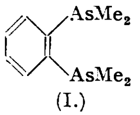
422. *Studies in Co-ordination Chemistry. Part V. Complexes of Bivalent and Tervalent Nickel with a Di(tertiary Arsine).*

By R. S. Nyholm.

By using the di(tertiary arsine) chelate group, *o*-phenylenebisdimethylarsine, a series of bivalent nickel salts of the general formula $[Ni(Diarsine)_2]X_2$ has been prepared, where X = Cl, Br, I, CNS, or ClO_4. These salts, which vary in colour from red to brown, are diamagnetic and it is concluded that the four nickel–arsenic bonds are covalent and planar. Aerial oxidation of the bivalent chloride in the presence of hydrochloric acid yields a paramagnetic, complex salt containing tervalent nickel. The formula, $[NiCl_2(Diarsine)_2]Cl$, has been confirmed by the preparation of a perchlorate and a platinichloride and by conductimetric, potentiometric, and magnetic measurements. The last of these indicate the presence of one unpaired electron. The corresponding bromide and thiocyanate complexes of tervalent nickel have been prepared and are shown to have properties similar to those of the chloride. The corresponding paramagnetic iodide was not obtained but an unusual diamagnetic iodide complex is described. The properties of this new series of tervalent nickel salts are discussed and consideration is given to the bond orbitals used. An octahedral trisdiarsine complex of bivalent nickel of the formula $[Ni(Diarsine)_3][ClO_4]_2$ is described.



(I.)

LITTLE previous work has been reported on the complexes of nickel with tertiary arsines and this investigation was undertaken to obtain information on the stereochemistry and stability of nickel complexes of the di(tertiary arsine) chelate group, *o*-phenylenebisdimethylarsine (I), with which both bivalent and tervalent iron have been shown to form stable complexes containing covalent bonds (Part III, *J.*, 1950, 851). This chelate group also forms strong covalent bonds with bivalent palladium (Chatt and Mann, *J.*, 1939, 1622), quadrivalent tin (Allison and Mann, *J.*, 1949, 2915), tervalent rhodium (Part IV, *J.*, 1950, 857) and bivalent and tervalent cobalt (Part VI, following paper).

The stereochemistry of bivalent nickel is of special interest because octahedral, tetrahedral, and square complexes are known, but the element shows a distinct preference for the co-ordination number four, rather than six, particularly in its covalent compounds (Nyholm, *Quart.*

Reviews, 1949, **3**, 321). The factors which determine whether the configuration of a four-covalent complex will be tetrahedral or planar are imperfectly understood, but the importance of the electronegativity of the attached groups has been established. It was shown by Mellor and Craig (*J. Proc. Roy. Soc. N.S.W.*, 1941, **74**, 475; see also Mellor, *Chem. Reviews*, 1943, **33**, 137) that the tendency to form tetrahedral complexes increases as the electronegativity of the attached atoms increases. Using the magnetic criterion of bond type, these workers found that when four oxygen atoms were attached to the nickel atom the complexes were always tetrahedral but the presence of the less electronegative nitrogen or sulphur atom tended to give a square arrangement; they considered, however, that steric factors were also important. Table I shows how the magnetic moment may be used to distinguish between the square arrangement (using dsp^2 bonds) and the tetrahedral configuration. Magnetic data do not give the type of bond in a tetrahedral complex since both ionic and tetrahedral sp^3 covalent bonds lead to the presence of two unpaired electrons.

The powerful chelate group used here co-ordinates much more strongly with bivalent nickel than do trialkylarsines. Jensen (*Z. anorg. Chem.*, 1936, **229**, 265) has shown that triethylarsine does not form very stable compounds with bivalent nickel. He isolated the compound di-iodobistriethylarsinenickel(II), $NiI_2,2AsEt_3$, but this substance decomposed readily in benzene solution; the corresponding chloride and bromide dissociated in alcohol too extensively to permit of their isolation. By using the similar trialkylphosphines, Jensen (*loc. cit.*) obtained more stable compounds which had the general formula $NiX_2,2PR_3$, where R = alkyl and X = Cl, Br, I or NO_3. With the exception of the nitrate, which was green and had a dipole moment of 8·85 D., all of these compounds were red to brown and in benzene solution their dipole moments were zero. Jensen concluded that all of these compounds had a *trans*-planar configuration, except the nitrate which he considered was either *cis*-planar or tetrahedral. Asmussen ("Magnetokemiske Undersøgelser over Uorganiske Kompleksforbindelser," Copenhagen, 1944, p. 221) has reported that the magnetic moment of this compound is 3·05 B.M. which indicates the tetrahedral configuration (iii in Table I).

In their investigation of the complexes of bivalent palladium with this chelate group, Chatt and Mann (*loc. cit.*) isolated the salt-like complexes $[Pd(Diarsine)_2][PdCl_4]$ and $[Pd(Diarsine)_2]Cl_2$, and the non-ionic complex $[PdCl_2(Diarsine)]$ (cf. II). Attempts to prepare the nickel analogue (II) of this non-ionic complex have been unsuccessful. The stereochemistry of compounds of this type with different halogens would be of great interest.

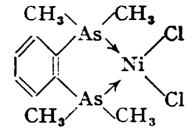
TABLE I.

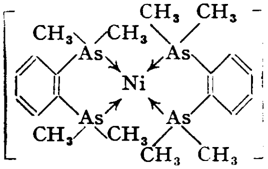
Calculated magnetic moments for nickel complexes.

Complex.	Electronic arrangement. 3*d*	4*s*	4*p*	4*d*(?)	Calculated magnetic moment μ (B.M.).
(i) Nickelous covalent planar (dsp^2 bonds)	[↓↑][↓↑][↓↑][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][ ]		0·0
(ii) Nickelous ionic, octahedral or tetrahedral	[↓↑][↓↑][↓↑][↓][↓]	[ ]	[ ][ ][ ]		2·83
(iii) Nickelous covalent tetrahedral (sp^3 bonds)	[↓↑][↓↑][↓↑][↓][↓]	[↓↑]	[↓↑][↓↑][↓↑]		2·83
(iv) Nickelous covalent octahedral (d^2sp^3 bonds)	[↓↑][↓↑][↓↑][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	[↓][↓]	2·83
(v) Nickelic covalent planar (dsp^2 bonds)	[↓↑][↓↑][↓↑][↓][↓↑]	[↓↑]	[↓↑][↓↑][ ]		1·73
(vi) Nickelic covalent octahedral (d^2sp^3 bonds)	[↑↓][↓↑][↓↑][↓↑][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]	[↓]	1·73
(vii) Nickelic covalent square pyramid (dsp^3 bonds)	[↓↑][↓↑][↓↑][↓][↓↑]	[↓↑]	[↓↑][↓↑][↓↑]		1·73

When a solution of nickel chloride in alcohol was treated with the diarsine a deep blood-red colour developed instantly and the compound isolated had the formula $[Ni(Diarsine)_2]Cl_2$. This substance, which is diamagnetic, is soluble in water to give a red solution, which is partly hydrolysed as shown by the development of the odour of the diarsine. Addition of perchloric acid to the aqueous solution gives the insoluble perchlorate. The compound is formulated as (III), being di-(*o*-phenylenebisdimethylarsine)nickel(II) chloride. The corresponding bromide, iodide, and thiocyanate were prepared and all these salts are diamagnetic. Their properties are summarised in Table II. The diamagnetism indicates the use of *dsp*^{2} bonds from the nickel atom and hence it is concluded that the four nickel–arsenic bonds are coplanar.

(II.)





(III.)

TABLE II.

Physical properties of bivalent and tervalent nickel complexes.

[A = *o*-Phenylenebis(dimethylarsine).]

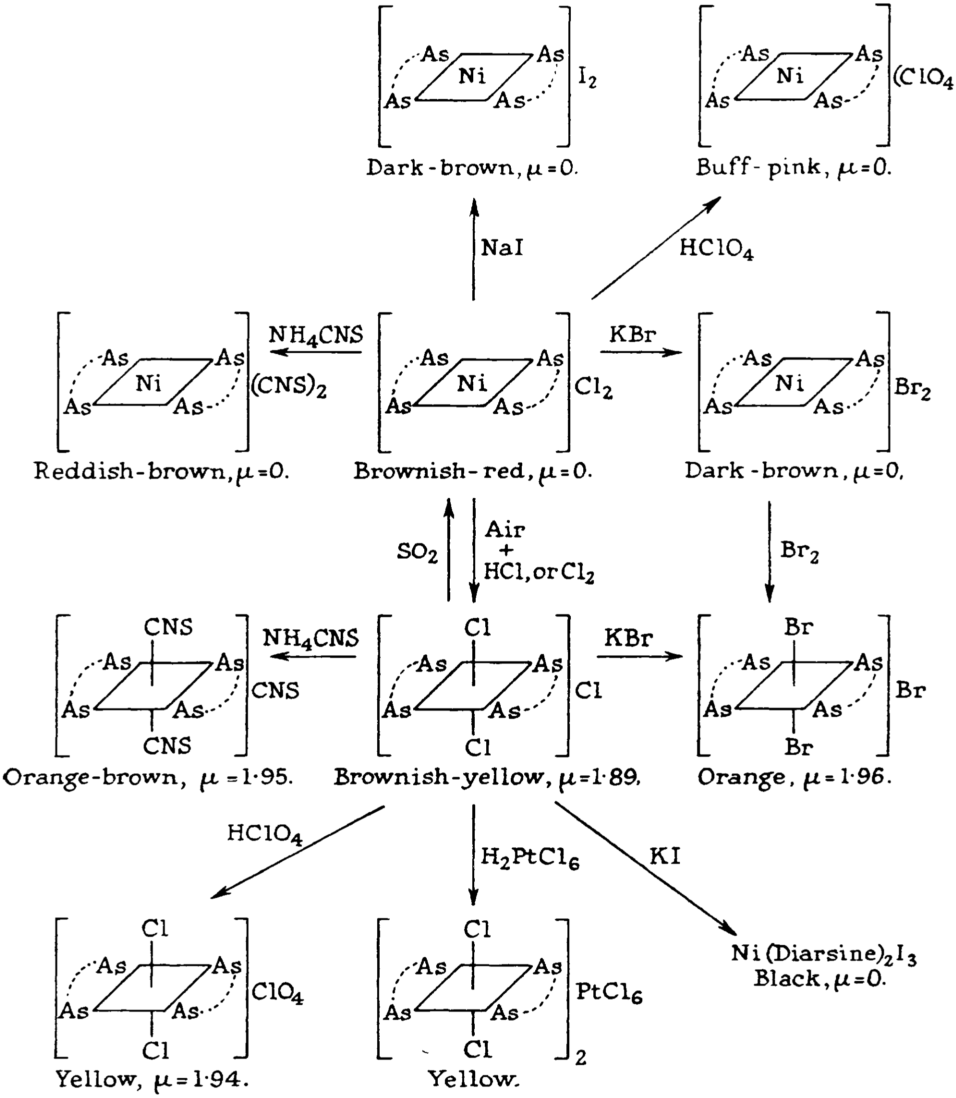
Compounds of bivalent nickel.			Compounds of tervalent nickel.		
Complex.	Colour.	μ (B.M.).	Complex.	Colour.	μ (B.M.).
$[NiA_2]Cl_2$	Red	0·0	$[NiCl_2A_2]Cl$	Yellow	1·89
$[NiA_2]Br_2$	Brown	0·0	$[NiBr_2A_2]Br$	Orange	1·96
$[NiA_2](CNS)_2$	Reddish-brown	0·0	$[Ni(CNS)_2A_2]CNS$	Orange-brown	1·95
$[NiA_2](ClO_4)_2$	Buff-pink	0·0	$[NiCl_2A_2]ClO_4$	Yellow	1·94
$[NiA_2]I_2$	Dark brown	0·0			
			NiI_3,A_2	Black	0·0

In attempts to prepare the compound (II), the nickel complex (III) was refluxed in alcoholic solution with excess of nickel chloride and hydrochloric acid. Chatt and Mann (*loc. cit.*) used this method to convert di-(*o*-phenylenebisdimethylarsine)palladous chloride (cf. III) into the non-ionic compound dichloro-(*o*-phenylenebisdimethylarsine)palladium (cf. II). In our work with nickel no precautions were taken initially to exclude air and it was found that oxidation took place with the formation of the first of a series of tervalent nickel salts. These have been investigated in some detail. As yet, attempts to obtain the compound (II) have been unsuccessful, even when precautions were taken to exclude air to prevent oxidation. Apparently such a compound is less stable than the bis(diarsine) salt, in which case the failure to isolate it under the conditions used can be understood.

When an alcoholic solution of the bivalent nickel chloride salt containing hydrochloric acid was heated under reflux in the presence of air a change in colour from deep red to a brownish-red occurred during a few hours and brown crystals were formed. When finely divided, this substance was brownish-yellow in colour. The compound had the empirical formula $NiCl_3(Diarsine)_2$ and it seemed likely that oxidation of the nickel to the tervalent state had occurred; the possibilities that the extra atom of chlorine was present as a molecule of hydrochloric acid or that partial oxidation of the diarsine had occurred were kept in mind, but the properties of the compound were incompatible therewith. The yellowish-brown compound was also produced in a less pure form by passing chlorine into an aqueous solution of the bivalent salt $[Ni(Diarsine)_2]Cl_2$; the red solution immediately became yellow when treated with chlorine, and the compound was precipitated. However, the compound $NiCl_3(Diarsine)_2$ itself reacts with chlorine to give a product containing more than three chlorine atoms, as will be discussed later, and hence this was not a convenient method for the preparation of the tervalent complex.

The compound dissolved readily in alcohol and was moderately soluble in water to give a green solution from which it was immediately reprecipitated by hydrochloric acid. This was taken to indicate that part, at least, of the chlorine was ionised. The aqueous solution was at first neutral to litmus. When kept for many hours the aqueous solution became orange and the odour of the diarsine developed; this hydrolysis was prevented by the addition of hydrochloric acid. The initial neutrality seemed to exclude the presence of hydrochloric acid in the molecule and it was observed that the diarsine does not react with hydrochloric acid by itself. The molecular conductivity of the aqueous solution at a dilution of 1024 litres was initially 120 mho; this figure gradually increased owing to hydrolysis but indicated the formation initially of two ions from each molecule of $NiCl_3(Diarsine)_2$. It thus seemed probable that the compound should be formulated as $[NiCl_2(Diarsine)_2]Cl$, (see Fig. 1), in which the tervalent nickel atom is octahedral. This formulation as dichlorodi-(*o*-phenylenebisdimethylarsine)-nickel(III) monochloride has been confirmed by other physical and chemical investigations to be described. In Fig. 1 the two chlorine atoms in the cation are shown as *trans*; this is probably correct, but without an *X*-ray crystallographic examination it must remain speculative.

FIG. 1.

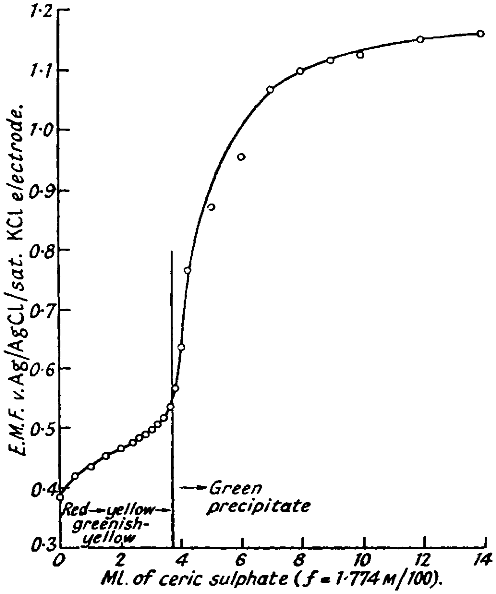


Treatment of the green solution of the complex in water with sulphur dioxide gave a red colour which suggested reduction to the bivalent nickel salt [Ni(Diarsine)$_2$]Cl$_2$. This was confirmed by the isolation of the buff-pink perchlorate of the bivalent complex, [Ni(Diarsine)$_2$][ClO$_4$]$_2$, which was identified by analysis and magnetic moment. This compound was also prepared by starting from a pure specimen of the bivalent nickel chloride complex and the two compounds are identical. When a solution of the tervalent complex was treated with perchloric acid a yellow precipitate of dichlorodi-(*o*-phenylenebisdimethylarsine)nickel(III) perchlorate, [NiCl$_2$(Diarsine)$_2$]ClO$_4$, was obtained. This compound is quite distinct from the perchlorate of the bivalent complex; whereas the compound [Ni(Diarsine)$_2$][ClO$_4$]$_2$ gave no precipitate on being heated with silver nitrate and nitric acid, the perchlorate of the tervalent complex soon lost the chlorine from the cation as silver chloride when similarly treated. Under these conditions the perchlorate ion does not react with silver nitrate. The platinichloride of the tervalent nickel complex was also prepared and has the formula $[NiCl_2(Diarsine)_2]_2[PtCl_6]$ as required.

Potentiometric titration of the bivalent complex with ceric sulphate gives conclusive evidence that the oxidation involves a one-electron change per nickel atom. Fig. 2 shows the curve obtained by titrating a solution of di-(*o*-phenylenebisdimethylarsine)nickel(II) chloride with ceric sulphate at 0°, in the presence of a little hydrochloric acid. The chloride-ion concentration was kept low to prevent precipitation of the tervalent complex by the common-ion effect. Also, the titration was carried out at 0° to minimise hydrolysis since this produced the diarsine which is a reducing agent. Permanganate and dichromate gave high results, probably owing to greater simultaneous oxidation of the diarsine. From the curve it can be seen that there is a sudden increase in the oxidation potential at the calculated end-point. It is possible to determine approximately the standard oxidation–reduction potential for the reaction

FIG. 2.

Potentiometric titration of $[Ni(Diarsine)_2]Cl_2$ *with ceric sulphate*; Pt *electrode.*



$$[Ni(Diarsine)_2]^{++} + 2Cl^- - e \longrightarrow [NiCl_2(Diarsine)_2]^+$$

from the figures obtained in this titration. The oxidation potential is given by the expression,

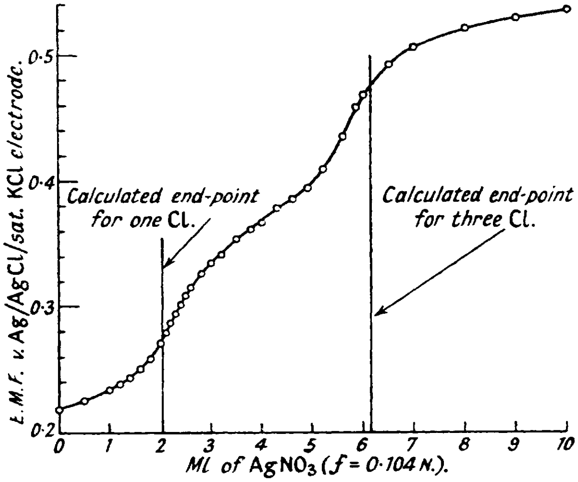
$$E = E_0 + \frac{RT}{F} \ln \frac{a_{[NiCl_2(Diarsine)_2]^+}}{a_{[Ni(Diarsine)_2]^{++}} \times a^2_{Cl^-}}$$

and hence the standard-oxidation reduction potential (E_0) is observed when all activities are unity. The activities of the oxidant and reductant are approximately equal when the bivalent nickel salt is 50% oxidised, but, as the activity of the chloride ion still affects the potential, it is possible to give E_0 to the nearest 0·1 v. only. By use of the above equation, E_0 is estimated to be *ca.* +0·7 v. on the standard hydrogen scale. This value explains why atmospheric oxygen can effect this oxidation : the reaction is thermodynamically feasible, since E_0 for the system $4e + O_2 + 4H^+ \longrightarrow 2H_2O$ is +1·23 v. The relative ease with which it occurs is unusual; the aerial oxidation of ferrous chloride in cold aqueous solution, for example, takes place only very slowly although E_0 for the system Fe^{++}/Fe^{+++} is +0·77 v. The conditions used in the present work are, however, much more favourable for oxidation ; the solution is boiling and the substance formed by oxidation is less soluble. The alcohol also has an effect on the equilibrium and in any case the kinetics of the process may be quite different from those involved in the oxidation of ferrous chloride. The red solution became greenish-yellow at the end-point and further addition of ceric sulphate produced a green precipitate. A similar green compound is obtained by the action of chlorine on an aqueous solution of the tervalent nickel complex salt and is possibly a derivative of quadrivalent nickel. This subject will be considered further in a later communication.

The result of a potentiometric titration using silver nitrate as titrant and a silver electrode as indicator is shown in Fig. 3. It was apparent from earlier experiments that the two chlorine atoms in the cation were not as strongly bound as in the similar tervalent rhodium salts (Part IV, *J.*, 1950, 857) or in the tervalent cobalt complex (Part VI, following paper), but by carrying out the titration in the presence of a large amount of alcohol it was possible to demonstrate that one of the three chlorine atoms reacted more readily than the other two. In Fig. 3 there is a definite inflexion in the curve after one equivalent of silver nitrate has been added, but on further addition of silver nitrate the other two chlorine atoms slowly react also.

FIG. 3.

Potentiometric titration of $[NiCl_2(Diarsine)_2]Cl$ *with* $AgNO_3$; *silver electrode.*



The magnetic susceptibility supports the valency of three assigned to the nickel atom. The compounds $[NiCl_2(Diarsine)_2]Cl$ and $[NiCl_2(Diarsine)_2]ClO_4$ are paramagnetic with magnetic moments of 1·89 and 1·94 B.M., respectively. This may be taken to indicate the presence of one unpaired electron since experimental magnetic moments are usually a little in excess of the calculated value of 1·73 B.M. Oxidation of nickel to the tervalent state necessarily leaves it with an odd number of electrons and since a moment corresponding to one unpaired electron was observed it seems that only one of the electron pairs in the 3*d* shell has been uncoupled (see Table I). It must be pointed out that the magnetic moment does not indicate definitely which orbitals are used by the metal atom, but it does support a valency of three for the nickel. The orbitals used by the metal atom will be considered later.

Two other tervalent nickel complexes have been prepared from the chloride $[NiCl_2(Diarsine)_2]Cl$. When an aqueous solution of this compound was treated with sodium bromide, the orange complex salt dibromodi-(*o*-phenylenebisdimethylarsine)nickel(III) bromide was precipitated. This compound was also obtained, but less pure, by oxidising the bivalent bromide complex with bromine in alcohol. The compound was less soluble than the chloride in both water and alcohol; a suspension of it in aqueous alcohol was reduced by sulphur dioxide to the brown bivalent complex. The magnetic moment (1·96 B.M.) again showed the presence of one unpaired electron. The tervalent nickel thiocyanate was prepared similarly by the action of ammonium thiocyanate on an aqueous solution of the chloride and the compound dithiocyanatodi-(*o*-phenylenebisdimethylarsine)nickel(III) thiocyanate was precipitated as an orange-brown powder. The magnetic moment of this compound (1·95 B.M.) was similar to that of the chloride and bromide. This thiocyanato-complex began to decompose in a few days, but the tervalent nickel chloride and bromide were stable indefinitely. As shown in Table II, the tervalent nickel complexes were all paler than the corresponding bivalent planar compounds.

The reaction of the tervalent nickel chloride complex with sodium iodide takes quite a different course from that of the bromide or thiocyanate, and a black compound of the empirical formula $NiI_3(Diarsine)_2$ was obtained. The very deep colour of this compound, compared with that of the bivalent iodide complex, suggested a different type of reaction and this was confirmed by the magnetic moment. Unlike the chloride, bromide, and thiocyanate of similar empirical formula, the compound was diamagnetic and it seemed possible that reduction to the bivalent state had occurred; such a reaction is to be expected from the oxidation–reduction potentials of the reactants. Since the oxidation potential of the couple $[NiCl_2(Diarsine)_2]^+/[Ni(Diarsine)_2]^{++}$ (*ca.* +0·7 v.) is higher than that of the couple I_2–I^- (+0·53 v.), oxidation of the iodide ion to iodine is expected with reduction of the nickel to the planar bivalent state, unless solubilities affect the equilibrium. Unless suitably stabilised, the iodides of metals in higher valency states are unstable; for example it was shown in Part III (*J.*, 1950, 851) that the iodide $[FeI_2(Diarsine)_2]I$, which is formed momentarily by the action of iodide ions on the ferric chloride complex, undergoes spontaneous oxidation–reduction to give the non-ionic octahedral ferrous complex $[FeI_2(Diarsine)_2]$. For this nickel complex, however, the reaction is not as simple, for no iodine is left in solution and its mode of attachment to the complex is doubtful. The diamagnetism seems to exclude the idea that the iodine is used to oxidise part of the diarsine, for it appears that the essential dsp^2 bonds from the four arsenic atoms to the metal are unaffected. The iodine could be present as I_3^- ions, but there is also the possibility that the compound is a polynuclear complex in which the polymerisation causes the diamagnetism. The deep colour lends some support to the latter suggestion, but these formulations remain at present speculative.

The stability of these tervalent nickel complexes is noteworthy. No value is available for the free energy of formation of a Ni^{+++} ion, but by comparison with cobalt, the oxidation potential of the couple Ni^{+++}–Ni^{++} must be near +2·0 v. At least it is known that the higher oxide of formula NiO_2 or Ni_2O_3 liberates oxygen when treated with acid, and this indicates an oxidation potential near +2·0 v. (Latimer, "Oxidation Potentials," Prentice Hall, N.Y., 1938, p. 190).* As the oxidation potential of the complex is only *ca.* +0·7 v., this decrease from +2·0 v. is a striking indication of the preferential stabilisation of the tervalent state. A qualitative demonstration of this is given by the behaviour of both complexes with water; the bivalent complex dissolves to a red solution which has a very pronounced odour of the di(tertiary arsine), which is produced by partial hydrolysis. Whereas, on the other hand, the green solution of the tervalent complex has initially no trace of an odour of the diarsine; after some hours the diarsine can be detected, but only because the hydroxy-complex formed by hydrolysis of the chloride decomposes. This decomposition is prevented by the addition of hydrochloric acid. Treatment of an aqueous solution of the bivalent complex with alcoholic dimethylglyoxime gave no precipitate until dilute aqueous ammonia was added to the solution, whereupon the usual red precipitate of bisdimethylglyoximenickel(II) was obtained. The tervalent complex, when similarly treated, gave no red precipitate initially but the solution developed a dark purple-red colour which may be due to a tervalent nickel complex with dimethylglyoxime. Jensen (private communication) has obtained such a complex by bromine oxidation of the bivalent complex. These experiments show that an aqueous solution of the compound $[NiCl_2(Diarsine)_2]Cl$ contains no bivalent nickel ion.

These nickel salts are the first examples of stabilised tervalent nickel complexes in which the metal atom is apparently octahedral. Jensen (*Acta Chem. Scand.*, 1949, **3**, 474) has recently investigated a relatively unstable non-ionic five-covalent complex of tervalent nickel which is formed when dibromo-*trans*-bistriethylphosphinenickel is oxidised with bromine. The compound has the formula $NiBr_3,2PEt_3$ and is monomeric in freezing benzene. The dipole moment in benzene is 2·3 D., which, together with the magnetic moment of 1·7—1·9 B.M., enabled Jensen to conclude that the complex has a square pyramidal structure. Daudel and Bucher (*J. Chim. physique*, 1945, **42**, 6) predicted that this shape would arise from the use of dsp^3 bonds by the metal atom, provided that the *d* orbital had a lower principal quantum number than the *s* and the *p* orbitals (see vii, Table I). Unlike the compounds described here, Jensen's complex decomposed within a few hours and thus an *X*-ray examination of its structure was not possible.

The compound tris-(*o*-phenylenebisdimethylarsine)nickel(II) perchlorate was obtained in small yield from the mother-liquors of the preparation of the tervalent chloride complex. The solution was still brownish-red after aerial oxidation for several weeks, and the addition of

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* By using the value +0·59 v. for the Ni/Ni^{+++} couple (estimated by Pauling, "V. Henri Memorial Volume," Liege, 1948, p. 7) and the value −0·25 v. for the Ni/Ni^{++} (Latimer, *loc. cit.*) we obtain +1·77 v. for the Ni^{++}/Ni^{+++} couple.

perchloric acid gave the required compound as a red precipitate. Its properties are unusual in some ways: unlike the corresponding tris-*o*-phenanthroline- and trisdipyridyl-nickel complexes, for which $\mu = 2{\cdot}8$ B.M. (Asmussen, *op. cit.*, p. 212), this substance is diamagnetic. Also, chlorine and ceric sulphate, but not air, oxidise this substance to an unstable green compound. The properties of this bivalent nickel complex and its oxidation product are being investigated further.

The orbitals used in these nickelous and nickelic complexes are of considerable interest. The diamagnetic four-covalent complexes obviously use dsp^2 bonds and are hence square, but the tervalent complexes are not so straightforward as it is not easy to decide which orbital is occupied by the unpaired electron. This unpaired electron could be in the $3d$ shell, in which case the use of d^2sp^3 bonding orbitals is not permissible (see vii, Table I), or it could be promoted to some level above $4p$, thereby enabling the metal atom to use the d^2sp^3 bond orbitals (vi, Table I).

With regard to the former possibility, it is conceivable that the first step in the oxidation of the square complex is the unpairing of the fourth $3d$ electron pair, it being assumed that the four $3d4s4p^2$ bonds are unaffected. The unpaired electron so obtained would then form a bond in the remaining $4p$ orbital, giving five dsp^3 bonds (see vii, Table I); then would follow immediately the accession to the cation of another chloride ion, to be held by an essentially ionic bond, giving a co-ordination number of six. Actually, the two chlorine atoms would probably be *trans* and some form of resonance between the two chlorine atoms would occur. This attainment of a co-ordination number of six is in keeping with the tendency of metals to reach the four- or six-covalent state when possible; this was not possible with Jensen's compound $NiBr_3,2PEt_3$ because the oxidation was carried out under anhydrous conditions where no anions were available to enter the co-ordination sphere. This method of formulation would explain the ease with which the two chlorine atoms in the cation reacted with silver nitrate.

The other possibility is that d^2sp^3 covalent bond orbitals are used with the promotion of the unpaired electron to the $4d$ shell (probably), as shown in vi, Table I. Some support is provided for this idea by preliminary experiments which suggest that this electron may be removed by oxidation, to give a quadrivalent nickel complex as would be expected. It must be emphasised however, that it is not yet possible to decide between these two hypotheses.

Fig. 1 summarises the relations between these nickel complexes; in each case the formula for the di(tertiary arsine) has been abbreviated to show only the two arsenic atoms.

EXPERIMENTAL.

Di-(o*-phenylenebisdimethylarsine)nickel*(II) *Chloride.*—Nickel chloride hexahydrate (1·5 g.) was dissolved in hot alcohol (30 ml.) and treated with *o*-phenylenebisdimethylarsine (2·0 g.) in alcohol (20 ml.). The blood-red solution which formed was heated on the water-bath for a few seconds and most of the alcohol then distilled off under reduced pressure at room temperature until the volume was about 10 ml. Brownish-red crystals had begun to separate, and, after cooling in ice water, the mixture was filtered and the *complex* (1·5 g.) washed many times with small quantities of alcohol, in which it was fairly soluble. The substance was then dried in a vacuum-desiccator and kept dry (Found: C, 34·2; H, 4·9; Cl, 10·2. $C_{20}H_{32}Cl_2As_4Ni$ requires C, 34·3; H, 4·6; Cl, 10·1%). Magnetic susceptibility: powder form, at 28°, $\chi = -0{\cdot}50 \times 10^{-6}$, whence $\mu = 0$. The complex dissolved readily in water to give a red solution which had a strong odour of the diarsine. It was insoluble in non-hydroxylic solvents such as benzene. An aqueous or alcoholic solution reacted instantly with silver nitrate, all of the chloride ion being precipitated.

Di-(o*-phenylenebisdimethylarsine)nickel*(II) *Bromide.*—Nickel chloride hexahydrate (1·3 g.) and sodium bromide (2·5 g.) were dissolved, by heating, in alcohol (40 ml.) containing distilled water (20 ml.) and the solution was filtered and treated with *o*-phenylenebisdimethylarsine (2·8 g.) in alcohol (30 ml.). The solution immediately developed a dark red colour and, after the solution had been warmed and shaken for a few seconds, beautiful, sparkling, brown plates crystallised. The solution was heated on the water-bath for a few minutes and then filtered, and the compound was well washed with alcohol in which it was slightly soluble to give a pink solution. The *complex* (3·4 g.) was finally dried in a vacuum-desiccator (Found: C, 31·1; H, 4·1; Br, 20·0. $C_{20}H_{32}Br_2As_4Ni$ requires C, 30·3; H, 4·0; Br, 20·2%). Magnetic susceptibility: powder form, at 20°, $\chi = -0{\cdot}46 \times 10^{-6}$, whence $\mu = 0$. The compound was much less soluble than the chloride in both water and alcohol, and was insoluble in solvents such as benzene. Treatment of an alcoholic solution with silver nitrate caused precipitation of all the bromide ion.

Di-(o*-phenylenebisdimethylarsine)nickel*(II) *Thiocyanate.*—Nickel chloride hexahydrate (0·22 g.) was dissolved in hot alcohol (30 ml.), and ammonium thiocyanate (2·0 g.) in distilled water (5 ml.) added. The hot solution was filtered and added to *o*-phenylenebisdimethylarsine (0·6 g.) in alcohol (20 ml.). The brownish-violet solution immediately became red, and dark brown crystals were precipitated. These were filtered off (0·55 g.) and well washed with alcohol, in which the *thiocyanate* dissolved slightly to give a pinkish-violet solution (Found: C, 35·6; H, 4·35; N, 3·9; S, 8·4; Ni, 8·1. $C_{22}H_{32}N_2S_2As_4Ni$ requires C, 35·4; H, 4·3; N, 3·8; S, 8·6; Ni, 7·9%). The compound was insoluble in water, but an alcoholic solution reacted immediately with silver nitrate to give a white precipitate.

In the above preparation a slight excess of the diarsine was used. If the nickel halide is in excess, an impure product is obtained, the analysis of which suggests that the impurity is almost certainly the tetrathiocyanatonickel(II) compound $[Ni(diarsine)_2][Ni(CNS)_4]$. As a further precaution to avoid the formation of this substance, the nickel solution was always added to the excess of diarsine.

Magnetic susceptibility: powder form; as there was insufficient of the compound to fill the tube, the susceptibility was not measured exactly but the compound was diamagnetic, whence $\mu = 0$.

Di-(o-*phenylenebisdimethylarsine*)*nickel*(II) *Iodide*.—Nickel chloride hexahydrate (1·2 g.) and lithium iodide (4 g.) were dissolved in alcohol (50 ml.), and the hot solution filtered and treated with *o*-phenylenebisdimethylarsine (1·4 g.) in alcohol (60 ml.). A blood-red colour developed immediately and, after warming and stirring of the solution, a brown precipitate formed. The solution was heated on the water-bath for a few minutes and, after standing for a short time, the precipitate was filtered off and washed many times with alcohol in which it was only very slightly soluble. The *iodide* (2·2 g.) was then dried in a vacuum-desiccator (Found: C, 27·3; H, 3·8; I, 28·8. $C_{20}H_{32}I_2As_4Ni$ requires C, 27·1; H, 3·6; I, 28·7%). Magnetic susceptibility: powder form: the compound was diamagnetic, but the susceptibility was not measured exactly, whence $\mu = 0$. The compound was only slightly soluble in water.

Di-(o-*phenylenebisdimethylarsine*)*nickel*(II) *Perchlorate*.—The bivalent nickel chloride complex (prepared as above) (0·2 g.) was dissolved in distilled water (10 ml.), to give a red solution, an excess of 30% perchloric acid was added immediately and the solution then diluted with distilled water (40 ml.). A buff-pink precipitate formed at once, and the odour of the diarsine, which is characteristic of a solution of the chloride complex, disappeared. The precipitated *perchlorate* was filtered off, washed many times with distilled water, in which it was insoluble, and dried in a vacuum-desiccator. A practically quantitative yield of just over 0·2 g. was obtained (Found: C, 29·3; H, 4·0; Ni, 7·2. $C_{20}H_{32}O_8Cl_2As_4Ni$ requires C, 29·0; H, 3·9; Ni, 7·1%).

Dichlorodi-(o-*phenylenebisdimethylarsine*)*nickel*(III) *Chloride*.—Nickel chloride hexahydrate (1·6 g.) was dissolved in alcohol (60 ml.) containing 10N-hydrochloric acid (7 ml.), and a solution of *o*-phenylenebisdimethylarsine (2·9 g.) in alcohol (30 ml.) was added. The blood-red solution was then refluxed, filtered air being allowed access to the surface of the solution. After about 2 hours brown crystals formed on the surface of the flask, but refluxing was continued for about 2 days. The solution was then cooled and filtered, and the compound washed many times with dilute hydrochloric acid and finally with alcohol. The washings were at first red and finally yellowish-green owing to a little of the *complex* dissolving. The substance (2·4 g.) was then dried in a vacuum-desiccator (Found: C, 32·5; H, 4·5; Cl, 14·4; Ni, 8·05. $C_{20}H_{32}Cl_3As_4Ni$ requires C, 32·6; H, 4·3; Cl, 14·5; Ni, 8·0%). An aqueous solution of the complex was green, but when kept it became orange after a few days, and during this time the odour of the diarsine developed in the solution. Addition of hydrochloric acid to an aqueous solution of the compound gave a yellow precipitate immediately, and this was a convenient method of purification. The substance is brown in the form of crystals, but when powdered has a yellowish-brown colour. It was quite insoluble in benzene or chloroform, but dissolved readily in alcohol.

The following results were obtained in determinations of the magnetic susceptibility of the powder form of four separately prepared specimens:

Temp.	$\chi \times 10^6$.	$\chi_M \times 10^6$.	$\chi_M \times 10^6$ (at 20°).	χ_M + Diamagnetic correction (452).	Magnetic moment, μ (B.M.).
21°	1·39	1024	1030	1482	1·87
27·5	1·51	1110	1140	1592	1·94
26·5	1·42	1040	1060	1512	1·89
20	1·41	1040	1040	1492	1·88

Mean magnetic moment = 1·89 B.M.

Dichlorodi-(o-*phenylenebisdimethylarsine*)*nickel*(III) *Platinichloride*.—A solution of the tervalent nickel monochloride complex $[NiCl_2(diarsine)_2]Cl$ (0·25 g.) in alcohol (50 ml.) was filtered, and an excess of a 10% aqueous solution of chloroplatinic acid added. A yellow precipitate of the *platinichloride* was formed immediately and, after coagulation by warming, this was filtered off and washed many times with distilled water and dried in a vacuum-desiccator (0·25 g.) (Found: C, 26·5; H, 3·7; Ni, 6·5; Pt, 10·6; Cl, 19·2. $C_{40}H_{64}Cl_{10}As_8Ni_2Pt$ requires C, 26·5; H, 3·5; Ni, 6·5; Pt, 10·66; Cl, 19·6%). Insufficient of the material was available for a determination of the magnetic moment.

Dichlorodi-(o-*phenylenebisdimethylarsine*)*nickel*(III) *Perchlorate*.—The tervalent nickel monochloride complex, $[NiCl_2(Diarsine)_2]Cl$ (0·7 g.), was moistened with alcohol and dissolved quickly in warm distilled water (200 ml.). The solution was filtered and the filtrate treated immediately with excess of a 30% solution of perchloric acid, with vigorous stirring. A yellow precipitate was obtained which settled after a few minutes. It was then filtered off and washed thoroughly with cold distilled water, in which it was practically insoluble. The *complex* (0·7 g.) was then dried in a vacuum desiccator and then had a brownish-yellow colour with a golden sheen (Found: C, 29·9; H, 3·8; Cl, 13·1; Ni, 7·5. $C_{20}H_{32}O_4Cl_3As_4Ni$ requires C, 29·95; H, 4·0; Cl, 13·3; Ni, 7·3%). Magnetic susceptibility: powder form, at 16°: $\chi = 1{\cdot}48 \times 10^{-6}$, $\chi_M = 1180 \times 10^{-6}$, correction for diamagnetism $= 459 \times 10^{-6}$, whence $\mu = 1{\cdot}94$ B.M.

Dibromodi-(o-*phenylenebisdimethylarsine*)*nickel*(III) *Bromide*.—The tervalent nickel monochloride complex, $[NiCl_2(Diarsine)_2]Cl$ (1·1 g.), was dissolved in warm water (300 ml.) as quickly as possible, after being first moistened with alcohol, and the solution filtered. The filtrate was treated immediately with a solution of sodium bromide (3 g.) in distilled water (10 ml.), with constant stirring. An orange-yellow precipitate appeared at once and, after a few minutes' stirring, this coagulated to an orange-brown, crystalline powder. This *bromide* (1·3 g.) was filtered off, washed many times with distilled water, in which it was only very slightly soluble, and dried in a vacuum-desiccator (Found : C, 27·6; H, 3·8; Br, 27·6; Ni, 6·9. $C_{20}H_{32}Br_3As_4Ni$ requires C, 27·6; H, 3·7; Br, 27·6; Ni, 6·75%). Magnetic susceptibility : powder form at 17° : $\chi = 1{\cdot}33 \times 10^{-6}$, $\chi_M = 1160 \times 10^{-6}$, correction for diamagnetism = 489 × 10^{-6}, whence $\mu = 1{\cdot}96$ B.M. The compound could be recrystallised from a large volume of alcohol containing a little hydrobromic acid. It was less soluble than the chloride in both water and alcohol, and was quite insoluble in benzene and chloroform.

Dithiocyanatodi-(o*-phenylenebisdimethylarsine*)*nickel*(III) *Thiocyanate*.—The tervalent nickel chloride complex, $[NiCl_2(Diarsine)_2]Cl$ (1·0 g.), was moistened with alcohol and dissolved quickly in warm distilled water (30 ml.). The solution was stirred vigorously and ammonium thiocyanate (3 g.) added; an orange-brown precipitate then formed at once. The solution was set aside for about 10 minutes with constant stirring, after which the *thiocyanate* had settled out. It (1·1 g.) was filtered off, well washed with cold distilled water, in which it was very slightly soluble, and dried in a vacuum-desiccator (Found : C, 34·3; H, 4·1; N, 4·8; S, 11·3; Ni, 7·3. $C_{23}H_{32}N_3S_3As_4Ni$ requires C, 34·3; H, 4·0; N, 5·2; S, 11·9; Ni, 7·3%). The compound dissolved in warm alcohol to an orange solution which reacted immediately with silver nitrate to give a white precipitate in a green solution. The solubility of this tervalent nickel complex in alcohol was greater than that of the bivalent complex. The compound had to be analysed and the magnetic moment determined as soon as it was prepared, for after a few days decomposition was apparent, the odour of organic sulphur compounds being detected. Magnetic susceptibility : powder form at 14° : $\chi = 1{\cdot}45 \times 10^{-6}$, $\chi_M = 1170 \times 10^{-6}$, correction for diamagnetism = 490 × 10^{-6}, whence $\mu = 1{\cdot}95$ B.M.

Di-(o*-phenylenedidimethylarsine*)*nickel Tri-iodide*.—The tervalent nickel chloride complex, $[NiCl_2(Diarsine)_2]Cl$ (1·4 g.), was dissolved in distilled water (350 ml.) as quickly as possible by gentle warming, and the solution filtered and treated at once with sodium iodide (5 g.) in distilled water (20 ml.). The green solution first became brown and then a black precipitate was formed. The latter was allowed to coagulate for a few minutes, then filtered off, and washed many times with distilled water until the washings had only a faint pink colour. The *complex* (1·7 g.) was dried in a vacuum-desiccator (Found : C, 23·7; H, 3·4; I, 37·9; Ni, 5·9. $C_{20}H_{32}I_3As_4Ni$ requires C, 23·7; H, 3·2; I, 37·6; Ni, 5·8%). Although insoluble in cold water or alcohol, the substance was slightly soluble in hot aqueous alcohol to a pink solution. Magnetic susceptibility : powder form at 22° : $\chi = -0{\cdot}46 \times 10^{-6}$, whence $\mu = 0$.

Tris-(o*-phenylenebisdimethylarsine*)*nickel*(II) *Perchlorate*.—This compound was obtained in a slightly impure form from the mother-liquors of the preparation of the tervalent nickel chloride complex. The red residues from several preparations of the compound $[NiCl_2(Diarsine)_2]Cl$ were treated with filtered air for about 3 weeks, a little extra hydrochloric acid being added to the solution. After this time the solution was still reddish-brown and a little more of the tervalent complex had crystallised out. The solution was then filtered, diluted to about 70 ml. with distilled water, and treated with excess of 30% perchloric acid. A reddish precipitate was obtained which was filtered off and well washed with distilled water, in which it was only very slightly soluble to give a pink solution. The filtrate was initially green owing to the excess nickel chloride present. The *perchlorate* was then dried in a vacuum-desiccator, the colour changing from red to brown, possibly owing to the loss of water of crystallisation (Found : C, 32·3; H, 4·2; Cl, 7·0; Ni, 5·55. $C_{30}H_{48}O_8Cl_2As_6Ni$ requires C, 32·3; H, 4·3; Cl, 6·4; Ni, 5·25%). The compound was soluble in warm water to give a red solution, but was insoluble in other solvents. It gave only a slight precipitate (corresponding to about 0·2—0·3% of chlorine) with silver nitrate and nitric acid after prolonged heating, showing that a trace of $[NiCl_2(Diarsine)_2]ClO_4$ probably was present. The perchlorate ion does not react with silver nitrate under the above conditions. Magnetic susceptibility; powder form at 21·5° : $\chi = -0{\cdot}38 \times 10^{-6}$, whence $\mu = 0$.

Potentiometric Titrations.—Oxidation–reduction. The red bivalent complex $[Ni(Diarsine)_2]Cl_2$ (0·0451 g.) was dissolved in ice-cold distilled water (50 ml.), 10N-hydrochloric acid (0·2 ml.) added, and the solution stirred vigorously in a 250-ml. vessel immersed in ice-water. A bright platinum electrode was placed in the solution which was connected to a silver–silver chloride–saturated potassium chloride electrode through a potassium chloride agar bridge. Ceric sulphate (0·01774M.) was run in immediately, the minimum time elapsing between dissolution of the compound and the titration. The result of the titration is shown in Fig. 2.

Chloride ion. The tervalent nickel chloride complex (0·1565 g.), was dissolved in absolute alcohol (70 ml.) and distilled water (30 ml.), and N-nitric acid (10 ml.) added just before titration. The solution was stirred vigorously in a 250-ml. vessel. A silver–silver chloride electrode was inserted and the solution connected to a silver–silver chloride–saturated potassium chloride reference electrode through an ammonium nitrate agar bridge. The temperature throughout was 20°. The solution was then titrated with silver nitrate solution (0·104N.) from a microburette. The results are shown in Fig. 3. It was necessary to use a high concentration of alcohol in the solvent for this titration, otherwise after the addition of 1 equivalent of silver nitrate no inflexion was observed.

Molecular Conductivity of Tervalent Nickel Chloride Complex.—Measurements were carried out in a pipette-type cell of volume about 15 ml. and cell constant 0·0508 cm.$^{-1}$; the conductivity water used had a specific conductance of 1·3 × 10^{-6} mho/cm.^{3} at 25°. The tervalent nickel chloride complex $[NiCl_2(Diarsine)_2]Cl$ (0·0720 g.) was well dried and finely powdered to hasten dissolution, and dissolved quickly in about 50 ml. of warm conductivity water and the solution adjusted to 100 ml. at 25°. This gave a solution containing one g.-mol. per 1024 l. The cell was then filled and the conductivity measured at 25° in a thermostat. Three lots of the solution were used, and the results showed that the conductivity increased a little more rapidly with time when the solution was in the cell than when kept in a flask in the thermostat; a slight catalytic effect of the platinum may be responsible, but in any case the differences were small and may not be significant. By extrapolation to zero time it is concluded that the initial molecular conductivity of the M/1024-solution was 120 mho, and hence it follows that the complex forms two ions in solution. The solution gradually lost the green colour, becoming first yellow, then finally orange-red, and the odour of the diarsine was observed after this decomposition had occurred. The following figures show how the molecular conductivity increased with time :

Solution no.	Time (mins.).	Molecular conductivity, mho.	Solution no.	Time (mins.).	Molecular conductivity, mho.
1	0	120 (estim.)	3	153	149 (estim.)
1	42	124	3	218	157
1	47	127	3	233	159
1	78	135	3	271	164
2	83	136	3	358	175
2	85	139	3	1598	269
2	91	143	3	2173	373
3	95	137	3	3073	450
3	105	142	3	3388 (2½ days)	450

Reduction of the Tervalent Nickel Chloride Complex.—The monochloride $[NiCl_2(Diarsine)_2]Cl$ (0·3 g.) was dissolved in distilled water (125 ml.) and filtered at once. Sulphur dioxide was passed into the green solution. Within a minute the solution became orange; finally it was red. After five minutes (to ensure that reduction was complete), excess of a 60% solution of perchloric acid was added and a buff-pink precipitate of the bivalent perchlorate $[Ni(Diarsine)_2][ClO_4]_2$ was obtained. This was filtered off and well washed with distilled water and identified by analysis (Found : C, 29·3; H, 3·8; Ni, 7·1). Calc. for $C_{20}H_{32}O_8Cl_2As_4Ni$: C, 29·0; H, 3·9; Ni, 7·1%). The compound was diamagnetic as required for a planar four-covalent complex of bivalent nickel.

Analysis.—Halogen was determined by heating about 0·1—0·2 g. of the compound with 20 ml. of 0·05N-silver nitrate in the presence of about 10 ml. of 15N-nitric acid on the water-bath until decomposition was complete. The excess of silver nitrate was then determined with standard ammonium thiocyanate solution. Total halogen in perchlorates was determined by the Carius method.

Nickel was determined by dimethylglyoxime after oxidation of organic matter and removal of the arsenic. About 0·2 g. of the compound was folded in a small filter paper and digested in a Kjeldahl flask with potassium sulphate (5 g.) and concentrated sulphuric acid (10 ml.). When the solution had become clear, distilled water (150 ml.) was added and the arsenic precipitated with hydrogen sulphide. The arsenious sulphide was then filtered off and the excess of hydrogen sulphide removed by boiling. The nickel was then precipitated with dimethylglyoxime in the usual manner and weighed.

Microanalyses for carbon, hydrogen, nitrogen, and sulphur were carried out by Messrs. Weiler and Strauss, Oxford.

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