108. *Studies in Co-ordination Chemistry. Part XV.* Complexes of Chromium with a Di(tertiary Arsine).*

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Sexicovalent complexes of chromium(III) with *o*-phenylenebisdimethylarsine (I) have been prepared and studied. These are the first complexes of chromium(III) with tertiary arsines to be described. Blue complexes containing one molecule of ligand to each chromium atom have been isolated and shown to be non-electrolytes of the type $[CrDiarsineX_3,H_2O]^0$, where X is a halogen atom. Green compounds having the empirical formula $2CrX_3,3Diarsine$ are considered to be salts of the type $[Cr(Diarsine)_2X_2][CrDiarsineX_4]$; from these salts the perchlorate, $[Cr(Diarsine)_2X_2]ClO_4$, can be prepared readily. The structures have been investigated by using electrical conductivity, cryoscopic, and magnetic measurements. In all the compounds investigated the magnetic moment is approximately 3·9 Bohr magnetons, thus indicating that no electron-pairing has taken place. All attempts to prepare complexes of bivalent chromium with the diarsine were unsuccessful, and no complexes were obtained containing three molecules of ligand co-ordinated to a single chromium atom.

These four papers deal with di(tertiary arsine) complexes of chromium, manganese, ruthenium, and osmium halides. Previous investigations here of the metal complexes of the di(tertiary arsine) chelate group (I) (*o*-phenylenebisdimethylarsine) [1] have been concerned mainly with the metals towards the end of each transition series. To put this work into perspective the abbreviated Periodic Table shown in Table 1 is helpful.

Earlier work [2] showed that the di(tertiary arsine) possesses marked capacity for effecting electron-pairing in transition-metal atoms and for the stabilisation of a wide variety of both common (*e.g.*, Ni^{II}) and uncommon (*e.g.*, Ni^{III} and Ni^{IV}) valency states.[2] The diamagnetism of $[Ni^{II}(Diarsine)_3][ClO_4]_2$ indicated that electron-pairing different from that expected on the basis of the simple Pauling theory could occur. To study these effects in more detail we examined the complexes of the transition metals with fewer non-bonding *d* electrons—particularly in the two later transition series. As a necessary preliminary, the complexes of the first transition series were examined. This paper deals with Cr complexes; Part XVI with those of Mn, and Parts XVII and XVIII with Ru and Os compounds which are compared with those of Fe^{II}, Fe^{III}, and Fe^{IV} previously reported.

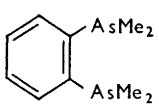
(I) 

Table 1.

Cr	Mn	**Fe**	**Co**	**Ni**	**Cu**	* Elements in **bold** type previously investigated; [2] in
Mo	Tc * †	Ru	**Rh**	**Pd**	*Ag*	*italics*, being studied at present; in roman (ordinary) type,
W	*Re*	Os	Ir	**Pt**	**Au**	being discussed in this Series.
						† It is intended to study Tc complexes.

Tervalent chromium is well known to give rise exclusively to sexicovalent complexes

* Part XIV, *J.*, 1952, 3579.

[1] Chatt and Mann, *J.*, 1939, 610.

[2] ($Fe^{II, III}$) Nyholm, *J.*, 1950, 851; (Fe^{IV}) Parish and Nyholm, *Chem. and Ind.*, 1956, 470; ($Co^{II, III}$) Nyholm, *J.*, 1950, 2070; ($Ni^{II, III}$) *idem*, *J.*, 1950, 2061; (Ni^{IV}) *idem*, *J.*, 1951, 2602; ($Ni^{0, II}$) *idem*, *J.*, 1952, 2906; (Cu^{I}) Kabesh and Nyholm, *J.*, 1951, 38; (Rh^{III}) Nyholm, *J.*, 1950, 857; (Pd^{II}) Chatt and Mann, *J.*, 1939, 1622; Harris, Nyholm, and Stephenson, *Nature*, 1956, 177, 1127; *J.*, 1956, 4375; (Pt^{II}) Harris, Nyholm, and Phillips (unpublished); ($Au^{I, III}$) Nyholm, *Nature*, 1951, **168**, 705; Harris, Nyholm, and Stephenson, *Rec. Trav. chim.*, 1956, **75**, 687; Harris and Nyholm, *J.*, 1957, 63.

when the donor atoms of the ligands are nitrogen and oxygen. These are very stable and react very slowly; as illustrations trisethylenediamine- and trioxalato-chromium(III) ions have been resolved [3] and the $[Cr(H_2O)_6]^{3+}$ ion exchanges [4] the water molecules only very slowly with $H_2{}^{18}O$. In this investigation with the di(tertiary arsine), again Cr^{III} gives rise to sexicovalent complexes only. Since the Cr^{3+} ion has a $(3d_\epsilon)^3$ configuration with two empty d_γ orbitals, the formation of an octahedral complex, even with ligands like CN^-, is not expected to lead to electron-pairing. However, the Cr^{2+} ion has one more electron and ligands like dipyridyl and the cyanide ion effect a reduction in the number of unpaired electrons from four to two.[5]

No reaction occurs between *o*-phenylenebisdimethylarsine and chromium-(II) or -(III) halides in water or in alcoholic solution when much water is present. When the solvent is only slightly moist, however, combination takes place between chromium(III) halides and the ligand in solvents such as methanol, ethanol, acetone, or dioxan, with formation of slightly soluble *green* complexes having the empirical formula $CrX_3,1\frac{1}{2}$Diarsine and very soluble *blue* compounds of the empirical formula CrDiarsineX_3Q, where Q represents one molecule of the solvent, usually water. The reactions are hastened by refluxing in the appropriate solvent or by warming for a few minutes on a water-bath. If the molar proportion of diarsine to chromic salt is in the ratio of 2 : 1, then the less soluble green complexes are preferentially obtained, whilst equimolecular proportions favour the formation of the soluble blue compounds. By refluxing an alcoholic solution of the latter with the diarsine, the less soluble green complexes were obtained. If excess of perchloric acid is added beforehand, perchlorates of the formula $[Cr(Diarsine)_2X_2]ClO_4$ are precipitated. Purification of the perchlorate of the *green* halide complexes is effected readily by adding diethyl ether, in which the blue mono-diarsine complex is readily soluble. After evaporation of this ether solution to dryness under reduced pressure, the bright blue compound can be obtained pure by repetitive extraction with chloroform and precipitation with light petroleum.

Structure of the Blue Soluble Complexes.—Since the solvent molecule Q, presumably occupying the sixth co-ordinating position, may be methanol, ethanol, or water, mixed blue complexes usually result unless the solvent used is free from water. Solvents such as acetone yielded blue complexes in which methanol appeared to have partly replaced the water molecule, traces of the former being present in the common solvent acetone. We therefore attempted to form a blue complex by using dioxan as the solvent; the presence of a co-ordinated molecule of this solvent would markedly affect the analysis. Unfortunately, anhydrous chromic salt would not dissolve in this solvent, and a little water was added to assist in the solution. The resulting blue chloro-compound had the composition $[CrDiarsineCl_3(H_2O)]^0$, H_2O completely replacing the dioxan to yield the aquo-complex. The structure of this chloride and of the bromo-derivative was established by conductivity measurements in nitrobenzene in which they are virtually non-electrolytes. Molecular-weight determinations in chloroform show that they are monomeric. The complexes are thus clearly sexicovalent non-electrolytes. Although un-ionised in nitrobenzene, the complexes react readily with silver nitrate in aqueous alcoholic solution to precipitate all of the halogen as silver halides. The properties of the compounds are shown in Table 2. In all cases the magnetic moment is very close to the spin-only value for three unpaired electrons (3·88 B.M.).

Structure of the Less-soluble Form.—The empirical formula $CrCl_3,1\frac{1}{2}$Diarsine must clearly be doubled at least, and the complex is then most readily formulated as $[Cr(Diarsine)_2Cl_2][CrDiarsineCl_4]$ or as $[Cr(Diarsine)_3][CrCl_6]$. Treatment of a solution of this salt with perchloric acid yields the salt $[Cr(Diarsine)_2Cl_2]ClO_4$, which reaction seems to favour the first structural formula. Furthermore, the $[CrDiarsineCl_4]^-$ anion

[3] Werner, *Ber.*, 1912, **45**, 3061; see also *ibid.*, 1911, **44**, 3132.
[4] Plane and Taube, *J. Phys. Chem.*, 1952, **56**, 33.
[5] Burstall and Nyholm, *J.*, 1952, 3570.

is apparently related to the soluble blue non-electrolyte complexes. The interconversion presumably occurs according to the reaction

$$[\text{CrDiarsineCl}_4]^- + H_2O \rightleftharpoons [\text{CrDiarsineCl}_3(H_2O)]^0 + Cl^-$$

since the formation of the salt-like complex ion on the left of the equation is favoured by the presence of a high concentration of HCl. The trisdiarsine formula is also made improbable because all attempts to prepare a $[\text{CrDiarsine}]_3^{3+}$ ion have been unsuccessful. Prolonged refluxing of the chromic perchlorate in ethanol with excess of the diarsine failed to produce any reaction or change from the purple colour of the hexa-aquochromic

TABLE 2. *Properties of chromium*(III) *di*(*tertiary arsine*) *complexes.*

		Molecular conductivity in $Ph{\cdot}NO_2$ at 25°		Magnetic susceptibility and moment at 20°				
Compound *	Colour	Λ_M	Concn. (10^{-3}M)	$\chi_g \times 10^{-6}$	$\chi_M \times 10^{-6}$	Diamag. corrn.	$\chi_M' \times 10^{-6}$	$\mu_{eff.}$ (B.M.)
$[\text{CrDCl}_3,H_2O]^0$	Bright blue	0·7	6·49	12·75	5885	264	6149	3·82
$[\text{CrDBr}_3,H_2O]^0$	Deep blue	0·6	4·00	10·15	6050	295	6345	3·87
$[\text{CrD}_2\text{Cl}_2][\text{CrDCl}_4]$	Bright green	40·0	0·97	10·30	12,100	699	12,799	3·88 †
$[\text{CrD}_2\text{Cl}_2]\text{ClO}_4$	Pale green	28·2	2·27	7·41	5900	456	6356	3·87
$[\text{CrD}_2\text{Br}_2][\text{CrDBr}_4]$	Dark green	38·1	1·25	8·39	12,100	736	12,836	3·88 †
$[\text{CrD}_2\text{Br}_2]\text{ClO}_4$	Deep green	26·9	0·71	7·02	6200	477	6677	3·96
$[\text{CrD}_2\text{I}_2][\text{CrDI}_4]$	Brown-green	41·9	0·384	7·01	12,090	823	12,913	3·89 †
$[\text{CrD}_2\text{I}_2]\text{ClO}_4$	Pale green	26·7	1·89	6·27	6140	497	6637	3·94

* D = Ditertiary arsine chelate group, see (I). † Per Cr^{III} atom.

ion; the original diarsine was recovered from the solution. The perchlorate $[\text{Cr(Diarsine)}_2\text{Cl}_2]\text{ClO}_4$ gives a molecular conductivity in nitrobenzene which indicates the expected two ions, and ebullioscopic determination of molecular weight in acetone also supports this, since a value corresponding to almost complete dissociation is obtained. Unfortunately, the low solubilities of the complexes of empirical formula $CrX_3,1\frac{1}{2}$Diarsine prevented determination of their molecular weights. As with the blue non-electrolyte complexes the magnetic moments are again close to the spin-only value for 3 unpaired electrons.

The only puzzling feature is the abnormally high conductivity of the $[\text{Cr(Diarsine)}_2X_2]^+[\text{CrDiarsine}X_4]^-$ complexes in nitrobenzene. This must presumably arise from dissociation of the anion in this solvent. This hypothesis finds support from the fact that stable complexes of the $[\text{CrDiarsine}X_4]^-$ anion could not be isolated by using simple cations such as K^+. An equilibrium of the type $[\text{CrDiarsineCl}_4]^- + 2Ph{\cdot}NO_2 \rightleftharpoons [\text{CrDiarsineCl}_2(Ph{\cdot}NO_2)_2]^+ + 2Cl^-$ is suggested as a possible explanation.

Absorption spectra of all these complexes have been recorded and their significance will be discussed in a later communication dealing with spectra of the di(tertiary arsine) complexes for all the transition metals.

All attempts to obtain halogeno-complexes of the diarsine with chromium(II) were unsuccessful, various solvents having been tried. In a later communication, however, we shall describe mixed di(tertiary arsine)–carbonyl complexes of chromium in which the chromium atom is bivalent. As with certain Ni^{II} complexes it seems to be necessary to start with a carbonyl rather than to attempt direct co-ordination.

EXPERIMENTAL

Dichlorodi-(o-phenylenebisdimethylarsine)chromium(III) *Tetrachloromono-(o-phenylenebis-dimethylarsine)chromate*(III).—Chromic chloride tetrahydrate (0·5 g.) was heated with excess of 10N-hydrochloric acid and evaporated almost to dryness. The purple residue was treated with 10N-hydrochloric acid (5 ml., and the mixture dissolved in acetone (50 ml.) and filtered. Diarsine (1·1 g.) in acetone (10 ml.) was added, and the mixture refluxed for 30 min., then concentrated to 6 ml. Ethyl ether was added with shaking to precipitate the *complex* as a fine green powder. The precipitate was washed well with ether to remove traces of the blue complex and dried *in vacuo* (Found: C, 30·7; H, 4·1; Cl, 18·0. $C_{30}H_{48}Cl_6As_6Cr_2$ requires C, 30·72; H, 4·04; Cl, 18·14%).

Dichlorodi-(o-phenylenebisdimethylarsine)chromium(III) *Perchlorate*.—The above procedure was repeated, 30% perchloric acid (2 ml.) being substituted for the 10N-hydrochloric acid. The pale green precipitate which settled out after refluxing with diarsine and the addition of ethyl ether was washed several times with ether and dried *in vacuo* [Found: C, 30·1; H, 4·1; Cl(chloro), 9·27%; *M*, ebullioscopic in 2·12% solution in acetone, 377. $C_{20}H_{32}O_4Cl_3As_4Cr$ requires C, 30·13; H, 4·06; Cl(chloro), 8·9%; *M*, 795].

Dibromodi-(o-phenylenebisdimethylarsine)chromium(III) *Tetrabromomono-(o-phenylenebisdimethylarsine)chromate*(III).—The procedure was the same as for the complex $[Cr(Diarsine)_2Cl_2][CrDiarsineCl_4]$, except that lithium bromide (3 g.) in ethanol was added before refluxing in acetone, and hydrobromic acid substituted for hydrochloric acid in the initial stages (Found: C, 25·2; H, 3·4; Br, 33·5. $C_{30}H_{48}Br_6As_6Cr_2$ requires C, 24·97; H, 3·32; Br, 33·3%).

Dibromodi-(o-phenylenebisdimethylarsine)chromium(III) *Perchlorate*.—The above experiment was repeated except that lithium bromide was omitted and 30% perchloric acid (2 ml.) added before refluxing in acetone (Found: C, 27·1; H, 3·7; Br, 18·1%; *M*, ebullioscopic in 1·42% solution in acetone, 342. $C_{20}H_{32}O_4ClBr_2As_4Cr$ requires C, 27·19; H, 3·65; Br, 18·1%; *M*, 884).

Di-iododi-(o-phenylenebisdimethylarsine)chromium(III) *Tetraiodomono-(o-phenylenebisdimethylarsine)chromium*(III).—Hydriodic acid and lithium iodide (3·0 g.) were substituted for lithium bromide and hydrobromic acid, and the rest of the procedure was as for the corresponding bromo-complex (Found: C, 21·0; H, 2·9; I, 43·3. $C_{30}H_{48}I_6As_6Cr_2$ requires C, 20·90; H, 2·81; I, 44·2%).

Di-iododi-(o-phenylenebisdimethylarsine)chromium(III) *Perchlorate*.—By omitting lithium iodide in the last preparation and including hydriodic acid and perchloric acid the pale green *compound* $[Cr(Diarsine)_2I_2]ClO_4$ was obtained. Owing to its appreciable solubility its solution must be made very concentrated before precipitation occurs (Found: C, 24·2; H, 3·1; I, 25·7%; *M*, ebullioscopic in 2·3% solution in acetone, 460. $C_{20}H_{32}O_4ClI_2As_4Cr$ requires C, 24·56; H, 3·29; I, 25·97%; *M*, 978).

Trichloromonoaquomono-(o-phenylenebisdimethylarsine)chromium(III).—Chromic chloride tetrahydrate (0·5 g.) and the diarsine (0·55 g.) were dissolved in dioxan (20 ml.), concentrated hydrochloric acid (5 ml.) added, and the mixture refluxed until a deep blue colour had developed. The mixture was then evaporated to 10 ml. on a water-bath under reduced pressure, and filtered. The filtrate was then treated with diethyl ether, stirred, and set aside. The green precipitate of the salt-like form was removed by centrifuging. The supernatant liquor was filtered and evaporated to dryness under reduced pressure; the residue was dissolved in a small quantity of chloroform, a little ether added, and the solution again filtered. The addition of light petroleum to the filtrate resulted in precipitation of the required *product* as a blue powder. The latter was then redissolved in ether, reprecipitated with light petroleum, and dried in a vacuum desiccator (Found: C, 26·2; H, 4·3; Cl, 22·8%; *M*, ebullioscopic in 2·26% solution in chloroform, 424. $C_{10}H_{18}OCl_3As_2Cr$ requires C, 25·97; H, 3·92; Cl, 23·00%; *M*, 462). The substance decomposes without melting between 240° and 245°.

Tribromomonoaquomono-(o-phenylenebisdimethylarsine)chromium(III).—The aforementioned procedure was repeated but hydrobromic acid was used instead of hydrochloric acid, and the corresponding *bromo-compound* was formed (Found: C, 19·7; H, 3·2; Br, 40·9%; *M*, ebullioscopic in 4·5% solution in chloroform, 610. $C_{10}H_{18}OBr_3As_2Cr$ requires C, 20·16; H, 3·05; Br, 40·3%; *M*, 596).

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