$Co(NH_3)_6{}^{3+}$, with no evidence for reactions 6a or 6d. The additional oxidation steps needed to obtain the final products are not involved in this competition as established by the lack of dependence of the stoichiometry on the concentration of added oxidant. One or both of these reactions involves an acidity dependence resulting in a net first-order dependence of the stoichiometry on acidity. In addition, there appears to be a stoichiometric (as well as kinetic) dependence on one or both of the buffer constituents. The stoichiometric observations allow one to calculate the ratio of the specific rate constants for reactions 6b and 6c if it is assumed that these reactions are both first order in the common intermediate Co^{III}–L$'$. This is possible because it is quite certain that neither Co^{2+} nor $Co(NH_3)_6{}^{3+}$ can undergo further reaction under the experimental conditions used. This approach leads to the relationship

$$(k_{6b}/k_{6c})_{65°} = 25[H^+] \qquad (7)$$

Thus in 0.5 M acid, 92.5% of the original cobalt is converted to the Co^{III} hexaammine whereas at 0.01 M H$^+$ only 20% is. The increase in yield of Co^{2+} with increasing temperature indicates that the intramolecular redox reaction has a *larger* activation energy than the hydrolytic reaction.

It is not possible to draw any conclusions from the present results relevant to the electron equivalency of the redox steps, since there is no way to establish whether L$'$ in reaction 6b is an odd-electron or even-electron species.

Mechanism.—Wilson and Harris[11] have suggested a mechanism for the SCN^-–H_2O_2 reaction which combines electrophilic attack of H_2O_2 on sulfur (and carbon) with hydrolytic steps.

The present results support the suggestion that initial attack occurs at the sulfur atom.[18] The subsequent reactions are more rapid and therefore not susceptible to elucidation by the usual kinetic methods. The stoichiometric results, however, establish the presence of a competitive step somewhere in the reaction sequence as described in the previous section. This competitive step involves an acid dependence which is *not* related to that shown by the rate law.

Activation Parameters.—The activation parameters reported in Table III for the $(H_3N)_5CoNCS^{2+}$ oxidation are for the second-order path; they are rather similar to values reported previously for oxidation by hydrogen peroxide and other peroxo oxidants.[19,20]

(18) Additional support is provided by unpublished observations of A. J. Sadowski of this laboratory that addition of Hg^{2+} ion to the reaction systems greatly reduces the rate of reaction. It is known that Hg^{2+} bonds strongly to the exposed sulfur of $(H_3N)_5CoNCS^{2+}$.

(19) Activation parameters for six second-order oxidations by hydrogen peroxide tabulated in ref 13 (p 92 ff) show the following ranges: $\Delta H^* = 12.8$–23.0 kcal/mole; $\Delta S^* = -25$ to -11 eu.

(20) Note Added in Proof.—We have just learned that the reaction of $(H_3N)_5CoNCS^{2+}$ with H_2O_2 has recently been studied by A. R. Norris and S. M. Caldwell (Queen's University, Kingston, Ontario). Working at 25° and in the range [H$^+$] = 0.05–0.50 they obtain a rate law in agreement with that reported here. They also have evidence that a significant fraction of the Co(III) product is in the form of a complex other than $Co(NH_3)_6{}^{3+}$.

Nickel Complexes with 2-Diethylphosphinoethyl Ethyl Sulfide

By J. F. SIECKHAUS and T. LAYLOFF

The new bidentate ligand diethylphosphinoethyl ethyl sulfide, DPES, has been synthesized, and a series of Ni(II) complexes characterized. Five-coordinate, diamagnetic complexes of general formula [Ni(DPES)$_2$X]ClO$_4$ (where X = Cl, Br, I) have been obtained, and spectral studies appear to be consistent with a square-pyramidal structure. The thiocyanate complex, Ni(DPES)$_2$(NCS)$_2$, exists in two isomeric forms, a diamagnetic, four-coordinate species in which DPES is believed to function as a monodentate ligand bonding only through phosphorus and a paramagnetic, octahedral adduct in which DPES is bidentate.

In recent years many nickel complexes with bidentate ligands containing phosphorus, arsenic, and sulfur have been reported. These include the complexes with o-phenylenebisdimethylarsine (DAS),[1] 1,2-bis(diethylphosphino)ethane,[2,3] 1,2-diethylthioethane,[4] and dimethyl-o-methylthiophenylarsine.[5] The physical properties of the bis-chelate adducts, Ni(chelate)$_2$X$_2$ (where X is a univalent anion), vary significantly with the nature of the bidentate ligand. For example, the diarsine and diphosphine complexes are diamagnetic and ionize in noncoordinating solvents as uni-univalent

(1) C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960).

(2) C. E. Wymore and J. C. Bailar, *J. Inorg. Nucl. Chem.*, **14**, 42 (1960).
(3) G. Booth and J. Chatt, *J. Chem. Soc.*, 3238 (1965).
(4) R. Backhouse, M. Foss, and R. S. Nyholm, *ibid.*, 1714 (1957).
(5) S. Livingstone, *ibid.*, 4222 (1958).

electrolytes when a halide is the anion and as bi-univalent electrolytes when perchlorate is the anion. The halide adducts are apparently five-coordinate in these solvents and tetragonal in the solid state.[1,6] The thioether and dimethyl-*o*-methylthiophenylarsine complexes, however, are octahedral. These latter complexes have magnetic moments indicative of two unpaired electrons and are nonelectrolytes in most solvents.

Tertiary phosphines are believed to be stronger field ligands than tertiary arsines,[7] and therefore the mixed-donor chelate, 2-diethylphosphinoethyl ethyl sulfide (DPES) (I), was synthesized in order to study the

$$(C_2H_5)_2PC_2H_4S(C_2H_5)$$

DPES

I

SP

II
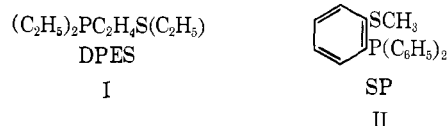
effects of phosphine and thioether linkages on the coordination number of Ni(II) halide complexes. A similar bidentate ligand, *o*-methylthiophenyldiphenylphosphine (SP) (II), was recently reported,[8] and nickel halide complexes with the two ligands are quite similar. However, a rather striking difference is noted in the behavior of these two ligands toward Ni(II) thiocyanate. Ligand II forms a five-coordinate cationic species, Ni(SP)$_2$(NCS)$^+$, which is similar to the halide adducts, while ligand I gives two isomeric complexes of formula Ni(DPES)$_2$(NCS)$_2$, neither of which has the structure and properties of the corresponding halide complexes.

Experimental Section

Diethylphosphinoethyl Ethyl Sulfide.—Diethylphosphinoethyl ethyl sulfide was prepared by the addition of 2-chloroethyl ethyl sulfide (Wateree Chemical Co.) to sodium diethyl phosphide in liquid ammonia. All operations were carried out under nitrogen at −78°. In a typical reaction 10 g of Na was dissolved in 600 ml of liquid ammonia in a 1-l. three-necked flask. Dry phosphine was bubbled through until the blue color of the metal ammonia solution had turned to yellow. The yellow color of this solution was dicharged by the addition of 47 g of ethyl bromide in 50 ml of diethyl ether. The mixture was allowed to stir for 15–20 min and then 17 g of sodium amide (Fisher Scientific Co.) was added. Stirring was continued for 2 hr during which time the mixture turned a dark green. This color was then discharged by the addition of 47 g of ethyl bromide. The subsequent addition of 17 g of sodium amide and vigorous stirring for 2–3 hr produced the dark red sodium diethyl phosphide. 2-Chloroethyl ethyl sulfide was then added dropwise until the red color was discharged. The amount of sulfide required was 43 g (theoretical, 53 g). After stirring for 15–20 min the Dry Ice bath was removed and the liquid ammonia was allowed to evaporate. To the remaining white solid were added 150 ml of freshly boiled water and 150 ml of diethyl ether. The ether layer was separated and dried over anhydrous sodium sulfate. The ether was removed by distillation at atmospheric pressure and the liquid which remained was vacuum distilled. A colorless liquid [bp 59° (0.4 mm)] which weighed 31 g (40%) was obtained.

Anal. Calcd for C$_8$H$_{19}$PS: C, 53.91; H, 10.67. Found: C, 53.93; H, 10.59.

(6) J. Lewis, R. S. Nyholm, and G. Rodley, *J. Chem. Soc.*, 1483 (1965).

(7) J. Chatt, G. Gamlen, and L. Orgel, *ibid.*, 1047 (1959).

(8) G. Dyer, D. Meek, M. Workman, and T. Du Bois, paper presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966; G. Dyer, M. O. Workman, and D. W. Meek, *Inorg. Chem.*, **6**, 1404 (1967).

[Ni(DPES)Br$_2$].—An acetone solution containing 3.0 g (0.014 mole) of NiBr$_2$ and 2.5 g (0.014 mole) of I was refluxed for 2 hr. The purple crystals which were obtained on cooling were recrystallized from acetone and dried over P$_2$O$_5$ *in vacuo*.

Anal. Calcd for C$_8$H$_{19}$PSBr$_2$Ni: C, 24.21; H, 4.79; S, 8.09; Ni, 14.80. Found: C, 24.10; H, 4.69; S, 8.28; Ni, 14.81.

[Ni(DPES)$_2$(ClO$_4$)$_2$].—To 2.88 g (0.0078 mole) of Ni(ClO$_4$)$_2$·6H$_2$O in 25 ml of hot butanol was added 2.8 g (0.016 mole) of ligand I. A yellow-brown oil formed immediately. The addition of 8–9 ml of absolute ethanol solidified the oil yielding 4.5 g of crude product. The compound was obtained as large rust-colored crystals by crystallization from an acetone–ethyl acetate mixture.

Anal. Calcd for C$_{16}$H$_{38}$P$_2$S$_2$Cl$_2$O$_8$Ni: C, 31.28; H, 6.19; Ni, 9.56. Found: C, 31.44; H, 6.30; Ni, 9.53.

[Ni(DPES)$_2$I$_2$].—To 10 ml of a saturated aqueous solution of KI was added 0.7 g of Ni(DPES)$_2$(ClO$_4$)$_2$ in 30 ml of acetone. The purple precipitate obtained by evaporating this solution was recrystallized from ethanol. This complex can also be prepared by the reaction of ligand I with NiI$_2$ in ethanol.

Anal. Calcd for C$_{16}$H$_{38}$P$_2$S$_2$I$_2$Ni: C, 28.70; H, 5.68; I, 37.96; Ni, 8.77. Found: C, 29.00; H, 5.81; I, 36.99; Ni, 8.74.

[Ni(DPES)$_2$IClO$_4$].—To 0.295 g (0.0019 mole) of NaI was added 1.203 g (0.0019 mole) of Ni(DPES)$_2$(ClO$_4$)$_2$ in 30 ml of acetone. A mixture of purple and maroon microcrystals was obtained from the purple solution after filtration and evaporation to 10 ml. These crystals were removed by filtration, and the addition of water to the mother liquor yielded a dark maroon crystalline precipitate. This precipitate was filtered, washed with water, and dried over P$_2$O$_5$ *in vacuo*.

Anal. Calcd for C$_{16}$H$_{38}$P$_2$S$_2$IClO$_4$Ni: C, 29.95; H, 5.92; I, 19.79; Ni, 9.15. Found: C, 31.08; H, 6.15; I, 19.20; Ni, 9.12.

[Ni(DPES)$_2$BrClO$_4$].—To 5 ml of a saturated aqueous solution of sodium bromide was added 2 g of Ni(DPES)$_2$(ClO$_4$)$_2$ in 20 ml of acetone. The resulting solution was filtered to remove the excess sodium bromide. The acetone was removed by distillation at reduced pressure and an oily material remained. The oil was redissolved in a small amount of acetone and the solution was cooled in an ice bath. The purple crystalline precipitate which formed was collected by filtration, washed with water, and dried over P$_2$O$_5$ *in vacuo*.

Anal. Calcd for C$_{16}$H$_{38}$P$_2$S$_2$BrClO$_4$Ni: C, 32.25; H, 6.39; Br, 13.45; Ni, 9.87. Found: C, 31.61; H, 6.13; Br, 14.06; Ni, 9.80.

[Ni(DPES)$_2$(ClO$_4$)$_2$·2Ni(DPES)$_2$ClClO$_4$].—To 5–10 ml of a saturated aqueous solution of NaCl was added 2 g of Ni(DPES)$_2$-(ClO$_4$)$_2$ in 20 ml of acetone. The excess NaCl was removed by filtration and a dark red crystalline precipitate was obtained by evaporating the red solution to near dryness. This precipitate was recrystallized from acetone and dried over P$_2$O$_5$ *in vacuo*.

Anal. Calcd for C$_{48}$H$_{114}$P$_6$S$_6$Cl$_6$O$_{16}$Ni$_3$: C, 33.65; H, 6.65; Ni, 10.28; Cl, 12.42. Found: C, 33.49; H, 6.74; Ni, 10.33; Cl, 12.76.

[Ni(DPES)$_2$(NCS)$_2$]. Yellow Isomer.—To 10 ml of a saturated aqueous solution of potassium thiocyanate was added 1 g of Ni-(DPES)$_2$(ClO$_4$)$_2$ in 10–20 ml of acetone. The red-brown solution was evaporated and a yellow precipitate was obtained. The complex was recrystallized as yellow flakes from an acetone–aqueous ethanol mixture and dried over P$_2$O$_5$ *in vacuo*.

Anal. Calcd for C$_{18}$H$_{38}$N$_2$P$_2$S$_4$Ni: C, 40.71; H, 7.15; Ni, 11.05. Found: C, 41.19; H, 7.27; Ni, 11.15.

Olive Isomer.—To 20 ml of a 75% ethanol solution containing 1.3 g of NiCl$_2$·6H$_2$O and 1.1 g of KSCN was added 1.9 g of ligand I. The green-brown precipitate which formed was recrystallized by precipitation from a dilute acetone solution with aqueous ethanol. The dark olive crystals were removed by filtration and dried over P$_2$O$_5$ *in vacuo*.

Anal. Calcd for C$_{18}$H$_{38}$N$_2$P$_2$S$_4$Ni: C, 40.71; H, 7.15; Ni, 11.05. Found: C, 41.01; H, 7.34; Ni, 10.97.

Physical Measurements and Analyses.—The magnetic sus-

ceptibilities of the solid complexes were obtained at room temperature by the Gouy method using $NiCl_2 \cdot 6H_2O$ as the standard. All are diamagnetic except the olive isomer of $Ni(DPES)_2$-$(NCS)_2$ which has a magnetic moment of 2.96 BM (corrected for diamagnetism).

Conductance measurements were made with an Electro-Measurements, Inc. Model 250-DA impedance bridge. Molar conductances were measured at 25° employing 10^{-3} M solutions and a bridge frequency of 1000 cps (Table I). Conductometric titrations were performed in acetone using the impedance bridge and a pair of platinum electrodes arbitrarily spaced (Figure 1).

TABLE I
PROPERTIES OF THE COMPLEXES

Complex	Color	Mp, °C	$\Lambda_M,^a$ cm²/ohm mole	Electronic absorption maxima, cm⁻¹ ^{b}
$Ni(DPES)Br_2$	Purple	139–141	0.1	19,230 (895); 26,320 (1180)
$Ni(DPES)_2(ClO_4)_2$	Rust	143–145	45.7	24,040 (500)
$Ni(DPES)_2(NCS)_2$	Yellow	68–69	3.3	22,730 sh (1150); 27,-550 (7000)
$Ni(DPES)_2(NCS)_2$	Olive	68–71	3.0	22,730 sh (1330); 27,-500 (8000) 9340; 10,100; 12,690; 13,240 (sh)^c
$Ni(DPES)_2I_2$	Purple	132–134	25.4	18,450 (1130); 27,470 (2400)
$Ni(DPES)_2I(ClO_4)$	Purple	128–130	29.0	20,000 (850); 27,320 (1000)
$Ni(DPES)_2Br(ClO_4)$	Purple	121–125	28.7	20,490 (760); 25,510 (1700)
$Ni(DPES)_2(ClO_4)_2 \cdot$ $2Ni(DPES)_2Cl(ClO_4)$	Dark red	139–141	37.9^d	22,220 (515)^e

^{a} For approximately 10^{-3} M nitrobenzene solutions at 25°. A uni-univalent electrolyte will have a value in the range 20–30 and a bi-univalent electrolyte will have a value in the range 40–60. ^{b} Acetone solutions unless otherwise noted; sh, shoulder; bracketed numbers are molar absorptivities. ^{c} This spectrum was obtained on a Nujol mull of the solid. The authors wish to thank one of the referees for pointing out this technique. ^{d} Conductance per $[Ni(DPES)_2^{2+}]$ moiety or $\Lambda_M/3$. ^{e} Absorptivity calculated per $[Ni(DPES)_2^{2+}]$ moiety. The band of $[Ni(DPES)_2Cl^+]$ appears at 21,500 cm⁻¹ (see text).

The spectra in the visible and ultraviolet regions were obtained with a Bausch and Lomb 505 spectrophotometer. A Beckman DU with cell compartment thermostated at 25° was used for stability constant determinations. Infrared spectra were obtained using a Perkin-Elmer Model 21 spectrophotometer.

Nickel was determined using a standard electrogravimetric method. Analyses of C, H, P, S, I, Br, and Cl were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Formation Constants.—For an equilibrium involving two complexes the reaction can be written

$$[Ni(DPES)_2^{2+}] + nX^- \underset{}{\overset{K_f}{\rightleftharpoons}} [Ni(DPES)_2X_n^{(2-n)+}] \quad (1)$$
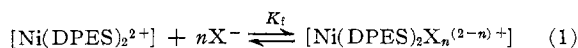
The combination of this expression with Beer's law yields

$$\log \frac{A_a - A_0}{A_\infty - A_a} = \log K_f + n \log [X^-] \quad (2)$$

where A_0, A_a, and A_∞ are the absorbancies at a specific wavelength of solutions of $Ni(DPES)_2^{2+}$ containing no X^-, a M X^-, and sufficient X^- to convert all $Ni(DPES)_2^{2+}$ to $[Ni(DPES)_2$-$X_n^{(2-n)+}]$, respectively. The plot of log $[(A_a - A_0)/(A_\infty - A_a)]$ vs. log $[X^-]$ has a slope equal to n. The value of K_f can then be calculated from eq 2.

Aqueous solutions of approximately 5×10^{-4} M $Ni(DPES)_2^{2+}$ were prepared by dissolving calculated amounts of $Ni(DPES)_2$-$(ClO_4)_2$ in water and diluting to 100 ml. Samples of these solutions were then transferred via a pipet to flasks containing appropriate amounts of KI, KBr, and KCl. The quantities of these salts were previously calculated to give the desired molarity upon dissolution in 10 ml of the $Ni(DPES)_2^{2+}$ solutions. The

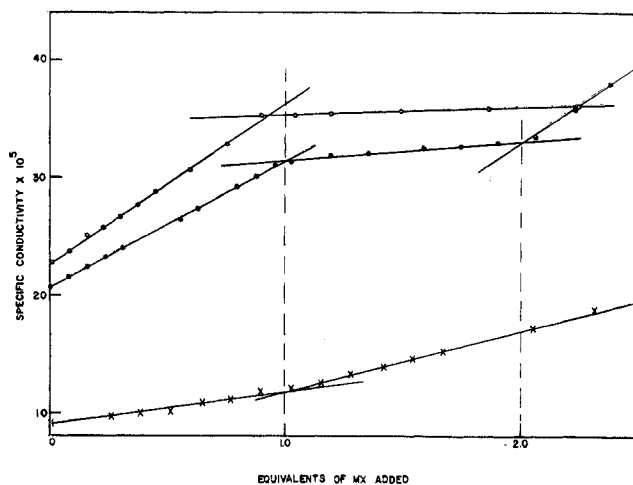Figure 1.—Conductometric titrations of $Ni(DPES)_2(ClO_4)_2$ in acetone with: ○, LiCl in acetone; ×, NaI in acetone; and ●, KSCN in acetone.

results of the plots are given in Table II together with the energies of the visible transitions of the four- and five-coordinate species in water and acetone.

TABLE II
FORMATION CONSTANT DATA FOR THE FIVE-COORDINATE $[Ni(DPES)_2X^+]$ CATIONS

Complex	ν_{max}, cm⁻¹ Acetone	Water	n	K_f
$Ni(DPES)_2(ClO_4)_2$	24,000	24,300	...	...
$Ni(DPES)_2Cl^+$	21,500	22,500	1.02	9.6 ± 0.6^a
$Ni(DPES)_2Br^+$	20,500	22,100	1.01	$(6.2 \pm 0.4) \times 10^b$
$Ni(DPES)_2I^+$	20,000	21,700	1.00	$(2.55 \pm 0.2) \times 10^{2\,a}$

^{a} Determined at 21,280 cm⁻¹. ^{b} Determined at 20,830 cm⁻¹.

Results and Discussion

DPES reacts with Ni(II) salts to form a wide variety of complexes, the structures and stoichiometries of which are highly dependent upon the anion employed. Crystalline complexes have been obtained in which the nickel atom is bonded to both one- and two-chelate donors and has coordination numbers ranging from four to six. All are diamagnetic except the olive isomer of $Ni(DPES)_2(NCS)_2$, and their properties are listed in Table I.

The perchlorate is a bi-univalent electrolyte in nitrobenzene and its infrared spectrum in Nujol shows only a single broad peak in the perchlorate stretching region at 1080 cm⁻¹. The absence of splitting in this band implies that the interaction between the metal and perchlorate ions[9] is predominantly ionic. This fact, coupled with the conductance and magnetic properties, is good evidence that this complex is four-coordinate with a square-planar structure.

Nickel bromide also forms a square-planar complex with I but nickel iodide gives the bis-chelate adduct, $Ni(DPES)_2I_2$. The molar conductance of this iodo complex is indicative of a uni-univalent electrolyte[10] and suggests that this complex exists as a five-coordi-

(9) B. Hathaway and A. Underhill, *J. Chem. Soc.*, 3091 (1961).
(10) A. Kabesh and R. Nyholm, *ibid.*, 38 (1951); C. M. Harris and R. S. Nyholm, *ibid.*, 4375 (1956).

nate species in solution. The break in the titration curve of $Ni(DPES)_2^{2+}$ with lithium chloride and the isolation of the iodo- and bromoperchlorate complexes, $Ni(DPES)_2X(ClO_4)$ (where X = I, Br), are good evidence that I is capable of effecting pentacoordination in Ni(II) halide complexes. The only chloro complex that could be isolated in crystalline form is the mixed salt, $Ni(DPES)_2(ClO_4)_2 \cdot 2Ni(DPES)_2Cl(ClO_4)$. This complex is similar to the diarsine adduct, $Ni(DAS)_2$-$(ClO_4)_2 \cdot 2Ni(DAS)_2I(ClO_4)$, reported by Harris, Nyholm, and Phillips.[1] The nature of this mixed salt was confirmed by elemental analyses (particularly carbon) and by the equivalent conductance value intermediate between that of a bi-univalent and a uni-univalent electrolyte.

Perhaps the most unusual of the nickel complexes with DPES is the thiocyanate adduct, $Ni(DPES)_2$-$(NCS)_2$. Two different forms of this compound have been obtained, a yellow crystalline-flake material and an olive-green microcrystalline complex. The yellow isomer is obtained by allowing $Ni(DPES)_2(ClO_4)_2$ to react with aqueous potassium thiocyanate in acetone, while the olive adduct is prepared by direct combination of $Ni(NCS)_2$ with DPES in ethanol. Recrystallization of either of these complexes generally produces the yellow adduct, but the olive isomer can be obtained by precipitation from a dilute acetone solution with aqueous ethanol.

The olive and yellow complexes exist in the same form in solution since their infrared and electronic spectra in acetone and their molar conductances in nitrobenzene are virtually identical. Both are diamagnetic in acetone, and while the yellow isomer is diamagnetic in the solid state also, the olive complex is paramagnetic with a moment of 2.96 BM. The C–S stretching frequencies of both adducts in Nujol are in the range generally attributed to N-bonded (as opposed to S-bonded) thiocyanate ion.[11] The yellow isomer absorbs at 857 cm^{-1} and the olive complex at 805 cm^{-1}. In acetone the C–S band appears at 857 cm^{-1} in the spectra of both complexes.

The rather unusual forms of structural isomerism in the solid state depicted in IIIa and b are suggested to account for the observed properties of these two complexes. The magnetic moment of the olive isomer results from the octahedral configuration of ligand-donor atoms about the nickel ion in structure IIIb. The

IIIa   IIIb
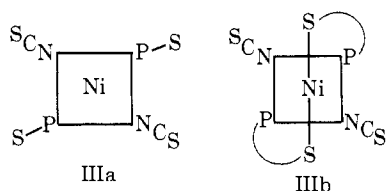
visible spectrum of the solid complex (Table I) is consistent with an octahedral structure and is quite similar to the spectra of other high-spin nickel(II) complexes which contain mixed-donor chelating ligands.[12,13]

The splitting of the band at *ca.* 10,000 cm^{-1} indicates some tetragonal distortion from regular O_h symmetry[14] and is expected in a complex which has two phosphorus, two sulfur, and two nitrogen atoms coordinated to the metal ion. When this adduct is dissolved in acetone or nitrobenzene the nickel–sulfur bonds are ruptured and the complex becomes four-coordinate and identical with the yellow isomer (structure IIIa). The instability of the nickel–sulfur bond in this complex is demonstrated by the conductometric titration of $Ni(DPES)_2$-$(ClO_4)_2$ with potassium thiocyanate in acetone in that the plot of this titration (Figure 1) has two breaks which occur at the first and second equivalence points. While this plot could also be interpreted by assuming the formation of a six-coordinate species, conductance and spectral studies indicate that DPES is functioning as a unidentate ligand, with coordination through the phosphorus atoms in the *trans* positions.

When methyl iodide is added to solutions of Ni-$(DPES)_2(NCS)_2$ (either isomer) in nitrobenzene, the conductance increases quite markedly. Since tertiary phosphines and dialkyl sulfides both undergo salt formation with alkyl halides,[15] this observation serves only as an indication that I is functioning as a unidentate ligand. The conductances of solutions of Ni-$(DPES)Br_2$, $Ni(DPES)_2I_2$, and $Ni(DPES)_2(ClO_4)_2$ (in which I is bidentate) do not increase when methyl iodide is added.

The assumption that I forms bonds through the phosphorus atoms in the *trans* positions is based on the comparison of the electronic spectra of $Ni(DPES)_2$-$(NCS)_2$ with that of *trans*-$Ni[(C_2H_5)_3P]_2(NCS)_2$ which has a known *trans*-planar arrangement of ligand donor atoms. Ligand I bonding only through phosphorus should be very similar to triethylphosphine and the spectra of *trans*-$Ni[(C_2H_5)_3P_2]_2(NCS)_2$ and $Ni(DPES)_2$-$(NCS)_2$ are similar (Table III). This assignment is further substantiated by comparing the spectrum of the analogous *cis*-planar adduct, $Ni[(C_2H_5)_2PC_2H_4P$-$(C_2H_5)_2](NCS)_2$, which has a noticeably different spectrum.

The behavior of the thiocyanate ion in this system is rather unusual and can best be explained by assuming that thiocyanate exerts a stronger ligand field than any of the halides. The high-spin moment of the olive isomer is evidence of that fact.

Since the thiocyanate ion reacts with $Ni(DPES)_2$-$(ClO_4)_2$ to give a complex in which it appears that the phosphorus atoms are *trans* to one another, it might be argued that the perchlorate adduct has a similar configuration, but one in which the sulfur atoms are bound to the nickel ion in the remaining sites in the square plane. Furthermore, since the five-coordinate halide

(11) J. Lewis, R. Nyholm, and P. Smith, *J. Chem. Soc.*, 4590 (1961); A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

(12) C. S. K. Chia, S. E. Livingstone, and T. N. Lockyer, *Australian J. Chem.*, **20**, 239 (1967).

(13) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *ibid.*, **20**, 471 (1967).

(14) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, Inc., New York, N. Y., 1966.

(15) E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. II, Chemical Publishing Co., Inc., New York, N. Y., 1960; G. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950.

TABLE III

ELECTRONIC SPECTRA OF SOME SQUARE-PLANAR
NICKEL–PHOSPHINE COMPLEXES IN BENZENE

Complex	$\bar{\nu}_{max}$	ϵ_{max}	Ref
Ni(DPES)$_2$(NCS)$_2$	27,030	7800	...
	22,730 sh	1100	
trans-Ni[(C$_2$H$_5$)$_3$P]$_2$(NCS)$_2$	27,170	9900	b
	22,222	1200	
cis-Ni[(C$_2$H$_5$)$_2$PC$_2$H$_4$P(C$_2$H$_5$)$_2$]- (NCS)$_2$	25,190^a	1900	c

^{a} Spectrum measured in aqueous ethanol. ^{b} D. Klos, Master's Thesis, St. Louis University, 1963. ^{c} J. Tentor, Master's Thesis, St. Louis University, 1963.

complexes were prepared by reaction of alkali halides with Ni(DPES)$_2$(ClO$_4$)$_2$, these adducts quite probably have the *trans* arrangement of ligand-donor atoms also. However, additional evidence is needed to establish these structures.

The structure of the five-coordinate Ni(DPES)$_2$X$^+$ cations appears to be square pyramidal since the electronic spectra of these complexes (Figure 2) differ from those of known trigonal-bipyramidal adducts. The spectra of these latter complexes are characterized by two absorptions in the visible region assignable to the $^1A_1 \rightarrow {}^1E(D)$ transitions in C_{3v} symmetry,[16] while the visible spectra of the DPES adducts of ligand I show only a single band near 21,000 cm^{-1}. Whereas the spectral evidence alone is not sufficient to rule out the trigonal-bipyramidal structure, the effect of solvent on these spectra and the formation constants of the five-coordinate species can be best interpreted on the basis of a square-pyramidal configuration.

Figgis has proposed that the d orbitals in a square-pyramidal complex are likely to be split in the order $d_{x^2-y^2} > d_{z^2} > d_{xz}, d_{yz}, > d_{xy}$.[14] Assuming that this scheme is correct, the first spin-allowed absorption band in the visible spectrum of a low-spin d^8 complex of C_{4v} symmetry would be that corresponding to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition ($^1A_1 \rightarrow {}^1B_2$). It is believed that the visible band which appears in the spectra of the five-coordinate Ni(DPES)$_2$X$^+$ complexes corresponds to this transition, and the following arguments are cited in evidence.

The energy separation between the d_{z^2} and $d_{x^2-y^2}$ orbitals is a measure of the difference in the perturbing effects of the axial and in-plane ligands on the d orbitals of the metal ion. As long as this difference is of a sufficient magnitude that the splitting energy is greater than the pairing energy (of the electrons in the d_{z^2} orbitals), the d^8 complex will remain diamagnetic. However, as the ligand field strength of the axial ligand increases, this energy separation becomes smaller; and, in the limiting case when the perturbation of the d_{z^2} and $d_{x^2-y^2}$ orbitals is approximately the same, the complex becomes paramagnetic. In the intermediate cases the energy of the $^1A_1 \rightarrow {}^1B_2$ transition decreases with increasing axial perturbation and the corresponding spectral bands shift to lower wavenumbers. Such an argument presupposes that the normal spectro-
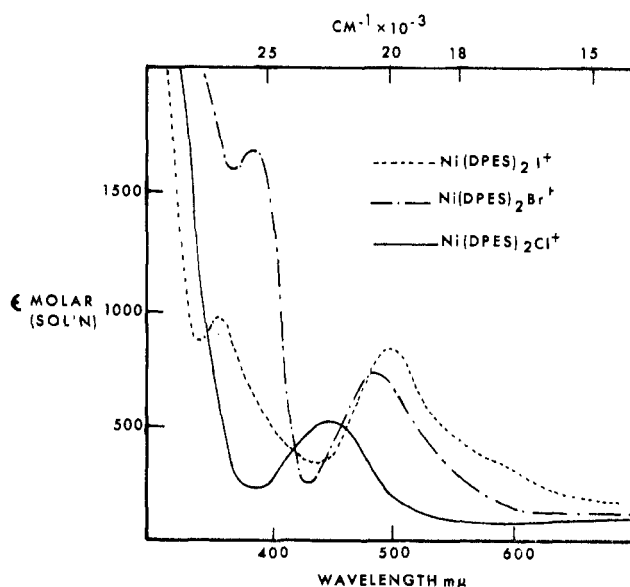
Figure 2.—Electronic absorption spectra of the Ni(DPES)$_2$X$^+$ ions (where X = Cl, Br, I) in acetone.

chemical series observed for transition metal ions will be reversed in this case, with the stronger field ligands, X, in a series of Ni(chelate)$_2$X$^+$ complexes absorbing at lower energies. An examination of the spectral data in Table I and Figure 2 shows that the energy of the visible band in the spectra of the five-coordinate cations increases in the order of the normal spectrochemical series for halide ions (I < Br < Cl). Evidence has been obtained, however, which suggests that iodide ion exerts a stronger ligand field than chloride ion in this system, and the arguments presented previously can still be successfully applied to the spectra of these five-coordinate complexes.

In nonaqueous solvents the Ni(DPES)$_2^{2+}$ substrate has an apparent high affinity for each of the halide ions, since reactions between equimolar quantities of these species go essentially to completion (*cf.* Figure 1). In water, however, the solvation energy of the halide ions competes with the metal–halogen bond energy, and the result is a decrease in interaction energy between the planar Ni(DPES)$_2^{2+}$ moiety and the halide ions. Consequently, the evaluation of K_f in aqueous media provides a means of determining the affinity of the Ni(II) substrate for the various halide ions. All three halides give five-coordinate complexes ($n = 1$ in each case), and a marked increase in stability is noted in the series Cl < Br < I (Table II). The apparent reversal in ligand field strengths of the halide ions in these complexes is unusual but not unique. A similar effect has been observed in the Ni(II) halide system involving the ligand diphenylphosphine. Both Ni[(C$_6$H$_5$)$_2$PH]$_3$I$_2$ and Ni[(C$_6$H$_5$)$_2$PH]$_3$Br$_2$ have been shown to have a pseudo-square-pyramidal structure,[17] but the five-coordinate bromo complex is diamagnetic while the corresponding iodo species is paramagnetic with a moment of 1.29 BM.[18] The energy separation between the d_{z^2} and $d_{x^2-y^2}$ orbitals is so small in this latter case that the

(16) G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964); G. Dyer and D. W. Meek, *ibid.*, **4**, 1398 (1965).

(17) J. Bertrand and D. Plymale, *ibid.*, **5**, 879 (1966).

(18) R. Hayter, *ibid.*, **2**, 932 (1963).

complex is near the "magnetic crossover point" where the ground state changes from a singlet to a triplet and population of both levels is possible. The fact that the bromide complex remains diamagnetic is a clear indication that the ligand field strength of the iodide ion is greater in this system too.

These data concur with the arguments for assignment of the first spin-allowed visible band in the spectra of these five-coordinate cations to the $^1A_1 \rightarrow {}^1B_2$ transition. In further support of this assignment is the fact that these bands occur at higher energy in water than they do in nonaqueous solvents. In water the axial perturbation caused by the halide ions is decreased relative to that in weaker solvating media such as acetone because of the competition between the solvent and the substrate for the anions. As a result the energy of the d_{z^2} orbital is much less affected and the $^1A_1 \rightarrow {}^1B_2$ transition occurs at higher energy.

A further aspect of the spectra of these five-coordinate $Ni(DPES)_2X^+$ cations must be noted since it may indicate a tendency of the nickel ion to increase its coordination number from five to six. When progressively larger amounts of lithium chloride are added to a solution of $Ni(DPES)_2(ClO_4)_2$ in acetone, the frequency of maximum absorption shifts to lower energy

$(24,040 \rightarrow 20,000$ cm$^{-1})$, and the extinction coefficient passes through a maximum of about 700 at 21,500 cm^{-1}. This maximum occurs at the 1:1 equiv point and is therefore believed to be characteristic of the five-coordinate $[Ni(DPES)_2Cl^+]$ species. A similar effect is observed in the spectra of the bromo and iodo complexes as the absorption bands of $[Ni(DPES)_2Br]$-(ClO_4) and $[Ni(DPES)_2I](ClO_4)$ are shifted from 20,490 to 19,380 cm^{-1} and 20,000 to 18,450 cm^{-1}, respectively, when excess bromide and iodide ions are added. In the latter case the band at 18,450 cm^{-1} is identical with that observed in the spectrum of $Ni(DPES)_2I_2$, and, since it is asymmetric to the high-energy side, it could be indicative of an equilibrium mixture of five- and six-coordinate species. This would be a plausible interpretation of the effects of excess halide on the spectra of the analogous five-coordinate bromo and chloro complexes also.

Kinetics of the Consecutive Substitutions of Ammonia by Chloride Ion in Tetraamminepalladium(II) Ion[1]

BY RICHARD A. REINHARDT AND ROBERT K. SPARKES

The reaction of $Pd(NH_3)_4{}^{2+}$ with Cl$^-$ in acid solution follows predominantly the course

$$Pd(NH_3)_4{}^{2+} \xrightarrow{k_A{}'} Pd(NH_3)_3Cl^+ \xrightarrow{k_B{}'} trans\text{-}Pd(NH_3)_2Cl_2$$
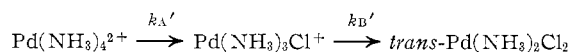
Each pseudo-first-order rate constant is found to obey the two-term rate law $k' = k_1 + k_2[Cl^-]$. Values found at 25° and $\mu = 1$ are $k_{A1} = 0.0011$ sec^{-1}, $k_{A2} = 0.0071$ M^{-1} sec^{-1}, $k_{B1} = 9 \times 10^{-4}$ sec^{-1}, and $k_{B2} = 0.030$ M^{-1} sec^{-1}. Activation enthalpies are smaller than for corresponding Pt(II) reactions; activation entropies are all negative. Estimate is made of the rate constants of the very slow step leading to $Pd(NH_3)Cl_3{}^-$: at 30°, $k_{C1} \sim 3 \times 10^{-6}$ sec^{-1} and $k_{C2} \sim 4 \times 10^{-6}$ M^- sec^{-1}. The *trans* and *cis* effects are discussed.

Introduction

Substitution reactions of square-planar platinum(II) complexes have been studied extensively and results have been summarized elsewhere.[2] Characteristics of these reactions to be noted here are two-term rate laws, *trans* and *cis* effects, and negative entropies of activation. The rates of reaction of analogous Pt(II) and

Pd(II) complexes[3] have been studied and it was found that the relative reactivity of Pd to Pt is *ca.* 10^5, presumably as a result of the increased tendency of Pd(II) to form the five-bonded intermediate.

In their studies of the substitution of various ligands into $Pd(acac)_2$ (acac = acetylacetonate), Pearson and Johnson[4] have established the fundamental similarity in the behavior of the complexes of the two metals. In particular, the two-term rate law was found and a very large *trans* effect was observed.

(1) This research has been supported by the Office of Naval Research. Portions are taken from the M.S. Thesis of R. K. Sparkes, Naval Postgraduate School, 1966.

(2) (a) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 388 (1962); (b) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 2; (c) U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

(3) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 4200 (1960).

(4) R. G. Pearson and D. A. Johnson, *ibid.*, **86**, 3983 (1964).