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Four- and Five-Coordinate Nickel(II) Complexes of 2,3-Butanedionebis(2-diphenylphosphinoethylimine)[1,2]

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The tetradentate ligand 2,3-butanedionebis(2-diphenylphosphinoethylimine), $(C_6H_5)_2PCH_2CH_2N\!\!=\!\!C(CH_3)C(CH_3)\!\!=\!\!NCH_2CH_2P(C_6H_5)_2$, forms the four-coordinate, square $[Ni(C_{32}H_{34}N_2P_2)](ClO_4)_2$ complex and the five-coordinate, diamagnetic, square-pyramidal complexes $[Ni(C_{32}H_{34}N_2P_2)X](ClO_4)\cdot0.5C_2H_5OH$ (X = Cl, Br, I) and $[Ni(C_{32}H_{34}N_2P_2)X](ClO_4)\cdot0.5\text{-}C_4H_9OH$ (X = Cl, Br). The compounds have been characterized by conductivity measurements, proton magnetic resonance spectra, infrared spectra, electronic absorption spectra, and elemental analyses. The electronic absorption spectra of the five-coordinate, square-pyramidal complexes are characterized by a distinct low-energy shoulder on a more intense high-energy absorption band.

Introduction

Although the relative crystal field stabilization energies for low-spin d^8 metal ions in trigonal-bipyramidal and square-pyramidal crystal fields indicate that the square pyramid should be the preferred structure,[3] numerous low-spin, five-coordinate d^8 transition metal complexes with "tripod-like" tetradentate ligands have been shown to possess the trigonal-bipyramidal structure. The structure of some of these complexes[4] has been attributed to such steric requirements of the ligand as the pyramidal nature of the central donor atom, the rigid nature of the carbon chain between donor atoms, and the steric bulk of the terminal donor atoms. The observation that "tripod-like" tetradentate ligands with flexible carbon chains between the donor atoms form trigonal-bipyramidal complexes rather than square-pyramidal complexes has been interpreted as illustrating the importance of electronic factors such as the repulsive interaction between bonding electron pairs and the π-acceptor ability of the ligand donor atoms in determining the structure of low-spin, five-coordinate d^8 complexes.[5,6]

The tetradentate arsenic ligand o-phenylenebis(o-dimethylarsinophenylmethylarsine) forms a square-pyramidal complex with platinum(II), in which one of the inner arsenic donor atoms occupies the apical position of a square pyramid. The formation of a square-pyramidal complex in preference to a trigonal-bipyramidal complex illustrates the importance of ligand field effect associated with the 5d platinum(II) ion in determining the structure of low-spin, five-coordinate d^4 complexes as opposed to steric and electronic factors associated with the ligand.[7] However, the arrangement of donor atoms about the square pyramid results in a relatively unstrained pyramidal arrangement of alkyl and aryl groups about each of the arsenic donor atoms. Thus a combination of ligand field effects and steric requirements of the ligand best accounts for the observed structure.

The more flexible tetradentate ligand 1,3-bis(3-diphenylphosphinopropylthio)propane forms five-coordinate trigonal-bipyramidal complexes with Ni(II) and five-coordinate square-pyramidal complexes with Pd(II) and Pt(II).[8] The square-pyramidal structures of the Pd(II) and Pt(II) complexes are associated with the relatively greater ligand field effects associated with 4d and 5d transition metal ions. The trigonal-bipyramidal structure of the nickel(II) complexes most probably arises from a combination of electronic factors associated with the ligand and steric interactions between the cis diphenylphosphino groups and the fifth donor atom in the corresponding square-pyramidal structure.

The ligand, 2,3-butanedionebis(2-diphenylphosphinoethylimine), was designed and synthesized to investigate (1) the electronic absorption spectra of low-spin, square-pyramidal nickel(II) complexes with a cis arrangement of donor atoms in the basal plane and (2) the steric interactions associated with the introduction of a fifth donor group into a square-planar complex having a cis arrangement of bulky donor groups.

Experimental Section

Reagents.—Reagent grade 1,4-dioxane was dried over sodium wire for several days and then distilled (bp 101°) from molten sodium under a dry nitrogen atmosphere. Dichloromethane was stirred over anhydrous calcium chloride and then distilled (bp 40°) from fresh anhydrous calcium chloride. Acetonitrile was refluxed over calcium hydride, decanted, and then distilled (bp 81°) from P_4O_{10}. 1-Butanol was dried over magnesium oxide and then distilled (bp 117°) from magnesium butoxide. Chlorodiphenylphosphine was vacuum distilled (bp 111° (5 mm)) and the second of three equal fractions was collected. Ethylenimine (Dow) was distilled (bp 55°) from sodium hydroxide. Absolute ethanol and anhydrous diethyl ether were used without further purification.

Synthesis of 2-Diphenylphosphinoethylamine.—2-Diphenylphosphinoethylamine was prepared according to the method of Issleib and Haferburg.[9]

Synthesis of 2,3-Butanedionebis(2-diphenylphosphinoethylimine).—To 5.20 g (22.7 mmol) of 2-diphenylphosphinoethylamine was added 0.977 g (11.35 mmol) of biacetyl under dry nitrogen. After approximately 2 hr sufficient solid had formed to make stirring difficult. Absolute ethanol (100 ml) was added to the reaction mixture and stirring was continued for an additional 48 hr. The white crystals were collected by filtration, washed with three 10-ml portions of absolute ethanol and three 10-ml portions of anhydrous diethyl ether, and dried in a stream of dry nitrogen. The crude product was recrystallized from

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(2) Presented at the 21st Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969; see Abstract No. 187.

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(7) T. L. Blundell and H. M. Powell, *J. Chem. Soc. A*, 1650 (1967).

(8) T. D. DuBois and D. W. Meek, *Inorg. Chem.*, **8**, 146 (1969).

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TABLE I

ELEMENTAL ANALYSES OF $C_{32}H_{34}N_2P_2$ AND ITS NICKEL(II) COMPLEXES[a]

Compound	% calcd					% found				
	C	H	N	P	X	C	H	N	P	X
$C_{32}H_{34}N_2P_2$	75.56	6.74	5.51	12.18	...	75.52	6.84	5.33	12.38	...
$[Ni(C_{32}H_{34}N_2P_2)](ClO_4)_2$	50.16	4.47	...	8.08	9.25	50.00	4.34	...	8.10	9.39
$[Ni(C_{32}H_{34}N_2P_2)Cl]ClO_4 \cdot 0.5C_2H_5OH$	54.66	5.14	3.86	...	4.89	54.49	5.10	3.77	...	4.86[b]
$[Ni(C_{32}H_{34}N_2P_2)Br]ClO_4 \cdot 0.5C_2H_5OH$	51.49	4.85	3.64	...	10.38	51.73	4.77	3.69	...	10.39[b]
$[Ni(C_{32}H_{34}N_2P_2)I]ClO_4 \cdot 0.5C_2H_5OH$	48.51	4.57	3.43	...	15.53	48.71	4.57	3.50	...	15.59[b]
$[Ni(C_{32}H_{34}N_2P_2)Cl]ClO_4 \cdot 0.5C_4H_9OH$	55.25	5.32	...	8.38	9.59	55.10	5.58	...	8.17	9.56[c]
$[Ni(C_{32}H_{34}N_2P_2)Br]ClO_4 \cdot 0.5C_4H_9OH$	52.11	5.01	...	7.90	9.05	52.33	5.24	...	7.63	9.39[c]

[a] Carbon, hydrogen, nitrogen, phosphorus, and total halogen analyses reported as per cent chlorine were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] Ionic halide determined gravimetrically as silver salts. [c] Total halogen reported as per cent chlorine.

butanol, dried in a stream of dry nitrogen, and finally dried *in vacuo* (3.0 g, 52% yield). The elemental analyses for 2,3-butanedionebis(2-diphenylphosphinoethylimine) (mp 144–145°) are reported in Table I.

Synthesis of $[Ni(C_{32}H_{34}N_2P_2)](ClO_4)_2$.—To an ethanol solution (10 ml) containing 0.3657 g (1 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ was added 0.5082 g (1 mmol) of $C_{32}H_{34}N_2P_2$ in dichloromethane (10 ml) under nitrogen. Yellow $[Ni(C_{32}H_{34}N_2P_2)](ClO_4)_2$ crystals separated from the reaction mixture with the slow evaporation of dichloromethane under a stream of dry nitrogen. The crystals were collected on a sintered-glass funnel, recrystallized from a 1:1 mixture of dichloromethane and ethanol, washed with ethanol, washed with diethyl ether, dried in a stream of dry air, and finally dried *in vacuo* (0.60 g, 78% yield). Elemental analyses are reported in Table I.

Synthesis of $[Ni(C_{32}H_{34}N_2P_2)X]ClO_4 \cdot 0.5C_2H_5OH$ (X = Cl, Br, I).—These complexes were prepared by adding 1 mmol of LiCl, NaBr, or NaI dissolved in absolute ethanol to a dichloromethane solution containing 1 mmol of $[Ni(C_{32}H_{34}N_2P_2)](ClO_4)_2$. The appropriate deeply colored complex separated from the solution with the evaporation of dichloromethane from the reaction mixture under a stream of dry nitrogen. The complexes were collected on a sintered-glass funnel, recrystallized from a 1:1 mixture of dichloromethane and ethanol, washed with ethanol, washed with diethyl ether, dried in a stream of dry air, and finally dried *in vacuo* (yields were approximately 80%). The elemental analyses are reported in Table I.

Synthesis of $[Ni(C_{32}H_{34}N_2P_2)X]ClO_4 \cdot 0.5C_4H_9OH$ (X = Cl, Br).—These complexes were prepared according to the procedure given for the $[Ni(C_{32}H_{34}N_2P_2)X]ClO_4 \cdot 0.5C_2H_5OH$ complexes except that 1-butanol was used rather than absolute ethanol in the preparative and recrystallization steps (yields were approximately 80%). The elemental analyses are reported in Table I.

Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 457 spectrophotometer. Spectra were recorded for Nujol mulls between crystalline KBr plates and for deuteriodichloromethane solutions in KBr cells. Visible and ultraviolet spectra of the complexes in solution were recorded with a Cary Model 14 spectrophotometer using matched 0.1- and 1.0-cm cells. The spectra of the complexes in the solid state were obtained with the Cary Model 14 spectrophotometer by using Nujol mulls suspended on filter paper.[10]

Conductance Measurements.—The measurements were performed with an Industrial Instruments Model RC-16B conductivity bridge. All measurements were made at 25.0 ± 0.1° and a frequency setting of 1000 cps for the electrolytes. The cell constant was 1.50. Dilution studies were carried out in acetonitrile over the concentration range of 1×10^{-2} to 1×10^{-4} N.

Pmr Spectra.—The pmr spectra were recorded with a Varian Associates T-60 spectrometer. Tetramethylsilane was used as an internal standard in deuteriodichloromethane solvent.

Results and Discussion

Four-Coordinate Square Complex.—The complex $[Ni(C_{32}H_{34}N_2P_2)](ClO_4)_2$ behaves as a 2:1 electrolyte in acetonitrile solution (Table II).[11–13] The infrared

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(11) G. J. Janz, F. J. Kelley, and H. V. Venkatassetty, "A Survey of Non-Aqueous Conductance Data," Rensselaer Polytechnic Institute, Troy, N. Y., 1962.

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(13) A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, **6**, 458 (1967).

TABLE II

CONDUCTANCE DATA FOR NICKEL(II) COMPLEXES OF $C_{32}H_{34}N_2P_2$ IN ACETONITRILE

Compound	$\Lambda_m{}^a$	$\Lambda_e{}^0$	$A_{exptl}{}^b$	Calcd slopes $A_{1:1}$	$A_{2:1}$
$[Ni(C_{32}N_{34}N_2P_2)](ClO_4)_2$	310	181.3	775	365	712
$[Ni(C_{32}N_{34}N_2P_2)Cl]ClO_4 \cdot 0.5C_2H_5OH$	140	150.7	346	342	650
$[Ni(C_{32}N_{34}N_2P_2)Br]ClO_4 \cdot 0.5C_2H_5OH$	146	156.4	344	346	661
$[Ni(C_{32}H_{34}N_2P_2)I]ClO_4 \cdot 0.5C_2H_5OH$	147	159.2	398	348	667

[a] Molar conductivities for approximately 10^{-3} M acetonitrile solutions. [b] Using the Onsager limiting law, $\Lambda_e{}^0 - \Lambda_e = Ac^{1/2}$, the value of the slope, A, was determined from a plot of equivalent conductivity, Λ_e, against $c^{1/2}$, where c is the equivalent concentration. The value of the limiting equivalent conductivity, $\Lambda_e{}^0$, was obtained by extrapolation of the same plot to $c^{1/2} = 0$.

bands at 625 and 1100 cm^{-1} associated with the perchlorate anion are not split in the solid-state Nujol spectrum indicating that the perchlorate anions are not coordinated.[14] The pmr data for the complex in deuteriodichloromethane indicate that all four donor atoms of the ligand $C_{32}H_{34}N_2P_2$ are coordinated to the nickel(II) cation since a downfield shift is observed for all protons bound to carbon atoms adjacent to the ligand donor groups (Table III).[15–17] Addition of methyl iodide to approximately 10^{-3} M acetonitrile solutions of the complex did not cause an increase in conductivity over a period of 4 weeks. Although a recent report indicates that the methyl iodide conductivity test is not a particularly reliable method for detecting ligand donor atoms which are not coordinated,[17] these observations are consistent with the conclusion drawn from the pmr data that all four ligand donor atoms are coordinated. The electronic absorption spectrum of the diamagnetic $[Ni(C_{32}H_{34}N_2P_2)]$-$(ClO_4)_2$ complex exhibits an absorption maximum at 26,200 cm^{-1} (ϵ 3100) with a low-energy shoulder at ~25,000 cm^{-1} in dichloromethane solution and in the solid state. The similarity of the solid state and the solution electronic spectra indicates that the complex possesses the same structure in dichloromethane solution and in the solid state. The electronic absorption spectrum is consistent with a square-planar arrangement of donor atoms about nickel(II). The low-energy shoulder and the maximum are assigned the transitions of d-orbital character $xy \rightarrow x^2 - y^2$ and $z^2 \rightarrow x^2 - y^2$, respectively.

Five-Coordinate Complexes.—Spectrophotometric titrations of $[Ni(C_{32}H_{34}N_2P_2)](ClO_4)_2$ with $(n\text{-}C_7H_{15})_4$-NCl, $(n\text{-}C_7H_{15})_4$NBr, and $(n\text{-}C_7H_{15})_4$NI in dichloro-

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TABLE III

PMR SPECTRA OF 2,3-BUTANEDIONEBIS(2-DIPHENYLPHOSPHINOETHYLIMINE) AND ITS
DIAMAGNETIC NICKEL(II) COMPLEXES[a]

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| | Proton assignment of resonance signals of ligand, δ, ppm | | | |
Compound	Singlet CH_3	Triplet CH_2P	Triplet CH_2N	Multiplet C_6H_5
$C_{32}H_{34}N_2P_2$	1.91 (5.9)	2.50 (4.1)	3.55 (4.0)	7.35 (20)
$[Ni(C_{32}H_{34}N_2P_2)](ClO_4)_2$	2.35 (6.0)	3.00 (4.0)	3.66 (4.0)	7.35 (20)
$[Ni(C_{32}H_{34}N_2P_2)Cl]ClO_4 \cdot 0.5C_2H_5OH$	2.35 (5.9)	3.11 (4.4)	3.78 (4.0)	7.35 (20)
$[Ni(C_{32}H_{34}N_2P_2)Br]ClO_4 \cdot 0.5C_2H_5OH$	2.35 (6.1)	3.11 (4.8)	3.81 (4.4)	7.35 (20)
$[Ni(C_{32}H_{34}N_2P_2)I]ClO_4 \cdot 0.5C_2H_5OH$	2.36 (6.2)	3.10 (4.6)	3.85 (4.0)	7.35 (20)
$[Ni(C_{32}H_{34}N_2P_2)Cl]ClO_4 \cdot 0.5C_4H_9OH$	2.33 (6.0)	3.16 (9.5)[b]	3.78	7.35 (20)
$[Ni(C_{32}H_{34}N_2P_2)Br]ClO_4 \cdot 0.5C_4H_9OH$	2.33 (6.0)	3.16 (8.8)[b]	3.78	7.35 (20)

[a] Resonance signals for the methyl group of C_2H_5OH and for the methyl group and methylene groups of C_4H_9OH do not overlap with the spectrum of the ligand and give integrated intensities consistent with the formulations. The resonance signals associated with the CH_2OH grouping of both alcohols overlap with the ligand spectrum. Integrated intensities, in parentheses, include the signals due to the CH_2OH protons. [b] Represents total integrated intensity for CH_2P and CH_2N groupings of ligand as well as CH_2OH grouping of butanol.

methane give sharp end points at 1:1 mole ratio of halide ion to the square cation (Figure 1) indicating the formation of five-coordinate cations in solution. Isosbestic points are observed at 350 and 421, 355 and 424, and 365 and 428 nm for Cl^-, Br^-, and I^-, respectively. The solid complexes are isolated as their one-half ethanol or one-half butanol solvates from these
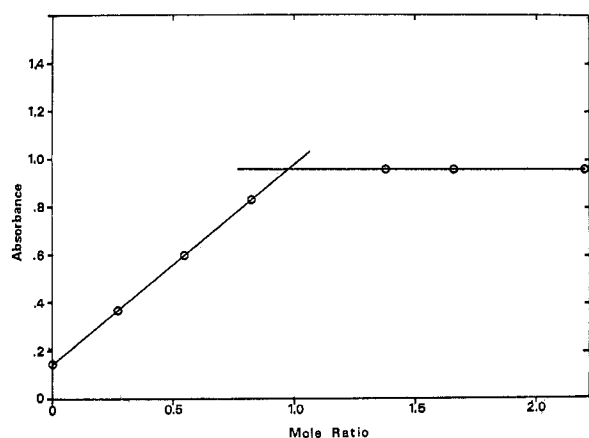

Figure 1.—Spectrophotometric titration of $[Ni(C_{32}H_{34}N_2P_2)]^{2+}$ with $(n\text{-}C_7H_{15})_4NBr$ in dichloromethane solution at 475 nm.

solvents. The ethanol and butanol molecules are not coordinated to the nickel(II) ion since the dichloromethane spectra of the solid complexes are identical with the spectra obtained in the spectrophotometric titrations of $[Ni(C_{32}H_{43}N_2P_2)](ClO_4)_2$ in dichloromethane solution where no ethanol or butanol is present. Further support for this conclusion is found in the fact that the O–H stretch in deuteriodichloromethane solutions of the complexes appears at $\sim$3620 cm^{-1} which is within the range generally observed for dilute solutions of free alcohols in non-hydrogen-bonding solvents.[18] Also, the O–H stretch in the solid state Nujol mulls appears at $\sim$3530 cm^{-1}. The complexes of the type $[M(C_2H_5OH)_6]X_2$ give O–H stretching frequencies for coordinated alcohol at $\sim$3400, 3480–3500, and 3200–3400 cm^{-1} for $X^- = ClO_4^-$, BF_4^-, and NO_3^-, respectively.[19] Finally, only 0.5 mol of alcohol is present for each mole of complex.

No splitting of the 625- and 1100-cm^{-1} infrared bands

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associated with the perchlorate anions is observed in the solid-state Nujol spectra of the $[Ni(C_{32}H_{34}N_2P_2)X]$-$ClO_4 \cdot 0.5ROH$ (R = C_2H_5 and C_4H_9) complexes indicating that the perchlorate anion is not coordinated in the solid complexes.[14] The C=N stretch which occurs at $\sim$1620 cm^{-1} in the free ligand is shifted to $\sim$1575 cm^{-1} on complexation.

The complexes $[Ni(C_{32}H_{34}N_2P_2)X]ClO_4 \cdot 0.5C_2H_5OH$ (X = Cl, Br, I) behave as uni-univalent electrolytes in acetonitrile solution (Table II). The molar conductivities are in the range generally accepted for 1:1 electrolytes in acetonitrile.[11] The slopes of plots of equivalent conductance against the square root of equivalent concentration are in good agreement with the values calculated for 1:1 electrolytes.[12,13] The acetonitrile solutions of the complexes obey Beer's law over the concentration range studied ($\sim$10^{-2} to $\sim$10^{-4} N) eliminating the possibility of equilibria involving either halide ion displacement or ligand donor atom displacement by the solvent.

The proton resonance signals for the five-coordinate complexes are shifted downfield with respect to the values of the free ligand (Table III). The signals for the five-coordinate complexes occur at the same or lower field positions than those for the four-coordinate
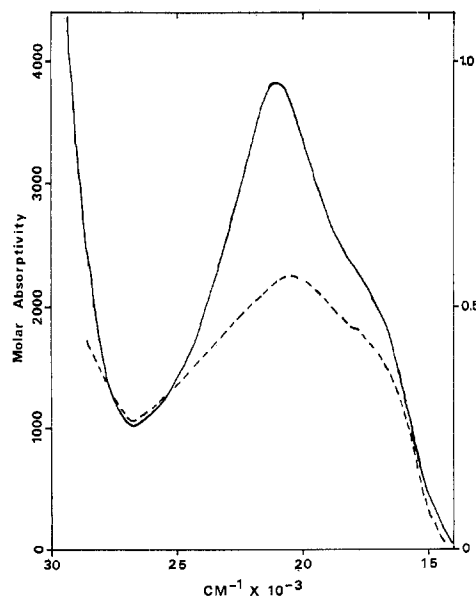

Figure 2.—Electronic absorption spectra of $[Ni(C_{32}H_{34}N_2P_2)Br]$-$ClO_4 \cdot 0.5C_2H_5OH$ in the solid state (— — — —) and in dichloromethane solution (————).

square [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)](ClO$_4$)$_2$ complex in which all four donor atoms of the ligand C$_{32}$H$_{34}$N$_2$P$_2$ clearly must be coordinated. These data strongly suggest that all four donor atoms of C$_{32}$H$_{34}$N$_2$P$_2$ are coordinated and that the complexes are five-coordinate.[15-17] Addition of methyl iodide to the acetonitrile solutions ($\sim$1 $\times$ 10^{-3} M) did not cause an increase in conductivity over a period of approximately 4 weeks. These observations are consistent with the conclusion based on the pmr data that all four ligand donor groups are coordinated.[4,15-17]

The electronic absorption spectra in the solid state and in dichloromethane and acetonitrile solutions exhibit the same absorption maxima (Figure 2) indicating that the complexes possess the same structure both in the solid state and in solution. The absorption maxima produce the usual spectrochemical series of Cl > Br > I (Figure 3). The molar absorptivities of these

Figure 4.—Electronic absorption spectra of [NiAs(o-C$_6$H$_4$As-Ph$_2$)$_3$Br]ClO$_4$ (————), [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)Br]ClO$_4$·0.5C$_2$H$_5$OH (————), and [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)](ClO$_4$)$_2$ (————) in dichloromethane solution.

Figure 3.—Electronic absorption spectra of [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)I]-ClO$_4$·0.5C$_2$H$_5$OH (————), [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)Br]ClO$_4$·0.5C$_2$H$_5$OH (————), and [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)Cl]ClO$_4$·0.5C$_2$H$_5$OH (————) in dichloromethane solution.

Figure 5.—Electronic absorption spectra of [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)-Br]ClO$_4$·0.5C$_2$H$_5$OH (————), [Ni{Ph$_2$P(o-C$_6$H$_4$AsPPh$_2$)}$_2$Br]-ClO$_4$ (————), and Ni{CH$_3$As(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_2$}Br$_2$ (————) in dichloromethane solution.

complexes are not sensitive to the halide donor atom and do not give a definite trend as the fifth donor atom is changed (Figure 3) whereas those of the trigonal-bipyramidal complexes are more sensitive and generally increase in intensity in the order I < Br < Cl.[20-22]

A comparison of the visible electronic absorption spectra of the [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)]$^{2+}$, [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)-Br]$^+$, and [Ni{As(o-C$_6$H$_4$AsPh$_2$)$_3$}Br]$^{+}$ [22,23] complex cations in dichloromethane solution (Figure 4) illustrates that the absorption maximum for the [Ni{C$_{32}$-H$_{34}$N$_2$P$_2$}Br]$^+$ cation occurs at considerably higher energy than that of the trigonal-bipyramidal [Ni{As-(o-C$_6$H$_4$AsPh$_2$)$_3$}Br]$^+$ cation. The spectrum of the five-coordinate cation [Ni(C$_{32}$H$_{34}$N$_2$P$_2$)Br]$^+$ is considerably more intense and shifted to lower energy compared to the spectrum of the square-planar [Ni(C$_{32}$H$_{34}$-

N$_2$P$_2$)]$^+$ cation. Since the spectra of the [Ni(C$_{32}$H$_{34}$-N$_2$P$_2$)X]$^+$ (X = Cl, Br, I) cations are not typical of trigonal-bipyramidal complexes which are characterized by an intense symmetrical absorption maximum at $\sim$16,000 cm^{-1} followed by a much less intense absorption at $\sim$21,000 cm^{-1},[20-24] these complexes are assigned a square-pyramidal structure with all four donor atoms of C$_{32}$H$_{34}$N$_2$P$_2$ being coordinated in the basal plane of the square pyramid. This structural assignment is consistent with the planar nature of the ligand. A trigonal-bipyramidal structure or a square-pyramidal structure in which one or more of the phosphorus donor atoms were not coordinated in the same

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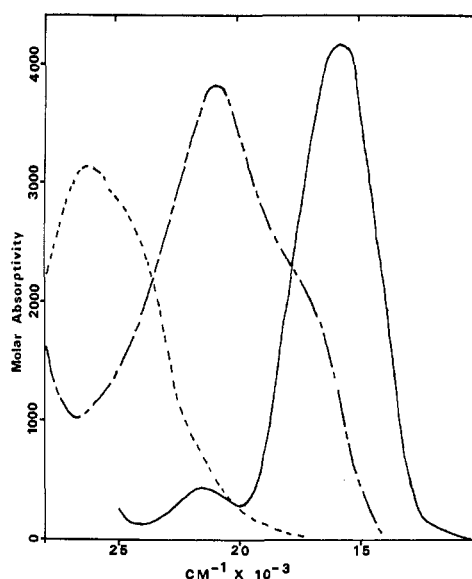(23) G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc., London*, 170 (1961).

(24) L. P. Haugen and R. Eisenberg, *Inorg. Chem.*, **8**, 1072 (1969).

plane as the C_2N_2Ni chelate ring would place excessive strain on the required planar nature of the C_2N_2Ni chelate ring. The low-energy shoulder at ~17,000 cm^{-1} and the maximum at ~21,000 cm^{-1} in the electronic absorption spectra of these five-coordinate, square-pyramidal complexes are assigned to transitions of d-orbital character $z^2 \rightarrow x^2 - y^2$ and $xy \rightarrow x^2 - y^2$, respectively.

The cis arrangement of donor atoms in the basal plane of the square-pyramidal structure yields complexes whose electronic absorption spectra are quite similar in energy position and contour to those of the $Ni\{CH_3-As(CH_2CH_2CH_2AsMe_2)_2\}Br_2$[25,26] (Figure 5) and $Ni\{CH_3N(CH_2CH_2PPh_2)_2\}Br_2$[27,28] complexes which are known to possess unsymmetrical square-pyramidal structures. This observation gives additional support to the assigned square-pyramidal structure. The dia-

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magnetic, five-coordinate nickel(II) complexes of the o-phenylene-bridged bidentate ligands $Ph_2P(o-C_6H_4-AsPh_2)$, $Ph_2P(o-C_6H_4SCH_3)$, and $Ph_2P(o-C_6H_4SeCH_3)$ have been assigned square-pyramidal structures on the basis of their electronic absorption spectra.[29,30] A comparison of the electronic absorption spectrum of the $[Ni\{Ph_2P(o-C_6H_4AsPh_2)\}_2Br]^+$ cation with that of the $[Ni(C_{32}H_{34}N_2P_2)Br]^+$ cation illustrates that the absorption maxima appear at similar energies (Figure 5). The lack of splitting in the absorption bands of the square-pyramidal nickel(II) complexes with the bidentate ligands suggests that these complexes have a trans arrangement of identical donor groups in the basal plane of the square pyramid rather than a cis arrangement of identical donor atoms.

The fact that monomeric complexes of the types $[Ni(C_{32}H_{34}N_2P_2)X]ClO_4 \cdot 0.5ROH$ (X = Cl, Br, I where R = C_2H_5 and X = Cl, Br where R = C_4H_9) can be prepared demonstrates that two diphenylphosphino groups can occupy cis positions in the basal plane of a square-pyramidal nickel(II) complex.

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Magnetic Titrations. Nickel(II) Complexes of C-Substituted Ethylenediamines

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The Quincke method of magnetic susceptibility measurement has been adapted for use in magnetic titrations. The technique has been employed to study the complex formation reactions of nickel(II) with ethylenediamine, 1,2-propanediamine, 2-methyl-1,2-propanediamine, and 2,3-dimethyl-2,3-butanediamine in 40% aqueous methanol solution. It was found that ethylenediamine and 1,2-propanediamine react with nickel(II) to give paramagnetic tris complexes, with no indication of intermediate diamagnetic species. 2-Methyl-1,2-propanediamine gives a paramagnetic tris complex with excess ligand but forms a diamagnetic intermediate species during the magnetic titration at a 2:1 ligand:metal ratio. 2,3-Dimethyl-2,3-butanediamine reacts with nickel(II) to give a diamagnetic bis complex with no indication of further interaction, even at large ligand:metal ratios. Increasing C-substitution of ethylenediamines causes an increase in the relative tendency to form stable diamagnetic bis complexes with nickel(II). This is due principally to steric interactions. The reaction of nickel(II) with *meso*-1,2-diphenylethylenediamine in 50% aqueous dioxane was also studied. A paramagnetic mono complex and a diamagnetic bis complex were formed during the course of the magnetic titration in this system.

Introduction

Nickel(II) complexes of ethylenediamines have been the subject of a number of investigations,[2-8] since the bonding characteristics and even the structure of the complexes are very sensitive to structural variations of the ligand. Ethylenediamine itself and other derivatives which are not highly substituted form blue, paramagentic complexes, whereas highly substituted ligands form yellow, diamagnetic complexes.

Basolo and collaborators have determined stepwise formation constants for the nickel(II) complexes of

several ethylenediamines,[3-5] including ethylenediamine (en), 1,2-propanediamine (pn), 2-methyl-1,2-propanediamine (*i*-bn), 2,3-dimethyl-2,3-butanediamine (tetra-Meen), and *meso*-1,2-diphenylethylenediamine (*ms*-stien). They found that en, pn, and *i*-bn form mono, bis, and tris complexes but that tetraMeen and *ms*-stien do not go beyond the bis complex. Furthermore, the order of stability constants was found to be anomalous for the tetraMeen complex, with K_2 being greater than K_1. In the same study the solid compounds Ni(tetraMeen)$_2$Cl$_2$ and Ni(*i*-bn)$_2$Cl$_2$ were isolated and found to be diamagnetic. It was concluded that the tendency to form yellow, diamagnetic compounds increases with increasing methyl substitution.

Wilkins[7] has studied the kinetics of the dissociation of the mono and bis nickel(II) complexes of all five of these diamines in aqueous acid. Although Basolo found no correlation between C-methyl and C-phenyl

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