatest, *i.e.*, when the axial ligands are those higher in the spectrochemical series. For ligands of interest here spectrochemical effects diminish according to $\text{CN}^- > \text{PMe}_3 > \text{Cl}^- > \text{Br}^- > \text{I}^-$.

If we accept that the complexes [NiX₂(PMe₃)₃] are to have one of three TBP structures 1-3, [Ni(CN)₂(PMe₃)₃] is predicted to have the D_{3h} stereochemistry 1. On the other hand, when X = Cl, Br, or I the C_{2v} structure 2 should be favored as there are two PMe₃ groups in the axial positions and $|E_0 - E_k|$ is a maximum. These predictions appear to be confirmed experimentally.

Acknowledgments. The research at the California Institute of Technology was supported by the National

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Science Foundation. We are most grateful to Dr. Gordon Rodley for synthesizing single crystals suitable for X-ray analysis.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary

material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-4428.

Kinetics and Thermodynamics of Rapid Structural Interconversions of Dichloro-1,1,7,7-tetraethyldiethylenetriaminenickel(II) in Acetonitrile

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Abstract: Spectrophotometric and conductometric studies in acetonitrile solutions of dichloro-1,1,7,7-tetraethyldiethylenetriaminenickel(II) (NiLCl_2 where L is the tridentate ligand 1,1,7,7-tetraethyldiethylenetriamine) are interpreted in terms of the following equilibria, where $\text{NiLCl}^+||\text{Cl}^-$ represents an outer-sphere complex: $\text{NiLCl}_2 \rightleftharpoons \text{NiLCl}^+||\text{Cl}^- \rightleftharpoons \text{NiLCl}^+ + \text{Cl}^-$ (eq 2). The equilibrium constants have the following values at 20°: $K_1 = k_{12}/k_{21} = 0.95$; $K_s = k_{23}/k_{32} = 8 \times 10^{-5} \text{ mol dm}^{-3}$; $K_d = K_1 K_s / (1 + K_1) = 3.9 \times 10^{-5} \text{ mol dm}^{-3}$. Values of ΔH° and ΔS° were also determined. Kinetic data for this system were obtained by relaxation methods, in which the equilibria were suddenly perturbed by an electric field jump or by means of a pulse of radiation from a Q-switched neodymium laser. The results were interpreted in terms of the above mechanism; values for the rate constants k_{21} and k_{32} were estimated to be $7 \times 10^5 \text{ sec}^{-1}$ and $2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, respectively, at 20°.

Although five-coordination is somewhat unusual¹ for nickel(II) compounds, a considerable number of complexes of this type have now been prepared and characterized.² The complexes frequently contain bulky, polydentate ligands so that the tendency to attain six-coordination is suppressed by crowding around the central metal ion. As well as being of stereochemical interest, five-coordinate species have frequently been proposed as intermediates in substitution reactions³ and structural interconversions^{4,5} of transition metal complexes.

One example of a nickel(II) compound which can exist in a stable five-coordinate form is dichloro-1,1,7,7-tetraethyldiethylenetriaminenickel(II), written as NiLCl_2 , where L is the tridentate ligand $\text{Et}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NEt}_2$. On the basis of spectral, magnetic, and conductometric evidence, Dori and Gray⁶ showed that in acetonitrile and other polar organic solvents this compound was capable of existing in at least two stereochemical modifications present in equilibrium: a five-coordinate, paramagnetic, un-ionized species NiLCl_2 (absorption maximum 450 nm) and a four-coordinate, square-planar, diamagnetic, ionized species NiLCl^+ (absorption maximum 530 nm). In describing

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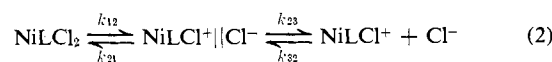
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these species as five- and four-coordinate, respectively, one is ignoring the possibility of weak coordination by the solvent. This point is discussed later.

In the present paper we describe a kinetic and thermodynamic investigation of this system in acetonitrile as solvent. Two chemical relaxation methods were applied. In the first method the position of the equilibrium was disturbed by application of an electric field pulse (second Wien effect).⁷ This method could be used because NiLCl_2 behaves as a moderately weak electrolyte in acetonitrile. The second method depends on the fact that NiLCl_2 absorbs at 1.06 μm , and it was found possible to disturb the equilibrium by means of a pulse of radiation from a Q-switched neodymium laser operating at this wavelength. Conductometric and spectrophotometric methods were used to monitor the relaxation processes as well as to investigate the equilibrium itself.

Both the kinetic and thermodynamic results indicate the participation of a third species in the equilibrium. This is postulated to be an outer-sphere complex written as $\text{NiLCl}^+||\text{Cl}^-$. The equilibria are thus represented by (2) where k_{12} , etc., denote the rate constants.



Experimental Section

Kinetics. The Q-switched neodymium laser and spectrophoto-

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