Preparation and Spectroscopic Properties of Some Low Spin Trigonal Bipyramidal d⁸ Metal Complexes

O.St.C. Headley[1], R.S. Nyholm, C.A. McAuliffe, L. Sindellari, M.L. Tobe, and L.M. Venanzi[2]

The preparation of $(o-Me_2As \cdot C_6H_4)_3As$, (Qas), and of complexes $[MX \, Qas]Y$ (M = Ni; X = Cl, Br, I, NCS, NO_2, N_3, NO_3, CH_3COO; Y = X^-, BF_4^- BPh_4^-: M = Pd or Pt; X = Cl, Br, I, NCS; Y = X^-, BF_4^-, BPh_4^-) are described. All the complexes are diamagnetic, five-coordinate species and behave as 1:1 electrolytes in polar solvents. The visible and near U–V spectra contain bands attributable to d–d transitions the intensities of which, although relatively high, are appreciably lower than those of the analogous complexes of $(o-Ph_2As \cdot C_6H_4)_3As$, (QAS). It is concluded that the ligand field bands in $[MX \, QAS]Y$ « borow » intensity from $\pi^* \leftarrow \pi$ transitions of the phenyl groups. Towards the metals used in this investigation Qas is a better ligand than the previously investigated QAS.

Results and Discussion

Trigonal bipyramidal complexes of the type $[M^{n+}X(L'(ZL)_3)]^{(n-1)+}$ (M = Fe^{II}, Co^{II}, Ni^{II}, Rh^{I}, Pd^{II} or Pt^{II}; X = anionic ligand; L = N, P or As; Z = $o-C_6H_4$, $CH_2CH_2CH_2$ or CH_2CH_2; L = NR$_2$, PR$_2$, AsR$_2$, SR or SeR). (I) are now quite common.[3]

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The complexes of nickel(II) with ligands of the above type have been the object of a particularly intense study as they can be both of high spin, *e.g.*, with N(CH$_2$CH$_2$NMe$_2$)$_2$ [3c] and of low spin type, *e.g.*, with $(o-Ph_2P \cdot C_6H_4)_3$ P[3a] and it has been of particular interest to ascertain precisely what modification of the various features of the quadridentate ligands are

responsibile for the spin multiplicity of the central metal atom.

The complexes of palladium(II) and platinum(II)[4] occur in low spin forms only and possibly for this reason have received less attention. However, they offer a promising series of substrates for the study of substitution reactions of 5-coordinate complexes containing stereorestrictive ligands[5] and also of the mechanism of transfer of non-garland multidentate ligands from one metal atom to another.[6]

While the high spin complexes possess electronic absortpion spectra which are in accord with theory both in terms of the position of the bands and the

Table I. Some Physical Properties of Complexes [MX-(Qas)]Y (M = Ni, Pd and Pt; Qas = $(o-Me_2As \cdot C_6H_4)_3As$; X = anionic ligand; Y = other anion).

	Compound	Colour	Decomp. pt.	Λ_M [a]
1.	[NiCl(Qas)][BF₄]	Deep blue	>360°	93
2.	[NiCl(Qas)][BPh₄]	Dark blue	236-240	18 [b]
3.	[NiBr(Qas)]Br	Dark blue	310-314	84
4.	[NiBr(Qas)][BF₄]	Dark blue	>360	82
5.	[NiBr(Qas)][BPh₄]	Dark blue	245-250	51
6.	[NiI(Qas)]I	Green	[c]	79
7.	[NiI(Qas)][BF₄]	Dark blue	>360	84
8.	[Ni(NCS)(Qas)](NCS)	Purple-blue	310-315	75
9.	[Ni(NCS)(Qas)][BPh₄]	Purple-blue	258-262	46
10.	[Ni(NO₂)(Qas)](NO₂)	Red-blue	[d]	83
11.	[Ni(NO₂)(Qas)][BPh₄]	Red-blue	[e]	54
12.	[Ni(N₃)(Qas)][BF₄]	Blue black	265-270	88
13.	[Ni(NO₃)(Qas)][BPh₄]	Dark blue	260-264	57
14.	[Ni(OAc)(Qas)][BPh₄]	Purple-blue	238-243	52
15.	[PdCl(Qas)][BF₄]	Orange-red	>330	97
16.	[PdCl(Qas)][BPh₄]	Red	248-250	19 [b]
17.	[PdBr(Qas)]Br	Red	290-294	73
18.	[PdBr(Qas)][BF₄]	Dark red	>330	90
19.	[PdI(Qas)]I	Dark red	290-295	78
20.	[Pd(NCS)(Qas)](NCS)	Dark red	240-244	91
21.	[PtCl(Qas)][BF₄]	Yellow	>330	88
22.	[PtCl(Qas)][BPh₄]	Yellow	288-290	18 [b]
23.	[PtBr(Qas)][BF₄]	Yellow	>330	95
24.	[PtI(Qas)]I	Yellow-brown	320-323	94

[a] In Ω^{-1} cm^2 M^{-1} for approx. 10^{-3} M nitromethane solutions, unless otherwise specified, at 25°. [b] For 10^{-3} M nitrobenzene solutions at 20°. [c] Slow decomposition above 330°. [d] Slow decomposition above 250°. [e] Slow decomposition above 320°.

(1) Present adress: Division of Chemistry, U. W. I., St. Augustine, Trinidad, W. I.
(2) Present adress: Department of Chemistry, State University of New York at Albany, N. Y. 12203.
(3) a) L. M. Venanzi, *Angew. Chem., Int. Ed.,* 3, 453 (1964). b) G. Dyer and D. W. Meek, *Inorg. Chem.,* 6, 149 (1967). c) M. Ciampolini and N. Nardi, *Inorg. Chem.,* 5. 41 (1966). d) L. Sacconi and L. Bertini, *J. Amer. Chem. Soc.,* 90. 5443 (1968).

(4) G. Dyer and L. M. Venanzi, *J. Chem. Soc.,* 2771 (1965) and references quoted therein.
(5) R. G. Pearson, M. M. Muir, and L. M. Venanzi, *J. Chem. Soc.,* 5221 (1965). T. M. D. Morgan and M. L. Tobe, unpublished results.
(6) W. W. Fee and M. L. Tobe, unpublished results.

intensities of their absorption,[3c] the low energy bands of the low spin complexes show molar extinction coefficients in the range 3000-8000 M^{-1} cm^{-1}, which would seem to be too high to be due to simple ligand field transitions.[4] However, investigation of a wide range of such complexes has led to the conclusion that these bands are essentially d–d transitions and it has been suggested that the high molar extinction coefficients arise from « large mixing-in of higher configurations belonging both to excited states of the metal ion and to charge transfer states by odd ligand field components ».[7] It has also been found that the intensities of these bands are strongly sensitive to the nature of the donor atoms[2b] and, therefore, it was of interest to establish the extent to which the intensities of the low energy bands in complexes [MX(QL)]$^+$ (M = Ni, Pd or Pt; X = anionic ligand) QL = quadridentate ligand of the type listed above) would be influenced by changes of substituents on the terminal donor atoms.

For these purposes, the ligand tris (o-dimethylarsino-phenyl)arsine, Qas, was synthesized and its complexing properties examined.

The complexes prepared, and some of their physical properties, are listed in Tables I and II while the relevant analytical data are presnted in Table III.

The complexes are all formulated as 1:1 electrolytes of the type [MX(Qas)]Y and the conductivities, magnetic susceptibilities and general features of the visible and ultra violet absorption spectra closely resemble those of the corresponding [MX(QAS)]Y species. Consequently, the Qas complexes have also been assigned trigonal bipyramidal structures.

In keeping with the greater donor ability expected for the —AsMe$_2$ group when compared to —AsPh$_2$ (from both electronic and steric effects), spectral studies show that on mixing equimolar amounts of [NiBr(QAS)]Br and Qas in dichloromethane there is rapid and quantitative formation of [NiBrQas]$^+$. On the other hand, a ten-fold excess of QAS will not displace Qas from [NiBr(Qas)]$^+$ in dichloromethane solution. The greater donor capacity of Qas is also reflected in its ability to form iron(II) complexes[8] whereas QAS does not.[9]

The electronic spectra of the corresponding complexes of Qas and QAS show a number of significant differences (Table IV). Thus, each Qas complex absorbs at higher energy than the corresponding QAS complex, an effect observed elsewhere and probably due to changes in the electron density.[10] The low energy bands of the Qas complexes have extinction coefficients which are about one half of those of the corresponding QAS derivatives, indicating that the high intensities of the latter are due, at least in part, to mixing of the d–d transitions with transitions of the type $\pi^* \leftarrow \pi$ of the benzene rings, an hypothesis which is supported by the observation that the low energy bands in the full aliphatic (qas) complexes [NiX(As(CH$_2$CH$_2$CH$_2$AsMe$_2$)$_3$)] have even lower intensities.[11] Most complexes, even those of nickel(II), show more or less pronounced splittings of the lowest energy band. These splitting were previously observed in the complexes [MX(QAS)]$^+$ (M = Pd or Pt, but not Ni)[4] and since they were found to be ligand dependent and therefore not attributable to spin-orbit coupling, they have been tentatively assigned to a combination of steric and electronic effects.[4] These features are, at present, under further investigation.

The infra-red spectra of the complexes have been examined and some of the absorptions have been assigned as follows: (1) In [NiNO$_2$(Qas)][BPh$_4$], bands

Table II. Visible and ultra violet spectra of complexes [MX(Qas(Y] (M = Ni, Pd or Pt; X = anionic ligand; Y = other anion) in dichloromethane solution.

Complex	E_{max} (cm^{-1})	ε_{max} cm^{-1} M^{-1}	E_{max} [a] (cm^{-1})	ε_{max} [a] cm^{-1} M^{-1}
1	17,800	2500	15,600	1140
	23,300	159	17,800	2500
			23,300	159
2	17,500	2100		
	ca. 23,300	sh		
	38,700	620		
4	17,300	2470	15,300	1250
	23,100	380	17,700	2410
			23,100	380
6	16,800	1900	16,300	1650
	22,700	415	18,500	922
	29,200	4500	22,700	415
			29,200	4500
7	16,600	2180		
	22,700	600		
	29,200	4800		
9	18,800	2550	16,700	2040
	23,500	605	19,200	1590
			23,800	420
10	20,000 [b]	3290		
	20,000	3100		
	28,600	3490		
11	19,800	3240		
	28,200	3780		
12	18,600	2660	16,000	1640
	23,400	1100	18,700	2580
			23,400	1050
13	18,300	1940	15,600	1940
			18,400	1060
			23,000	250
14	19,000	2610	16,500	1730
			19,400	2330
15	ca. 21,300	sh	21,500	1400
	27,500	3650	27,500	3650
16	ca. 21,400	sh		
	27,400	4380		
	ca. 33,800	sh		
17	ca. 20,400	sh	20,200	1800
	24,600	2720	24,600	2720
18	ca. 20,400	sh	20,200	2000
	24,600	2760	24,600	2760
19	20,800	2900		
	28,600	5180		
20	20,700	2320		
	24,400	3300		
21	24,100	2960		
	27,200	3720		
22	24,200	3120		
	27,200	3860		
23	23,400	2820		
	26,700	3090		
24	22,700	2740		
	24,200	2720		

[a] Values from Gaussian analysis. [b] In aqueous solution.

(7) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, J. Chem. Soc., (A), 540 (1967).
(8) O. St. C. Headley, Ph. D. Thesis, London (1967).
(9) H. T. Halfpenny, J. G. Hartley and L. M. Venanzi, J. Chem. Soc., (A), 627 (1967)..
(10) C. R. C. Coussmaker, M. Hely Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, J. Chem. Soc., 2705 (1961).
(11) G. S. Benner and D. W. Meek, Inorg. Chem., 6, 1399 (1967).

Table III. Some analytical data on complexes [MX(Qas)]Y

Method of prep.	Solvent of recryst.	Yield %	C(%) Found	C(%) Reqd.	H(%) Found	H(%) Reqd.	Metal(%) Found	Metal(%) Reqd.	As(%) Found	As(%) Reqd.	Hal. or S(%) Found	Hal. or S(%) Reqd.	N(%) Found	N(%) Reqd.
1. B	CH₂Cl₂/EtOH	60	36.2	36.1	3.9	3.8	7.3	7.4	37.7	37.6	4.5	4.5		
2. C	CH₂Cl₂/EtOH	75	55.9	56.0	4.9	5.0	5.7	5.7	29.1	29.1				
3. A	Not recryst.	70	34.6	34.4	4.0	3.6	7.1	7.1						
4. B	CH₂Cl₂/EtOH	85	34.2	34.2	3.9	3.6	6.8	7.0	35.7	35.6	9.3	9.5		
5. C	CH₂Cl₂/EtOH	70	54.5	53.6	5.0	4.7	5.5	5.5						
6. A	Not recryst.	70	30.8	31.0	3.2	3.2	6.4	6.3						
7. B	CH₂Cl₂/EtOH	70	32.0	32.4	3.2	3.4	6.4	6.6	33.3	33.7	14.2	14.2		
8. A	Not recryst.	75	39.7	39.4	4.0	3.8	7.1	7.4						
9. C	CH₂Cl₂/EtOH	95	54.3	55.8	5.0	4.7	5.4	5.6			2.7	3.0	1.0	1.3
10. A ^{a}	CH₂Cl₂/Et₂O	65	36.8	37.7	4.2	3.1	7.6	7.7					3.2	3.6
11. C	CH₂Cl₂/EtOH	94	55.2	55.3	4.8	4.8	5.6	5.7					1.2	1.3
12. B	Not recryst.	80	35.7	35.7	3.4	3.7	7.3	7.3						
13. C	CH₂Cl₂/EtOH	85	55.6	54.6	4.8	4.7	5.1	4.7					1.2	1.3
14. C	CH₂Cl₂/EtOH	95	57.3	56.9	4.9	5.0	5.5	5.6						
15. D	CH₂Cl₂/EtOH	70	34.3	34.0	3.5	3.5	12.5	12.6						
16. E	CH₂Cl₂/EtOH	75	53.9	53.4	5.1	4.7	9.9	9.9	27.6	27.8				
17. F	CH₂Cl₂/EtOH	80	31.8	32.6	3.4	3.4	18.1	18.1						
18. G	CH₂Cl₂/EtOH	68	32.7	32.3	3.5	3.4	11.8	11.9						
19. F	CH₂Cl₂/EtOH	90	29.5	29.5	3.0	3.1	10.8	10.9						
20. F	CH₂Cl₂/EtOH	70	36.8	37.2	3.5	3.6	12.5	12.5						
21. H	Acetone	64	31.5	30.8	3.4	3.2	20.6	20.8						
22. I	CH₂Cl₂/EtOH	70	48.4	49.4	4.3	4.3	16.9	16.7	25.3	25.7				
23. J	Acetone	60	30.5	29.4	3.1	3.1	20.0	19.9						
24. K	Not recryst.	75	26.7	27.0	2.7	2.8	18.4	18.3						

^{a} The crude product was precipitated by addition of ether, redissolved in a small amount of dichloromethane, filtered off from solid sodium nitrate, and re-precipitated by addition of ether.

Table IV. Absorption maxima, E_{max} (cm⁻¹) and molar absorptivities, $\varepsilon_{max}(M^{-1}$ cm⁻¹) of the low-energy bands in complexes [MI(QL)]Y (M = Ni, Pd and Pt; QL = QAS and Qa;s Y = other anion).

[MI(QL)]⁺	M	QL = QAS		QL = Qas		QL = qas ^{a}
E_{max}	Ni	15,000	21,000	16,600	22,700	15,670
ε_{max}		3,460	1,160	2,180	600	1,560
E_{max}	Pd	18,900	26,000	20,800	28,600	
ε_{max}		7,800	8,800	2,900	5,180	
E_{max}	Pt	20,800	22,900	22,700	24,200	
ε_{max}		4,500	4,500	2,740	2,720	

^{a} Ref. 11.

at 1366, 1307 and 816 cm⁻¹ have been assigned to the NO_2 asymmetric stretch, symmetric stretch and deformation respectively and it is concluded that the ligand is bonded to the metal through the nitrogen atom.[12]   (2) In [NiNO₃(Qas)][BPh₄] bands at 1490, 1256, 976 and 792 cm⁻¹ have been assigned to the asymmetric stretch, the NO_2 symmetric stretch, the N–O stretch and the non-planar rock, as found in other complexes containing coordinated nitrate.[13]   (3) In [Ni(NCS)(Qas)]SCN bands at 2097 and 827 cm⁻¹ have been assigned to the C–N stretch and the C–S stretch of N-bonded thiocyanate, while bands at 2055 and 719 cm⁻¹ have been assigned to corresponding modes of ionic thiocyanate.[14]   In the corresponding palladium(II) complex, the above bands occur at 2109, 834, 2049 and 775 cm⁻¹ respectively, suggesting similar modes of bonding.   (4) In [Ni(N₃)(Qas)][BF₄] the band at 2041 cm⁻¹ has been assigned to the asymmetric N–N stretch of coordinated azide.[15]

(12) D. M. Adams, « Metal-Ligand and Related Vibrations », Arnold, London, 1967. P. 273.
(13) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).
(14) D. W. Adams, *loc. cit.*, p. 318.
(15) D. M. Adams, *loc. cit.*, p. 287.

Experimental Section

o-Bromophenyldimethylarsine was prepared from, either *o*-nitroaniline or *o*-bromoaniline by standard methods.[16]

Tris-(o-dimethylarsinophenyl)arsine.   *o*-Bromophenyldimethylarsine (42 g., 0.16 moles) was dissolved in dry, purified[17] light petroleum (b.pt. 40-60°, 300 ml) and a solution of *n*-butyl lithium in light petroleum (196 ml 0.905 M; 0.177 moles) was added under nitrogen, the mixture stirred under reflux for 1.5 hours during which time the lithiated species separated as pale yellow crystals. Arsenic trichloride (10.6 g; 0.59 moles) dissolved in light petroleum (100 ml) was slowly added to the refluxing mixture and heating and stirring continued until the reaction mixture was decolorised (*ca.* 1 hour). After cooling, it was hydrolysed with N/20 hydrochloric acid (200 ml). The organic layer, after drying and evaporation of the solvent, left a viscous oil which gave a crystalline product after dissolution in ethanol (400 ml) and methanol (200 ml). The solution was left at room temperature until the first crystals formed and then cooled in ice-water. Yield 15 g; M.pt. 115°. The p.m.r. spectrum in CDCl₃ shows a single methyl resonance at $\tau = 8.85$. *Anal.* Calcd. for C₂₄H₃₀As: C, 46.7; H,4.9; As, 48.5. Found: C, 46.7; H, 5.0; As, 48.2.

Preparation of the complexes. Nickel complexes. Ethanolic solutions of the nickel salts were prepared either from commercial products where available or else by adding a 3 to 6 fold excess of the required

(16) W. A. Jacobs, M. Heidelberger, and I. P. Rolf, *J. Am. Chem. Soc.*, 40, 1580 (1918). H. Burton and C. S. Gibson, *J. Chem. Soc.*, 457 (1926). E. R. H. Iones and F. G. Mann, *J. Chem. Soc.*, 4472 (1955). R. D. Cannon, B. Chiswell, and L. M. Venanzi, *J. Chem. Soc.* (A), 1277 (1967).
(17) The solvent was purified by shaking it with concentrated sulphuric acid and then distilling the petroleum layer under an atmosphere of nitrogen into a flask containing freshly extruded sodium.

sodium salt to an ethanolic solution of hydrated nickel nitrate. On cooling, sodium nitrate separated out and was filtered off. The complexes of the type [NiX(Qas)]X were obtained by adding equimolar amounts of the arsine, dissolved in a mixture of dichloromethane and ethanol to the ethanolic solution of the nickel salt. In a typical preparation, X = Cl, 0.001 moles of nickel chloride in 10 ml ethanol were treated with 0.001 moles of the arsine dissolved in 2 ml dichloromethane and 10 ml ethanol. Complexes formed immediately and no heating was required. The products either separated out on cooling or after concentration. (*Method A*). The fluoroborate salts separated out on addition of aqueous fluoroboric acid (42%) to the solutions obtained by Method A (*Method B*) and the tetraphenylborate salts were obtained in a similar way by adding an ethanolic solution of sodium tetraphenyl borate. (*Method C*).

Palladium complexes. Finely powdered palladium(II) chloride, suspended in ethanol, and a slight excess of the arsine, in dichloromethane-ethanol, were refluxed together for 30 minutes; the solution was filtered and 42% fluoroboric acid was added. (*Method D*). Equimolar ethanolic solutions of $Na_2[PdCl_4]$ and the ligand were refluxed for 30 minutes and the product was then precipitated from the filtered and cooled solution by adding sodium tetraphenyl borate. (*Method E*). A finely ground mixture of palladium(II) bromide and a five-fold excess of the appropriate sodium salt was extracted with ethanol and treated with an ethanolic solution of the ligand. (*Method F*). A solution of palladium(II) bromide in dimethylformamide was treated with a solution of the arsine in ethanol. The product was obtained on addition of 42% fluoroboric acid. (*Method G*).

Platinum complexes. The arsine, (0.0011 moles) in dichloromethane-ethanol, was added to an ethanolic solution of platinum(IV) chloride (0.0010 moles), the precipitate filtered off and redissolved in dimethylformamide. The production was then precipitated by the addition of 42% fluoroboric acid, (*Method H*). An ethanolic solution of $Na_2[PtCl_4]$ was used as indicated in method E, (*Method I*). Mixtures of platinum(II) halide and the appropriate sodium halide were used as described in method F, (*Method J*). The complex was prepared as for method J and the product precipitated out on addition of 42% fluoroboric acid, (*Method K*). All the com-

pounds were dried at 80°, 10^{-3} mm.

Analysis. Nickel was determined, after breaking down the complex by refluxing with a mixture of concentrated sulphuric and nitric acids, either by EDTA titration[18] or else spectrophotometrically.[19] Palladium was determined gravimetrically either as the metal[20] or as the dimethylglyoxime complex[21] after first decomposing the complexes. Platinum was determined either gravimetrically as the metal[22] or spectrophotometrically.[23] Carbon, hydrogen, arsenic, halogen and sulphur were determined by standard methods by (a) A. Stone, Department of Chemistry, University College, London, (b) Drs Weiler and Strauss, Oxford and (c) Dr. A. Bernhardt, Max Plank Institut für Kohlenforschung, Mülheim. Halogens were also determined by Volhard's method after charring the organic matter with a mixture of sodium and potassium carbonates. Arsenic was also determined spectrophotometrically.[19]

Physical measurements. Conductivities were measured, either with a Wayne-Kerr Universal Bridge, Model 221B, or with a Cambridge Instruments Conductivity bridge, using bright platinum electrodes and « AnalaR » nitrobenzene or spectroscopic grade nitromethane as solvents. The magnetic susceptibilities of powdered samples were measured by either the Gouy or the Faraday method. Visible and ultra violet spectra of solutions were recorded on Unicam SP 500, 700 and 800 spectrophotometers and infrared spectra were recorded with either a Perkin-Elmer, Model 337, or a Grubb-Parsons, Type G.S. 2A spectrophotometer.

(18) A. I. Vogel, « Quantitative Inorganic Analysis », 3rd Ed., Longmans, London, 1961, p. 345.
(19) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).
(20) R. W. Schoeller and A. R. Powell, « The Analysis of Minerals and Ores of the Rarer Elements », 3rd Ed., Griffin, London, 1955, p. 358.
(21) *idem ibid.*, p. 359.
(22) *idem ibid.*, p. 357.
(23) J. A. Brewster, C. A. Savage, and L. M. Venanzi, *J. Chem. Soc.*, 3699 (1961).