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Four- and Five-Coordinate Nickel(II) and Four-Coordinate Palladium(II) Complexes of 1,2-Bis(diethylphosphino)ethane

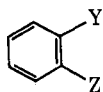
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1,2-Bis(diethylphosphino)ethane (TEP) forms five-coordinate, diamagnetic $[\text{Ni}(\text{TEP})_2\text{X}]\text{B}(\text{C}_6\text{H}_5)_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) complexes, as well as the four-coordinate, diamagnetic $[\text{Ni}(\text{TEP})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{CN}$) complexes. The compounds were characterized by conductivity and magnetic measurements, electronic and infrared spectra, and elemental analyses. The five-coordinate complexes $[\text{Ni}(\text{TEP})_2\text{X}]\text{B}(\text{C}_6\text{H}_5)_4$ are assigned a square-pyramidal structure on the basis of their electronic spectra and an X-ray structure determination of $[\text{Ni}(\text{TEP})_2\text{I}]\text{I}$. By comparing the electronic spectra with this $[\text{Ni}(\text{TEP})_2\text{X}]^+$ series, the square-pyramidal structures previously assigned²⁻⁴ to other pentacoordinate $[\text{Ni}(\text{bidentate})_2\text{X}]^+$ complexes on the basis of electronic spectra are strongly supported by the structure of $[\text{Ni}(\text{TEP})_2\text{I}]\text{I}$. The square-planar complexes $[\text{Ni}(\text{TEP})\text{X}_2]$ add one dimethylphenylphosphine molecule to form pentacoordinate $[\text{Ni}(\text{TEP})(\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2)\text{X}_2]$ complexes in dichloromethane solutions. Palladium(II) forms the diamagnetic, four-coordinate $[\text{Pd}(\text{TEP})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{CN}$) complexes but shows no tendency to form pentacoordinate complexes. Vibrational spectra indicate that the thiocyanate complex $[\text{Pd}(\text{TEP})(\text{CNS})_2]$ contains both N- and S-bonded thiocyanate groups.

Introduction

The *o*-phenylene ligands I-IV form several series of five-coordinate $[\text{Ni}(\text{YZ})_2\text{X}]^+$ complexes that have been assigned square-pyramidal structures.^{2,3} Recently, the



- I, Y = $\text{As}(\text{CH}_3)_2$, Z = $\text{As}(\text{CH}_3)_2$, L = DAS
 II, Y = $\text{As}(\text{C}_6\text{H}_5)_2$, Z = $\text{P}(\text{C}_6\text{H}_5)_2$, L = AsP
 III, Y = SCH_3 , Z = $\text{P}(\text{C}_6\text{H}_5)_2$, L = SP
 IV, Y = SeCH_3 , Z = $\text{P}(\text{C}_6\text{H}_5)_2$, L = SeP
 V, Y = $\text{N}(\text{CH}_3)_2$, Z = $\text{P}(\text{C}_6\text{H}_5)_2$, L = PN
 VI, Y = $\text{N}(\text{CH}_3)_2$, Z = $\text{P}(\text{C}_2\text{H}_5)_2$, L = P'N

diphosphine ligand *cis*-1,2-bis(diphenylphosphino)ethylene (VPP) was shown to form pentacoordinate $[\text{Ni}(\text{VPP})_2\text{X}]^+$ complexes⁴ although attempts to isolate five-coordinate nickel(II) halide complexes with the saturated analog 1,2-bis(diphenylphosphino)ethane (DPE) have been unsuccessful.⁴⁻⁶ However nickel(II) cyanide and DPE have recently been shown to form the neutral five-coordinate complex $\text{Ni}(\text{DPE})_2(\text{CN})_2$, which has a dangling phosphino group.⁷ Booth and Chatt found that the 1:2 complexes $[\text{Ni}(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2\text{X}_2]$ ($\text{X} = \text{Br}, \text{I}, \text{R} = \text{CH}_3$; $\text{X} = \text{I}, \text{R} = \text{C}_2\text{H}_5$; $\text{X} = \text{I}, \text{Br}, \text{R} = \text{C}_6\text{H}_5$) behave as electrolytes in nitrobenzene but they assumed that the nickel was six-coordinate in the solid state.⁸ Similarly the complexes $[\text{M}(\text{DAS})_2\text{X}_2]$ ($\text{M} = \text{Ni}, \text{Pd}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$)⁹ have been classified as tetragonal in the solid state on the basis of an X-ray structural study on $[\text{Pd}(\text{DAS})_2\text{I}_2]$,¹⁰ even though they are uni-univalent electrolytes in nitrobenzene.

Palladium(II) generally exhibits a smaller tendency than nickel(II) to form five-coordinate complexes.^{11,12} However, five-coordinate palladium(II) complexes are formed with certain ligands. For example, the monodentate ligand 2-phenylisophosphindoline gives a distorted square-pyramidal Pd(II) complex¹³ and the sterically rigid tetradentate ligands $\text{As}(\text{o}-\text{C}_6\text{H}_4\text{As}(\text{C}_6\text{H}_5)_2)_3$ (QAS) and $\text{P}(\text{o}-\text{C}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2)_3$ (QP) form trigonal-bipyramidal palladium(II) complexes.^{14,15} With ligand V, palladium(II) forms only four-coordinate $[\text{Pd}(\text{PN})\text{X}_2]$ complexes¹⁴ but the ligand VI is said to give five-coordinate $[\text{Pd}(\text{P}'\text{N})_2\text{X}]^+$ ($\text{X} = \text{Cl}, \text{Br}$) complexes in nitrobenzene.¹⁶ In contrast to the unsuccessful attempts to obtain five-coordinate nickel(II) halide complexes with DPE,⁴⁻⁶ Westland reported the existence of $[\text{Pd}(\text{DPE})_2\text{X}]^+$ complexes in solution.¹⁷

All of the above bidentate ligands except DPE contain the somewhat rigid, π -conjugated, *o*-phenylene or ethylene linkages. As a continuation of our investigation into the factors that promote five-coordination,^{3,4,18} we have prepared nickel(II) and palladium(II) complexes of the flexible diphosphine 1,2-bis(diethylphosphino)ethane (TEP). Except for Wymore and Bailar's¹⁹ broad survey of the TEP complexes that resulted with different metals, few complexes of this diphosphine have been reported in the literature.^{8,20}

Experimental Section

Reagents.—All nickel salts were anhydrous except for $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Sodium tetrachloropalladate(II) and palladium(II) iodide were obtained from Engelhard and used without further purification. Bis(diethylphosphino)ethane (TEP) was used as supplied by Strem Chemicals and Orgmet, Inc. Absolute ethanol and reagent grade dichloromethane were used without further purification. Ethanol was

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TABLE I
 PROPERTIES AND ANALYTICAL DATA ON THE TEP COMPLEXES

| Compound ^b | Color | —Λ _m , cm ² /(ohm mol)— | | Analysis | | | | | |
|---|--------------|---|-------|----------|-------|-------|-------|---------|------------|
| | | c | e | % C | | % H | | % other | |
| | | | | Calcd | Found | Calcd | Found | Calcd | Found |
| NiCl ₂ | Yellow-brown | 6.0 | ... | 35.76 | 35.16 | 7.20 | 7.56 | 21.11 | 20.61 (Cl) |
| NiBr ₂ | Red-brown | ... | 21.3 | 28.25 | 27.67 | 5.70 | 5.59 | 37.63 | 38.22 (Br) |
| NiI ₂ ^d | Dark brown | ... | 74.0 | 23.15 | 22.86 | 4.67 | 4.99 | 48.93 | 48.76 (I) |
| NiL(NCS) ₂ | Orange | 21.6 | 22.8 | 37.80 | 37.95 | 6.34 | 6.47 | 7.35 | 6.49 (N) |
| NiL(CN) ₂ ^e | Yellow | 0.5 | ... | 45.42 | 44.99 | 7.57 | 7.76 | 8.84 | 8.60 (N) |
| [NiL ₂ I]I | Red | 90.5 | 115.8 | 33.10 | 32.99 | 6.68 | 6.76 | 35.00 | 35.07 (I) |
| [NiL ₂ I]B(C ₆ H ₅) ₄ ^e | Red-orange | 63.0 | ... | 57.10 | 54.56 | 7.42 | 7.36 | 13.75 | 14.32 (I) |
| [NiL ₂ Cl]B(C ₆ H ₅) ₄ ^e | Yellow | 57.9 | 146.2 | 63.80 | 62.41 | 8.30 | 7.65 | 4.29 | 5.13 (Cl) |
| [NiL ₂ Br]B(C ₆ H ₅) ₄ | Orange | ... | 131.0 | 60.65 | 61.32 | 7.87 | 7.99 | 9.18 | 9.55 (Br) |
| [NiL ₂ (NCS)]B(C ₆ H ₅) ₄ ^e | Red | 70.0 | ... | 63.60 | 63.30 | 8.08 | 7.97 | 1.65 | 1.62 (N) |
| PdLCl ₂ | Pale yellow | 10.7 | ... | 31.30 | 31.03 | 6.31 | 6.34 | 18.50 | 18.45 (Cl) |
| PdLBr ₂ | Pale yellow | 12.5 | 3.8 | 25.40 | 25.17 | 5.12 | 4.89 | 33.82 | 33.74 (Br) |
| PdL ₂ ^e | Yellow | ... | 3.7 | 21.22 | 21.15 | 4.27 | 4.49 | 44.80 | 45.06 (I) |
| PdL(CNS) ₂ ^f | Pale yellow | ... | ... | 33.59 | 32.77 | 5.64 | 5.57 | 6.52 | 6.16 (N) |
| PdL(CN) ₂ | White | ... | 1.5 | 39.50 | 39.35 | 6.64 | 6.65 | 7.68 | 7.51 (N) |
| L(CH ₃ I) ₂ | White | 152.0 | 288.5 | 29.40 | 28.92 | 6.18 | 5.98 | 51.75 | 50.98 (I) |

^a All of these complexes were shown to be diamagnetic. ^b L = (C₂H₅)₂PCH₂CH₂P(C₂H₅)₂, TEP. ^c Molar conductance value of ~10⁻³ M solution in nitromethane; (CH₃)₃BuAsI gave a Λ value of 92.7 cm²/(ohm mol). ^d Calcd mol wt 518; found mol wt 558 in chloroform at 37°. ^e Molar conductance value of ~10⁻³ M solution in acetonitrile; NaB(C₆H₅)₄ gave a Λ value of 153.5 cm²/(ohm mol). ^f See footnote 22 for notation on thiocyanate.

also dried by azeotropic distillation with benzene and distilled at 77–78°.

Preparation of the Complexes.—All preparative work was carried out under an atmosphere of dry nitrogen to prevent oxidation of the diphosphine. Since all of the syntheses followed the same general procedure of adding the phosphine to the appropriate nickel salt in absolute ethanol, only the preparation of one example of each type of complex is presented in detail.

[Ni(TEP)₂].—The diphosphine (0.2 g, 1 mmol) was transferred *via* a syringe into a brown solution of NiI₂·6H₂O (0.42 g, 1 mmol) in absolute ethanol (10 ml). The dark precipitate that formed was dissolved by the addition of dichloromethane and the solution was filtered. A dark brown crystalline solid formed as the solution was concentrated on a rotary evaporator. These crystals were collected on a sintered-glass frit and washed with hexane.

[Ni(TEP)₂][B(C₆H₅)₄]₂.—The diphosphine (0.2 g, 1 mmol) was transferred *via* a syringe into a yellow solution of Ni(NO₃)₂·6H₂O (0.145 g, 0.5 mmol) in absolute ethanol (10 ml). The resulting reddish brown solution was stirred and sodium tetraphenylborate (0.35 g, 1 mmol) in ethanol (10 ml) was added. The cream-colored powder that separated immediately was collected on a sintered-glass frit and washed with ethanol and hexane; yield was ~100%.

[Ni(TEP)₂NCS]B(C₆H₅)₄.—Potassium thiocyanate (0.021 g, 0.22 mmol) was added to [Ni(TEP)₂][B(C₆H₅)₄]₂ (0.22 g, 0.20 mmol) in absolute ethanol (10 ml). Dichloromethane (*ca.* 15 ml) was added and the mixture was stirred and warmed. The resulting red solution was filtered when only a slight precipitate remained in the flask and was concentrated on a rotary evaporator. The dark red crystalline solid (0.12 g) that was subsequently collected on a frit represented a yield of 71%.

[Pd(TEP)Cl₂].—The diphosphine (0.44 g, 2.1 mmol) was transferred *via* a syringe into a partially dissolved mixture of Na₂PdCl₄ in absolute ethanol (15 ml). A tan compound began to precipitate immediately but the mixture was warmed briefly and then stirred overnight. After removal of all the solvent, the product was extracted with dichloromethane and the remaining brown solid was washed with ethanol. Concentration of the yellow dichloromethane-ethanol solution on a rotary evaporator gave a pale yellow crystalline solid that was collected on a frit and washed with ethanol and hexane; yield, 68%.

[Pd(TEP)Br₂].—Sodium bromide (0.6 g, 3 mmol) was added to an acetone solution of [Pd(TEP)Cl₂] (0.19 g, 0.05 mmol) and the yellow solution was warmed briefly. After removal of acetone, the resulting solid was extracted with dichloromethane and washed with ethanol. Concentration of the dichloromethane-ethanol solution gave a yellow crystalline product that was collected on a frit and washed with hexane. Except for [Pd(TEP)I₂], which was prepared directly from palladium iodide, the other [Pd(TEP)X₂] compounds were prepared in an analogous manner from [Pd(TEP)Cl₂] by metathesis with the appropriate sodium salt.

Physical Measurements.—Electronic and infrared spectra and

conductance and magnetic measurements were obtained as previously described.³ Elemental analyses and molecular weight measurements were determined by M-H-W Laboratories, Garden City, Mich.

Results and Discussion

The physical properties and analytical data of the four- and five-coordinate compounds are listed in Table I. The band maxima and extinction coefficients of the electronic absorption spectra are given in Table II.

Four-Coordinate Complexes.—1,2-Bis(diethylphosphino)ethane (TEP) forms diamagnetic, four-coordinate Ni(TEP)X₂ (X = I, Br, Cl, NCS, CN) complexes when mixed with nickel(II) salts in a 1:1 stoichiometric ratio (Table I). The cream-colored [Ni(TEP)₂][B(C₆H₅)₄]₂ compound precipitated when sodium tetraphenylborate was added to an ethanolic solution of nickel nitrate and the diphosphine. The tetraphenylborate complex is a di-univalent electrolyte in nitromethane; its molar conductance value (146.5 cm²/(ohm mol)) agrees well with the value obtained for the bis(methyl iodide) derivative of the diphosphine (152.0 cm²/(ohm mol)). In the case of the [Ni(TEP)(NCS)₂] complex the conductance (21.6 cm²/(ohm mol)) indicates significant ionization, but the other [Ni(TEP)X₂] complexes are essentially nonconductors. The above complexes exhibit electronic absorption bands in the visible region (Table II) consistent with a four-coordinate, planar structure.^{4,18} The band maxima of the lowest energy band produce the typical spectrochemical series, *i.e.*, CN > NCS > Cl > Br > I. A comparison of these spectral data with those previously obtained⁴ for complexes of *cis*-1,2-bis(diphenylphosphino)ethylene (VPP) and bis(diphenylphosphino)ethane (DPE) shows that bis(diethylphosphino)ethane exhibits the highest ligand field strength of these three diphosphine ligands. This is consistent with its more basic diethylphosphino groups. Both thiocyanate groups are N bonded in [Ni(TEP)(NCS)₂] since the λ_{max} and ε_{max} in the electronic spectra are greater than those of the corresponding chloride complex.²¹ Also, the infrared spectrum of the orange complex shows only a strong, broad peak

TABLE II
 ELECTRONIC ABSORPTION SPECTRA OF THE TEP COMPLEXES

| Compound ^a | E_{\max} , cm^{-1} | | Nujol mulls of the solid at $\sim 300^\circ\text{K}$ |
|--|--|--|--|
| | CH_2Cl_2 soln ^b | | |
| NiLi_2 | 20,600 (2200), 29,400 (3640) sh, 32,600 (8700) sh, ^c 36,000 (26,400), 40,000 (27,000) | | 20,900, 23,700 sh ^c |
| NiLBr_2 | 22,000 (1490), 29,200 (812) sh, ^c 32,800 (2750) sh, 37,000 (12,100) | | 21,900 |
| NiLCl_2 | 22,900 (1040), 33,100 (2810), 39,700 (13,100) | | 23,300 |
| $\text{NiL}(\text{NCS})_2$ | 24,500 (2310), 34,200 (12,500) | | 25,600 |
| $\text{NiL}(\text{CN})_2$ | 31,500 (3350) sh, 33,800 (5400) | | |
| $[\text{NiL}_2\text{I}]$ | 20,600 (2600), 23,200 (1030) sh, 29,400 (4370), 32,800 (11,200), 36,200 (31,400), 40,300 (28,700) | | 20,800, 23,300 sh |
| $[\text{NiL}_2\text{I}]\text{B}(\text{C}_6\text{H}_5)_4$ | 20,000 (730), 23,300 (1210), 32,300 (11,400), 37,000 (24,300), 40,800 (52,000) | | 20,400 sh, 23,900 |
| $[\text{NiL}_2\text{Br}]\text{B}(\text{C}_6\text{H}_5)_4$ | 23,800 (1145), 32,500 (8950), 41,500 (33,400) | | 24,100 |
| $[\text{NiL}_2\text{Cl}]\text{B}(\text{C}_6\text{H}_5)_4$ | 25,500 (1080), 32,700 (5100), 36,800 (14,000) | | 25,800 |
| $[\text{NiL}_2\text{NCS}]\text{B}(\text{C}_6\text{H}_5)_4$ | 24,200 (1430), 33,900 (5640) | | 24,500 |
| PdLi_2 | 26,600 (6900), 37,000 (18,200) sh | | 26,800 |
| PdLBr_2 | 30,100 (5200), 33,600 (2520) sh | | |
| PdLCl_2 | 32,300 (4430), 38,500 (2700) | | |
| $\text{PdL}(\text{CNS})_2$ | 31,300 (5200), 36,800 (16,800), 40,000 (24,000) | | |
| $\text{PdL}(\text{CN})_2$ | 42,900 (12,000) | | |

^a L = $(\text{C}_2\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_5)_2$, TEP. ^b Molar extinction coefficients in parentheses. ^c sh, shoulder on a more intense absorption band.

at 2095 cm^{-1} in the cyanide stretching region, indicative of N-bonded thiocyanate.

The lower energy band in the planar $\text{Ni}(\text{TEP})\text{X}_2$ complexes is assigned to the ligand field transition ${}^1\text{A}_1 \rightarrow {}^1\text{B}_2$ in C_{2v} symmetry; this involves the orbitals $b_2(d_{xy}) \rightarrow b_1(d_{x^2-y^2})$.⁶ The strong absorption at ca. $33,000\text{ cm}^{-1}$ (Table II) is assigned to a nickel-phosphorus charge-transfer band; its relatively constant value rules out its assignment as a nickel-halogen charge-transfer band.

In their survey of the complexes of TEP,¹⁹ Wymore and Bailar isolated the palladium compound $[\text{Pd}(\text{TEP})\text{Cl}_2]$. The series of diamagnetic, square-planar palladium(II) complexes $[\text{Pd}(\text{TEP})\text{X}_2]$ has been extended in this study to include X = Cl, Br, I, CNS, CN.²² Although the ability of palladium(II) to form stable square-planar complexes $[\text{Pd}(\text{PR}_3)_2\text{X}_2]$ with many tertiary phosphines is well known,²³ there are few reports of a series with X being various anionic ligands and especially with X = CN.²⁴ The complexes $[\text{Pd}(\text{TEP})\text{X}_2]$ are essentially nonelectrolytes in nitromethane (Table I) and are pale yellow to white. The white complex $[\text{Pd}(\text{TEP})(\text{CN})_2]$ has two sharp infrared bands in the cyanide stretching region, at 2130 and 2135 cm^{-1} , indicative of cis-cyanide groups in the planar complex.

The infrared spectrum (dichloromethane solution) of the pale yellow $[\text{Pd}(\text{TEP})(\text{CNS})_2]$ ²² complex shows a strong, sharp absorption at 2110 cm^{-1} and a strong, broader peak at 2083 cm^{-1} . This splitting is too large to be due to cis SCN^- groups; both the integrated intensities and the positions of the $\text{C}\equiv\text{N}$ infrared bands ($2.4 \times 10^4\text{ M}^{-1}\text{ cm}^{-2}$, 2110 cm^{-1} ; $6.5 \times 10^4\text{ M}^{-1}\text{ cm}^{-2}$, 2083 cm^{-1}) are consistent with one S-bonded and one N-bonded thiocyanate.^{21,26} The λ_{\max}

and ϵ_{\max} values of the lowest energy electronic absorption band (Table II) support this conclusion, as they are intermediate between those found for $[\text{Pd}(\text{TEP})\text{Cl}_2]$ and $[\text{Pd}(\text{TEP})\text{Br}_2]$. This complex is another example of the limited number of molecular thiocyanate complexes that contain both N-bonded and S-bonded thiocyanate groups.²⁵⁻²⁷

The electronic absorption bands (Table II) of the $[\text{Pd}(\text{TEP})\text{X}_2]$ complexes are in good agreement with those reported for other square-planar palladium(II) complexes when the high ligand field strength of TEP is taken into account.^{21,28} With the exception of the thiocyanate complex, the lowest energy electronic band gives the same spectrochemical series as was observed for the $[\text{Ni}(\text{TEP})\text{X}_2]$ complexes, *i.e.*, $\text{CN} > \text{Cl} > \text{CNS} > \text{Br} > \text{I}$. This band is assigned to the ${}^1\text{A}_1 \rightarrow {}^1\text{B}_2$ transition in C_{2v} symmetry.⁶

Five-Coordinate Complexes.—In contrast to the unsuccessful attempts to prepare the complexes $[\text{Ni}(\text{DPE})_2\text{X}]^+$ (DPE = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$),⁴⁻⁶ the five-coordinate $[\text{Ni}(\text{TEP})_2\text{X}]\text{B}(\text{C}_6\text{H}_5)_4$ complexes can be isolated from the deeply colored solutions that result from mixing the appropriate potassium or sodium salt with the cream-colored $[\text{Ni}(\text{TEP})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$ complex in ethanol-dichloromethane. The chloride and bromide complexes have also been prepared by the addition of a solution of sodium tetraphenylborate to the dichloromethane-ethanol solution of TEP mixed with the nickel(II) halide in a 2:1 mole ratio. The solids were purified by dissolving them in dichloromethane-ethanol and slowly evaporating the dichloromethane. The dark red $[\text{Ni}(\text{TEP})_2\text{I}]$ complex formed when $\text{NiLi}_2 \cdot 6\text{H}_2\text{O}$ and TEP were mixed in a 1:2 mole ratio in ethanol; it was crystallized from ethanol-hexane as dark red needles.

The $[\text{Ni}(\text{TEP})_2\text{X}]\text{B}(\text{C}_6\text{H}_5)_4$ complexes are diamagnetic and 1:1 electrolytes in nitromethane. Since the electronic spectra (Table II) are similar in the solid state (Nujol mulls) and in dichloromethane solution, it is concluded that five-coordinate cations are present both in solution and in the solid state. At 77°K the

(22) Throughout this paper the thiocyanate ion is written as CNS whenever the specific type of bonding is unknown or is not to be represented; a formula written as $[\text{ML}(\text{SCN})_2]$ implies M-SCN linkages, whereas $[\text{ML}(\text{NCS})_2]$ implies M-NCS bonding.

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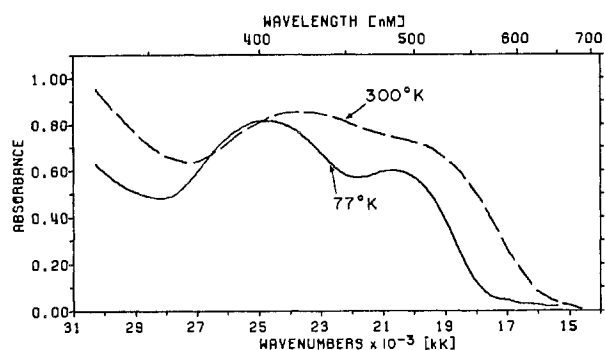


Figure 1.—Electronic spectra of the solid five-coordinate $[\text{Ni}(\text{TEP})_2\text{I}]\text{B}(\text{C}_6\text{H}_5)_4$ complex suspended in Nujol at 77°K (—) and at $\sim 300^\circ\text{K}$ (---). The absorbance scale is arbitrary.

peak maxima in the spectra of the solids are resolved better, as illustrated in Figure 1, but their positions remain virtually unaffected. Although Booth and Chatt had shown that $[\text{Ni}(\text{TEP})_2\text{I}]\text{I}$ was a uni-univalent electrolyte in nitrobenzene,⁸ they presumed it to be octahedrally coordinated in the solid. The ϵ_{max} values and the positions of the electronic absorption bands of these $[\text{Ni}(\text{TEP})_2\text{X}]^+$ complexes are very similar to those of $[\text{Ni}(\text{SP})_2\text{X}]^+$,³ $[\text{Ni}(\text{VPP})_2\text{X}]^+$,⁴ and $\text{Ni}(\text{DSP})\text{X}_2$,^{3,28} which have been interpreted previously in terms of a square-pyramidal coordination geometry around the nickel ion. An X-ray structure determination of $[\text{Ni}(\text{TEP})_2\text{I}]\text{I}$ by Professor Palenik has confirmed a somewhat distorted square-pyramidal geometry. The inner coordination sphere of the cation, along with some important bond distances and angles, is shown in Figure 2.

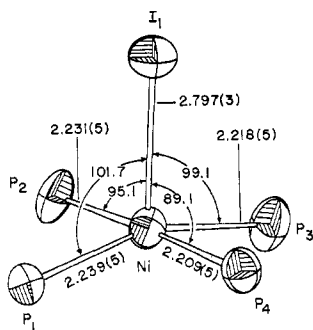


Figure 2.—The bond distances and angles of the inner coordination sphere of the five-coordinate complex $[\text{Ni}(\text{TEP})_2\text{I}]\text{I}$.

Since the low-energy bands of the pentacoordinate complexes produce the usual spectrochemical series, $\text{NCS} \sim \text{Cl} > \text{Br} > \text{I}$, the same square-pyramidal geometry may be assumed for all of the $[\text{Ni}(\text{TEP})_2\text{X}]^+$ species. At the same time, the similarity of electronic spectra with complexes of the type $[\text{Ni}(\text{YZ})_2\text{X}]^+$ with the chelating ligands I–IV and with $[\text{Ni}(\text{VPP})_2\text{X}]^+$ strongly supports their previous characterization as square-pyramidal structures.^{1–4}

The red crystalline $[\text{Ni}(\text{TEP})_2(\text{NCS})]\text{B}(\text{C}_6\text{H}_5)_4$ complex exhibits one $\text{C}\equiv\text{N}$ infrared absorption at 2070 cm^{-1} (s, b), characteristic of N-bonded thiocyanate.²⁵ Unlike the analogous $[\text{Ni}(\text{VPP})_2(\text{NCS})]\text{B}(\text{C}_6\text{H}_5)_4$ complex which has $\mu_{\text{eff}} = 1.86$ BM,⁴ this thiocyanate complex is diamagnetic at room temperature; also the similarity of the electronic spectrum in the solid state

to that in dichloromethane solution confirms that the square-pyramidal structure exists in both states.

Previous studies showed that the square-planar $[\text{NiL}_2\text{X}_2]$ ($\text{L} = \text{phenyldimethylphosphine}$) complexes become trigonal-pyramidal $[\text{NiL}_3\text{X}_2]$ ($\text{X} = \text{I}, \text{Cl}, \text{Br}, \text{NO}_2$) complexes by the addition of excess phosphine to solutions of the square-planar $[\text{NiL}_2\text{X}_2]$ complexes.¹⁸ In the present study, phenyldimethylphosphine was added to solutions of the $[\text{Ni}(\text{TEP})\text{X}_2]$ complexes to determine the tendency of the four-coordinate complexes to attain pentacoordination. New absorption bands appear at lower energy than was observed for the corresponding four-coordinate complex when $\text{X} = \text{CN}, \text{I}, \text{Br}$. The band positions and color changes that occur when phenyldimethylphosphine is added correspond with those reported for trigonal-bipyramidal nickel(II) complexes.^{18,29} The visible spectrum of $[\text{Ni}(\text{TEP})(\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2)(\text{CN})_2]$ (Figure 3) shows two

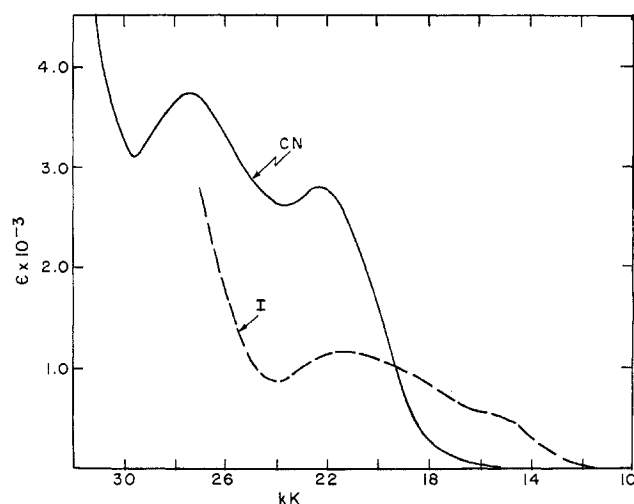


Figure 3.—Electronic spectra of the five-coordinate $[\text{Ni}(\text{TEP})(\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2)\text{X}_2]$ complexes in dichloromethane: —, $\text{X} = \text{CN}$, $1.42 \times 10^{-3} M$ $[\text{Ni}(\text{TEP})\text{X}_2]$ containing $0.055 M$ $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$; ---, $\text{X} = \text{I}$, $0.81 \times 10^{-3} M$ $[\text{Ni}(\text{TEP})\text{X}_2]$ containing $0.034 M$ $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$.

ligand-field bands in agreement with the theoretical expectations³⁰ for low-spin, trigonal-bipyramidal nickel(II) complexes and with the observed patterns of other diamagnetic, trigonal-bipyramidal complexes.^{18,29} Therefore, the new bands at 21,700 cm^{-1} (ϵ 2740) and at 27,400 cm^{-1} (ϵ 3730) in the red solutions of $[\text{Ni}(\text{TEP})(\text{CN})_2]$ containing excess $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$ are attributed to the five-coordinate compound $[\text{Ni}(\text{TEP})(\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2)(\text{CN})_2]$ and are assigned to the ${}^1\text{A}_1 \rightarrow \text{a}^1\text{E}$ and ${}^1\text{A}_1 \rightarrow \text{b}^1\text{E}$ transitions, respectively, of a trigonal-bipyramidal nickel(II) complex.¹⁸

The dark green dichloromethane solutions of $[\text{Ni}(\text{TEP})\text{I}_2]$ containing excess $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$ show an absorption band at 16,000 cm^{-1} (Figure 3) which increases in intensity with increasing concentration of the monodentate phosphine. This band corresponds to that found at 16,300 cm^{-1} in $[\text{Ni}(\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2)_3\text{I}_2]$ and is assigned to the ${}^1\text{A}_1 \rightarrow \text{a}^1\text{E}$ transition of a trigonal-bipyramidal structure. Similarly, a reddish brown solution of $[\text{Ni}(\text{TEP})\text{Br}_2]$ becomes dark green on the addition of a large excess of $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$ and the new

(29) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc. A*, 540 (1967), and references cited therein.

(30) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).

(28) D. W. Meek and J. A. Ibers, *Inorg. Chem.*, **8**, 1913 (1969).

visible absorption band at $16,700\text{ cm}^{-1}$ (shoulder on the $23,800\text{-cm}^{-1}$ band) can be attributed to a penta-coordinate complex. An analogous color change was observed for solutions of $[\text{Ni}(\text{TEP})\text{Cl}_2]$ containing a large excess (200:1 mole ratio) of the monodentate phosphine. The cream-colored $[\text{Ni}(\text{TEP})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$ is insoluble in dichloromethane ($26,000\text{ cm}^{-1}$, ϵ 940 in CH_3CN) but forms a yellow solution with a large excess of $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$ (101:1 molar ratio) that shows a symmetrical visible band at $24,100\text{ cm}^{-1}$ (ϵ 930). Spectral comparison with other $[\text{Ni}(\text{bidentate})_2\text{X}]^+$ species, where bidentate = AsP, SP, and SeP (ligands II–IV), indicates that the lowest electronic absorption band of the planar $[\text{Ni}(\text{bidentate})_2]^{2+}$ cation generally shifts a few thousand reciprocal centimeters to lower energy when the five-coordinate complex is formed.³ Also, since the trigonal-bipyramidal species $[\text{Ni}(\text{phosphite})_5]^{2+}$, where phosphite = $\text{P}(\text{OCH}_3)_3(\text{CH}_2)_3$ and $\text{P}(\text{OCH}_3)_3$, absorb near $20,000\text{ cm}^{-1}$,³¹ it is reasonable to assign the $24,100\text{-cm}^{-1}$ band to the square-pyramidal $[\text{Ni}(\text{TEP})_2\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2]^{2+}$ cation, where the monodentate phosphine is loosely held in the apical position. To test the ease of replacing a halide from the $[\text{Ni}(\text{TEP})_2\text{X}]^+$ cations in the presence of excess $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$, the visible absorption spectrum of $[\text{Ni}(\text{TEP})_2\text{Br}]^+$

(31) J. M. Jenkins, T. J. Huttemann, and J. G. Verkade, *Advan. Chem. Ser.*, **No. 62**, 604 (1967); E. F. Riedel and R. A. Jacobson, Abstracts, Meeting of the American Crystallographic Association, Minneapolis, Minn., No. P-10.

$[\text{B}(\text{C}_6\text{H}_5)_4]$ is unchanged in the presence of a 48:1 molar ratio excess of $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$; thus the bromide was not replaced by $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$.

The tendency of the $[\text{Ni}(\text{TEP})\text{X}_2]$ complexes to become pentacoordinate depends upon the anion and appears to follow the order of polarizability of the anions rather than their relative positions in the spectrochemical series; evidence to support this general conclusion has been reported previously^{4,11,18,32} particularly for the series $[\text{Ni}(\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2)_2\text{X}_2]$.¹⁸

The failure to obtain a palladium complex containing two chelating diphosphine groups has been reported by Wymore and Bailar.¹⁹ In this work, the reaction of PdI_2 with TEP in a 1:2 mole ratio yielded only the yellow, square-planar $[\text{Pd}(\text{TEP})\text{I}_2]$ complex. Dichloromethane solutions of this complex remained yellow in the presence of a large excess of $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$. Attempts to isolate complexes of the type $[\text{Pd}(\text{TEP})_2\text{X}]^+$ gave only the previously discussed square-planar complexes.

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(32) R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963).

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA ANALITICA ED ElettROCHIMICA DELL'UNIVERSITÀ, PISA, ITALY

Kinetics of the Reaction of the Bis(oxalato)platinate(II) Ion with Thiocyanate

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Rate data for the reaction of $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ with SCN^- in the presence of various cations and at several temperatures are reported. The reaction gives $\text{Pt}(\text{SCN})_4^{2-}$ and occurs in at least two steps, as shown by the change of optical density with time. An intermediate product was isolated and identified as *trans*- $\text{K}_4[\text{Pt}(\text{C}_2\text{O}_4)_2(\text{SCN})_2] \cdot 3\text{H}_2\text{O}$. An examination of this product has shown that the overall reaction is more complicated than shown by the optical density–time curve. The rate and the equilibrium constant of an intermediate or possibly parallel reaction were measured at 25° , as well as the activation parameters of the main reactions. The results are interpreted in terms of a ring-opening mechanism, involving intermediates containing unidentate oxalato ligands.

Introduction

Many substitution reactions of square-planar platinum(II) complexes, mostly involving unidentate ligands, have been studied kinetically. In general these reactions have been found to exhibit a two-term rate law¹

$$\text{rate} = k_{\text{H}_2\text{O}}[\text{complex}] + k_1[\text{complex}][\text{L}] \quad (\text{L} = \text{entering ligand})$$

However substitution reactions on Pt(II) complexes with chelating ligands have been infrequently studied, possibly because such reactions are generally very slow. For instance, $k_{\text{H}_2\text{O}}$ and k_1 for the $\text{C}_2\text{O}_4^{2-}$ exchange with $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ are smaller by about 4 orders of magnitude than the values for comparable unidentate complexes.²

For this reaction, as well as for the racemization and exchange reactions of tris(oxalato) octahedral complexes,³ an intramolecular mechanism has been proposed, which involves the opening of the chelate ring and the existence of unidentate oxalato complexes as intermediates. To the best of our knowledge, such intermediates have not been isolated, and for Pt(II) only very few complexes containing acid oxalato groups⁴ or amino acids with a free carboxyl group⁵ are known.

In an attempt to clarify the mechanism of such reactions we have measured the rate of the reaction of $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ with SCN^- , considering also the salt effects, which are already known for many reactions

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, Chapter 4, pp 300–328.

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