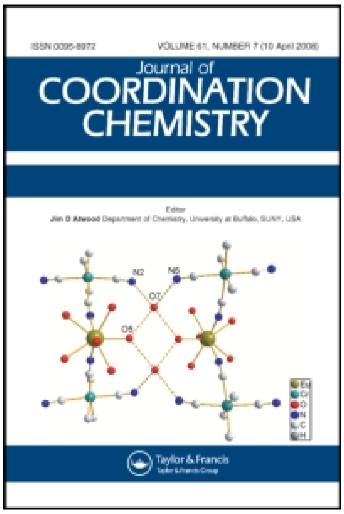

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COORDINATION COMPLEXES CONTAINING MULTI DENTATE LIGANDS. PART IV. REARRANGEMENT REACTIONS OF LOW SPIN PENTACOORDINATE NICKEL (II) COMPLEXES WITH SODIUM TETRAPHENYLBORATE TO PRODUCE POLYNUCLEAR COMPLEX SPECIES

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COORDINATION COMPLEXES CONTAINING MULTI DENTATE LIGANDS. PART IV. REARRANGEMENT REACTIONS OF LOW SPIN PENTACOORDINATE NICKEL (II) COMPLEXES WITH SODIUM TETRAPHENYLBORATE TO PRODUCE POLYNUCLEAR COMPLEX SPECIES.

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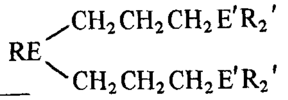
The reaction of the terdentate arsine bis(3-dimethylarsinopropyl)phenylarsine, tasp, with nickel(II) halides produces the diamagnetic, square-pyramidal $[Ni(tasp)X_2]$ (X = Cl, Br, I) complexes. In contrast to bis(3-dimethylarsinopropyl)methylarsine, the tasp ligand does not form a simple $[Ni(ligand)(NCS)_2]$ complex, but forms $[Ni_2(tasp)(NCS)_4]$, which can be subsequently converted to $[Ni_2(tasp)_3(NCS)_4]$. Reaction of $[Ni_2(tasp)_3(H_2O)](ClO_4)_4$ with varying amounts of sodium tetraphenylborate produces the polynuclear species $[Ni_2(tasp)_3(H_2O)](ClO_4)(BPh_4)_3$, $[Ni_3(tasp)_5](ClO_4)_5(BPh_4)$, and $[Ni(tasp)_2](BPh_4)_2$. Similar reactions with $[Ni(tasp)I_2]$ produce the polynuclear $[Ni_2(tasp)_2I_3]BPh_4$, $[Ni_4(tasp)_4I_7]BPh_4$, and $Ni_2(tasp)_3I_4$ species. All these polynuclear complexes are pentacoordinate and essentially square-pyramidal. The complexes were characterised by elemental analyses, magnetic, and visible and infrared spectral measurements, and by conductivity studies. The spectra and structures of the complexes are discussed.

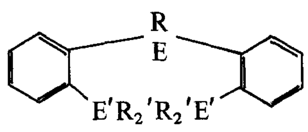
INTRODUCTION

Nickel(II) complexes of several terdentate ligands containing phosphorus or arsenic donors have been reported. These include the five-coordinate square pyramidal $[NiLX_2]$ (L = tas,[2,3] dap,[3] ptas,[4] and ttas[5]; X = halide). The perchlorate complexes which have been isolated are of the type $[Ni_2L_3(H_2O)](ClO_4)_4$ (L = tas,[3,6] dap,[3] ptas,[4] ptap[4]) and $[Ni(ttas)_2](ClO_4)_2$.[5] In a previous study[3] the reaction of $Ni(dap)I_2$ with $NaBPh_4$ to yield the trimeric $[Ni_3(dap)_3I_5]BPh_4$ complex was reported. We have extended this series of complexes by the preparation of nickel(II) derivatives of bis(3-dimethylarsinopropyl)phenylarsine (tasp), and have studied the reactions of $Ni(tasp)I_2$ and $[Ni_2(tasp)_3(H_2O)](ClO_4)_4$ with sodium tetraphenylborate in various ratios. Although nickel(II) halide complexes of these ligands are best described in the solid state as molecular five-coordinate $[NiLX_2]$ species, almost all exhibit appreciable conductivities in solution,



$$RE\begin{matrix} \nearrow CH_2CH_2CH_2E'R_2' \\ \searrow CH_2CH_2CH_2E'R_2' \end{matrix}$$

R = R′ = Me, E = E′ = As tas
R = Ph, R′ = Me, E = P, E′ = As dap
R = Ph, R′ = Me, E = E′ = As tasp



R = R′ = Ph, E = E′ = As ptas
R = R′ = Ph, E = P, E′ = As ptap
R = R′ = Me, E = E′ = As ttas

indicating an equilibrium of the type

$$[NiLX_2] \rightleftharpoons [NiLX]^+ \quad X^-$$

Indeed it has been shown[3] possible to isolate four-coordinate $[NiLX]^+$ (L = dap) derivatives. However, reaction between $[Ni(dap)I_2]$ and $NaBPh_4$ did not lead to the simple $[Ni(dap)I]^+$ cation,[3] and so our main purpose in this study was to prepare further polymeric complexes.

EXPERIMENTAL

The bis(3-dimethylarsinopropyl)phenylarsine ligand, tasp, was prepared by reaction of phenyldichloro-

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† Address enquiries to this author.

arsine with the Grignard reagent formed from 3-chloropropyldimethylarsine.[7] The product is a yellow-brown oil, which was dissolved in ethanol to give a solution of known concentration, and aliquot portions of this solution used in the complex preparations.

Preparation of [Ni(tasp)X_2] (X = Cl, Br, I)

The method is exemplified by the preparation of [Ni(tasp)Cl_2]; to nickel(II) chloride hexahydrate (0.68 g, 2.9 mmol) in ethanol (20 ml) was added a solution of tasp (1.6 g, 2.9 mmol) *via* a syringe, and the mixture was stirred for 15 minutes. The deep purple solution was rotatory evaporated to dryness and then crystallised from CH_2Cl_2/EtOH to afford small purple crystals in 77% yield.

[Ni_2(tasp)$_3$(H_2O)](ClO_4)$_4$ was prepared in an analogous manner using a 2:3 $Ni(ClO_4)_2.6H_2O$: tasp ratio. Recrystallisation from CH_2Cl_2/EtOH gave purple-black crystals in 93% yield.

Ni_2(tasp)(CNS)$_4$ Method 1. Nickel(II) chloride hexahydrate (0.68 g, 2.9 mmol) in ethanol (20 ml) was treated with a slight excess of an ethanolic solution of potassium thiocyanate. The solution was filtered and tasp (1.6 g, 2.9 mmol) in ethanol was added *via* a syringe. The resulting dark solution was stirred for 15 minutes and then rotatory evaporated to dryness. Subsequent extraction with hot dichloromethane, filtration, and crystallisation afforded Ni_2(tasp)(CNS)$_4$. *Method 2.* An ethanolic solution of [Ni(tasp)I_2] was refluxed with excess potassium thiocyanate for 30 minutes. A dark brown solid was deposited, which was recrystallised from CH_2Cl_2/EtOH to yield dark brown crystals of Ni_2(tasp)(CNS)$_4$.

Reaction of [Ni(tasp)I_2] and [Ni_2(tasp)$_3$ (H_2O)](ClO_4)$_4$ with $NaBPh_4$.

General Method. The nickel(II) complex was dissolved in warm ethanol ($\sim$30°C) containing enough dichloromethane to achieve solution. The deeply coloured solution was stirred and the calculated quantity of sodium tetraphenylborate in ethanol added dropwise. The mixture lightened in colour and, after stirring for 10 minutes, was rotatory evaporated to dryness. The product was stirred with cold dichloromethane, filtered, and evaporated to a volume of $\sim$20 ml. The dark product separated out, leaving a pale yellow or green filtrate.

TABLE I
Analytical data and some physical properties of the complexes

Compound	Colour	M.Pt. (°C)	% C$^{(a)}$	% H	% Other$^{(b)}$	$\Lambda_M$$^{(c)}$	Slope$^{(d)}$
[Ni(tasp)Cl_2]	red-purple	222(d)	32.5(33.4)	5.2(5.0)	12.0(12.3)	21$^{(e)}$	
[Ni(tasp)Br_2]	red-purple	>250(d)	28.6(28.8)	4.5(4.5)	24.0(24.1)	30$^{(e)}$	
[Ni(tasp)I_2]	green-black	>250(d)	25.5(25.2)	3.7(3.3)	33.2(33.5)	32.4$^{(e)}$	
[Ni_2(tasp)(NCS)$_4$]$^{(f)}$	brown-black	246	30.1(29.9)	3.8(3.6)	6.8(7.0)	insol.	
$^{(g)}$		243	30.6	3.9	6.9	insol.	
[Ni_2(tasp)$_3$(NCS)$_4$]	black	~100(d)	37.1(36.8)	4.8(5.1)	3.7(3.3)	insol.	
[Ni_2(tasp)$_3$(H_2O)](ClO_4)$_4$	purple	142(d)	31.0(30.8)	5.1(4.8)	7.8(7.6)	338$^{(h)}$	6,950
[Ni_2(tasp)$_3$(H_2O)](ClO_4)(BPh_4)$_3$	blue-purple	146(d)	57.0(56.9)	5.7(5.9)	1.5(1.4)	344$^{(h)}$	5,750
[Ni_3(tasp)$_5$](ClO_4)$_5$(BPh_4)	blue-purple	149(d)	38.1(38.5)	5.1(5.4)	1.3(1.1)	470$^{(h)}$	14,650
[Ni(tasp)$_2$](BPh_4)$_2$$^{(j)}$	blue	148(d)	60.1(60.5)	5.9(6.0)		222$^{(h)}$	3,330
$^{(k)}$		147(d)	60.1	6.0		214$^{(h)}$	3,320
[Ni_2(tasp)$_2$$I_3$]$BPh_4$	black	230(d)	39.6(39.1)	4.9(4.6)	23.0(22.5)	102$^{(h)}$	1,780
[Ni_4(tasp)$_4$$I_7$]$BPh_4$	black	280(d)	32.7(33.1)	4.6(4.3)	28.6(28.8)	95$^{(h)}$	1,875
[Ni_2(tasp)$_3$$I_4$]	black	264(d)	30.3(29.5)	4.3(4.4)	26.0(25.8)		

(a) found(calc.); (b) nitrogen or halogen; (c) 10^{-3} M solution; (d) $\Lambda_o - \Lambda_e)/\sqrt{C}$; (e) in nitromethane; (f) from $Ni(NCS)_2$ + tasp; (g) from [Ni(tasp)I_2] + KNCS; (h) in acetone; (j) from [Ni_2(tasp)$_3$(H_2O)](ClO_4)$_4$ + 3$NaBPh_4$; (k) from [Ni_2(tasp)$_3$(H_2O)](ClO_4)$_4$ + 4$NaBPh_4$.

Physical Measurements. Conductivity studies, infrared and electronic spectra were obtained as previously described.[8]

RESULTS AND DISCUSSION

Nickel(II) Halide Complexes

Nickel(II) halides react with tasp in ethanol to yield [Ni(tasp)X_2] complexes, which are diamagnetic and essentially non-electrolytes in nitromethane (Table I). Their electronic spectra (Table II, Figures 1 and 2) closely resemble that of [Ni(tas)Br_2], which is known to be a five-coordinate distorted square-pyramidal complex,[9] and consequently the [Ni(tasp)X_2] complexes are assigned a similar structure. The main d–d transition occurs in the range 17–21 kK and is assigned to the transition of d-orbital character $d_{z^2} \rightarrow d_{x^2-y^2}$; whilst the band at ∿33.5 kK in all three halide complexes may, because of its constant energy, be assigned to nickel-arsenic charge transfer. While the energy of this latter band is constant it is noticeable that its intensity varies as the coordinated halide is changed, I > Br > Cl. A comparison of the spectra with those of the analogous tas and dap complexes[3] shows that for the same halide the main ligand field band moves to higher energy in the order dap > tasp > tas. In the cases of dap and tasp this is expected, i.e. donor set $As_2P > As_3$, but that tasp exerts an apparently stronger ligand field strength than tas is surprising, implying that PhAs$<$ is greater than MeAs$<$ grouping. Compression effects, which produce greater than normal field strengths have been observed in multidentate ligands containing *o*-phenylene bridging groups,[10] but no such mechanism is possible here, both tas and tasp having identical trimethylene bridges between donor groups. The effect must be electronic in origin and the nature of it must await more detailed study.

It has previously been observed in the quadridentate "tripod" ligand complexes, [Ni(As_4)X]$^+$, that as the number of aryl groups was decreased, from (o-$C_6H_4AsPh_2)_3As$ to (o-$C_6H_4AsMe_2)_3As$, the

TABLE II
Electronic and infrared spectral data

	Electronic Spectra (kK)		
Compound	Solution$^{(a)}$	Solid Reflectance	Infrared Spectra (cm^{-1})
[Ni(tasp)Cl_2]	14.40(~100)$^{(c)}$	~15.5(sh)	
	20.97(460)	19.8	
	29.07(4,460)		
	33.62(3,700)		
[Ni(tasp)Br_2]	13.30(348)$^{(c)}$	14.2	
	18.00(sh)		
	20.56(820)	19.2	
	27.35(6,650)	27.2	
	33.49(13,000)		
	38.35(17,000)		
[Ni(tasp)I_2]	13.22(1,100)$^{(c)}$	13.4	
	17.21(1,750)	17.1	
	19.62(~1,400)(sh)		
	24.90(2,850)	24.2	
	33.55(28,300)		
	36.90(19,000)		

continued . . . . .

Compound	Electronic Spectra (kK)		Infrared Spectra (cm^{-1})
	Solution$^{(a)}$	Solid Reflectance$^{(b)}$	
$[Ni_2(tasp)(NCS)_4]$		16.7	2100, 2070(sh) (CN);
		22.75	~820 (CS)
$[Ni_2(tasp)_3(NCS)_4]$		9.3	2100(sh), 2080 (CN)
		17.0(sh)	
		21.45	
$[Ni_2(tasp)_3(H_2O)](ClO_4)_4$	18.3(2,920)$^{(d)}$	17.4	3300, 1630 (H_2O)
	20.2(sh)		1075(v.br) (ClO_4^-)
$[Ni_3(tasp)_5](ClO_4)_5(BPh_4)$	18.4 (4,319)$^{(d)}$	17.7	1085 (v.st.)(ClO_4^-)
	21.5(sh)		1573 (BPh_4^-)
$[Ni_2(tasp)_3(H_2O)](ClO_4)(BPh_4)_3$	18.5 (3,180)$^{(d)}$	17.7	3300, 1630 (H_2O)
	21.0 (sh)		1080(br) (ClO_4^-)
			1573 (BPh_4^-)
$[Ni(tasp)_2](BPh_4)_2$	18.5 (1,859)$^{(d)}$	17.85	No ClO_4^- absorptions
		19.7(sh)	1573 (BPh_4^-)
$Ni_2(tasp)_3I_4$	13.40(888)$^{(d)}$	13.1	
	16.90(1,515)	17.75	
	19.75(1,188)	20.0	
	24,30(2,624)	24.6	
$[Ni_4(tasp)_4I_7]BPh_4$	12.60 (2,900)$^{(d)}$	13.9	1573 (BPh_4^-)
	17.10(5,140)	16.4(sh)	
	19.85(4,370)	18.85	
	24.70(9.100)	25.0	
$[Ni_2(tasp)_2I_3]BPh_4$	17.30(1,611)$^{(d)}$	17.7(sh)	1573 (BPh_4^-)
	19.75(1,830)	19.2	
	25.50(4,630)		

(a) molar extinction coefficient in parenthesis;
(b) only recorded in the range 5–28 kK;
(c) dichloromethane solution;
(d) aceton solution in the range 5–30 kK.

intensity of the main d–d transitions fell quite dramatically, indicating that much of the intensity of the d–d bands in the tripod tetradentates synthesised and studied by Venanzi and co-workers derived from the "borrowing" of intensity from the π–π^* transitions localised on the aryl groups.[11] In comparing the complexes derived from the totally aliphatic tas ligand, $MeAs(CH_2CH_2CH_2AsMe_2)_2$, with those from the phenyl-substituted tas ligand, tasp, $PhAs(CH_2CH_2CH_2AsMe_2)_2$, we have been presented with an excellent chance to re-examine this phenomenon. We found that the extinction coefficients of the $[Ni(tasp)X_2]$ complexes (Table II) were indeed greater than those of the tas analogues,[3] though the increase was only of the order of ∿10% and may not be significant.

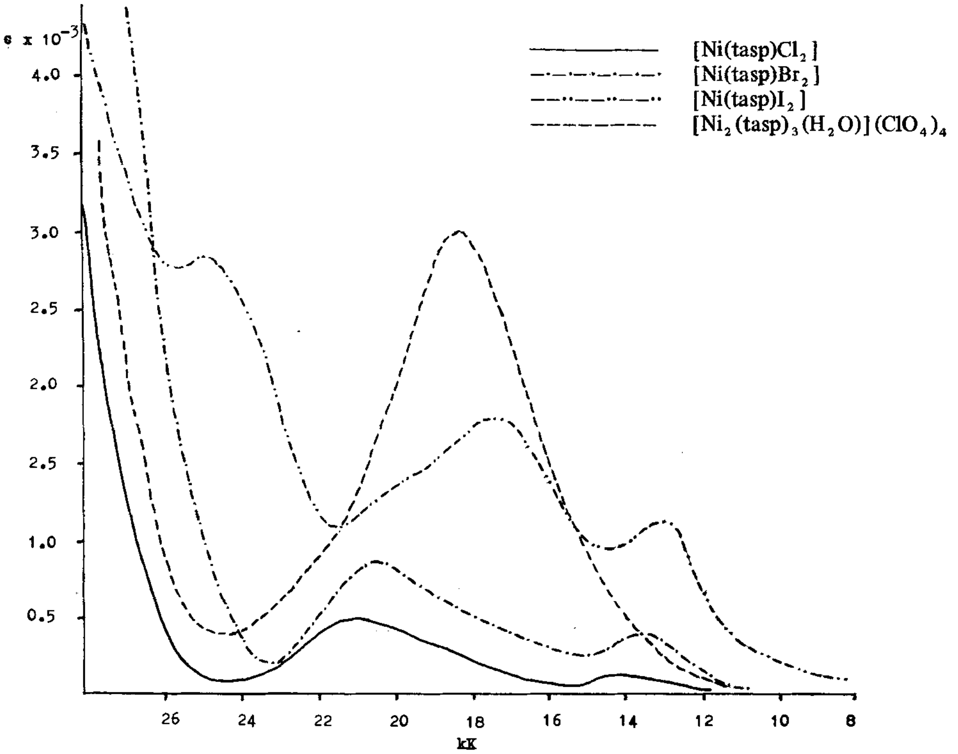

FIGURE 1. Electronic solution spectra

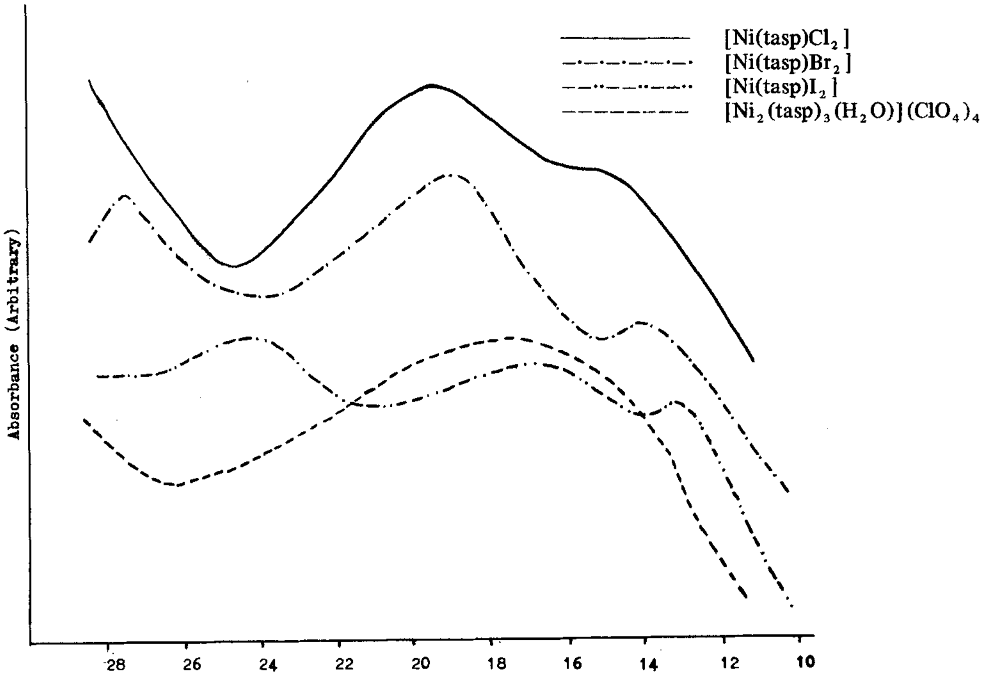

FIGURE 2. Solid state electronic spectra

Surprisingly, a [Ni(tasp)(NCS)$_2$] complex could not be obtained (*cf.* [Ni(tas)(NCS)$_2$][3]). The reaction of Ni(NCS)$_2$ with tasp or of Ni(tasp)I$_2$ with KNCS in ethanolic solution produced [Ni$_2$(tasp)(NCS)$_4$]. This diamagnetic complex dissolved in dichloromethane and could be recovered on rapidly removing the solvent, but on standing the solution decomposed. This instability in solution precluded solution spectral studies; however, the mull IR spectrum suggests that only Ni-*N*CS bonding is present which produces the intriguing possibility of only seven donors [As$_3$N$_4$] about the two nickel atoms. On refluxing in ethanol Ni$_2$(tasp)(NCS)$_4$ rearranges to form the dichloromethane soluble brown Ni$_2$(tasp)$_3$(NCS)$_4$ and the insoluble yellow Ni(NCS)$_2$. In the solid state Ni$_2$(tasp)$_3$(NCS)$_4$ also only shows the presence of Ni-*N*CS coordination, but once again lack of long-term solution stability prevented further study. This dimer is diamagnetic and the electronic spectrum shows no evidence of the Ni(NCS)$_4^{2-}$ ion, thus ruling out the [Ni(tasp)$_3$] [Ni(NCS)$_4$] formulation, but in the absence of crystallographic measurements the actual structure must remain in doubt.

Polynuclear Complexes.

The reaction of Ni(ClO$_4$)$_2$.6H$_2$O with tasp produces only [Ni$_2$(tasp)$_3$(H$_2$O)](ClO$_4$)$_4$, analogous to the complexes of tas, dap,[6] pdap, and ptas.[4] Its spectroscopic properties are almost identical with those of [Ni$_2$(tas)$_3$(H$_2$O)](ClO$_4$)$_4$[6] and are consistent with square pyramidal nickel(II).

Following indications[3] that the triarsine complexes may be capable of rearrangement and polymerisation in solution, we investigated the reactions between [Ni$_2$(tasp)$_3$(H$_2$O)](ClO$_4$)$_4$ and NaBPh$_4$ in various ratios. The work was complicated by the low solubility of the products and by their rapid decomposition in most solvents. These polynuclear species decomposed very rapidly in nitromethane, ethanol, acetonitrile, and, more slowly, in dichloromethane. However, conductivity measurements on acetone solutions of the complexes were found to be effectively unchanged over a 5 hour period, indicating that the solutions were stable at least for this period of time.

Reaction of [Ni$_2$(tasp)$_3$(H$_2$O)](ClO$_4$)$_4$ with NaBPh$_4$ in a 1:1 molar ratio yielded a blue-purple homogeneous powder. Repeated reactions gave the same product, the analysis of which (Table I) indicated the product to be [Ni$_3$(tasp)$_5$](ClO$_4$)$_5$ (BPh$_4$).† Repeated reactions of [Ni$_2$(tasp)$_3$(H$_2$O)] (ClO$_4$)$_4$ with two equivalents of NaBPh$_4$ yielded [Ni$_2$(tasp)$_3$](ClO$_4$)(BPh$_4$)$_3$. From [Ni$_2$(tasp)$_3$ (H$_2$O)](ClO$_4$)$_4$ and NaBPh$_4$ in a 1:3 or 1:4 ratio blue complexes consistently analysing as [Ni(tasp)$_2$] (BPh$_4$)$_2$ were obtained. The visible spectra of all these complexes in acetone exhibit an intense broad asymmetric absorption at $\sim$18.5 kK; the diffuse reflectance spectra are generally similar (Table II). Addition of small amounts of water or nitromethane to these acetone solutions resulted in rapid decomposition, the intense purple colour changing to yellow-brown. The visible spectra of these decomposed solutions showed only weak, poorly resolved absorptions and we have been unable to identify the species present (*cf.* ref. 5).

The electronic spectra of all these complexes are characteristic of five-coordinate, square-pyramidal nickel(II) with an As$_5$ or As$_4$L donor set similar to that found for [Ni$_2$(tasp)$_3$(H$_2$O)](ClO$_4$)$_4$. The infrared spectra confirm the presence of tetraphenylborate and also show that the perchlorate groups present are uncoordinated – evidenced by the broad, unsplit absorption at $\sim$1080 cm^{-1}.[14] Few studies have been made on conductivities of coordination complexes in acetone,[15] and to our knowledge $\Lambda_0 - \Lambda_e$ *vs* $\sqrt{C}$ plots for various electrolyte types[16] have not been reported. Geary[15] quotes the Λ_M values for 10^{-3} M solutions in acetone as 1:1 100–140, 2:1 160–200, 3:1 $\sim$270, 4:1 $\sim$360 ohm^{-1} cm^2 M^{-1}. Thus, [Ni$_2$(tasp)$_3$(H$_2$O)](ClO$_4$)(BPh$_4$)$_3$ behaves as a 1:4 electrolyte, [Ni$_3$(tasp)$_5$](ClO$_4$)$_5$(BPh$_4$) has the very high value Λ_M = 470 ohm^{-1} cm^2 M^{-1}, which is not unreasonable for a 1:6 electrolyte with such large ions, and [Ni(tasp)$_2$](BPh$_4$)$_2$ is a 1:2 electrolyte. The conductivity values are also internally consistent; *cf.* [Ni$_2$(tasp)$_3$(H$_2$O)](ClO$_4$)(BPh$_4$)$_3$ and [Ni$_2$(tasp)$_3$(H$_2$O)](ClO$_4$)$_4$.

The isolation of [Ni(tasp)$_2$](BPh$_4$)$_2$ provides another example of a [Ni(tridentate)$_2$]$^{2+}$ species. The first species of this type reported was [Ni(tas)$_2$] (ClO$_4$)$_2$,[2] and at that time this complex was formulated as a low-spin octahedral nickel(II) complex

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†Attempts to analyse these polymeric complexes for nickel by EDTA titrations and gravimetrically by dimethylglyoxime were not successful. We have analysed for C, H, N, and Hal wherever possible, and the excellent fit of these analyses to those calculated assure us of the accuracy of our formulations. In particular, we would like to stress that many repetitions of these reactions produced complexes which gave constant analyses. We are indebted to the microanalytical service of this Department for their painstaking work.

similar to $[Ni(diarsine)_3](ClO_4)_2$ (diarsine = *o*-phenylenebisdimethylarsine). Subsequently both of these species have been shown to contain the pentacoordinate $[Ni(As_4O)]^{2+}$ [6] and $[Ni(As_5)]^{2+}$ [17] coordination moieties, respectively. Similar species are $[Ni(ttas)_2](ClO_4)_2$,[5] and the $[NiI]^{2+}$ (L = the potentially hexadentate *o*-phenylenebis di-(3-dimethylarsinopropyl)arsine).[18] There is no good evidence to suggest that such species are anything but pentacoordinate, and the $[Ni(tasp)_2](BPh_4)_2$ complex reported here clearly contains an $NiAs_5$ chromophore. Attempts to confirm this by ^1H n.m.r. spectroscopy (to detect the uncoordinated $-AsMe_2$ group) were not successful, due to poor solubility in suitable solvents.

Since both $[Ni(tasp)Br_2]$ and $[Ni(tasp)I_2]$ complexes have appreciable conductivities in nitromethane (although too low for 1:1 electrolytes), we also studied the reaction of the latter with varying amounts of sodium tetraphenylborate. A large excess (∿6 fold) of tetraphenylborate produced a black homogeneous solid, $[Ni_2(tasp)_2I_3]BPh_4$, whilst a 1:2 molar ratio of $[Ni(tasp)I_2]$:$NaBPh_4$ gave $[Ni_4(tasp)_4I_7]BPh_4$; both are 1:1 electrolytes and have electronic spectra (Table II) indicative of pentacoordination similar to that in the parent $[Ni(tasp)I_2]$. Reaction of $[Ni(tasp)I_2]$ with $NaBPh_4$ in a 1:1 molar ratio produced the complex $Ni_2(tasp)_3I_4$, which exhibited no IR absorptions characteristic of BPh_4^-; qualitative tests for boron were negative.

Molecular weight values in acetone solution for several of these complexes were of the correct order but about 15% higher than the calculated values, probably due to ion pairing.

Thus the reaction of $[Ni_2(tasp)_3(H_2O)](ClO_4)_4$ and $[Ni(tasp)I_2]$ with $NaBPh_4$ under suitable conditions leads to rearrangement, producing various polynuclear cations. The stoichiometry of these products vary considerably and bear little relationship to the ratio of the reactants. Presumably lattice energy and, to a lesser extent, steric factors within the cations themselves are the governing factors. In the absence of X-ray structural data further speculation, other than to point out that all the polynuclear species appear to be pentacoordinate and essentially square-pyramidal, seems premature. It should be stressed that the species reported here are the products of reactions repeated a number of times to ensure molecular purity. It is also clear that in the rearrangement reactions the products isolated were only the major products, because from the stoichiometry, other nickel containing species must be produced; presumably these are present in the green or yellow filtrates after isolation of the major products.

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