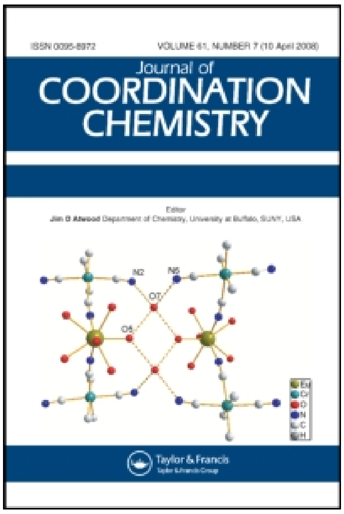

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PALLADIUM(II), PLATINUM(II) AND RHODIUM(III) COMLEXES OF THE DITERTIARY STIBINE, BIS(DIPHENYLSTIBINO)METHANE

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PALLADIUM(II), PLATINUM(II) AND RHODIUM(III) COMLEXES OF THE DITERTIARY STIBINE, BIS(DIPHENYLSTIBINO)METHANE

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Eighteen complexes of the ditertiary stibine, bisdiphenylstibinomethane, dsbm, have been isolated and characterized by conductivity and electronic and infrared spectral measurements. Information concerning the structures and of the probable nature of the bonding between the metal and the ligand in the complexes $[M(dsbm)X_2]_2$ and $M(dsbm)_2X_2$ (M = Pd, Pt; X = Cl, Br, I) and $Rh(dsbm)_2X_3$ (X = Cl, Br, I) has been obtained from these measurements. Reactions between Ag(I) and Hg(II) salts led to the isolation of the $(AgI)_2$.dsbm and $(HgI_2)_2$.dsbm derivatives. The ligand reacts with manganese(III) chloride, iron(III) chloride and copper(II) chloride to form bis(dichlorodiphenylstibino)methane, $Ph_2Sb(Cl_2)CH_2Sb(Cl_2)Ph_2$.

INTRODUCTION

Triphenylstibine complexes of many transition metals have been reported.[1] The majority contain the metal ion in a low formal oxidation state, although the 'softer' class *b* acceptors – the platinum metals and Cu, Ag, Au, Hg – form stibine complexes in normal oxidation states.

Antimony has been incorporated into a bidentate arsenic-antimony chelate, *o*-(dimethylstibinophenyl)-dimethylarsine,[2] and into quadridentate chelating ligand systems such as tris-(*o*-diphenylphosphinophenyl)stibine,[3] tris-(3-dimethylarsinopropyl)-stibine,[4] and tris-(*o*-dimethylarsinophenyl)stibine.[5,6] However, until the preparation of bisdiphenylstibinomethane, dsbm, by Matsumura and Okawara[7] no chelating agent containing only antimony donors was known. A study of the coordination chemistry of ditertiary stibine ligands has hitherto been prevented by the lack of preparative routes to the ligands.

Fukumoto, Matsumura and Okawara synthesized complexes of dsbm with the carbonyls of chromium, molybdenum, tungsten, and iron, in which the ligand behaves as a monodentate or rarely, as a bridging bidentate ligand.[8] We wish here to report the reaction of dsbm with salts of Pd(II), Pt(II), Rh(III), Ir(III), Cu(II), Hg(II), Ag(I), Mn(III), and Fe(III).

EXPERIMENTAL SECTION

Preparation of the Ligand

Bisdiphenylstibinomethane was prepared as described.[8] Found: C, 53.2: H, 4.1%. Calculated for $C_{25}H_{22}Sb_2$: C, 53.1, H, 3.9%. M.Pt. 83° (reported[8] 82–83°C).

Preparation of the Complexes

$[Pd(dsbm)Cl_2]_2$. An acetone solution (15 ml) of dsbm (0.57 g; 1.0 mmole) was added to a stirred solution of K_2PdCl_4 (0.327 g; 1.0 mmole) in water (15 ml). The oily precipitate which formed was dissolved by dropwise addition of acetone. On further stirring a yellow microcrystalline precipitate formed, which was filtered off, rinsed with water (5 ml), acetone (5 ml), and dried *in vacuo.* Yield 70%.

$[Pd(dsbm)X_2]_2$ (X = Br, I) were similarly obtained by this reaction in the presence of excess NaX.

$Pd(dsbm)_2Cl_2$. A solution of Na_2PdCl_4 (0.3 g; 1.0 mmole) in water (10 ml) was added dropwise to a stirred solution of dsbm (1.1 g; 2.0 mmole) in acetone (20 ml). The initial dark colored solution was treated dropwise with acetone until all solid material had dissolved. On further stirring a yellow solid separated. After washing with acetone (5 ml) this was dried *in vacuo.* Yield ~45%.

$[Pt(dsbm)X_2]_2$ were prepared in a manner analogous to that used for the palladium derivatives.

$Pt(dsbm)_2X_2$ (X = Cl, Br, I). The appropriate $[Pt(dsbm)X_2]_2$ (1.0 mmole) in acetone (30 ml) was warmed with a solution of dsbm (2.0 mmole) in

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acetone (20 ml) for 2 hr, and the solution evaporated cautiously until precipitation occurred. The product was rinsed with acetone and dried. Yield 70–85%. (The final solutions should not be evaporated too quickly as this tends to result in the formation of sticky products.)

Rh(dsbm)$_2$Cl$_3$. Rhodium trichloride ($RhCl_3 \cdot xH_2O$; 0.2 g; ~1 mmole) in ethanol (20 ml) was stirred with a solution of dsbm (1.1 g; 2.0 mmole) in acetone (10 ml). After stirring for 1 hr the solution was cautiously evaporated in a stream of nitrogen at room temperature until a fine red precipitate formed. Yield ~35%.

Rh(dsbm)$_2$X$_3$ (X = Br, I). Rhodium trichloride (0.2 g, ~1 mmole) in water (15 ml) was treated with an excess of NaX and the resulting solution was filtered into one containing dsbm (1.1 g; 2.0 mmole) in acetone (20 ml). On concentration in a stream of nitrogen the complex precipitated. Yield ~50%.

(AgI)$_2$.dsbm. Silver(I) nitrate (0.17 g; 1.0 mmole) in hot ethanol (20 ml) was stirred with dsbm (0.57 g; 1.0 mmole) forming a colorless solution. Dropwise addition of sodium iodide (0.2 g) in ethanol (10 ml) resulted in the immediate precipitation of a yellow solid. This was filtered, rinsed with hot ethanol (50 ml), and dried *in vacuo*. Yield ~55%.

Reaction with Copper(II) Chloride. Copper(II) chloride (0.23 g; 2.0 mmole) in ethanol (10 ml) was added to a warm solution of dsbm (0.56 g; 1.0 mmole) in acetone (20 ml). The blue color rapidly discharged and a white precipitate formed. This was filtered off, rinsed with ethanol (25 ml) and dried *in vacuo*. Crystallization of the filtrate from hot ethanol produced a white microcrystalline solid.

Reaction with Ferric Chloride. The ligand (1.0 g) was refluxed with iron(III) chloride (2.0 g) in ethanol (50 ml) for 2 days, the initial orange-yellow solution turning red-brown and depositing a precipitate after 7 hr. The solution was evaporated to dryness, extracted with dichloromethane and the filtrate resulting was treated with ether. A cream precipitate was obtained, which was filtered and dried *in vacuo*.

Physical Measurements were obtained as previously described.[6]

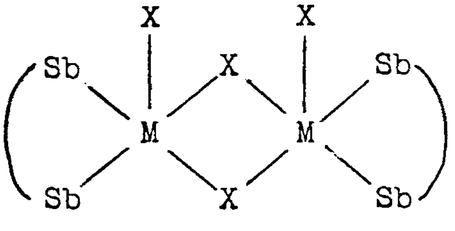
Analytical measurements were obtained by the micro-analytical service of this Department.

RESULTS AND DISCUSSION

Bisdiphenylstibinomethane, $Ph_2SbCH_2SbPh_2$, dsbm, reacts with palladium(II), platinum(II), and rhodium(III) salts in ethanol/dichloromethane mixtures to produce deeply colored solutions. On evaporation the complexes are usually obtained as red or orange oils, from which solids can only be obtained with considerable difficulty. The same difficulties were experienced on attempts at recrystallization from halogenated solvents. After investigation of a number of solvent systems we conclude that the best preparative route to these complexes is via reaction in aqueous acetone, from which, if care is paid to the ratio of the reactants, the complexes eventually precipitate in a state of high purity, thus obviating the need to recrystallize. When recrystallization was found to be necessary the best method was found to be dissolution of the complex in warm acetone, followed by evaporation or by precipitation by dropwise addition of water to the rapidly stirred solution. The complexes, together with physical properties and analytical data, are listed in Table I.

Palladium(II) and Platinum(II) Complexes

1:1 Complexes, [M(dsbm)X$_2$]$_2$. The addition of an acetone solution of dsbm to the appropriate alkali tetrahalopalladate(II) or tetrahaloplatinate(II) in water (1:1 molar ratio) resulted in the precipitation of complexes analyzing as M(dsbm)X_2 (M = Pd, Pt; X = Cl, Br, I). These complexes are insoluble in nitromethane, but behaved as non-electrolytes in 1,2-dichloroethane solution. Molecular weight determinations of selected complexes in chloroform indicate that they exist as dimeric M_2(dsbm)$_2X_4$ species in this solvent (Table I). The similarity of the ultraviolet-visible spectra of these complexes in the solid state and in solution in chlorinated hydrocarbon solvents (Table 2) suggests that the dimeric structure is maintained in the solid state as well as in solution. On the basis of these results three structures obviously appear possible:

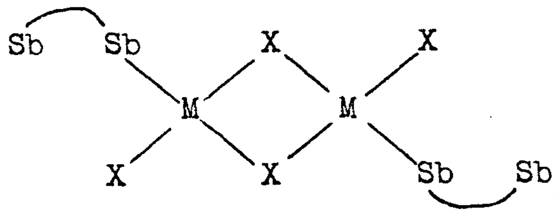


I

TABLE I
Analytical and physical data

Complex(a)	Color	Dec.Pt.	% Carbon		% Hydrogen		% Metal		% Halogen		Mol.Wt.(b)
		°C	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	
$[Pd(dsbm)Cl_2]_2$	Orange	140-2	39.8	40.2	3.1	2.9	14.4	14.3	9.5	9.5	1297(1486)
$[Pd(dsbm)Br_2]_2$	Orange-red	156-8	36.7	36.2	2.9	2.7	13.0	12.8	19.4	19.2	1603(1664)
$[Pd(dsbm)I_2]_2$	Dark brown	198-200	32.6	32.5	2.6	2.4	11.7	11.5	27.7	27.4	
$[Pt(dsbm)Cl_2]_2$	Yellow	172	35.8	36.0	2.6	2.6	23.7	23.4	8.7	8.5	1629(1664)
$[Pt(dsbm)Br_2]_2$	Yellow	158-160	32.6	32.6	2.8	2.4	21.4	21.2	17.5	17.4	
$[Pt(dsbm)I_2]_2$	Yellow	160	29.7	29.6	2.4	2.2	19.4	19.2	24.7	25.0	
$Pd(dsbm)_2Cl_2$	Yellow	168	46.1	45.9	3.7	3.4	8.1	8.1	5.3	5.4	1340(1309)
(c)	Yellow	166-168	46.0	45.9	3.7	3.4	8.3	8.1	5.2	5.4	
$Pd(dsbm)_2Br_2$	Deep yellow	172	43.2	42.9	3.4	3.1	7.9	7.6	11.7	11.4	
$Pd(dsbm)_2I_2$	Orange	162-170	40.2	40.2	3.0	2.9	7.2	7.1	16.8	17.0	
$Pt(dsbm)_2Cl_2$	Pale yellow	190-2	42.6	42.9	3.0	3.1	13.7	13.9	5.0	5.1	1375(1398)
$Pt(dsbm)_2Br_2$	Yellow	198-200	40.4	40.4	3.4	3.0	13.4	13.1	10.9	10.8	
$Pt(dsbm)_2I_2$	Orange	146-8	37.8	37.9	3.3	2.9	12.4	12.3	15.8	16.1	
$Pt_2(dsbm)_3Cl_4$	Yellow	166-8	40.4	40.2	3.2	3.0	17.8	17.5	6.4	6.4	1140(2230)
$Rh(dsbm)_2Cl_3$	Orange-red	220	44.8	44.8	2.9	2.9			7.9	8.0	1290(1342)
$Rh(dsbm)_2Br_3$	Red	244-6	40.4	40.2	3.3	3.3			14.9	15.2	
$Rh(dsbm)_2I_3$	Dark brown	228-230	37.4	37.1	3.4	3.0			23.0	23.6	1542(1616)
$(AgI)_2.dsbm$	Yellow	90-92	29.3	29.1	2.9	2.7			24.2	24.5	
$(HgI_2)_2.dsbm$	Yellow	230	20.0	20.2	2.5	2.2			34.8	34.4	
$Ph_2Sb(Cl_2)CH_2Sb(Cl_2)Ph_2$(d)	White	205	4.24	42.5	2.8	3.0			19.7	20.1	
(e)	White	208-210	42.4	42.5	2.9	3.0			20.0	20.1	
(f)	White	207	42.7	42.5	3.2	3.0			19.8	20.1	

(a) All soluble complexes are non-conductors in 1,2-dichloroethane; (b) Found (Calculated); chloroform solution
(c) Synthesised from $[Pd(dsbm)Cl_2]_2$ and dsbm; (d) from $CuCl_2$; (e) From $FeCl_3$; (f) from $MnCl_3$.



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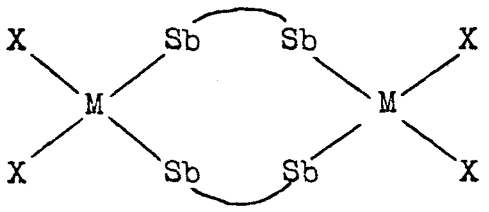

III

TABLE II
Electronic and infrared spectral data

Complex	Solution$^{(a)}$ (ε_{mol}) kK	Reflectance$^{(b)}$ kK	ν(M-X)$^{(c)}$ cm^{-1}
$[Pd(dsbm)Cl_2]_2$	33.2(30,780), 25.9(15,170), ~22.8(sh)(7,780)	26.0, 22.7	342, 310
$[Pd(dsbm)Br_2]_2$	32.6(28,850), 25.5(11,864), ~22.3(sh)(5,120)	24.7, 21.9	280(sh), 210
$[Pd(dsbm)I_2]_2$	30.3(18,540), 21.2(9,300)	20.6	
$Pd(dsbm)_2Cl_2$	32.3(26,930), ~29.0(sh)	27.0(sh)	310(W), 280
$Pd(dsbm)_2Br_2$	31.3(21,940), ~28.3(sh)	23.5	
$Pd(dsbm)_2I_2$	30.7(13,350), 21.8(6,200)	26.7, 20.2	
$[Pt(dsbm)Cl_2]_2$	31.5(21,940)		340, 310
$[Pt(dsbm)Br_2]_2$	30.7(23,740), 26.6(3,460)	26.1	
$[Pt(dsbm)I_2]_2$	30.3(20,920), 26.3(2,280)	26.3	
$Pt(dsbm)_2Cl_2$	36.3(19,700), 30.2(sh)(3,300)		320(sh), 285
$Pt(dsbm)_2Br_2$	~29.0(sh)(3,900)	23.8	
$Pt(dsbm)_2I_2$	25.3(6,800)	26.7, 20.4	
$Rh(dsbm)_2Cl_3$	32.4(13,560), 26.4(16,300)	25.6	350, 335
$Rh(dsbm)_2Br_3$	33.7(6,900), 25.5(13,000)	25.3	210
$Rh(dsbm)_2I_3$	~32.1(20,000), 28.3(sh), 23.8(9,250)	22.2	

(a) in 1,2-dichloroethane; (b) range 30-15 kK; (c) in Nujol.

The electronic spectra of these $M_2(dsbm)_2X_4$ complexes in dichloromethane exhibit the lowest energy absorptions at frequencies similar to those reported by Goggin *et al*[9] in compounds containing planar MSb_2X_2 chromophores. Moreover, pentacoordinate Pd(II) and Pt(II) complexes absorb at considerably lower frequencies than their 4-coordinate planar analogues.[10] Thus, structure I may be effectively discounted. We have used the metal-halogen vibrations in the far infrared spectra to distinguish between structures II and III, Figure 1, but we are aware that there are inherent dangers in predicting structures from spectral data, and conclusive structural assignments must await X-ray analysis.

Structure II is expected to exhibit three $\nu(M{-}X)$ vibrations: $\nu(M{-}X)_{terminal}$, $\nu(M{-}X)_{bridging}$ (trans to X), and $\nu(M{-}X)_{bridging}$ (trans to L); whilst structure III can be considered as essentially the same as a *cis*-ML_2X_2 system and should exhibit two $\nu(M{-}X)$ bands. Unfortunately, strong ligand absorptions make identification of the $\nu(M{-}X)$ frequencies difficult, and totally obscure most of the $\nu(M{-}Br)$.† The position of terminal $\nu(M{-}Cl)$ in the chlorine-bridged complexes $M_2L_2X_4$ of a wide range of phosphorus and arsenic donors are insensitive to the nature of L and occur at ~330–350 cm.[11–13] A second absorption assignable as $\nu(M{-}Cl)_{bridging}$ (trans to Cl) occurs at ~300 cm^{-1}. The third $\nu(M{-}Cl)$, that of bridging chlorine trans to L is sensitive to the identity of L and is expected to appear below 300 cm^{-1}.

Assuming that structure III would produce similar spectra to *cis*-ML_2X_2 (L = monodentate P, As, Sb ligand), the two $\nu(M{-}Cl)$ bands will lie in the range ~320–260 cm^{-1}.[12,14,15] In fact, no such absorptions are observed. The spectra of the [Pd(dsbm)

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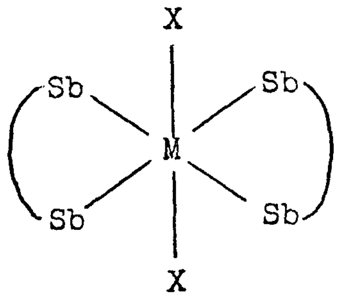
†A referee has pointed out to us that in one of the complexes in which we were fortunate enough to be able to record ν(Pd–Br), that of $[Pd(dsbm)X_2]_2$, the two absorptions are much farther apart than they are in the analogous chloro complex, Table 2. We can only ascribe this phenomenon to solid state effects.

$Cl_2]_2$ and $[Pt(dsbm)Cl_2]_2$ complexes exhibit $\nu(M\text{–}Cl)$ bands at 342,310 cm^{-1} and 340,310 cm^{-1}, respectively, which are assignable as $\nu(M\text{–}Cl)_{terminal}$ and $\nu(M\text{–}Cl)_{bridging}$ (trans to Cl) of structure II, with the third $\nu(M\text{–}Cl)$ being obscured, presumably, by ligand absorptions. It may be pointed out in particular, that the band at ~340 cm^{-1} in each complex is at too high a frequency to be due to a *cis*-ML_2Cl_2 species. Due to the difficulty mentioned above for the $\nu(M\text{–}Br)$ frequencies, and because the $\nu(M\text{–}I)$ absorptions occur below 200 cm^{-1}, we can only infer that the bromo and iodo derivatives, because their other properties are similar to the chloro complexes, can also be assigned structure II. An attempt to demonstrate the presence of uncoordinated $-SbPh_2$ groups by studying the variation of the conductance of a solution of $[Pt(dsbm)Cl_2]_2$ in 1,2-dichloroethane upon addition of methyl iodide was unsuccessful. After an initial small change in conductance a precipitate began to form, and thus meaningful results were not possible.

Attempts to isolate thiocyanate derivatives did not meet with success. Reaction of $M(SCN)_4{}^{2-}$ (M = Pd, Pt) with dsbm, or of $[M(dsbm)Cl_2]_2$ with KCNS, produced only dark oils which could not be induced to solidify.

1:2 Complexes, $M(dsbm)_2X_2$. Stirring together Na_2PdX_4 (X = Cl, Br) with dsbm in aqueous acetone produced complexes $Pd(dsbm)_2X_2$ which are monomeric in chloroform and non-electrolytes in 1,2-dichloroethane. There are four possible structures:



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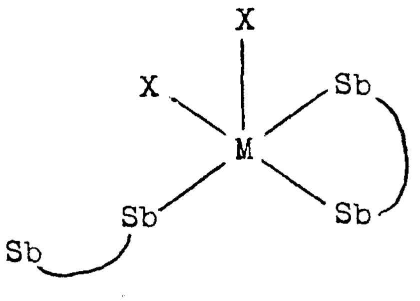

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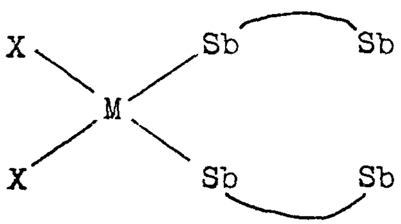
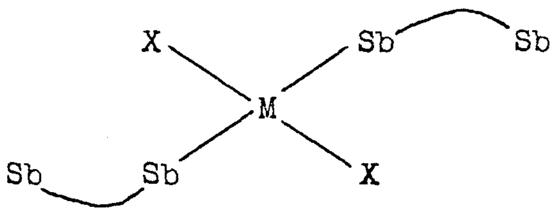


VI



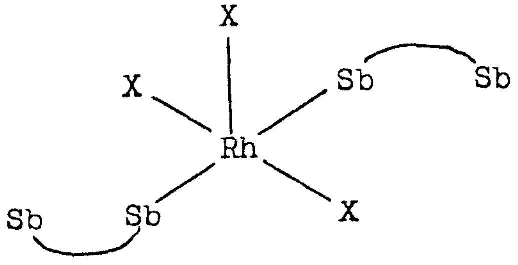
VII

Structure IV is not known for $[M(\text{bidentate})_2X_2]$ (M = Pd, Pt) complexes in solution, and while it is a possible structure there is evidence to suggest that the complexes have another structure. The electronic spectra of the $Pd(dsbm)_2X_2$ complexes fall into two categories: (a) when X = Cl, Br the electronic spectra in the solid state and in solution are quite distinctly different, the solution absorptions being at much higher energies; (b) when $X = I$, the visible absorption occurs at the same energy both in the solid state and in solution and this band is at very low energy. We therefore suggest that in solution $Pd(dsbm)_2X_2$ (X = Cl, Br) are four-coordinate and have either structure VI or VII, though the known prediliction of monodentate stibines to produce complexes of type cis-PdL_2X_2[1] suggests that structure VI may be more likely in solution. However, in the solid state the visible spectral bands suggest pentacoordination,[10] and indeed one of the observable $\nu(M\text{–}Cl)$ bands occurs in the range for bridging chlorines. This would exclude structure V and suggest bridging of an X group of structure VI to produce an effectively pentacoordinate solid state complex. For $Pd(dsbm)_2I_2$ it appears that the complex is pentacoordinate in the solid state and in solution.

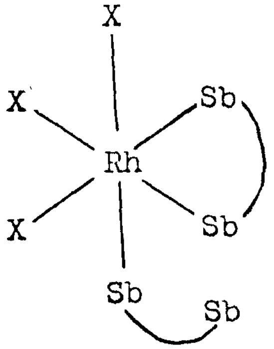
The platinum(II) complexes, $Pt(dsbm)_2X_2$, are produced only with difficulty by reaction of Na_2PtX_4 with dsbm in a 1:2 ratio in aqueous acetone, but are readily formed by warming $[Pt(dsbm)X_2]_2$ with dsbm in acetone. By analogous arguments to that used for the Pd analogues, they are assigned similar structures.

By reaction of Na_2PtCl_4 with dsbm in a 1:2 molar ratio in aqueous acetone a complex of composition $Pt_2(dsbm)_3Cl_4$ precipitates. This preparation is quite readily reproducible and yields a complex of constant composition. However, the molecular weight in chloroform is only 1140 (calculated for $Pt_2(dsbm)_3Cl_4$ is 2230), and so the nature of the complex is uncertain. It is possible that the complex in the solid state is effectively a complex combination of $Pt(dsbm)Cl_2$ and $Pt(dsbm)_2Cl_2$, and in chloroform dissociation into these two species occurs.

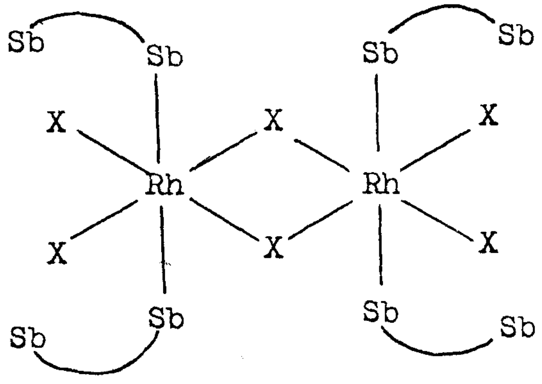
Rhodium(III) Complexes. Reaction of rhodium trihalides with dsbm in 1:1 or 1:2 molar ratios in aqueous acetone produced low yields of $Rh(dsbm)_2X_3$ (X = Cl, Br, I). In solution these complexes are monomeric and non-electrolytes. There are essentially two types of possible structure, pentacoordinate VIII or octahedral IX (or its trans isomer) or X (or its cis isomer). Although pentacoordination for rhodium(III) is virtually unknown, it may exist in the $[Rh(dsbm)_2X_3]$ complexes because of the tendency of dsbm to be monodentate, and bulky ligands such as dsbm would also favor a lower coordination number. However, as the infrared spectrum of the $[Rh(dsbm)_2Cl_3]$ (Table 2, Figure 1) contains ν(Rh–Cl) frequencies assignable to both terminal and bridging chlorines,[16] then structure X seems to be the most plausible solid state structure. Such dimeric rhodium(III) complexes are fairly well established. A comparison of the electronic spectra in solution and in the solid state shows significant differences, this is probably due to dissociation of the chlorine bridges.



VIII



IX



X

Other Complexes. The reaction of dsbm with a variety of other transition metal salts was attempted.

Iridium(III) halides react very slowly with the ligand in refluxing acetone or ethanol, and only very small yields of complexes of composition approximating to $Ir(dsbm)X_3$ were obtained, but these could never be obtained absolutely pure. The formation of a complex in solution between nickel(II) iodide and dsbm in dichloromethane has been reported[17] but no evidence of complexation between the ligand and other 3d transition metal ions in their normal oxidation states were observed, although manganese(III) chloride[18] rapidly, and iron(III) chloride slowly under reflux, convert dsbm into the antimony(v) chlorocompound $Ph_2Sb(Cl_2)CH_2Sb(Cl_2)Ph_2$. In the former case the other product is manganese(II) chloride, but the iron-containing product in the latter reaction has not been identified. Copper(II) chloride also chlorinates dsbm to bis(dichlorodiphenylstibino)methane. Similar chlorination reactions of triphenylstibine with $FeCl_3$[18] and $CuCl_2$[19] are known.

Silver(I) nitrate and dsbm appeared to react in ethanol but no complex could be isolated. However, upon addition of ethanolic sodium iodide, instant precipitation of yellow $(AgI)_2$.dsbm occurred. This complex is presumably a linear dimer containing bridging dsbm. Direct reaction of mercury(II) iodide

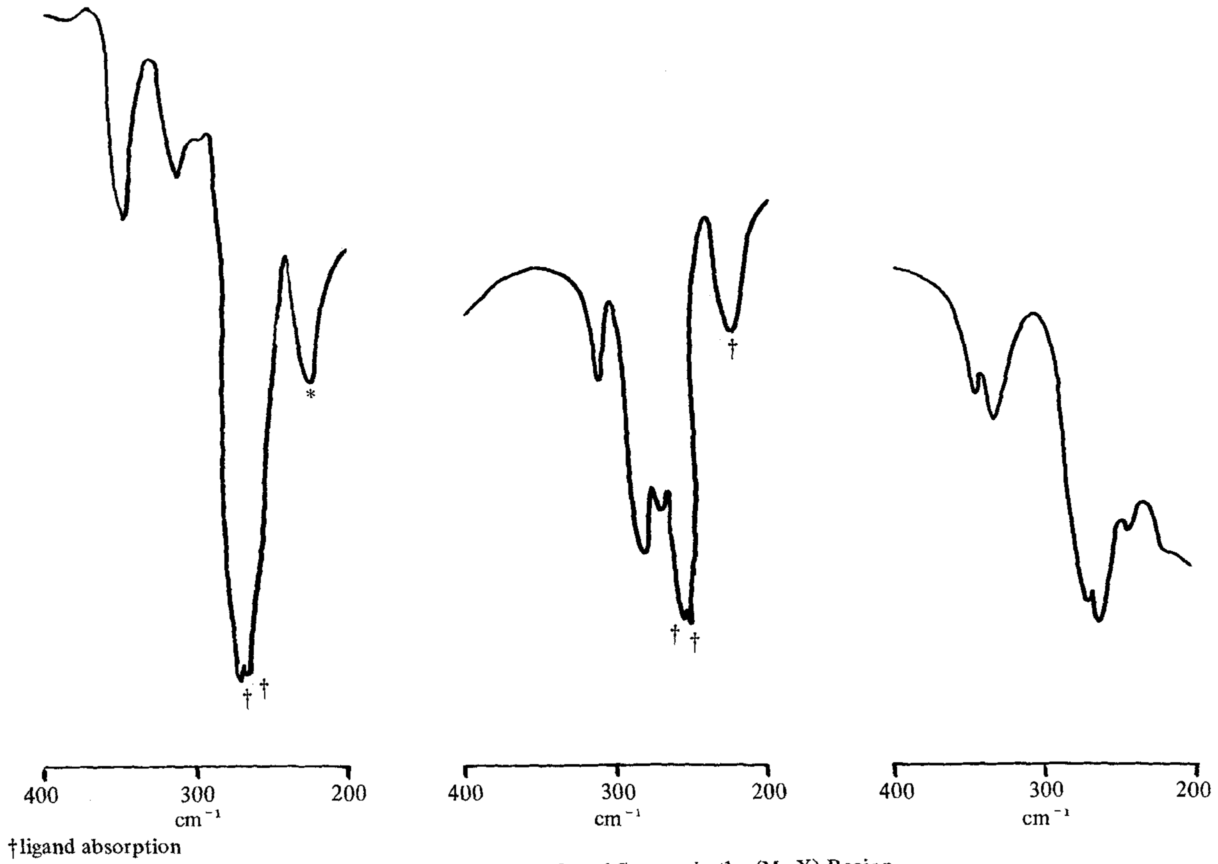


FIGURE 1 Infrared Spectra in the (M–X) Region

and dsbm in ethanol produced yellow $(HgI_2)_2$.dsbm. The insolubility of this complex in a large number of organic solvents suggests a polymeric structure.

CONCLUSIONS

We have found no direct evidence in this study for chelating behavior of dsbm; only evidence for monodentate coordination is available and no complexes of the type analogous to $[M(dpm)_2]^{2+}$ (M = Pd, Pt; dpm = bisdiphenylphosphinomethane), containing chelating dpm,[20,21] have been obtained. Presumably, the larger size of the antimony atom makes the formation of a four-membered chelate ring even more strained than in the case of dpm (which itself frequently acts as a monodentate ligand[22-24]).

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