580. *Studies in Co-ordination Chemistry. Part IX.* Quadrivalent Nickel.*

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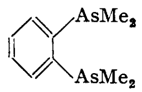
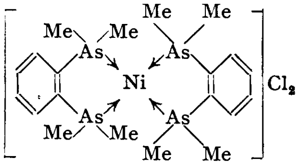
The action of several oxidising agents on the compound $[NiCl_2(diarsine)_2]Cl$ has been studied, where " diarsine " represents *o*-phenylenebisdimethylarsine. Chlorine and ceric sulphate give rise to deep green compounds which are easily reduced. Concentrated nitric acid forms an intensely blue solution from which aqueous perchloric acid precipitates the deep blue compound $[NiCl_2(diarsine)_2[ClO_4]_2$. The chemical and physical properties of this compound indicate that the nickel atom is quadrivalent. The compound is diamagnetic as required for an octahedral complex of Ni(IV) with covalent $3d^24s4p^3$ bonds. The compound is practically insoluble in water but an aqueous suspension is easily reduced by sulphur dioxide to the yellow compound $[NiCl_2(diarsine)_2]ClO_4$. The corresponding bromide, $[NiBr_2(diarsine)_2][ClO_4]_2$, has been prepared also by the action of nitric acid and perchloric acid upon the compound $[NiBr_2(diarsine)_2]Br$. This new compound is deep green and is also diamagnetic. The properties of these compounds are discussed and the literature dealing with ter- and quadri-valent nickel is reviewed.

IN Part V of this series (*J.*, 1950, 2061) the compounds formed by nickel salts with the ditertiary arsine chelate group *o*-phenylenebisdimethylarsine (I) were described. Bivalent nickel gives rise to a series of red complex salts with the general formula $[Ni(diarsine)_2]X_2$ (X = Cl, Br, I, CNS, ClO_4), as in (II); from the diamagnetism of these it is concluded that the four bonds to the metal atom are square planar, the bonds being $3d4s4p^2$. Oxidation of (II) with chlorine

(I.)





(II.)

in aqueous solution, or preferably, with air and hydrochloric acid in alcoholic solution, gave a brownish-yellow compound with the formula $[NiCl_2(diarsine)_2]Cl$. The anion of this complex salt may be replaced by ClO_4^- and $\frac{1}{2}PtCl_6^{--}$; treatment of the compound with sodium bromide and thiocyanate in aqueous solution gives the corresponding bromide and thiocyanate, *i.e.*, $[NiBr_2(diarsine)_2]Br$ and $[Ni(CNS)_2(diarsine)_2]CNS$. The magnetic moments of these compounds (*ca.* 1·9 Bohr magnetons), as well as other chemical and physical properties, led to the conclusion that they are octahedrally co-ordinated complexes of tervalent nickel, as shown in (III), the two Cl atoms being shown as *trans* for convenience. The location of the unpaired electron is uncertain, but the use by the nickel atom of $3d^24s4p^3$ octahedral covalent bonds in the usual configuration scheme necessitates its promotion above the 4*p* level, probably into a 5*s* orbital (see Table I). Such a promotion should facilitate its removal by oxidation to give an octahedral diamagnetic complex of quadrivalent nickel, the latter then being isoelectronic with tervalent cobalt. Some evidence which suggested that this promotion took place was mentioned in Part V (*loc. cit.*); in a potentiometric titration, with ceric sulphate as the oxidant, it was shown that the bivalent compound $[Ni(diarsine)_2]Cl_2$ could be oxidised to the compound $[NiCl_2(diarsine)_2]Cl$ with an end-point after one equivalent of oxidising agent had been added. After the end-point had been passed further addition of ceric sulphate gave a deep green precipitate, and it was suggested that this might contain quadrivalent nickel.

The compound $[NiCl_2(diarsine)_2]Cl$ has now been treated with several other oxidising agents in an attempt to achieve this oxidation. When chlorine is bubbled through an aqueous solution of this substance the colour changes very quickly from a pale green to a deeper emerald-green. Addition of hydrochloric acid then yields a bright green precipitate; this substance is fairly soluble in water, and since it is precipitated by hydrochloric acid the anion

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* Part VIII, *J.*, 1951, 1767.

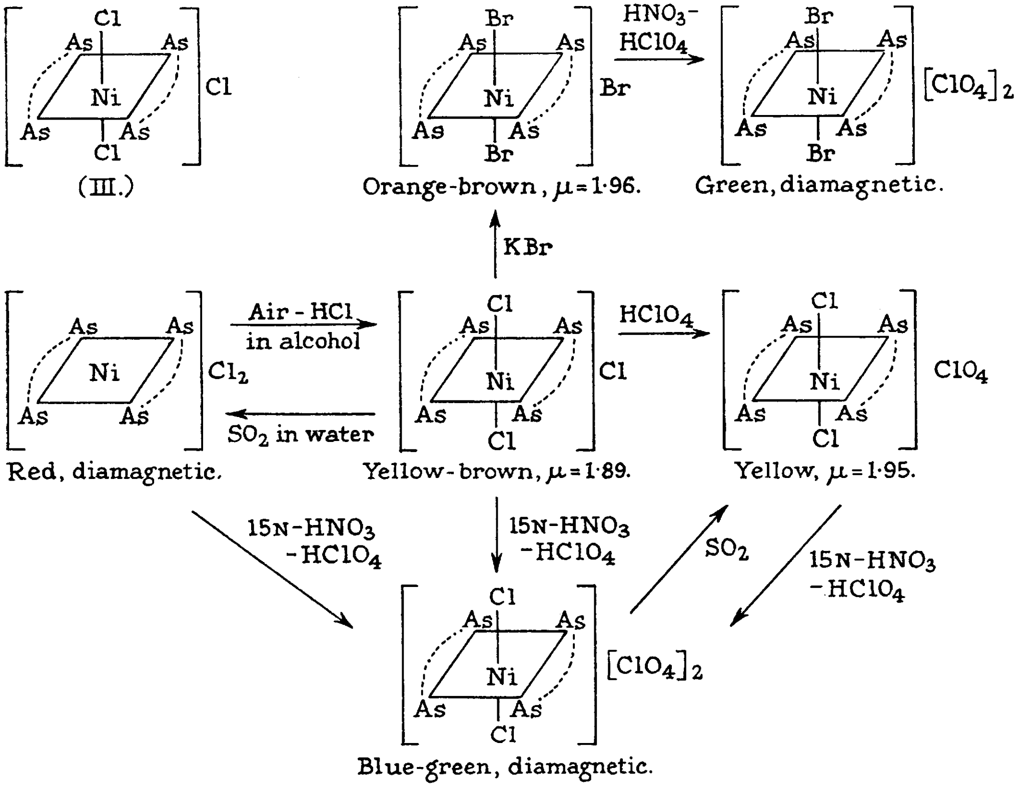
TABLE I.

Predicted magnetic moments for various nickel complexes.

Valency.	Bond type.	Unpaired electrons.	Calc. mag. moment (μ, B.M.).
II	Ionic (or $4s4p^3$ tetrahedral; or $4s4p^34d^2$ octahedral)	2	2·83
II	Covalent $3d4s4p^2$ square planar	0	0·00
II	Covalent $3d^24s4p^3$ octahedral	0 *	0·00
III	Ionic (or $4s4p^34d^2$ octahedral)	3	3·88
III	Covalent $3d^24s4p^3$ octahedral	1	1·73
IV	Ionic (or $4s4p^34d^2$ octahedral)	4	4·90
IV	Covalent $3d^24s4p^3$ octahedral	0	0·00

* It is assumed that 2 electrons are promoted to a 5*s* orbital in which they are paired.

is apparently the chloride ion. On storage, the compound becomes yellow within a few hours. Analysed after being dried in a desiccator in presence of chlorine, the compound contained about 90% of the chlorine required for the formula $[NiCl_2(diarsine)_2]Cl_2$. The magnetic susceptibility was not measured exactly, but the substance was paramagnetic and the paramagnetic susceptibility gradually increased. As this compound was clearly too unstable for investigation, the precipitation of the corresponding perchlorate was attempted. When aqueous perchloric acid is added to the emerald-green solution obtained by chlorine oxidation, a green precipitate is obtained which is much less soluble than the chloride. The magnetic susceptibility of this compound ($\chi_g = 1·0 \times 10^{-6}$) was less than that of the tervalent perchlorate $[NiCl_2(diarsine)_2]ClO_4$ for which $\chi_g = 1·46 \times 10^{-6}$, suggesting that some formation of a diamagnetic complex had taken place; however, the chlorine analysis was too high for the compound $[NiCl_2(diarsine)_2][ClO_4]_2$ which one might expect to be formed. The method of oxidation appeared to be unsatisfactory probably because the dilution necessary to get the tervalent complex into aqueous solution resulted in some oxidation of the tertiary arsine. Both of these green compounds were easily reduced by sulphur dioxide. The chloride first becomes yellow and finally red, owing to the eventual formation of the $[Ni(diarsine)_2]^{++}$ ion. The perchlorate


(III.)

was readily reduced to the yellow compound $[NiCl_2(diarsine)_2]ClO_4$, the insolubility of which makes it more resistant to the action of sulphur dioxide.

Treatment of an aqueous solution of $[NiCl_2(diarsine)_2]Cl$ with ceric sulphate in sulphuric acid solution gives a deep green precipitate, analysis of which suggests the formula $[NiCl_2(diarsine)_2][Ce(SO_4)_3]$, both metals being quadrivalent. The compound became yellow when kept. It was isolated in small amounts only, and the magnetic susceptibility was not measured. The freshly prepared compound reacts with aqueous perchloric acid to give a more stable deep blue-green compound, more easily prepared as follows.

Concentrated nitric acid has been found to be a very effective oxidising agent. When added to 15N-nitric acid, the finely divided tervalent compound $[NiCl_2(diarsine)_2]Cl$ dissolved at once to an intensely blue-black solution. The solution was treated almost immediately with perchloric acid, followed by a large volume of water, and a deep bluish-green precipitate was obtained. This substance is practically insoluble in water and its analysis agreed fairly closely with the formula $[NiCl_2(diarsine)_2][ClO_4]_2$; it does not contain nitrogen, confirming that the colour is not due to a nitrosyl group. Similar reactions occur when the compounds $[Ni(diarsine)_2]Cl_2$ and $[NiCl_2(diarsine)_2]ClO_4$ are treated with concentrated nitric acid and perchloric acid. The deep blue product is fairly stable on storage but undergoes some decomposition if left exposed to sunlight or when freely exposed to the atmosphere for some days, becoming yellow in the process.

Owing to its insolubility in water, it is not easy to carry out many chemical reactions with the compound. However, it redissolves in concentrated nitric acid to give a deep blue solution, the colour of which gradually fades owing to slow decomposition of the complex. The compound is unaffected by cold concentrated hydrochloric acid, but on being warmed the blue-green suspension quickly becomes yellow. This yellow suspension, and the original compound, are both easily reduced by stannous chloride to give a buff-pink precipitate, the colour of which indicates the presence of the $[Ni(diarsine)_2]^{++}$ ion. An aqueous suspension of the complex becomes yellow when treated with sulphur dioxide; the yellow product is paramagnetic and its analysis is correct for the compound $[NiCl_2(diarsine)_2]ClO_4$. When the blue-green complex is treated with potassium iodide and starch solution, a blue colour develops and a black precipitate is formed. This black compound has been described previously, its formula (when pure) being $NiI_3(diarsine)_2$ (see Part V); it is diamagnetic and of uncertain constitution. This formation of a blue colour with starch indicates the liberation of iodine and provides strong evidence for a higher valency state of nickel. Unfortunately, the reaction could not be carried out stoicheiometrically; since both the starting material and the product are highly insoluble in water only a limited amount of iodine is obtained. The compound $NiI_3(diarsine)_2$ appears to form a coating over the quadrivalent complex; this has been confirmed by isolating the product. Analysis confirms that only partial conversion into the complex iodide has occurred.

The substance has been found to be diamagnetic ($\chi_g = -0{\cdot}3 \times 10^{-6}$). After correction for atomic diamagnetism, the molar susceptibility corresponds to a magnetic moment of about 0·7 Bohr magneton; the corrected molar susceptibility is only about one-eighth of that usually observed for paramagnetic compounds containing only one unpaired electron. This small moment is clearly not due to any integral number of unpaired electrons and is ascribed partly to the uncertainty of the diamagnetic correction and partly to impurities. For comparative figures of the magnetic susceptibilities and moments of the complexes of bi-, ter-, and quadrivalent nickel with the ditertiary arsine, see Table II. Data for a typical bivalent nickel compound with "ionic" bonds, $[Ni(NH_3)_6]Br_2$, are also included. It should be noted that even the diamagnetic compound $[Ni(diarsine)_2]Cl_2$ has a moment of 0·5 B.M. after correction for atomic diamagnetism. Data for two other diamagnetic octahedral complexes of cobalt are also quoted to show the size of the moment after the diamagnetic correction is made. When used to indicate the number of unpaired electrons, it is considered that μ may safely be taken as formally zero when the corrected molar susceptibility from which it is calculated is less than 250, which is the case here.

As shown in Table I, diamagnetism is also expected for square four-covalent complexes of Ni(II) and for octahedral covalent $3d^24s4p^3$ Ni(II) complexes such as $[Ni(diarsine)_3][ClO_4]_2$. However, it has not been found possible to formulate the compound $[NiCl_2(diarsine)_2][ClO_4]_2$ as either of these stereochemical types whereas it is readily formulated as an octahedral Ni(IV) complex.

By treating the orange compound $[NiBr_2(diarsine)_2]Br$ with concentrated nitric acid followed by perchloric acid a similar reaction to that shown by the chloride takes place. A deep green perchlorate is obtained, analysis of which indicates the formula $[NiBr_2(diarsine)_2][ClO_4]_2$. Like the corresponding chloride, this compound is diamagnetic. It reacts with potassium iodide–starch solution to give a blue colour and is reduced by sulphur dioxide to the orange perchlorate of the lower valency state.

TABLE II.

Magnetic susceptibilities (at 20°) of nickel complexes.

Valency of Ni.	Compound.*	χ_g.†	χ_M.†	Diamag. corrn.[a]	$\chi_{corr.}$.†	Moment (μ, B.M.).
II	$[NiX_2]Cl_2$	−0·50	−351	436	85	(0·5)
II	$[Ni(NH_3)_6]Br_2$	12·7	4099	152	4251	3·16
III	$[NiCl_2X_2]Cl$	1·41	1065	452	1517	1·89
III	$[NiCl_2X_2]ClO_4$	1·46	1170	455	1625	1·95
III	$[NiBr_2X_2]Br$	1·32	1150	489	1639	1·96
IV	$[NiCl_2X_2][ClO_4]_2$	−0·30	−272	478	206	(0·7)
IV	$[NiBr_2X_2][ClO_4]_2$	−0·29	−287	505	217	(0·7)
III	$[CoCl_2X_2]ClO_4$ [b]	−0·50	−365	455	90	(0·5)
III	$[Co\,en_3][ClO_4]_3$ [c]	−0·45	−155	210	55	(0·36)

* X = *o*-Phenylenebisdimethylarsine.

† χ_g = g.-susceptibility, χ_M = molar susceptibility, $\chi_{corr.}$ = latter after correction, × 10^{-6} in each case.

[a] The diamagnetism of the metal atom has been ignored in all cases. [b] Part VI, *J.*, 1950, 2071.

[c] Asmussen, "Magnetokemiske Undersøgelser over Uorganiske Kompleksforbindelser," Copenhagen, 1944, p. 163.

On the basis, therefore, of the method of preparation of these compounds, which involves oxidation, and of the analyses, the action on reducing agents and on potassium iodide, and finally the diamagnetism, it seems reasonable to formulate both these compounds as octahedral complexes of quadrivalent nickel with covalent $3d^24s4p^3$ bonds. An *X*-ray crystallographic examination of these compounds is most desirable but in its absence their properties are most satisfactorily accounted for on the assumption that the nickel atom is quadrivalent. The compounds are therefore named: dichloro- and dibromo-di-*o*-phenylenebisdimethylarsine-nickel(IV) perchlorate. The relation between these compounds and other nickel complexes of the ditertiary arsine, showing the structures which are proposed for the new compounds, are summarised in the diagram, the two halogen atoms being shown as *trans* for convenience.

Unfortunately, it has not been found practicable to determine by direct measurement the oxidation–reduction potential of the tervalent–quadrivalent couple, as suggested by Mr. Terrey, but this can be estimated from the method of preparation. The oxidation is readily effected by ceric sulphate (*ca.* 1·6 v.), by chlorine (*ca.* 1·36 v.), and by concentrated nitric acid (which liberates chlorine from hydrogen chloride), so the E_0 value of the couple

$$[NiCl_2(diarsine)_2]^{++}/[NiCl_2(diarsine)_2]^{+}$$

would be approximately 1·3—1·4 v. The oxidation–reduction potential for the bivalent–tervalent couple with the diarsine, $[NiCl_2(diarsine)_2]^{+}/[Ni(diarsine)_2]^{++}$, is approximately 0·7 v. (see Part V, *loc. cit.*).

In view of the suggestion that the nickel atom is quadrivalent in the above compounds, it is of interest to review other evidence in the literature for ter- and quadri-valency of nickel in complex compounds. Much work has been done during the last few years but, earlier, Hofmann and Ehrhardt (*Ber.*, 1913, **46**, 1457) claimed to have prepared the compound trisodium hexaformoximonickelate(III), and Dubsky and Kuras (*Chem. Zentr.*, 1931, **102**, I, 2045) stated that they had isolated a tervalent nickel complex of benzamidoxime. Malatesta (*Gazzetta*, 1940, **70**, 842) disagreed with the conclusions of Dubsky and Kuras, showing that the compound is diamagnetic. Feigl (*Ber.*, 1924, **57**, 758) stated that the red solution obtained by treating nickel(II) bisdimethylglyoxime with ammonia in the presence of oxidising agents contained ter- or quadri-valent nickel. However, Okac and Polster (*Coll. Czech. Chem. Comm.*, 1948, **13**, 561, 572) have asserted that the oxime rather than the nickel undergoes oxidation; they claim that the red precipitate formed by neutralisation of the red oxidised solution is obtained only when lead dioxide is used as the oxidising agent, and that lead is an essential constituent of the red precipitate. The oxidation of square nickel complexes of dioximes has also been studied by Edelman (*J. Amer. Chem. Soc.*, 1950, **72**, 5765). By the action of bromine on nickel(II) bis-α-benzildioxime a dark brown compound, considered to be bis-α-benzildioxime-nickel(III) bromide, was isolated. This substance loses the bromine on moderate heating, reverting to the bivalent complex. The corresponding iodide was obtained as bronze crystals by a similar method of oxidation. Unfortunately, the magnetic moments were not reported. In oxidation of metal complexes in which the metal atom is attached to organic groups there is always the possibility of oxidising the latter rather than the metal and the magnetic moment is therefore specially helpful. The possibility that the tertiary arsine rather than the nickel atom was being oxidised has been considered very carefully in all work with these ditertiary arsine complexes, but no evidence that this is taking place has been obtained. Edelman's compounds certainly appear to be tervalent, but in view of the previous uncertainty concerning the valency of the nickel atom in these compounds a more complete investigation of the physical properties and chemical reactions of the compounds formed by the oxidation of nickel complexes of dioximes would be desirable.

Jensen has also examined the action of halogens on square diamagnetic nickel(II) complexes. By the action of bromine on the red *trans*-bistriethylphosphinedibromonickel(II) the compound bistriethylphosphinetribromonickel(III), $NiBr_3,2PEt_3$, was obtained as violet-black crystals (*Z. anorg. Chem.*, 1936, **229**, 265). Later (*Acta Chem. Scand.*, 1949, **3**, 474) Jensen measured both the magnetic moment (1·7—1·9 B.M.) and the dipole moment (2·5 D.) and presented a sound case for the tervalency of the nickel atom, the co-ordination number of the metal atom being 5. The electric dipole moment was interpreted to mean that the shape of the molecule was a square pyramid. This substance might well be regarded as the first clearly established case for tervalent nickel in complex compounds. Jensen (*ibid.*, p. 481) also examined the action of atmospheric oxygen on the complexes of nickel with mono-, di-, and tri-aminoguanidine and suggested that the oxidation is initiated by the formation of a complex of ter- or quadri-valent nickel which then decomposes. The spontaneous oxidation of these compounds is remarkably fast.

The preparation of some complex heteropolymolybdates of quadrivalent nickel has been claimed by Hall (*J. Amer. Chem. Soc.*, 1907, **29**, 692); a compound of the formula $3BaO,NiO_2,9MoO_3,12H_2O$ was isolated. This substance is diamagnetic (Ray and Sarma, *Nature*, 1946, **157**, 627; *J. Ind. Chem. Soc.*, 1948, **25**, 205) from which it was concluded that octahedral covalent $3d^24s4p^3$ bonds are formed by a quadrivalent nickel atom. Ray and Sarma (*loc. cit.*) also described a dark purple periodate of the formula $Na(K)NiIO_6,xH_2O$ which is weakly paramagnetic (μ = 1·1—1·3 B.M.). The small paramagnetism was attributed to a slight amount of dissociation, it being claimed that the compound was an octahedral complex of quadrivalent nickel. Some difficulty was experienced in formulating this compound with the necessary six octahedral bonds. In view of the very electronegative groups to which the nickel(IV) is attached, the low moment is a little surprising at first sight, for it might be thought that the bonds would be ionic (μ = 4·90 B.M.). However, the isoelectronic cobalt(III) is diamagnetic even when connected to six oxygen atoms also, *e.g.*, in hydrated cobaltic sulphate. Lander (*Acta Cryst.*, 1951, **4**, 148; see also Lander and Wooten, *J. Amer. Chem. Soc.*, 1951, **73**, 2452) has recently described another quadrivalent nickel complex in which the nickel atom is connected to very electronegative groups. This is the compound $BaNiO_3$, obtained as a black powder. The magnetic moment (0·8 B.M.) is attributed to a small amount of dissociation. The crystal structure of this compound has been determined and it is found that the nickel atom is octahedrally co-ordinated to six oxygen atoms. A complex fluoride of quadrivalent nickel, K_2NiF_6, has been described by Klemm and Huss (*Z. anorg. Chem.*, 1949, **258**, 221), but its magnetic moment has not been reported.

The preparation of two binuclear quadrivalent nickel complexes in which the metal atom is octahedral has been reported by Hieber and Brücks (*Naturwiss.*, 1949, **36**, 312). On use, as the chelate group of *o*-mercaptoaniline, a deep blue complex was isolated, the structure of which is considered to involve a bridge of two oxygen atoms between two Ni(IV) atoms.

As the above summary indicates, the higher valency states of nickel offer a fruitful field for investigation; a more detailed study of the oxidation of square nickel complexes should prove very profitable.

EXPERIMENTAL.

*Dichlorodi-*o*-phenylenebisdimethylarsinenickel* (IV) *Perchlorate*.—The tervalent complex, $[NiCl_2(diarsine)_2]Cl$ (0·7 g.), prepared as in Part V, was very finely ground and added with stirring to cold 15N-nitric acid (30 ml.), giving a deep inky-blue solution, which was well stirred for 4 minutes, during which no change in colour was observed. After being filtered through a sintered-glass crucible, to remove any traces of insoluble matter, the blue solution was treated with 30% perchloric acid (10 ml.), followed immediately by distilled water (200 ml.), with vigorous stirring. A blue-black precipitate appeared and the solution was allowed to settle for 5 minutes. The *perchlorate* (0·78 g.) was then filtered off, well washed with distilled water, and dried *in vacuo* [Found: C, 27·0; H, 3·5; Cl (excluding ClO_4), 7·9; Ni, 6·8. $C_{20}H_{32}O_8Cl_4As_4Ni$ requires C, 26·65; H, 3·5; Cl (excluding ClO_4), 7·9; Ni, 6·52%]. No nitrogen was obtained in three separate determinations. The compound is insoluble in water and in organic solvents but dissolves in concentrated nitric acid with eventual decomposition. When heated, it becomes red at about 190° and decomposes explosively at 270°.

Reduction with sulphur dioxide. The finely divided blue nickel(IV) compound, prepared as above (0·3 g.), was suspended in water (20 ml.), and sulphur dioxide passed into the suspension. The colour changed to yellow immediately. After a few minutes the yellow compound (0·25 g.) was filtered off, well washed with distilled water, and dried. It was then paramagnetic, reduction to the tervalent *perchlorate* $[NiCl_2(diarsine)_2]ClO_4$ having taken place [Found: C, 30·2; H, 4·15; Cl (excluding ClO_4), 8·65. $C_{20}H_{32}O_4Cl_3As_4Ni$ requires C, 29·95; H, 4·0; Cl (excluding ClO_4), 8·85%].

Action of Other Oxidising Agents on $[NiCl_2(diarsine)_2]Cl$.—*Chlorine.* The chloride (0·84 g.) was dissolved in distilled water (700 ml.), the solution filtered and cooled to 10°, and chlorine passed in for 3 minutes. The colour changed from a pale to a deep emerald-green. Excess of 30% perchloric acid (20 ml.) was then added, a green precipitate being formed, which during about 10 minutes gradually darkened in colour. The compound was then filtered off, washed with distilled water saturated with chlorine, and dried over concentrated sulphuric acid in a desiccator filled with chlorine. The compound (0·75 g.) was analysed and its magnetic moment determined as soon as it was dry {Found: C, 29·4; H, 3·9; Cl (excluding ClO_4), 10·0; Ni, 7·2%. Cf. analysis for pure $[NiCl_2(diarsine)_2][ClO_4]_2$, above}. The magnetic susceptibility is given on p. 2603. On storage, the compound gradually became yellow.

Ceric sulphate. The chloride (0·3 g.), dissolved in distilled water (200 ml.), was treated with excess of ceric sulphate dissolved in dilute sulphuric acid, and a deep green precipitate was formed. This was filtered off and dried quickly; it had a formula approximating to $[NiCl_2(diarsine)_2][Ce(SO_4)_3]$ (Found: C, 20·3; H, 4·1. $C_{20}H_{32}O_{12}Cl_2S_3As_4CeNi$ requires C, 21·3; H, 2·9%). The *substance* decomposed when kept and could not be obtained pure. An aqueous solution reacted instantly with perchloric acid to give a deep blue precipitate of the compound obtained by oxidation with nitric acid. When sulphur dioxide was passed into a green solution of the compound, it became first yellow then orange-red.

*Dibromodi-*o*-phenylenebisdimethylarsinenickel*(IV) *Perchlorate.*—The finely divided orange tervalent compound, $[NiBr_2(diarsine)_2]Br$ (0·32 g.), was added to 15N-nitric acid (20 ml.) with vigorous stirring; it dissolved to form a deep green solution which was filtered through sintered glass after about 3 minutes. The filtrate was treated immediately with excess of 30% perchloric acid (5 ml.), followed by distilled water (200 ml.), a deep green crystalline precipitate being formed. After about 5 minutes the *perchlorate* (0·3 g.) was filtered off and well washed with distilled water, the last washings having a pale green colour; it was dried *in vacuo* (Found: C, 24·9; H, 3·6; Br, 16·2; Ni, 6·1. $C_{20}H_{32}O_8Br_2Cl_2As_4Ni$ requires C, 24·25; H, 3·2; Br, 16·16; Ni, 5·93%). The analysis shows that the compound could not be obtained as pure as the chloride. The substance is insoluble in organic solvents and is only slightly soluble in water. When treated with sulphur dioxide, the green suspension becomes orange at once owing to reduction. When heated the compound becomes red at about 190° and decomposes above 200°.

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