227. *Some Trigonal-bipyramidal Nickel*(II) *Complexes with Quadridentate Phosphines and Arsines.*

By G. Dyer, J. G. Hartley, and L. M. Venanzi.

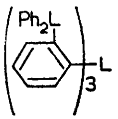
Tris-(*o*-diphenylphosphinophenyl)phosphine and the arsenic analogue form complexes with nickel(II) of the type [NiX(chelate)]$^+$ which are five-co-ordinate with trigonal-bipyramidal structure. Nitrate and perchlorate ions co-ordinate strongly to nickel in these complexes.

Recent investigations have shown that nickel(II) tends to form five-co-ordinate complexes more often than suspected hitherto. The majority of such compounds have been obtained by using phosphorus and arsenic donors. Thus *o*-phenylenebis(dimethylarsine) (I) (das) forms complexes of the type [MX(das)$_2$]$^+$ in solution, and solid salts such as [MX(das)$_2$][PF$_6$] have been isolated.[1] The terdentate ligand, bis-(3-dimethylarsinopropyl)methylarsine (II) (tas), gives complexes of the type [NiX$_2$(tas)], the solid bromo-compounds having a distorted square-pyramidal structure.[2]

$o\text{-}C_6H_4(AsMe_2)_2$ (I) (das)

$Me{\cdot}As(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}AsMe_2)_2$ (II) (tas)

We report here the preparation and properties of a number of complexes with two quadridentate ligands, one of phosphorus (QP; III*a*) and the other of arsenic (QAS; III*b*). The complexes prepared and some of their physical properties are listed in Table 1. These are 1 : 1 electrolytes in nitrobenzene, and the conductance does not increase when iodomethane is added, indicating that all four arsine or phosphine groups are co-ordinated, and therefore that the complexes are five-co-ordinate. The complexes with two co-ordinating anions remain five-co-ordinate even in the solid state as shown by the virtual identity of the spectra of the series of complexes [NiBr(QAS)]Y (Y = Br, ClO$_4$, BPh$_4$), both in solution and in the solid state. They are of low spin, and their properties are very similar to the corresponding palladium(II) and platinum(II) compounds.[3]



L = P; (III*a*) (QP)
L = As; (III*b*) (QAS)

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[1] Barker, Harris, and McKenzie, *Proc. Chem. Soc.*, 1961, 335.
[2] Mair, Powell, and Henn, *Proc. Chem. Soc.*, 1960, 415.
[3] Hartley, Venanzi, and Goodall, *J.*, 1963, 3930, and previous references therein.

TABLE 1.

Colours, decomposition points, conductivities, and analyses (%) of nickel(II) complexes with the ligands (IV*a*; QP) and (IV*b*; QAS).

Compound	Colour	Decomp. pt.	Λ_M * (mho)	Ni Found	Ni Reqd.	As or P Found	As or P Reqd.	C Found	C Reqd.	H Found	H Reqd.	N Found	N Reqd.
[NiCl(QAS)](ClO$_4$)	Dark blue	321—322°	23·9	4·9	4·9	25·4	25·3	54·6	54·8	4·0	3·6		
[NiBr(QAS)]Br	Blue-black	329—333	20·6	4·7	4·8	24·7	24·8	53·4	53·6	3·7	3·5		
[NiBr(QAS)](ClO$_4$)	Dark blue	321—322	23·0	4·7	4·8	24·3	24·4	52·4	52·8	3·6	3·5		
[NiBr(QAS)][BPh$_4$]	Dark blue	225—228	15·7	4·0	4·0	20·5	20·7						
[NiI(QAS)]I	Blue-black	330—331	24·8	4·6	4·5	22·9	23·0						
[NiI(QAS)](ClO$_4$)	Blue-black	338—339	23·8	4·6	4·6	23·4	23·5						
[Ni(NCS)(QAS)](ClO$_4$) ...	Black	316—318	24·3	4·8	4·9	24·7	24·8					1·4	1·2
[Ni(CN)(QAS)](ClO$_4$) ...	Brown	338—339	23·2	4·9	5·0	25·3	25·5					1·0	1·2
[Ni(NO$_3$)(QAS)](ClO$_4$) ...	Dark blue	293—296	25·2	4·8	4·8	24·6	24·8					1·0	1·15
[Ni(ClO$_4$)(QAS)](ClO$_4$) ...	Dark blue	†	32·5	4·6	4·7	24·1	24·0	52·0	52·1	3·6	3·4		
[NiCl(QP)](ClO$_4$)	Deep purple	353—356	22·7	5·9	5·8	12·2	12·3						
[Ni(NO$_3$)(QP)](ClO$_4$) ...	Deep purple	282—285	22·8	5·6	5·7	11·9	11·9					1·1	1·35
[Ni(ClO$_4$)(QP)](ClO$_4$) ...	Royal blue	†	34·2	5·5	5·5	11·5	11·5						

* For 10^{-3}M-nitrobenzene solutions at 20°. † Gradual decomposition above 250°. N.B. All complexes were diamagnetic; values of χ_M (corrected) at room temperature were within the range -20 to $+70 \times 10^{-6}$.

TABLE 2.

Visible and ultra-violet spectra of nickel(II) complexes with the ligands (IV*a*; QP) and (IV*b*; QAS).

Complex	Dichloromethane solution $E_{max.}$ (cm.$^{-1}$)	Dichloromethane solution $\varepsilon_{max.}$	Solid $E_{max.}$ (cm.$^{-1}$)
[NiCl(QAS)](ClO$_4$)	39,200sh	22,300	39,200sh
	31,300	15,400	31,000
	21,800	330	22,000
	16,200	4470	16,000
[NiBr(QAS)]Br	37,800	23,500	37,800
	31,200	15,000	31,000
	21,800	450	21,800
	15,800	4000	15,400
[NiBr(QAS)](ClO$_4$)	37,800	25,500	37,800
	31,200	15,900	31,000
	21,800	450	21,800
	15,800	4150	15,400
[NiBr(QAS)][BPh$_4$]	37,800	28,000	37,800sh
	31,200	15,500	31,000
	21,800	450	21,800
	15,800	4100	15,500
[NiI(QAS)]I	37,300	22,800	36,300sh
	31,000	16,000	30,800
	21,200	910	21,000
	15,200	3700	14,700
[NiI(QAS)](ClO$_4$)	36,300	22,200	36,300sh
	30,800	17,000	30,800
	21,000	1160	21,000
	15,000	3460	14,700
[Ni(NCS)(QAS)](ClO$_4$)	38,500sh	28,400	—
	31,600	24,000	31,400
	22,400	1900	22,200
	17,100	9800	17,000
[Ni(CN)(QAS)](ClO$_4$)	38,600sh	22,000	38,000sh
	34,200	18,000	34,500sh
	21,500	5750	21,500
[Ni(NO$_3$)(QAS)](ClO$_4$)	38,500sh	30,000	38,200sh
	33,500sh	13,000	33,000sh
	16,500 [a]	2200	16,200
[Ni(ClO$_4$)(QAS)](ClO$_4$)	38,400sh	18,100	38,500sh
	31,400	11,400	33,000sh
	16,900 [b]	3730	16,000
[NiCl(QP)](ClO$_4$)	36,200 [c]	20,800	36,300sh
	17,500	4950	17,500
[Ni(NO$_3$)(QP)](ClO$_4$)	37,300 [c]	21,200	37,000sh
	17,600	5400	17,600
[Ni(ClO$_4$)(QP)](ClO$_4$)	37,300sh [c]	19,200	37,000sh
	18,100	4150	17,000

[a] Gaussian analysis shows another band at 22,000 cm.$^{-1}$ ($\varepsilon = 270$). [b] Gaussian analysis shows another band at 21,700 cm.$^{-1}$ ($\varepsilon = 213$). [c] Gaussian analysis shows that the broad bands in the QP complexes can be resolved into bands (ε in parentheses) at: chloro-complex, 34,700 (17,000), 30,500 (6000), 26,600 (2100); nitrato-complex, 34,700 (16,300), 30,600 (7400), 27,800 (2450); perchlorato-complex, 34,500 (15,000), 30,600 (7200), 28,000 (2300).

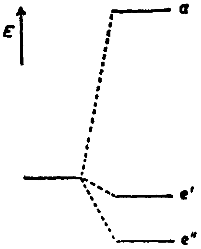
The nitrato- and perchlorato-complexes, like all our other complexes, are 1 : 1 electrolytes, and the evidence indicates that the oxy-anion is co-ordinated to the central metal atom.

Co-ordination of nitrate ion to transition-metal ions is not uncommon, and the effect of co-ordination on its vibrational spectrum has been investigated by Gatehouse *et al.*[4] The complexes $[Ni(NO_3)(QP)](ClO_4)$ and $[Ni(NO_3)(QAS)](ClO_4)$ show strong bands at 1480, 1275, and 1000 cm.$^{-1}$ (phosphorus compound) and 1490, 1260, and 980 cm.$^{-1}$ (arsenic compound), assignable to ν_4 (asymmetric stretch), ν_1 (NO_2 symmetric stretch), and ν_2 (N–O stretch) respectively, for a co-ordinated nitrate, confirming the above formulation.

Co-ordination of the perchlorate ion has been observed in complexes of nickel(II) and copper(II) with 1,10-phenanthroline and 2,2′-bipyridyl, and the low conductivity of a nitrobenzene solution of $\{Ni(ClO_4)_2(das)_2\}$ has been attributed to the formation of the ion $[Ni(ClO_4)(das)_2]^+$.[1] It has also been reported recently that $\{Ni(3,5\text{-lutidine})_4(ClO_4)_2\}$ contains co-ordinated perchlorate.[5] Hathaway and Underhill [6] have shown that, in co-ordinated perchlorates, the triply degenerate asymmetrical stretch ν_3 of T_d (at 1080—1100 cm.$^{-1}$) is split into a non-degenerate symmetric stretch ν_1 and a doubly degenerate asymmetric bend ν_4 of the C_{3v} group. It was also observed that when the oxygen atom was only weakly bonded, the two stretches ν_1 and ν_4 were not fully resolved, a broad band being observed. The spectra of $[NiCl(QP)](ClO_4)$ and $[NiCl(QAS)](ClO_4)$ show a single intense band at 1080 cm.$^{-1}$ due to ionic perchlorate. The corresponding perchlorato–perchlorate complexes, on the other hand, show three distinct bands in the same region: at 1155, 1080, and 1005 cm.$^{-1}$ showing conclusively that one of the perchlorates is strongly bonded to the central metal atom. They also show a band at 850—860 cm.$^{-1}$ which may be assigned to the non-degenerate Cl–O stretch ν_2.

The differences in visible and ultraviolet spectra of corresponding compounds of nickel, palladium, and platinum are in accord with the increase in orbital splitting in the series Ni $<$ Pd $<$ Pt, thus establishing that the nickel(II) complexes have trigonal-bipyramidal structure like their palladium(II) and platinum(II) analogues.

Two main sets of bands of fairly low energy are observed: one more intense set at 15,000—17,000 cm.$^{-1}$ and the other less intense set at 21,000—22,000 cm.$^{-1}$ in the arsine complexes. For the phosphine complexes they occur at 17,000—18,000 and 26,000—28,000 cm.$^{-1}$ respectively (see Table 2). The *d*-energy level splitting in trigonal-bipyramidal complexes is shown in the Figure. Nickel(II) then has two filled subshells, $(e'')^4(e')^4$, and the observed bands have been assigned to $e' \longrightarrow a_1'$ and $e'' \longrightarrow a_1'$ transitions respectively,[7] despite their fairly high intensities ($\varepsilon_{max.}$ 3500—10,000 for the lower and 200—1900 for the higher energy bands).



d-Energy level splitting for a trigonal-bipyramidal field.

These transitions become allowed, at least to a certain extent, because the d_{z^2} and the p_z orbitals of the metal ion in C_{3v} symmetry have a_1 symmetry and, therefore, will mix. Furthermore, transitions can gain intensity from σ-bonding owing to mixing of e' and ligand orbitals.

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[4] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.
[5] Buffagni, Vallarino, and Quagliano, *Inorg. Chem.*, 1964, **3**, 480.
[6] Hathaway and Underhill, *J.*, 1960, 3091.
[7] Jørgensen, "Inorganic Complexes," Academic Press, London, 1963, p. 165.

The extinction coefficients of the higher frequency bands are about 1/10 to 1/4 of those of the lower frequency bands. This is in keeping with the idea that while the enhancement of intensities of the lower frequency bands is caused by both of the above factors, the intensities of the higher frequency bands would be little affected by the second factor unless extensive π-bonding occurred.

The spectrochemical series of ligands X in the complexes [NiX(QAS)](ClO_4) is readily constructed, and is of interest as it clearly shows the positions of the nitrato- and perchlorato-groups, which cannot usually be included:

$$I < Br < Cl < NO_3 < ClO_4 < NCS < CN.$$

Our five-co-ordinate complexes with QAS and QP contrast strikingly with complexes of the tetratertiary ligand tris-(3-dimethylarsinopropyl)arsine (IV) (qas),[8] which may be

$As(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}AsMe_2)_3$ (IV) (qas)

regarded as an aliphatic analogue of QAS. Complexes of qas with nickel(II) were found to be unstable, readily becoming oxidised to nickel(III) derivatives; the only nickel(II) compound which could be isolated was [NiI_2(qas)], which was octahedral. The differences in behaviour towards nickel(II) between qas and QAS may be steric, as the latter has the more rigid structure, although octahedral complexes of QAS of the type [MX_2(QAS)] (M = Ru, Os) are known.[3]

EXPERIMENTAL

The tetratertiary phosphine was prepared by the method of Hartley *et al.*,[3] and the tetratertiary arsine by the method of Howell *et al.*[9] Unless otherwise stated, all complexes were recrystallised twice by dissolving in dichloromethane, filtering, adding ethanol, and removing dichloromethane. Yields refer to recrystallised *complexes*. The nitrate and cyanide complexes were pumped at 60°/10^{-4} mm. for 24 hr. to remove solvent.

[NiCl(QAS)](ClO_4).—On refluxing nickel chloride hexahydrate (0·12 g.) and nickel perchlorate hexahydrate (0·18 g.) in ethanol (5 ml.), and QAS (1 g.) in dichloromethane (20 ml.), an intense blue solution was obtained. This was diluted with ethanol (20 ml.), and dichloromethane was removed (yield 0·65 g., 55%).

[NiBr(QAS)]Br.—Nickel bromide trihydrate (0·21 g.) and QAS (0·5 g.) in ethanol (20 ml.) were refluxed and the intensely coloured solution, when cooled, produced blue-black crystals which were recrystallised from ethanol (yield 0·3 g., 49%).

[NiBr(QAS)](ClO_4).—Boiling ethanolic solutions of sodium perchlorate (0·2 g.) and [NiBr(QAS)]Br (0·3 g.) were mixed, and allowed to cool. The precipitate was recrystallised once (yield 0·22 g., 72%).

[NiBr(QAS)][BPh_4].—Hot ethanolic solutions of sodium tetraphenylboron (0·1 g.) and [NiBr(QAS)]Br (0·3 g.) were mixed and cooled. The product was recrystallised once (yield 0·32 g., 88%).

[NiI(QAS)]I.—Nickel nitrate hexahydrate (0·2 g. in 5 ml. of ethanol) and sodium iodide (0·21 g. in 5 ml. of ethanol) were mixed and sodium nitrate was filtered off. The filtrate (diluted with ethanol to 20 ml.) on refluxing with QAS (0·5 g.) gave black sparingly soluble crystals (yield 0·2 g., 30%).

[NiI(QAS)](ClO_4).—The boiling iodo–iodide reaction mixture (see above) was filtered when only a small quantity of black crystals had separated into hot sodium perchlorate (0·3 g.) in ethanol (20 ml.). The product was recrystallised once (yield 0·44 g., 68%).

[Ni(NCS)(QAS)](ClO_4).—Nickel nitrate hexahydrate (0·2 g. in 5 ml. of ethanol) and sodium thiocyanate (0·11 g. in 5 ml. of ethanol) were mixed and filtered into QAS (0·5 g.) in dichloromethane (10 ml.). After refluxing, the intensely coloured solution was filtered into sodium perchlorate (0·5 g.) in ethanol (10 ml.), and dichloromethane was removed (yield 0·26 g., 43%).

[Ni(CN)(QAS)](ClO_4).—[NiI(QAS)](ClO_4) (0·33 g.) in warm dichloromethane (20 ml.) was treated dropwise with sodium cyanide (0·0128 g.) in ethanol (20 ml.); dichloromethane was boiled off (yield 0·13 g., 42%).

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[8] Barclay and Barnard, *J.*, 1961, 4269.
[9] Howell, Pratt, and Venanzi, *J.*, 1961, 3167.

$[Ni(NO_3)(QAS)](ClO_4)$.—A solution of nickel nitrate hexahydrate (0·29 g.) and nickel perchlorate hexahydrate (0·367 g.) in ethanol (2 ml.) was added dropwise to QAS (2 g.) in boiling chlorobenzene (10 ml.). The mixture was refluxed for 2 hr., then cooled. The product crystallised slowly during 24 hr. It was purified by dissolving in dichloromethane (25 ml.) and chlorobenzene (7·5 ml.), and removing dichloromethane (yield 1·34 g., 55%).

$[Ni(ClO_4)(QAS)](ClO_4)$.—Nickel perchlorate hexahydrate (0·367 g.) in ethanol (2 ml.) was added dropwise to QAS (1 g.) in boiling chlorobenzene (10 ml.). After refluxing, the solution was concentrated to half its volume, and allowed to stand 24 hr. The product was recrystallised once using dichloromethane and chlorobenzene (yield 0·6 g., 48%).

$[NiCl(QP)](ClO_4)$.—Nickel chloride hexahydrate (0·16 g.) in ethanol (15 ml.) and QP (0·41 g.) in dichloromethane (15 ml.) were refluxed for 2 hr., then filtered into sodium perchlorate (0·4 g.) in ethanol (10 ml.). Dichloromethane was removed, and indigo crystals separated rapidly (yield 0·3 g., 60%).

$[Ni(NO_3)(QP)](ClO_4)$.—It was prepared as above from nickel nitrate hexahydrate (0·072 g.) and nickel perchlorate hexahydrate (0·092 g.) in ethanol (10 mls.) and QP (0·41 g.) in dichloromethane (10 ml.) (yield 0·39 g., 75%).

$[Ni(ClO_4)(QP)](ClO_4)$.—It was prepared as $[Ni(ClO_4)(QAS)](ClO_4)$ using QP (0·82 g.) instead of QAS (yield 0·43 g., 40%).

Analytical.—Nickel, arsenic, and phosphorus were determined by spectrophotometry. For nickel, samples (about 25 mg.) were refluxed with concentrated nitric and 72% perchloric acids (2 ml. each) for 2 hr., diluted to 100 ml., and neutralised (litmus) with 2N-sodium hydroxide. Citric acid (2 ml. of 10% aqueous solution), potassium persulphate (6 ml. of 2% aqueous solution), sodium hydroxide (30 ml. of 2N), and dimethylglyoxime (4 ml. of 1% ethanolic solution) were added. The solutions were warmed at 75° for 7 min., diluted to 500 ml., and the absorbances at 465 mμ were measured after 1 hr.

For arsenic and phosphorus, samples (about 25 mg.) were refluxed with 72% perchloric acid (5 ml.) and ammonium vanadate (about 25 mg.) for 2 hr., and diluted to 500 ml. Aliquot parts (5 ml.) were treated with 5 ml. of molybdate reagent (prepared to dissolving 8 g. of ammonium molybdate in a cold mixture of 80 ml. concentrated sulphuric acid, 320 ml. water and 1600 ml. 1N-hydrochloric acid) and 2 ml. of hydrazine sulphate (0·05% aqueous solution). The mixtures were diluted to 25 ml., heated at 100°c for 15 min., and cooled. The absorbances at 840 mμ were measured after 1 hr.

Visible and Ultraviolet Spectra.—A Unicam S.P. 700 recording spectrophotometer was used. Solution spectra were obtained for 10^{-3}—10^{-5}M-solutions. Solid spectra were obtained by impregnating small filter papers with solutions of samples (2—5 mg.) in dichloromethane (about 1 ml.). The dichloromethane evaporated in a few seconds, leaving dry coloured filter papers, which were made translucent by painting with Nujol. These were placed over the entrance to the photocell housing, with a Nujol-treated blank filter paper on the reference side. An air-only base-line was used; bands with extinction coefficients up to 5000 had apparent absorbances in the 0—1·1 range, while those with extinction coefficients up to 40,000 were recorded in the absorbance range 0·9—2. Tests showed peak and shoulder positions identical with those of reflectance spectra of powdered complexes obtained by manual operation of a reflection attachment S.P. 540 on a Unicam S.P. 500 spectrophotometer.

Infrared Spectra.—These were recorded in Nujol and hexachlorobutadiene mulls in the sodium chloride and cæsium bromide regions on a Perkin-Elmer model 221 spectrophotometer. The C–N and C–S stretches in $[Ni(NCS)(QAS)](ClO_4)$ occur at 2090 and 833 cm.$^{-1}$, respectively, indicating *N*-bonding.

Conductivity and Magnetic Susceptibility.—See ref. 3.

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INORGANIC CHEMISTRY LABORATORY, OXFORD UNIVERSITY. [*Received, June* 25*th*, 1964.]