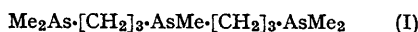


1105. *Tertiary Arsinic Complexes of Bi- and Ter-valent Cobalt.*

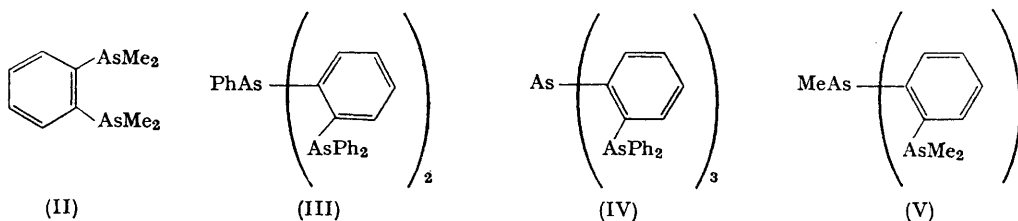
By R. G. CUNNINGHAME, R. S. NYHOLM, and M. L. TOBE.

The terdentate ligand, bis-(*o*-dimethylarsinophenyl)methylarsine (TTAS) has been synthesised and its complexes with cobalt prepared. The octahedral cobalt(II) complex, $[\text{Co}(\text{TTAS})_2]^{2+}$, has been characterised as its perchlorate and tetrachlorocobaltate(II). A series of cobalt(III) complexes of the type $[\text{CoTTASX}_3]^0$ has been prepared, where X = Cl, Br, I, NCS, NO_2 , and NO , and the properties of these are reported. In each, only one of the two possible isomers could be obtained and, in the case of X = Cl, Br, I, and NCS, the compounds are isomorphous and therefore have the same isomeric form. With the exception of the trinitrato-complex, which apparently undergoes considerable solvolysis, these complexes are all non-electrolytes in nitromethane.

SOME years ago¹ we described the preparation and properties of the aliphatic tertiary arsinic (I) and have since reported on the type and structure of the complexes which it forms with a number of transition metals.²⁻⁴



Although it gives rise to interesting stereochemical arrangements, notably square pyramidal bivalent nickel compounds,⁵ the compounds formed by this terdentate ligand with most first-row transition metals are too labile for simple kinetic and many thermodynamic investigations. We set out, therefore, to synthesise a ligand which resembled more closely the well-known bidentate chelate group, *o*-phenylenebisdimethylarsine (II), which we have found



forms very stable compounds with most of the first-row transition elements. Venanzi⁶ has synthesised a wholly aromatic terdentate molecule (III), and has reported the complexes of this ligand with palladium,⁷ platinum,⁸ and rhenium.⁹ The corresponding potentially quadridentate molecule (IV) has also been prepared by Venanzi.⁶ We have prepared the terdentate arsine, bis-(*o*-dimethylarsinophenyl)methylarsine (V), because it was expected that the presence of the methyl groups would enhance its donor properties. The complexes which it forms with bi- and ter-valent cobalt are described in this paper. Cobalt(III) complexes of the type $[\text{CoTTASX}_3]^0$, where X is a relatively labile ligand, are of particular interest for kinetic studies because they do not carry any net charge and therefore lead to a minimal ion-association with anionic reagents. They are, as hoped, soluble in a number of aprotic solvents.

¹ Barclay and Nyholm, *Chem. and Ind.*, 1953, 378.

² Barclay, Nyholm, and Parish, *J.*, 1961, 4433.

³ Masek, Nyholm, and Stiddard, *Coll. Czech. Chem. Comm.* 1964, 29, 1714.

⁴ Howard, Ph.D. thesis, London, 1963.

⁵ Mair, Powell, and Helm, *Proc. Chem. Soc.*, 1961, 415.

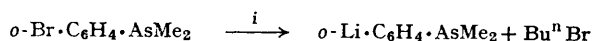
⁶ Howell, Pratt, and Venanzi, *J.*, 1961, 3167.

⁷ Savage and Venanzi, *J.*, 1962, 1548.

⁸ Brewster, Savage, and Venanzi, *J.*, 1961, 3699.

⁹ Mawby and Venanzi, *J.*, 1962, 4447.

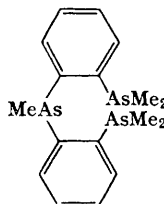
As described in the Experimental section, the terdentate ligand was prepared by the sequence of reactions given below; the *o*-bromophenyldimethylarsine was prepared by well-known reactions starting from *o*-arsanilic acid.¹⁰



↓
ii

i Bu^nLi in petroleum (b.p. 40—60°)

ii MeAsCl_2 in benzene



The ligand was isolated as a viscous oil which formed a white solid, m. p. 64—68°, on being seeded with crystals from an earlier preparation. On recrystallisation from ethanol, white material, m. p. 37.5°, was obtained. This had an analysis identical with that of the crude arsine and had the same chemical properties. The high- and low-melting-point forms have a mixed melting point of 59—65°. N.m.r. studies now in progress indicate that there is restricted rotation about the As-Ph bond and we are of the opinion that the above behaviour can be explained in terms of this restricted rotation.

Complexes of Bivalent Cobalt.—When cobalt(II) perchlorate, in aqueous acetone, is treated with an excess of the triarsine, a yellow-green complex of the formula $[\text{Co}(\text{TTAS})_2](\text{ClO}_4)_2$ is isolated. The properties of this compound are shown in Table 1; it is clearly a spin-paired d^7 bi-univalent electrolyte. The magnetic moment indicates one unpaired electron and, although one must exercise some caution, the value of μ_{eff} (1.96 B.M. at 24.5°) is consistent with the assignment of a small tetragonal distortion of the octahedral structure.¹¹ The corresponding tetrachlorocobaltate(II) derivative, $[\text{Co}(\text{TTAS})_2][\text{CoCl}_4]$, has been isolated; its properties are given in Table 1. The strong paramagnetism is clearly attributable to the $[\text{CoCl}_4]^{2-}$ anion since χ_m is consistent with the sum of the cationic and anionic contributions.

Attempts to prepare 5-co-ordinate derivatives of the type $[\text{CoTTASX}_2]$ have led, so far, to the isolation of unstable materials.

Complexes of Trivalent Cobalt.—The trichloro-, tribromo-, and tri-iodo-complexes are prepared by aerial oxidation of a mixture of the corresponding cobalt(II) halide and the triarsine in alcohol. The tri-isothiocyanato-, trinitro-, and trinitrato-complexes are obtained from the trichloro-complex by displacing the chlorine with the appropriate anion. The trinitro-complex can also be easily prepared by the action of the triarsine on a solution of sodium cobaltinitrite. The reaction paths are outlined in Chart 1.

With the exception of the trinitrato-complex, all these compounds are virtually non-electrolytes in nitromethane. All the cobalt(III) complexes are diamagnetic. A study of spectra (infrared absorption, visible absorption, and visible reflectance) lead us to believe that all these complexes have the same stereoisomeric form. The X-ray powder patterns suggest that the chloro-, bromo-, iodo-, and isothiocyanato-complexes are isomorphous. In addition, the tribromo-cobalt(III) complex is isomorphous with the corresponding chromium(III) complex which will be reported in another communication.¹² We cannot say, at this stage, whether or not these complexes have a vicinal arrangement of the three anionic ligands (and hence the three As atoms). A model of the ligand suggests that the vicinal arrangement

¹⁰ Burton and Gibson, *J.*, 1926, 457; Jones and Mann, *J.*, 1955, 4472.

¹¹ Figgis and Nyholm, *J.*, 1959, 338.

¹² Cook, Nyholm, and Tobe, *J.*, submitted for publication.

would be less strained, but since the complex, $[\text{PtTTASCl}]\text{Cl}$, has been prepared¹³ such arguments should not be considered as compelling.

The physical properties of these compounds are collected in Table 1.

TABLE 1.
Properties of cobalt-triarsine complexes.

Complex	Colour	M. p. (decomp.)	Molecular conductivity* in CH_3NO_2 (mhos)	Magnetic moment (B.M.)
$[\text{Co}(\text{TTAS})_2](\text{ClO}_4)_2$	Yellow-green	275—280°	195 ($5 \times 10^{-4}\text{M}$)	1.96 (24.5°)
$[\text{Co}(\text{TTAS})_2][\text{CoCl}_4]$	Light-green			2.21† (20.5°)
$[\text{CoTTASCl}_3]$	Purple	260—265°	0.7 ($1 \times 10^{-3}\text{M}$)	Diamagnetic
$[\text{CoTTASBr}_3]$	Black	265—268°	2.9 ($5 \times 10^{-4}\text{M}$)	
$[\text{CoTTASI}_3]$	Black	275—285°	9.3 ($8 \times 10^{-4}\text{M}$)	„
$[\text{CoTTAS}(\text{NCS})_3]$	Red	232—235°	0.7 ($8 \times 10^{-4}\text{M}$)	„
$[\text{CoTTAS}(\text{NO}_2)_3]$	Orange	235—238°	0.8 ($5 \times 10^{-4}\text{M}$)	„
$[\text{CoTTAS}(\text{NO}_3)_3]$	Magenta	220—225°	58 ($5.5 \times 10^{-4}\text{M}$)	„

* Measured at 25°.

† The paramagnetic contribution from the CoCl_4^{2-} ion has been subtracted. The high moment is probably due to an excess of $[\text{CoCl}_4]^{2-}$ associated with slight oxidation of the complex cation.

The visible absorption spectra deserve some comment. The intensities of the absorptions are large, a common characteristic of cobalt(III) complexes with arsenic chromophores¹⁴, and two peaks are observed, the one at shorter wavelength often forming a shoulder on the high-intensity ultraviolet absorption band. The absorption at the second peak is generally similar to that at the first, except in the case of the trichloro-complex, where the extinction coefficient of the shorter-wavelength peak is only about 15% of that of the longer-wavelength band. This effect is also observed in the analogous d^3 chromium(III) complex.¹⁰ The spectra of the triacido-cobalt(III) complexes (Figs. 1 and 2) are affected by their environment (Table 2). A change of solvent from dichloromethane to nitromethane leads to a change in the extinction coefficients and, in the case of the tri-isothiocyanato-complex, causes a shift of the maximum. The relative intensities of the maxima in solution differ from those observed in the reflectance spectra.

The infrared spectra of all these complexes, in Nujol mulls, have been examined in the region 2.5μ to 15μ . There are several strong bands in this region arising from vibrations of the triarsine ligand but these have yet to be assigned. Attention has been focused on the absorption bands arising from vibrations of the polyatomic anionic ligands, NCS, NO_2 , and NO_3 . The following assignments have been made:

$[\text{CoTTAS}(\text{NCS})_3]$, C—N stretch, antisymmetric, 2083s, 2051s; C—S stretch, symmetric, 833m, 828m, 820sh cm^{-1} ; the NCS bending mode was not observed. The C—S stretching frequencies at $820\text{—}833 \text{ cm}^{-1}$ are indicative of metal–nitrogen bonding¹⁵ and the C—N stretching frequencies also lie within the usual range found for isothiocyanato-complexes.

$[\text{CoTTAS}(\text{NO}_2)_3]$ N—O, stretch, asymmetric, 1404s and 1385s cm^{-1} . These are measured in a hexachlorobutadiene mull and there is some interference from ligand absorptions at 1441 and 1420 cm^{-1} : N—O stretch, symmetric, 1309sh 1294s, 1276s; NO_2 stretch, 820s, 813s, and 810s cm^{-1} . All these absorptions are due to co-ordinated, nitrogen-bonded nitro-groups but it is not possible to say whether there is a *cis*- or a *trans*-arrangement of the co-ordinated groups.¹⁶ Comparison with the spectra of *cis*- and *trans*- $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ ¹⁷ does not allow an assignment of structure.

$[\text{CoTTAS}(\text{NO}_3)_3]$, NO_2 stretch, symmetric, 1297sh, 1285sh, 1269s; N—O stretch, 1016s; non-planar rock, 801mw cm^{-1} . The asymmetric N—O stretch at $1530\text{—}1480 \text{ cm}^{-1}$ is

¹³ Cunninghame, unpublished results.

¹⁴ Dunn and Yamada, *J.*, 1962, 1564.

¹⁵ Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

¹⁶ Chatt, Duncanson, Gatehouse, Lewis, Nyholm, Tobe, Todd, and Venanzi, *J.*, 1959, 4073.

¹⁷ Majuda, Duval, and Lecompte, *Compt. rend.*, 1938, 247, 302.

masked by absorptions of the arsine ligand. The spectrum indicates that, in the solid, all three nitrate-groups are co-ordinated to the metal.¹⁸ The absence of a band at 1050 cm^{-1} is also evidence for the absence of unco-ordinated nitrate ions in the solid.

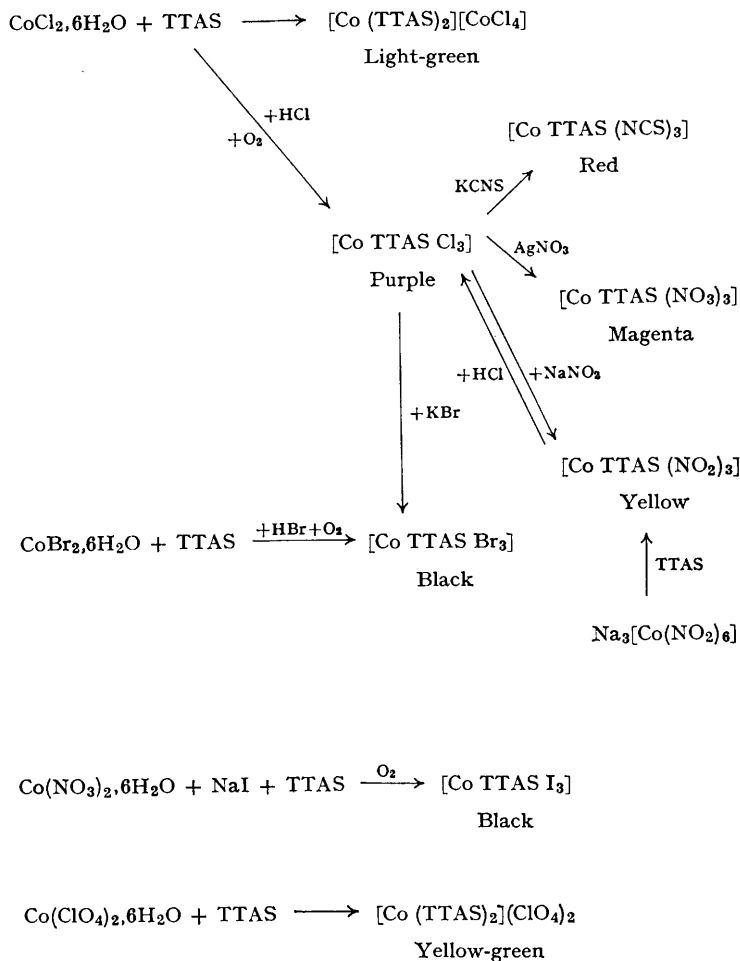


CHART I. Reaction schemes for cobalt-triarsine complexes.

The trinitrato-complex is of interest because of its relatively high lability and low stability. The conductivity measurements indicate that the nitrate-groups can be severally replaced by solvent, the extent of solvolysis depending upon the nature of the solvent; in water, for example, the high conductivity (440 mhos for a $5.2 \times 10^{-4}\text{M}$ solution at 25°) suggests that all three nitrate-groups have been replaced. In nitromethane, the equivalent conductivity (58 mhos for a $5.5 \times 10^{-4}\text{M}$ solution at 25°) is slightly less than would be expected for a 1:1 electrolyte. These solvolyses are also apparent from the way in which the absorption spectra depend quite markedly upon the solvent (Fig. 3). The reflectance spectrum has a maximum at 18,900 cm^{-1} which is similar to that in dichloromethane (19,000 cm^{-1} , $\epsilon_{\text{max.}} = 1150 \text{ cm}^2\text{mole}^{-1}$), but in nitromethane and water the peak shifts to higher frequencies (19,500 and 19,650 cm^{-1} respectively). It should be pointed out, however, that $[\text{Co TTAS (NCS)}_3]$ exhibits a similar solvent shift of 400 cm^{-1} but is still a non-electrolyte in nitromethane.

¹⁸ Gatehouse, Livingston, and Nyholm, *J.*, 1959, 4222.

Some test-tube reactions of solutions of the trinitrato-complex are given in Chart 2. The colour change on adding a drop of concentrated hydrochloric acid to the solution in nitromethane is virtually instantaneous at room temperature but the formation of the trichloromethane in aqueous solution is much slower. At this stage, any discussion based on relative rates must be speculative until catalytic effects, which are quite common in the reactions of other cobalt(III)-arsine complexes,¹⁹ are ruled out. The formation of a yellow colour on

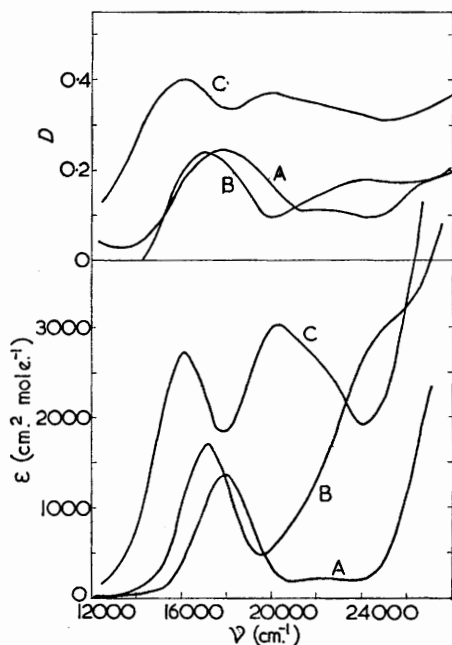


FIG. 1. Diffuse reflectance spectra (top) in MgCO_3 mulls and visible absorption spectra (bottom) of dichloromethane solutions of: (A) $[\text{CoTTASCl}_3]$, (B) $[\text{CoTTASBr}_3]$, and (C) $[\text{CoTTASI}_3]$.

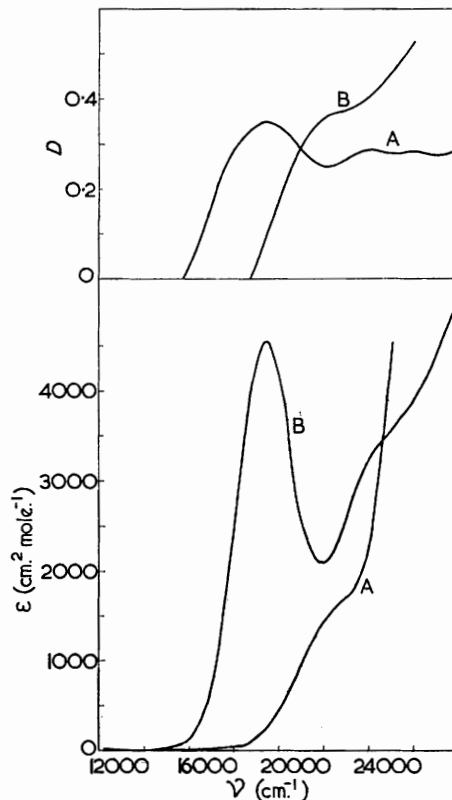


FIG. 2. Diffuse reflectance spectra (top) in MgCO_3 mulls and visible absorption spectra (bottom) of dichloromethane solutions of: (A) $[\text{CoTTAS(NCS)}_3]$ and (B) $[\text{CoTTAS(NO}_2)_3]$.

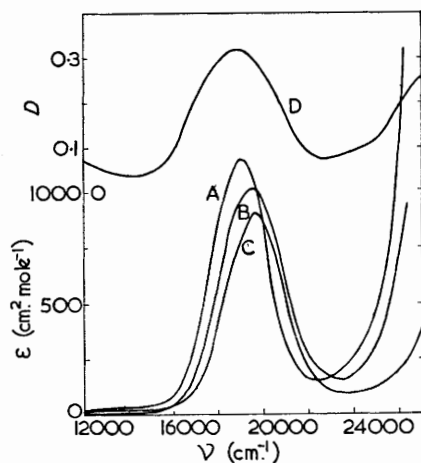


FIG. 3. Absorption spectra of $[\text{CoTTAS(NO}_2)_3]$ in: (A) dichloromethane solution; (B) nitromethane solution; and (C) aqueous solution. The diffuse reflectance in magnesium carbonate mull (D) is shown above for comparison.

¹⁹ Peloso and Tobe, *J.*, 1964, 5063, and unpublished work.

TABLE 2.

The effect of solvent upon the absorption spectra of [Co TTAS X₃].

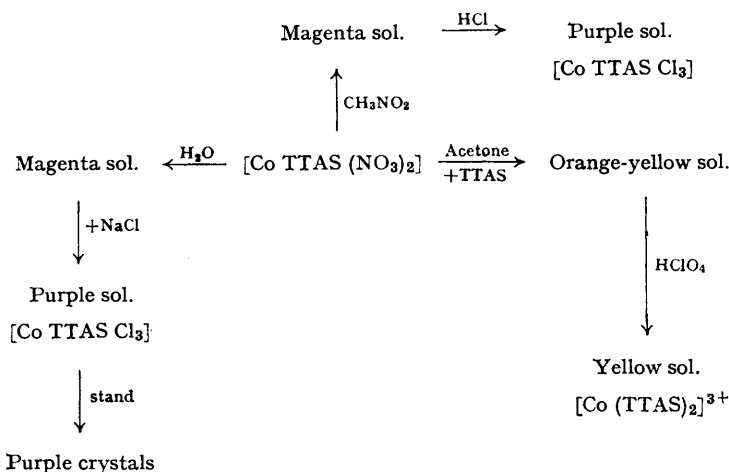
Complex	CH ₂ Cl ₂ soln.		CH ₃ ·NO ₂ soln.		MgCO ₃ mull	
	$\nu_{\max.}$ (cm. ⁻¹)	$\epsilon_{\max.}$	$\nu_{\max.}$ (cm. ⁻¹)	$\epsilon_{\max.}$	$\nu_{\max.}$ (cm. ⁻¹)	"D" [†] $\nu_{\max.}$ \ddagger
[Co TTAS Cl ₃]	18,000	1350	17,900	2100	17,900	0.245
	22,500	200	22,500	300	22,500	0.11
[Co TTAS Br ₃]	17,250	1700			17,100	0.24
	25,000 sh	3000*			24,300	0.18
[Co TTAS I ₃]	16,150	2750			16,150	0.40
	20,300	3050			20,000	0.37
[Co TTAS (NCS) ₃]	19,500	4550	19,900	3450	19,500	0.35
	24,500 sh	3400*			24,200	0.29
[Co TTAS (NO ₂) ₃]	23,200 sh	1750*			23,000 sh	
[Co TTAS (NO ₃) ₃] [†]	19,000	1150	19,500	1000	18,900	0.32

* Value of the extinction coefficient at the point of inflection.

† In water there is a peak at 19,650 cm.⁻¹ with an extinction coefficient of 900.

‡ Uncorrected optical density readings.

adding excess triarsine to the solution in acetone is fairly rapid on warming and is consistent with the formation of [Co(TTAS)₂]³⁺ but this complex, although obtainable in an impure form, has not yet been adequately characterised.* The trinitrato-complex will therefore be a very useful intermediate for the preparation of other complexes of this series and a kinetic and equilibrium study of its reactions is in hand.

CHART 2. Some test-tube reactions of [Co TTAS (NO₃)₃].

EXPERIMENTAL

Bis-(o-dimethylarsinophenyl)methylarsine (TTAS).—*o*-Bromophenyldimethylarsine was prepared from arsenic acid by methods previously described.¹⁰ It should be noted that the crude *o*-bromophenyldichloroarsine obtained from the SO₂-HCl reduction of the arsenic acid should be purified by distillation before conversion into the *o*-bromophenyldimethylarsine.

A light petroleum (b. p. 40—80°) solution of *n*-butyl-lithium (150 ml.; 1.18M) was slowly added during 15 min. to a solution of *o*-bromophenyldimethylarsine (46.1 g.) in dry ether (300 ml.). The clear, slightly yellowish, solution was refluxed for 30 min and then methylchloroarsine (14.2 g.) in dry benzene (100 ml.) was added slowly. During the addition the reaction mixture turned pale-yellow but this colour faded and at the end of the reaction the mixture was chalk-white. This was

* Note added in proof. This complex has now been isolated by Dr. R. Nanda from the mother liquor of the large-scale preparation of [Co TTAS Cl₃]. It has been characterised as the yellow chloride and perchlorate.

stirred for 30 min. and then hydrolysed with water (200 ml.). The colourless organic layer was separated and dried overnight over a molecular sieve (Type 4A). The solvents were removed in a stream of nitrogen and the residue distilled under reduced pressure. A viscous oil (24.5 g., 61%), b. p. 184—190°/0.5 mm., was obtained and this slowly crystallised to a white solid on being seeded with a previous preparation, m. p. 64—68° (Found: C, 45.3; H, 5.1; As, 49.65. $C_{17}H_{23}As_3$ requires C, 45.2; H, 5.1; As, 49.7%). This solid can be recrystallised from ethanol and is then obtained as a white solid, m. p. 37.5° (Found: C, 45.2; H, 5.0; As, 49.65%).

The analysis is not altered by this recrystallisation and the infrared spectrum shows no evidence for absorptions characteristic of ethanol and is virtually identical with that of the original preparation, except that a single peak at 888 cm^{-1} is split into two peaks at 891 and 881 cm^{-1} in the original compound. A mixture of the two forms melts at 60—68°.

Bis(di-o-dimethylarsinophenylmethylarsine)cobalt(II) Perchlorate.—Cobalt(II) perchlorate hexahydrate (0.30 g.) in 50% acetone-water (20 ml.) was added to a solution of the triarsine (0.71 g.) in boiling acetone (100 ml.) under an atmosphere of nitrogen. The yellow-green solution was refluxed for 1 hr. and the solution was concentrated to about 40 ml. and left to cool. Yellow-green needles (0.64 g.) separated out and were filtered off, washed with ice-cold acetone and ether, and dried in a vacuum desiccator. The compound is diamagnetic, $\chi_g = 0.918 \times 10^{-6}$ c.g.s. units at 24.5°, diamagnetic correction = $+537 \times 10^{-6}$ c.g.s. units (the value calculated for the ligand using Pascal's constants does not differ significantly from the directly measured diamagnetism of the free ligand), hence $\mu_{\text{eff}} = 1.96$ B.M. (Found: C, 35.2; H, 3.9; As, 38.75; Co, 5.4, 5.9. $C_{34}H_{46}As_6Cl_2CoO_8$ requires C, 35.1; H, 3.95; As, 38.7; Co, 5.1%).

Bis(di-o-dimethylarsinophenylmethylarsine)cobalt(II) Tetrachlorocobaltate.—Cobalt chloride hexahydrate (0.24 g.) in ethanol (10 ml.) was added to a solution of the triarsine (0.45 g.) in ethanol (15 ml.). The light-green precipitate (0.5 g.) was filtered off, washed with acetone, and dried in a vacuum desiccator (Found: C, 33.5; H, 4.3; Co, 10.4, 10.6. $C_{34}H_{46}As_6Cl_4Co_2$ requires C, 35.1; H, 3.95; Co, 10.1%). The compound is slightly soluble in acetone, ethanol, and nitromethane.

The reflectance spectrum and the absorption spectrum in nitromethane clearly show the presence of the $CoCl_4^{2-}$ ion. The complex is paramagnetic, $\chi_g = 9.55 \times 10^{-6}$ c.g.s. units at 20.5°. Using the value 4.69 B.M. for μ_{eff} of the $CoCl_4^{2-}$ ion it can be calculated that the contribution made to χ_g by the $[Co(TTAS)_2]^{2+}$ cation is $1.66 \pm 0.30 \times 10^{-6}$ c.g.s. units. By using a diamagnetic correction of 473×10^{-6} c.g.s. units it is found that $\mu_{\text{eff}} = 2.21 \pm 0.16$ B.M. The analyses clearly indicate that the compound is not pure, possibly containing some Co(III) cation. The correction for the susceptibility of the $CoCl_4^{2-}$ ion is therefore only approximate.

Trichloro(bis-o-dimethylarsinophenylarsine)cobalt(III).—Cobalt chloride hexahydrate (0.24 g.) in ethanol (15 ml.) was added to a solution of the triarsine (0.45 g.) in ethanol (50 ml.). Concentrated hydrochloric acid (1 ml.) was added to the mixture (containing a green precipitate) and air was passed over the stirred suspension for several hours and the purple precipitate (0.44 g.) was filtered off, washed with acetone, and dried in a vacuum desiccator. The crude product was crystallised from 70% ethanol-water containing a little hydrochloric acid. Red-purple crystals (0.30 g.) were obtained (Found: C, 33.4; H, 4.6; As, 36.8; Cl, 17.2; Co, 9.2. $C_{17}H_{23}As_3Cl_3Co$ requires C, 33.1; H, 3.7; As, 36.5; Cl, 17.1; Co, 9.6%). The complex is insoluble in water, benzene, and carbon tetrachloride but is soluble in methanol, ethanol, chloroform, acetone, dichloromethane, and nitromethane. In the last-named solvent it is a non-electrolyte. The compound is diamagnetic, $10^6\chi_g = -0.43$ c.g.s. units.

Tribromo(bis-o-dimethylarsinophenylmethylarsine)cobalt(III).—Cobalt bromide hexahydrate (0.33 g.) in warm ethanol (20 ml.) was added to a solution of the triarsine (0.46 g.) in warm ethanol (40 ml.). Hydrobromic acid (2 ml.; 46%) was added to the suspension and air was passed over the stirred reaction mixture for 6 hr. The black precipitate (0.58 g.) was filtered off, washed with ice-cold ethanol, and dried in a vacuum desiccator. It could be crystallised from acetone or dichloromethane but the acetone-recrystallised sample contained acetone of crystallisation. The dark-purple needles obtained from dichloromethane are free from solvent (Found: C, 27.3; H, 3.0. $C_{17}H_{23}As_3Br_3Co$ requires C, 27.15; H, 3.05%). The compound is insoluble in water, benzene, and carbon tetrachloride but is soluble in methanol, chloroform, dichloromethane, acetone, and nitromethane. In the last-named solvent it is virtually a non-electrolyte, the small conductivity possibly arising from a little solvolysis.

Aqueous potassium bromide (10 ml.; 0.198M) was added to a suspension of $[CoTTASCl_3]$ (0.177 g.) in ethanol (100 ml.) and the mixture refluxed for 5 hr. and set aside for 3 days. The solution was concentrated to 50 ml. and water (5 ml.) was added. The black crystalline precipitate

(0.175 g.) was filtered off, washed several times with water, and dried in a vacuum desiccator (Found: C, 27.85; H, 3.35%). The reflectance spectra of the two preparations are identical.

Tri-iodo(bis-o-dimethylarsinophenylmethylarsine)cobalt(III).—The triarsine (0.45 g.) in ethanol (10 ml.) was added to a solution of cobalt nitrate hexahydrate (0.29 g.) and sodium iodide (0.98 g.) in hot ethanol (40 ml.). The black mixture was stirred for 3 hr. while air was passed over the surface. The mixture was set aside for 8 days with occasional stirring and shaking. The red-brown solution was decanted from the black precipitate which was then washed with methanol (50 ml.) and then dry ether (3 × 50 ml.). The dark-grey product (0.55 g.) was dried in a stream of air and recrystallised from 70% dichloromethane-methanol whereby small black crystals were obtained (Found: C, 23.25; H, 3.3. $C_{17}H_{23}As_3CoI_3$ requires, C, 23.2; H, 2.6%). The complex is insoluble in water and carbon tetrachloride but dissolves in nitromethane and in dichloromethane. In the former it is almost a non-electrolyte, the small conductivity probably arising from a little solvolysis.

Tri-isothiocyanato(bis-o-dimethylarsinophenylmethylarsine)cobalt(III).—Potassium thiocyanate (0.5 g.) in ethanol (40 ml.) was added to a boiling solution of $[CoTTASCl_3]$ (0.14 g.) in methanol (60 ml.). The purple solution turned bright red almost immediately and, after it had been refluxed for 2 hr., 70 ml. of methanol was distilled from it. Red crystals (0.12 g.) separated on cooling and were filtered off, washed with water, ice-cold methanol, and ether, and dried in a vacuum desiccator (Found: C, 35.6; H, 3.7. $C_{20}H_{23}As_3CoN_3S_3$ requires C, 35.1; H, 3.4%). The compound is insoluble in water but dissolves in methanol, acetone, dichloromethane, and nitromethane; in the last-named it is a non-electrolyte.

Trinitro(bis-o-dimethylarsinophenylmethylarsine)cobalt(III).—Sodium nitrite (0.5 g.) in methanol (40 ml.) was added to a solution of $[CoTTASCl_3]$ (0.125 g.) in boiling methanol (60 ml.). The purple solution turned red and finally became orange after 15 min. It was refluxed for a further hour and set aside overnight. The orange-brown crystals (0.08 g.) were filtered off, washed with ice-cold methanol and ether, and dried in a vacuum desiccator (Found: C, 32.0; H, 4.0. $C_{17}H_{23}As_3CoN_3O_6$ requires C, 31.4; H, 3.55; As, 34.7; Co, 9.1%). The complex is soluble in methanol, acetone, dichloromethane, and nitromethane and is a non-electrolyte in the last solvent. The complex could also be prepared by the following method. Triarsine (0.45 g.) in hot methanol (85 ml.) was added to a solution of sodium hexanitrocobaltate(III) (0.40 g.) in 60% methanol-water (15 ml.). A yellow-orange solid was precipitated and the mixture was refluxed for 6 hr. and set aside for several days. The orange precipitate (0.55 g.) was filtered off, washed with ethanol, acetone, and ether, and dried in a vacuum desiccator (Found: C, 31.5; H, 3.8; As, 34.55; Co, 9.75%). The absorption spectrum of this complex in dichloromethane is identical with that of the complex prepared from the trichloro-complex.

Trinitrato(bis-o-dimethylarsinophenylmethylarsine)cobalt(III).— $[CoTTASCl_3]$ (0.152 g.) was dissolved in 6*M*-nitric acid (30 ml.), and aqueous silver nitrate solution (15 ml.; 0.10*N*) was added to the bright-red solution, whereby silver chloride was precipitated. The mixture was digested on a steam bath for ten hours and set aside overnight. The silver chloride was filtered off* and the bright magenta-coloured filtrate was extracted several times with dichloromethane. The organic layers were collected, dried, and concentrated to a volume of 10 ml., and benzene (10 ml.) was added. The magenta precipitate (0.09 g.) was filtered off, washed with ice-cold methanol, benzene, and ether, and dried in a vacuum desiccator (Found: C, 29.4; H, 3.9. $C_{17}H_{23}As_3CoN_3O_9$ requires C, 29.3; H, 3.3%).

Magnetic susceptibilities were measured by the Gouy method. Conductances were measured in a glass cell with shiny platinum electrodes by a Wayne Kerr B 221 universal bridge. Infrared spectra were obtained with Nujol or hexachlorobutadiene mulls and a Grubb-Parsons GS 2A spectrophotometer. U.v. and visible absorption and reflectance spectra were measured with a Unicam SP 500 spectrophotometer.

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* The silver chloride was collected in a weighed crucible, washed, and dried to constant weight; 0.1004 g. of silver chloride was obtained, corresponding to 94.5% of the chloride in the starting material, which had not been recrystallised.