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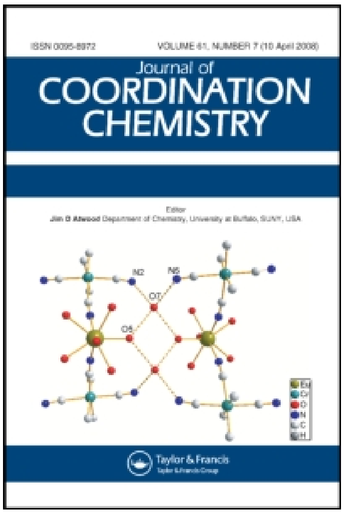

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

FOUR- AND FIVE-COORDINATE NICKEL(II) COMPLEXES OF THE ALIPHATIC, TRIDENTATE LIGANDS BIS(3-DIMETHYLARSINOPROPYL)METHYLARSINE AND BIS(3-DIMETHYLARSINOPROPYL)PHENYLPHOSPHINE

C. A. McAuliffe[a]; M. O. Workman[a]; Devon W. Meek[a]
[a] Department of Chemistry, The Ohio State University, Columbus, Ohio

To cite this Article McAuliffe, C. A. , Workman, M. O. and Meek, Devon W.(1972) 'FOUR- AND FIVE-COORDINATE NICKEL(II) COMPLEXES OF THE ALIPHATIC, TRIDENTATE LIGANDS BIS(3-DIMETHYLARSINOPROPYL)METHYLARSINE AND BIS(3-DIMETHYLARSINOPROPYL)PHENYLPHOSPHINE', Journal of Coordination Chemistry, 2: 2, 137 — 143

To link to this Article: DOI: 10.1080/00958977208072963

URL: http://dx.doi.org/10.1080/00958977208072963

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J. Coord. Chem., 1972, Vol. 2, pp. 137–144

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Printed in Woking, England

FOUR- AND FIVE-COORDINATE NICKEL(II) COMPLEXES OF THE ALIPHATIC, TRIDENTATE LIGANDS BIS(3-DIMETHYLARSINOPROPYL)METHYLARSINE AND BIS(3-DIMETHYLARSINOPROPYL)PHENYLPHOSPHINE[1]

C. A. McAULIFFE[2], M. O. WORKMAN[3], and DEVON W. MEEK*

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

(*Received December* 10, 1971; *in final form March* 23, 1972)

Fifteen diamagnetic nickel(II) complexes of the flexible, tridentate ligands bis(3-dimethylarsinopropyl)phenylphosphine(dap) and bis(3-dimethylarsinopropyl)methylarsine(tas) were isolated and characterized. The molecular, five-coordinate complexes Ni(ligand)X_2 (ligand = dap; X = Cl, Br, I, NCS, CN: ligand = tas; X = Br, I, NCS, CN) and the four-coordinate complexes [Ni(dap)Cl]ClO_4 and [Ni(dap)NO_3]NO_3 were studied by electronic and infrared spectra, magnetic, conductivity, and molecular weight measurements. On the basis of X-ray structural determinations of Ni(tas)Br_2 and Ni(dap)$(CN)_2 \cdot H_2O$ and the similar electronic spectra of the dap and tas series of complexes, the inner coordination geometry of all these complexes can be represented as a distorted square pyramid. The method of isolation and the properties of the polynuclear complexes $[Ni_2L_3(H_2O)](ClO_4)_4$ (L = dap and tas) and $[Ni_3(dap)_3I_5]B(C_6H_5)_4$ are also discussed.

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INTRODUCTION

Our previous studies with the "tripod-like", flexible, tetradentate ligands $D[CH_2CH_2CH_2As(CH_3)_2]_3$ (D = P[4], As[5], Sb[6]) revealed that the resultant five-coordinate nickel(II) complexes possessed trigonal-bipyramidal structures.[6,7] Even though accurate molecular models show that other four, five-, and six coordinate nickel(II) complexes are possible with these tetradentate ligands, one might logically suggest that the pyramidal nature of the Group V apex atom contributes significantly to the formation of the trigonal-bipyramidal $[Ni(ligand)X]^+$ complexes. In order to remove this symmetry factor from the ligands, we have examined several series of five-coordinate nickel(II) complexes that may be prepared from bidentate and monodentate phosphine and arsine ligands.[8]

In the $[Ni(bidentate)_2X]^+$ complexes, small changes in the nature of the ligands apparently can stabilize square-pyramidal structures in some cases and trigonal-bipyramidal structures in other cases.[8c] To remove any possible structural contributions from the ionic lattice in the $[Ni(bidentate)_2X]^+$ and the $[Ni(tetradentate)X]^+$ complexes, we have examined the molecular compounds Ni(ligand)X_2 that can be prepared from flexible, aliphatic arsine and phosphine tridentate ligands. This paper reports the results obtained with the new "mixed" ligand $C_6H_5P[CH_2CH_2CH_2As(CH_3)_2]_2$(dap). In addition, we have extended the known series of $CH_3As[CH_2CH_2CH_2As(CH_3)_2]_2$(tas) complexes for comparison with the dap complexes.

EXPERIMENTAL SECTION

Preparation of the Ligands

Both $CH_3As[CH_2CH_2CH_2As(CH_3)_2]_2$ and $C_6H_5P[CH_2CH_2CH_2As(CH_3)_2]_2$ were prepared by Benner's[4,5] improvements and modifications of the method used by Barclay *et al.* to prepare tas.[9]

Preparation of the Complexes: $[Ni(L)X_2]$ (L = *tas*, X = *Br, I, NCS, CN*; L = *dap*, X = *Cl, Br, I, NCS, CN*)

All of the complexes were prepared by a general method described specifically for $[Ni(dap)Br_2]$: Anhydrous nickel(II) bromide (0.29 g; 1.3 mmole) was dissolved in ethanol (15 ml) and filtered into a solution of dap (0.56 g; 1.3 mmole) in ethanol (5 ml). The intensely colored purple solution was cooled overnight at 0° and purple needles separated. These were collected, washed with ether, and dried *in vacuo*. Yield, 81%.

$[Ni_2(L)_3(H_2O)](ClO_4)_4$ (L = *tas, dap*). These complexes were prepared by the method reported for $[Ni(tas)_2](ClO_4)_2$.[9]

$[Ni(dap)Cl]ClO_4$. (a) A mixture of $[Ni(H_2O)_6]Cl_2$ (0.32 g, 1.3 mmole) and $[Ni(H_2O)_6](ClO_4)_2$ (0.49 g; 1.3 mmole) was dehydrated with 12 ml of 2,2-dimethoxypropane. To this solution was added dropwise an ethanolic solution (5 ml) of dap (1.1 g, 2.7 mmole). A yellow solid soon separated; this was collected, washed with ethanol, and dried *in vacuo*. (b) When the purple $[Ni_2(dap)_3(H_2O)](ClO_4)_4$ complex (0.5 g) is heated in boiling methanol (15ml), the purple solution becomes lighter in color after a few minutes and a yellow complex separates. This was collected, washed with ethanol, and dried *in vacuo*. Yield, 69%.

CAUTION! *This reaction is potentially very hazardous and should be carried out with care and behind a safety shield.*

$[Ni(dap)(NO_3)]NO_3$. To $[Ni(H_2O)_6](NO_3)_2$ (0.38 g, 1.3 mmole) in ethanol (15 ml) was added an ethanolic solution (5 ml) of dap (0.55 g, 1.3 mmole). On standing at 5° for 3 days, dark red crystals separated; these were collected and dried. Yield, 63%.

Physical Measurements

Spectral, conductivity, and magnetic measurements were carried out as described previously.[10] The conductivity studies at different concentrations were carried out as described by DuBois,[11] which is a modification of the method of Feltham and Hayter.[12]

Elemental Analyses

These were performed by Galbraith Laboratories, Knoxville, Tenn., or by M.H.W. Laboratories, Garden City, Michigan.

RESULTS AND DISCUSSION

Five-Coordinate Complexes

The flexible tridentate ligands bis(3-dimethylarsinopropyl)methylarsine, tas, and bis(3-dimethyl-

TABLE I

Physical properties and analytical data of the nickel(II) complexes[a]

	% Carbon		% Hydrogen		% Other			
	Calc.	Found	Calc.	Found	Calc.	Found	Color	Conductance (in mhos)[c]
$[Ni(tas)(NCS)_2]$	27.91	28.14	4.83	4.98	5.01[b]	4.87	Brown	8.3
$[Ni(tas)Br_2]$	21.89	22.04	4.48	4.73			Purple	4.7
$[Ni(tas)I_2]$	18.94	18.97	3.87	3.99			Black	6.1
$[Ni(tas)(CN)_2]$	31.52	30.97	5.45	5.32	5.66[b]	5.81	Red	1.9
$[Ni_2(tas)_3(H_2O)](ClO_4)_4$[h]	23.50	23.80	4.92	5.25	8.41[d]	8.25	Purple	273
$[Ni(dap)Cl_2]$	36.13	36.10	5.49	5.60	13.33[d]	13.17	Purple	16.4
$[Ni(dap)Br_2]$	30.95	31.07	4.70	4.80	25.75[d]	25.54	Purple	11.7
$[Ni(dap)I_2]$	26.66	26.79	4.05	4.11	36.05[d]	35.85	Black	13.1
$[Ni(dap)(CN)_2]$	42.11	42.18	5.65	5.80	5.46[b]	5.70	Red	3.0
$[Ni(dap)(NCS)_2]$	37.44	36.63	5.03	5.35	4.85[b]	4.64	Brown	9.3
$[Ni(dap)(NO_3)](NO_3$	32.85	33.10	5.00	5.12	4.79[b]	4.68	Red-orange	208[e]
$[Ni(dap)NO_3]B(C_6H_5)_4$	57.01	56.80	5.82	5.64	1.66[b]	1.73	Light orange	183[e]
$[Ni_2(dap)_3(H_2O)](ClO_4)_4$	33.11	33.49	5.12	5.26	8.15[d]	7.77	Purple	292
$[Ni(dap)Cl]ClO_4$[f,g]	32.25	31.96	4.91	4.91	11.90[d]	12.07	Yellow	143[e]
	32.25	31.38	4.91	4.90	11.90[d]	12.96	Yellow	147[e]
$[Ni_3(dap)_3I_5]B(C_6H_5)_4$	36.97	36.70	4.75	4.64	27.17[d]	27.06	Black	

[a] All the complexes listed are diamagnetic.

[b] nitrogen analysis.

[c] In freshly prepared ~$10^{-3}M$ nitromethane solutions.

[d] halogen analysis.

[e] Conductance obtained in acetonitrile, approx. $10^{-3}M$.

Prepared from a mixture of equimolar quantities of $Ni(H_2O)_6(ClO_4)_2$, $Ni(H_2O)_6Cl_2$ and dap.

[g] Prepared from the isolated $[Ni_2(dap)_3(H_2O)](ClO_4)_4$ complex in methanol.

[h] Ni: Calc, 6.93%; Fd., 6.97%; O: Calc., 16.02%; Fd., 16.14%.

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arsinopropyl)phenylphosphine, dap, give the dark brown or black complexes $[\mathrm{Ni}LX_2]$ (L = tas, X = Br, I, NCS, CN; L = dap, X = Cl, Br, I, NCS, CN) when mixed with anhydrous nickel(II) salts. Table I lists the analytical, magnetic and conductance data for the complexes that were isolated. All are diamagnetic and very nearly non-electrolytes in nitromethane. Table II and Figures 1–3 contain details of the electronic spectra. In general, the spectra of analogous complexes of both tridentate ligands are similar; the implication, therefore, is that the stereochemistry of the two series of complexes is closely related. The dap complexes have electronic absorptions uniformly at higher energy than the corresponding tas complexes, presumably because of the higher ligand field strength of the central phosphorus donor atom in the dap ligand. The electronic spectra of the $[\mathrm{Ni(dap)}X_2]$(X = Cl, Br, I) complexes closely resemble each other, and the unsymmetrical absorption band (~22,000 cm^{-1}) shifts to lower energy in the order Cl > Br > I; in the case of the iodide, the spectrum is resolved into two components (Table II). The spectra of the complexes $[\mathrm{Ni(tas)}X_2]$ (X = Br, I) are very similar, and both are remarkably similar to the previously reported

TABLE II

Electronic absorption spectra of the nickel(II) complexes of dap and tas

Complex	E_{max}, cm^{-1} CH_2Cl_2 Solution (ϵ)[a]	E_{max}, cm^{-1} Nujol mulls at ~300°K
Ni(tas)Br_2	14,040 (~306)	14,340
	17,780sh (~575)	17,900
	20,510 (782)	20,300sh[b]
	27,360 (6,060)	27,500
	32,310 (9,880)	– – – –[c]
	37,810 (15,950)	– – – –
Ni(tas)I_2	13,120 (632)	13,400
	16,860 (1,200)	16,830
	19,530 (973)	
	25,000 (2,270)	25,000
	32,310 (20,340)	– – – –[c]
	36,100 (19,200)	– – – –
Ni(tas)$(NCS)_2$	16,300sh[b] (~305)	16,450
	21,980 (2,150)	22,050
	29,110 (6,365)	29,300
	32,570 (20,570)	
	34,480 (14,770)	
	39,920 (20,370)	
Ni(tas)$(CN)_2$	21,400 (380)	21,700
	27,780 (11,160)	27,900
	35,400 (14,450)	
	36,700 (12,840)	
Ni(dap)Cl_2	15,970 (235)	15,900
	22,550 (1,065)	21,800
	30,200 (12,310)	30,300
	33,840 (9,770)	– – – –[c]
Ni(dap)Br_2	14,930 (348)	15,600
	19,230sh[b] (723)	20,400
	21,980 (951)	
	28,330 (8,975)	28,600
	33,783 (18,020)	– – – –[c]
	39,840 (26,130)	– – – –
Ni(dap)I_2	14,080 (521)	14,400
	18,420 (1,086)	18,870
	20,830 (984)	
	26,000sh (~1,990)	25,800
	33,444 (20,100)	– – – –[c]
	37,453 (16,450)	– – – –
Ni(dap)$(NCS)_2$	17,400 (217)	17,910
	23,500 (1,883)	23,700
	29,960 (5,710)	29,800
	36,340 (13,150)	
Ni(dap)$(CN)_2$	20,200 (229)	18,740
	28,250 (1,202)	26,360
	35,520 (19,430)	
[Ni(dap)NO_3]NO_3	23,300 (943)[d]	22,330
[Ni(dap)NO_3]$B(C_6H_5)_4$	23,260 (899)	22,220
[Ni(dap)Cl]ClO_4	22,800 (1,050)[e]	22,730
	22,950 (1,020)[f]	
		18,800sh
$[Ni_2(dap)_3H_2O](ClO_4)_4$	21,640 (817)	21,000
$[Ni_3(dap)_3I_5]B(C_6H_5)_4$[g]	14,390 (503)	
	18,870sh (~990)	
	20,830 (1,117)	
	26,320sh (~2,210)	
	33,610 (22,040)	
	37,450 (25,550)	

[a] Molar absorptivity values are given in parentheses.
[b] sh, shoulder on a more intense absorption.
[c] The solid state spectra were not recorded beyond 32,000 cm^{-1}.
[d] Spectrum obtained in acetonitrile.
[e] Synthesized directly from an equimolar mixture of $[Ni(H_2O)_6]Cl_2$, $[Ni(H_2O)_6](ClO_4)_2$, and the ligand dap.
[f] Synthesized from the isolated complex $[Ni_2(dap)_3H_2O](ClO_4)_4$ by heating it in boiling methanol.
[g] The spectrum of this compound obtained in nitromethane had maxima at 14,400(497)[a], 18,850(970), and 20,820 (1142).

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spectrum of the bromide complex.[9] The [Ni(tas)Br$_2$] complex has a distorted square-pyramidal structure that has been rationalized[9, 13] on the basis of steric interactions of the dimethylarsino groups with the bromide in the basal plane. If these steric factors are important, the magnitude of the distortion should vary as the size of the halide changes. Such a structural distortion seems to explain the spectral data as the visible bands become more asymmetric in the order Cl < Br < I. The shapes of the electronic spectra are very similar in both the solid state and in solutions; a few of the solid state spectra are illustrated in Figure 3.

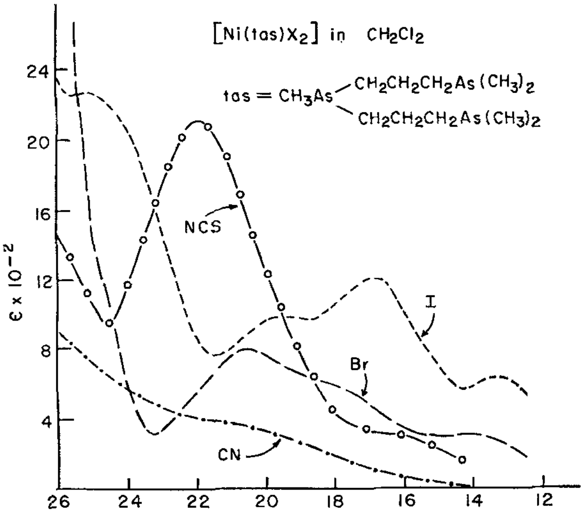

FIGURE 1 Electronic absorption spectra of the complexes [Ni(tas)X$_2$](tas = CH$_3$As[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_2$; X = I, Br, NCS and CN) in dichloromethane solutions.

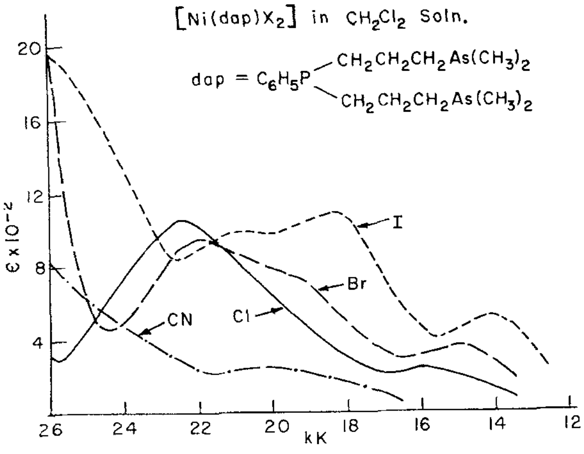

FIGURE 2 Electronic absorption spectra of the complexes [Ni(dap)X_2](dap = C$_6$H$_5$P[CH$_2$CH$_2$CH$_2$As(CH$_3$)$_2$]$_2$; X = I, Br, Cl, CN) in dichloromethane solutions.

The infrared spectra of the dap and tas thiocyanate complexes show two strong C ≡ N absorptions both in the solid state and in dichloromethane solutions. For Ni(dap)(NCS)$_2$, the C ≡ N stretching frequency occurs at 2072 cm^{-1} and 2099 cm^{-1} in a Nujol mull and at 2076 (A = 7.21 × 10^4 cm^{-2}M^{-1}) and 2094 cm^{-1} (A = 7.49 × 10^4 cm^{-2}M^{-1}) in dichloromethane. Similar absorptions are observed for Ni(tas)(NCS)$_2$ at 2070 and 2090 cm^{-1} in the solid state and at 2071 (A = 6.84 × 10^4 cm^{-2}M^{-1}) and 2092 cm^{-1} (A = 7.35 × 10^4 cm^{-2}M^{-1}) in dichloromethane solutions. These infrared data support isothiocyanato coordination by both NCS groups[14] and the two absorption bands are consistent with a C$_s$ microsymmetry for both Ni(ligand)(NCS)$_2$ complexes. Thus, the coordination geometry of the thiocyanate complexes is probably very similar to the square-pyramidal structure of the Ni(dap)(CN)$_2$ complex that is discussed in the following section.

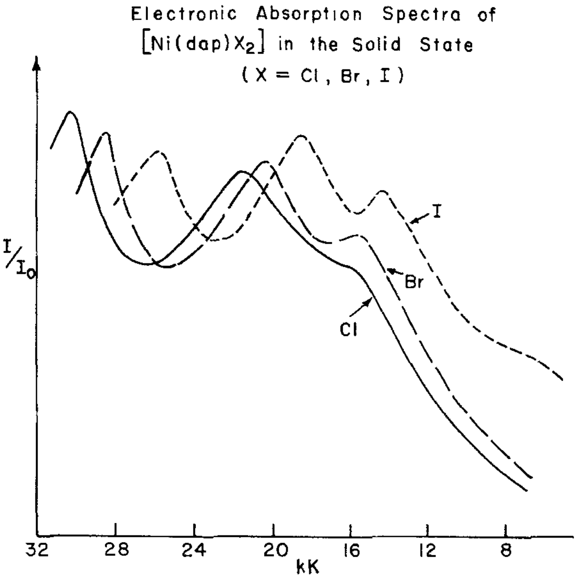

FIGURE 3 Electronic absorption spectra of the complexes [Ni(dap)X_2](X = Cl, Br, I) as Nujol mulls of the solids at ~300° K.

The deep red cyano complexes Ni(dap)(CN)$_2$ and Ni(tas)(CN)$_2$ exhibit two electronic absorption bands at ca. 19kK and 26kK as illustrated in Figure 4. The visible spectrum of the solid in a Nujol mull, both at 77°K and ~300°K, exhibits

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the same spectral contours as the solution spectrum, indicating that the structure of the complex in the solid persists in solution. It is concluded on the basis of conductivity, magnetic, and infrared and visible spectral measurements that both Ni(ligand)$(CN)_2$ complexes are pentacoordinate in the solid state and in solution. The infrared spectra (Nujol mulls) show two sharp peaks at 2097 and 2102 cm^{-1} for Ni(dap)$(CN)_2$ and at 2094 and 2099 cm^{-1} for Ni(tas)$(CN)_2$. In dichloromethane solution Ni(dap)$(CN)_2$ gives two sharp absorptions at 2095 and 2101 cm^{-1} with a weak peak at 2118 cm^{-1} (Figure 5). The electronic spectra indicate a square-pyramidal geometry and the infrared spectra show that the two cyanides are non-equivalent. These structural features have been confirmed by Palenik and Rendle[15] with an X-ray crystal structure determination of Ni(dap)$(CN)_2 \cdot H_2O$.

The electronic spectra of Ni(dap)$(CN)_2$ and Ni(tas)$(CN)_2$ are assigned on the basis of C_s microsymmetry (Figure 5). There would be four spin-allowed transitions, $^1A' \rightarrow {}^1A'(d_{z^2} \rightarrow d_{x^2-y^2})$, $^1A' \rightarrow {}^1A''(d_{xz} \rightarrow d_{x^2-y^2}$, $^1A' \rightarrow {}^1A''(d_{yz} \rightarrow d_{x^2-y^2}$, and $^1A' \rightarrow {}^1A'(d_{xy} \rightarrow d_{x^2-y^2})$. Two of these transitions $(d_{z^2} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2})$ are also orbitally allowed and would be expected to give the two most intense electronic absorptions; they are assigned to the bands at ca. 19 kK and 26 kK, respectively.

The constancy of the electronic band at ~32.3 kK in the [Ni(tas)X_2] (X = Br, I) complexes suggests that this absorption is due to an arsenic-nickel charge-transfer transition, and the band which occurs at ca. 33.7 kK in the [Ni(dap)X_2] (X = Cl, Br, I) complexes may be tentatively assigned to a phosphorus-nickel charge-transfer transition. The bands at 30.2 kK (Cl), 28.3 kK (Br), and 26.0 kK (I) in the [Ni(dap)X_2] complexes can be tentatively assigned to halide-nickel charge transfer, and a similar assignment is proposed for the bands at 27.4 kK (Br) and 25.0 kK (I) in the [Ni(tas)X_2] complexes.

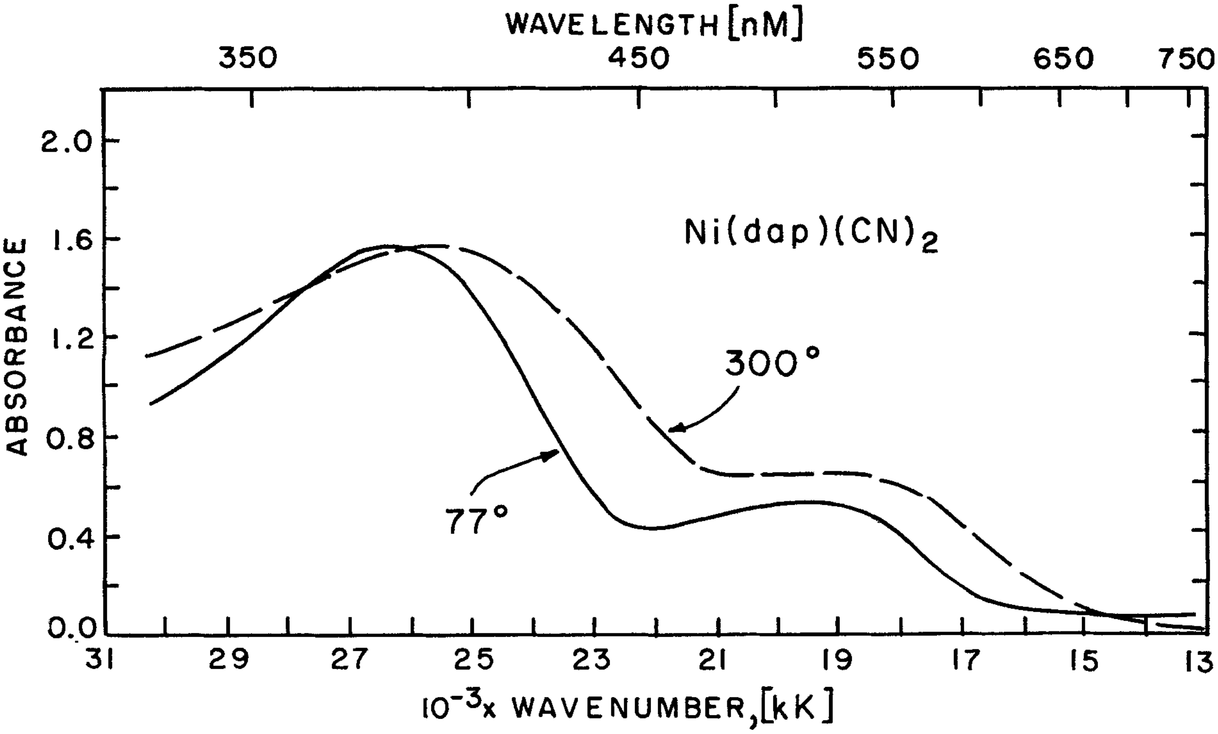

FIGURE 4 Electronic spectra of the square-pyramidal complex [Ni(dap)$(CN)_2$] as a Nujol mull at ~300° — — — and at 77°K——.

Four-Coordinate Complexes

Three four-coordinate, planar complexes were prepared. The synthesis of [Ni(dap)Cl]ClO_4 was

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carried out by mixing dap with a solution containing equimolar quantities of $[Ni(H_2O)_6](ClO_4)_2$ and $[Ni(H_2O)_6]Cl_2$. The resultant $[Ni(dap)Cl]ClO_4$ complex can be recrystallized without change from acetonitrile or chloroform, and its conductance in acetonitrile (143 mhos) is indicative of a uni-univalent electrolyte. The electronic spectrum exhibits one symmetrical band at 22,800 cm^{-1} ($\epsilon = 1{,}050$) in acetonitrile (at 22,730 cm^{-1} in a Nujol mull). The red-orange nitrate complex, $[Ni(dap)(NO_3)]NO_3$ is a uni-univalent electrolyte in acetonitrile, and the infrared spectrum (Nujol mull) provides evidence for both coordinated and uncoordinated nitrate groups.[16] The electronic spectrum has a symmetrical absorption at 23,300 cm^{-1} ($\epsilon = 943$). The shift in the visible absorption, *i.e.*, $NO_3 > Cl$, is consistent with the usual spectrochemical order of these anions. A metathetical reaction between sodium tetraphenylborate and $Ni(dap)(NO_3)_2$ resulted in the replacement of one nitrate by tetraphenylborate without significant changes in the visible spectrum, *i.e.*, the spectrum of $[Ni(dap)NO_3]B(C_6H_5)_4$ is very similar to that of $[Ni(dap)NO_3]NO_3$.

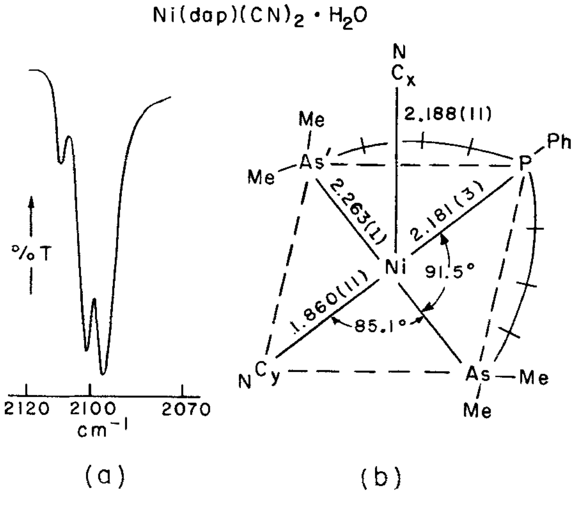

FIGURE 5 (a) Infrared spectrum of $Ni(dap)(CN)_2{\cdot}H_2O$ in the $\nu_{C\equiv N}$ region in dichloromethane solution. (b) Representation of the geometry of the inner coordination sphere of the same complex; other angles of importance are: P—Ni—C_x = 96.3(1)°; As—Ni—C_x = 98.2(2)°; C_x—Ni—C_y = 108.6(4)°.[15]

Since some of the dap complexes exhibit appreciable conductance in nitromethane we investigated the possibility of isolating cations from solutions of $[Ni(dap)I_2]$ with large non-coordinating anions. A homogeneous complex of elemental composition $[Ni_3(dap)_3I_5]BPH_4$ was obtained when excess sodium tetraphenylborate was added to a solution of $Ni(dap)I_2$. Feltham and Hayter[12] have described a method for determining the ion type and molecular complexity of electrolytes by measuring Λo–Λe as a function of concentration; using this method we find the limiting slope of $[Ni_3(dap)_3I_5]BPh_4$ to be 173 in nitromethane, which is within the range for 1:1 electrolytes.[12] This trinuclear complex has essentially the same electronic spectrum in dichloromethane solution and in the solid state (Table II) and is very similar to the spectrum of $[Ni(dap)I_2]$.

We have repeated the reaction of tas with $[Ni(H_2O)_6](ClO_4)_2$ several times according to the method of Barclay *et al.*[9] Each time a purple compound was isolated whose total analysis corresponds to the formulation $[Ni_2(tas)_3(H_2O)](ClO_4)_4$; we have been unable to fit the analytical data to any other reasonable formula.[17] A similar complex $[Ni_2(dap)_3(H_2O)](ClO_4)_4$ was obtained from the reaction of dap with $[Ni(H_2O)_6](ClO_4)_2$. Infrared bands due to coordinated water are present at ~3300 and 1650 cm^{-1}. In nitromethane, the molar conductivity values are 273 and 292 mhos for the tas and dap complexes respectively; these values may be considered reasonable for a 4:1 electrolyte containing such a large cation. Both $[Ni_2(tas)_3(H_2O)](ClO_4)_4$ and $[Ni_2(dap)_3(H_2O)](ClO_4)_4$ are diamagnetic, and their electronic absorption maxima occur at the same positions in dichloromethane solutions as in the solid state. The absorption maxima (Table II) (ca. 19,000 cm^{-1}) are consistent with diamagnetic, square-pyramidal nickel(II) complexes.[10] The similarity of the spectra for these dinuclear dap and the tas complexes indicates that they have similar structures. The asymmetry of the band may result from two slightly different coordination environments around the two nickel atoms.

When $[Ni_2(dap)_3H_2O](ClO_4)_4$ is heated in methanol, it undergoes an interesting reaction. The original purple color of the solution becomes lighter in color and a yellow-orange complex separates after a few minutes. Elemental analysis indicates that the latter complex is $[Ni(dap)Cl]ClO_4$. Its electronic spectrum exhibits one symmetrical band at 22,900 ($\epsilon = 1020$) which is almost identical with the values for an authentic sample of $[Ni(dap)Cl]ClO_4$ (Table II) that was prepared by a direct route. Recently two other cases have been reported[18, 19] where a tertiary phosphine reduced the perchlorate ion. In each of several experiments the chloride analysis was always slightly high. This may be due to co-crystallization of a second chloride ion along with the perchlorate complex. Attempts to study the stoichiometry of this redox reaction have been unsuccessful, as only part of the $[Ni_2(dap)_3(H_2O)](ClO_4)_4$ sample is reduced; some of the original purple complex remains in solution. However, during the perchlorate reduction, it is likely that some of the dap ligand is converted to its oxide. Under comparable conditions, the corresponding tas complex $[Ni_2(tas)_3(H_2O)](ClO_4)_4$ does not undergo the redox reaction in methanol.

Conclusions

The flexible, tridentate ligands dap and tas give rise to several different types of nickel(II) complexes, depending on the stoichiometry of the reagents, the reaction conditions, and the nature of the anion present in solution. The ligands function as tridentates in the diamagnetic planar $[Ni(ligand)X]^+$ cations as well as in the square-pyramidal $Ni(ligand)X_2$ molecules.

As the dap and tas tridentate ligands are quite flexible and the energy difference between a trigonal-bipyramidal and a square-pyramidal complex is known to be small,[20] one could question why the square-pyramidal geometry is formed for these $Ni(tridentate)X_2$ complexes. The preference for the square pyramid may result from the π-bonding contributions. A square pyramid with the central metal in the basal plane represents the best five-coordinate geometry for efficient π-backbonding from the metal *d*-orbitals.[21] The length and flexibility of the six-member chelate chain in the dap and tas ligands permits attainment of nearly ideal ($\sim$90°) As-Ni-P bond angles and Ni-P and Ni-As bond distances.[22]

ACKNOWLEDGMENT

We are grateful to the National Science Foundation for partial financial support of this research.

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