against several solutions provided a check on the slope of the e.m.f.–pH straight line. Standardization before and after a titration showed reproducibility better than 0.01 pH unit, and the method of titration with a piston buret[3] was equally reliable. We have therefore estimated random errors in the equilibrium constants by applying the usual statistical tests to our calculations.

Where a constant was evaluated singly, so that one value was derived from each experimental point, we quote the mean pK or log K and its standard error. Overlapping acid dissociation constants were evaluated by least-squaring the linear regression equation. The table quotes standard errors of pK derived in the usual way from the standard errors of intercept and slope. Errors in stability constants were considered from two points of view; the statistical errors of the regression lines were evaluated as before, and the propagation of errors of pK or molar extinction coefficient into log β_2 was also estimated. The figures quoted in the table represent approximate standard errors from a combination of these several sources. The values of the constants for PAPHY are reproduced from the earlier paper, but with revised figures for pK_1' and pK_2'.

It has previously[3] been concluded from spectrophotometric evidence and from comparison with other pyridine compounds that pK_1 (2.87) and pK_2 (5.71) for PAPHY refer to the acid–base equilibria of the two heterocyclic nitrogen atoms. While tautomerism is common in polyfunctional pyridine derivatives, so that pK values measured by titration cannot be assigned unequivocally to given groups in the molecule, nevertheless the greater susceptibility of pK_1 to the influence of the methyl group in I suggests that it is concerned principally with ring A.

When B is a pyrimidyl or methylpyrazinyl ring, whose basic properties are known[7] to be weak, the low observed values of pK_1 indicate that it is now principally measuring the equilibrium at ring B. In ligands II and III, pK_2 is now a characteristic chiefly of ring A and is to be compared with pK_1 of PAPHY (2.87) and of ligand I (3.65). Its comparatively high values no doubt stem from the lower net positive charge on the dissociating species.

All the ligands considered here resemble PAPHY and *o*-phenanthroline in forming strongly colored cationic iron(II) complexes and in favoring the bis complex in solution. Only for III is log $\beta_1 > {}^1/_2$ log β_2, and for PAPHY itself β_1 could not be detected spectrophotometrically, suggesting that log β_1 was probably less than ${}^1/_2$ log $\beta_2 - 1$. Ligand I provides an example of the familiar influence of a methyl group adjacent to the pyridine donor nitrogen in reducing complex stability by steric hindrance in spite of its base-strengthening effect.

The acid-strengthening effect of coordinated metal on the imino group has already[3] been shown to depend on the nature of the metal. Comparison of the iron(II) complexes of the four ligands now shows the effect to be almost independent of modifications to the periphery of the ligand. It may be measured by $\Delta \text{p}K_3 = \text{p}K_3 - {}^1/_2(\text{p}K_1' + \text{p}K_2')$ and then appears for ligand I, as for PAPHY, to be about 8 pK units but cannot be determined more precisely because of the uncertainty in pK_3. However, in II and III, where the imino group is initially more acidic and pK_3 is better defined, ΔpK_3 has the value 8.0. We therefore conclude that the electron-withdrawing influence of a coordinated metal, transmitted through the conjugated system of the ligand, is not affected by changes in the ligand outside the chelate rings.

Acknowledgment.—The authors gratefully acknowledge a grant from the Petroleum Research Fund of the American Chemical Society which has made this work possible.

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[7] A. Albert, "Heterocyclic Chemistry," Athlone Press, London, 1959, p. 344.

Contribution from the Department of Chemistry,
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Five-Coordinate Nickel(II) Complexes with Tris(3-dimethylarsinopropyl)phosphine[1]

By Gereld S. Benner, William E. Hatfield, and Devon W. Meek

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Chemical analyses, magnetic moments, electronic absorption spectra, and molar conductance values indicate that tris-(3-dimethylarsinopropyl)phosphine (TAP) reacts with nickel(II) salts to form the five-coordinate cations $[\text{Ni(TAP)X}]^+$ (where X is a monodentate anion). The aquo complex $[\text{Ni(TAP)H}_2\text{O}]^{2+}$ is analogous. The absorption spectra suggest that the cation has a trigonal-bipyramidal structure in which the organic molecule functions as a tetradentate ligand. The electronic absorption spectra and the chemical reactions of the complexes are discussed.

Introduction

Although many complexes have been reported with mono-, bi-, and tridentate arsenic and phosphorus ligands, relatively little work has been done with tetradentate arsenic or phosphorus ligands. The complexes of tetradentate molecules of the type $\text{D}[(\text{CH}_2)_n\text{DR}_2]_3$ (where $n = 2$ and 3) reported thus far contain ligands in which all four donor atoms are alike. Thus the

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tetradentate nitrogen ligands, tris(2-aminoethyl)amine (tren) and tris(3-aminopropyl)amine (trpn), have been studied since 1925,[2-6] whereas the analogous tetradentate phosphorus[7] or arsenic ligands[8-11] have been synthesized only recently. No metal complexes of a tetradentate ligand with a mixed donor system of one phosphorus and three arsenic atoms have been reported, although one aryl compound of this type is known.[12]

The geometry of a tetradentate ligand very sharply limits the stereochemical possibilities of the complex; *i.e.*, models of these molecules which contain three donor atoms connected to a central donor by trimethylene or ethylene bridges show that they can coordinate readily if the metal uses tetrahedral or octahedral bonding orbitals, but not if the bonds are square-planar. Such a ligand could also coordinate to four of the five positions around either a square-pyramidal or a trigonal-bipyramidal structure of a five-coordinate complex.

Very few five-coordinate nickel complexes have been reported. On the basis of molecular weight determinations and dipole moment measurements, Jensen[13] proposed a square-pyramidal structure for the compound $[Ni\{P(C_2H_5)_3\}_2Br_3]$. Harris, Nyholm, and Phillips[14] reported that the square-planar $[Ni(DAS)_2](ClO_4)_2$ [where DAS = *o*-bis(dimethylarsino)benzene] added one mole of halide to form a five-coordinate complex in solution. Recently, the complexes $[Ni\{P(CH_3)_3\}_3Br_2]$[15] and $[Ni\{HP(C_6H_5)_2\}_3X_2]$[16] were prepared from nickel halides and monodentate phosphine ligands. The five-coordinate nickel bromide complex[17] of the tritertiary arsine, $CH_3As[CH_2CH_2CH_2As(CH_3)_2]_2$ (TAS), was shown to possess a distorted square-pyramidal structure.[18]

We are interested in studying the properties and structures of the transition metal complexes which may be prepared from a tetradentate ligand containing two different donor atoms. This initial study in the series reports the complexes obtained from Ni(II) and the ligand $P[CH_2CH_2CH_2As(CH_3)_2]_3$ (TAP).

Experimental

Reagents.—Commercial hydrated cobalt chloride, $CoCl_2 \cdot 6H_2O$, was dehydrated with $SOCl_2$.[19] Anhydrous nickel chloride and cobalt bromide were obtained by drying the hydrated substances in an oven at 110°. The 3-chloropropanol (from Aceto Chemical Co.) was distilled *in vacuo* [b.p. 60–65° (10 mm.)] immediately before use.

Reagent grade methanol was refluxed over magnesium and then fractionated (b.p. 64.5°). Technical grade dichloromethane was fractionated (b.p. 40–41°). The nitromethane was washed with 5% aqueous $NaHCO_3$, then fractionated (b.p. 100–101°). Other reagent grade materials were used without further treatment.

Conductivity Measurements.—The conductivity values were obtained with a Fisher Scientific Products Co. cell in nitromethane or doubly distilled demineralized water with an Industrial Instruments, Inc., Model RC-16B2 conductance bridge.

Spectra.—The electronic absorption spectra were obtained on a Cary Model 14 spectrophotometer with 1 and 5 cm. matched quartz cells. The diffuse reflectance spectra were taken on a Beckman Model DU spectrophotometer equipped with a standard reflectance attachment using $MgCO_3$ as a standard. The infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer with the samples mounted as KBr disks. The polystyrene spectrum was used for calibration.

Molecular Weight Measurements.—Molecular weights were determined in benzene at 37° with a Mechrolab, Inc., vapor pressure osmometer, Model 301A, calibrated with benzil. Concentrations of the solutions were approximately 10^{-2} *M*. The results are reproducible to ±2%.

Magnetic Measurements.—The magnetic moments were determined by Dr. W. E. Hatfield at the University of Illinois with a Faraday balance.

Analyses.—The microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Drs. G. Weiler and F. B. Strauss, Oxford, England.

Synthesis of Tris(3-dimethylarsinopropyl)phosphine (TAP).—For the preparation of the ligand $P[CH_2CH_2CH_2As(CH_3)_2]_3$, we usually began with 3-dichloroarsinopropyl chloride which was prepared by modifications of Gough and King's synthesis of the compound.[8,20] From 100 g. of freshly distilled 3-dichloroarsinopropyl chloride one is able to obtain, *via* a stoichiometrically controlled Grignard reaction, 65–70 g. (80–86% of theory) of 3-dimethylarsinopropyl chloride, b.p. 62° (10 mm.).

The final step of the ligand synthesis involved preparation of the Grignard of 3-dimethylarsinopropyl chloride and its subsequent reaction with phosphorus trichloride. After normal workup of the Grignard reaction and removal of the ether, the distillation flask was evacuated to less than 1 mm. and the oil bath temperature raised to 120°. All volatile fractions were removed by vacuum distillation at this temperature. The yellow residual oil was dissolved in hot methanol, filtered, and crystallized in a Dry Ice–ethanol cold bath. The yields were 25–26 g. (~44% of theory). The white crystals were dissolved in 500 ml. of absolute ethanol which contained 0.05 g. of hydroquinone or in benzene which contained hydroquinone. Aliquots of these stock solutions were used for syntheses of the Ni(II) complexes.

Preparation of the Tetrasulfide of Tris(3-dimethylarsinopropyl)phosphine.—A solution of 0.125 g. of recrystallized sulfur in 6 ml. of ethylenediamine[21] was added to a solution of 0.25 g. of TAP in 2 ml. of benzene. After 3 min., this mixture was poured into 75 ml. of water and the resultant precipitate was separated by filtration. The white solid was recrystallized twice from N,N-dimethylformamide, washed with benzene and ether, and dried *in vacuo* at 56°; decomposition point 271–271.5° (sealed tube). *Anal.* Calcd. for $C_{15}H_{36}As_3PS_4$: C, 30.01; H, 6.04. Found: C, 30.54, 30.48; H, 6.25, 6.14.

Synthesis of the Coordination Compounds. $[Ni(TAP)X]ClO_4$, where X = Cl, Br.—A solution of 1.70 g. of $LiClO_4$ (0.016 mole) and 0.016 mole of anhydrous NiX_2 in 50 ml. of deaerated absolute ethanol was mixed with a solution of 6.9 g. of tris(3-

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[2] F. G. Mann and W. J. Pope, *Proc. Roy. Soc.* (London), **A109**, 444 (1925); *J. Chem. Soc.*, 482 (1926).

[3] F. G. Mann and W. J. Pope, *Chem. Ind.* (London), **44**, 833 (1925).

[4] F. G. Mann and W. J. Pope, *J. Chem. Soc.*, 489 (1926).

[5] F. G. Mann and W. J. Pope, *ibid.*, 409 (1929).

[6] G. A. Barclay and A. K. Bernard, *ibid.*, 2540 (1958); S. K. Madan, *Dissertation Abstr.*, **21**, 1366 (1960).

[7] J. G. Hartley, L. M. Venanzi, and D. C. Goodall, *J. Chem. Soc.*, 3930 (1963).

[8] G. A. Barclay and A. K. Bernard, *ibid.*, 4269 (1961).

[9] J. A. Brewster, C. A. Savage, and L. M. Venanzi, *ibid.*, 3699 (1961).

[10] J. G. Hartley and L. M. Venanzi, *ibid.*, 182 (1962).

[11] C. A. Savage and L. M. Venanzi, *ibid.*, 1548 (1962).

[12] T. E. W. Howell, S. A. J. Pratt, and L. M. Venanzi, *ibid.*, 3167 (1961).

[13] K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 265 (1936); K. A. Jensen and B. Nygaard, *Acta Chem. Scand.*, **3**, 474 (1949).

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

[15] K. A. Jensen, P. H. Nielsen, and C. T. Pedersen, *Acta Chem. Scand.*, **17**, 1115 (1963).

[16] R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963).

[17] G. A. Barclay and R. S. Nyholm, *Chem. Ind.* (London), 378 (1953).

[18] G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc.*, 415 (1960).

[19] A. R. Pray, *Inorg. Syn.*, **5**, 153 (1957).

[20] G. A. C. Gough and H. King, *J. Chem. Soc.*, 2432 (1928).

[21] W. A. Hodgson, S. A. Buckler, and G. Peters, *J. Am. Chem. Soc.*, **85**, 543 (1963).

TABLE I

PROPERTIES AND ANALYSES OF THE Ni(II) COMPLEXES[a]

Complex	Color	Yield, %	Molar conductance, cm.²/ohm M^g	C, %		H, %		Halogen, %		Other, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[Ni(TAP)Cl]B(C_6H_5)_4$	Violet	95	81.9	52.88	52.75	6.38	6.28	4.02	4.06		
$[Ni(TAP)Br]B(C_6H_5)_4$	Blue	98, 99	60.7	50.37	50.33	6.07	6.18	8.59	8.75		
$[Ni(TAP)I]B(C_6H_5)_4$	Blue	82, 95	60.1	47.94	47.94	5.78	5.99	12.99	13.12		
$[Ni(TAP)Cl]ClO_4$	Violet	55	95.1	27.06	26.37	5.45	5.24	10.75	11.11		
$[Ni(TAP)Br]ClO_4$	Blue	69	96.6	25.37	26.25	5.11	5.13	22.50[h]	22.58[h]		
$[Ni(TAP)I]ClO_4$	Blue	62	99.3	23.79	24.01	4.79	4.96	...	...		
$[Ni(TAP)NO_2]ClO_4$	Maroon	72	89.1	27.04	27.08	5.44	5.61	5.32	5.32	N, 2.10	N, 2.02
$[Ni(TAP)CN]ClO_4$	Deep red	85	92.1	29.28	29.50	5.53	5.65	...	...	N, 2.13	N, 2.20
$[Ni(TAP)NCS]ClO_4$[f]	Maroon	37	90.0	27.92	28.24	5.27	5.45	5.15	5.45		
$[Ni(TAP)(SC_2H_5)]ClO_4$	Blue	68	104[b]	29.53	29.64	5.98	6.01	5.13	5.27	S, 4.64	S, 4.40
$[Ni(TAP)H_2O](ClO_4)_2$[e]	Maroon	46	165	24.09	26.97	5.12	5.66	9.48	8.12		
$[Ni(TAP)I]_2[NiI_4]$	Brown	87	Insoluble	19.15	19.36	3.86	4.14	40.46	41.51	P, 3.29	P, 3.32
$[Ni(TAP)Br_2]$[c]	Deep red	24	83	26.08	26.67	5.25	5.36	23.14	23.63		
$[Ni(TAP)I_2]$[d]	Deep red	25	66	22.96	23.14	4.62	4.60	32.35	32.56		

[a] All of the complexes are diamagnetic except for $[Ni(TAP)I]_2[NiI_4]$, which exhibits χ'_M values of 6878, 8233, and 14851 × 10^{-6} at 298.5, 198.2, and 77°K., respectively. Assuming that the cation $[Ni(TAP)I]^+$ is diamagnetic, the corrected magnetic susceptibility of the compound at 298.5°K. is 6878 × 10^{-6}. This corresponds to μ_{eff} = 4.07 B.M., in excellent agreement with the calculation for a tetrahedral Ni(II) complex [N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959)]. However, this value is higher than has ever been observed for $[NiI_4]^{2-}$. [b] The conductance value is for a 1 × 10^{-3} *M* solution in methanol; the compound decomposed in CH_3NO_2. [c] The experimental molecular weight in a 10^{-2} *M* benzene solution was 707 (calculated value for $[Ni(TAP)Br_2]$ = 690.7. [d] The experimental molecular weight in a 10^{-2} *M* benzene solution was 814 (calculated value for $[Ni(TAP)I_2]$ = 784). [e] After repeated purification attempts, this compound gave high values for C and H; however, it readily reacted as $[Ni(TAP)H_2O](ClO_4)_2$ in the synthetic procedures. A typical value is given. [f] Both the electronic absorption spectrum and the infrared spectrum indicate that the thiocyanate group is bonded through the nitrogen atom. [g] Determined in 1 × 10^{-3} *M* nitromethane solutions. [h] Total halogen as Br.

dimethylarsinopropyl)phosphine (0.0145 mole) in 150 ml. of ethanol. The crystals were collected on a filter and washed with ether. Each of the complexes was recrystallized from a minimum of hot chloroform and then dried *in vacuo* at 56°.

$[Ni(TAP)Y]ClO_4$, where Y = NO_2, CN, SCN, SC_2H_5.—$[Ni(TAP)Cl]ClO_4$ (0.5 g., 0.00075 mole) dissolved in 2.5 ml. of chloroform was mixed with a methanol solution of NaY. Each of the resulting solutions was cooled to −18° for several hours and then the crystals were collected on a filter, washed with ether, and dried. The compounds were recrystallized from methanol and dried *in vacuo* at 56°.

Aquotris(3-dimethylarsinopropyl)phosphinenickel(II) Perchlorate.—A solution of 3.65 g. of hexaaquonickel(II) perchlorate (0.01 mole) dissolved in 25 ml. of ethanol was mixed slowly with 100 ml. of a 4.3% ethanol solution of tris(3-dimethylarsinopropyl)-phosphine (0.0091 mole) while stirring. The maroon powder was collected on a filter, redissolved, and subsequently precipitated from a mixture of 10% nitromethane and 90% acetone with ether. The compound was washed with ether and dried *in vacuo* at room temperature. The compound gave high analytical values for C and H after repeated purification attempts. It probably contained excess ligand but will be referred to as $[Ni(TAP)H_2O](ClO_4)_2$ in the following synthetic interconversions.

$[Ni(TAP)X]B(C_6H_5)_4$, where X = Cl, Br, I. (a) By Ligand Substitution.—A solution of 0.5 g. of $[Ni(TAP)H_2O](ClO_4)_2$ (0.00067 mole) in 5 ml. of nitromethane was mixed with 1 ml. of an ethanol solution which was saturated with the corresponding lithium halide. Then 0.46 g. of sodium tetraphenylborate (0.00134 mole) dissolved in 5 ml. of ethanol was added, while stirring, to each of the blue solutions. The crystals were collected on a filter, recrystallized from nitromethane, and dried at 56°; yields 85–98%. The visible and near-ultraviolet absorption spectra of the tetraphenylborate complexes were identical with those of the corresponding $[Ni(TAP)X]ClO_4$.

(b) **By Metathesis.**—$[Ni(TAP)X]ClO_4$ (1.4 mmoles) was dissolved in 5 ml. of chloroform and mixed with a solution of 2.8 mmoles of $NaB(C_6H_5)_4$ in 5 ml. of ethanol. The blue crystals, which precipitated immediately, were collected, recrystallized twice from nitromethane, and then dried at 56°; yields 90–98% of theory.

Iodotris(3-dimethylarsinopropyl)phosphinenickel(II) Tetraiodonickelate(II), $[Ni(TAP)I]_2[NiI_4]$.—Anhydrous nickel iodide was prepared *in situ* by mixing 1.226 g. of anhydrous nickel chloride and 2.836 g. of sodium iodide in 100 ml. of absolute ethanol. The sodium chloride was removed by filtration, and the solution of NiI_2 was added to 4.05 g. (0.0086 mole) of TAP in 75 ml. of ethanol. The brown material, which precipitated on combination of the reagents, was collected, dissolved in dichloromethane, and reprecipitated by addition of pentane at −78°.

Diiodotris(3-dimethylarsinopropyl)phosphinenickel(II), $[Ni(TAP)I_2]$.—A slurry of 0.6 g. (1.9 mmoles) of anhydrous nickel(II) iodide was stirred overnight under N_2 with 0.95 g. (2.0 mmoles) of TAP in 60 ml. of benzene. The red brown solution was filtered and evaporated *in vacuo*. The residual oil was crystallized from benzene to yield deep red crystals.

Dibromotris(3-dimethylarsinopropyl)phosphinenickel(II), $[Ni(TAP)Br_2]$.—This compound was obtained in an analogous manner as the above iodide complex.

Discussion

Inference of the Structure of the Complexes.—The conductivity data (Table I) strongly suggest that the complexes possess five-coordinate cations in nitromethane. One possible explanation consistent with the diamagnetism and the conductivity values of the complexes would envisage that one of the dimethylarsino groups remains uncoordinated. The nickel complex then would exhibit a four-coordinate structure with the phosphine functioning as a tridentate ligand. However, one can eliminate this possibility from consideration since the electronic absorption spectra of the complexes differ significantly from those of known four-coordinate Ni(II) complexes.[22,23]

The absorption spectra of the TAP complexes exhibit an intense (ϵ ~2200), broad band at 500–700 mμ and

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(22) G. Maki, *J. Chem. Phys.*, **29**, 1129 (1958).

(23) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

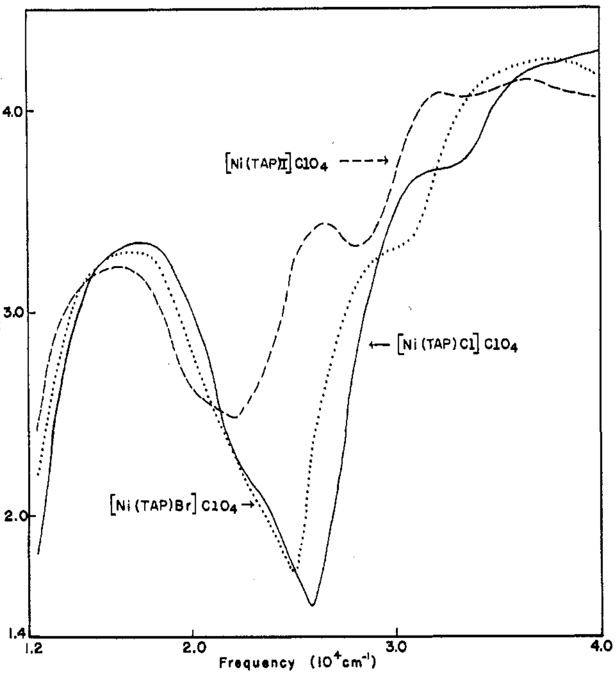

Fig. 1.—Absorption spectra of tris(3-dimethylarsinopropyl)phosphine complexes of nickel(II) in dichloromethane.

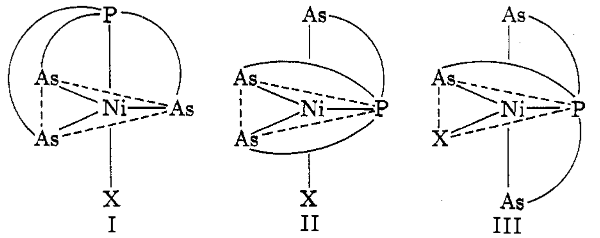

Fig. 2.—Three possible isomers for trigonal-bipyramidal [Ni(TAP)X]$^+$ ions.

more intense peaks in the ultraviolet region. No weak intensity bands were observed up to 1700 mμ. The spectra are quite different from those of other Ni(II) arsine or phosphine complexes which exhibit a coordination number of either four or six. The spectra of the nickel complexes (Fig. 1) exhibit very similar contours to the spectra of the platinum complexes [Pt(QAS)I]X where QAS = As[*o*-$C_6H_4As(C_6H_5)_2$]$_3$.[9] Also, the extinction coefficients and λ_{max} of the [Ni(QAS)X]ClO$_4$ compounds agree remarkably well with those of the corresponding TAP complexes.[24] X-Ray studies by Mair, Powell, and Venanzi[25] have shown that the cation [Pt(QAS)I]$^+$ exhibits a trigonal-bipyramidal structure. From the close similarity of the [Pt(QAS)I]$^+$ and [Ni(QAS)X]$^+$ spectra with the [Ni(TAP)X]$^+$ spectra, our nickel TAP complexes also are assigned a trigonal-bipyramidal structure.

A comparison of the diffuse reflectance spectrum of solid [Ni(TAP)Cl][B(C_6H_5)$_4$] with the spectrum of the same complex dissolved in dichloromethane or nitromethane shows that the coordination number does not change on dissolution. Thus, the complexes have five-coordinate trigonal-bipyramidal structures both in solution and in the solid state. An X-ray investigation is in progress to determine which of the three possible isomers of [Ni(TAP)X]$^+$ is formed (Fig. 2).

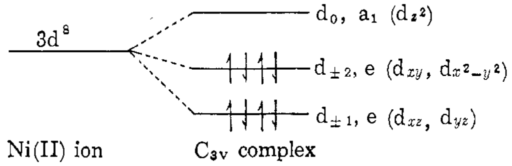

Fig. 3.—Energy level diagram for a d^8 C_{3v} complex.

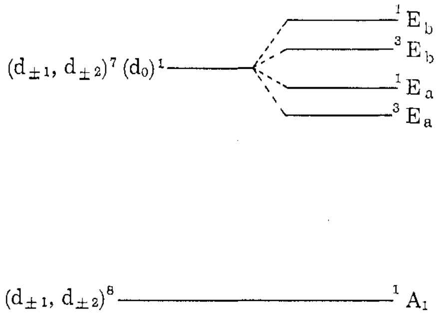

Fig. 4.—Ground and lowest excited states for the C_{3v} complexes.

Since the complexes [Ni(TAP)X]$^+$ approximate C_{3v} symmetry, the d-orbital energy level diagram should consist of three levels (Fig. 3). If the energy separation between the highest e level and the a_1 level is more than the electron pairing energy of the Ni(II) complex, the energy level diagram (Fig. 3) would account for the uniformly diamagnetic character of the five-coordinate TAP complexes. The absorption spectra confirm the separation since the first observed transition (e → a_1) occurs at 14,000–20,000 cm.$^{-1}$ in each complex, far in excess of the pairing energy of Ni(II).

The broad peak in the visible region can be resolved cleanly into two Gaussian curves. For the halide complexes, [Ni(TAP)X]ClO$_4$, the lower energy band (14,170–15,400 cm.$^{-1}$) exhibits ϵ_{max} values of 676–880, whereas the ϵ_{max} values are 1736–2285 for the higher energy band (16,740–17,840 cm.$^{-1}$). The first excited state electronic configuration $(d_{\pm1})^4(d_{\pm2})^3(d_0)^1$ will be mixed strongly with $(d_{\pm1})^3(d_{\pm2})^4(d_0)^1$. Such a configuration produces two ^1E and two ^3E levels[26] (Fig. 4). This situation should allow two bands of similar energies, $^1A_1 \rightarrow {}^1E_a$ and $^1A_1 \rightarrow {}^1E_b$, in agreement with the observed transitions.[27] The intensities are much higher than expected for simple d–d transitions; however, the complexes do not possess a center of symmetry and the metal p-orbitals must be mixed strongly with the two e sets. Also extensive π-bonding involving the empty d-orbitals on P and As may be involved. All these contributions would raise the transition intensities.

Chemical Behavior of the Complexes.—The nickel(II) complexes are very labile toward substitution of the nonchelating ligand. The blue halide complexes

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(24) L. M. Venanzi, private communication (1964).

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

(26) T. S. Piper, private communication (1964).

(27) Of course, one could further resolve the two Gaussian curves into four curves and speculate that the less intense set of bands is due to forbidden transitions from $^1A_1$ to ^3E_a and ^3E_b. However, the ratio of intensities between the two sets of bands would be ~3:1 and one would expect a much larger intensity difference for the spin-forbidden transitions compared to the spin-allowed transitions.

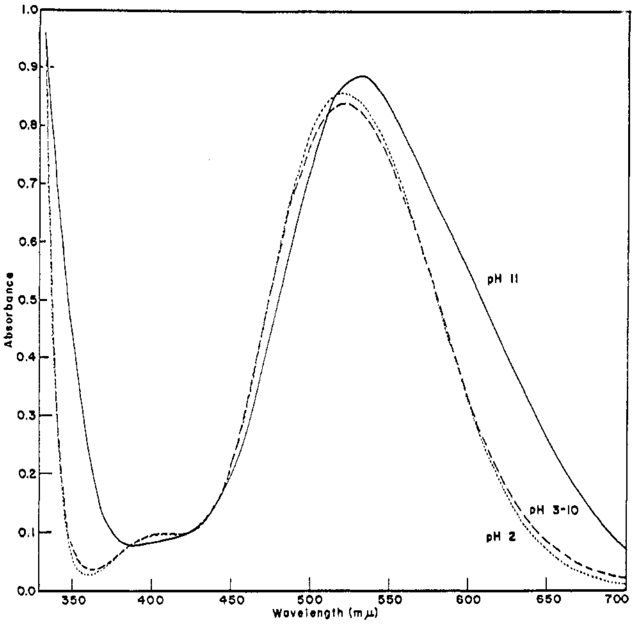


Fig. 5.—Spectrum of $[Ni(TAP)H_2O](ClO_4)_2$ in water at various pH values; [Ni] = 5.6×10^{-4} *M*.

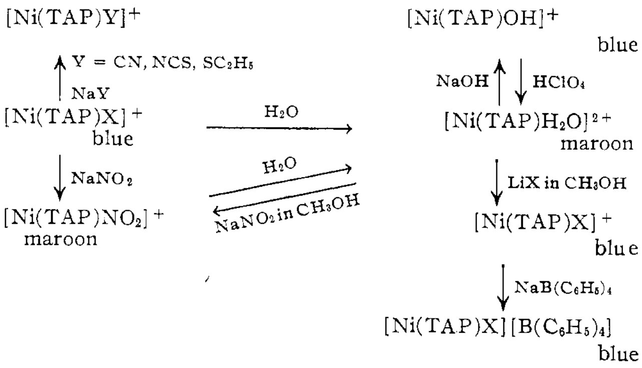
convert rapidly to the maroon aquo complex. The electronic absorption spectra of the resulting solutions correspond exactly to that of $[Ni(TAP)H_2O]^{2+}$. Also the conductance values (193–206 cm.^{2}/ohm *M* in 10^{-3} *M* solutions) indicate that bi-univalent electrolytes are formed immediately on dissolution of the halide complexes in water.

In order to identify and characterize some of the rapid color transformations which occurred when concentrated halide solutions were mixed with the aquo complex, the blue halide complexes were isolated from the respective solutions as the more insoluble tetraphenylborate salts. The $[Ni(TAP)X]B(C_6H_5)_4$ (where X = Cl, Br, I, CN, NO_2) complexes were prepared (1) by adding excess lithium halide to a solution of the aquo complex; (2) by direct synthesis from $[Ni(H_2O)_6](ClO_4)_2$, LiX, and TAP; and (3) by a metathesis reaction between $[Ni(TAP)X]ClO_4$ and $NaB(C_6H_5)_4$. Absorption λ_{max} and ϵ_{max} values for the complex cations were identical (within experimental error) with those of the corresponding perchlorate salts. Excess sodium tetraphenylborate did not replace both anions from the $[Ni(TAP)X]ClO_4$ complexes; only complexes of the type $[Ni(TAP)X][B(C_6H_5)_4]$ were obtained in nearly quantitative yields. The X ligand is not replaced by noncoordinating anions.

If a strong base is added to an aqueous solution of $[Ni(TAP)H_2O]^{2+}$, the solution turns blue; if perchloric acid is then added, the maroon color returns. This cycle can be repeated several times without any apparent decomposition of the complex. Figure 5 shows that the pH must be above 10 before the blue color appears in water, whereas slightly basic (pH ~8.5) alcohol solutions are blue.

The substitution reactions of the five-coordinate Ni(II) complexes can be summarized as in Scheme I. The immediate color changes which occur on combination of the reagents and the isolation and characterization of the pure complexes demonstrate that the rates of the substitution reactions are very rapid and proceed essentially to completion.

Scheme I



In contrast to the chloride and bromide complexes, a large excess of LiI in methanol converts only 80% of $[Ni(TAP)H_2O]^{2+}$ to the $[Ni(TAP)I]^+$ cation. In fact, very large ratios of I:Ni actually decrease the absorptivity of the solutions at 600 mμ. An isosbestic point in the spectra of the reaction mixtures indicates that two principal absorbing species are present in solution. This suggests the equilibrium

$$[Ni(TAP)I]^+ + I^- \rightleftharpoons [Ni(TAP)I_2]$$

The six-coordinate complex $[Ni(TAP)I_2]$ could not be isolated from methanol solutions, but it was prepared by reaction of anhydrous NiI_2 with TAP in benzene. The analogous $[Ni(TAP)Br_2]$ was prepared similarly. The molecular weight determinations of the two compounds agree very well for the six-coordinate complexes in benzene (Table I). However, both complexes convert immediately to the blue five-coordinate complexes when dissolved in any hydroxylic solvent such as methanol or when dissolved in high dielectric constant solvents such as nitromethane. Absorption spectra and the conductance values demonstrate that the six-coordinate complexes ionize to $[Ni(TAP)X]^+ + X^-$ in a 10^{-3} *M* nitromethane solution.

Recently Barclay and Bernard[6] reported that the tetra-tertiary arsine $As[CH_2CH_2CH_2As(CH_3)_2]_3$ preferentially formed octahedral Ni(III) complexes rather than Ni(II) complexes. In fact, they were able to obtain only one Ni(II) complex.

Many attempted oxidations of the $[Ni(TAP)X]ClO_4$ complexes resulted in decomposition of the complexes when strong oxidants were employed. However, nitrogen(IV) oxide or bromine converted the complexes into diamagnetic, four-coordinate Ni(II) arsonic acid complexes. These will be discussed in a subsequent paper. We have not been able to isolate any pure Ni(III) complex. The relative ease of preparation of the five-coordinate Ni(II) complexes, $[Ni(TAP)X]ClO_4$, and the difficulty of the oxidation experiments are in direct contrast to the observations of Barclay and Bernard. This discrepancy is not easily explained since it is expected that the coordination properties of the ligands $As[CH_2CH_2CH_2As(CH_3)_2]_3$ and $P[CH_2CH_2CH_2As(CH_3)_2]_3$ should not differ so markedly.

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The Effect of Coordination on the Reactivity of Aromatic Ligands.
X. Electrophilic Reactions of Bis(8-hydroxyquinolinato)copper(II)

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Bis(8-hydroxyquinolinato)copper(II) has been found to undergo a large number of electrophilic substitution reactions. Benzoylation, sulfonation, nitration, thiocyanation, mercuration, and condensation with formaldehyde can be effected readily on the complex. Iodination can be effected, but only in poor yields, while acetylation failed. A kinetic study of the mercuration of 8-hydroxyquinoline and its copper(II) complex has been carried out in glacial acetic acid. The rate of mercuration varies in the order copper complex $\gg$ 8-hydroxyquinoline. The rate of mercuration of the copper complex is significantly changed by the addition of either copper(II) acetate or 8-hydroxyquinoline. An improved method of preparing 8-hydroxyquinoline-5-sulfonic acid has been developed.

The studies reported in earlier papers in this series[1] were limited to a relatively small fraction of the possible electrophilic substitution reactions which are possible with complexes of aromatic ligands. The present work was undertaken to extend these studies to a number of other substitution reactions and to determine which of these are suitable for more detailed kinetic studies. The reactions were carried out on bis(8-hydroxyquinolinato)copper(II) because previous work[1] had shown that it possessed sufficient stability to survive most of the reactions of this sort without loss of copper, yet could be decomposed into ligand and copper sulfide. The specific reactions examined were (1) benzoylation with benzoyl chloride in the presence of anhydrous aluminum chloride, (2) sulfonation, (3) nitration, (4) iodination, (5) thiocyanation, (6) mercuration, (7) acid-catalyzed condensation with formaldehyde, and (8) acetylation. Of these, mercuration showed itself amenable to kinetic studies. As a consequence, kinetic studies were carried out on the mercuration of the copper(II) and zinc(II) complexes as well as the free ligand, all in the solvent glacial acetic acid.

Experimental

Bis(8-hydroxyquinolinato)copper(II) and Other Materials Used.—The copper complex was prepared as described previously.[1] The 8-hydroxyquinoline used was Eastman White Label, and the other chemicals used were of reagent or ACS grade wherever possible. The glacial acetic acid used in the kinetic studies was from a lot which assayed 100% acetic acid and was used without further purification.

Benzoylation.—The copper chelate (17.5 g., 0.05 mole) was suspended in dry carbon disulfide (300 ml.) in a three-neck flask fitted with a reflux condenser and a mechanical stirrer, and the mixture was cooled to 0–5° by means of an ice bath. To this, a solution of benzoyl chloride (14 g., 0.10 mole) in carbon disulfide was added over a period of 30–40 min. Anhydrous aluminum chloride (26 g., 0.19 mole) was added over a period of about 1 hr. during which time the temperature of the reaction mixture was not allowed to rise above 5°. This was refluxed for 36 hr., and the slurry was then transferred to a beaker; the carbon disulfide was removed by evaporation. The beaker was then placed in ice, cooled to 0–5°, and concentrated hydrochloric acid (150 ml.) was added dropwise, with stirring, over a period of 60–80 min. The product was filtered and the residue was saturated with hydrogen sulfide. This was continued over a period of 6 hr., until the copper was completely precipitated as copper sulfide, which was removed by filtration. The filtrate was extracted with ether and the ether extract was washed with water until the wash water was no longer acidic. This was then dried over anhydrous calcium chloride and filtered; the filtrate was allowed to evaporate. Recrystallization from ethanol or ether gave a product, m.p. 107–111°, which was not increased upon further recrystallization. The infrared spectrum in a KBr disk indicated the presence of a carbonyl group.

This product was sublimed under vacuum to obtain a pure white product, 5-benzoyl-8-hydroxyquinoline, m.p. 118.5–119.5° (lit.[2] 118–119°). *Anal.* Calcd. for $C_{16}H_{10}NO_2 \cdot H_2O$: C, 67.8; H, 4.6. Found: C, 67.5; H, 4.9.

This material was also prepared from benzoyl chloride, 8-hydroxyquinoline, and aluminum chloride, using the procedure given by Matsumura. The melting point and infrared spectrum (KBr disk) were identical with those of the compound prepared from the complex. A mixture melting point of the two products was not depressed.

The yields of 5-benzoyl-8-hydroxyquinoline from the copper complex were 36% when carbon disulfide was used as the solvent and 34% when nitrobenzene was used in parallel experiments.

Sulfonation.—The copper complex (10 g., 0.028 mole) was gradually treated with seven times its weight of concentrated sulfuric acid at 0–10°. The mixture was kept 3–4 hr. at room temperature and was then poured over crushed ice. The resulting solid was collected on a filter, washed with cold water, and finally

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[1] K. D. Maguire and M. M. Jones, *J. Am. Chem. Soc.*, **84**, 2316(1962); *ibid.*, **85**, 154 (1963).

[2] K. Matsumura, *ibid.*, **52**, 4433 (1930).