Some Tritertiary Arsine Complexes of Nickel, Palladium, and Platinum

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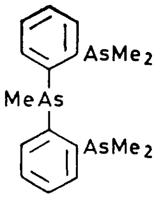
A series of complexes of composition M(ttas)X_2 [ttas = bis-(*o*-dimethylarsinophenyl)methylarsine; M = Ni; X = Cl, Br, I, SCN; M = Pd, Pt; X = Cl, Br, I] have been prepared and characterised in the solid state and in solution. The Pd and Pt complexes are generally 1:1 electrolytes indicating a four-co-ordinate geometry but there is a slight tendency towards association under certain circumstances. The Ni^{II} analogues are very sensitive to the nature of X and the solvent. Five-co-ordinate monomers are favoured and are most likely in non-polar solvents. Hydroxylic solvents favour disproportionation to $[Ni(ttas)_2]^{2+}$ and either NiX_4^{2-} or its solvolysis products. A series of complexes of the type $M(ttas)_2Y_2$ (M = Ni; Y = ClO_4^-, NO_3^-, I^-; M = Pd, Pt; Y = ClO_4) have also been described but the assignment in terms of a six-co-ordinate M is in doubt. An octahedral Ni^{III} complex *mer*-[Ni(ttas)Br_3] is also described.

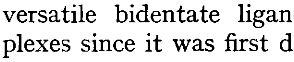
COMPLEXES formed by the bivalent d^8 metal ions, Ni^{II}, Pd^{II}, and Pt^{II}, give rise to complexes with varying co-ordination number and stereochemistry. In particular, the relationship between the structure of the ligand, co-ordination number, stereochemistry, magnetism and spectra has been studied by many investigators.[1]

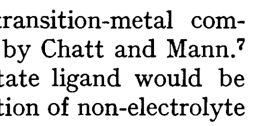
In the case of Ni^{II} it is possible to find high and low spin complexes,[2] four-, five-, and six-co-ordination and often a rapid conversion from one form into another[3] can be observed.

As part of our studies on the complexes formed by multidentate arsine ligands[4-6] we have examined the


(I)


(II)


(III)


(IV)

reactions of the terdentate ligand bis(*o*-dimethylarsinophenyl)methylarsine = ttas, (I), with nickel, palladium, and platinum. The ligand is an attempt to produce a terdentate analogue of *o*-phenylenebis(dimethylarsine) = dias, (II), which has proved to be one of the most versatile bidentate ligands for transition-metal complexes since it was first described by Chatt and Mann.[7] For bivalent metal ions a terdentate ligand would be eminently suitable for the preparation of non-electrolyte five-co-ordinate complexes and when this work was started in the early sixties, five-co-ordinate transition-metal complexes were uncommon.

RESULTS

Mono(*triarsine*) *Complexes*.—by treating ethanolic solutions of nickel chloride, and an excess of alkali-metal salt MX (X = Br, I, SCN) when X ≠ Cl, with equimolar quantities of the triarsine, compounds analysing for NiX_2(ttas) were obtained. Characteristic features and analyses are recorded in Table 1. The solid chloro-complex was obtained as a poorly defined amorphous brown powder with no definite *X*-ray diffraction pattern. It reacted with atmospheric moisture to form a brown tar but appeared to give well defined compounds in solution. The bromo- and iodo-compounds are stable towards atmospheric moisture and are diamagnetic. The chloro- and thiocyanato-complexes are paramagnetic in the solid state with effective magnetic moments of 2·84 (24°) and 2·23 (26·8°) B.M. respectively, based on the formulation NiX_2(ttas). The value for the chloro-complex is close to the spin-only value for the high spin d^8 Ni^{II} species but the moment of the thiocyanate species is much less than expected. The diffuse-reflectance spectrum of the latter species is consistent with the presence of diamagnetic $Ni(ttas)_2^{2+}$ (see below) and $Ni(NCS)_4^{2-}$ whose broad group of peaks[8] at 15,000—18,000 cm^{-1} would tend to broaden the absorption due to the cation in this region and shift it to longer wavelengths. With this formulation, a magnetic moment of 3·16 ± 0·03 B.M. (26·8°) can be assigned to the anionic species. This is considerably less than the value reported[8] for $[Ph_4As]_2[Ni(NCS)_4]$, 3·66 B.M. at 17°. The cause of this discrepancy must remain undecided until a proper structural analysis is made on the solid. The chloro-complex, if formulated as $[Ni(ttas)_2][NiCl_4]$, would require a magnetic moment of 3·91 ± 0·05 B.M. (24°) for the paramagnetic anion, which compares favourably with literature values of 3·89 B.M. for $[MePh_3As]_2[NiCl_4]$ at 27°[9] and 3·85 B.M. for $[Et_4N]_2[NiCl_4]$ at 27°.[10] The

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[1] R. S. Nyholm, *Chem. Rev.*, 1953, **53**, 263; J. R. Miller, *Adv. Inorg. Chem. Radiochem.*, 1962, **4**, 147; L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199.

[2] L. Sacconi, *J. Chem. Soc.* (*A*), 1970, 248.

[3] G. N. La Mar and E. O. Sherman, *J. Amer. Chem. Soc.*, 1970, **92**, 2691; R. G. Wilkins, R. Yelin, D. W. Margerum, and D. C. Weatherburn, *ibid.*, 1969, **91**, 4326.

[4] R. G. Cunninghame, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1964, 5800.

[5] C. D. Cook, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1965, 4194.

[6] R. G. Cunninghame, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.* (*A*), 1971, 227.

[7] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1939, 1624.

[8] D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 1965, **4**, 823.

[9] B. N. Figgis, J. Lewis, F. Mabbs, and G. A. Webb, *J. Chem. Soc.* (*A*), 1966, 1411.

[10] L. Sacconi, M. Ciampolini, and N. Nardi, *Inorg. Chem.*, 1965, **4**, 407.

diffuse-reflectance spectrum, Figure 1a, is broad and mainly featureless but does not contradict this formulation. Attempts to prepare this compound by mixing ethanolic solutions of $[Et_4N]_2NiCl_4$ and $[Ni(ttas)_2](ClO_4)_2$ were unsuccessful and evaporation of the blue-green solution yielded only the starting materials.

TABLE 1

	Colour	μ_{eff} B.M. *	C (%)		H (%)		As (%)		Halogen (%)		Metal (%)		Molar conductivity [d] (Ω^{-1} cm^2 mol^{-1})	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Nitromethane	Acetone
$Ni(ttas)Cl_2$	Dark brown	2·84 (24°)	35·1	35·0	4·0	3·3	38·7	38·6	12·2	12·6	10·1	10·2	See Figure 2	
$Ni(ttas)Br_2$	Purple	D	30·4	29·6	3·4	3·9	33·6	33·3			8·8	8·7	See Figure 2	
$Ni(ttas)I_2$	Purple	D	26·6	26·0	3·0	3·4							See Figure 2	
$Ni(ttas)I_2,2CH_2Cl_2$	Purple	D									6·3	6·2		
$Pd(ttas)Cl_2$	Pale orange	D	32·4	32·3	3·7	3·9	35·5	35·5	11·3	11·6			66	45
$Pd(ttas)Br_2$	Orange	D	28·4	28·4	3·2	3·6			22·2	21·3	14·9	15·1	79	72
$Pd(ttas)I_2$	Red	D	25·1	24·8	2·8	3·0	27·7	27·8			13·1	13·1	76	64
$Pt(ttas)Cl_2$	White	D	28·4	29·1	3·2	3·2			5·0	4·8 [a]	27·2	26·8	82	
$Pt(ttas)Br_2$	Pale yellow	D	25·3	24·8	2·9	2·8			19·8	19·8	24·2	23·7	73	
$Pt(ttas)I_2$	Dark yellow	D	22·6	23·2	2·6	2·9			28·2	27·6	21·7	21·2	91	
$Pt(ttas)Cl,ClO_4$	Pale cream	D	26·1	26·2	2·9	3·5							120	
$Ni(ttas)_2(ClO_4)_2$	Dark green	D	35·2	34·9	4·0	4·2					5·1	4·9	170	195
$Ni(ttas)_2(NO_3)_2$ [b]	Bright green	D	37·6	36·8	4·2	4·8					5·4	5·1		
$Ni(ttas)_2Ni(NCS)_4$	Green	2·23 (26·8°)	36·4	36·6	3·7	4·0	35·9	32·9			9·4	9·0		
$Ni(ttas)_2I_2$	Dark green	D	33·6	33·8	3·8	4·0			20·9	20·1			172	
$Pd(ttas)_2(ClO_4)_2$	Bright orange	D	33·8	33·8	3·8	4·1	37·2	36·6						230
$Pt(ttas)_2(ClO_4)_2$	Yellow	D	31·5	32·2	3·6	3·6	34·7	35·1			15·1	15·4	202	
$Ni(ttas)Br_3$	Red	2·5 ± 0·3 [c] (20°)	27·2	25·6	3·1	3·9			32·0	31·3	7·8	7·9	20	

* D = diamagnetic.

[a] 'Ionic' chloride = ½ total, estimated by direct titration of a solution of the complex with standard silver nitrate. [b] There are indications that some water is present and cannot be removed by heating *in vacuo*. [c] Inadequate sample for a more accurate determination. [d] Molecular conductivities for 1 : 1, and 2 : 1 electrolytes at 10^{-3}M are 70—90, and 150—180 Ω^{-1} cm^2 mol^{-1} in nitromethane and 120—150 and 200—250 Ω^{-1} cm^2 mol^{-1} in acetone.

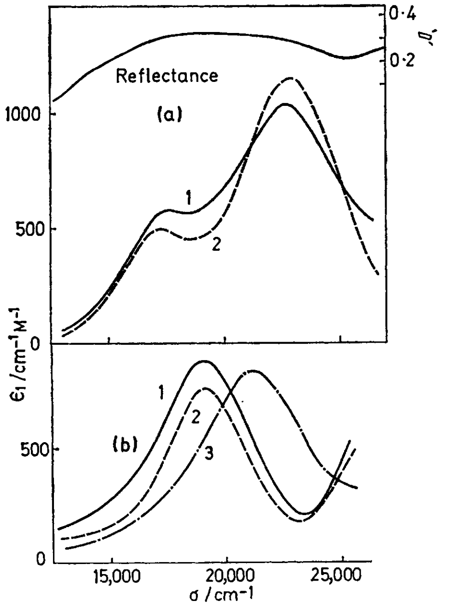

FIGURE 1 Electronic absorption spectra of $NiCl_2(ttas)$: (a) (1) in ethanol, (2) in water; (b) (1) in dichloromethane, (2) in acetone, (3) in nitromethane

TABLE 2

Visible absorption spectral characteristics of some Ni^{II} bis(triarsine) and related complexes

	State	$\sigma_{max.}$/cm^{-1}	$\epsilon_{max.}$ /M^{-1} cm^{-1}
$Ni(ttas)_2(ClO_4)_2$	Solid	23,350	0·43 [a]
	Solid	16,700	0·37 [a]
	Me_2CO	22,620	1370
		17,060	645
	$MeNO_2$	22,800	1400
		17,100	650
$Ni(ttas)_2I_2$	Solid	23,350	0·57 [a]
		16,700	0·32 [a]
	$MeNO_2$	22,600	1350
		17,100	630
$Ni(ttas)_2 (NO_3)_2$	Me_2CO	22,700	1400
		17,400	700
$[Ni(ttas)_2][Ni(CNS)_4]$	Solid	23,000	0·25 [a]
		15,800	0·19 [a]
$[Ni(dias)ttas](ClO_4)_2$	Water	23,000	1950 [b]
		18,900	1000 [b]
	Water	22,750	1680 [c]
		18,800	860 [c]
$[Ni(tas)_2](ClO_4)_2$ [d]		23,200	300
		18,450	2050
$[Ni(sas)](ClO_4)_2$ [e]		21,500	4000 [f]

[a] Uncorrected 'optical density' readings. [b] B. Bosnich, R. Bramley, R. S. Nyholm, and M. L. Tobe, *J. Amer. Chem. Soc.*, 1966, **88**, 3926. [c] D. J. Phillips, Ph.D. Thesis, London, 1958. [d] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 1961, 4433. [e] sas = *o*-Phenylenebis[di(3-dimethylarsinopropyl)arsine]. [f] G. A. Barclay, C. M. Harris, and J. V. Kingston, *Chem. Comm.*, 1968, 965.

The compounds are soluble in several common solvents and conductivity and spectral studies indicate that the form taken by the complex is very sensitive to the nature of both X and the solvent. Thus, while the diffuse-reflectance spectrum of $Ni(ttas)Cl_2$, Figure 1a, gives no indication of the nature of the complex the spectrum of its aqueous solution, Figure 1a (2), has peaks at 22,900 cm^{-1} (1150 cm^{-1} M^{-1}) and 17,240 (490 cm^{-1} M^{-1}) which are reasonably close to those observed for the $Ni(ttas)_2^{2+}$ cation (Table 2). In a disproportionation such as

$$2[Ni(ttas)Cl_2] \xrightarrow{H_2O} [Ni(ttas)_2]^{2+} + Ni^{2+}aq + 4Cl^-$$

the absorption due to the cation will dominate the observed spectrum and the molar extinction coefficients, calculated on the assumption that this disproportionation is complete, are somewhat lower than those of the authentic bis(triarsine) species. The equivalent conductance of a 10^{-3}M solution (Figure 2) (244 cm^2 Ω^{-1} mol^{-1}, based on the $Ni(ttas)Cl_2$ formulation) is well within the region expected for a 2 : 1 electrolyte (240—260 cm^2 Ω^{-1} mol^{-1}) which, in fact, the product is. The solution in ethanol [Figure 1a (1)] repeats the spectral features of the bis(triarsine) species to a certain extent but the equivalent conductivity (40·0 cm^2 Ω^{-1} mol^{-1}, based on the monomeric formulation) is far too low for the 2 : 1 electrolyte (60—90 cm^2 Ω^{-1} mol^{-1}). However, the greater stability of simple chloro-complexes should result in considerable reduction of the observed conductance. Extensive formation of $[\mathrm{NiCl_4}]^{2-}$ would not be expected in the absence of an excess of chloride ions and the absorbance in the region 15,300—14,180 cm^{-1} where the tetrachloro-anion has maxima (*ca.* 200 cm^{-1} M^{-1})[11] does not suggest a large amount of this species, although it may be indicated in the diffuse-reflectance spectrum. The solutions in dichloromethane and acetone have similar spectra, Figure 1b, with only one absorption in the range 12,000—25,000 cm^{-1}. The conductivity in acetone (13·2 cm^2 Ω^{-1} mol^{-1}, 10^{-3}M) is very much less than that expected for a 1 : 1 electrolyte, suggesting an equilibrium of the type

$$[\mathrm{Ni(ttas)Cl_2}]^0 \rightleftharpoons [\mathrm{Ni(ttas)Cl}]^+ + \mathrm{Cl}^-$$

The similarity of the spectra in acetone and dichloromethane would suggest that solvolysis is not involved and while it has not yet been possible to prove that all three donors of the ligand are co-ordinating in the non-electrolyte species, a five-co-ordinate formulation is not unlikely. In nitromethane the conductivity is close to that of a 1 : 1 electrolyte and the absorption peak is shifted to shorter wavelengths. This is quite consistent with a change from five- to four-co-ordination.

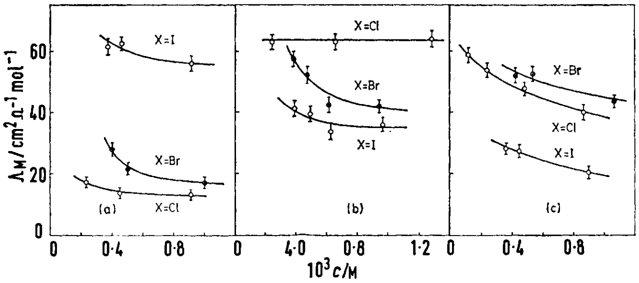

FIGURE 2 Molar conductivities of solutions of $\mathrm{NiX_2(ttas)}$ in (a) acetone, (b) nitromethane, and (c) ethanol; concentrations are expressed in terms of $\mathrm{NiX_2(ttas)}$ but in ethanol, for X = Cl, and Br, the complex disproportionates into $[\mathrm{Ni(ttas)_2}]$ $(\mathrm{NiX_4})$

The $\mathrm{Ni(ttas)Br_2}$ species behaves in a similar way but the diffuse-reflectance spectrum, while still broad, Figure 3, takes on some of the characteristics of the spectra in acetone and dichloromethane. The conductivity in nitromethane is considerably less than that of the chloro-complex (42·0 cm^2 Ω^{-1} mol^{-1}, as compared to 64·0 cm^2 Ω^{-1} mol^{-1} at 10^{-3}M) but the behaviour, on dilution, indicates further dissociation, Figure 2. The spectrum was measured in more dilute solutions where dissociation is likely to be complete. Experiments with mixed solvents indicate that the various species are rapidly interconvertible and preliminary studies have been made of the kinetics and equilibria of these changes. Addition of water to an acetone solution of $\mathrm{Ni(ttas)Br_2}$ causes an immediate colour change from purple to brown and green crystals of $[\mathrm{Ni(ttas)_2}](\mathrm{ClO_4})_2$ separate out when lithium perchlorate is added. The complex $\mathrm{Ni(tas)Br_2}$[12] [tas = bis-(3-dimethylarsinopropyl)methylarsine, (III)] behaves in a similar way.

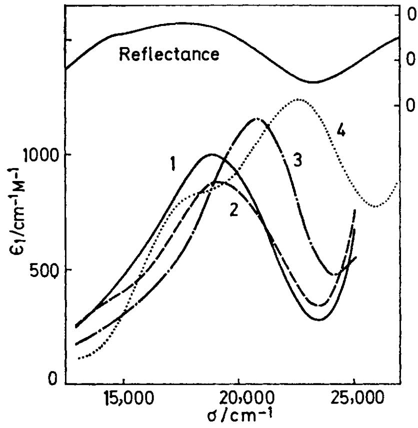

FIGURE 3 Electronic absorption spectra of $\mathrm{NiBr_2(ttas)}$: (1) in dichloromethane, (2) in acetone, (3) in nitromethane, (4) in ethanol

The iodo-complex adopts a different behaviour and, apart from a marked displacement of the major peak to shorter wavelengths in nitromethane, the solution and diffuse-reflectance spectra are fairly similar (Figure 4). The spectrum in ethanol indicates that little, if any, $[\mathrm{Ni(ttas)_2}]^{2+}$ is present since there is a minimum at 23,000 cm^{-1} where this species should have a major absorption peak. The conductance in ethanol is approximately one half of that expected for a 1 : 1 electrolyte and probably arises from a dissociation of the type observed for the other species in acetone.

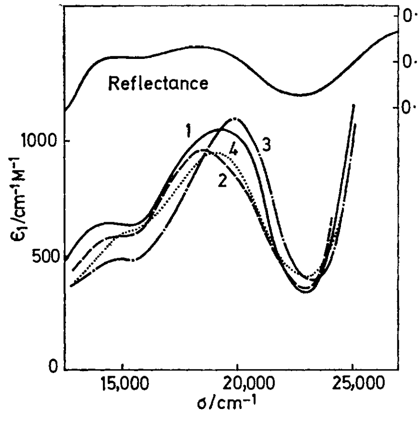

FIGURE 4 Electronic absorption spectra of $\mathrm{NiI_2(ttas)}$ (1) in acetone, (2) in dichloromethane, (3) in nitromethane, (4) in ethanol

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[11] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1961, **83**, 4161.

[12] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 1961, 4433.

The triarsine reacts with PdX_4^{2-} ions in ethanol to give $Pd(ttas)X_2$ (X = Cl, Br, I) (Table 1). These are 1 : 1 electrolytes in nitromethane, but in acetone the conductivities are approximately one half of that expected for a 1 : 1 electrolyte.

Na_2PtCl_4 reacts with the triarsine in ethanol to give, eventually, $PtCl_2(ttas)$ (Table 1). The bromo-analogue cannot be obtained pure by using a mixture of Na_2PtCl_4 and an excess of lithium bromide, but is conveniently obtained by the reaction of the ligand with $PtBr_2$ in chloroform. The iodo-derivative can be obtained quite easily from Na_2PtCl_4, lithium iodide, and the ligand. All three complexes are 1 : 1 electrolytes in nitromethane. The complex $[PtCl(ttas)]ClO_4$ has also been obtained in small yield. Its conductivity in nitromethane is high for a 1 : 1 electrolyte. There is no indication of any disproportionation of the Pd^{II} and Pt^{II} complexes in the way observed for the Ni^{II} analogues.

Bis-(triarsine) Complexes.—The bis-triarsine complexes of the type $[M(ttas)_2]X_2$ have been obtained for M = Pd, Pt; X = ClO_4; M = Ni; X = ClO_4, NO_3, I, and $\frac{1}{2}Ni(NCS)_4$ (Table 1). The nickel complexes were made by treating an aqueous ethanolic solution of the appropriate nickel salt with 2 molar equivalents of the triarsine. The presence of water seems to favour the formation of the bis-species, indeed, it was difficult to prepare any other type of complex under these conditions irrespective of the Ni : ligand ratios employed. The Pd^{II} and Pt^{II} analogues were prepared from the appropriate Na_2MCl_4 in ethanol by reaction with 2 molar equivalents of the ligand and subsequent addition of perchloric acid or lithium perchlorate. All complexes behave as 2 : 1 electrolytes in nitromethane or acetone and the addition of methyl iodide to a nitromethane solution leads to no significant increase in the conductivity even after 12½ days. This indicates the absence of reactive unco-ordinated arsenic but is not necessarily diagnostic of the absence of an unco-ordinated arsenic. Even after refluxing the free ligand with a large excess of methyl iodide it has only been possible to isolate the dimethiodide. All of the complexes, except $[Ni(ttas)_2][Ni(SCN)_4]$ are diamagnetic and even in this case the paramagnetism is confined to the complex anion. The electronic spectra of bis(triarsine)Ni^{II} complexes have been recorded and are collected in Table 2 where they are compared with those of other Ni^{II} complexes.

The *X*-ray diffraction patterns of the powdered perchlorates were recorded. Those of $Pt(ttas)_2(ClO_4)_2$ and the Pd analogue were identical but contained only a few lines. That for the Ni complex contained all the lines observed for Pd and Pt, but also many others and so, while it is clear that Pd and Pt complexes are isomorphous their relationship with the structure of the Ni^{II} analogue is ambiguous.

The nature of the Ni^{II} complexes with six potential arsenic donors deserves some comment. Diamagnetic complexes of the type $[Ni(tas)_2]X_2$, have been reported[12] as well as the complex $[NiL]X_2$ where L is the potential sexidentate, *o*-phenylenebis[di-(3-dimethylarsinopropyl)-arsine] (IV).[13] It has been generally accepted that these are indeed six-co-ordinate complexes with a tetragonally distorted octahedral geometry to account for the diamagnetism. The cation $[Ni(ttas)_2]^{2+}$ falls closely into this category. With the exception of that with the sexidentate ligand, solution absorption spectra of these complexes, where known, are reasonably similar, having two peaks in the visible region at 22,500—22,800 cm^{-1} and 17,100—18,450 cm^{-1} respectively although relative intensities of these peaks differ from compound to compound. Only one peak, at 21,500 cm^{-1}, is reported for the complex with the sexidentate ligand but the reported purple colour would suggest significant absorption at longer wavelength. The six-co-ordinate assignment is, however, thrown into doubt by the properties of the complex $[Ni(dias)(ttas)]^{2+}$. This complex, which has been shown to contain square pyramidal five-co-ordinate complex cations in the crystal,[14] was originally formulated as $[Ni(dias)_3]^{3+}$ and has a spectrum that is closely similar to the other potentially six-co-ordinate Ni^{II} arsine complexes (Table 2). It is possible that all of these complexes are five-co-ordinate in the sense that at any moment, one of the six arsenic atoms is unco-ordinated, or at most loosely attached to the nickel.

The nickel(II) complex $[Ni(ttas)Br_2]$ can be oxidised by bromine in $CHCl_3$–CCl_4 solution to the red Ni^{III} analogue, $Ni(ttas)Br_3$. This is soluble in acetone, chloroform, dichloromethane, and nitromethane and the red solutions do not change colour over a period of several hours. The conductivity in nitromethane (20 cm^2 Ω^{-1} mol^{-1}, $7{\cdot}5 \times 10^{-4}$M) while being appreciable, is very low for a 1 : 1 electrolyte (70—90 cm^2 Ω^{-1} mol^{-1}, 10^{-3}M). In ethanol, the original red colour changes to pale yellow over a period of 10—20 min and the compound, while insoluble in water, slowly reacts with it to form a yellow solution. The i.r. spectrum closely resembles that of the analogous *mer*-$RhX_3(ttas)$ complexes[6] and indeed the compound is isomorphous with *mer*-$RhBr_3(ttas)$. An attempt to prepare the iodo-analogue gave a brown paramagnetic iodine adduct of intermediate composition and there was evidence of oxidation at arsenic rather than nickel.

EXPERIMENTAL

Bis(*o*-dimethylarsinophenyl)methylarsine was prepared by the published method.[4]

*Dichloro[bis(*o*-dimethylarsinophenyl)methylarsine]nickel-*(II).—The triarsine (0·45 g, 1 mol) in ethanol (20 ml) was added to a solution of nickel(II) chloride hexahydrate (0·24 g, 1 mol) in ethanol (25 ml) and the dark brown solution was refluxed for 2 h under nitrogen before the bulk of the ethanol was distilled off. Addition of diethyl ether precipitated a purple-brown compound which was filtered off and dried *in vacuo*. The crude product was dissolved in hot dichloromethane (25 ml) and benzene (40 ml) was added

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[13] G. A. Barclay, C. M. Harris, and J. V. Kingston, *Chem. Comm.*, 1968, 965.

[14] B. Bosnich, R. S. Nyholm, P. J. Pauling, and M. L. Tobe, *J. Amer. Chem. Soc.*, 1968, **90**, 4741.

to the purple solution which was then concentrated. The finely divided product was filtered off, washed with ether, and dried (yield 0·47 g).

*Dibromo[bis(*o*-dimethylarsinophenyl)methylarsine]nickel*(II).—Nickel(II) chloride hexahydrate (0·25 g, 1 mol) and sodium bromide (0·28 g, 2·7 mol) were dissolved in ethanol (18 ml) and water (2 ml) and treated with a solution of the triarsine (0·45 g, 1 mol) in ethanol (15 ml). The dark solution was refluxed for 30 min, concentrated to 15 ml, and cooled to 0 °C. After the crystallised sodium chloride and sodium bromide had been filtered off, the dark brown filtrate was concentrated to small bulk and extracted several times with boiling benzene. The purple solution was concentrated and, on cooling, yielded fine purple crystals that were filtered off, washed with ice-cold ether, and dried *in vacuo* (yield 0·45 g).

*Di-iodo[bis-(*o*-dimethylarsinophenyl)methylarsine]nickel*(II).—A method analogous to that used for $Ni(ttas)Br_2$ gives a mixture of the required compound and $[Ni(ttas)_2]I_2$. The required product can be extracted by acetone. The following gave better yields. A solution of the triarsine (0·60 g, 1 mol) in hot acetone (25 ml) was added to a solution of nickel chloride hexahydrate (0·32 g, 1 mol) and lithium iodide (1·0 g, 6 mol) in boiling acetone (20 ml) and ethanol (5 ml). The deep purple solution was refluxed for 1 h, concentrated, and treated with benzene (10 ml). A purple crystalline mass separated on cooling and was filtered off and extracted with dichloromethane. The extract was filtered, concentrated to small bulk (5 ml), and hot benzene was added to it. On cooling, deep purple crystals separated and were filtered off, washed with benzene and ether, and dried *in vacuo* (yield 1·0 g). This method produces a compound with 2 molecular equivalents of dichloromethane of crystallisation which cannot readily be removed by heating *in vacuo*. Apart from the characteristic bands of CH_2Cl_2 the i.r. spectrum is identical with that of the simple species.

*Bis[di-(*o*-dimethylarsinophenyl)methylarsine]nickel*(II) *Perchlorate*.—A solution of nickel perchlorate heptahydrate (0·286 g, 1 mol) in water (5 ml) was heated with an ethanolic (20 ml) solution of the triarsine (0·69 g, 2 mol) and the green-brown solution was refluxed for 1 h during which time green crystals separated. These were filtered off, washed with a little ice-cold acetone and chloroform, and dried *in vacuo* (yield 0·68 g).

*Bis[di-(*o*-dimethylarsinophenyl)methylarsine]nickel*(II) *Nitrate*.—This compound was obtained when equimolar amounts of nickel nitrate hexahydrate and triarsine were allowed to react by the method used to prepare $Ni(ttas)Cl_2$. The bright green crystalline product was contaminated with a brown material which was removed by washing with acetone.

*Bis[di-(*o*-dimethylarsinophenyl)methylarsine]nickel*(II) *Tetrathiocyanatonickelate*(II).—This complex was obtained as the product of an attempt to prepare $[Ni(ttas)(CNS)_2]$ using the method for the dibromo-complex with potassium thiocyanate in place of sodium bromide. The dark purple solution deposited green crystals during two days. These were washed with water and dried *in vacuo*.

*Bis[di-(*o*-dimethylarsinophenyl)methylarsine]nickel*(II) *Iodide*.—Nickel iodide (0·24 g, 1 mol) was allowed to react with the triarsine (0·69 g, 2 mol) in methanol (110 ml). The mixture was refluxed for 4 h and lithium iodide (1 g) in ethanol (5 ml) and water (5 ml) were added to the cooled solution which was then concentrated under reduced pressure. A dark green crystalline product separated and was filtered off, washed successively with water, ice-cold ethanol, benzene and diethyl ether, and dried (yield 0·54 g).

*Tribromo[bis-(*o*-dimethylarsinophenyl)methylarsine]nickel*(III).—The complex $Ni(ttas)Br_2$ (0·244 g, 1 mol) in chloroform (75 ml) was treated with bromine (0·017 g, 0·5 mol) in carbon tetrachloride (0·65 ml). The deep purple solution became bright red and was set aside 30 min. Light petroleum (b.p. 40—60°) was added to precipitate the red product which was filtered off, washed with ether, and dried *in vacuo* (yield 0·11 g).

*Dichloro[bis-(*o*-dimethylarsinophenyl)methylarsine]palladium*(II).—The triarsine (0·46 g, 1 mol) in hot ethanol (30 ml) was added to a solution of sodium tetrachloropalladate tetrahydrate (0·37 g, 1 mol) in hot ethanol (30 ml). A pale orange precipitate formed but re-dissolved after a few minutes of heating under reflux. A small quantity of palladium was filtered off and the pale orange filtrate was refluxed for a further 4 h and then concentrated. Addition of diethyl ether precipitated a pale orange compound which was filtered off, washed with a little acetone and ether, and dried *in vacuo* at 80 °C (yield 0·48 g).

*Dibromo[bis-(*o*-dimethylarsinophenyl)methylarsine]palladium*(II) was prepared by the same method as the chloro-complex but adding an excess (1·0 g) of lithium bromide. Bright orange crystals were filtered off, washed with water, ice-cold ethanol and ether, and dried *in vacuo* (yield 0·52 g).

*Bis-[di(*o*-dimethylarsinophenyl)methylarsine]palladium*(II) *Perchlorate*.—A solution of the triarsine (0·61 g, 2 mol) in hot ethanol (30 ml) was added to one of sodium tetrachloropalladate tetrahydrate (0·20 g, 1 mol) in hot ethanol (30 ml). An orange precipitate formed immediately but dissolved rapidly to give a red solution. This was filtered free from a small amount of solid material and lithium perchlorate (2·0 g) in hot ethanol (10 ml) was added to the hot solution; a bright orange product separated. The reaction mixture was warmed on a steam-bath for 10 min and the product was filtered off, washed with a little ethanol and ether, and dried *in vacuo* (yield 0·63 g).

*Chloro[bis-(*o*-dimethylarsinophenyl)methylarsine]platinum*(II) *chloride* was prepared from $Na_2PtCl_4,4H_2O$ in a way similar to the palladium analogue. The yellow ethanolic solution was filtered free from the precipitated sodium chloride and evaporated to dryness under nitrogen. The yellow residue was extracted with hot chloroform, and benzene was added to the extract. On concentration a white crystalline product separated and was filtered off, washed with acetone and ether, and dried *in vacuo* (yield 0·40 g from 0·54 g triarsine).

*Chloro[bis-(*o*-dimethylarsinophenyl)methylarsine]platinum*(II) *perchlorate* was obtained by adding lithium perchlorate to an ethanol–ether solution of the chloride.

*Bromo[bis-(*o*-dimethylarsinophenyl)methylarsine]platinum*(II) *Bromide*.—A suspension of platinum(II) bromide (0·71 g, 2 mol) in chloroform (100 ml) was stirred with the triarsine (0·46 g, 1 mol) for 5 h under nitrogen. The mixture was set aside overnight and the unchanged $PtBr_2$ was filtered off. The clear yellow filtrate was concentrated and light petroleum (b.p. 100—120°) and a little acetone was added to precipitate the pale yellow product which was filtered off, washed with light petroleum (b.p. 40—60°) and ether, and dried *in vacuo* (yield 0·64 g). Attempts to make this compound from Na_2PtCl_4 and NaBr led to products containing both halogens.

*Iodo[bis-(*o*-dimethylarsinophenyl)methylarsine]platinum*(II)

Iodide.—Sodium tetrachloroplatinate tetrahydrate (0·51 g, 1 mol) in hot ethanol (20 ml) was added to a solution of lithium iodide (1·0 g) in boiling ethanol (20 ml) and refluxed under nitrogen for 10 min. The triarsine (0·52 g, 1 mol) in hot ethanol (20 ml) was then added to the mixture and after the initially formed precipitate had redissolved the mixture was refluxed for 5 h and then concentrated. The crude product was precipitated by ether and was washed, dried, and extracted with hot dichloromethane. The orange solution was concentrated and the product was precipitated by ether and recrystallised from 60% acetone–ethanol (yield 0·45 g).

*Bis[di-(*o*-dimethylarsinophenyl)methylarsine]platinum*(II).—Sodium tetrachloroplatinate tetrahydrate (0·30 g, 1 mol) in 40% aqueous ethanol (10 ml) was added to a warm solution of the triarsine (0·61 g, 2 mol) in ethanol (40 ml) and the mixture was warmed on a steam-bath for 5 min. Perchloric acid (10 ml, 60°) and lithium perchlorate (1·0 g) in ethanol (10 ml) were added to the solution which was then set aside to crystallise overnight. The yellow crystalline product was filtered off, washed with ice-cold ethanol, and dried *in vacuo* (yield 0·57 g).

Conductance measurements were made with a Wayne-Kerr B221 Universal bridge and a cell with bright platinum electrodes. Visible and u.v. absorption spectra of solutions and diffuse-reflectance spectra of magnesium carbonate mulls of the solids were measured with a Unicam SP 500 spectrophotometer. Magnetic susceptibilities of the powdered solids were measured by the Gouy method using a permanent magnet of field strength *ca.* 7000 G. The measured diamagnetic correction for the triarsine ($202 \pm 15 \times 10^{-6}$ c.g.s.u. mol^{-1}, 20°) agrees quite closely with that calculated from Pascals constants (230×10^{-6} c.g.s.u. mol^{-1}).

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