easily provide a pathway for the small lattice interaction.

Conclusions

The magnetic and structural properties of these four complexes are summarized in Table II. The copper–copper separations of two of the complexes are greater than 3 Å, and this distance is considered to be too great to allow any significant orbital overlap between copper atoms; moreover, an interaction of this type must be antiferromagnetic in nature. The remaining two complexes, which are very similar in structure, show a negative correlation between the Cu–Cu separation and the value of $2J$. These facts indicate that the spin–spin interaction is of the type proposed by Goodenough,[5] in which the ligand atoms are instrumental in the exchange interaction. Further evidence for the superexchange mechanism is provided by the Cu–O–Cu bridge angles. The assumption that the s-orbital contribution increases as the bridge angle increases from 90° suggests that the value of $2J$ will decrease as the bridge angle increases; our experimental observations are consistent with this postulation.

The pathways available for the intradimer magnetic coupling have been discussed in some detail elsewhere.[2,3,5,17] All major pathways for the exchange interaction make positive contributions to J. Our magnetization studies, which are the first studies of this type of copper(II) compounds, provide strong evidence for the confirmation of the triplet ground state for these complexes.

The molecular field approximation used in the analysis of the data is basically that of Weiss. Although more sophisticated treatments could be used, the more simple method describes the experimental data reasonably well.

Table II. Structural and Magnetic Properties

Complex	Bridge angle, deg	Cu–Cu, Å	$2J$, cm^{-1}	Θ, deg	Ref
$[Cu(Et_2dtc)_2]_2$		3.59	24	−1.15	2, 14
$[Cu(pyO)_2(NO_3)_2]_2$	102.9	3.459	15	−0.50	1, 15
$[Cu(bipy)OH]_2SO_4 \cdot 5H_2O$	97	2.893	48	−0.50	3. 16
$[Cu(bipy)OH]_2(NO_3)_2$	95.6	2.847	172	−0.45	4, 10

Some comment should be made about the relation of the Θ value to the magnetic ordering temperature T_i (i = N or C, depending upon whether the ordering is antiferromagnetic or ferromagnetic, respectively). Although Θ may approximate T_C for ferromagnetic ordering, this is not true for Θ and T_N when antiferromagnetic ordering occurs.[8] Since the interdimer interactions of the systems studied here are antiferromagnetic, we are unable to predict the ordering temperature. It is noteworthy that all of the interdimer interactions that have been observed for copper(II) complexes have been antiferromagnetic in nature.

Registry No. Tetrakis(*N,N*-diethyldithiocarbamato)dicopper(II), 37897-35-1; di-μ-(pyridine *N*-oxide)-bis[bis(nitrato)(pyridine *N*-oxide)copper(II)], 26507-58-4; di-μ-hydroxo-bis(2,2′-bipyridyl)dicopper(II) sulfate pentahydrate, 37838-57-6; di-μ-hydroxo-bis(2,2′-bipyridyl)dicopper(II) nitrate, 37897-36-2; copper(II) nitrate, 3251-23-8.

Acknowledgments. This research was supported by the National Science Foundation through Grant GP-22887 and by the Materials Research Center of the University of North Carolina under Contract DAHC-15-67-C-0223 with the Advanced Research Projects Agency. We wish to thank Mr. Van H. Crawford, Mr. Robert F. Drake, and Mr. Richard P. Eckberg for experimental assistance.

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Ligand-Bridged Five-Coordinate Nickel(II) Complexes

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The tetradentate ligand 2,3-butanedione bis(2-diphenylarsinoethylimine), $(C_6H_5)_2AsCH_2CH_2N{=}C(CH_3)C(CH_3){=}NCH_2CH_2As(C_6H_5)_2$, forms the four-coordinate, square-planar $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$ complex and the five-coordinate, ligand-bridged $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ (X = Cl, Br, I) complexes. The coordination compounds have been characterized by conductivity measurements, molecular weight measurements, proton magnetic resonance spectra, infrared spectra, electronic absorption spectra and elemental analyses. The electronic absorption spectra of the five-coordinate, ligand-bridged complexes of the type $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ are consistent with a square-pyramidal arrangement of donor atoms about the nickel(II) ion.

Introduction

In general it has been observed that five-coordinate, low-spin, trigonal-bipyramidal complexes of nickel(II) give electronic absorption spectra which are characterized by a rather intense symmetrical absorption band followed by a band of much lower intensity at higher energy. The positions of the absorption bands of the trigonal-bipyramidal complexes depend upon the relative crystal field strength of the donor atoms of the ligands.[1] In comparison the five-coordinate, low-spin, square-pyramidal complexes of nickel(II) give electronic absorption bands at relatively higher energies than the more intense band of the trigonal-bipyramidal complexes with the same or similar ligand donor atoms.[2-5]

The contour of the electronic absorption bands of the square-pyramidal complexes is quite sensitive to the arrangement of donor atoms in the base of the square pyramid. The

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Table I. Analyses of $C_{32}H_{34}N_2As_2$ and Its Nickel(II) Complexes[a]

	% calcd					% found				
	C	H	N	As	X[b]	C	H	N	As	X[b]
$C_{32}H_{34}N_2As_2$	66.44	5.75	4.70	25.12		64.52	5.83	4.63	25.36	
$[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$	45.00	4.02	3.28	17.54	8.30	45.24	4.22	3.30	17.64	8.52
$[Ni(C_{32}H_{34}N_2As_2)Cl]_n(ClO_4)_n$	48.64	4.35	3.55	18.96	8.98	48.95	4.58		18.70	8.67
$[Ni(C_{32}H_{34}N_2As_2)Br]_n(ClO_4)_n$	46.05	4.11	3.36	17.95	8.50	45.68	4.12	3.37	18.27	8.21
$[Ni(C_{32}H_{34}N_2As_2)I]_n(ClO_4)_n$	43.59	3.90	3.18	17.00	8.04	43.48	3.96	3.18	17.32	8.29

[a] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [b] Total halogen calculated and reported as per cent chlorine.

square-pyramidal $[Ni\{MeN(CH_2CH_2PPh_2)_2\}Br_2]$ and $[Ni\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}Br_2]$ complexes possess a nonequivalent set of donor atoms in the basal plane of the square pyramid. The electronic absorption spectra of these complexes are characterized by a definite low-energy shoulder on a more intense high-energy band.[2-5] The low-spin, five-coordinate nickel(II) complexes of the *o*-phenylene-bridged bidentate ligands $Ph_2P(o\text{-}C_6H_4AsPh_2)$, $Ph_2P(o\text{-}C_6H_4SCH_3)$, and $Ph_2P(o\text{-}C_6H_4SeCH_3)$ have been assigned square-pyramidal structures on the basis of the energy position of the broad symmetrical electronic absorption band in their electronic absorption spectra.[6,7] The electronic absorption spectra of the five-coordinate, diamagnetic complexes of the type $[Ni(C_{32}H_{34}N_2P_2)X]ClO_4$ (where X = Cl, Br, or I and $C_{32}H_{34}N_2P_2$ is a planar tetradentate nitrogen-phosphorus ligand) are quite similar in contour and energy position to those of $[Ni\{MeN(CH_2CH_2PPh_2)_2\}Br_2]$ and $[Ni\{MeAs(CH_2CH_2CH_2AsMe_2)_2\}Br_2]$ and have been assigned a square-pyramidal structure with all four ligand donor atoms occupying the coordination sites in the base of the square pyramid. These observations in conjunction with the planar cis arrangement of donor atoms in the 2,3-butanedione bis(2-diphenylphosphinoethylimine) have been interpreted as indicating that the diphenylphosphino groups of the *o*-phenylene-bridged bidentate ligands occupy trans positions in the basal plane of their five-coordinate, square-pyramidal nickel(II) complexes.[8]

To gain further information concerning (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 a cis arrangement of bulky terminal groups in a square plane and the introduction of a fifth donor group, the ligand 2,3-butanedione bis(2-diphenylarsinoethylimine) has been synthesized and its complexing properties with nickel(II) have been investigated.

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 calcium chloride and then distilled (bp 40°) from fresh calcium chloride. Acetonitrile was refluxed over calcium hydride, decanted, and then distilled (bp 81°) from a small amount of P_4O_{10}. Triphenylarsine (Aldrich), ethylenimine (Dow), butanol, 95% ethanol, anhydrous diethyl ether, and petroleum ether were used without further purification.

Synthesis of 2,3-Butanedione Bis(2-diphenylarsinoethylimine). All glassware was dried overnight at 110° and assembled with dry nitrogen purge while hot. All steps of the reaction, including weighing and transferring of reagents, were performed under dry nitrogen. All solvents were deaerated by bubbling dry N_2 gas through them for approximately 1 hr before they were used.

To 8.2 g (0.21 mol) of potassium metal in 300 ml of dioxane was added 30.6 g (0.10 mol) of triphenylarsine. The reaction mixture was refluxed for 3 hr, cooled to room temperature, and treated dropwise over a 2-hr period with 10.3 ml (0.20 mol) of ethylenimine in 25 ml of dioxane. After the resulting mixture was refluxed for 2 hr, it was cooled to room temperature and 10 ml of 95% ethanol was added to destroy the excess potassium metal. The reaction mixture was then hydrolyzed with 150 ml of deaerated water, the ether and water layers were separated, and the water layer was extracted with two 75-ml portions of deaerated diethyl ether. The combined ether portions were dried over anhydrous sodium sulfate and decanted onto molecular sieves, and the diethyl ether-dioxane solvent mixture was removed by distillation. The resulting light yellow oil was heated at 180° (0.5 mm) for 6 hr to remove any diphenylarsine and/or 1-amino-2-phenylethane. Neither of the possible side reaction products were separated from the light yellow liquid under these conditions. An attempt to purify the 2-diphenylarsinoethylamine, $C_{14}H_{16}AsN$, by vacuum distillation at higher temperatures (220° (0.5 mm)) caused a slight darkening of the light yellow liquid. Since the 2-diphenylarsinoethylamine could not be purified by vacuum distillation, the mobile yellow liquid was treated dropwise with 3.5 ml (0.04 mol assuming an 80% yield of $C_{14}H_{16}AsN$) of biacetyl in 50 ml of butanol. A white solid began to form with the addition of the biacetyl solution. The mixture was stirred for 16 hr at room temperature and then for 2 hr at Dry Ice temperatures. The solid white product, 2,3-butanedione bis(2-diphenylarsinoethylimine), was collected by filtration, washed with ten 25-ml portions of petroleum ether, recrystallized from hot butanol, washed with petroleum ether, and dried *in vacuo* (mp 140°, yield 32%). Elemental analyses for 2,3-butanedione bis(2-diphenylarsinoethylimine) are given in Table I.

Synthesis of Complexes. Preparative manipulations with the uncoordinated ligand were performed under a nitrogen atmosphere to prevent its possible oxidation. The nickel(II) complexes were collected on a sintered-glass funnel, recrystallized from a 1:1 mixture of dichloromethane and butanol, washed with butanol, washed with diethyl ether, dried in a stream of dry air and finally dried *in vacuo*. Elemental analyses for the complexes are presented in Table I. Yields of the recrystallized complexes were approximately 70%.

$[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$. A butanol solution of 0.366 g (1 mmol) of $[Ni(H_2O)_6](ClO_4)_2$ was heated in a closed hood at reflux for 15 min in an attempt to distil some of the water of hydration from the reaction mixture. A dichloromethane solution containing 0.597 g (1 mmol) of the ligand, $C_{32}H_{34}N_2As_2$, was added to the cooled butanol solution with stirring. Orange crystals of $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$ separated from the reaction mixture with the slow evaporation of dichloromethane under a stream of dry nitrogen.

$[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$. A dichloromethane solution containing 0.597 g (1 mmol) of $C_{32}H_{34}N_2As_2$ was added to butanol solutions of "$NiXClO_4$" (1 mmol) which had been heated in a closed hood at reflux for 15 min and then cooled to room temperature. The "$NiXClO_4$" solutions were prepared *in situ* by mixing equimolar amounts of $[Ni(H_2O)_6](ClO_4)_2$ and NiX_2 (X = Cl, Br, I) in butanol. Crystals of the deeply colored nickel(II) complexes separated on evaporation of dichloromethane from the reaction mixtures with a stream of dry nitrogen.

Spectra. Infrared spectra were obtained with Perkin-Elmer Models 137 and 457 spectrophotometers using Nujol mulls between crystalline potassium bromide plates. Visible and ultraviolet spectra of the complexes in solution were taken with a Cary Model 14 spectrophotometer using matched 0.1- and 1.0-cm quartz 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.[9]

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Table II. Pmr Spectra of 2,3-Butanedione Bis(2-diphenylarsinoethylimine) and Its Diamagnetic Nickel(II) Complexes

	δ, ppm			
Compound	CH_3 protons[a]	$-CH_2-As$ protons	$-CH_2-N$ protons	C_6H_5 protons
$C_{32}H_{34}N_2As_2$	1.83 (3.0)	2.38 (2.0)	3.61 (2.0)	7.30 (10)
$[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$	2.38 (3.1)	3.03 (2.1)	3.78 (2.1)	7.40 (9.6)
$[Ni(C_{32}H_{34}N_2As_2)Cl]_n(ClO_4)_n$	2.34 (3.1)	3.14 (2.0)	3.90 (2.0)	7.40 (10)
$[Ni(C_{32}H_{34}N_2As_2)Br]_n(ClO_4)_n$	2.40 (3.0)	3.10 (2.0)	3.91 (2.0)	7.40 (9.9)
$[Ni(C_{32}H_{34}N_2As_2)I]_n(ClO_4)_n$	2.34 (3.0)	3.20 (2.0)	4.00 (2.0)	7.37 (9.8)

[a] The relative integrated intensities of the signals are reported in parentheses.

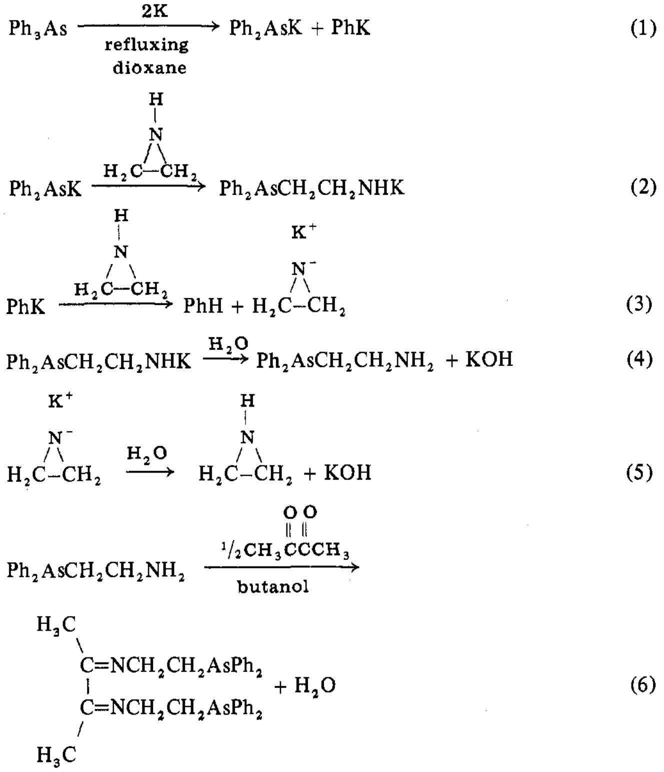
Conductance Measurements. The measurements were performed with an Industrial Instruments Model RC-16B conductivity bridge. All measurements were made at 25.0 ± 0.1° and a frequency setting of 1000 cps for the electrolytes. The cell constant was 1.50. Dilution studies were carried out in acetonitrile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

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

Results and Discussion

Synthesis of the Ligand. The steps involved in the synthesis of 2,3-butanedionebis(2-diphenylarsinoethylimine) are carried out as indicated in Scheme I. In the first step triphenylarsine is converted to potassium diphenylarsenide and phenylpotassium. In the second step (reactions 2 and 3 of Scheme I) the diphenylarsenide nucleophile opens the ethylenimine ring in a manner analogous to the corresponding diphenylphosphide nucleophile.[10] The phenylpotassium formed in reaction 1 most probably acts as a base to extract the proton from the nitrogen atom of ethylenimine in much the same manner as CH_3Li rather than as a ring-opening nucleophile.[11] This behavior (reaction 3 of Scheme I) accounts for the fact that no 1-amino-2-phenylethane could be separated from the reaction mixture by vacuum distillation. Also, the presence of a relatively high concentration of the ethylenimine anion or ethylenimine served to ensure complete reaction of the diphenylarsenide nucleophile. The hydrolysis step (reactions 4 and 5 of Scheme I) generates ethylenimine and 2-diphenylarsinoethylamine. The intermediate, 2-diphenylarsinoethylamine, is condensed (2:1 mole ratio) with 2,3-butanedione in dry butanol.

Scheme I



The results of elemental analyses for C, H, N, and As are in excellent agreement with those calculated for the ligand, $C_{32}H_{34}N_2As_2$ (Table I). The infrared spectrum of the ligand exhibits a strong sharp band at about 1615 cm^{-1} which is assigned to the C=N grouping of the ligand. The pmr spectrum (Table II) of the ligand is fully consistent with the assigned structure. The peaks at δ 1.83 (singlet), 2.38 (triplet), 3.61 (triplet), 7.30 (broad multiplet) are assigned to methyl protons, methylene protons on the carbon atom adjacent to arsenic, methylene protons on the carbon atom adjacent to nitrogen, and phenyl protons, respectively. The relative integrated intensities reported in Table II are consistent with these assignments.

Four-Coordinate Square Complex. The complex $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$ behaves as a 2:1 electrolyte in acetonitrile solution (Table III). The perchlorate anions are not coordinated in the solid state since the infrared bands at ∿625 and ∿1100 cm^{-1} are not split.[12] The pmr data for deuteriodichloromethane solutions (Table II) indicate that all four donor atoms of the ligand are coordinated to nickel(II) since a downfield shift is observed for all protons bound to carbon atoms adjacent to the ligand donor groups.[13-15] Addition of methyl iodide to acetonitrile solutions of the complex did not cause an increase in the conductivity over a 24-hr period. Although a recent report indicates that the methyl iodide conductivity test is not exceptionally reliable,[15] these data are consistent with the pmr data and support the contention that all four donor atoms of the ligand are coordinated to nickel(II). The electronic absorption spectrum of the diamagnetic $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$ complex exhibits a single absorption maximum at 25,000 cm^{-1} (ϵ 3260) in dichloromethane solution and in the solid state. The similarity of the solid state and solution electronic spectra indicates that the complex possesses the same structure in dichloromethane solution and in the solid state. The single, intense, high-energy absorption band is consistent with a square-planar arrangement of donor atoms about nickel(II) and is assigned to the transition of d-orbital character $xz, yz \rightarrow x^2 - y^2$.[16]

Five-Coordinate Complexes. Spectrophotometric titration of $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$ with $(n\text{-}C_7H_{15})_4NI$ in dichloromethane gives a sharp end point at the 1:1 mole

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Table III. Conductance Data for Nickel(II) Complexes of $C_{32}H_{34}N_2As_2$ in Acetonitrile

	Exptl values[a]		Calcd values of A			
	Λ_e^0	$-A_{exptl}$[b]	1:1	2:1	3:1	4:1
$[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$	171	706	357	691	1045	1418
$[Ni(C_{32}H_{34}N_2As_2)Cl]_n(ClO_4)_n$	233	957	403	820	1260	1716
$[Ni(C_{32}H_{34}N_2As_2)Br]_n(ClO_4)_n$	231	939	403	820	1260	1716
$[Ni(C_{32}H_{34}N_2As_2)I]_n(ClO_4)_n$	154	493	345	656	990	1343

[a] Acetonitrile solvent; experimental values are corrected for the specific conductivity of acetonitrile at 25° ($K_0 = 7.6 \times 10^{-7}$ ohm^{-1}). [b] Using the Onsager limiting law, $\Lambda_e^0 - \Lambda_e = AN^{1/2}$, the value of the slope, A, was determined from a plot of equivalent conductivity, Λ_e, against $N^{1/2}$, where N is the equivalent concentration. The value of the limiting equivalent conductivity, Λ_e^0, was obtained by extrapolation of the same plot to $N^{1/2} = 0$.

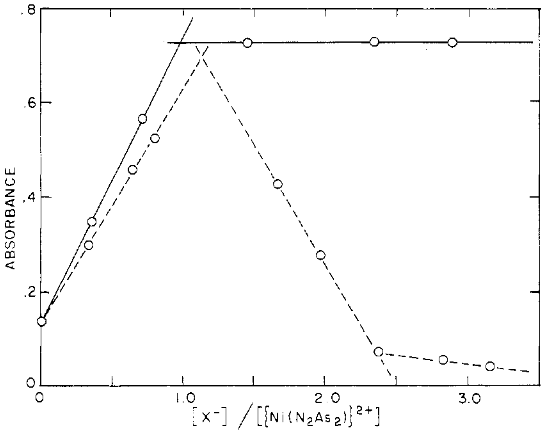

Figure 1. Plots of absorbance against increasing mole ratio of $(n\text{-}C_7H_{15})_4NI$ (———) and $(n\text{-}C_7H_{15})_4NCl$ (– – – – –) to $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$ in dichloromethane ($N_2As_2 = C_{32}H_{34}N_2As_2$).

ratio (Figure 1) indicating that a five-coordinate cation is formed or that the iodide ion has displaced one of the four ligand donor atoms in the square cation, $[Ni(C_{32}H_{34}N_2As_2)]^{2+}$. Spectrometric titration of the square complex with $(n\text{-}C_7H_{15})_4NX$ ($X^- = Cl^-, Br^-$) in dichloromethane gives sharp breaks at 1:1 and 2:1 mole ratios of halide ion to the square cation (Figure 1) indicating that both five-coordinate and six-coordinate complexes are formed or that one and two donor atoms of the ligand have been displaced from the square cation.

The isolated complexes of the type $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ (X = Cl, Br, I) do not behave as 1:1 electrolytes in acetonitrile solution as indicated by plots of equivalent conductivity against the square root of normality (Table III).[17,18] The chloro and bromo complexes give experimental slopes which are intermediate between values calculated for 2:1 and 3:1 electrolytes and the iodo complex gives an experimental slope which is intermediate between values calculated for 1:1 and 2:1 electrolytes. The lack of curvature in the plots of Λ_e against $N^{1/2}$ and the fact that Beer's law is obeyed over the concentration range studied illustrate that an equilibrium situation involving halide ion displacement by the acetonitrile solvent cannot account for the observed intermediate values of the experimental slopes. The slopes are most consistent with a mixture (n = 2, 3 for Cl and Br and n = 1, 2 for I) of different ligand-bridged cationic species in acetonitrile solution. The fact that the molecular weight of the bromo complex (570[19]) is intermediate between the values calculated for a 2:1 electrolyte (556 calcd) and a 3:1 electrolyte (626 calcd) in acetone solvent is also consistent with a mixture of $[Ni(C_{32}H_{34}N_2As_2)Br]_2(ClO_4)_2$ and $[Ni(C_{32}H_{34}N_2As_2)Br]_3(ClO_4)_3$ ligand-bridged complexes.

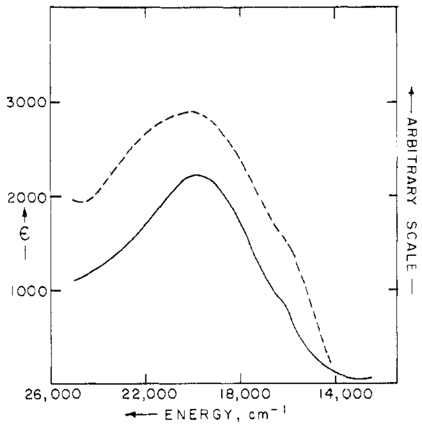

Figure 2. Electronic absorption spectra of $[Ni(C_{32}H_{34}N_2As_2)Br]_n(ClO_4)_n$ in acetonitrile (———) and the solid compound suspended in a Nujol mull (– – – –). An arbitrary scale is used for the solid-state spectrum.

The resonance positions for the protons on carbon atoms adjacent to donor groups in the complexes $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ (X = Cl, Br, I) are shifted downfield from the free ligand and have values nearly equal to or below those of the square complex (Table II). In the square $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$ complex all ligand donor atoms are coordinated (Table II). Thus, the pmr data indicate that all four ligand donor atoms are coordinated to the nickel(II) ion in the $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ complexes.[13-15] Also, addition of methyl iodide to acetonitrile solutions of the complexes does not cause an increase in the conductivity of the solutions over a 24-hr period. The pmr spectra of the isolated complexes of the type $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ in deuteriodichloromethane solution, the dilution conductivity studies, the Beer's law plots, the methyl iodide conductivity tests on acetonitrile solutions, and the sharp breaks at the 1:1 mole ratio in the spectrophotometric titration of $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$ with halide ion in dichloromethane solution strongly support the conclusion that the halide ion and all four donor atoms of the ligand are coordinated to nickel(II).

The electronic absorption spectra in the solid state and in dichloromethane and acetonitrile solutions exhibit the same absorption maxima (Figure 1) indicating that the $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ (X = Cl, Br, I) complexes have the same structure both in the solid state and in solution. The absorption maxima produce the usual spectrochemical series of Cl (20,200 cm^{-1}) > Br (19,850 cm^{-1}) > I (19,300 cm^{-1}) and the trend in molar absorptivity parallels the increasing polarizability of the halogens I (ϵ 4310) > Br (ϵ 2200) > Cl (ϵ 1250). The shapes of the electronic absorption bands for the chloro and iodo complexes are nearly identical to that of the bromo complex (Figure 2).

In the absence of X-ray data the coordination geometry of these complexes has been deduced by comparing the observed magnetic properties and electronic absorption spectra of the $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ (where X = Cl, Br, I) complexes with those of complexes of known structure. The electronic absorption spectra of the diamagnetic $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ complexes are characterized by a broad band at approximately 20,000 cm^{-1} with a low-energy shoulder at approximately 16,000 cm^{-1} (Figure 2).

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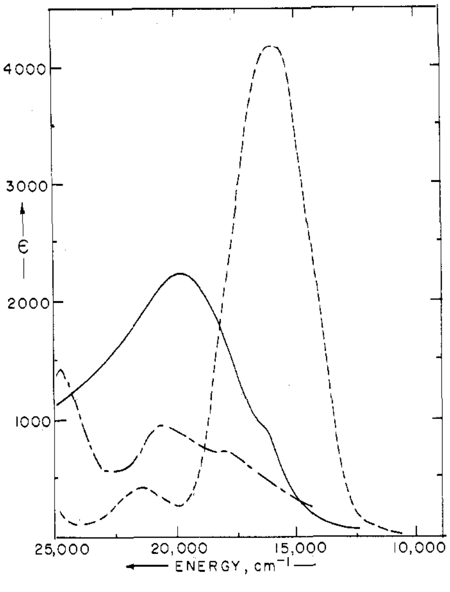

Figure 3. Electronic absorption spectra of $[Ni(C_{32}H_{34}N_2As_2)Br]_n(ClO_4)_n$ (———), [Ni(QAS)Br]ClO_4 (– – – –), and Ni(triars)Br_2 (——— —) in dichloromethane solvent. QAS is As[o-C_6H_4As$(C_6H_5)_2]_3$ and triars is $CH_3As[CH_2CH_2CH_2As(CH_3)_2]_2$.

The broad asymmetric electronic absorption band of the $[Ni(C_{32}H_{34}N_2As_2)Br]_n^{n+}$ cation occurs at considerably higher energy than the more symmetrical absorption band of the trigonal-bipyramidal $[NiAs(o\text{-}C_6H_4AsPh_2)_3Br]^+$ cation (Figure 3).[20,21] In contrast to this, the spectral bands compare well in position and contour with those of the square-pyramidal $[Ni\{Me(AsCH_2CH_2CH_2AsMe_2)_2\}Br_2]$[2,3] (Figure 3) and $[Ni\{MeN(CH_2CH_2PPh_2)_2\}Br_2]$[4,5] complexes. On this basis the $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ complexes are assigned square-pyramidal structures and the two components of the broad asymmetric bands in these low-spin complexes are assigned to transitions of d-orbital character $z^2 \rightarrow x^2 - y^2$ and $xz, yz \rightarrow x^2 - y^2$.[16]

The electronic absorption spectra of the $[Ni(C_{32}H_{34}N_2P_2)X]^+$ and $[Ni(C_{32}H_{34}N_2As_2)X]_n^{n+}$ (X = Cl, Br, I) cations exhibit similar contours with the maximum and shoulder for the $[Ni(C_{32}H_{34}N_2P_2)X]^+$ cations appearing at higher energies than those of the corresponding $[Ni(C_{32}H_{34}N_2As_2)X]_n^{n+}$ cations in accord with the greater ligand field strength of P relative to As (Figure 4). The intensities of the electronic absorption bands of the $[Ni(C_{32}H_{34}N_2P_2)X]^+$ cations are higher than those of the $[Ni(C_{32}H_{34}N_2As_2)X]_n^{n+}$ cations. Extensive mixing of ligand and metal orbitals is thought to account for the high intensities of the electronic absorption bands of low-spin, five-coordinate nickel(II) complexes.[1] Therefore, the relatively high intensities of the electronic absorption bands of $[Ni(C_{32}H_{34}N_2P_2)X]^+$ cations are most probably associated with the fact that all four π-acceptor donor groups of the tetradentate nitrogen-phosphorus ligand are bound to the nickel(II) ion in the base of the square pyramid since this arrangement of π-acceptor donor atoms permits extensive mixing of the filled metal d orbitals with the empty π-antibonding orbitals of the C=N donor groups and the empty d orbitals of the P donor atoms. Nickel(II) complexes with two C=N and two As donor groups about the base of a square pyramid would be expected to give absorption bands with intensities quite similar to those of $[Ni(C_{32}H_{34}N_2P_2)X]^+$ cations. Since the intensities of the electronic absorption bands of the $[Ni(C_{32}H_{34}N_2As_2)X]_n^{n+}$ cations are considerably less than those of the $[Ni(C_{32}H_{34}N_2P_2)X]^+$ cations, the ligand-bridged $[Ni(C_{32}H_{34}N_2As_2)X]_n^{n+}$ cations probably have structures in which the apical position of the square-pyramid is occupied by an As donor atom and one of the coordination sites in the base of the square-pyramid is occupied by a halide donor (Figure 5). This proposed arrangement of donor atoms about the square pyramid also minimizes steric interactions between the phenyl substituents bound to the As donor atoms of the ligand.

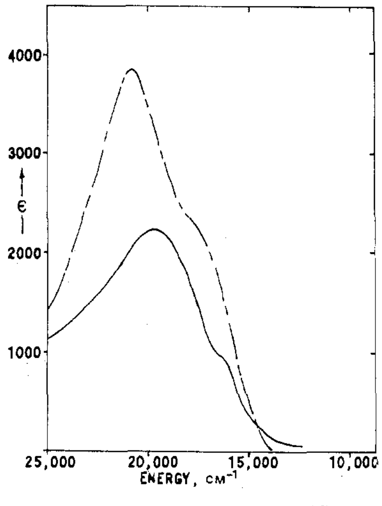

Figure 4. Electronic absorption spectra of $[Ni(C_{32}H_{34}N_2As_2)Br]_n(ClO_4)_n$ (———) and $[Ni(C_{32}H_{34}N_2P_2)Br]ClO_4$ (——— —) in dichloromethane solution.

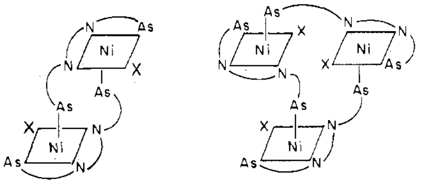

Figure 5. Most probable square-pyramidal structures for the $[Ni(C_{32}H_{34}N_2As_2)X]_n(ClO_4)_n$ (X = Cl, Br, I) complexes.

The fact that the square $[Ni(C_{32}H_{34}N_2As_2)]^{2+}$ cation forms ligand-bridged, square-pyramidal cations when it is treated with an equimolar amount of halide while the corresponding square $[Ni(C_{32}H_{34}N_2P_2)]^{2+}$ cation forms monomeric, square-pyramidal cations may be attributed to a combination of steric and electronic factors. The greater tetrahedral covalent radius of arsenic relative to phosphorus (∿0.08 Å) tends to relieve steric strain between the cis diphenylarsino groups through a longer metal to donor atom distance. However, this relief of steric interaction through the longer metal to donor atom distance is more than offset by the longer As-C_6H_5 bonds which leads to greater steric interactions since the four phenyl groups on the two As or two P donor atoms must lie side to side in the square $[Ni(C_{32}H_{34}N_2D_2)]^{2+}$ (D = As, P) cations. In addition, to the added steric requirements of the cis diphenylarsino groups, work by Chatt and Wilkins[22] indicates that M→L type dπ-dπ bonding remains essentially constant while the σ-bonding component decreases in going from P to As to Sb in the $\{(C_2H_5)_3M\}_2PtCl_2$ (M = P, As, Sb) complexes. Thus, it is reasonable to suggest that the greater steric interactions between the phenyl groups of the cis diphenylarsino groups and the weaker Ni-As σ-bond strength are responsible for

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the fact that 2,3-butanedione bis(2-diphenylarsinoethylimine) forms ligand-bridged square-pyramidal nickel(II) complexes rather than monomeric, square-pyramidal nickel(II) complexes as does 2,3-butanedione bis(2-diphenylphosphinoethylimine).

Registry No. $C_{32}H_{34}N_2As_2$, 37862-12-7; Ph_2AsK, 21498-51-1; $(CH_2)_2NH$, 151-56-4; $[Ni(C_{32}H_{34}N_2As_2)](ClO_4)_2$, 37862-13-8; $[Ni(C_{32}H_{34}N_2As_2)Cl]_n(ClO_4)_n$, 37862-14-9; $[Ni(C_{32}H_{34}N_2As_2)Br]_n(ClO_4)_n$, 37862-15-0; $[Ni(C_{32}H_{34}N_2As_2)I]_n(ClO_4)_n$, 38050-89-4; $CH_3C(O)C(O)CH_3$, 431-03-8; $Ph_2AsCH_2CH_2NH_2$, 31699-82-8.

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Photochemical Reactivity of *trans*-Diacidotetracyanocobaltate(III) Complexes

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The photochemistry of *trans*-$Co(CN)_4(SO_3)(X)^{n-}$ ($X = SO_3^{2-}$, OH^-, or OH_2) is reported. The principal photoreactions involve substitution of the sulfito group yielding aquation products. Photoreduction to yield Co(II) is a minor reaction. Disappearance quantum yields are in the range 0.1–0.6 and are modestly affected by variation in the wavelength of the exciting light.

Excited-state decay processes of a number of cyanometalate complexes have been reported.[2] Luminescence has been observed in a few cases at low temperature and in rigid media,[3] while chemical decay paths dominate in fluid solutions for many cyanometalate complexes.[2] Both redox and ligand substitution processes are observed upon irradiation of such complexes.

Population of ligand field excited states of cyanocobaltate(III) complexes leads to facile ligand substitution processes. The octahedral complex $Co(CN)_6^{3-}$ undergoes photoaquation[4] with a quantum yield of 0.31 which is independent of the exciting wavelength[4b] (254, 313, or 366 nm) and the acidity of the solution[4b] (in the range pH 2.0–7.5). The photoaquation is thought to occur *via* an interchange mechanism,[5] and the wavelength-independent quantum yields and triplet-sensitized aquation yields[6] support the notion that decay proceeds *via* the $^3T_{1g}(t_{2g}{}^5e_g{}^1)$ excited state.[2]

Cyanocobaltate(III) complexes of C_{4v} symmetry, $Co(CN)_5(X)^{n-}$ ($X = Cl^-$, Br^-, I^-, or OH_2), also give $Co(CN)_5(OH_2)^{2-}$ in high yield[4a,7] upon population of low-lying ligand field excited states. The photoaquation of $Co(CN)_5(X)^{n-}$ species apparently occurs *via* a dissociative type mechanism[5,7] and like $Co(CN)_6^{3-}$ preliminary results[6b] suggest that decay proceeds through the lowest ligand field triplet excited state. Thermal substitution of $Co(CN)_5(X)^{n-}$ also yields $Co(CN)_5(OH_2)^{2-}$ by a dissociative mechanism.[8] In marked contrast to $Co(NH_3)_5(X)^{n+}$ systems[2] the cyanocobaltate(III) complexes do not yield Co(II) upon direct irradiation.

We have extended the study of the photochemical behavior of cyanocobaltate(III) complexes to species of the type *trans*-$Co(CN)_4(SO_3)(X)^{n-}$ ($X = SO_3^{2-}$, OH^-, or OH_2). These complexes are of considerable interest because as reported herein their excited-state reactivity patterns show important differences from their ground-state behavior.

Experimental Section

Materials. The previously published preparation of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ was used to obtain samples of both the sodium and potassium salts.[9,10] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory for $K_5Co(CN)_4(SO_3)_2$. *Anal.* Calcd: C, 9.26; N, 1080; S, 12.36. Found: C, 9.30; N, 10.78; S, 10.64. Solutions of the *trans*-$Co(CN)_4(SO_3)(H_2O)^{3-}$ were prepared by dissolving appropriate amounts of $K_5Co(CN)_4(SO_3)_2$ in 0.01 *M* $HClO_4$. Formation of *trans*-$Co(CN)_4(SO_3)(H_2O)^{3-}$ is rapid and quantitative under these conditions.[10] Preparation of *trans*-$Co(CN)_4(SO_3)(OH)^{4-}$ was achieved by making solutions of *trans*-$Co(CN)_4(SO_3)(OH_2)^{3-}$ 0.1 *M* in NaOH.

Irradiation Procedures. Samples were irradiated using merry-go-rounds.[11] In various experiments different filter systems were used to isolate the group of lines near 254, 313, 366, or 436 nm in the spectrum of a mercury lamp. Light intensities were measured using ferrioxalate actinometry.[12] Three-milliliter samples were used and the light intensities were of the order of 10^{-7} einstein min^{-1}. Thermal aquation of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ was sufficiently rapid to compete with photolysis. Correction was made by measuring rates in parallel control experiments. Both *trans*-$Co(CN)_4(SO_3)(OH)^{4-}$ and *trans*-$Co(CN)_4(SO_3)(H_2O)^{3-}$ are thermally inert under the reaction conditions.

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