

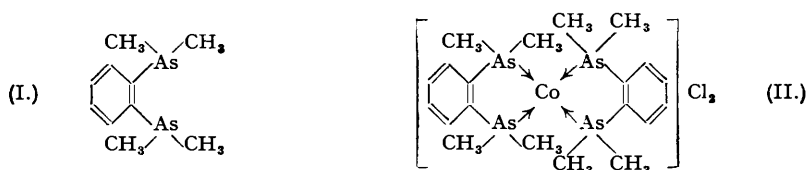
**423.** *Studies in Co-ordination Chemistry. Part VI. Complexes of Bivalent and Tervalent Cobalt with a Di(tertiary Arsine).*

By R. S. NYHOLM.

A series of complex salts of bivalent and trivalent cobalt with the di(tertiary arsine) chelate group, *o*-phenylenebisdimethylarsine, has been prepared and studied. Cobaltous halides form stable, slightly soluble salts of the formula  $[\text{Co}(\text{Diarsine})_2]\text{X}_2$ , where X = Cl, Br, I, or CNS. From the magnetic moments of these compounds it is concluded that the four bonds to the cobalt atom are covalent and planar. Aerial oxidation of these cobaltous salts gives very stable trivalent octahedral complexes, in which the diamagnetic cation contains two halogen atoms and two molecules of the chelate group attached to a cobaltic atom; the anion may be either a halogen atom or the group  $[\text{CoX}_4]^-$ , where X = Cl or CNS. The chloride, bromide, iodide, and thiocyanate complexes have been prepared and their properties are discussed. The behaviour of iron, cobalt, and nickel with this di(tertiary arsine) are compared.

In previous papers (Parts III, IV, and V, *J.*, 1950, 851, 857, 2061) the complexes of iron, rhodium, and nickel with the chelate group *o*-phenylenebisdimethylarsine (I) were investigated, and their stereochemistry was determined. It was decided to investigate the complexes of bivalent and trivalent cobalt with this chelate group since compounds of tertiary arsines with cobalt had not been described previously. With the results of this investigation available it is possible to compare and contrast the compounds of iron, cobalt, and nickel with this di(tertiary arsine);

all of these elements from covalent bonds with this chelate group in both the trivalent and the bivalent state.



The stereochemistry of bivalent cobalt is of unusual interest since octahedral complexes (both covalent and ionic), planar four-covalent complexes, and tetrahedral complexes are known. When the compound is tetrahedral, the magnetic moment does not enable one to decide whether the bonding is ionic or covalent using  $sp^3$  bonds, because the number of unpaired electrons is the same in both cases (see i and ii in Table I). The octahedral complexes usually have ionic bonds with magnetic moments between 4 and 5 B.M., e.g.,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$  has a magnetic moment

TABLE I.

Calculated magnetic moments for cobalt complexes.

Complex.	Electronic arrangement.			Calculated magnetic moment $\mu$ (B.M.).
	3d	4s	4p	
(i) Cobaltous (ionic) (tetrahedral or octahedral)	$\uparrow\downarrow\uparrow\downarrow\downarrow\downarrow$	$\square$	$\square\square\square$	3.88
(ii) Cobaltous (tetrahedral) ( $sp^3$ bonds)	$\uparrow\downarrow\uparrow\downarrow\downarrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	3.88
(iii) Cobaltous, planar ( $d^2sp^2$ bonds)	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	1.73
(iv) Cobaltous, octahedral ( $d^2sp^3$ bonds)	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	4d(?) 1.73
(v) Cobaltic (ionic)	$\uparrow\downarrow\downarrow\downarrow\downarrow\downarrow$	$\square$	$\square\square\square$	4.90
(vi) Cobaltic, octahedral ( $d^2sp^3$ bonds)	$\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$	0.0

of 5.25 B.M. (Klemm and Schuth, *Z. anorg. Chem.*, 1933, **210**, 33), but at least one octahedral complex with covalent bonds is known. This is the compound dipotassium calcium hexanitrocobalt(II)  $[\text{K}_2\text{CaCo}(\text{NO}_2)_6]$  for which Cambi, Ferrari, and Colla (*Gazzetta*, 1936, **65**, 1162) reported a magnetic moment of 1.9 B.M. As may be seen from Table I (iv) the calculated magnetic moment for an octahedral complex of bivalent cobalt with covalent bonds is 1.73 B.M., corresponding to one unpaired electron. A magnetic moment of 1.73 is also predicted for planar four-covalent complexes because this shape requires the use of  $d^2sp^2$  bonds (see iii, Table I).<sup>\*</sup> It should thus be easy to distinguish between planar four-covalent complexes and tetrahedral complexes by magnetic susceptibility measurements, since the magnetic moments are so different (1.73 B.M., compared with 3.88 B.M.). In practice the magnetic moments of both the square and the tetrahedral complexes are rather larger than these figures, probably owing to a considerable orbital contribution to the magnetic moment (Selwood, "Magnetochemistry," Interscience N.Y., 1943, p. 163). Mellor and Craig (*J. Proc. Roy. Soc. N.S.W.*, 1940, **74**, 495) reported magnetic moments between 1.8 and 2.8 B.M. for a series of planar complexes, and values between 4.2 and 5.3 B.M. for tetrahedral complexes; Selwood (*ibid.*, p. 174) and Pauling ("Nature of the Chemical Bond," N.Y., 1945, p. 114) have reported similar values. When the bonds are ionic, bivalent cobalt forms either octahedral, e.g.,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ , or tetrahedral complexes, e.g.,  $\text{M}^I_2[\text{CoCl}_4]$ . The co-ordination number is, as a rule, six in cationic complexes, and four in anionic complexes. When the cobalt atom forms covalent bonds the co-ordination number four is more common than six. Little is known of the conditions leading to square complexes; it seems, however, that if the co-ordination number is four then planar complexes are obtained only when the cobalt atom is joined to the less electro-negative atoms. Mellor and Craig (*loc. cit.*) found that four sulphur atoms tended to give the planar arrangement,

<sup>\*</sup> Calvin and his co-workers (*J. Amer. Chem. Soc.*, 1946, **68**, 2254) have shown recently by use of X-rays that certain four-covalent complexes of bivalent cobalt with one unpaired electron are planar.

but four oxygen atoms gave the tetrahedral configuration. It is apparent that bivalent cobalt forms square complexes less readily than does bivalent nickel, and increasing the electro-negativity of the attached groups results in a change to the tetrahedral configuration more readily in the former case; for example, although the compound  $\text{NiCl}_2 \cdot 2\text{PET}_3$  is planar,  $\text{CoCl}_2 \cdot 2\text{PET}_3$  is tetrahedral.

Although no complexes of bivalent cobalt with tertiary arsines have been reported previously, Jensen (*Z. anorg. Chem.*, 1936, **229**, 282) described the compound dichlorobis(triethylphosphine)cobalt(II),  $\text{CoCl}_2 \cdot 2\text{PET}_3$ , as well as the tripropylphosphine analogue, but he made no reference to the corresponding tertiary arsine complex. These phosphine complexes were unstable. Tertiary arsines usually form complexes similar to those given by tertiary phosphines, but as a rule the arsine complexes are less stable: with bivalent nickel, for example, the only tertiary arsine complex isolated by Jensen (*ibid.*, p. 265) had the formula  $\text{NiI}_2 \cdot 2\text{AsEt}_3$ , but this was less stable than the corresponding phosphine compound. For the compound  $\text{CoCl}_2 \cdot 2\text{PET}_3$ , Jensen (*ibid.*, p. 282) reported a dipole moment of 8.7 D. in benzene solution; this was taken to indicate the tetrahedral configuration rather than the less likely *cis*-planar arrangement, and the magnetic moment of this compound, 3.5 B.M. (Jensen, private communication), seems to confirm this.

When a solution of cobaltous chloride in alcohol was treated with the di(tertiary arsine), one obtained immediately a yellow precipitate of the compound di(*o*-phenylenebisdimethylarsine)cobalt(II) chloride,  $[\text{Co}(\text{Diarsine})_2]\text{Cl}_2$ , see (II). This substance was insoluble in benzene or chloroform, but was slightly soluble in warm water or warm alcohol. The aqueous solution reacted at once with silver nitrate, showing that the chlorine was ionised, but the low solubility in water, combined with the pronounced hydrolysis, vitiated attempts to determine the molecular conductivity. These properties support the assignment of the salt-like structure to this compound, and, as the magnetic moment (2.1 B.M.) indicated the presence of one unpaired electron, the four *dsp^2* cobalt-arsenic bonds are apparently planar (see iii, Table I). The bromide, iodide, and thiocyanate were prepared in a similar manner, and had magnetic moments which indicated the presence of one unpaired electron (see figure). These compounds were only very slightly soluble in water and their colours varied from yellow to brown. The colour is some guide to the stereochemistry, for Mellor and Craig (*loc. cit.*) noticed that square complexes of bivalent cobalt were some shade of brown while the ionic or tetrahedral complexes varied in colour from pink or mauve to blue; the correlation between colour and magnetic susceptibility is, however, not so well established as with the corresponding compounds of nickel. The moist chloride became green on the surface in air, owing to oxidation, and all of these bivalent complexes oxidised readily in air to give very stable complexes of trivalent cobalt.

Attempts to isolate a non-ionic complex of the formula  $[\text{Co}(\text{Hal})_2(\text{Diarsine})]$  by refluxing an alcoholic solution of cobaltous chloride with the complex salt  $[\text{Co}(\text{Diarsine})_2]\text{Cl}_2$  in an inert atmosphere were unsuccessful. When air was admitted to the reaction mixture, oxidation took place rapidly and the cobaltous salt dissolved to give a green solution from which a green complex of trivalent cobalt was obtained on cooling. The formula of this substance,  $\text{Co}_3\text{Cl}_8(\text{Diarsine})_4$ , indicates that two cobaltic and one cobaltous atom are present. The mean magnetic moment is 2.7 B.M., but on the assumption that the two cobaltic atoms are diamagnetic the moment of the cobaltous atom is 4.4 B.M. The low solubility of the compound suggested that it was a salt, and it was found that half the chlorine could be titrated with silver nitrate in alcohol solution. These facts suggested the formula  $[\text{CoCl}_2(\text{Diarsine})_2]_2[\text{CoCl}_4]$ , namely bis[dichlorodi(*o*-phenylenebisdimethylarsine)cobalt(III)] tetrachlorocobalt(II), and this was confirmed by chemical investigations. When a solution of the compound in alcohol was treated with perchloric acid the  $[\text{CoCl}_4]^-$  ion was replaced and the blue-green diamagnetic compound dichlorodi(*o*-phenylenebisdimethylarsine)cobalt(III) perchlorate,  $[\text{CoCl}_2(\text{Diarsine})_2]\text{ClO}_4$ , was precipitated. By subtracting the diamagnetic susceptibility of the cation in this compound from the magnetic susceptibility of the compound  $[\text{CoCl}_2(\text{Diarsine})_2]_2[\text{CoCl}_4]$  one obtains the magnetic susceptibility of the  $[\text{CoCl}_4]^-$  ion. These figures are given in Table II and the magnetic moment of the  $[\text{CoCl}_4]^-$  ion (4.4 B.M.) indicates three unpaired electrons and hence a tetrahedral arrangement. The magnetic moment of the  $[\text{CoCl}_4]^-$  ion was measured earlier by Barkworth and Sugden (Barkworth, Ph.D. thesis, University of London, 1937, p. 53) using the compound  $[\text{QH}]_2[\text{CoCl}_4]$ , where Q = quinoline, and these workers reported the value of 4.57 B.M.

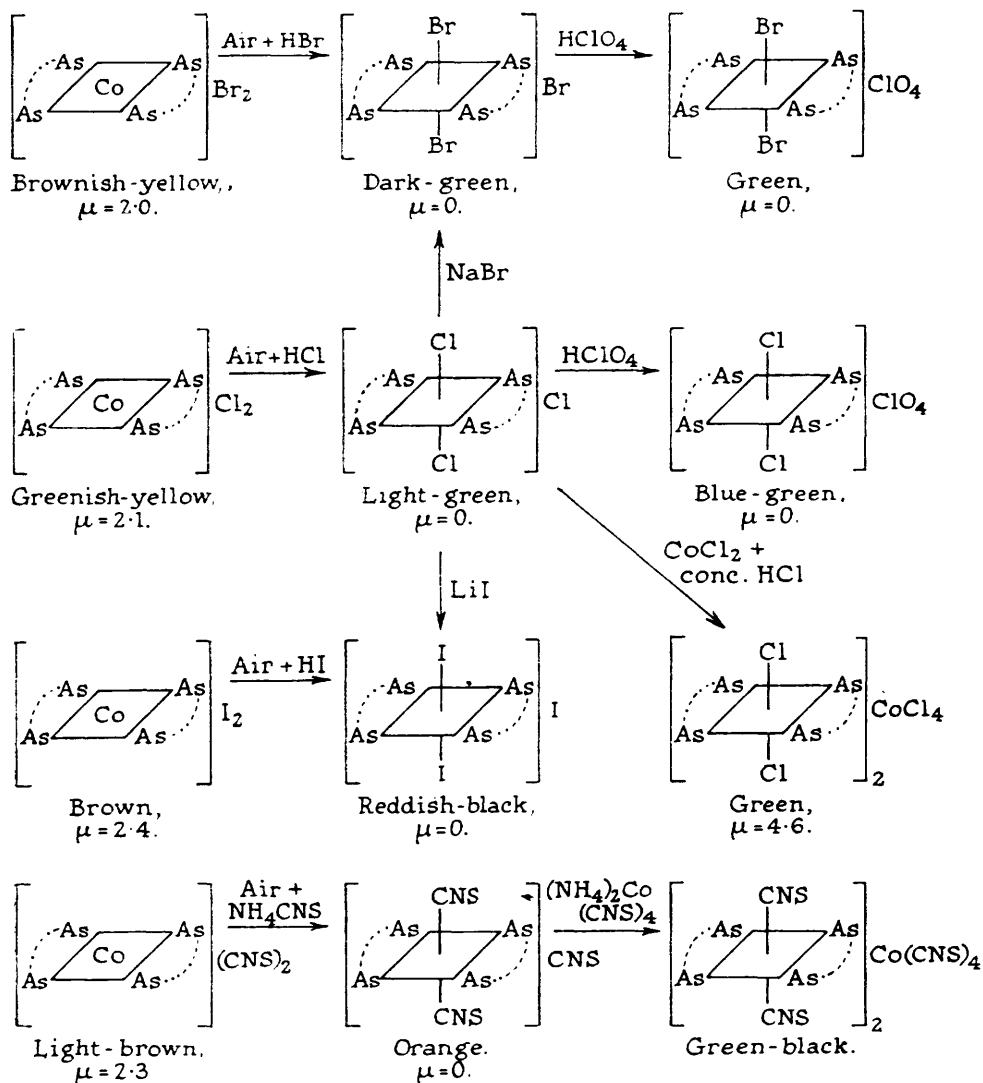
The compound dichlorodi(*o*-phenylenebisdimethylarsine)cobalt(III) chloride,  $[\text{CoCl}_2(\text{Diarsine})_2]\text{Cl}$ , is produced when the bivalent cobalt complex is oxidised in the absence of cobaltous chloride, but the product usually contains some of the less soluble  $[\text{CoCl}_4]^-$  compound because some decomposition of the cobaltous salt occurs with the formation of cobalt chloride. The

TABLE II.

Experimental magnetic susceptibilities of some cobalt complexes.

A = *o*-Phenylenebisdimethylarsine.

Compound.	$\chi_M$ (20°), $\times 10^6$ .	Diamagnetic correction, $\times 10^6$ .	$\chi_M$ (corrected for diamagnetism), $\times 10^6$ .	Magnetic moment (mean $\mu$ per cobalt atom), B.M.
(1) $[\text{CoCl}_2\text{A}_2]_2[\text{CoCl}_4]$ .....	7520	1200	8700	2.7
(2) $[\text{CoCl}_2\text{A}_2]\text{ClO}_4$ .....	-400	—	—	0.0
(3) $[\text{CoCl}_2\text{A}_2]^+$ .....	-370	—	—	0.0
(4) $[\text{CoCl}_4]^-$ .....	8260	94	8350	4.4



diamagnetic monochloride was obtained free from the  $[\text{CoCl}_4]^-$  compound by making use of the solubility of the former in a mixture of chloroform and alcohol.

When the cobaltous bromide complex was heated in air with hydrobromic acid in boiling alcoholic solution the octahedral complex  $[\text{CoBr}_2(\text{Diarsine})_2]\text{Br}$  was obtained. This compound, which is deep green, is diamagnetic like the chloride but is less soluble in alcohol. The compound

was also prepared by the action of sodium bromide on the chloride complex. No complex with the  $[\text{CoBr}_4]^-$  anion was obtained. The corresponding reddish-black trivalent iodide,  $[\text{CoI}_2(\text{Diarsine})_2]\text{I}$ , was obtained by oxidising the cobaltous iodide complex with air in the presence of hydriodic acid. This compound was conveniently prepared by treating the chloride with a suitable iodide in alcohol; like the chloride and bromide it is diamagnetic. The thiocyanate complexes of trivalent cobalt were also investigated. A deeply coloured paramagnetic compound containing the  $[\text{Co}(\text{CNS})_4]^-$  ion was obtained when the bivalent complex was oxidised in the presence of cobaltous thiocyanate; this has a constitution similar to that of the tetrachlorocobalt(II) complex, and has the formula  $[\text{Co}(\text{CNS})_2(\text{Diarsine})_2][\text{Co}(\text{CNS})_4]$ . By treating this substance with perchloric acid the orange perchlorate  $[\text{Co}(\text{CNS})_2(\text{Diarsine})_2]\text{ClO}_4$  was obtained, and this showed the expected diamagnetism. Aerial oxidation of the bivalent thiocyanate complexes takes place extremely readily even in cold alcoholic solution.

The most noteworthy property of these complexes is the very marked increase in stability in passing from the bivalent to the trivalent state; the stability of these complexes of trivalent cobalt is of special interest because the metal atom is co-ordinated with atoms of fairly low electronegativity. Pauling (*op. cit.*, p. 257) has pointed out that the atoms and groups which occur in the octahedral complexes of trivalent cobalt are in the main strongly electronegative, and instances the fact that chlorine is introduced more readily than iodine. In the trivalent iodide complex described here there are four arsenic and two iodine atoms attached to the cobalt, and all of these are of much lower electronegativity than atoms such as nitrogen or oxygen. The fact that this complex is quite stable, although it contains a metal in a high valency state attached to easily oxidisable groups like tertiary arsines and the iodide ion, emphasises the strength of the bonds. All of these trivalent complexes must be heated with silver nitrate and concentrated nitric acid for some hours to remove the halogen from the cation. Although compounds containing one iodine atom attached to a cobaltic atom are known, *e.g.*,  $[\text{Co}(\text{NH}_3)_5\text{I}]\text{X}_2$  (where X = a univalent anion) (J. W. Mellor, "Comprehensive Treatise on Inorganic Chemistry," 1935, Vol. IX, p. 695), the compound  $[\text{CoI}_2(\text{Diarsine})_2]\text{I}$  is one of the few cobaltic complexes known in which two iodine atoms are attached to the cobalt atom. Unlike  $\text{Fe}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$  derivatives, no octahedral complexes of bivalent cobalt were isolated.

The compounds prepared in this investigation and the relations between them are shown in the figure. In the trivalent complexes the two halogen atoms in the cation are shown as *trans*, but as with the corresponding trivalent compounds of iron, rhodium, and nickel it must remain speculative until proved by X-ray crystallography or until the *cis*-arrangement is established by optical resolution.

TABLE III.

Complex salts formed by iron, cobalt, and nickel with a di(tertiary arsine).

A = *o*-Phenylenebisdimethylarsine.

Iron.	Cobalt.	Nickel.
<i>Bivalent</i> $[\text{FeA}_2\text{X}_2]^0$ .	<i>Bivalent</i> $[\text{CoA}_2]\text{X}_2$ .	<i>Bivalent</i> $[\text{NiA}_2]\text{X}_2$ .
X = Br, I, CNS; non-electrolytes, diamagnetic, $\mu = 0$ , covalent $d^2sp^3$ bonds.	X = Cl, Br, I, CNS; salts, paramagnetic, $\mu = 2.0-2.4$ , covalent $dsp^3$ bonds.	X = Cl, Br, I, CNS, $\text{ClO}_4$ ; salts, diamagnetic, $\mu = 0$ , covalent $dsp^3$ bonds.
<i>Octahedral</i> (six-covalent).	<i>Planar</i> (four-covalent).	<i>Planar</i> (four-covalent) $[\text{NiA}_3](\text{ClO}_4)_2$ ; diamagnetic, $\mu = 0$ .
<i>Tervalent</i> $[\text{FeX}_2\text{A}_2][\text{FeX}_4]$ .	<i>Tervalent</i> $[\text{CoX}_2\text{A}_2][\text{CoX}_4]$ .	<i>Tervalent</i> $[\text{NiX}_2\text{A}_2]\text{X}$ .
X = Cl, Br; paramagnetic, $\mu = 2.3$ for cation and $\mu = 5.9$ for anion.	X = Cl, CNS; paramagnetic, $\mu = 0$ for cation and $\mu = 4.4$ for anion.	X = Cl, Br, CNS; paramagnetic, $\mu = 1.9$ .
$[\text{FeCl}_2\text{A}_2]\text{ClO}_4$ .	$[\text{CoX}_2\text{A}_2]\text{X}$ .	$[\text{NiCl}_2\text{A}_2]\text{B}$ .
Paramagnetic, $\mu = 2.3$ .	X = Cl, Br, I, CNS, cation contains covalent $d^2sp^3$ bonds.	B = $\text{ClO}_4$ , $\frac{1}{2}\text{PtCl}_6$ , $\mu = 1.9$ , orbitals doubtful.
$[\text{FeBr}_2\text{A}_2]\text{X}$ .	<i>Octahedral</i> .	<i>Octahedral</i> .
X = Br, $\text{ClO}_4$ , cation covalent, $d^2sp^3$ bonds.		
<i>Octahedral</i> .		

In Table III the behaviour of iron, cobalt, and nickel with this di(tertiary arsine) is compared so far as these investigations have proceeded. This chelate group provides a unique opportunity

for comparing the behaviour of these three metals because they form stable complexes with this diarsine in both the bivalent and trivalent states. The bonds were in all cases covalent but no unusual co-ordination numbers were observed. In the bivalent state iron forms solely octahedral complexes; the iodide and bromide are stable in air, but the chloride undergoes aerial oxidation very readily. Bivalent cobalt and nickel both form square four-covalent complexes but in addition nickel gives rise to an octahedral complex. The reluctance of bivalent cobalt to form octahedral complexes with covalent bonds is well known and towards this chelate group the ease with which these three metals form such compounds is  $\text{Fe} > \text{Ni} \gg \text{Co}$ ; this order has also been observed with other co-ordinating groups, e.g., dipyriddy.

In the trivalent state all of these elements give octahedral covalent complexes of marked stability, the cobaltic complexes containing particularly strong bonds.

This chelate group also co-ordinates readily with univalent copper, and complexes with the formulæ  $[\text{Cu}(\text{Diarsine})_2]\text{X}$  and  $[\text{CuX}, \text{Diarsine}]_2$  have been prepared, where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ . This work, in collaboration with Mr. A. Kabesh, will be described in Part VII of this series.

#### EXPERIMENTAL.

*Di-(o-phenylenebisdimethylarsine)cobalt(II) Chloride.*—Cobalt chloride hexahydrate (1.2 g.) in alcohol (20 ml.) was treated with *o*-phenylenebisdimethylarsine (1.4 g.) in alcohol (40 ml.), and the solution well shaken. A greenish-yellow powder was precipitated immediately and after being heated on the water-bath for a few minutes the mixture was cooled and filtered. The *chloride* (1.3 g.) was well washed with cold alcohol, in which it was slightly soluble, and dried in a vacuum-desiccator (Found: C, 33.9; H, 4.6; Cl, 10.1.  $\text{C}_{20}\text{H}_{32}\text{Cl}_2\text{As}_2\text{Co}$  requires C, 34.2; H, 4.55; Cl, 10.1%). The compound dissolved in hot water to an orange-brown solution, some decomposition occurring as was shown by the odour of the diarsine. It was also soluble to some extent in alcohol, and treatment of the alcoholic solution with silver nitrate gave a precipitate of silver chloride at once. The compound was insoluble in benzene or chloroform. When left in the air in a moist condition the compound turned green on the surface owing to oxidation. Unless tightly stoppered it developed the odour of the diarsine fairly quickly when kept owing to decomposition. Prolonged refluxing of this compound with alcoholic cobaltous chloride in carbon dioxide caused no change, but in the presence of air rapid oxidation to a cobaltic complex occurred. Magnetic susceptibility: powder form at  $28.5^\circ$ :  $\chi = 2.02 \times 10^{-6}$ ,  $\chi_M = 1420 \times 10^{-6}$ , correction for diamagnetism =  $436 \times 10^{-6}$ , whence  $\mu = 2.1$  B.M.

*Di-(o-phenylenebisdimethylarsine)cobalt(II) Bromide.*—Cobalt chloride hexahydrate (0.9 g.) and sodium bromide (4 g.) were dissolved in a mixture of alcohol (70 ml.) and distilled water (30 ml.) by heat, and the solution was treated with *o*-phenylenebisdimethylarsine (1.5 g.) in alcohol (50 ml.). The solution was well shaken. A brownish-yellow precipitate appeared immediately. After the mixture had been heated on the water-bath for a few minutes the *bromide* was filtered off and well washed with alcohol in which it was very slightly soluble. The substance (1.4 g.) was then dried in a vacuum-desiccator (Found: C, 30.7; H, 4.3; Br, 20.0.  $\text{C}_{20}\text{H}_{32}\text{Br}_2\text{As}_2\text{Co}$  requires C, 30.3; H, 4.05; Br, 20.2%). The compound was slightly soluble in hot water to a brownish-orange solution which had a marked odour of the diarsine owing to hydrolysis. It was insoluble in benzene or chloroform. Magnetic susceptibility: powder form at  $22^\circ$ :  $\chi = 1.46 \times 10^{-6}$ ,  $\chi_M = 1155 \times 10^{-6}$ , correction for diamagnetism =  $468 \times 10^{-6}$ , whence  $\mu = 2.0$  B.M.

*Di-(o-phenylenebisdimethylarsine)cobalt(II) Iodide.*—Cobalt chloride hexahydrate (1.2 g.) and lithium iodide (3 g.) were dissolved in alcohol and the filtered solution was treated with *o*-phenylenebisdimethylarsine (1.5 g.) in alcohol (75 ml.). A brown precipitate was formed immediately and after the mixture had been heated on the water-bath for a few minutes the *iodide* was filtered off, well washed with alcohol, in which it was practically insoluble, and dried in a vacuum-desiccator (yield, 1.8 g.) (Found: C, 26.8; H, 3.8.  $\text{C}_{20}\text{H}_{32}\text{I}_2\text{As}_2\text{Co}$  requires C, 27.1; H, 3.6%). The compound was much less soluble than the chloride or the bromide in both alcohol and water, but hot water produced the odour of the diarsine, showing that some dissolution with decomposition took place. Magnetic susceptibility: powder form at  $15^\circ$ :  $\chi = 2.30 \times 10^{-6}$ ,  $\chi_M = 2040 \times 10^{-6}$ , correction for diamagnetism =  $490 \times 10^{-6}$ , whence  $\mu = 2.4$  B.M.

*Di-(o-phenylenebisdimethylarsine)cobalt(II) Thiocyanate.*—Cobaltous chloride hexahydrate (0.7 g.) and ammonium thiocyanate (1.5 g.) were dissolved in alcohol (40 ml.) and distilled water (5 ml.), and the deep-blue solution was added to *o*-phenylenebisdimethylarsine (1.45 g.) in alcohol (40 ml.). A grey precipitate was obtained immediately, and after 5 minutes' heating on the water-bath the solution was cooled and filtered, and the residue well washed with alcohol. The filtrate was red, owing to partial oxidation to form the trivalent cobalt complex. The *thiocyanate* (1.6 g.) was dried in a vacuum-desiccator (Found: C, 34.5; H, 4.1.  $\text{C}_{22}\text{H}_{32}\text{N}_2\text{S}_2\text{As}_2\text{Co}$  requires C, 35.3; H, 4.3%). The compound was insoluble in water or alcohol but in the presence of air dissolved rapidly in alcohol owing to oxidation. When preparing this compound it was difficult to avoid the formation of some of the compound  $[\text{Co}(\text{Diarsine})_2][\text{Co}(\text{CNS})_4]$ , and the presence of a small amount of this substance is suggested by the analysis. Magnetic susceptibility: powder form at  $20^\circ$ :  $\chi = 2.34 \times 10^{-6}$ ,  $\chi_M = 1740 \times 10^{-6}$ , correction for diamagnetism =  $450 \times 10^{-6}$ , whence  $\mu = 2.3$  B.M.

*Bis[dichloro-di-(o-phenylenebisdimethylarsine)cobalt(III)]tetrachlorocobalt(II).*—The cobaltous chloride complex,  $[\text{Co}(\text{Diarsine})_2]\text{Cl}_2$  (2.0 g.), was added to a filtered solution of cobaltous chloride hexahydrate (0.9 g.) in alcohol (210 ml.) containing 10N-hydrochloric acid (5 ml.). The solution was then heated under reflux, filtered air being brought into contact with the surface of the solution. After about 1 hour green crystals began to form, and the cobaltous complex gradually dissolved. After about 4 hours all

of the cobaltous salt had been oxidised to give a deep-green solution. This was then filtered hot, and on cooling green crystals (2.2 g.) of the required compound were obtained (Found: C, 29.8; H, 3.9; Cl, 17.8; Co, 10.9.  $C_{40}H_{64}Cl_3As_3Co_3$  requires C, 29.9; H, 4.0; Cl, 17.7; Co, 11.0%). The compound could be recrystallised from alcohol containing a little hydrochloric acid and cobaltous chloride; in the absence of these, some formation of the more soluble monochloride occurred. As expected from the formula, potentiometric titrations with silver nitrate and a silver electrode showed that half of the total chlorine was ionised. The compound was insoluble in water, but dissolved in a large volume of alcohol, but in this solvent it was very much less soluble than the monochloride. Magnetic susceptibility: powder form at 24°:  $\chi = 4.63 \times 10^{-6}$ ,  $\chi_M = 7440 \times 10^{-6}$ , correction for diamagnetism =  $1200 \times 10^{-6}$ , whence mean  $\mu$  per Co atom = 2.7 B.M., and  $\mu$  for one Co atom (in the  $[CoCl_4]^-$  anion) = 4.6 B.M.

*Dichlorodi-(o-phenylenebisdimethylarsine)cobalt(III) Chloride*.—This compound is obtained in alcoholic solution contaminated with the above tetrachlorocobalt(II) compound by aerial oxidation under reflux of the bivalent salt  $[Co(Diarsine)_2]Cl_2$  in the presence of a little hydrochloric acid. Some decomposition of the cobaltous salt gives rise to some cobaltous chloride which forms the complex anion. The substance was prepared more conveniently from the tetrachlorocobalt(II) compound as follows.

The compound  $[CoCl_2(Diarsine)_2]_2[CoCl_4]$  (1.6 g.), containing a little of the monochloride, was dissolved in alcohol (250 ml.) by heat, water (100 ml.) containing 10N-hydrochloric acid (2 ml.) added, and the cooled solution shaken immediately with chloroform (250 ml.) in a separating funnel. The extraction was repeated twice. The chloroform solution was filtered, concentrated to about 75 ml., and treated with light petroleum at the b. p. until just cloudy. On cooling, beautiful bright green needles of the required chloride (0.9 g.) were obtained (Found: C, 31.9; H, 4.4; Cl, 14.7; Co, 8.0.  $C_{20}H_{32}Cl_3As_2Co$  requires C, 32.5; H, 4.3; Cl, 14.5; Co, 8.0%). The compound was very soluble in alcohol, slightly soluble in water, and soluble in chloroform containing a little alcohol. The alcoholic solution reacted instantly with silver nitrate solution to give a precipitate of silver chloride, but the solution remained green because the chlorine in the cation did not react. Magnetic susceptibility: powder form at 14.5°:  $\chi = -0.40 \times 10^{-6}$ , whence  $\mu = 0$ .

*Dichlorodi-(o-phenylenebisdimethylarsine)cobalt(III) Perchlorate*.—The tetrachlorocobalt(II) compound,  $[CoCl_2(Diarsine)_2]_2[CoCl_4]$  (0.7 g.), was dissolved in alcohol (50 ml.) and, after it had cooled, 30% perchloric acid was added in considerable excess. A beautiful greenish-blue precipitate was obtained immediately; this was filtered off and washed many times with alcohol, in which it was insoluble (0.6 g.) (Found: C, 30.2; H, 4.0.  $C_{20}H_{32}O_4Cl_3As_2Co$  requires C, 30.0; H, 4.0%). The compound was insoluble in water and other solvents. On heating it exploded above 300°. Magnetic susceptibility: powder form at 19°:  $\chi = -0.50 \times 10^{-6}$ , whence  $\mu = 0$ .

*Dibromodi-(o-phenylenebisdimethylarsine)cobalt(III) Bromide*.—The cobaltous bromide complex,  $[Co(Diarsine)_2]Br_2$  (1.2 g.), was added to alcohol (125 ml.) containing 48% hydrobromic acid (5 ml.), and the solution refluxed for several hours with free access of filtered air to the surface of the solution. The cobaltous salt, which was initially in suspension, gradually dissolved to form a deep-green solution. A green compound began to crystallise from the solution after about 1 hour; at the end of 12 hours all the cobaltous salt had disappeared and the flask contained a mixture of green crystals and a deep-green solution. The hot solution was then filtered, the green crystals were dissolved in hot alcohol (125 ml.), and the solution was filtered and added to the first filtrate. The whole solution was then concentrated on the steam-bath to half its bulk and allowed to cool. Dark green flat rhombs of the required bromide (0.2 g.) crystallised on cooling (Found: C, 27.8; H, 4.1; Br, 27.4; Co, 6.85.  $C_{20}H_{32}Br_2As_2Co$  requires C, 27.5; H, 3.7; Br, 27.5; Co, 6.75%). The compound was readily soluble in alcohol but insoluble in water; it dissolved in chloroform containing a little alcohol. The alcoholic solution reacted instantly with silver nitrate to precipitate only the anionic bromine, for the solution remained green. The two covalently bound bromine atoms in the cation could be made to react with silver nitrate only by prolonged heating in the presence of concentrated nitric acid. Magnetic susceptibility: powder form at 20°:  $\chi = -0.40 \times 10^{-6}$ , whence  $\mu = 0$ .

*Dibromodi-(o-phenylenebisdimethylarsine)cobalt(III) Perchlorate*.—The mother-liquors from the recrystallisation of the monobromide,  $[CoBr_2(Diarsine)_2]Br$ , were treated with an excess of 30% perchloric acid, and the light green precipitate of perchlorate which formed immediately was filtered off and washed several times with alcohol, in which it was insoluble. It (0.25 g.) was washed finally with water and dried in a vacuum-desiccator (Found: C, 27.2; H, 3.8.  $C_{20}H_{32}O_4ClBr_2As_2Co$  requires C, 27.0; H, 3.6%). When heated, the compound exploded above 300°. Magnetic susceptibility: powder form: from the diamagnetism,  $\mu = 0$ .

*Di-iododi-(o-phenylenebisdimethylarsine)cobalt(III) Iodide*.—This compound was prepared by two methods each leading to the same product. The first of these is preferable since the second involves a reaction which starts with one insoluble compound and finishes with another, the purification of which is difficult.

The cobaltic monochloride complex,  $[CoCl_2(Diarsine)_2]Cl$  (0.6 g.), was dissolved in alcohol (100 ml.), and the solution filtered and treated with lithium iodide (4 g.) in warm alcohol (25 ml.). The solution was heated under reflux, the colour slowly changing from green through violet to dark red. A black crystalline precipitate was formed and after 1 hour the solution was cooled and the black crystalline complex (0.8 g.) was filtered off and well washed with alcohol (Found: C, 23.9; H, 3.4; Co, 5.8.  $C_{20}H_{32}I_3As_2Co$  requires C, 23.75; H, 3.4; Co, 5.8%).

The second method of preparation involved the aerial oxidation of the cobaltous complex in the presence of hydriodic acid. Cobalt chloride hexahydrate (0.7 g.) and lithium iodide (5 g.) were dissolved in alcohol (120 ml.), and the solution was filtered and treated with *o*-phenylenebisdimethylarsine (1.5 g.) in alcohol (30 ml.). A brown precipitate of the cobaltous complex appeared at once; to the

solution was then added 57% hydriodic acid (3 ml.), and the solution was heated under reflux with free access of air to the surface of the solution. After 3 days all of the light brown cobaltous salt had been replaced by a black precipitate (in a violet solution). The solution was cooled and filtered and the residue recrystallised from a large volume of alcohol (yield, 2.4 g.).

Under the microscope the compound consists of very dark red hexagonal crystals which are almost black by reflected light. The compound was much less soluble than the chloride or bromide in alcohol. It was slightly soluble in alcohol and in chloroform containing a little alcohol, but was insoluble in water. Magnetic susceptibility: powder form at 21°:  $\chi = -0.45 \times 10^{-6}$ , whence  $\mu = 0$ .

*Bis[dithiocyanatodi-(o-phenylenebisdimethylarsine)cobalt(III)]tetrathiocyanatocobalt(II)*.—This compound was prepared after unsuccessful attempts to obtain the compound  $[\text{Co}(\text{CNS})_2(\text{Diarsine})]$ .

Cobaltous chloride hexahydrate (0.16 g.) and ammonium thiocyanate (0.16 g.) were dissolved in alcohol (40 ml.) and distilled water (5 ml.), and the solution was added to the compound  $[\text{Co}(\text{Diarsine})_2](\text{CNS})_2$  (0.5 g.) in a 100-ml. flask. Carbon dioxide was then passed in, to exclude air, and the solution refluxed for 1 hour. Vigorous bumping occurred throughout, but no obvious change took place either in the solution or the insoluble bis(diarsine) complex. The solution was cooled, but no change had occurred. Air was then bubbled through the solution, and refluxing continued. Oxidation occurred rapidly, and after 1 hour the brown amorphous cobaltous salt had been converted into dark blue crystals (in a deep blue solution). On cooling, more greenish-black crystals separated. These (0.25 g.) were filtered off and washed with alcohol and dried in a vacuum-desiccator (Found: C, 32.4; H, 3.7.  $\text{C}_{48}\text{H}_{32}\text{N}_8\text{S}_8\text{As}_2\text{Co}_2$  requires C, 32.3; H, 3.6%). Magnetic susceptibility: The compound was shown to be paramagnetic, owing to the  $[\text{Co}(\text{CNS})_4]^-$  anion, but the amount did not permit of an exact determination of the susceptibility.

The compound was insoluble in alcohol and water but dissolved readily in acetone to give a violet-green solution which reacted instantly with silver nitrate, leaving a pink solution of the nitrate of the complex salt.

*Dithiocyanatodi-(o-phenylenebisdimethylarsine)cobalt(III) perchlorate*.—The above tetrathiocyanatocobalt(II) compound (0.2 g.) was dissolved in acetone (20 ml.) diluted with distilled water (20 ml.), and excess of perchloric acid added. Distilled water (50 ml.) was then added with stirring, giving an orange precipitate of the perchlorate (0.15 g.) in an almost colourless solution (Found: C, 31.7; H, 3.7; N, 3.2; Cl, 4.5.  $\text{C}_{22}\text{H}_{12}\text{O}_4\text{N}_2\text{ClS}_2\text{Co}$  requires C, 31.2; H, 3.8; N, 3.3; Cl, 4.2%). The compound was diamagnetic, whence  $\mu = 0$ .

The magnetic measurements on the compounds described in this and the preceding paper were carried out as described in Part III (*J.*, 1950, 851).

This work was carried out during the tenure of an Imperial Chemical Industries Fellowship awarded by the University of London. The author is indebted to Professor C. K. Ingold, F.R.S., for his continued interest in this work.

SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,  
UNIVERSITY COLLEGE, LONDON, W.C.1.

[Received, March 9th, 1950.]