

ANIONIC DIMETHYLPLATINUM(IV) SCHIFF-BASE CHELATE COMPLEXES

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SUMMARY

Anionic dimethylplatinum(IV) complexes with bidentate *N*-organosalicylaldimines of the form $[\text{Me}_2\text{PtX}_2(\text{Sal}=\text{N}-\text{R})]^-$ ($\text{X} = \text{Br}, \text{Cl}$) have been synthesized from Me_2PtX_2 and isolated as thallium, tetraalkylammonium and tetraphenylarsonium salts. The ^1H NMR and infrared spectra indicate an octahedral structure with the halogen atoms mutually *trans*. Measurement of $^{195}\text{Pt}-^1\text{H}$ coupling constants has been used to study some aspects of coordination of the Schiff-bases in these complexes. A binuclear complex involving a quadridentate Schiff-base ligand is also reported.

INTRODUCTION

Most studies of the coordination chemistry of organoplatinum(IV) compounds have been concerned with trimethylplatinum derivatives¹, these including the only examples of organoplatinum Schiff-base complexes². There have been some reports of dimethylplatinum complexes, these being mostly with tertiary phosphine and arsine ligands³⁻⁵ which are difficult to replace. More recently the halogen-bridged polymeric compounds $[\text{Me}_2\text{PtX}_2]_n$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been prepared^{6,7} and coordination compounds with simple monodentate ligands and ethylenediamine obtained. As a continuation of our studies on organometallic Schiff-base chelates we have investigated the reactions of Me_2PtX_2 compounds with a variety of salicylaldimine Schiff-bases and their derivatives. These reactions have yielded anionic complexes of the type $[\text{Me}_2\text{PtX}_2(\text{Sal}=\text{N}-\text{R})]^-$ ($\text{Sal}=\text{N}-\text{R} = N$ -substituted salicylaldiminato anion), which can be isolated as salts of large cations, such as Tl^+ , Bu_4N^+ and Ph_4As^+ . Some spectroscopic studies have been made on the compounds.

RESULTS AND DISCUSSION

Syntheses

Reactions of Me_2PtBr_2 with $\text{TlSal}=\text{N}-\text{R}$ and Tl_2Salen [$\text{SalenH}_2 = N, N'$ -ethylenebis(salicylaldimine)] in an attempt to synthesize complexes of the type $\text{Me}_2\text{Pt}(\text{Sal}=\text{N}-\text{R})_2$ and $\text{Me}_2\text{PtSalen}$ with elimination of TlBr failed to give the desired products, the Pt-Br bond being retained. When the solid material formed by reaction

of Me_2PtBr_2 with an equimolar quantity of $\text{TlSal=N-C}_6\text{H}_5$ in benzene was recrystallized from a large volume of dichloromethane a yellow solid was obtained with an analytical composition corresponding to $\text{Tl}[\text{Me}_2\text{PtBr}_2(\text{Sal=N-C}_6\text{H}_5)]$. The compound is soluble in dichloromethane or acetone but the solutions are unstable, slowly becoming cloudy on standing as do thallium(I) salts of Schiff-bases⁸. The NMR spectrum shows resonances at $\delta = 1.24$ and 2.06 ppm with ^{195}Pt satellites corresponding to $J(\text{Pt-H})$ values of 73 and 69 Hz respectively.

Me_2PtBr_2 , which is insoluble in non-coordinating solvents, will dissolve in solutions of *N*-alkyl and -aryl salicylaldimines in ethanol when heated for a short time (prolonged heating results in deposition of metallic platinum) and after addition of a salt of a large cation and an equimolar amount of potassium hydroxide, salts of the anions $[\text{Me}_2\text{PtBr}_2(\text{Sal=N-R})]^-$ can be isolated from the solution. The salts $[\text{Bu}_4\text{N}][\text{Me}_2\text{PtBr}_2(\text{Sal=N-R})]$ ($\text{Bu} = n\text{-butyl}$) and $[\text{Ph}_4\text{As}][\text{Me}_2\text{PtBr}_2(\text{Sal=N-R})]$ where $\text{R} = \text{CH}_3, \text{C}_6\text{H}_{11}$ and C_6H_5 , as well as $[\text{Me}_4\text{N}][\text{Me}_2\text{PtBr}_2(\text{Sal=N-C}_6\text{H}_5)]$ have been made by this method. The tetrabutylammonium salts crystallize readily while the tetraphenylarsonium salts and the tetramethylammonium salt are more difficult to isolate. $[\text{Bu}_4\text{N}][\text{Me}_2\text{PtCl}_2(\text{Sal=N-C}_6\text{H}_5)]$ has been prepared analogously from Me_2PtCl_2 . However Me_2PtI_2 does not dissolve in a hot ethanol solution of $\text{HSal=N-C}_6\text{H}_5$, even on prolonged heating under reflux, nor does it react with $\text{TlSal=N-C}_6\text{H}_5$.

Conductance measurements in acetone for $[\text{Bu}_4\text{N}][\text{Me}_2\text{PtBr}_2(\text{Sal=N-C}_6\text{H}_5)]$ and $[\text{Ph}_4\text{As}][\text{Me}_2\text{PtBr}_2(\text{Sal=N-R})]$ ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) give molar conductances of 129, 126 and 128 $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$ respectively at 20° which are typical values for 1/1 electrolytes, serving to confirm the ionic formulation given. The yellow compounds are all readily soluble in acetone, alcohols and chloroform (with the exception of the tetramethylammonium salt) but insoluble in water.

Me_2PtBr_2 also dissolves in hot ethanol containing SalenH_2 and addition of potassium hydroxide and Ph_4AsBr produces a yellow solid sparingly soluble in organic solvents with the composition $[\text{Ph}_4\text{As}][(\text{Me}_2\text{PtBr}_2)_2\text{Salen}]$, where the anion is presumed to have a binuclear structure with Salen behaving as a bridging ligand as has been proposed for other organometallic compounds⁹⁻¹². Reaction of Me_2PtBr_2 with Tl_2Salen in ethanol gave an insoluble solid, presumed to be $\text{Tl}_2[(\text{Me}_2\text{PtBr}_2)_2\text{Salen}]$, which on reaction with Ph_4AsBr gives $[\text{Ph}_4\text{As}]_2[(\text{Me}_2\text{PtBr}_2)_2\text{Salen}]$.

Spectra and structure

The ^1H NMR spectra of the salts have been measured and are shown in Table 1. Low solubility prevented a spectrum of the Salen complex from being obtained. As there are two different resonances for the methyl groups attached to platinum these must be *cis*, as would be expected. $\text{Me}_2\text{PtBr}_2\text{Py}_2$ displays only one methyl group resonance at $\delta 2.06$ ppm implying that both methyl groups must have the same substituent in the *trans* position. Assuming that Sal=N-R occupies the same coordination positions as does pyridine the only possible structure for the salicylaldimine complex anions which satisfies the above criteria is that shown in the figure. This is also the structure which would be expected from a preferential breaking of the halide bridges of the polymeric Me_2PtX_2 in the positions *trans* to the methyl groups, which have a high *trans* effect¹³.

The methyl groups (1) and (2) are assigned on the basis of the upfield shift when the salicylaldimine is changed from alkyl to aryl caused by the anisotropic shielding

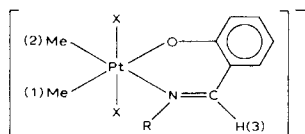
TABLE 1

¹H NMR SPECTRA OF SALTS OF [Me₂PtX₂(Sal=N-R)]^{-a}

Cation	X	R	δ Values (ppm downfield from internal TMS)					$J(^{195}\text{Pt}-^1\text{H})$ values ^b (Hz)		
			Me(1)	Me(2)	Aromatic	H(3)	Other	J ₁	J ₂	J ₃
Bu ₄ N	Br	CH ₃	1 83	1 99	6 15-7 18	7 75	Bu ₄ N 0 8-3 1 CH ₃ ^c 3 54	73 1	67 3	26 4
Bu ₄ N	Br	C ₆ H ₁₁	1 71	1 96	6 13-7 16	7 21	Bu ₄ N 0 8-3 1 C ₆ H ₁₁ , Obs -4 1 ^d	72 6	67 2	27 1
Bu ₄ N	Br	C ₆ H ₅	1 27	2 02	6 17-7 37	7 81	Bu ₄ N 0 8-3 2	73 0	69 1	24 1
Ph ₄ As	Br	CH ₃	1 74	1 93	6 02-7 86	^e	CH ₃ ^f 3 50	73 1	67 1	
Ph ₄ As	Br	C ₆ H ₁₁	1 67	1 93	6 01-7 86	^e	C ₆ H ₁₁ 1 1-4 2	72 7	67 5	
Ph ₄ As	Br	C ₆ H ₅	1 22	1 99	6 03-7 81	^e		73 4	69 5	
Me ₄ N ^g	Br	C ₆ H ₅	1 24	2 00	6 14-7 46	7 84	Me ₄ N 3 31	73 6	69 9	24 4
Bu ₄ N	Cl	C ₆ H ₅	1 11	1 85	6 17-7 34	7 88	Bu ₄ N 0 8-3 1	71 7	68 2	22 4

^a In CDCl₃ ^b J₁, J₂ and J₃ refer to coupling of Pt with Me(1), Me(2) and H(3) respectively ^c J(Pt-CH₃) 13 0, J(H(3)-CH₃) 1 2 Hz ^d Upfield end of range obscured by Bu₄N⁺ resonances ^e Obscured by Ph₄As⁺ resonances ^f J(Pt-CH₃) = 13 2, J(H(3)-CH₃) = 1 2 Hz ^g In acetone-d₆

due to the ring current of the benzene ring, as has been done previously in assigning spectra of organometallic Schiff-base complexes of palladium^{10,11}, platinum¹¹, and gold¹². As has been found with dimethylgold complexes¹² this implies that the more shielded of the two methyl groups is that *trans* to the oxygen of the salicylaldehyde. The chemical shift differences and the upfield shift due to the aryl Schiff-base are similar in magnitude to those observed for the gold complexes, which must be assumed to be square planar, and hence serve to confirm the proposed structure shown in the figure. No significant correlations can be seen in the chemical shifts, although the methyl groups appear to be more shielded in the chloride complex possibly because the smaller chlorine atoms are less able to delocalize the negative charge on the anion than are bromine atoms.

Fig 1 Structure of [Me₂PtX₂(Sal=N-R)]⁻

The ¹⁹⁵Pt-¹H coupling constants however do show clearer patterns. A fairly successful approach to the theory of couplings through two bonds of the type ²J(X-CH) has assumed the coupling constant to be directly proportional to the *s* character of the hybrid orbital of X used in the X-C bond¹⁴ and hence the covalency of the bond. Therefore in methyl platinum compounds a higher value of J(Pt-H) for a methyl group indicates a stronger platinum carbon bond, a feature which has been used to study *trans* effects in methylplatinum(II) complexes¹⁵ and more recently in trimethylplati-

num(IV) complexes¹⁶. It may first be noted for the compounds studied here that $J_1 > J_2$, *i.e.* the *trans* nitrogen donor reduces the covalency of the Pt–C bond more than does the oxygen donor, as found for N and O donors in trimethylplatinum complexes¹⁶.

Values of J_1 show no significant variation on changing the nature of the Schiff-base but J_2 is clearly raised when $R = C_6H_5$ indicating a smaller *trans* effect on the Pt–C bond, probably due to the greater electron withdrawing properties of the aryl group. A similar effect has been noted in (*N,N*-dimethylbenzylamine-2-*C,N*) platinum(II) complexes where the coupling is through three bonds via a coordinated nitrogen atom *trans* to the imine nitrogen¹¹. Both J_1 and J_2 are lowered in the chloro complex indicating a weakening of the Pt–C bond, although no appreciable *cis* effect of this kind was found in trimethylplatinum compounds¹⁶.

The coupling constant J_3 is through three bonds and is influenced by the effect of R on the C=N bond as well as the strength of Pt–N bonding. It appears again that the phenyl derivative has a lower value of J_3 , which is a similar trend to that observed in platinum(II) complexes¹¹. Comparison with these complexes also reveals that the magnitude of J_3 is approximately one-third that of the corresponding coupling constant in the platinum(II) derivatives. The value of a coupling constant directly proportional to the *s* character of the platinum hybrid orbital used in bonding should, in a six coordinate complex, be two-thirds that in a corresponding four coordinate complex. This factor has been found reasonably accurate for the direct coupling constant $^1J(\text{Pt–P})$ in phosphine complexes¹⁵. However this reduction assumes equal sharing of the platinum 6s orbital among the ligands, and the $^2J(\text{Pt–CH})$ values found here and in trimethylplatinum(IV) complexes¹⁶ do not show such a reduction from values in platinum(II) compounds¹⁵ so other factors must be operating. The reasons for the large reduction of J_3 are not clear but much weaker coordination of the Schiff-base in the platinum(IV) compounds is suggested, possibly due, at least in part, to the effect of the methyl group in the *trans* position and the anionic nature of the complex. In the chloro complex J_3 shows a small reduction in magnitude similar to that in J_1 and J_2 .

The infrared spectrum of $[\text{Bu}_4\text{N}][\text{Me}_2\text{PtCl}_2(\text{Sal}=\text{N–C}_6\text{H}_5)]$ shows a band at 324 cm^{-1} which is not present in the spectrum of the corresponding bromo complex and can be assigned to $\nu(\text{Pt–Cl})$. The presence of a single such band gives further confirmation of the structure with *trans* halogen atoms. No $\nu(\text{Pt–Br})$ could be found above 200 cm^{-1} in $[\text{Bu}_4\text{N}][\text{Me}_2\text{PtBr}_2(\text{Sal}=\text{N–C}_6\text{H}_5)]$, the spectrum being identical to that of the chloro complex apart from the absence of the band at 324 cm^{-1} . The spectra are in general typical of salicylaldimine chelate complexes.

EXPERIMENTAL

Instrumentation

NMR spectra were obtained with a Varian Associates HA-100 spectrometer and the infrared spectra recorded on a Jasco DS-4036 spectrophotometer as Nujol mulls. Conductance measurements were made with a Wayne Kerr B221A bridge.

Starting materials

The platinum compounds Me_2PtX_2 ⁶ and the thallium(I) Schiff-base derivatives⁸ were prepared as described in the literature.

TABLE 2

ANALYTICAL DATA AND YIELDS

Complex	Formula	Analyses found (calcd) (%)				Yield (%)
		C	H	N	X	
Tl[Me ₂ PtBr ₂ (Sal=N-C ₆ H ₅)]	C ₁₅ H ₁₆ NOBr ₂ TlPt	22.48 (22.93)	2.15 (2.05)	1.95 (1.78)	21.0 (20.3)	
[Bu ₄ N][Me ₂ PtBr ₂ (Sal=N-CH ₃)]	C ₂₆ H ₅₀ N ₂ OBr ₂ Pt	41.32 (41.00)	6.71 (6.62)	3.42 (3.68)	20.8 (21.0)	69
[Bu ₄ N][Me ₂ PtBr ₂ (Sal=N-C ₆ H ₁₁)]	C ₃₁ H ₅₈ N ₂ OBr ₂ Pt	44.53 (44.88)	7.11 (7.05)	3.04 (3.32)	18.9 (19.3)	78
[Bu ₄ N][Me ₂ PtBr ₂ (Sal=N-C ₆ H ₅)]	C ₃₁ H ₅₂ N ₂ OBr ₂ Pt	44.74 (45.20)	5.98 (6.36)	3.23 (3.40)	19.1 (19.4)	63
[Ph ₄ As][Me ₂ PtBr ₂ (Sal=N-CH ₃)]	C ₃₄ H ₃₄ NOBr ₂ AsPt	44.97 (45.25)	4.10 (3.79)	1.81 (1.55)	17.4 (17.7)	62
[Ph ₄ As][Me ₂ PtBr ₂ (Sal=N-C ₆ H ₁₁)]	C ₃₉ H ₄₂ NOBr ₂ AsPt	47.09 (48.26)	4.45 (4.36)	1.43 (1.44)	16.8 (16.5)	82
[PhAs][Me ₂ PtBr ₂ (Sal=N-C ₆ H ₅)]	C ₃₉ H ₃₆ NOBr ₂ AsPt	48.55 (48.56)	4.31 (3.76)	1.31 (1.45)	17.0 (16.6)	48
[Me ₄ N][Me ₂ PtBr ₂ (Sal=N-C ₆ H ₅)]	C ₁₉ H ₂₈ N ₂ OBr ₂ Pt	34.41 (34.82)	4.20 (4.31)	3.98 (4.27)	24.6 (24.4)	57
[Bu ₄ N][Me ₂ PtCl ₂ (Sal=N-C ₆ H ₅)]	C ₃₁ H ₅₂ N ₂ OCl ₂ Pt	50.98 (50.67)	7.01 (7.13)	3.87 (3.81)	10.0 (9.7)	77
[Ph ₄ As] ₂ [(Me ₂ PtBr ₂) ₂ Salen]	C ₆₈ H ₆₆ N ₂ O ₂ Br ₄ As ₂ Pt ₂	45.36 (45.30)	3.82 (3.69)	1.55 (1.55)	17.5 (17.7)	71

Syntheses

Analytical figures and yields for all the compounds are given in Table 2. Tl[Me₂PtBr₂(Sal=N-C₆H₅)]. Me₂PtBr₂ (100 mg, 0.26 mmole) suspended in benzene (20 ml) was treated with TlSal=N-C₆H₅ (105 mg, 0.26 mmole) and stirred at room temperature for 2 days. The solid was filtered off, dissolved in a large volume of dichloromethane and after filtering hexane was added and the solution partly evaporated under reduced pressure to give the product as a yellow crystalline solid.

Quaternary ammonium and arsonium salts of [Me₂PtX₂(Sal=N-R)]⁻ (X = Br, Cl; R = CH₃, C₆H₁₁, C₆H₅). Me₂PtX₂ (0.26 mmole) was suspended in a solution of HSal=N-R (0.26 mmole) in ethanol (20 ml) and the mixture heated while stirring until the platinum compound had dissolved. After cooling and filtering, potassium hydroxide (0.3 mmole as a 10% aqueous solution) and a small excess of Bu₄NBr or Ph₄AsBr in a little ethanol, or Me₄NBr in water, were added, followed by water. The tetrabutylammonium salts crystallized readily on reduction of the volume under reduced pressure, and were filtered off, washed with water and dried *in vacuo*. Other salts crystallized less readily and with the exception of [Ph₄As][Me₂PtBr₂(Sal=N-C₆H₅)] could not be obtained in a crystalline form. The other tetraphenylarsonium salts were obtained by evaporating under reduced pressure to the first sign of cloudiness, cooling to -20° overnight and quickly filtering off the solid formed, washing with water and drying *in vacuo*. (On warming to room temperature in the mother liquor the solid forms a gum.) In the case of the tetramethylammonium salt the solution was evaporated under reduced pressure until the cloudy material had coagulated, this was then filtered off, washed with water and dried *in vacuo*.

$[Ph_4As]_2[(Me_2PtBr_2)_2Salen]$, (a). Me_2PtBr_2 (100 mg, 0.26 mmole) was dissolved by heating in ethanol (20 ml) containing $SalenH_2$ (35 mg, 0.13 mmole) and after cooling and filtering potassium hydroxide (15 mg, 0.26 mmole as a 10% aqueous solution) and Ph_4AsBr (150 mg, 0.33 mmole, in a small volume of ethanol) were added. There was a small amount of immediate yellow precipitate and after adding water and partly evaporating the solid was filtered off, washed with water and dried *in vacuo*.

(b) Me_2PtBr_2 (100 mg, 0.26 mmole) and Tl_2Salen (90 mg, 0.13 mmole) suspended in ethanol (20 ml) and heated under reflux for several hours. The solid was filtered off and found to be insoluble in dichloromethane and acetone. It was suspended in acetone (100 ml) and treated with Ph_4AsBr (150 mg, 0.33 mmole) in a small volume of methanol. After stirring for a half hour the mixture was filtered, water added to the filtrate and the volume reduced. The yellow solid was filtered off, washed with water and a little acetone and dried *in vacuo*.

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REFERENCES

- 1 J S Thayer, *Organometal Chem Rev Sect A*, 5 (1970) 53
- 2 V Romano, R Badalamenti, T Pizzino and F Maggio, *J Organometal Chem*, 42 (1972) 199
- 3 J Chatt and B L Shaw, *J Chem Soc*, (1959) 705
- 4 J D Ruddick and B L Shaw, *J Chem Soc A*, (1969) 2801
- 5 J D. Ruddick and B L Shaw, *J Chem Soc A*, (1969) 2961
- 6 J R. Hall and G A Swile, *Aust J Chem*, 24 (1971) 423
- 7 H C Clark and L. E. Manzer, *J. Organometal Chem.*, 38 (1972) C41
- 8 R J Cozens, K S Murray and B O West, *Aust J Chem*, 23 (1970) 683
- 9 R J Cozens, K. S Murray and B O West, *J Organometal Chem*, 27 (1971) 399
- 10 B E Reichert and B O West, *J Organometal Chem*, 36 (1972) C29
- 11 B E Reichert and B O West, *J Organometal Chem*, 54 (1973) 391
- 12 K. S Murray, B E. Reichert and B. O. West, *J Organometal. Chem*, 61 (1973) 451
- 13 D M Adams, J Chatt, J Gerratt and A. D Westland, *J Chem Soc*, (1964) 734
- 14 C W Smith, *J Chem Phys*, 39 (1963) 2031
- 15 F H Allen and A Pidcock, *J Chem Soc A*, (1968) 2700
- 16 D E Clegg, J R Hall and G A Swile, *J Organometal Chem*, 38 (1972) 403