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Complexes of Platinum(II) with *cis*- and *trans*-1, 2-Bis(dimethylarsino) ethylene

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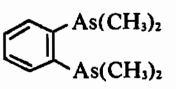
cis-*1,2-Dichloroethylene reacts with sodium dimethylarsenide to give a colourless oil containing the* trans- *and* cis-*isomers of 1,2-bis(dimethylarsino) ethylene (edas) in a ratio of about 10 to 1, as indicated by proton nmr measurements. The infrared spectrum and an approximate determination of the dipole moment support this conclusion. The oil reacts with potassium tetrachloroplatinate(II) to give an insoluble complex* $PtCl_2(edas)$ *and a water-soluble complex* $[Pt_2(edas)_4]Cl_4 . 3H_2O$*, which readily loses two molecules of ligand forming the insoluble complex. Derivatives of formula* $[Pt_2(edas)_4]X_4$ ($X = PF_6^-$, ClO_4^-, $\frac{1}{2}PtCl_6^{2-}$) *can also be isolated. The hexafluorophosphate and perchlorate derivatives behave as 4:1 electrolytes in* ca. 10^{-3} M *nitromethane solution, while the chloride shows behaviour intermediate between that of a 1:1 and 2:1 electrolyte. The infrared spectra suggest that these complexes contain the* trans-*olefinic ditertiary arsine, and structures are suggested in which this ligand bridges two platinum atoms. Ultraviolet irradiation of solutions of the complex* Pt_2Cl_4(trans-*edas*)$_4$ *yields an isomeric, water-soluble complex which is formulated as* $[Pt($cis-*edas*$)_2]Cl_2$ *on the basis of its infrared spectrum. Derivatives of formula* $[Pt($cis-*edas*$)_2]^{2+}X_2$ ($X = PF_6^-$, ClO_4^-, $\frac{1}{2}PtCl_6^{2-}$) *can also be isolated; these, and the dichloride, behave as 2:1 electrolytes in* ca. 10^{-3} M *nitromethane solution. These complexes are believed to contain two molecules of* cis-*1,2-bis(dimethylarsino)ethylene acting as a bidentate chelate ligand. The mechanisms for the observed isomerizations are briefly discussed.*

Introduction

The complexes formed with transition metals by tertiary phosphines and arsines, especially bidentate chelate ligands, exhibit a wide range of oxidation states and coordination numbers.[2] A particularly versatile chelate ligand is 1,2-bis(dimethylarsino)-benzene(I).[3] The simple preparation of this ligand recently reported by Feltham, Kasenally and Nyholm,[4] which involves the reaction of *o*-dichlorobenzene with sodium dimethylarsenide, led us to attempt the preparation of the *cis*-ethylenic analogue (II) by a similar reaction using *cis*-dichloroethylene in place of *o*-dichlorobenzene, in order to compare the complexing properties of the aromatic and *cis*-olefinic ditertiary arsines. The *trans*-olefinic arsine (III) is also of interest as a potential bridging ligand which could form binuclear or polymeric complexes.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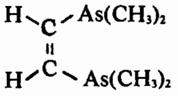
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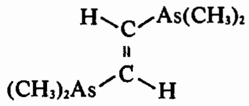
(III)

While the present work was in progress, the reaction of *cis*-dichloroethylene with sodium dimethylarsenide was reported briefly,[5] but the configuration of the product was not established. A number of ligands related to (II) and (III) and some derived metal complexes have been described recently, *e.g.* *cis*- and *trans*-1,2-bis(diphenylphosphino) ethylene,[6-8] *cis*- and *trans*-1,2-bis(diphenylarsino)ethylene,[9] 1,2-bis-(diphenylarsino)tetrafluoro-cyclobutene and its diphenylphosphino analogue.[10]

Experimental Section

Starting Materials. Tetrahydrofuran was dried over molecular sieve and distilled from sodium benzophenone ketyl before use. Dimethyliodoarsine was

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[2] (a) G. Booth, *Advan. Inorg. Radiochem.*, *6*, 1 (1964); (b) T. A. Manuel, *Advan. Organometal Chem.*, *3*, 181 (1965).

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[4] (a) R. D. Feltham, A. Kasenally, and R. S. Nyholm, *J. Organometal Chem.*, *7*, 285 (1967); (b) R. D. Feltham and W. Silverthorn, *Inorg. Synth.*, *10*, 159 (1967).

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[6] A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, *86*, 2299 (1964).

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[9] A. M. Aguiar, J. T. Mague, H. J. Aguiar, T. G. Archibald, and G. Prejean, *J. Org. Chem.*, *33*, 1681 (1968).

[10] W. R. Cullen, P. S. Dahliwal, and C. J. Stewart, *Inorg. Chem.*, *6*, 2256 (1967).

prepared from cacodylic acid by the method of Burrows and Turner.[11]

Measurements. The infrared spectra of tertiary arsines were measured on liquid films and in cyclohexane solution on a Perkin-Elmer 237 double beam spectrophotometer (Cambridge) and on a Grubb-Parsons G.S. 2A double beam grating spectrophotometer (London) in the range 4000-650 cm^{-1}. The infrared spectra of the complexes were measured in Nujol and hexachlorobutadiene mulls. Proton magnetic resonance spectra were measured at 60 MHz on a Perkin-Elmer R-10 instrument and at 100 MHz on a Varian HA 100 instrument. Deuteriochloroform or carbon tetrachloride solutions containing *ca.* 1% tetramethylsilane as the internal standard were used for the ligand, while the complexes were measured in deuterium oxide solutions using tetramethylsilane as external reference. Conductance measurements were carried out at 25° on *ca.* 10^{-3} *M* solutions in Analar nitromethane using a Wayne-Kerr Universal bridge, Type B 221, and conventional dip-type platinum electrodes.

The dipole moment of 1,2-bis(dimethylarsino)-ethylene in benzene solution was measured by Mrs. R. M. Canadine, ICI Petrochemicals and Polymer Laboratory, Runcorn, Cheshire.

Microanalyses were carried out by the microanalytical laboratories of the Department of Chemistry, University of Cambridge and University College London, by Messrs. Weiler and Strauss, Oxford, and by the Max-Planck Institut für Kohlenforschung, Mülheim, Germany. Platinum was determined by direct ignition to the metal after moistening with concentrated sulphuric acid.

Reaction of cis-*Dichloroethylene with Sodium Dimethylarsenide.* Sodium wire (19.3 g., 2.5 moles) was cut into small pieces and added to dry tetrahydrofuran (240 ml.). The mixture was cooled to 0°C in a nitrogen atmosphere and dimethyliodoarsine (77.9 g., 1 mole) was added dropwise with stirring over one hour, the temperature being maintained at 0-5°C. The yellow-green suspension was stirred for 30 min. at this temperature, then cooled to −40°C and treated dropwise with *cis*-dichloroethylene (12.9 ml., 0.5 mole), the temperature being kept below −30°C. The reaction mixture was allowed to warm to room temperature and the solvent was removed at reduced pressure. The residue was hydrolyzed cautiously with water and the organic layer was separated and distilled, giving a small amount of tetramethyldiarsine and 1,2-bis(dimethylarsino)etheylene (mainly the *trans*-isomer) as a colorless, air-sensitive liquid, b.p. 66-70°/6 mm Hg (16.5 g., 41% yield).

Anal. Calcd. for $C_6H_{14}As_2$: C, 30.5; H, 6.0; As, 63.5. Found: C, 30.5, 30.1; H, 5.8, 6.4; As, 63.7, 63.5 (analyses on samples from two independent preparations).

The liquid reacts with methyl iodide at room temperature giving a colorless dimethiodide, which melts at 240°C after recrystallization from ethanol (literature value,[5] 260°C).

Anal. Calcd. for $C_8H_{20}As_2I_2$: C, 18.5; H, 3.8; I, 48.8. Found: C, 18.5; H, 3.6; I, 49.6.

A similar reaction was carried out using *trans*-dichloroethylene in place of *cis*-dichloroethylene. Distillation at 56°/ 5 mm. gave an exceedingly air-sensitive liquid, probably tetramethyldiarsine; the infrared spectrum gave no indication of the presence of 1,2-bis(dimethylarsino)ethylene.

*Dichloro[*trans-*1,2-bis(dimethylarsino)ethylene]-platinum(II),* $[PtCl_2(\text{trans-}edas)]_n$. Potassium tetrachloroplatinate (II) (1 g., 1 mole) in water (40 ml.) was added dropwise with stirring to a solution of the ligand (0.57 g., 1 mole) in ethanol (40 ml.) which had been warmed on the steam-bath. The complex, which precipitated immediately, was filtered and washed with acetone and ether (80% yield). It forms fine white crystals which decompose above 300°C and are insoluble in common organic solvents.

Anal. Calcd. for $C_6H_{14}As_2Cl_2Pt$: C, 14.3; H, 2.7; Cl, 13.7; Pt, 38.9. Found: C, 13.7; H, 3.2; Cl, 14.0; Pt, 39.0.

*Tetra-μ-[*trans-*1,2-bis(dimethylarsino)ethylene]diplatinum(II)tetrachloride trihydrate,* $[Pt_2(\text{trans-}edas)_4]Cl_4 3H_2O$. Potassium tetrachloroplatinate(II) (1.75 g., 1 mole) in water (20 ml.) was added to the ligand (2.1 g., 2 moles) in ethanol (15 ml.), and the yellow solution was stirred for 30 min. On cooling, bright yellow crystals were obtained (83% yield).

Anal. Calcd. for $C_{12}H_{28}As_4Cl_2Pt.1.5H_2O$: C, 18.8; H, 4.1; Cl, 9.3; Pt, 25.5. Found: C, 18.6; H, 4.3; Cl, 9.4; Pt, 25.2.

At room temperature in vacuo, the complex lost water and became deep orange. The orange complex still contained water, as shown by the infrared spectrum, and on exposure to the atmosphere, the yellow hydrate was rapidly re-formed. On heating to 95°C in vacuo, or on heating in acetone or chloroform, the complex $[PtCl_2(\textit{trans-}edas)]_n$ was formed. Thermogravimetry and differential thermal analysis on $Pt(\textit{trans-}edas)_2Cl_2 1.5H_2O$ also showed a weight loss corresponding to one molecule of ligand at *ca.* 130°C, followed by more complicated decomposition at *ca.* 300°C.

Tetraperchlorate Derivative, $[Pt_2(\text{trans-}edas)_4](ClO_4)_4$. An aqueous solution of the tetrachloride was treated with 30% aqueous perchloric acid. The white powder which precipitated was filtered and air-dried. Analytical data could not be obtained owing to the explosiveness of the compound. The infrared spectrum was similar to those of the PF_6^- and $PtCl_6^{2-}$ derivatives, and it was assumed to be pure for the purpose of conductivity measurements.

Tetrakis(hexafluorophosphate) Derivative, $[Pt_2(\text{trans-}edas)_4](PF_6)_4$. An ethanolic solution of the tetrachloride was treated with a saturated aqueous solution of ammonium hexafluorophosphate. The white solid was recrystallized from 1:1 acetone/ethanol. The infrared spectrum showed the presence of some water.

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(11) G. J. Burrows and E. E. Turner, *J. Chem. Soc.*, *119*, 428 (1921).

Anal. Calcd. for $C_{12}H_{28}As_4F_{12}P_2Pt$: C, 15.0; H, 2.9; F, 23.8. Foudn: C, 15.6; H, 3.2; F, 23.3.

Bis(hexachloroplatinate) Derivative, $[Pt_2(\text{trans-}edas)_4](PtCl_6)_2$. An ethanolic solution of the complex was treated with a saturated solution of potassium hexachloroplatinate in aqueous ethanol. The yellow insoluble precipitate was washed with water and ethanol, and dried at 25°/0.1 mm.

Anal. Calcd. for $C_{12}H_{28}As_4Cl_2Pt_2$: C, 13.4; H, 2.6; Pt, 36.3. Found: C, 13.5; H, 2.8; Pt, 37.1.

*Bis(*cis*-1,2-bis(dimethylarsino)ethylene]platinum(II) dihexafluorophosphate,* $[Pt(\text{cis-}edas)_2](PF_6)_2$ *and the Corresponding Dichloride,* $[Pt(\text{cis-}edas)_2]Cl_2$. The complex $[Pt_2(\textit{trans}\text{-edas})_4]Cl_4$ (0.2 g.) in ethanol (50 ml.) was irradiated with ultraviolet light for 12 hrs. using a Hanovia medium-pressure photochemical reactor. The resulting colourless solution was filtered and added dropwise with vigorous stirring to ether (50 ml.). The crude dichloride precipitated as a white, hygroscopic powder (45% yield) which was filtered and dried in a dry-box. Analyses at this stage gave high chloride and low carbon and hydrogen values. Treatment of the aqueous solution of the chloride with potassium hexafluorophosphate gave $[Pt(\textit{cis}\text{-edas})_2](PF_6)_2$ as a colourless powder which was recrystallized from acetone.

Anal. Calcd. for $C_{12}H_{28}As_4F_{12}P_2Pt$: C, 15.0; H, 2.9; F, 23.8. Found: C, 15.3; H, 2.9; F, 24.3.

The hexafluorophosphate derivatives in acetone solution was treated with a fourfold excess of lithium chloride in acetone. The dichloride precipitated immediately as a white powder, which was filtered in a dry-box and dried at 25°/0.1 mm (50% yield). Analyses for carbon and hydrogen were satisfactory, although chlorine analyses were consistently high.

Anal. Calcd. for $C_{12}H_{28}As_4Cl_2Pt$: C, 19.5, H, 3.8; Cl, 9.6. Found: C, 19.2; H, 4.4; Cl, 11.0.

Diperchlorate Derivative, $[Pt(\text{cis-}edas)_2](ClO_4)_2$. An aqueous solution of the dichloride was treated with 30% aqueous perchloric acid. The precipitated white powder was filtered and dried at 25°/0.1 mm.

Anal. Calcd. for $C_{12}H_{28}As_4Cl_2O_8Pt$: C, 16.6; H, 2.7. Found: C, 16.8; H, 3.2.

Hexachloroplatinate Derivative, $[Pt(\text{cis-}edas)_2](PtCl_6)$. An aqueous solution of the dichloride was treated with a saturated aqueous solution of hexachloroplatinic acid. The insoluble yellow powder was filtered off and dried at 25°/0.1 mm.

Anal. Calcd. for $C_{12}H_{28}As_4Cl_6Pt_2$: C, 13.4; H, 2.6; Cl, 19.8; Pt, 36.3. Found: C, 13.7; H, 2.5; Cl, 19.9; Pt, 37.9. The platinum analysis was not very accurate owing to the small amount of available sample.

Results and Discussion

The ditertiary arsine of formula $C_6H_{14}As_2$ isolated from the reaction of *cis*-dichloroethylene with sodium dimethylarsenide is a colourless, high-boiling oil which is readily oxidized by air, but is stable under nitrogen. The nmr spectrum measured in $CDCl_3$ shows two signals assignable to vinyl protons at τ 3.17 and τ 3.35 in a ratio of approximately 1 to 10 and a singlet due to methyl protons at τ 9.00. The ratio of vinyl to methyl absorptions is 1:6. The infrared spectrum (Table I) shows a strong band at *ca.* 970 cm^{-1} which is characteristic of *trans*-disubstituted derivatives of ethylene[12] and can be assigned to the olefinic C–H deformation mode; there are also weak absorptions in the 700 cm^{-1} region characteristic of *cis*-disubstituted ethylenes. Strong absorptions in the regions 1420 cm^{-1}, 1280-1255 cm^{-1}, and 890-834 cm^{-1} are assigned to various modes of the $As(CH_3)_2$ group (Table I), following the assignment of the corresponding frequencies in 1,2-bis-(dimethylarsino)benzene.[13] The infrared spectrum of a liquid film of the compound shows a weak band at *ca.* 1560 cm^{-1}, which is probably due to a C=C stretching vibration, but the band is not visible if the spectrum is measured in cyclohexane solution. For a *trans*-disubstituted ethylenic derivative, the C=C stretching vibration should be infrared-inactive. The dipole moment of the ligand in benzene is approximately 1.2 D, which may be compared with the dipole moments of *cis*- and *trans*-dichloroethylene (1.80 and 0 D respectively),[14] *cis*- and *trans*-1,2-bis-(diphenylphosphino)ethylene (1.96 and 0.99 D respectively) and the *cis*- and *trans*-diphenylarsino analogues (1.37 and 0.97 D respectively).[9]

The ligand reacts readily with methyl iodide to form a dimethiodide (also isolated by Phillips and Vis[5]), the infrared spectrum of which shows no band due to C=C stretching at 1560 cm^{-1}. Evaporation to dryness after removal of the dimethiodide gives a crude product which has not been obtained in sufficient quantity for purification; its infrared spectrum shows a medium band at 1560 cm^{-1}. It may be noted that the aromatic ditertiary arsine I forms only a monomethiodide under the same conditions.[15]

From these data, and from the types of complex formed with platinum(II) (see below), it is concluded that the ligand contains predominantly (*ca.* 90%) the *trans*-isomer (III), with a small amount (*ca.* 10%) of the *cis*-isomer (II). The proton resonances at τ 3.17 and τ 3.35 are assigned to the vinyl protons of (II) and (III) respectively. These conclusions are supported by the fact that the ligand reacts with nickel(II) salts in ethanol to give *ca.* 10% yields of complexes derived from (II) and 70-80% yields of complexes derived from (III).[16] Displacement of the ligands from these complexes has given small amounts of the pure isomers (II) and (III), which show singlet vinyl proton resonances in $CDCl_3$ at τ 3.17 and τ 3.35 respectively, in agreement with the above assignments.[16] Attempts to separate the isomers by fractional distillation or v.p.c. have not so far been successful.

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(12) L. J. Bellamy, «The Infrared Spectra of Complex Molecules», Methuen and Co. Ltd., London, England, pp. 45-48 (1960).
(13) G. A. Rodley, Thesis, University of London (1963).
(14) R. Bramley, C. G. Le Fevre, and B. P. Rao, *J. Chem. Soc.*, 1183 (1959).
(15) F. G. Mann and F. C. Baker, *J. Chem. Soc.*, 4147 (1952).
(16) M. A. Bennett and J. D. Wild, unpublished work.

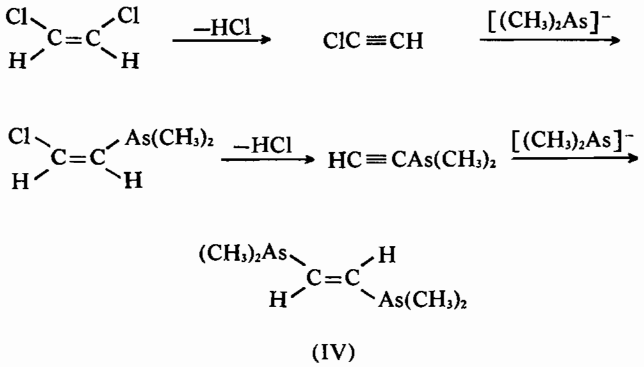
Table I. Infrared absorption bands in the region 3400-650 cm^{-1} for *trans*-edas and its platinum(II) complexes

Assignment	Ligand [a]	Dimethodide of *trans*-edas	$[Pt_2(trans\text{-}edas)_4]Cl_4 . 3H_2O$	$[PtCl_2(trans\text{-}edas)]_n$	$[Pt_2(trans\text{-}edas)_4][PtCl_6]_2$
O–H str. (H_2O)		not measured	3400 m		not measured
olef C–H str	3000 s		3000 w	3000 w	
C–H str of $As(CH_3)_2$	2920 s 2820 w		2920 s 2740 w	2920 s	
H–O–H def. (H_2O)			1635 ms		1610 w, br
olef C=C str. [b]	1560 m				
asym C–H def. of $As(CH_3)_2$	1420 vs	1420 m	1420 s	1410 s	1410 m
sym C–H def. of $As(CH_3)_2$	1280 s 1255 s	1300 m 1280 w 1268 m	1264 m	1270 m 1255 m	1269 w
olef C–H i.p. def. [c]	1142 ms 1120 w	1199 m	1176 vs	1180 m	1179 w, sh 1162 w, sh 1158 w
olef C–H o.o.p. def.	969 s	962 vs, sh 953 vs 930 vs	1026 m	975 s	970 m
C–H rock of $As(CH_3)_2$	890 vs 846 vs 834 s 790 m 735 m	881 sh 872 s	914 s 870 vs 826 s	920 s 890 s 860 m	917-909 m 890 ms 882 ms 870 m, sh

[a] Probably a mixture of approximately 90% *trans* and 10% *cis*-edas (see text). [b] May be due to *cis*-isomer. [c] Tentative assignment. Abbreviations: vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; sh, shoulder; br, broad.

The only product we obtained from the reaction of *trans*-dichloroethylene with sodium dimethylarsenide is tetramethyl-diarsine (cacodyl)$[(CH_3)_2As{-}]_2$. Phillips and Vis[5] report that an unidentified dimethylarsinoethylene is also produced, but this could not be separated from the cacodyl.

At present, the mechanism of the observed isomerization is unknown. It occurs even when the excess of sodium is removed by filtration before the dichloroethylene is added and despite the low temperatures (<–30°C) maintained during the reaction. This suggests that sodium dimethylarsenide is sufficiently basic to cause the isomerization. One possible mechanism involves a series of base-catalyzed eliminations and additions, with acetylenic intermediates:[17]



(IV)

This mechanism explains the lack of reactivity of *trans*-1,2-dichloroethylene, since dehydrohalogenation is known to take place preferentially from *trans*-positions.[17] The stereochemistry of the final product obviously depends on the mode of addition of $[(CH_3)_2As]^-$ to the acetylenic intermediate (IV), which in this case must be mainly *cis*, giving predominantly the *trans*-product. It should be noted, however, that the reactions of *cis*-dichloroethylene with a number of related nucleophiles *e.g.* $[(C_6H_5)_2P]^-$,[6] $[(C_6H_5)_2As]^-$,[9] and $[p\text{-}CH_3C_6H_4S]^-$ [18] are reported to occur with retention of the *cis*-configuration. Also, the first one reacts with *trans*-dichloroethylene with retention of the *trans*-configuration,[6] the second one gives only 10% of the *trans*-product,[9] while the third fails to react. On the other hand, both *cis*- and *trans*-dichloroethylene react with sodium *t*-butylmercaptide giving the *cis*-disubstituted derivative.[19] It appears that a number of mechanisms may be operative in nucleophilic substitutions on double bonds.

Platinum(II) Complexes. Aqueous potassium tetrachloroplatinate(II) (1 mole) reacts with the ligand (1 mole) to give an insoluble, white, finely crystalline solid of formula $PtCl_2(edas)$. Its infrared spectrum (Table I) shows no band at 1560 cm^{-1} and is otherwise similar to that of the original ligand; the appearance of a strong band at *ca.* 970 cm^{-1} suggests that the complex contains the *trans*-ligand (III). Models show that (III) cannot act as a chelate group, so that the complex must be either dimeric or polymeric with bridging ligand molecules. Two obvious possibilities are shown in (V) and (VI). A polymeric structure similar to (V) has been suggested for the rhodium (I) carbonyl complex of *trans*-1,2-bis(diphenylarsino)ethylene.[9]

From the reaction of an aqueous ethanolic solution of potassium tetrachloroplatinate(II) with two equivalents of the ligand, bright yellow crystals of formula $Pt(edas)_2Cl_2 . 1.5H_2O$ can be isolated. The infrared spectrum (Table I) shows strong bands due to water and other bands characteristic of (III), although the olefinic C–H deformation frequency is shifted from its position at 969 cm^{-1} in the free ligand to 1026

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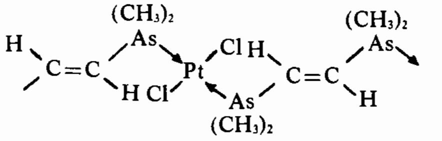
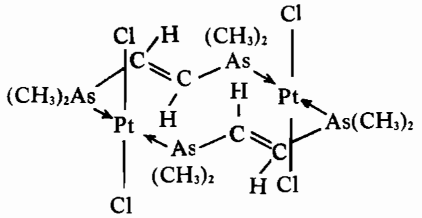
(17) S. Patai and Z. Rappaport, «The Chemistry of Alkenes», S. Patai, Ed., Interscience, New York, N. Y., Chapter 8, p. 528, et. sep., and references cited therein (1964).

(18) W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. MacManimie, *J. Am. Chem. Soc.*, *78*, 2743 (1956).

(19) J. J. Flynn, Jr. and W. E. Truce, *Diss. Abs.*, *27*, 406-B (1966).

cm^{-1}. The 60 MHz nmr spectrum in D_2O consists of two broad bands (6.6 Hz at half-height) at τ 2.55 and τ 8.05, of relative intensity 1:6, due to the vinyl and methyl protons of (III), together with a sharp band at τ 5.25 due to water. The complex readily loses ligand on heating in high vacuum or in acetone or chloroform forming $[PtCl_2(\textit{trans}\text{-edas})]_n$. A reasonable dimeric structure for $[Pt(\textit{trans}\text{-edas})_2]Cl_2$ is shown in (VII). The loss of two ligand molecules, giving structure (VI), can be readily envisaged, and is analogous to the well-known formation of complexes of the type $PtCl_2(PR_3)_2$ from ionic chloride derivatives of $[Pt(PR_3)_4]^{2+}$.[20]


(V)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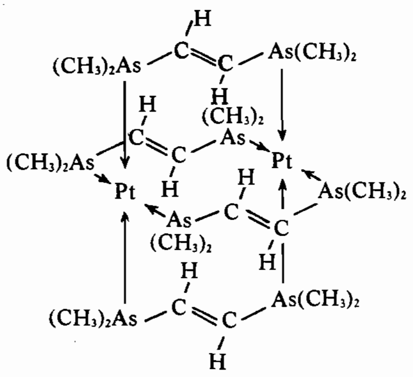
(VII)

The complex $[Pt_2(\textit{trans}\text{-edas})_4]Cl_4$ forms a number of derivatives of general formula $[Pt_2(\textit{trans}\text{-edas})_4]X_4$ ($X = PF_6^-$, ClO_4^-, and $\frac{1}{2}PtCl_6^{2-}$), which have infrared spectra similar to that of the *trans*-ligand. They tenaciously retain water, even on heating *in vacuo*. Their conductances have been measured in nitromethane solution at 25°C over a range of concentration and interpreted by the method of Feltham and Hayter.[21] Plots of Λ_{equiv} *vs.* $\sqrt{C_{equiv}}$ are shown in Figure 1. The perchlorate is not very soluble in nitromethane, so that the range of concentration studied for this complex is limited, but the similarity of equivalent conductivities at comparable concentrations for the perchlorate and hexafluorophosphate derivatives indicates a similar degree of dissociation. For these two derivatives, the slopes of the curves for $C < 10^{-3}$ equivs. per liter are approximately 1400. This compares with a value of 1020 for the 3:1 electrolyte $[Co(bipy)_3](ClO_4)_3$;[21] no values for a 4:1 electrolyte are available. The molar conductivity of $[Pt_2(\textit{trans}\text{-edas})_4](PF_6)_4$ at $10^{-3}\,M$ concentration in nitromethane is 196 ohm^{-1} cm^2 mol^{-1}, which is about the value expected for a 3:1 electrolyte, but, as can be seen in Figure 1, ion-pairing is extensive and complete dissociation to a 4:1 electrolyte is unlikely. Therefore, the conductance data support the formulation of these compounds as $[Pt_2(\textit{trans}\text{-edas})_4]^{4+}X_4^-$ ($X = PF_6$, ClO_4).

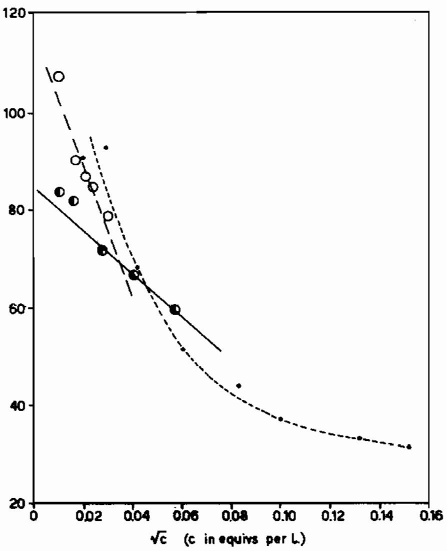

Figure 1. Equivalent conductivities of platinum(II) complexes of *trans*-edas in nitromethane. ○, $[Pt_2(\textit{trans}\text{-edas})_4](ClO_4)_4$; ——·——, $[Pt_2(\textit{trans}\text{-edas})_4](PF_6)_4$; ◐, $[Pt_2(\textit{trans}\text{-edas})_4]Cl_4$.

The slope of the $\Lambda_{equiv}/\sqrt{C}$ plot for $[Pt_2(\textit{trans}\text{-edas})_4]Cl_4$ is 340. This is intermediate between the values of 216 for $Na[B(C_6H_5)_4]$ and 465 for $[Ni(\text{o-phen})_3]Cl_2$,[21] sugesting that the tetrachloride is intermediate in behaviour between a 1:1 and 2:1 electrolyte. The molar conductivity of a $10^{-3}\,M$ solution of the complex is 71.0 ohm^{-1} cm^2 mol^{-1}, which can be compared with a value of 73.0 ohm^{-1} cm^2 mol^{-1} for $[NiCl(diars)_2]^+Cl^-$ (diars = ligand (I)) at the same concentration.[3c] It seems likely that, in nitromethane solution, $[Pt_2(\textit{trans}\text{-edas})_4]Cl_4$ can dissociate as follows, the extent of dissociation depending on concentration: $[Pt_2Cl_3(\textit{trans}\text{-edas})_4]^+Cl^- \rightleftharpoons [Pt_2Cl_2(\textit{trans}\text{-edas})_4]^{2+} + 2Cl^-$. Possibly chloride ions can coordinate to platinum in the *trans*-positions of (VII), and the change in colour from yellow to deep orange as water is removed from the trihydrate may be due to the replacement of coordinated water molecules by chloride ions outside the coordination sphere.

Ultraviolet irradiation of an ethanolic solution of the complex $[Pt_2(\textit{trans}\text{-edas})_4]Cl_4$ causes the yellow colour to disappear, and addition of ether precipitates a white, extremely hygroscopic powder. Analysis of this crude product suggests the approximate formula to be $Pt(edas)_2Cl_2$. Treatment of the irradiated solution, or of an ethanolic solution of the new dichloride, with perchlorate, hexafluorophosphate or chloroplatinate (IV) ions gives derivatives of general formula $Pt(edas)_2X_2$ ($X = ClO_4^-$, PF_6^- or $\frac{1}{2}PtCl_6^{2-}$), and

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(20) K. A. Jensen, *Z. anorg. Chem.*, 229, 225 (1936).

(21) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

Table II. Infrared absorption bands in the region 3400-650 cm^{-1} for platinum(II) complexes of *cis*-edas [a]

Assignment	[Pt(*cis*-edas)$_2$]Cl$_2$	[Pt(*cis*-edas)$_2$](PF$_6$)$_2$	[Pt(*cis*-edas)$_2$][PtCl$_6$]
O—H str. (H$_2$O)	3400 m, br		
olef. C—H str.		3010 s	not measured
C—H str. of As(CH$_3$)$_2$		2930 w	
H—O—H def. (H$_2$O)	1640 m	1620 w	
olef. C=C str.	1570 w	1570 w	1572 vw
asym. C—H def. of As(CH$_3$)$_2$	1420 m	1420 s	1415 ms
sym. C—H def. of As(CH$_3$)$_2$	1260 m	1268 m	1260 m
		1250 w	
		1163 w	1158 m
		1150 w, br	
		1100 w	1108 w
olef. C–H i.p. def. [b]	1090 m	1090 m	1085 m
C–H rock of As(CH$_3$)$_2$	930 vs	922 s	918 s
	890 vs	876 vs	870 vs
			845 s
P–F str. (PF$_6^-$)		830 vs, br	
		772 m	764 w
		738 m	
olef. C–H o.o.p. def.	720 vs	702 s	704 w

[a] Abbreviations as in Table I. [b] Tentative assignment.

by treatment of the hexafluorophosphate derivative with lithium chloride the original complex Pt(edas)$_2$Cl$_2$ can be obtained in a fairly pure state. The infrared spectra of these complexes show medium or strong bands at *ca.* 1570 cm^{-1}, 1090 cm^{-1} and *ca.* 700 cm^{-1} which are absent from the spectra of the complexes of (III), while the band at *ca.* 970 cm^{-1} characteristic of (III) and its complexes has completely disappeared (Table II). A strong band in the 700 cm^{-1} region is characteristic of the out-of-plane CH deformation vibration of a *cis*-disubstituted ethylenic derivative[12] and the band at 1570 cm^{-1} is readily assigned to an infrared-active C=C stretching mode. The infrared spectral evidence therefore strongly suggests that a *trans*→*cis*-isomerization has occurred under the influence of ultraviolet irradiation, and that the new complexes contain *cis*-1,2-bis(dimethylarsino)-ethylene *cis*-edas (II), acting as a bidentate chelate group similarly to its aromatic analogue (I). The band at *ca.* 1090 cm^{-1} cannot be assigned with certainty, but it may arise from the corresponding in-plane CH-deformation vibration of (II).

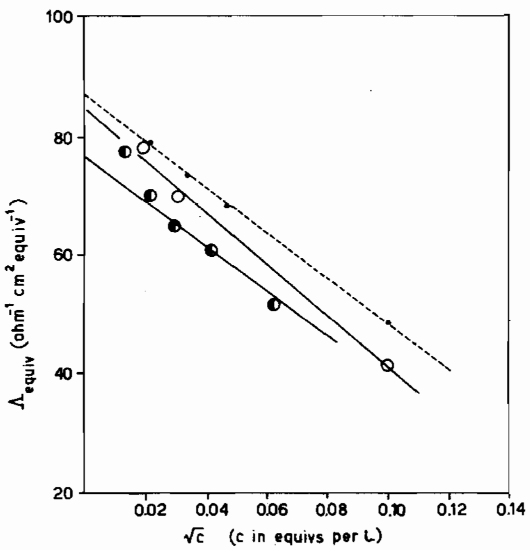
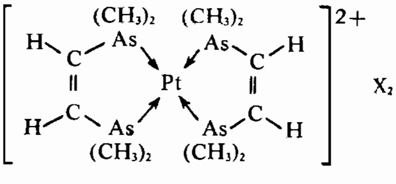


Figure 2. Equivalent conductivities of platinum(II) complexes of *cis*-edas in nitromethane. ○, [Pt(*cis*-edas)$_2$](ClO$_4$)$_2$; — — · — —, [Pt(*cis*-edas)$_2$](PF$_6$)$_2$; ◐, [Pt(*cis*-edas)$_2$]Cl$_2$.

The 60 MHz nmr spectrum of the complex Pt-(*cis*-edas)$_2$Cl$_2$ in deuterium oxide shows two sharp bands at τ 2.75 and τ 7.95 of relative intensity 1:6, due to the vinyl and methyl protons of (II), together with a band at τ 5.25 due to water.

The conductances of the complexes of the *cis*-ligand (II) have been measured over a range of concentration in nitromethane solution. Plots of Λ_{equiv} *vs.* $\sqrt{C_{equiv}}$ are shown in Figure 2. The slopes of the curves for the perchlorate and hexafluorophosphate derivatives are 405 and 400 respectively, showing that these behave as 2:1 electrolytes in nitromethane. In agreement with this, the molar conductivities are about 160 ohm^{-1} cm^2 mol^{-1} The slope of the curve for the dichloride is about 370, which suggests that this also is a 2:1 electrolyte in nitromethane, although the molar conductivity at 10^{-3} *M* is 64 ohm^{-1} cm^2 mol^{-1}, which is in the range expected for a 1:1 electrolyte. On the basis of conductance data, it has been suggested[3c] that the complex [Pt(diars)$_2$]-(ClO$_4$)$_2$ contains the square planar [Pt(diars)$_2$]$^{2+}$ cation, whereas the complex Pt(diars)$_2$Cl$_2$ contains the five-coordinate [PtCl(diars)$_2$]$^+$ cation (diars=ligand (I)). However, an X-ray study[22] of Pt(diars)$_2$Cl$_2$ shows that, in the solid state, this complex contains the planar [Pt(diars)$_2$]$^{2+}$ cation, and that interaction between this cation and chloride ions is electrostatic only, since the Pt–Cl distance is 4.16 Å. It is concluded by analogy that all the complexes of general formula [Pt(*cis*-edas)$_2$]X$_2$ (X=Cl$^-$, PF$_6^-$, ClO$_4^-$, ½PtCl$_6^{2-}$) contain two molecules of (II) coordinated to platinum (II) in a square planar configuration (VIII).

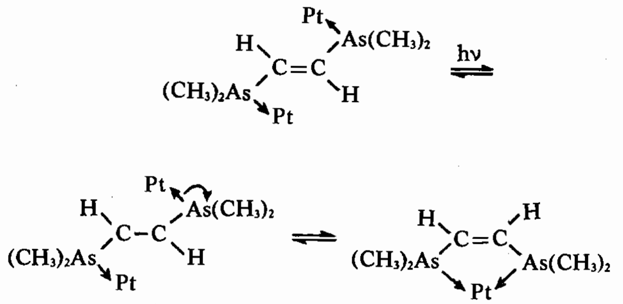


(VIII)

In the case of the dichloride, it is possible that there is an equilibrium in solution of the following type:

$$[\mathrm{PtCl}(cis\text{-edas})_2]^+\mathrm{Cl}^- \rightleftharpoons [\mathrm{Pt}(cis\text{-edas})_2]^{2+} + 2\mathrm{Cl}^-$$

All attempts to prepare the *cis*-ditertiary arsine (II) by ultraviolet irradiation of the original ligand have been unsuccessful. It seems likely that the first step in the ligand isomerization which occurs on irradiation of the complex $[\mathrm{Pt}_2(trans\text{-edas})_4]\mathrm{Cl}_4$ is rupture of one of the Pt–As bonds. This can be followed by excitation to a diradical (IX) which is still coordinated to the metal:



(IX)

The diradical (IX) could either return to the original complex, or, by rotation about the C–C bond, it could form the complex of the *cis*-ligand. The second alternative is evidently favoured by the strong chelate effect of the *cis*-ligand.

The irradiation method for the preparation of complexes of ligand (II) has been extended to nickel(II) and cobalt(II).[16] This work will be reported in a future publication, together with a comparison of the complexing properties of the *cis*-olefinic and aromatic ditertiary arsines[23]

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(22) N. C. Stephenson, *Acta Cryst.*, *17*, 1517 (1964).

(23) Complexes of *cis*-edas with iron and cobalt have recently been reported by R.D. Feltham, H.G. Metzger and W. Silverthorn, *Inorg. Chem.*, *7*, 2003 (1968), and personal communication (R.D.F.).