499. *The Visible and Ultaviolet Spectra of Trigonal Bipyramidal Complexes of Nickel*(II), *Palladium*(II), *and Platinum*(II)

By G. Dyer and L. M. Venanzi

Complexes $[MX(QAS)](ClO_4)_n$, where M = Pd or Pt and $n = 1$ for X = CN, NO_2, NO_3, or $CH_2{\cdot}NO_2$, and $n = 2$ for X = thiourea or dimethyl sulphide have been prepared. The ultraviolet and visible spectra of these complexes and of those with X = Cl, Br, I, or NCS have been examined, and some assignments made for *d–d* transitions in a trigonal bipyramidal field. An explanation is offered for the deviation from perfect trigonal symmetry in these complexes.

Trigonal bipyramidal complexes of palladium(II) and platinum(II) with the quadridentate arsine ligand tris-(*o*-diphenylarsinophenyl)arsine, $(o\text{-}Ph_2As{\cdot}C_6H_4)_3As$ (QAS), containing the $[MX(QAS)]^+$ ion, where M = Pd or Pt and X = Cl, Br, I, or NCS have previously been reported.[1] As nickel(II) forms complexes with QAS that contain strongly co-ordinated nitrato- and perchlorato-groups,[2] it was of interest to see whether corresponding complexes with palladium(II) and platinum(II) could be prepared.

Complexes were prepared by the scheme shown for platinum, and by an almost identical scheme for palladium. Their physical properties are listed in Table 1.

The reaction of $[MBr(QAS)](ClO_4)$ with nitrite was slow, but practically instantaneous with cyanide or thiourea. Excess of cyanide gave QAS and presumably $[M(CN)_4]^{2-}$. No product could be isolated by using ammonium hydroxide or sodium hydroxide.

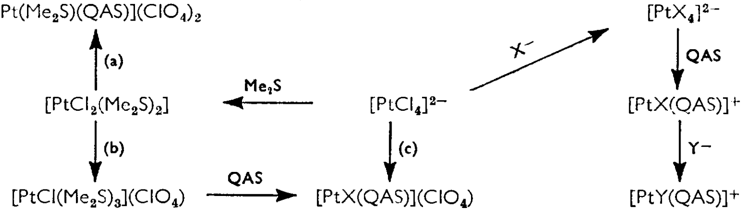
In a further attempt to prepare a hydroxide complex, a solution of $[MBr(QAS)](ClO_4)$ in nitromethane and ethanol was shaken with moist silver oxide; under these conditions $(CH_2{\cdot}NO_2)^-$ ions, produced by reaction of nitromethane with silver oxide, co-ordinated

$$\text{"AgOH"} + CH_3{\cdot}NO_2 + [MBr(QAS)]^+ \longrightarrow [M(CH_2{\cdot}NO_2)(QAS)]^+ + AgBr + H_2O.$$

An attempt to prepare nitrato-nitrate complexes from $[MCl_2(MeS)_2]$ by addition of dimethyl sulphide and silver nitrate, and reaction with QAS, gave products that could not be obtained analytically pure. Their infrared spectra, however, showed the presence of both co-ordinated and ionic nitrate. But the nitrato-complexes $[Pd(NO_3)(QAS)][BPh_4]$ and $[Pd(NO_3)(QAS)](ClO_4)$ could be prepared. The conductance of nitrobenzene solutions of the nitrato-complexes increased when pyridine was added, presumably because of the formation of $[M(pyridine)(QAS)]^{2+}$ which, however, could not be isolated.

Attempts to prepare a perchlorato-complex as indicated in the scheme failed because of the insolubility of $[PtCl(Me_2S)_3](ClO_4)$.

Preparative scheme



[X = Br, I, NCS; a = (1) Me_2S, (2) $AgNO_3$ or AgF, (3) QAS, (4) $NaClO_4$; b = (1) Me_2S, (2) $AgClO_4$ or $NaClO_4$; c = (1) QAS, (2) ClO_4; Y = CN, NO_2, CH_2NO_2 starting from X = Br]

The complexes obtained, together with the nickel complexes [2] $[NiX(QAS)](ClO_4)$ where X = I, Br, Cl, NO_3, ClO_4, NCS, or CN, provide an extensive series for studies of ultraviolet

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[1] J. A. Brewster, C. A. Savage, and L. M. Venanzi, *J.*, 1961, 3699; C. A. Savage and L. M. Venanzi, *J.*, 1962, 1548.

[2] G. Dyer, J. G. Hartley, and L. M. Venanzi, *J.*, 1965, 1293.

TABLE 1

Colours, decomposition points, conductivities, and analyses of palladium(II) and platinum(II) complexes with the ligand (I; QAS)

No.	Complex	Colour	Decomp. pt.	Λ_M * (mho)
1	$[PdBr(QAS)](ClO_4)$	Dark red-purple	318—320°	24·7
2	$[PdI(QAS)](ClO_4)$	Dark purple	325—328	24·9
3	$[Pd(CN)(QAS)](ClO_4)$	Bright yellow	300—303	24·3
4	$[Pd(NO_2)(QAS)](ClO_4)$	Orange	299—300	24·2
5	$[Pd(thiourea)(QAS)](ClO_4)_2$	Deep red	310—311	43·2
6	$[Pd(CH_2NO_2)(QAS)](ClO_4)$	Scarlet	267—270	23·8
7	$[Pd(NO_3)(QAS)](ClO_4)$	Deep red	278—282	27·5
8	$[Pd(NO_3)(QAS)][BPh_4]$	Deep red	243—246	15·7
9	$[Pd(Me_2S)(QAS)](ClO_4)_2$	Red	300—302	47·3
10	$[PtBr(QAS)](ClO_4)$	Orange	359—360	24·8
11	$[Pt(NCS)(QAS)](ClO_4)$	Orange	356—358	28·5
12	$[Pt(CN)(QAS)](ClO_4)$	Very pale yellow	368—369	22·0
13	$[Pt(NO_2)(QAS)](ClO_4)$	Yellow	372—373	22·8
14	$[Pt(thiourea)(QAS)](ClO_4)_2$	Yellow-orange	344—345	42·8
15	$[Pt(CH_2NO_2)(QAS)](ClO_4)$	Yellow	338—341	25·6
16	$[Pt(Me_2S)(QAS)](ClO_4)_2$	Yellow-orange	349—351	47·1

	Pd or Pt		As		C		H		N	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
No.	(%)		(%)		(%)		(%)		(%)	
1	8·3	8·4	23·6	23·5						
2	8·1	8·0	22·8	22·6						
3	8·7	8·7	24·3	24·5					0·9	1·1
4	8·5	8·6	24·3	24·1					0·9	1·1
5	7·7	7·8	21·8	21·8						
6	8·3	8·5	23·6	23·8						
7	8·3	8·5	23·7	23·8						
8	7·1	7·2	20·4	20·3	63·4	63·4	4·8	4·2	0·8	0·9
9	7·9	7·9	22·1	22·1						
10	14·2	14·3	21·9	22·0						
11	14·4	14·6	22·4	22·4						
12	15·0	14·9	22·8	22·9	50·8	50·4	3·4	3·2		
13	14·6	14·7	22·3	22·5	48·7	48·7	3·1	3·2	1·0	1·0
14	13·3	13·4	20·4	20·5	45·5	45·2	3·3	3·2	2·0	1·9
15	14·4	14·5	22·5	22·3	48·8	49·1	3·1	3·3		
16	13·4	13·5	20·7	20·7					2·0 †	2·2 †

* 10^{-3}M-solutions in nitrobenzene at 20°. † Sulphur analysis.

TABLE 2

Visible and ultraviolet spectra of palladium(II) and platinum(II) complexes with the ligand (I; QAS)

		Dichloromethane soln.			
	Solid	Obs.		Gaussian curves	
Complex	$E_{max.}$ (cm.$^{-1}$)	$E_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$	$E_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$
$[Pd(CN)(QAS)](ClO_4)$	38,600(sh)	38,500	22,500	35,000	11,800
	26,000	26,400	15,500	27,000	13,200
	24,800(sh)	24,700(sh)	13,000	24.300	11,000
$[Pd(NO_2)(QAS)](ClO_4)$	38,500(sh)	38,800(sh)	26,500	—	—
	28,700(sh)	28,400	7000	28,400	7000
	22,800	23,200	11,000	23,700	9500
	21,600(sh)	21,800(sh)	10,500	20,600	6500
$[Pd(Me_2S)(QAS)](ClO_4)_2$	38,700(sh)	37,800	27,000	—	—
	—	31,500(sh)	11,000	30,500	4400
	22,000	22,400	11,500	22,900	10,500
	20,500(sh)	20,800(sh)	10,000	20,000	6600
$[Pd(thiourea)(QAS)](ClO_4)_2$	38,400(sh)	39,400(sh)	30,000	—	—
	35,000(sh)	35,000(sh)	24,000	—	—
	28,500(sh)	28,000	4300	28,000	4300
	22,000	22,400	9500	22,400	9500
	19,500(sh)	19,800(sh)	6500	19,200	5200

TABLE 2 (*Continued*)

		Dichloromethane soln.			
	Solid	Obs.		Gaussian curves	
Complex	$E_{max.}$ (cm.$^{-1}$)	$E_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$	$E_{max.}$ (cm.$^{-1}$)	$\varepsilon_{max.}$
[Pd(NCS)(QAS)](ClO$_4$)	38,000(sh)	38,000	20,600	—	—
	34,000(sh)	34,200	18,000	—	—
	31,000(sh)	32,600(sh)	17,500	—	—
	26,600	26,600	5500	26,600	5500
	21,600	21,900	7300	21,900	7300
	18,700	18,800	5700	18,800	5400
[Pd(NO$_3$)(QAS)](ClO$_4$)	39,000(sh)	39,800	31,300	—	—
	—	—	—	27,800	3700
	21,100	21,100	7700	21,700	7000
	—	—	—	19,000	4800
[PdCl(QAS)](ClO$_4$)	39,000(sh)	39,000	26,800	—	—
	—	34,600(sh)	17,500	—	—
	29,700(sh)	29,700(sh)	6000	28,000	3300
	20,200	20,800	8200	20,900	8000
	19,000(sh)	19,400(sh)	7500	18,300	5000
[PdBr(QAS)](ClO$_4$)	38,500(sh)	38,800	29,000	—	—
	29,600(sh)	29,800(sh)	6700	28,200	3500
	20,200	20,600	8700	20,700	8500
	19,000(sh)	19,300(sh)	7800	18,200	5000
[PdI(QAS)](ClO$_4$)	38,600	39,000	26,300	—	—
	33,500	34,000	22,300	—	—
	25,500	26,000	8800	26,000	8800
	18,400	18,900	7800	18,900	7800
[Pt(CN)(QAS)](ClO$_4$)	38,000(sh)	38,200	22,500	37,300	6000
	30,200	30,600	16,900	30,900	15,000
	—	29,200(sh)	13,300	27,600	7600
[Pt(NO$_2$)(QAS)](ClO$_4$)	38,000(sh)	38,600(sh)	27,000	—	—
	—	—	—	31,800	7600
	26,800	27,100	10,700	27,600	9800
	—	—	—	24,600	7000
[Pt(Me$_2$S)(QAS)](ClO$_4$)$_2$	—	39,000(sh)	28,400	—	—
	—	—	—	32,200	6600
	25,200	25,500	11,200	26,000	10.800
	—	—	—	22,800	5400
[Pt(thiourea)(QAS)](ClO$_4$)$_2$	—	39,500(sh)	31,600	—	—
	—	33,700(sh)	13,800	31,700	8600
	25,200	25,200	9000	25,800	8000
	—	23,600(sh)	7400	22,800	6500
[Pt(NCS)(QAS)](ClO$_4$)	38,000(sh)	38,000	27,500	—	—
	32,000(sh)	32,000	10,600	31,500	6500
	24,700	24,700	7200	25,300	7000
	22,600(sh)	23,000(sh)	5800	22,200	5000
[PtCl(QAS)](ClO$_4$)	39,000(sh)	39,000(sh)	22,300	—	—
	—	33,800(sh)	13,300	31,000	5000
	24,500	24,500	8100	25,000	7600
	22,900(sh)	23,200(sh)	7300	22,000	5500
	—	39,500(sh)	24,700	—	—
	—	34,200(sh)	14,700	31,700	8000
	23,700	23,700	7600	24,200	7400
	21,900(sh)	22,200(sh)	6800	21,300	4900
[PtI(QAS)](ClO$_4$)	—	39,500(sh)	32,500	—	—
	31,400(sh)	31,200	13,600	30,700	10,000
	21.600	21.900	6300	22,900	4500
	—	—	—	20,800	4500

and visible spectra of trigonal bipyramidal complexes of d^8 ions. Examination of the spectra, including Gaussian analysis where necessary (see Table 2 and Figure 1), shows that:

(*a*) for nickel, the two low-energy bands (Gaussian curves) move to higher energy in the order I $<$ Br $<$ Cl $<$ NO$_3$ $<$ ClO$_4$ $<$ NCS $<$ CN,[2] as expected from the spectrochemical series.

(*b*) for palladium, the same two bands are readily recognised, at rather higher energy;

for platinum they occur at higher energy still. This is in accordance with the fact that *d*-orbital energy-level splitting increases in the order Ni < Pd < Pt.

(*c*) for palladium and platinum, the lower-energy band is a double peak, consisting of two Gaussian curves separated by about 3000 cm.$^{-1}$.

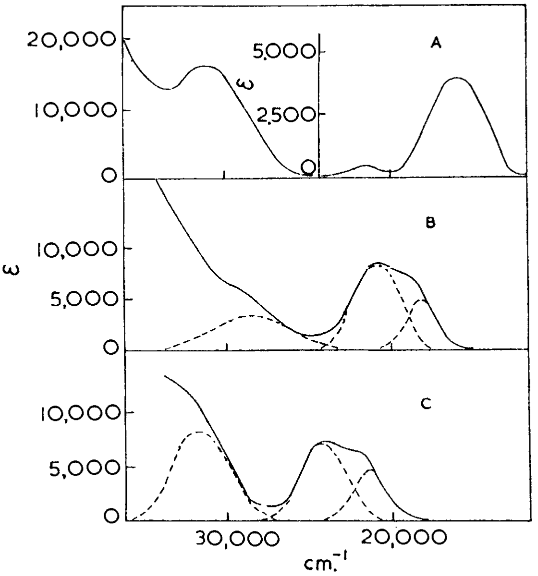

FIGURE 1. The visible and ultraviolet spectra of bromo-perchlorate complexes
A, [NiBr(QAS)](ClO$_4$). *B*, [PdBr(QAS)](ClO$_4$). *C*, [PtBr(QAS)](ClO$_4$)

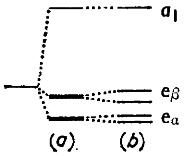

FIGURE 2. *d*-Orbital energy-level splitting:
(*a*) in a regular trigonal bipyramidal field
(*b*) in a field with distorted trigonal symmetry

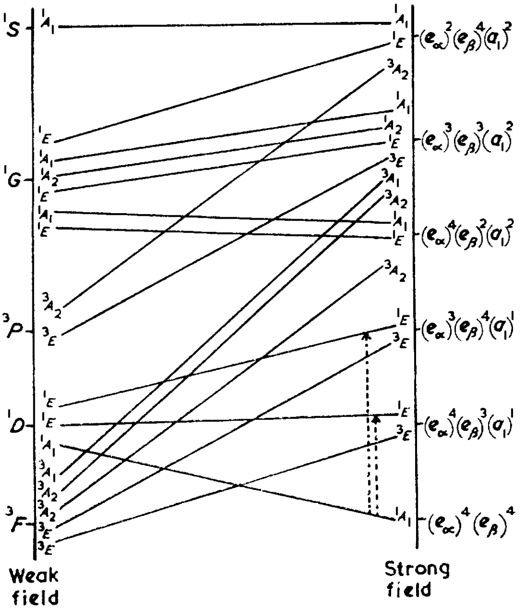

FIGURE 3. Energy-level correlation diagram for a d^8-ion in a field of C_{3v} symmetry

The ligand field-splitting for a trigonal bipyramidal complex is shown in Figure 2(*a*), and the energy-level correlation diagram for a d^8 ion in a field of C_{3v} symmetry is shown in Figure 3. In a strong field one would expect two spin-allowed transitions, from the

${}^1A_1$ state to the two ${}^1E(D)$ states, which correspond to electron-transitions between the orbitals $e_\alpha \longrightarrow a_1$ and $e_\beta \longrightarrow a_1$. The two low-energy bands observed in all the complexes have been assigned to these transitions.

The splitting of the lower-energy band in the palladium and platinum complexes is too great to be accounted for by spin-orbit coupling. *X*-Ray analysis of [PtI(QAS)][BPh$_4$] has shown that in the equatorial plane the As–Pt–As bond angles are 122, 119, and 103°, and the As–Pt bond distances opposite to these angles are 2·49 Å, 2·43 Å, and 2·45 Å, respectively.[3] The major effect of this distortion would be to remove the degeneracy of the e_β level [see Figure 2(*b*)].

The observation that the splitting of the e_β level occurs only in the palladium and platinum cases suggests that the nickel complexes have a regular (or nearly regular) structure. This difference may be due to steric effects: palladium(II) and platinum(II) have the same covalent radii, which are larger than that of nickel(II), as is shown by the M–Br distances in [NiBr$_2$(PEt$_3$)$_2$]$_2$] (2·30 Å), and [PtBr$_2$(NH$_3$)$_2$] (2·63 Å), and the M–Cl distances [4] in [PtCl$_2$(NH$_3$)$_2$] (2·30 Å), and K$_2$[PdCl$_4$] (2·30 Å).

The observation that the splitting of the e_β level increases slightly with the ligand field indicates that electronic effects may also be responsible for the observed distortions. The crystal-field stabilisation energy of a d^8 ion is much smaller in a trigonal bipyramidal field, as in [ML$_5$], than in a square planar field, as [5] in [ML$_4$].

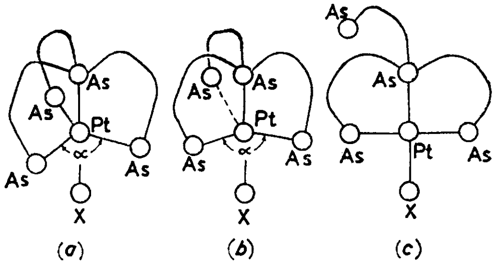

FIGURE 4. Distortion of trigonal structure towards a square planar structure
(*a*) $\alpha = 120°$. Equatorial As–Pt bonds equal;
(*b*) $\alpha > 120°$. One equatorial As–Pt bond longer;
(*c*) $\alpha = 180°$. Only 3 of the 4 arsine groups co-ordinated

The complexes of the tetradentate arsine with d^8 ions are five-co-ordinate, presumably because the energy gained by forming a fifth bond overcomes the difference in crystal-field stabilisation energy between the four- and five-co-ordinate structures. This is in agreement with the distortion observed in [PtI(QAS)][BPh$_4$], where the long As–Pt bond is opposite to the large As–Pt–As angle (see Figure 4).

EXPERIMENTAL

Preparation of Complexes.—Unless otherwise stated, all complexes were crystallised twice by dissolution in dichloromethane, filtration, addition of ethanol and removal of the dichloromethane. They were then evacuated at 60°/10^{-4} mm. for 24 hr. Yields refer to recrystallised compounds.

The tetratertiary arsine was prepared by the method of Howell *et al.*[6] The preparations of [PdX(QAS)](ClO$_4$), where X = Cl or NCS, and of [PtX(QAS)](ClO$_4$), where X = Cl or I, have already been described.[1]

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[3] G. A. Mair, H. M. Powell, and L. M. Venanzi, *Proc. Chem. Soc.*, 1961, 170; G. A. Mair and H. M. Powell, private communication.

[4] L. E. Sutton, " Interatomic Distances," London, 1958, *Chem. Soc. Special Publ.*, *No.* 11, pp. 98—101; G. Giacometti, V. Scatturin, and A. Turco, *Gazzetta*, 1958, **88**, 434.

[5] F. Basolo and R. G. Pearson, " Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 55.

[6] T. E. W. Howell, S. A. J. Pratt, and L. M. Venanzi, *J.*, 1961, 3167.

[PdBr(QAS)](ClO$_4$). Sodium chloropalladite tetrahydrate (0·183 g.) and sodium bromide (0·26 g.) in ethanol (50 c.c.) were refluxed with the arsine (0·5 g.) for 2 hr. After filtration the solution was treated with sodium perchlorate (0·1 g.) in ethanol (10 c.c.), and the product crystallised out, (yield 0·27, 42%).

[PdI(QAS)](ClO$_4$). This was prepared analogously by using sodium iodide (0·37 g.) instead of sodium bromide; solid iodo-iodide, which separated during the reaction with the arsine, was dissolved in dichloromethane (50 c.c.) before treatment with sodium perchlorate (yield 0·32 g., 48%).

[Pd(CN)(QAS)](ClO$_4$). A boiling solution of the chloro-complex (0·56 g.) in methanol (100 c.c.) was treated slowly with sodium cyanide (0·38 g.) in methanol (50 c.c.). The resulting yellow solution was filtered and cooled; the product (0·4 g.), which slowly separated, was crystallised from dichloromethane–anisole (yield 0·33 g., 59%).

[Pd(NO$_2$)(QAS)](ClO$_4$). The chloro-complex (0·77 g.) was refluxed with sodium nitrate (0·4 g.) in methanol (80 c.c.) for 8 hr., during which time the product (0·68 g.) was precipitated; it was recrystallised from dichloromethane–anisole (yield 0·43 g., 55%).

[Pd(thiourea)(QAS)](ClO$_4$)$_2$. A boiling suspension of the chloro-complex (0·61 g.) in methanol (50 c.c.) was treated with thiourea (0·4 g.). A clear red solution rapidly formed, to which sodium perchlorate (0·25 g. in 5 c.c. of methanol) was added. The product was precipitated on the addition of water (120 c.c.); it was recrystallised from dichloromethane–anisole (yield 0·46 g., 68%).

[Pd(CH$_2$·NO$_2$)(QAS)](ClO$_4$). The chloro-complex (0·61 g.) in nitromethane (25 c.c.) and ethanol (50 c.c.) was shaken with moist, freshly prepared silver oxide (0·5 g.) for 2 hr. The solution was filtered and concentrated in a vacuum to 15 c.c. The precipitate was crystallised from nitromethane (yield 0·23 g., 37%).

[Pd(NO$_3$)(QAS)][BPh$_4$]. Bis(dimethyl sulphide)dichloropalladium(II) (0·6 g.) was shaken with dimethyl sulphide (0·5 c.c.) in water (10 c.c.) until an orange solution formed. Silver nitrate (0·68 g.) in water (5 c.c.) was added. The solution was filtered and refluxed with the arsine (2 g.) in ethanol (150 c.c.) for 1 hr. One half of the solution was evaporated to dryness and treated as follows: the residue was crystallised from nitromethane to give crude [Pd(NO$_3$)(QAS)](NO$_3$); when a portion (0·41 g.) of this was dissolved in ethanol (25 c.c.) and treated with sodium tetraphenylborate (0·2 g.) in ethanol (10 c.c.), the product was precipitated (yield 0·22 g., 45%). When silver fluoride was used instead of silver nitrate, decomposition to palladium black occurred.

[Pd(Me$_2$S)(QAS)](ClO$_4$)$_2$. The other half of the solution obtained in the above preparation was treated with sodium perchlorate (0·5 g.) in ethanol (20 c.c.); the product crystallised out (yield 0·8 g., 60%).

[Pd(NO$_3$)(QAS)](ClO$_4$). Palladous nitrate dihydrate (0·41 g.) and QAS (1·4 g.) in tetrahydrofuran (40 c.c.) were refluxed together for $\frac{1}{2}$ hr. The solution was filtered and treated with sodium perchlorate (0·5 g.) in tetrahydrofuran. The precipitate was crystallised from tetrahydrofuran (yield 1·14 g., 64%).

Attempted preparation of [Pd(ClO$_4$)(QAS)](ClO$_4$). Palladous perchlorate (1 c.c. of a 1M-solution in 6N-perchloric acid) in ethanol (50 c.c.) with QAS (1 g.) gave a complex containing no co-ordinated perchlorate.

[PtBr(QAS)](ClO$_4$) *and* [Pt(NCS)(QAS)](ClO$_4$). These complexes were prepared in the same way as the palladium analogues, by using sodium chloroplatinite (yields 45 and 39%, respectively).

[Pt(CN)(QAS)](ClO$_4$). A boiling solution of the bromo-complex (0·68 g.) in methanol (200 c.c.) was treated slowly with sodium cyanide (0·04 g.) in methanol (50 c.c.). The product (0·4 g.), which separated slowly, was crystallised from nitromethane–anisole (yield 0·2 g., 61%).

[Pt(NO$_2$)(QAS)](ClO$_4$). The bromo-complex (0·68 g.) was refluxed with sodium nitrite, (0·35 g.) in methanol (100 c.c.) for 8 hr. The precipitate was crystallised from nitromethane. (yield 0·35 g., 53%).

[Pt(thiourea)(QAS)](ClO$_4$)$_2$. The bromo-complex (0·68 g.), thiourea (0·4 g.) and sodium perchlorate (0·2 g.) were refluxed in methanol (80 c.c.) for 1 hr. Water (100 c.c.) was added; the precipitate (0·6 g.) was crystallised from nitromethane–anisole (yield 0·35 g., 49%).

[Pt(CH$_2$NO$_2$)(QAS)](ClO$_4$). This complex was prepared in the same way as the palladium analogue (yield 44%).

[Pt(Me$_2$S)(QAS)](ClO$_4$)$_2$. Bis(dimethyl sulphide)dichloroplatinum(II) (0·39 g.), dimethyl sulphide (0·5 c.c.) and water (3 c.c.) were shaken for 12 hr., and treated with silver nitrate (1 c.c. of a 2N-aqueous solution). The filtrate was refluxed with the arsine (1 g.) in ethanol (75 c.c.) for 2 hr. After filtration, the solution (from which impure $[Pt(NO_3)(QAS)](NO_3)$ could be obtained by evaporation to dryness) was treated with sodium perchlorate (0·4 g.) in ethanol (20 c.c.) to give the product in a crystalline form (yield 0·8 g., 55%). The use of silver fluoride instead of silver nitrate gave the same product.

Attempted preparation of $[Pt(ClO_4)(QAS)](ClO_4)$. When silver perchlorate was used instead of silver nitrate in the above preparation, the platinum was precipitated with the silver chloride as $[PtCl(Me_2S)_3](ClO_4)$. This compound was prepared by adding sodium perchlorate to the solution obtained by shaking $[PtCl_2(Me_2S)_2]$ and dimethyl sulphide in water; it crystallised from water as white needles (Found: Pt, 37·6; S, 18·7. $C_6H_{18}Cl_2O_4PtS_3$ requires Pt, 37·8; S, 18·6%).

Attempted preparation of $[MX(QAS)]Y_2$, *where* M = Pd *or* Pt, *and* X = NH_3 *or pyridine, and* Y = NO_3, BPh_4 *or* ClO_4. Ammonia gas or pyridine caused a change in colour of nitromethane solutions of crude nitrato-nitrate complexes, but only impure starting materials could be isolated as solids by evaporation or precipitation with ether. Addition of sodium tetraphenylborate in nitromethane gave precipitates of sodium nitrate; the filtrates gave impure products containing co-ordinated $(CH_2{\cdot}NO_2)^-$, produced from the solvent by the bases ammonia and pyridine. Carrying out the reactions in ethanol gave products whose infrared spectra showed little evidence of co-ordinated base; similar results were obtained by using sodium perchlorate instead of sodium tetraphenylborate. No reaction occurred when QAS was refluxed with compounds containing the $[Pt(NH_3)_4]^{2+}$ ion.

Analyses.—Platinum [1] and arsenic [2] analyses were carried out spectrophotometrically as previously described.—For palladium, a modification of the method of Menis and Rains [7] was used. Samples (containing about 0·5 mg. of (Pd) were refluxed with concentrated nitric and 72% perchloric acids (3 c.c. of each) for 2 hr. Concentrated hydrochloric acid (5 c.c.) was then added, and the solutions concentrated to 3 c.c.; the hydrochloric acid treatment was repeated, and finally a further quantity (5 c.c.) of hydrochloric acid was added, and the solutions were diluted to 500 c.c. Portions (10 c.c.) were transferred to standard flasks containing water (70 c.c.), ethanol (10 c.c.), and concentrated hydrochloric acid (4 c.c.). A solution of α-furildioxime (in 30 c.c. of ethanol diluted to 100 c.c. with water) was added, and each mixture was diluted to 100 c.c. with water. After 2 hr. the absorbances at 420 mμ were measured in 10 cm. cells.

Visible and Ultraviolet Spectra.—A Unicam model S.P. 700 recording spectrophotometer was used to record the spectra of solids and solutions (in dichloromethane) by methods described elsewhere.[2]

Infrared Spectra.—Infrared spectra in Nujol and hexachlorobutadiene mulls were recorded in the sodium chloride region with a Perkin-Elmer model 221 spectrophotometer. Cyano-complexes show sharp bands due to the C–N stretching vibration at 2110 (nickel), 2125 (palladium), and 2130 cm.$^{-1}$ (platinum complex).[8a] In the thiocyanato-complexes, the C–N stretching bands occur at 2090 (nickel), 2118 (palladium), and 2124 cm.$^{-1}$ (platinum). The bands associated with the C–S bond would be expected at about 820 cm.$^{-1}$ for *N*-bonding or 700 cm.$^{-1}$ for *S*-bonding.[8b] They are found at 833 (nickel), 845 (palladium), and 850 cm.$^{-1}$ (platinum), indicating *N*-bonding in each case, in agreement with the recent observation that for palladium(II) and platinum(II) complexes, co-ordinated thiocyanate is usually *S*-bonded, as in $[M(SCN)_4]^{2-}$ and $[M(SCN)_2(NH_3)_2]$, but is *N*-bonded when there is other phosphine or arsine ligand present, as [9] in $[M(NCS)_2(PEt_3)_2]$. The thiourea complexes show three N–H stretching bands, at 3460, 3300, and 3200 cm.$^{-1}$, and a strong double band at 1620, 1640 cm.$^{-1}$ (associated with the NH_2 rock, N–C–N stretch and C–S stretch).[10] The nitro-complexes show bands at 1400 [$\nu_{as}(NO_2)$], 1310 [$\nu_s(NO_2)$], and 815 cm.$^{-1}$ [$\nu(ONO)$].[8c] Co-ordinated nitrate was indicated by strong bands [11] at 1490 and 1260 cm.$^{-1}$. The nitromethane ion, which has not been used as a ligand before, when co-ordinated shows a very characteristic strong band at

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1505 cm.$^{-1}$, presumably [12] $\nu_{as}(NO_2)$. There was no evidence of decomposition to fulminate, which would show strong bands [13] at 2150 and 1150 cm.$^{-1}$.

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