

771. Octahedral Ditertiary Arsine Complexes of Tervalent Gallium and Indium

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The preparation and properties of a series of ditertiary arsine complexes of the trivalent d^{10} metals gallium(III) and indium(III) are reported. As a rule, complexes of the type $[M(\text{Diars})_2X_2][MX_4]$ ($X = \text{Cl, Br, and I}$) are formed, but GaCl_3 and InI_3 are unusual and give rise to $[\text{Ga}(\text{Diars})_2\text{Cl}_2][\text{Ga}_3\text{Cl}_{10}]$ and $[\text{In}(\text{Diars})_2\text{I}_2][\text{In}(\text{Diars})\text{I}_4]$, respectively. Electrical conductivity and molecular weight studies in nitrobenzene solution show that in all cases the compounds behave as 1 : 1 electrolytes. The $[MX_4]^-$ anions can be isolated as tetraphenylarsonium salts and, in special circumstances, a perchlorate of the $[M(\text{Diars})_2X_2]^+$ cation {*e.g.*, with $[\text{In}(\text{Diars})_2\text{Br}_2]^+$ } can be prepared. In all cases, the metal atom is six-co-ordinate when attached to the diarsine. No complexes of univalent gallium, indium, or thallium, or of thallium(III) could be isolated.

FOLLOWING earlier¹ studies on the behaviour of uni- and bi-valent d^{10} metal ions towards tertiary arsines, in particular *o*-phenylenebisdimethylarsine,² we report here studies of the complexes formed by the trivalent d^{10} metals, gallium, indium, and thallium with this chelate group. Considerable interest attaches to these Group III metals because they show four- and six-co-ordination, depending upon the attached ligand. As pointed out by Greenwood³ in his detailed review, nearly all previously prepared complexes have involved the use of halide ions or nitrogen or oxygen atoms as donors. It was of particular interest to determine whether five-co-ordinate derivatives of the type $[M(\text{Diars})X_3]^0$ ($X = \text{halogen}$) could be prepared.

Owing to the extreme ease with which the anhydrous halides of gallium, indium, and thallium undergo hydrolysis it was necessary to carry out all operations in anhydrous solvents; benzene and diethyl ether were convenient.

Gallium Compounds.—These derivatives were prepared by treating a solution of the gallium trihalide in benzene or ether with the stoichiometric amount of diarsine. Two

¹ J. Lewis, R. S. Nyholm, and D. J. Phillips, *J.*, 1962, 2177.

² J. Chatt and F. G. Mann, *J.*, 1939, 610.

³ N. N. Greenwood, *Adv. Inorg. Chem. Radiochem.*, 1963, 5, 91.

types of complex have been isolated: gallium trichloride yields a derivative having the empirical formula $\text{GaCl}_3 \cdot 0.5\text{Diars}$, whereas for the tribromide and tri-iodide the empirical formulæ are $\text{GaBr}_3 \cdot \text{Diars}$ and $\text{GaI}_3 \cdot \text{Diars}$. All these compounds are white and diamagnetic, and are soluble in nitrobenzene, nitromethane, and tetrahydrofuran (solvents which dissolve electrolytes) and slightly soluble in benzene and diethyl ether; they are stable in moist air for several hours. The results of conductivity and molecular weight measurements in nitrobenzene (see Table 1) strongly suggest salt-like structures (at least in solution). The bromide and iodide are clearly of the general type $[\text{M}^{\text{III}}(\text{Diars})_2\text{X}_2][\text{M}^{\text{III}}\text{X}_4]$, already well known with ferric chloride and bromide.⁴ However, it is necessary to postulate that the chloride has the molecular formula $[\text{Ga}(\text{Diars})_2\text{Cl}_2][\text{Ga}_3\text{Cl}_{10}]$.

The presence of $[\text{GaBr}_4]^-$ and $[\text{GaI}_4]^-$ ions is supported by the behaviour of the complexes with tetraphenylarsonium salts in alcoholic solution; complexes of the type $[\text{Ph}_4\text{As}][\text{GaX}_4]$ are precipitated when *one* mole of $[\text{Ph}_4\text{As}]\text{X}$ is added. However, with the chloride the complex gives readily three moles of $[\text{Ph}_4\text{As}][\text{GaCl}_4]$ per $[\text{Ga}(\text{Diars})_2\text{Cl}_2][\text{Ga}_3\text{Cl}_{10}]$ unit. When excess of $[\text{Ph}_4\text{As}]^+\text{Cl}^-$ is added, a fourth mole of $[\text{Ph}_4\text{As}][\text{GaCl}_4]$ can be precipitated, provided that the complex cation is decomposed with hydrochloric acid. Nevertheless, the compound $[\text{Ph}_4\text{As}][\text{GaCl}_4]$ is precipitated quantitatively only from concentrated solutions.

The $[\text{Ga}(\text{Diars})_2\text{X}_2]^+$ cation is obviously octahedral, but one does not know whether the two halogen atoms are *cis* or *trans*. In principle, this can be decided by studying the number of Ga-Br and Ga-I stretching bands, but the wavelengths of these lie outside the range of readily available long-wave infrared spectrophotometers ($>200 \text{ cm.}^{-1}$). All our experience with trivalent transition-metal atoms suggests that the most likely configuration is *trans*-octahedral.

TABLE I
Properties of gallium(III) and indium(III) diarsine complexes

Complex *	Mol. conduct ($\text{ohm}^{-1} \text{ cm.}^{-2}$) in PhNO_2 at 25°		Mol. wt. in freezing PhNO_2	
	Found	Concn. $\times 10^{-3}$ (M)	Calc.	Found
$[\text{GaD}_2\text{Cl}_2][\text{Ga}_3\text{Cl}_{10}]$	29.9	0.93	1277	609 †
$[\text{GaD}_2\text{Br}_2][\text{GaBr}_4]$	34.7	1.03	1191	640
$[\text{GaD}_2\text{I}_2][\text{GaI}_4]$	34.9	1.01	1473	798
$[\text{InD}_2\text{Cl}_2][\text{InCl}_4]$	29.8	0.94	1014	641
$[\text{InD}_2\text{Br}_2][\text{InBr}_4]$	29.8	1.06	1281	668
$[\text{InD}_2\text{I}_2][\text{InDI}_4]$	27.3	1.00	1849	632 ‡

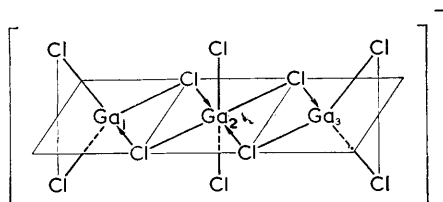
* D = diarsine. † Mean of 3 determinations, all within $\pm 5\%$. ‡ Mean of 2 determinations both within $\pm 4\%$.

The structure of the $[\text{GaBr}_4]^-$ and $[\text{GaI}_4]^-$ anions is undoubtedly tetrahedral, but great interest attaches to the suggested $[\text{Ga}_3\text{Cl}_{10}]^-$ anion. As is well known, the co-ordination number tends to fall as formal (positive) charge on the metal ion decreases and as the polarisability of the attached ligand increases. Thus, for trivalent iron the preferred co-ordination number increases from four to six as we pass from the $[\text{FeCl}_4]^-$ to the $[\text{FeF}_6]^{3-}$ anion. Hence there is the possibility of an increase in passing from the bromide and iodide to the chloride in the gallium complexes. A $[\text{GaCl}_6]^{3-}$ anion has not been isolated but the presence of octahedral gallium(III) in the $[\text{Ga}_3\text{Cl}_{10}]^-$ anion offers a reasonable explanation for the structure of this entity. If, as shown in the Figure, there were two (terminal) tetrahedral gallium(III) atoms and one central octahedral gallium(III) atom, a reasonable structure can be proposed. Six-co-ordination for the central gallium(III) atom is made more likely by the fact that the four bridging Cl atoms are effectively less electronegative than the terminal Cl atoms, thus making six-co-ordination more feasible. Unfortunately, long-wave infrared studies did not assist in establishing the definite presence of bridging Cl groups, because of other absorptions in the same region. Similarly, nuclear magnetic resonance studies on the gallium(III) atoms by Dr. R. Bramley were

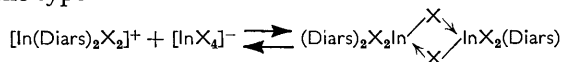
⁴ R. S. Nyholm, *J.*, 1950, 851.

inconclusive, because the compounds had to be studied in the solid state. Clearly, an X-ray investigation is necessary to confirm the suggested structure for the anion.

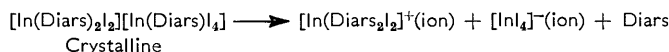
It is noteworthy that no derivatives of the $[\text{Ga}(\text{Diars})_3]^{3+}$ cation could be isolated. This is not surprising, since with cobalt(III) the $[\text{Co}(\text{Diars})_3]^{3+}$ ion is converted rapidly into the $[\text{Co}(\text{Diars})_2\text{Cl}_2]^+$ ion in the presence of chloride⁵ ions. In all our investigations, the use of halide ions to ensure the solubility of the gallium salt was essential. It should be mentioned that Sutton⁶ and Ivanov,⁷ using *o*-phenanthroline have isolated tris-chelate derivatives of the type $[\text{Ga}(\textit{o}-phenanthroline)₃]³⁺, but this ligand is much more basic than diarsine.$



Indium Compounds.—Following exploratory experiments to determine optimum conditions, the metal trihalides were treated with the diarsine in benzene or ether solution in the ratio 1 : 1 at room temperature. The complexes isolated had the empirical formulæ $[\text{InX}_3, \text{Diars}]$ ($\text{X} = \text{Cl}$ or Br) and $[\text{InI}_3 \cdot 5\text{Diars}]$, respectively. The chloro- and bromo-complexes were precipitated immediately, but to obtain the iodo-derivatives the solution needed concentration or the addition of light petroleum. (In view of the commonly observed lower solubility of iodo-complexes in a homologous series, this strongly suggested the formation of complexes of a different structural type.) Conductivity and molecular-weight data are given in Table 1. For the chloro- and bromo-derivatives, the structural formulæ are clearly of the type $[\text{In}(\text{Diars})_2\text{X}_2][\text{InX}_4]$. The cryoscopic data suggest that some association of the two ions in the following equation takes place, perhaps owing to an equilibrium of the type



as has been postulated^{1,8} for some copper(I) and silver(I) diarsine complexes; the variation of the conductivity with concentration seems to support this hypothesis. However, we are forced to conclude that the iodo-derivative is of the type $[\text{In}(\text{Diars})_2\text{I}_2][\text{In}(\text{Diars})\text{I}_4]$ in the solid state. Analogous structures have been postulated previously for certain trivalent chromium complexes.⁹ It is difficult to see why the $[\text{In}(\text{Diars})\text{I}_4]^-$ anion should be formed in place of the $[\text{InI}_4]^-$ ion; the tentative explanation we offer is that, in spite of the lower stability of the $[\text{In}(\text{Diars})\text{I}_4]^-$ ion as compared with the $[\text{InI}_4]^-$ ion in solution, the lattice energy of the solid complex $[\text{In}(\text{Diars})_2\text{I}_2][\text{In}(\text{Diars})\text{I}_4]$ is greater than that of the $[\text{In}(\text{Diars})_2\text{I}_2][\text{InI}_4]$ compound, *i.e.*, the solubility of the latter is higher, hence preferential precipitation of the former occurs. Dissociation of the diarsine molecule from the $[\text{In}(\text{Diars})\text{I}_4]^-$ anion is supported by the fact that molecular-weight data indicate that $[\text{In}(\text{Diars})_2\text{I}_2][\text{In}(\text{Diars})\text{I}_4]$ forms *three* particles in solution, presumably owing to the following dissociation,



The unusual nature of the $[\text{In}(\text{Diars})\text{I}_4]^-$ anion has prompted us to attempt to stabilise it with a different cation. Treatment of an alcoholic solution of the $[\text{In}(\text{Diars})_2\text{I}_2][\text{In}(\text{Diars})\text{I}_4]$ compound with a solution of tetraphenylarsonium iodide yields a compound containing diarsine, presumably impure $[\text{Ph}_4\text{As}][\text{In}(\text{Diars})\text{I}_4]$ but analytical data strongly

⁵ R. S. Nyholm, *J.*, 1950, 2072.

⁶ G. J. Sutton, *Austral. J. Chem.*, 1958, 11, 120.

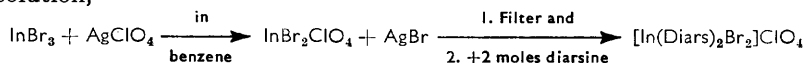
⁷ B. N. Ivanov-Emin, *Russ. J. Inorg. Chem.*, 1961, 5, 583.

⁸ A. Kabesh and R. S. Nyholm, *J.*, 1951, 38.

⁹ R. S. Nyholm and G. J. Sutton, *J.*, 1958, 560.

suggest that some $[\text{Ph}_4\text{As}][\text{InI}_4]$ is present. This tendency for indium to increase its co-ordination number as compared with gallium is not so surprising when one recalls that corresponding decreases in effective electronegativity occur as one passes from copper to silver and from zinc to cadmium.

We have also attempted to isolate perchlorates of the type $[\text{In}(\text{Diars})_2\text{X}_2]\text{ClO}_4$. The usual method involving the addition of perchloric acid to solutions of $[\text{In}(\text{Diars})_2\text{X}_2][\text{InX}_4]$ compounds was not successful, but the following reaction sequence yielded a complex approximating to the composition $[\text{In}(\text{Diars})_2\text{Br}_2]\text{ClO}_4$; this is a 1 : 1 electrolyte in nitrobenzene solution,



Analytical data for this compound were not very satisfactory (cf. Found: C, 22.9. Req'd., 25.4), but this is presumably due to the presence of some of the compound $[\text{In}(\text{Diars})_2\text{Br}_2][\text{InBr}_4]$, for which the required carbon content is 18.8%. All attempts to isolate the $[\text{In}(\text{Diars})_2\text{X}_2]^+$ cations by precipitation with other anions, such as $[\text{BPh}_4]^-$,

TABLE 2

Characteristic infrared bands for diarsine (cm^{-1})¹⁰

$[\text{Ga}(\text{Diars})_2\text{Cl}_2]^+$	756, 890, 921	$[\text{In}(\text{Diars})_2\text{Cl}_2]^+$	756, 873, 910
$[\text{Ga}(\text{Diars})_2\text{Br}_2]^+$	749, 885, 917	$[\text{In}(\text{Diars})_2\text{Br}_2]^+$	758, 877, 911
$[\text{Ga}(\text{Diars})_2\text{I}_2]^+$	745, 877, 912	$[\text{In}(\text{Diars})_2\text{I}_2]^+$	747, 865, 906

were unsuccessful, presumably because in the solvent which had to be used, namely water, alcohol, and acetone, the cation undergoes decomposition.

The infrared spectra of all gallium and indium complexes were studied. Earlier work by Rodley had shown that the characteristic spectra of co-ordinated diarsine involves bands at about 750, 880, and 910 cm^{-1} . As shown in Table 2 these are clearly present in the complexes studied and support the hypothesis that the $[\text{M}(\text{Diars})_2\text{X}_2]^+$ ion is present.

Thallium Complexes.—All attempts to prepare thallium(III)-diarsine complexes were unsuccessful. As expected, the thallium(III) effected oxidation of the ligand. Attempts to prepare diarsine compounds by replacement of *o*-phenanthroline (or bipyridyl) from complexes of the type ⁶ $[\text{Tl}(\text{o-phen})_2\text{X}_2][\text{TlX}_4]$ were also unsuccessful; attempts to use higher temperatures to effect displacement resulted only in reduction of the anion.

EXPERIMENTAL

All preparations were carried out under dry, purified nitrogen; all solvents were thoroughly dried, and were stored over sodium wire. The gallium and indium halides were prepared as described earlier.¹¹ The complexes were stored under nitrogen, although they are stable to air and moisture for some time. All the complexes described are diamagnetic, colourless powders or crystals.

Analyses.—Gallium was determined gravimetrically as hydroxyquinolate, and indium by volumetric titration with EDTA.¹²

Dichlorodi-(o-phenylenebisdimethylarsine)gallium(III) Salt of $[\text{Ga}_3\text{Cl}_{10}]^-$ Anion.—Anhydrous gallium trichloride (2.0 g.) in benzene (30 ml.) was added slowly at room temperature, with effective stirring, to a solution of diarsine (1.63 g.) in benzene (20 ml.), the mole ratio GaCl_3 : diarsine being 2 : 1. The white to pale pink complex (3.6 g.), which was precipitated immediately, was filtered off, washed with light petroleum, and dried *in vacuo*. It did not melt, but decomposition started slowly at about 190° (Found: C, 19.0; H, 2.8; Cl, 32.8; Ga, 22.1. Calc. for $[\text{GaDiars}_2\text{Cl}_2][\text{Ga}_3\text{Cl}_{10}]$: C, 18.8; H, 2.5; Cl, 33.3; Ga, 21.85%). The complex is soluble in nitrobenzene, sparingly in benzene, ether, and tetrahydrofuran; it is decomposed by water, alcohols, and acetone.

Dibromodi-(o-phenylenebisdimethylarsine)gallium(III) Tetrabromogallate.—The same procedure was used with gallium tribromide as with the trichloride, with a molar ratio GaBr_3 : diarsine of 1 : 1. The white product melted at 95° (decomp.) (Found: C, 19.9; H, 2.9; Br, 39.8; Ga, 12.05. $[\text{GaDiars}_2\text{Br}_2][\text{GaBr}_4]$ requires C, 20.2; H, 2.7; Br, 40.3; Ga, 11.71%). The compound has solubilities similar to those of the chloro-compound.

¹⁰ R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J.*, 1962, 2460.

¹¹ Brauer, "Handbuch der preparativen anorganischen Chemie," Stuttgart, 1960, pp. 749 ff.

¹² Schwarzenbach, "Complexometric Titrations," Methuen, London, 1957, p. 91.

Di-iododi-(o-phenylenebisdimethylarsine)gallium(III) Tetraiodogallate.—This compound, prepared by the above procedure by substituting GaI_3 dissolved in diethyl ether for GaCl_3 , was also obtained in nearly quantitative yield after removing part of the solvent [m. p. 127—130° (decomp.)] (Found: C, 16.2; H, 2.4; Ga, 9.5; I, 52.8. $[\text{GaDiars}_2\text{I}_2][\text{GaI}_4]$ requires C, 16.3; H, 2.2; Ga, 9.5; I, 51.7%). The complex is more soluble than the chloro- and bromo-compounds in the solvents mentioned above.

Dichlorodi-(o-phenylenebisdimethylarsine)indium(III) Tetrachloroindate.—Indium trichloride was dissolved in ether, and diarsine in benzene solution was added at room temperature in a mole ratio of 1 : 1. The precipitate was isolated in the usual manner. The complex started to decompose at about 175° (Found: C, 23.6; H, 3.5; Cl, 20.6; In, 23.3. $[\text{InDiars}_2\text{Cl}_2][\text{InCl}_4]$ requires C, 23.7; H, 3.2; Cl, 21.0; In, 22.6. The compound is soluble in nitrobenzene, very sparingly in ether and benzene, and is decomposed by water, acetone, and alcohols.

Dibromodi-(o-phenylenebisdimethylarsine)indium(III) Tetrabromoindate.—The same procedure was used with indium tribromide in benzene, yielding a white powder, melting at 296—298° (decomp.) (Found: C, 18.8; H, 2.7; Br, 37.0; In, 18.1. $[\text{InDiars}_2\text{Br}_2][\text{InBr}_4]$ requires C, 18.75; H, 2.5; Br, 37.4; In, 17.9%). The complex has solubilities similar to those of the chloro-compound.

Di-iododi-(o-phenylenebisdimethylarsine)indium(III) Mono-(o-phenylenebisdimethylarsine)-tetraiodoindate.—A procedure similar to that used for the bromide was employed. The presence of free iodine in preparations of InI_3 must be carefully avoided. The complex was crystallised by evaporation of the solvent, or by precipitation by adding light petroleum or other non-polar solvents. The white product can be recrystallised from hot benzene [m. p. 135—138° (decomp.)] (Found: C, 19.2; H, 2.6; I, 42.3; In, 11.3. $[\text{InDiars}_2\text{I}_2][\text{InDiarsI}_4]$ requires C, 19.5; H, 2.6; I, 41.2; In, 12.4%).

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