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DIMETHYLPLATINUM(IV) COMPOUNDS. V. PREPARATION AND REACTIONS OF BIS(SALICYLALDEHYDATO) COMPLEXES

J.R. HALL and G.A. SWILE
Department of Chemistry, University of Queensland,
Brisbane, Australia 4067.
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Summary

Two geometrical isomers of $Pt(CH_3)_2(Sal)_2$ have been prepared and identified by ^1H NMR spectra. Some reactions of isomer A (phenolic oxygen atoms *trans* to CH_3) and isomer B (aldehydic oxygen atoms *trans* to CH_3) are reported. Isomer B reacts with C_5D_5N to produce species containing unidentate Sal in solution, while isomer A tends to lose Sal with formation of hydroxo species. Primary amines react with isomer B to form salicylaldimine complexes. Isomer A reacts with en to form $Pt(CH_3)_2en(OH)_2$.

Introduction

Although a large range of β-dicarbonyl complexes of both trimethylplatinum(IV) [1-6] and dimethylplatinum(IV) [7-8] are known, there has been far less work on salicylaldehydato complexes. A compound of formula $Pt(CH_3)_3Sa$ was prepared by reaction of $[Pt(CH_3)_3I]_4$ with TlSal [9] and was found to be dimeric with bridging phenolic oxygen atoms both in the solid state [9,10] and in solution [11], but no reactions of the compound were reported. In the dimethylplatinum(IV) system only the compound $Bu_4N[Pt(CH_3)_2Br_2Sal]$ which is monomeric with Sal *trans* to CH_3 groups has been reported [12]. In this paper we report the preparation of geometrical isomers of formula $Pt(CH_3)_2(Sal)_2$ and a number of reactions of these compounds with pyridine-d_5 and amines. Preliminary results have been reported [8].

Results and Discussion

Preparation and identification of the compounds $Pt(CH_3)_2(Sal)_2$

$Pt(CH_3)_2(OH)_2 \cdot 2H_2O$* dissolves in boiling salicylaldehyde and from such solutions a compound of formula $Pt(CH_3)_2(Sal)_2$ may be isolated. The product is an orange-yellow crystalline solid which is soluble in organic solvents such as chloroform and benzene but decomposed by 95% ethanol or aqueous acetone to reform the hydroxo compound.

Assuming bidentate salicylaldehyde and *cis*-methyl groups are present, three geometrical isomers are possible for $Pt(CH_3)_2(Sal)_2$ (see Fig. 1).

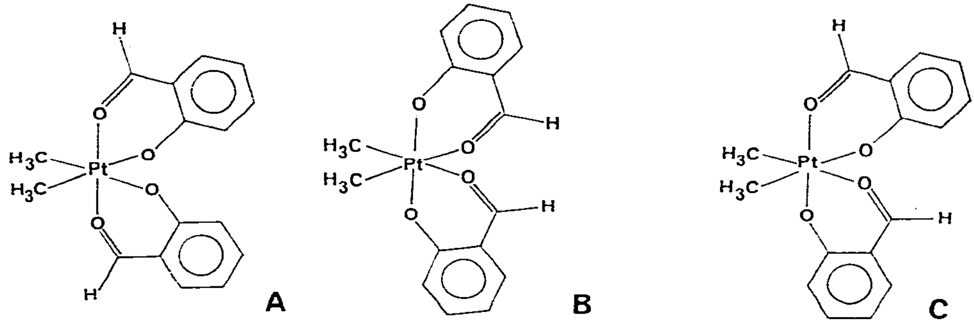

Fig. 1. Isomers of *cis*-dimethyl-*bis*(salicylaldehydato)platinum(IV), $Pt(CH_3)_2(Sal)_2$.

The ^1H NMR spectrum of the compound in $CDCl_3$ (Fig. 2a) indicates the presence of only one isomer since only a single methyl-platinum resonance (with satellites due to coupling between the methyl protons and ^{195}Pt ($I = \frac{1}{2}$, 34% abundance)) is observed. Isomer C may be ruled out since for this isomer two non-equivalent methyl-platinum

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* The compound $Pt(CH_3)_2(OH)_2 \cdot 2H_2O$ has been reported from the reaction of $[Pt(CH_3)_2Br_2]_n$ with NaOH [8]. Subsequent preparations indicate that freshly prepared samples approach this formulation, but there is loss of weight with ageing and the compound is probably better described as $Pt(CH_3)_2(OH)_2 nH_2O (n=1-2)$.

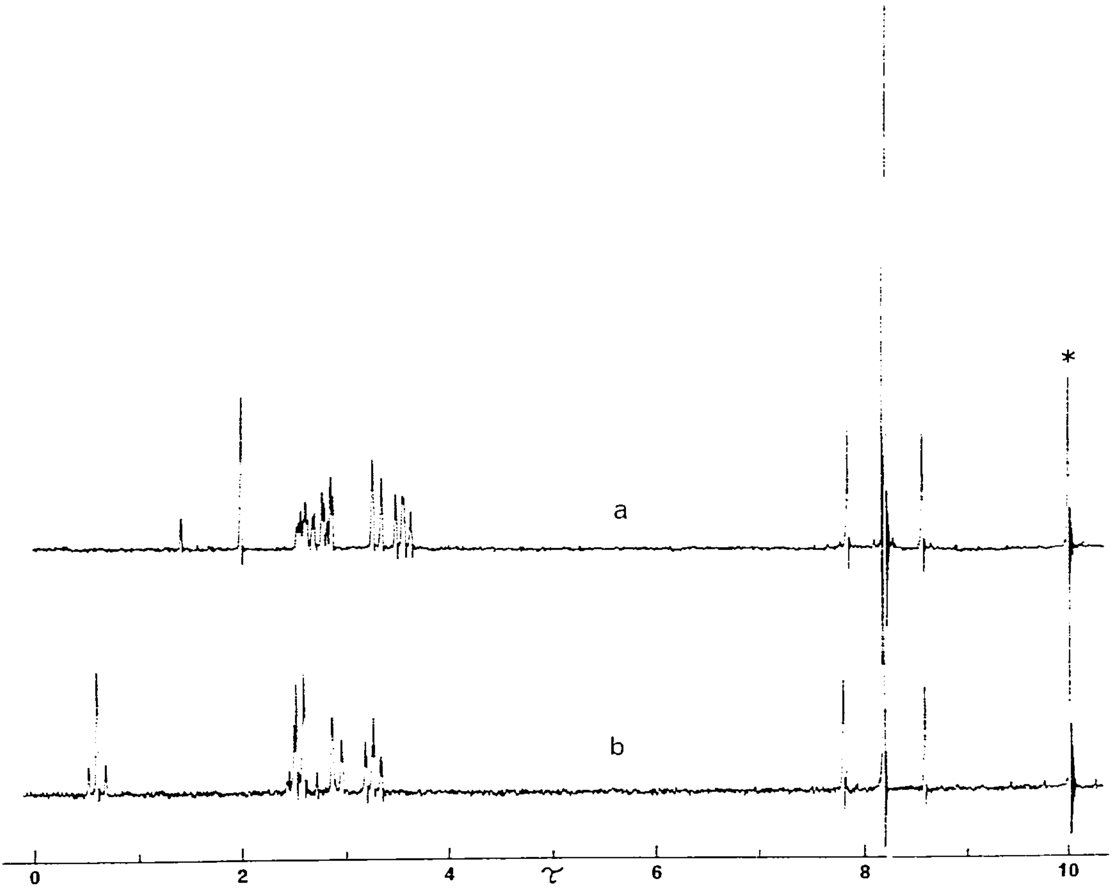

Fig. 2. ^1H n.m.r. spectra of $Pt(CH_3)_2(Sal)_2$ in $CDCl_3$; (a), isomer A and (b), isomer B. *TMS.

resonances with different coupling constants would be expected due to the influence of different types of donor atoms in the *trans* positions [13]. The magnitude of the coupling constant observed (72.4 Hz, Table 1) is consistent with the presence of oxygen donor atoms *trans* to CH_3 [13] and appears to be more consistent with CH_3 *trans* to phenolic oxygens when compared with the values obtained for CH_3 *trans* to phenolic (74.1 Hz) and aldehydic (78.6 Hz) in $Bu_4N[Pt(CH_3)_2Br_2Sal]$ [12].

Reference to Table 1 shows that the aldehydic protons of the salicylaldehydato ligands couple to ^{195}Pt with a magnitude of 121.0 Hz. This value is substantially higher than that expected for either isomer B of Fig. 1 (where the coupling would be expected to be of the same

TABLE 1

^1H NMR SPECTRA OF ISOMERS OF $Pt(CH_3)_2(Sal)_2$ AND THEIR REACTION PRODUCTS

Compound		$Pt-CH_3$		$Pt-O=CH$		$Pt-N=CH$		$Pt-N-CH_3$	
		τ	J	τ	J	τ	J	τ	J
In *m*-dichlorobenzene									
$Pt(CH_3)_2(Sal)_2$	A	8.19	72.5						
	B	8.12	77.5						
	C	8.07	77.2						
		8.23	72.7						
In $CDCl_3$									
$Pt(CH_3)_2(Sal)_2$	A	8.23	72.4	1.89	121.0				
	B	8.19	77.5	0.62	16.3				
$Pt(CH_3)_2Sal(Sal{=}N{-}CH_3)$		8.31	79.1	0.67	15.9	1.89	22.0	6.61	8.7[a]
		8.55	67.1						
$Pt(CH_3)_2(Sal{=}N{-}CH_3)_2$		8.66	68.4			1.95	22.5	6.67	9.1[b]
$Pt(CH_3)_2(Sal)(Sal{=}N{-}C_6H_5)$		8.14	78.7	0.78	16.0	1.83	19.6		
		8.44	68.5						
$Pt(CH_3)_2(Sal{=}N{-}C_6H_5)(Sal{=}N{-}CH_3)$		8.49	68.4			2.04	22.2	6.58	9.1[c]
		8.55	70.4			1.90	19.2		
$Pt(CH_3)_2(Sal)_2$,B + en:									
Initial Products:	Major	8.32	78.8	0.68	15.4	1.83	19[d]		
		8.52	66.6						
	Minor	8.40 8.52	79.1 66.6	0.61	15.2	1.93	20[d]		
Final Products:	Major	8.64	68.6			1.92	21.2		
	Minor	8.65	69.0			[e]			
In $CDCl_3$-C_5D_5N									
$Pt(CH_3)_2(Sal)_2C_5D_5N$		8.02[f]	77.1	0.62[g]	17.2				
		8.57[f]	71.6	-0.62[h]	—				
$Pt(CH_3)_2(Sal)_2(C_5D_5N)_2$		8.07	71.4	-0.48	—				
$Pt(CH_3)_2(Sal)(C_5D_5N)OH$		8.31[f]	73.2	1.46	76.2				
		8.49[f]	72.0	0.09[f]	—				
$Pt(CH_3)_2(C_5D_5N)_2(OH)_2$		8.63	71.8						
In D_2O									
$Pt(CH_3)_2en(OH)_2$		8.87	70.7						

[a] $^3J(CH_3{-}N{=}CH)$ 1.2 Hz. [b] $^3J(CH_3{-}N{=}CH)$ 1.4 Hz. [c] $^3J(CH_3{-}N{=}CH)$ 1.3 Hz.

[d] Error ±1 Hz. [e] Region complex, only major peaks identified.

[f] Slight downfield shift (3-4 Hz) as C_5D_5N concentration increased to 50% by volume. [g] Slight upfield shift (2 Hz) as C_5D_5N concentration increased to 50% by volume. [h] Peak moves to τ -0.73 as C_5D_5N concentration increased to 50% by volume.

order as that found in the complexes $[Pt(CH_3)_2Br_2Sal{=}N{-}R]^-$ (22-27 Hz) [14] since the coupling in each case is *trans* to CH_3) or isomer A of Fig. 1 (where a somewhat higher value (~ 60 Hz) might be expected when allowance is made for the smaller *trans* influence of O compared with CH_3 [13] (cf., $[Pt(CH_3)_2(CH_3NH_2)_4]^{2+}$, where the couplings of the methylamine methyl protons *trans* to CH_3 and CH_3NH_2 are 15 and 40 Hz respectively [15])). The abnormally high value of 121 Hz for this coupling can only be rationalized in terms of a favourable orientation of the Pt—O═C—H groups. Similar large couplings have been found for *trans* Pt—C═C—H couplings in alkenylplatinum(II) compounds (120-148 Hz) [16]. The above evidence, although more consistent with isomer A, does not allow an unequivocal assignment to a particular isomer, and it is only by comparison of these results with those found for the other isomer reported below that the compound can be assigned to isomer A of Fig. 1.

Although the compound is stable indefinitely in the solid state, heating solutions in high boiling solvents such as tetrachloroethylene, *m*-dichlorobenzene and dicyclopentadiene results in the formation of several new species according to ^1H NMR spectra. The rate of formation of these new species is dependent on the temperature of reaction, and the reactions are usually accompanied by some decomposition to metallic platinum.

According to ^1H NMR spectra of *m*-dichlorobenzene solutions (Table 1), three new methyl-platinum resonances appear during the reaction. Two of these resonances (τ 8.07, J 77.2 Hz; τ 8.23, J 72.7 Hz) remain at equal intensity throughout the reaction and so probably arise from a single species with non-equivalent methyl groups. This species is postulated to be isomer C of Fig. 1 but was never present in more than one-third of the total species in solution and no attempt was made to isolate it.

The third methyl-platinum resonance (τ 8.12, J 77.5 Hz) gradually increased in intensity as the reaction proceeded and was ultimately the only such resonance present. From solutions containing this species a yellow solid analysing for $Pt(CH_3)_2(Sal)_2$ was isolated. This solid is soluble in chloroform and benzene and, in contrast to the previous isomer, dissolves in ethanol and acetone without decomposition.

The ^1H NMR spectrum of this isomer in $CDCl_3$ is shown in Fig. 2b. The NMR data (Table 1) are consistent with this compound being isomer B of Fig. 1. A single methyl-platinum resonance is observed with a coupling constant of 77.5 Hz consistent with CH_3 *trans* to oxygen donors [13] while the salicylaldehyde aldehydic protons couple with ^{195}Pt with a magnitude of 16.3 Hz, comparable with the coupling of the aldimine proton in $[Pt(CH_3)_2Br_2Sal{=}N{-}R]^-$ [14]. It may be noted that for this isomer there is no enhanced coupling of the aldehydic proton to ^{195}Pt.

Since the magnitude of the coupling constant gives an indication of bond strength [13] it would be predicted that the coupling constant of a methyl group *trans* to an aldehyde group as in isomer B would be greater than that *trans* to a phenolic oxygen as in isomer A. The couplings observed for the two isomers (77.5 Hz for isomer B; 72.4 Hz for the initial isomer) tend to confirm that the initial isomer is isomer A.

Reactions of the compounds $Pt(CH_3)_2(Sal)_2$

(a) *Pyridine-d_5**

When C_5D_5N is added dropwise to a $CDCl_3$ solution of isomer B, two new methyl-platinum resonances appear in the NMR spectrum (Table 1). These resonances are of equal intensity and are presumably due to a single species with non-equivalent methyl groups. The coupling constants, 71.6 and 77.1 Hz are consistent with methyl groups *trans* to C_5D_5N and an aldehydic oxygen respectively, so that

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* C_5D_5N rather than C_5H_5N was used to enable the aldehydic proton resonances to be observed.

the species is presumed to be $Pt(CH_3)_2(Sal)_2(C_5D_5N)$ with one bidentate and one unidentate (via the phenolic oxygen atom) salicylaldehyde ligand. The aldehydic proton region supports the presence of such a species since two separate resonances are observed, one at τ 0.62 (J 17.2 Hz) which is attributable to bidentate Sal with the aldehydic group *trans* to CH_3 and a second at τ-0.62 which is broader than the first and shows no evidence for coupling with ^{195}Pt. There is apparently an equilibrium between isomer B and this species since there is still an appreciable amount of isomer B present on addition of more than two moles of C_5D_5N per mole of $Pt(CH_3)_2(Sal)_2$. There is no further change in the spectrum on allowing the solution to stand. On the other hand, the relative amounts of each species are altered by changing the concentration of $CDCl_3$.

Further addition of C_5D_5N results in increased formation of $Pt(CH_3)_2(Sal)_2(C_5D_5N)$, slight changes in the chemical shifts of the methyl and coordinated aldehydic protons and a more marked downfield shift of the free aldehyde proton which also tends to sharpen. Continued addition of C_5D_5N results in the formation of a new species with only a single methyl-platinum resonance (τ 8.07, J 71.4 Hz) which is postulated to be $Pt(CH_3)_2(Sal)_2(C_5D_5N)_2$ with C_5D_5N *trans* to CH_3 and two unidentate (via the phenolic oxygen atom) salicylaldehyde ligands. A single sharp resonance (τ - 0.48) appears in the aldehydic proton region with no evidence for coupling with ^{195}Pt. Further addition of C_5D_5N increases the amount of this species at the expense of $Pt(CH_3)_2(Sal)_2(C_5D_5N)$ until only the bis pyridine species is present. On allowing such solutions to stand for several days decomposition apparently occurs, since the colour of the solution becomes deep red and the NMR spectrum shows a large number of new peaks in the methyl-platinum region.

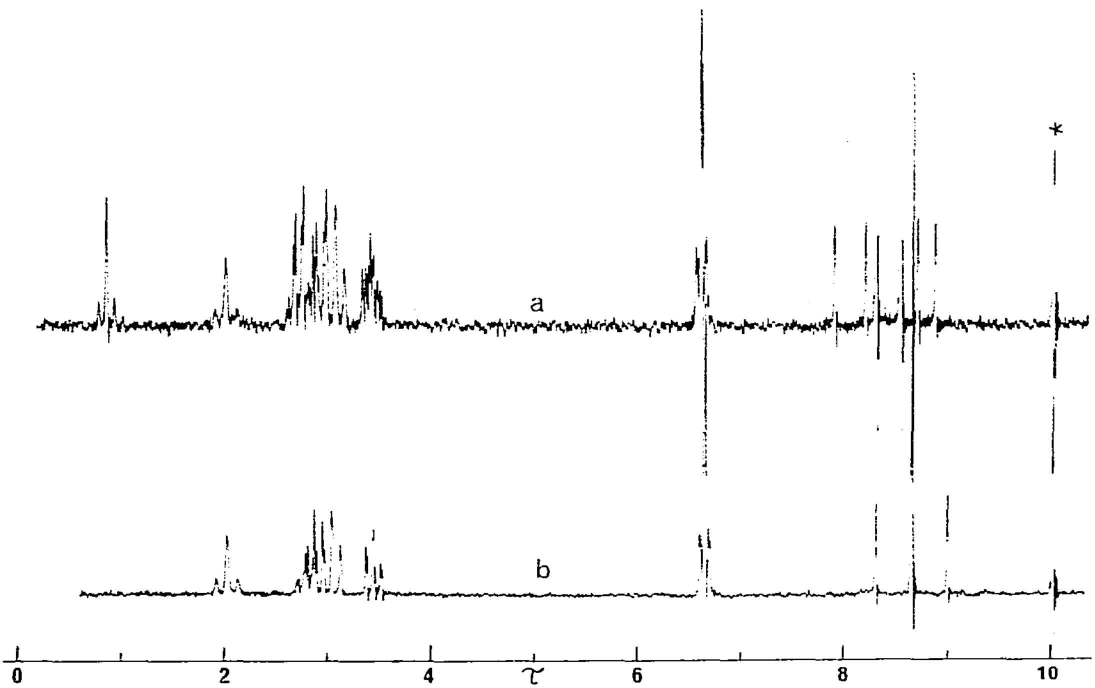
When a solution of isomer A is treated dropwise with C_5D_5N, two new methyl-platinum resonances appear in the NMR spectrum. The resonances are of equal intensity and presumably arise from a single species with non-equivalent methyl-platinum groups. The coupling constants observed (72.0 and 73.2 Hz) may be assigned to CH_3 groups *trans* to C_5D_5N and phenolic oxygen respectively. On allowing the solution to stand in the presence of more than two moles of C_5D_5N per mole of platinum, this second species gradually increases at the expense of isomer A. Two aldehydic resonances are present for the second species. One resonance (τ 1.46) shows coupling with ^{195}Pt(76.2 Hz) and can be assigned to a proton on an aldehydic group bonded to platinum in a position *cis* to the methyl groups, so that one bidentate salicylaldehyde is present in the compound. The second resonance is a sharp singlet at τ0.09 which is probably due to free salicylaldehyde since its chemical shift is almost identical with that found for salicylaldehyde in similar solutions (τ 0.06). The species present in solution could be either $[Pt(CH_3)_2Sal(C_5D_5N)_2]^+$ or $Pt(CH_3)_2Sal(C_5D_5N)OH$ with C_5D_5N or OH *trans* to the aldehydic oxygen atom. The latter formulation appears more likely since evaporation of solutions containing this species yields a product with OH vibrations in the infrared spectrum. The large decrease in the coupling constant of the coordinated aldehyde from 121.0 Hz in isomer A to 76.2 Hz in this species is also consistent with the coupling arising from a particular orientation of the aldehyde group in each compound, since a *trans* influence effect would not result in a change of this magnitude.

Addition of further C_5D_5N produces a second species exhibiting a single methyl-platinum resonance (τ 8.63, J 71.8 Hz) (Table 1) consistent with CH_3 groups *trans* to C_5D_5N while the aldehyde proton resonance observed previously (shifted to τ 0.06) increases in intensity. Furthermore, the aromatic region of the spectrum resembles the pattern found in free salicylaldehyde. This indicates that both Sal ligands have been displaced and the methyl-platinum species is most probably $Pt(CH_3)_2(C_5D_5N)_2(OH)_2$. Support for this formulation is obtained by evaporation of the solution to give a solid containing both coordinated OH and C_5D_5N as confirmed by IR. The compound is however unstable and loses C_5D_5N to form $Pt(CH_3)_2(OH)_2nH_2O$ on standing.

(b) Amines

When a one mole ratio of methylamine is added to a solution of $Pt(CH_3)_2(Sal)_2$ (isomer B) in $CDCl_3$ there is an immediate formation of a new species with two non-equivalent methyl-platinum groups as evidenced by the presence of two methyl-platinum resonances of equal intensity in the NMR spectrum (Fig. 3a). The spectrum can be interpreted in terms of the structure in Fig. 4A ($R=CH_3$), where methylamine has condensed with one of the salicylaldehyde ligands to form an N-methyl salicylaldimine complex. Thus the two methyl-platinum resonances have coupling constants of 79.1 and 67.1 Hz (Table 1), which are consistent with CH_3 *trans* to an aldehydic oxygen (cf., 77.5 Hz

Fig. 3. $Pt(CH_3)_2(Sal)_2$ (isomer B) plus (a) 1 mol of CH_3NH_2; (b) 2 mol of CH_3NH_2. *TMS.



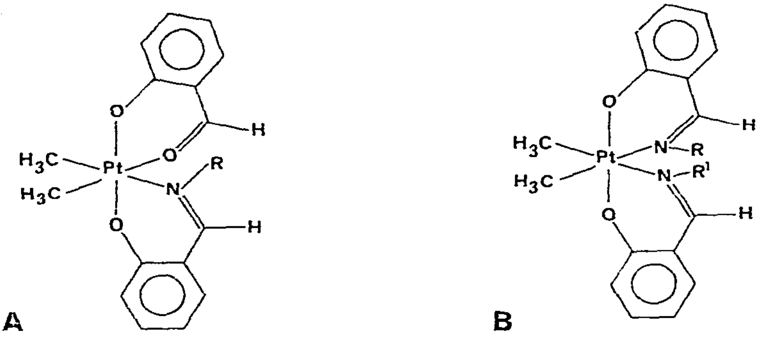


Fig. 4. Structures of the reaction products of isomer B with one mol of CH_3NH_2 (A) and two mol of CH_3NH_2 (B)

in isomer B) and *trans* to an aldimine group (cf., 67.1 in $Ph_4As[Pt(CH_3)_2Br_2Sal{=}N\text{-}CH_3]$ [14]). The N-methyl resonance consists of a central doublet due to coupling between the CH_3 group and the imine proton ($^3J(HC{=}NCH_3)$ 1.2Hz) together with satellites due to coupling with ^{195}Pt (Fig. 3a). The magnitude of this latter coupling (8.7 Hz) is somewhat less than those found in $M[Pt(CH_3)_2Br_2Sal{=}N\text{-}CH_3]$ (13.0-13.2 Hz) [14] and $[Pt(CH_3)_3Sal{=}N\text{-}CH_3L]$ (14-16 Hz) [17] indicating a weaker Pt-N bond in $Pt(CH_3)_2(Sal)(Sal{=}N\text{-}CH_3)$. This is supported also by the magnitude of the coupling of the aldimine proton with ^{195}Pt (22.0 Hz) which is less than that in $Bu_4N[Pt(CH_3)_2Br_2Sal{=}N\text{-}CH_3]$ (26.4 Hz) [14]. The aldehydic proton couples with ^{195}Pt with a magnitude of 15.9 Hz, which is of the same order as that found in isomer B (16.3 Hz).

Addition of a two mole ratio of methylamine to a $CDCl_3$ solution of $Pt(CH_3)_2(Sal)_2$ (isomer B) immediately produces $Pt(CH_3)_2Sal(Sal{=}N\text{-}CH_3)$ as for a one mole ratio. However, on allowing the solution to stand, formation of a new species, whose spectrum is shown in Fig. 3b, occurs over a period of about 30 minutes. The spectrum indicates that the compound is the bis (N-methylsalicylaldimine) compound whose structure is shown in Fig. 4B ($R{=}R^1{=}CH_3$). Thus a single methyl-platinum resonance is observed with a coupling constant of 68.4 Hz, while coupling of ^{195}Pt with both the N-methyl group (9.1 Hz) and the aldimine proton (22.5 Hz) are of the same order as is found for these couplings in the compound $Pt(CH_3)_2Sal(Sal{=}N\text{-}CH_3)$.

Although a second mole of CH_3NH_2 reacted quite readily with $Pt(CH_3)_2Sal(Sal{=}N{-}CH_3)$ as shown above, an attempt to react the latter species with α-methylbenzylamine was unsuccessful since no apparent reaction occurred after heating for 10 hours at 55°C.

Reaction of isomer B with a two mole ratio of aniline was extremely slow at room temperature but at 55°C reaction occurred over a period of 9 hours to produce a species whose NMR spectrum was consistent with $Pt(CH_3)_2Sal(Sal{=}N{-}C_6H_5)$ (Fig. 4A, $R{=}C_6H_5$). Thus two non-equivalent methyl-platinum resonances are observed with coupling constants of 78.7 Hz (*trans* to aldehyde group) and 68.5 Hz (*trans* to aldimine group). Both aldehydic (τ 0.78, J 16.0 Hz) and aldimine (τ 1.83, J 19.6 Hz) protons were observed (Table 1). The larger value of $^2J(^{195}Pt{-}CH_3)$ *trans* to N and the smaller value of $^3J(^{195}Pt{-}N{=}CH)$ compared with the values in $Pt(CH_3)_2Sal(Sal{=}N{-}CH_3)$ indicate a weaker Pt-N bond in the former compound, consistent with the greater electron - withdrawing properties of the aryl group [14].

No attempt was made to extend the reaction to the formation of the bis (N-phenylsalicylaldiminato) compound in view of the extreme slowness of such a reaction.* However, reaction of a solution of $Pt(CH_3)_2Sal$ $(Sal{=}N{-}C_6H_5)$ with CH_3NH_2 proceeded at a reasonable rate with the reaction being complete after 6 hours at 55°C. The product of the reaction was $Pt(CH_3)_2(Sal{=}N{-}C_6H_5)(Sal{=}N{-}CH_3)$ (Fig. 4B, $R{=}CH_3;R^1{=}C_6H_5$) according to ^1H NMR. Two methyl-platinum resonances are observed with coupling constants of 70.4 Hz (CH_3 *trans* to $N{-}C_6H_5$) and 68.4 Hz (CH_3 *trans* to $N{-}CH_3$) and two aldimine proton resonances at τ 1.90, J 19.2 Hz ($\underline{H}C{-}N{-}C_6H_5$) and τ 2.04, J 22.2 Hz ($\underline{H}C{-}N{-}CH_3$).

Reaction of $Pt(CH_3)_2(Sal)_2$ (isomer B) with ethylenediamine is more complex than the above reactions and the results more equivocal. Dropwise addition of en to a $CDCl_3$ solution of isomer B produces three new methyl-platinum resonances in the ^1H NMR spectrum. The intensities of these

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* Species of the type $Pt(CH_3)_2(Sal{=}N{-}R)_2$ would probably be best prepared by reaction of $Pt(CH_3)_2(OH)_2{\cdot}nH_2O$ with HSal=N-R as has been done with H acac=N-R ligands [6].

resonances indicate that two species, each with two non-equivalent methyl groups are present in solution in the approximate ratio of 2:1 with one resonance from each species being accidentally degenerate (Table 1). The magnitudes of the coupling constants indicate that for each species one CH_3 group is *trans* to an aldehyde oxygen (78.8 and 79.1 Hz respectively) and one *trans* to an aldimine group (66.6 Hz for each). Each species exhibits one aldehyde (τ 0.68 and τ 0.61 respectively) and one aldimine (τ 1.83 and τ 1.93 respectively) resonance. Fig. 5 shows two possible structures which would give non-equivalent methyl-platinum resonances but it is impossible to assign structures from the NMR spectra.

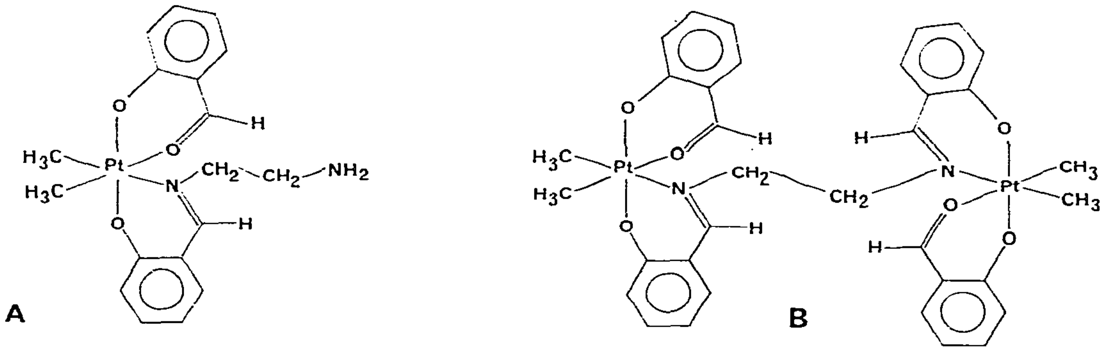

Fig. 5. Possible products of the reaction of isomer B with en.

Further addition of ethylenediamine produces two new species each with equivalent methyl groups *trans* to aldimine ligands (Table 1). A large number of monomeric, dimeric and even polymeric structures could be postulated with equivalent methyl groups so that the species cannot be identified by ^1H NMR spectra. The formation of insoluble material probably indicates that polymeric species have formed in the reaction. Reaction of $Pt(CH_3)_2(Sal)_2$(isomer A) with ethylenediamine results in immediate precipitation of a white microcrystalline solid which analyses for $Pt(CH_3)_2en(OH)_2$*. The ^1H NMR spectrum of this compound in D_2O exhibits a single methylplatinum resonance with a coupling constant of 70.7 Hz, consistent with CH_3 group *trans* to nitrogen donor

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* The same species may be prepared by reaction of $Pt(CH_3)_2(OH)_2 \cdot nH_2O$ with en.

atoms [13]. The infrared spectrum of the compound contains peaks due to coordinated OH at 3591 (ν(OH)), 989 and 969 (δ(OH)) and 558 cm^{-1} (ν(Pt-O)). From the filtrate of the above reaction, yellow crystals of bis-(salicylaldehyde)ethylenediimine can be obtained as confirmed by IR spectra.

The above reactions indicate that in $Pt(CH_3)_2(Sal)_2$ (isomer A) the coordinated aldehyde groups are readily displaced by OH groups in the presence of a variety of ligands such as C_5D_5N, ethylenediamine and even aqueous ethanol and acetone. Since the methyl groups tend to weaken the Pt-O (phenolic) in *trans* positions due to their high *trans* influence [13], this results in complete displacement of the salicylaldehyde ligands. On the other hand, in isomer B the phenolic groups do not appear to be displaced by OH groups and it is only the Pt-O (aldehydic) bonds *trans* to the methyl groups which are involved in either displacement reactions (C_5D_5N) or condensation reactions (amines). The lack of formation of hydroxo species in such systems suggests that the Pt-O (phenolic) bonds remain intact during the formation of the Schiff base complexes.

Experimental

Analytical results for the compounds are listed in Table 2.

Preparation of $Pt(CH_3)_2(Sal)_2$ (isomer A)

$Pt(CH_3)_2(OH)_2 \cdot nH_2O$ (0.6g) was suspended in salicylaldehyde (5 ml) and the mixture heated to boiling. The solid usually dissolved after several minutes heating although addition of ethanol (0.5 ml) was sometimes required for ready dissolution. The resultant orange solution was evaporated to dryness on the water bath in a stream of air. The orange-yellow crystalline solid was dissolved in chloroform, the solution filtered, concentrated to a small volume and *n*-hexane added to induce crystallization. The product, in the form of orange-yellow plates was filtered off, washed with *n*-hexane and air dried. Yield 95%.

The compound appears to be stable indefinitely in the solid state, one sample remaining unchanged after 4 months. When chloroform solutions of the compound are treated with 95% ethanol or aqueous

TABLE 2

ANALYTICAL DATA

Compound		Empirical formula	Analysis (calcd. (found)) (%)		
			C	H	N
$Pt(CH_3)_2(Sal)_2$	A	$C_{15}H_{16}O_4Pt$	41.1	3.5	
			(41.2)	(3.5)	
	B	$C_{16}H_{16}O_4Pt$	41.1	3.5	
			(41.2)	(3.5)	
$Pt(CH_3)_2(Sal)(Sal{=}N{-}CH_3)$		$C_{17}H_{19}NO_3Pt$	42.5	4.0	2.9
			(42.3)	(4.0)	(3.0)
$Pt(CH_3)_2(Sal{=}N{-}CH_3)_2$		$C_{18}H_{22}N_2O_2Pt$	43.8	4.5	5.7
			(43.9)	(4.6)	(5.6)
$Pt(CH_3)_2(Sal{=}N{-}C_6H_5)(Sal{=}N{-}CH_3)$		$C_{23}H_{24}N_2O_2Pt$	49.7	4.4	5.0
			(49.7)	(4.5)	(5.0)
$Pt(CH_3)_2en(OH)_2$		$C_4H_{16}N_2O_2Pt$	15.0	5.1	8.8
			(14.8)	(5.5)	(8.4)

acetone the solution becomes cloudy and the odour of salicylaldehyde becomes noticeable. Evaporation of the solution and extraction with chloroform leaves a pale yellow residue which has an identical infrared spectrum to that of $Pt(CH_3)_2(OH)_2 \cdot nH_2O$.

Preparation of $Pt(CH_3)_2(Sal)_2$ (isomer B)

$Pt(CH_3)_2(Sal)_2$ (isomer A) (0.5g) was dissolved in *m*-dichlorobenzene (8 ml) and the solution heated to boiling. Metallic platinum began to precipitate from solution after 30 seconds but heating was continued for 8 minutes at which time the ^1H NMR spectrum confirmed that only a single species was present in solution. The solvent was then evaporated by heating on a water bath in a stream of air. The residue was extracted with chloroform, charcoal added to adsorb the colloidal platinum, and the solution filtered. The filtrate was concentrated to a small volume and the yellow crystalline product precipitated by addition of *n*-hexane. A second recrystallization with charcoal is sometimes necessary to remove all traces of platinum. Yield 80%. The compound appears to be stable indefinitely both in the solid state and in solutions of chloroform, ethanol and acetone.

Several other high boiling solvents were investigated for the preparation of isomer B. With tetrachloroethylene, reaction was much slower, NMR spectra indicating complete conversion only after 2 hours boiling. Initial platinum formation was also slower, but the total amount of platinum formed eventually was about the same as in the *m*-dichlorobenzene reaction. With dicyclopentadiene, complete reaction occurred within 5 minutes of heating and there was no evidence for formation of platinum metal. However, isolation of the product was difficult as intractable tars tended to be formed. A similar result was found with pyridine solutions although in this case there was also substantial formation of $Pt(CH_3)_2py_2(OH)_2$.

^1H NMR spectra indicated that isomer A, in both tetrachloroethylene and *m*-dichlorobenzene decreased at the expense of two new species, isomers B and C. Both isomers were present throughout the reaction, although in *m*-dichlorobenzene isomer C was never present to an extent greater than 30-40%, the amount remaining fairly constant while isomer B increased at the expense of isomer A. In the lower-boiling solvent, tetrachloroethylene, it appeared that the amount of isomer C did in fact rise to almost 50% of the total species present. There was no evidence for free salicylaldehyde at any stage throughout the reaction. On the other hand NMR spectra of isomer A in both dicyclopentadiene and pyridine showed the presence of a free aldehyde group which suggests that the dicyclopentadiene may be coordinated to platinum in the former solution.

Reaction of $Pt(CH_3)_2(Sal)_2$ (isomer A) with C_5D_5N

$Pt(CH_3)_2(Sal)_2$ (isomer A) (0.04g) was dissolved in $CDCl_3$ (0.5 ml) in an NMR tube. Neat C_5D_5N was added dropwise to the solution and the reaction monitored by ^1H NMR spectra. When reaction was complete (approx. 50:50 $CDCl_3$:C_5D_5N) the solution was evaporated to dryness in a stream of air. The solid was extracted with chloroform leaving a residue confirmed to be $Pt(CH_3)_2(OH)_2 \cdot nH_2O$ by its infrared spectrum. The solution contained $Pt(CH_3)_2Sal(C_5D_5N)OH$ as confirmed by ^1H NMR.

Reaction of $Pt(CH_3)_2(Sal)_2$ *(isomer B) with* C_5D_5N

$Pt(CH_3)_2(Sal)_2$ (isomer B) (0.04g), dissolved in $CDCl_3$, was treated with C_5D_5N as for isomer A. The final solution was allowed to stand for 3 days during which time it changed from yellow to deep red and ^1H NMR spectra indicated a number of decomposition products in solution.

Preparation of $Pt(CH_3)_2Sal(Sal{=}N{-}CH_3)$

$Pt(CH_3)_2(Sal)_2$ (isomer B) (0.04g) was dissolved in $CDCl_3$ (0.5 ml) in an NMR tube. A solution of CH_3NH_2 in $CDCl_3$ was added dropwise until ^1H NMR spectra indicated complete formation of the desired product. The solution was then transferred to a beaker, concentrated to a small volume and *n*-hexane added. On allowing the solution to stand, yellow crystals of the product separated. These were filtered off and air-dried. Yield 90%.

Preparation of $Pt(CH_3)_2(Sal{=}N{-}CH_3)_2$

$Pt(CH_3)_2(Sal)_2$ (isomer B) (0.04g) was dissolved in $CDCl_3$ (0.5 ml) in an NMR tube. A solution of CH_3NH_2 in $CDCl_3$ was added dropwise until slightly more than 2 moles of CH_3NH_2 per mole of platinum were added, the amount required being estimated by comparison of the intensities of the free methyl resonance of CH_3NH_2 and the methyl-platinum resonances of $Pt(CH_3)_2Sal(Sal{=}N{-}CH_3)$. NMR spectra indicated the formation of the product after 30 minutes at room temperature. The solution was then transferred to a beaker, concentrated to a small volume and *n*-hexane added. On allowing the solution to stand yellow prisms of the product separated. These were filtered off and air-dried. Yield 95%.

Reaction of $Pt(CH_3)_2(Sal)_2$ (isomer B) with aniline

$Pt(CH_3)_2(Sal)_2$ (isomer B) (0.03g) was dissolved in $CDCl_3$ (0.5 ml) in an NMR tube and a solution of aniline in $CDCl_3$ (1:10) added dropwise. The solution initially contained $Pt(CH_3)_2(Sal)_2$ and unreacted aniline as confirmed by ^1H NMR spectra, but heating the solution at 55°C for 9 hours produced a single species whose NMR spectrum was consistent with $Pt(CH_3)_2Sal(Sal{=}N{-}C_6H_5)$. The solution became reddish during this time. Attempts to isolate this product in pure form were unsuccessful as intractable gums tended to form on evaporation of the solution.

Preparation of $Pt(CH_3)_2(Sal{=}N{-}C_6H_5)(Sal{=}N{-}CH_3)$

To a solution containing $Pt(CH_3)_2Sal(Sal{=}N{-}C_6H_5)$ prepared as described above, a solution of CH_3NH_2 in $CDCl_3$ was added dropwise until one mole of CH_3NH_2 per platinum was present as indicated by relative intensities of methylamine methyl and methyl-platinum resonances. After 6 hours at room temperature, NMR spectra indicated complete formation of the product. The reddish solution was transferred to a beaker, chloroform added, and the solution then heated with activated charcoal. After filtration the yellow solution was concentrated to a small volume and *n*-hexane added. On standing, yellow crystals of the product formed and were filtered off and air-dried. Yield 90%.

Reaction of $Pt(CH_3)_2(Sal)_2$ (isomer B) with ethylenediamine

$Pt(CH_3)_2(Sal)_2$ (isomer B) (0.05g) was dissolved in $CDCl_3$ (0.5 ml) in an NMR tube and a solution of ethylenediamine in $CDCl_3$ added dropwise. After the NMR spectrum of the intermediates had been recorded, excess ethylenediamine solution was added and the solution allowed to stand for 2 hours at which time reaction appeared to be complete. The solution was then filtered to remove a small amount of precipitated solid, the filtrate concentrated to a small volume and *n*-hexane added to precipitate a yellow solid. Analytical data for this solid indicated that there was a mixture of compounds present.

Reaction of $Pt(CH_3)_2(Sal)_2$ (isomer A) with ethylenediamine

$Pt(CH_3)_2(Sal)_2$ (0.03g) was dissolved in chloroform (2 ml) and a solution of ethylenediamine in chloroform added dropwise. There was immediate formation of an off-white microcrystalline precipitate. This was filtered off, dissolved in ethanol and treated with activated charcoal. After filtration, the solution was concentrated to a small volume and *n*-hexane added to precipitate the product as a white crystalline solid. The product analysed for $Pt(CH_3)_2en(OH)_2$ and was obtained in 70% yield. From the initial filtrate a yellow solid was obtained by concentration and addition of *n*-hexane. This was confirmed to be bis-(salicylaldehyde) ethylenediimine by its IR spectrum.

^1H NMR spectra were recorded on a JEOL PS-100 spectrometer on internal lock (TMS) using sweep width 270 Hz. Chemical shifts are considered accurate to ±0.01ppm and coupling constants to ±0.5 Hz.

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