The Hexa-arsine: Tetrakis-(3-dimethylarsinopropyl)-*o*-phenylenediarsine: a New Sexadentate Chelating Agent

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THE hexa-arsine, tetrakis-(3-dimethylarsinopropyl)-*o*-phenylenediarsine ($C_{26}H_{52}As_6 \equiv$ SAS, Figure) has been synthesised by the interaction of *o*-phenylenebisdichloroarsine[1] and a Grignard reagent prepared from 3-chloropropyldimethylarsine,[2] and isolated as a colourless viscous oil. Complexes with transition metals have been isolated from the reaction of hexa-arsine with the transition-metal salt in ethanol or aqueous ethanol. A selection of these compounds together with their magnetic properties, molar conductivities, and visible absorption spectra in nitromethane are listed in the Table.

This is the first compound to be synthesised

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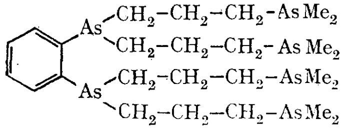
Some metal complexes of tetrakis-(3-dimethylarsinopropyl)-o-phenylenediarsine

Complex	Colour	Molar conductivity 10^{-3} M-MeNO$_2$ at 25°	Magnetic properties	Visible absorption spectra in MeNO$_2$ (357—600 mμ) λ max	ϵ max
$[Fe^{II}(SAS)](ClO_4)_2,3H_2O$	Mauve	160	diamag.	$<$ 375	—
$[Co^{II}(SAS)](ClO_4)_2,3H_2O$	Brown	161	$\mu = 2{\cdot}5$ B.M.	515	920
$[Co^{III}(SAS)](ClO_4)_3,3H_2O$	Red	212	diamag.	—	—
$[Co^{III}(SAS)]I_3$	Deep red	220	diamag.	485	2100
$[Ni^{II}(SAS)]I_2$	Purple	162	diamag.	—	—
$[Ni^{II}(SAS)](ClO_4)_2,3H_2O$	Purple	170	diamag.	465	4000
$[Pd^{II}(SAS)](ClO_4)_2,3H_2O$	Orange	170	diamag.	445	880
$[Pt^{II}(SAS)](ClO_4)_2,3H_2O$	Yellow	174	diamag.	395	1050

with six arsenic atoms in positions suitable for co-ordination to the one metal atom. Models show that these six arsenic atoms can be arranged to occupy the corners of an octahedron.

The reaction of hexa-aquo-iron(II) perchlorate in ethanol with the hexa-arsine forms a purple solution from which the mauve iron(II) complex $[Fe(SAS)](ClO_4)_2,3H_2O$ slowly separates. The compound is diamagnetic and a di–univalent electrolyte in nitromethane. The diamagnetism of this $[^2H_6]$complex is compatible with a six co-ordinate spin-paired arrangement. In a similar manner the cobalt(II) complex $[Co(SAS)](ClO_4)_2,3H_2O$ is isolated, from which the tervalent cobalt complex $[Co(SAS)](ClO_4)_3,3H_2O$ is prepared by nitric acid oxidation. An anhydrous cobalt(III) compound $[Co(SAS)]I_3$ is obtained when lithium iodide is added to an ethanolic solution containing the hexa-arsine and cobalt(II) chloride through which air has been passed. The bivalent cobalt complex has a magnetic moment of 2·5 B.M. and is a di–univalent electrolyte while the tervalent complexes are diamagnetic and tri–univalent electrolytes. The ability to oxidise the bivalent cobalt compound $[Co(SAS)](ClO_4)_2,3H_2O$ to the analogous cobalt(III) compound, without oxidation of the tertiary arsine groups, would suggest that in the case of the cobalt(II) complex all six arsenic atoms are co-ordinated.

The purple nickel(II) complexes $[Ni(SAS)](ClO_4)_2,3H_2O$ and $[Ni(SAS)]I_2$ are readily prepared from ethanolic solutions of the hexa-arsine and the appropriate nickel(II) salt. Both compounds are diamagnetic and di–univalent electrolytes. Bivalent palladium and platinum complexes have also been investigated with this ligand. The orange palladium compound $[Pd(SAS)](ClO_4)_2,3H_2O$ and the yellow platinum complex $[Pt(SAS)](ClO_4)_2,3H_2O$ are diamagnetic and di–univalent electrolytes. The colours of the hexa-arsine complexes of nickel, palladium, and platinum are similar to those of the corresponding bis-complexes of the tri-arsine, bis(bis-3-dimethylarsinopropyl)-arsine.[3]



The purple nickel hexa-arsine complex has an intense absorption band at 465 mμ ($\epsilon = 4000$) while the bis-triarsine complex possesses an intense absorption band at 540 mμ ($\epsilon = 2000$) and has been postulated as a six co-ordinate tetragonal structure.[3] The red tris-diarsine complex $Ni(diars)_3(ClO_4)_2$ (diars = *o*-phenylenebisdimethylarsine) has two absorption bands in this region at 435 and 530 mμ both of high intensity (ϵ *ca.* 2000 and 1100 respectively) and is postulated as a regular octahedral cation.[4]

Examination of the reaction between the nickel and palladium complexes, $[M(SAS)](ClO_4)_2,3H_2O$, with methyl iodide in nitromethane solution shows no change in their molar conductivities after a period of 50 hr., while a similar reaction between the ligand and methyl iodide showed a marked change in conductivity over 24 hr., when the molar conductance reaches a limiting value of 164 ohm^{-1} at 25°. This lack of reactivity of tertiary arsine metal complexes has been used by others[5] as evidence for suggesting that no free tertiary arsine groups are present.

It seems reasonable to assume that the metal complexes studied so far are six co-ordinate with the hexa-arsine acting as a sexadentate ligand.

(*Received, June 17th*, 1968; *Com.* 792.)

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