500. *Ditertiary Arsine Complexes of Octahedral Bivalent Molybdenum.*

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The preparation and properties of a series of ditertiary-arsine complexes of bivalent molybdenum, $Mo^{II}(Diarsine)_2Hal_2$, are reported, where Hal = Cl, Br, or I. Their magnetic moments are in the range 2·8—2·9 B.M., the deviation from the spin-only value for two unpaired spins being very small. The compounds are initially non-electrolytes in nitromethane but are rapidly oxidised. They are isomorphous with the corresponding $[Re(Diarsine)_2Hal_2]^0$ and $[Tc\ Diarsine_2Hal_2]^0$ compounds and appear to be the first known examples of octahedral bivalent molybdenum, having a d_ϵ^4-configuration. The spectra of the complexes have been measured and are consistent with the assumed octahedral arrangement of the ligands.

Apart from the polymeric dihalides and the diacetate [1] and certain substituted seven-co-ordinate carbonyl compounds (*e.g.*, Mo^{II} Diarsine$(CO)_3I_2)$,[2] few bivalent molybdenum compounds are known. The dihalides are unusual in that, unlike the corresponding chromous salts, they are stable to air and to most oxidising agents. Whereas the chromous halides are spin-free and have a tetragonal structure,[3] arising from the $d_\epsilon^3 d_\gamma^1$-configuration, the complex molybdenum chlorides involve [4] a cubic nucleus of the type $[Mo_6Cl_8]^{4+}$; a molybdenum atom is located at the centre of each face of the cube and a chlorine atom at each corner. For reasons discussed elsewhere [5] the molybdenum atom is conveniently regarded as having a valency of six, with metal–metal bonds, even though the formal oxidation state is only +2. Compounds of the type MoDiarsine$(CO)_3X_2$ are obtained by the action of a halogen on a tetracarbonyl, MoDiarsine$(CO)_4$, but no six-co-ordinate mononuclear molybdenum(II) complex has been previously reported.

The d^4 non-bonding configuration is of special interest owing to the range of co-ordination numbers and stereochemical arrangements to which it can give rise. If there are four unpaired electrons, tetragonal, square-planar, or even square-pyramidal arrangements are possible; if there are two unpaired electrons, (d_ϵ^4) octahedral co-ordination, as in $K_4Cr(CN)_6$, is expected. When there are no unpaired electrons, both four-co-ordination ($KReCl_4$) and seven-co-ordination (see above) are observed.

The absence of an example of octahedral molybdenum(II) complexes prompted us to investigate the behaviour of molybdenum halides with the ditertiary arsine chelate group *o*-phenylenebisdimethylarsine (Diarsine).[6] This chelate group has been shown previously to be an extremely versatile ligand for the stabilisation of a wide variety of oxidation states of most transition metals.

The compounds described here are obtained by treating a solution of the $[Mo^{III}(H_2O)Cl_5]^{2-}$ or the $[Mo^{III}Cl_6]^{3-}$ ion with Diarsine in a mixture of alcohol and water containing hydrochloric acid. Air must be excluded during all operations. Warming yields the bright yellow compound $Mo^{II}(Diarsine)_2Cl_2$, the tervalent molybdenum having been reduced to the bivalent state. The use of the molybdenum(III) bromide or iodide complex ions leads to the corresponding bromo- or iodo-complexes. These are more deeply coloured, the properties of the three complexes being shown in the Table. The reactions are slow at room temperature but are complete in about 12 hours at 40—50°.

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[1] Bannister and Wilkinson, *Chem. and Ind.*, 1960, 319.
[2] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1806.
[3] Oswald, *Helv. Chim. Acta*, 1961, **44**, 1049.
[4] Brosset, *Arkiv Kemi, Min., Geol.*, 1945, A20.
[5] Sheldon, *Nature*, 1959, **184**, 1210; L. Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, New York, 3rd edn., 1960.
[6] Chatt and Mann, *J.*, 1939, 610.

The complex dihalides are sensitive to air, the stability to oxidation being iodide > bromide ≫ chloride, which is the sequence usually observed.

Compound †	Colour of solid	Mol. conductivity * in nitromethane (c = 0·001M) (ohm^{-1} cm.^{2})	μ_{eff}, Magnetic moment at 25° (B.M.)
$[MoDiarsine_2Cl_2]^0$	Bright yellow	8	$2{\cdot}8_5$
$[MoDiarsine_2Br_2]^0$	Fawn or buff	20	2·9
$[MoDiarsine_2I_2]^0$	Light brown	23	2·8

* These values increase rapidly on storage. † Each of these compounds is isomorphous (X-ray powder pattern) with the corresponding technetium complex.

The complexes have a limited solubility in nitromethane and in chloroform. Although the colour of the solution is originally the same as that of the solid compound, it changes fairly rapidly and the compounds decompose. This is indicated by the molecular conductivities of the compounds which were determined as quickly as possible after dissolution. The change is probably due to aerial oxidation. For a uni-univalent electrolyte in nitromethane a molecular conductivity of about 90 mho is expected for a 10^{-3}M-solution. The values observed (20 mho or less) are clearly consistent with the presence of a non-electrolyte which has undergone some decomposition.

A study of the X-ray powder photographs reveals that each of the $[Mo^{II}Diarsine_2Hal_2]^0$ halides is isomorphous with the corresponding bivalent rhenium,[7] bivalent technetium,[8] and bivalent iron [9] complexes. The similarity of the powder patterns of the molybdenum and technetium complexes is specially noteworthy. The rhenium derivatives have been shown to be monomeric in solution and hence we may conclude that the Mo^{II} atom is six-co-ordinate.

The magnetic susceptibility of the various derivatives have been measured at room temperature and, in the case of the chloride, over the range from −180° to +20° C; a calculation of the magnetic moment (μ_{eff}), based on the room-temperature susceptibility, leads to a value of $\mu_{\text{eff}} = 2{\cdot}8$—$2{\cdot}9$ B.M. These results suggest that the complexes have a d_ϵ^4-configuration; as such, they are the first strong field paramagnetic molybdenum(II) derivatives described. The spin-only moment for two unpaired electrons is 2·83 B.M.; however, Kotani [10] has shown that for a d_ϵ^4 ion in a regular octahedron of negative charges the value of μ_{eff} can vary from 0·00 to 3·14 B.M. depending on the relative values of the spin–orbit coupling constant (λ) and the value of kT. The value of λ for the free ion at room temperature (at which $kT = 200$ cm.$^{-1}$) is about −1390 cm.$^{-1}$.[11] This leads to a value of $\mu_{\text{eff}} = 2{\cdot}3$ B.M. However, this value needs to be modified in two ways. First, the spin–orbit coupling constant is probably smaller in the complex than in the free ion (see above); this is a general phenomenon [12, 13] which occurs on complex formation owing to a decrease in the effective positive charge which is felt by the d-electrons. This reduction in λ will tend to increase the value of μ_{eff}. Secondly, the electrical field is undoubtedly not cubic, and probably the two halogen atoms in the complex are *trans* to one another. However, Figgis [14] has shown that, whether the two halogen atoms are *cis*- or *trans*-related, such distortions generally operate so as to destroy orbital degeneracy and hence to favour moments which approach the spin-only value. Studies of the temperature–susceptibility curve support this view; the value of θ computed from the expression $\chi \propto 1/(T + \theta)$ is of the order of 20°, but divergence from a linear plot is observed. The magnetic moment varies from 2·59 to 2·84 B.M. over the temperature range 78—300° K.

[7] Curtis, Fergusson, and Nyholm, *Chem. and Ind.*, 1958, 625.
[8] Fergusson and Nyholm, *Nature*, 1959, **183**, 1039.
[9] Nyholm, *J.*, 1950, 851.
[10] Kotani, *J. Phys. Soc., Japan*, 1949, **4**, 293.
[11] Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.
[12] Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183.
[13] Dunn, *J.*, 1959, 623; see also Pauling, *J.*, 1948, 1461.
[14] Figgis, *Trans. Faraday Soc.*, 1960, **57**, 198, 204.

One of the most interesting features of the reaction between the molybdenum(III) halides and Diarsine is that one can isolate molybdenum(V) as well as molybdenum(II) compounds. This suggests that the formation of molybdenum(II) arises from a disproportionation of molybdenum(III) in the presence of the Diarsine. Diarsine complexes of molybdenum in the higher oxidation state have been isolated and these will be described later in detail.[15]

It will be seen from the Experimental section that the compound $Mo(Diarsine)_2I_2$ was not obtained free from the chloride. This arises from the difficulty of displacing chloride by iodide. In other experiments exchange between bromide and chloride in $Mo(Diarsine)_2Cl_2$ in ethanol was found to be very slow. Steric factors may be involved but there is also the question of class A or B character.[16] For class A metals (*e.g.*, Be^{2+}, Al^{3+}) co-ordination of halogen in aqueous solution follows the order $Cl^- > Br^- > I^-$. We regard molybdenum(II) as being of the class A type for the reasons discussed elsewhere.[17]

Reflectance spectra of the chloride and bromide complexes have been obtained over the range 10,000—30,000 cm.$^{-1}$. In $Mo(Diarsine)_2Cl_2$ a band is observed with a maximum at ~10,800 cm.$^{-1}$, with some evidence of a shoulder at 11,100 cm.$^{-1}$, the half-widths being ($\delta-$) 700 and ($\delta+$) 800 cm.$^{-1}$. No other band is observed before the onset of the electron-transfer band absorption [18] at 17,000 cm.$^{-1}$. For the bromide, only the edge of the first band is visible at 10,000 cm.$^{-1}$, but the maximum is estimated at >9000 cm.$^{-1}$ by comparison with the chloride; in addition, a shoulder at 22,700 cm.$^{-1}$ appears on the edge of the electron-transfer band.

The first band can be assigned as the first ligand-field band, *i.e.*, to the ${}^5E \longleftarrow {}^3T_1$ transition. By extrapolation [19] a free-ion value of 535 cm.$^{-1}$ for the Racah B parameter is obtained, whilst for the complex ~400 cm.$^{-1}$ would be expected. For the chloride a Dq value of 2200—2400 cm.$^{-1}$ is expected also, account being taken of the position of Diarsine in the spectrochemical series.[18] When these values are used in conjunction with the Tanabe–Sugano diagram [20, 21] the predicted band positions are in reasonable agreement with those observed, although the weak ${}^1A_1 \longleftarrow {}^3T_1$ transition is not accounted for if the splitting on the first band is ascribed to the effect of tetragonal distortion.

The spectra of these complexes is of some general interest in view of the rarity of low-spin d_ϵ^4 octahedral complexes with accessible ligand-field bands. The solution spectra of the isoelectronic $[Re^{III}Diarsine_2Hal_2]^+$ complex ions have been determined [22] and these show features similar to those of the corresponding molybdenum(II) complexes.

EXPERIMENTAL

All the preparative work was carried out in an apparatus which had been first degassed and then filled with pure nitrogen. Rigid exclusion of oxygen is essential.

*Dichlorobis-*o*-phenylenebisdimethylarsinemolybdenum*(II).—Dipotassium pentachloroaquomolybdate(III) (0·62 g.) was treated with 6N-hydrochloric acid (5 ml.), and the solution was warmed and added to Diarsine (1·4 g.) in ethanol (50 ml.). The mixture was heated to about 50°, the colour changing from the original orange-red to darker orange. A bright yellow powder was gradually deposited, leaving a pink supernatant liquor. The reaction appeared to be complete in about 24 hr. The solid *complex* (0·5 g.) was filtered off, washed with dilute hydrochloric acid to remove any precipitated potassium chloride, and dried *in vacuo* (Found: C, 32·6; H, 4·6; Cl, 9·6; Mo, 12·7. $C_{20}H_{32}As_4Cl_2Mo$ requires C, 32·5; H, 4·4; Cl, 9·6; Mo, 13·0%).

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[15] Irving, Lewis, Nyholm, and Smith, unpublished work.

[16] Ahrland, Chatt and Davies, *Quart. Rev.*, 1958, **12**, 265.

[17] Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

[18] Dunn, Nyholm, and Yamada, *J.*, 1962, 1564.

[19] Jorgensen, unpublished work.

[20] Tanabe and Sugano, *J. Phys. Soc., Japan*, 1959, **9**, 766.

[21] Dunn, in "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ. Inc., 1960.

[22] Fergusson, Ph.D. Thesis, London, 1960.

Alternatively one may use tripotassium hexachloromolybdate(III), or ideally a tervalent molybdenum chloride solution obtained by electrolytic reduction.

*Dibromobis-*o*-phenylenebisdimethylarsinemolybdenum*(II).—A solution (~4 ml.) of tervalent molybdenum (0·4M in molybdenum and 7M in hydrochloric acid) was electrolytically reduced, and evaporated to dryness *in vacuo*, then treated with concentrated hydrobromic acid (*d* 1·46) and evaporated to dryness again. After two further similar treatments the residue was dissolved in oxygen-free concentrated hydrobromic acid, a little water added, and the solution warmed until clear. To the solution was then added Diarsine (1·3 g.) in ethanol (40 ml.), and the reaction was completed as for the chloride. The *product* (0·46 g.) was of a buff colour and had properties similar to those of the dichloride (Found: C, 29·3; H, 4·1; Br, 18·3; As, 33·9; Mo, 11·5. $C_{20}H_{32}As_4Br_2Mo$ requires C, 29·0; H, 3·9; Br, 19·3; As, 36·2; Mo, 11·6%).

*Di-iodobis-*o*-phenylenebisdimethylarsinemolybdenum*(II).—Dipotassium pentachloroaquomolybdate(III) (1·0 g.) was dissolved in freshly purified hydriodic acid (*d* 1·7; 2 ml.) containing lithium iodide (2·0 g.), and water (5 ml.) was added. After gentle heating, the Diarsine (1·43 g.), dissolved in ethanol (50 ml.), was added. The compound (0·5 g.) was isolated as in the previous preparations and had a light brown colour. Contamination with the dichloro-complex was unavoidable owing to the method of preparation and this is reflected in the analysis (Found: C, 27·0; H, 4·1; Cl, 1·1; I, 23·3; Mo, 11·0. Calc. for $C_{20}H_{32}As_4I_2Mo$: C, 26·0_5; H, 3·5; I, 27·5; Mo, 10·4%). The analysis agrees with a composition of about 85% of $Mo(Diarsine)_2I_2$ and 15% of $Mo(Diarsine)_2Cl_2$.

Analyses.—Molybdenum was estimated colorimetrically by an adaptation of the method of Cox and Pollitt.[23] Decomposition was effected by treatment with concentrated sulphuric acid followed by ignition at $<500°$.[24] Halogens were estimated either gravimetrically, after decomposition with concentrated nitric acid in the presence of silver nitrate [25] followed by reprecipitation, and on occasions by microanalysis.

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[23] Cox and Pollitt, *J. Soc. Chem. Ind.*, 1944, **63**, 375.
[24] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1803.
[25] Nyholm, *J.*, 1950, 2061.