

## TRIMETHYLPLATINUM(IV) COMPLEXES WITH O-N BIDENTATE LIGANDS

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### SUMMARY

Complexes of the trimethylplatinum(IV) moiety with bidentate monobasic salicylaldimines  $C_6H_5(OH)CH=NR$  ( $R$  = ethyl, propyl, phenyl) have been prepared and characterized by IR, UV and NMR spectra and magnetic susceptibility measurements. The complexes are dimeric with double Pt-O-Pt bridges, and the metal appears to be pseudo-octahedrally hexacoordinated.

### INTRODUCTION

Trimethylplatinum(IV) is among the most stable organometallic moieties. It gives complexes with monodentate ligands, *e.g.* the halides, with bidentate ligands, *e.g.*  $\beta$ -diketones, and with mixed ligands, *i.e.* with more than one type of ligand<sup>1</sup>. In all these complexes the platinum is hexacoordinated<sup>1</sup>. As far as we know, no trimethylplatinum(IV) complex of *N*-substituted salicylaldimines has been reported. The different electronic and steric characteristics of substituents on the nitrogen play an important role in determining the type of stereochemistry of complexes containing such ligands<sup>2-5</sup>.

As part of our study of organoplatinum(IV) chemistry, we describe below the preparation of compounds obtained by reacting trimethylplatinum(IV) iodide with monobasic *N*-alkylsalicylaldimines, where alkyl = ethyl, propyl, tert-butyl, phenyl. They were characterized by measurements of molecular weight, IR, UV and NMR spectra and magnetic susceptibility. For comparative studies we have also prepared trimethyl platinum(IV) oxinate, the crystal structure of which has been previously reported<sup>6-7</sup>.

### EXPERIMENTAL

Analytical grade reagents were used throughout.

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### Preparation of the ligands

The ligands, which are represented as H-Sal=N-R, were prepared by refluxing salicylaldehyde with the equimolar amount of the appropriate amine. The oils obtained were purified by vacuum distillation at 25 mmHg; H-Sal=N-Et (b.p. 127°) is reddish while H-Sal=N-Pr (b.p. 140°) and H-Sal=N-t-Bu (b.p. 160°) are yellow.

H-Sal=N-Ph was prepared in ethanol and recrystallized from the same solvent as a yellow solid, m.p. 49°.

### Preparation and analysis of the complexes

Trimethylplatinum(IV) complexes, denoted Me<sub>3</sub>Pt-Sal=N-R, were obtained by mixing chloroform solutions of (CH<sub>3</sub>)<sub>3</sub>PtI<sup>8</sup> (3 mmoles in 500 ml) with equimolar amounts of thallium(I) ethoxide<sup>9</sup> and H-Sal=N-R. After 8 h of refluxing, yellow-brown TII separated from the solution. The cool solution was filtered and evaporated to dryness on a steam bath. The solid was extracted with 50 ml of benzene, and the resulting solution filtered and concentrated to small volume (5-10 ml); addition of petroleum ether then caused separation of the complexes Me<sub>3</sub>Pt-Sal=N-R. They were recrystallized from a benzene/petroleum ether mixture, filtered through a Hirsch funnel and pump-dried. Microanalytical determinations of Pt<sup>10</sup>, C, N, H and O were carried out. Some chemical and physical characteristics are as follows:

*Me<sub>3</sub>Pt-Sal=N-Et.* Dark yellow solid decomposing above 193°. (Found: C, 37.4; H, 5.03; N, 3.51; O, 4.26; Pt, 50.5. C<sub>12</sub>H<sub>18</sub>NOPt calcd.: C, 37.4; H, 4.93; N, 3.61; O, 4.12; Pt, 50.2%.)

*Me<sub>3</sub>Pt-Sal=N-Pr.* Mustard coloured solid, decomposing above 195°. (Found: C, 38.5; H, 5.15; N, 3.65; O, 3.78; Pt, 48.0. C<sub>13</sub>H<sub>20</sub>NOPt calcd.: C, 38.8; H, 5.26; N, 3.48; O, 3.98; Pt, 48.5%.)

*Me<sub>3</sub>Pt-Sal=N-Ph.* Yellow solid decomposing above 233°. (Found: C, 45.0; H, 4.37; N, 3.47; O, 3.96; Pt, 43.5. C<sub>16</sub>H<sub>18</sub>NOPt calcd.: C, 44.0; H, 4.38; N, 3.21; O, 3.66; Pt, 44.6%.)

An attempt to make the complex of trimethylplatinum(IV) with H-Sal=N-t-Bu under the same conditions was unsuccessful. Probably steric hindrance by the bulky substituent on nitrogen is among the factors contributing to this failure.

### Molecular weights

Because of low solubility of the Me<sub>3</sub>Pt-Sal=N-R compounds, molecular weights were measured at 25° in very dilute (10<sup>-3</sup> M) benzene solution, by a vapour pressure osmometer Mechrolab 301 A. They are: 807 ± 150 (Me<sub>3</sub>Pt-Sal=N-Et); 712 ± 80 (Me<sub>3</sub>Pt-Sal=N-Pr) and 861 ± 150 (Me<sub>3</sub>Pt-Sal=N-Ph).

### IR spectra

Vibrational spectra were taken on Nujol or hexachlorobutadiene mulls by a Perkin-Elmer 700 in the 4000-650 cm<sup>-1</sup> range and by a Perkin-Elmer 457 in the 650-250 cm<sup>-1</sup> range, using CsI plates. The instruments were calibrated with a polystyrene film.

### UV spectra

The electronic spectra of the ligands and complexes (Table 1 and Fig. 1) were measured in the 1000-200 nm range, at room temperature, in CCl<sub>4</sub> solution, using

TABLE 1

ELECTRONIC ABSORPTION SPECTRA OF H-Sal=N-R LIGANDS AND Me<sub>3</sub>Pt-Sal=N-R COMPLEXES

The wavelengths ( $\lambda$  (nm)) and absorptivities ( $\epsilon \times 10^3, l \cdot M^{-1} \cdot \text{cm}^{-1}$ ) refer to the band maxima.

Compounds	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$	$\lambda$	$\epsilon$
H-Sal=N-Et	259	2.79	263	3.77	320	2.23
Me <sub>3</sub> Pt-Sal=N-Et	259	10.6	265	10.9	357	5.23
H-Sal=N-Pr	260	8.50	263	9.59	316	5.24
Me <sub>3</sub> Pt-Sal=N-Pr	260	10.0	267	10.9	365	3.63
H-Sal=N-Ph	261	24.0	273	33.2	302	24.0
			316	26.3	345	29.3
Me <sub>3</sub> Pt-Sal=N-Ph	260	14.5	264	15.0	375	2.82
Oxine	257	7.47			316	2.61
Me <sub>3</sub> Pt oxinate	261	21.5			372	5.00

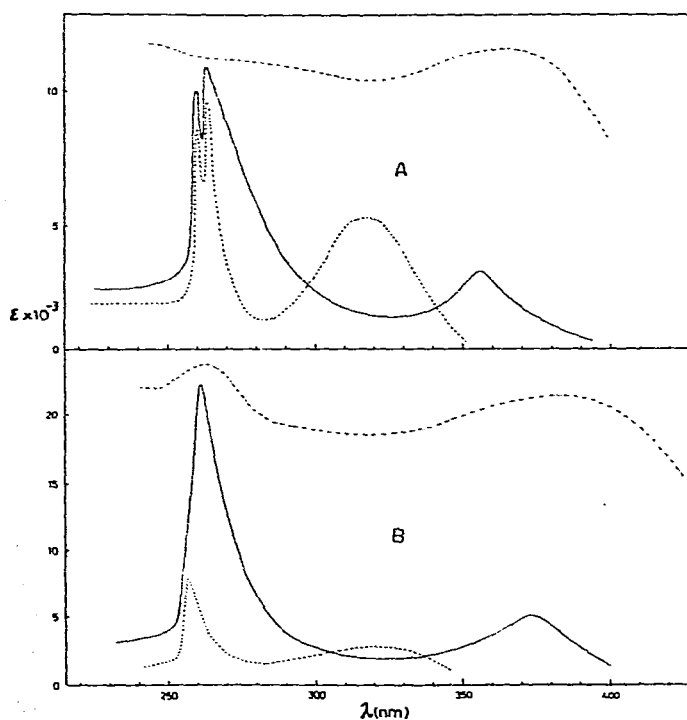


Fig. 1. A: Absorption spectra of H-Sal=N-Pr (-----), Me<sub>3</sub>Pt-Sal=N-Pr (—) and diffuse reflectance spectrum of Me<sub>3</sub>Pt-Sal=N-Pr (· · · · ·). B: Absorption spectra of oxine (-----), Me<sub>3</sub>Pt oxinate (—) and diffuse reflectance spectrum of Me<sub>3</sub>Pt oxinate. Both the reflectance spectra are on arbitrary scales.

a Beckman DK 2A spectrometer with 1 cm optical path silica cells. The complexes obey Beer's law at the studied wavelengths. The diffuse reflectance spectra of the complexes were measured with the same instrument equipped with a special attachment; MgO was used as reference.

*Magnetic susceptibility measurements*

The magnetic behaviour of the  $\text{Me}_3\text{Pt-Sal=N-R}$  complexes was investigated by the Gouy method using the previously described apparatus<sup>11</sup>. Two field intensities were used ( $H$  5000 and 8000 Oersted). Recrystallized saccharose was used for calibration<sup>12</sup>.

*NMR spectra*

NMR spectra were recorded at 25° with a Jeol C 60 spectrometer at 60 MHz on saturated  $\text{CDCl}_3$  or  $\text{CS}_2$  solutions of the complexes, with TMS as internal standard. The data are listed in Table 2.

TABLE 2

NMR SPECTRA OF  $\text{Me}_3\text{Pt-Sal=N-R}$  COMPLEXES IN THE  $\text{PtCH}_3$  RANGE

Compounds	Solvent	Number of peaks	$\tau(\text{CH}_3)$	$J(^{195}\text{Pt-CH})$ (Hz)
$\text{Me}_3\text{Pt-Sal=N-Et}$	$\text{CS}_2$	3	9.48	78.0
			9.55	76.5
			9.61	73.5
$\text{Me}_3\text{Pt-Sal=N-Pr}$	$\text{CS}_2$	3	9.49	
			9.56	
			9.64	
$\text{Me}_3\text{Pt-Sal=N-Ph}$	$\text{CDCl}_3$	3	8.79	
			9.13	
			9.51	
$\text{Me}_3\text{Pt oxinate}$	$\text{CDCl}_3$	3	8.40	70.5
			8.86	75.8
			9.51	80.0

## RESULTS AND DISCUSSION

The analytical data indicate that the  $\text{Me}_3\text{Pt-Sal=N-R}$  complexes are dimeric with a 1/1 trimethylplatinum(IV)/ligand ratio. The ligands are in the anionic form, as can be deduced from the analytical data, and from a comparison between the infrared spectra of the ligands and those of the corresponding complexes; in the latter the characteristic broad band ( $3200\text{--}2500\text{ cm}^{-1}$ ) of the OH stretching vibration disappears. The differences between the IR spectra of the complexes and those of the ligands in the  $2950\text{--}2800$ ,  $1400\text{--}1200$ ,  $650\text{--}250\text{ cm}^{-1}$  ranges are mainly due to the C-H stretch, to the platinum-bonded  $\text{CH}_3$  deformations and to the Pt-C<sup>13</sup>, Pt-O and Pt-N vibrations<sup>14</sup>.

The electronic absorbance spectra of the ligands and complexes (Table 1 and Fig. 1) show very similar systems of bands in the 280–250 nm range. These strong absorbance bands can be assigned to  $\pi^* \leftarrow \pi$  transitions of the ligands' aromatic system<sup>15</sup>, indicating that some structural features of the ligands are unchanged in the complexes. Another intense band in the 400–315 nm range is found for both the

ligands and complexes, shifted towards higher wavelengths in the latter. It is not easy to decide if in the complexes this is a charge transfer band<sup>16</sup> or attributable to the ligand, since it involved the bands at lower wavelengths. A band appearing in the 315–400 nm range in the spectra of many oxinates has been attributed to a bathochromic shift of the 315 nm band found in the free oxine, following the chelation of this ligand<sup>17–23</sup>. Similar effects are found for other ligands<sup>18</sup>. We can thus assume that the ligands in the  $\text{Me}_3\text{Pt-Sal=N-R}$  complexes in  $\text{CCl}_4$  act as chelating bidentate bases.

The diffuse reflectance spectra of the  $\text{Me}_3\text{Pt-Sal=N-R}$  complexes, measured in the 200–1000 nm range, are not resolved below 300 nm (*cf.* Fig. 1); this is quite usual with solid spectra<sup>24</sup>. However, the trimethylplatinum(IV) oxinate spectrum shows a band in this range. In the 300–400 nm range the resolution is satisfactory, and all the complexes show a band.

A comparison between the reflectance and absorbance spectra shows that, while in the case of the trimethylplatinum(IV) oxinate there is a complete identity, in the other cases this identity is restricted to the range above 300 nm, where the resolution of the spectra is sufficiently good. We can therefore infer that the same dimeric chelated species is present in solution and in the solid. The dimeric species could in principle, be formed through a Pt–Pt bond or Pt–O–Pt bridges. The magnetic susceptibility measurements allow us to discard the first hypothesis since the complexes are diamagnetic, while simple application of valence bond theory predicts that there would be unpaired electrons in the first case<sup>12</sup>. This diamagnetism suggests that, as with most platinum(IV) species, the new complexes are pseudo-octahedrally hexacoordinated<sup>25</sup>. Since the vibrational features of the  $(\text{CH}_3)_3\text{Pt}^{\text{IV}}$  moiety in these complexes are similar with those in the  $(\text{CH}_3)_3\text{PtX}$  compounds ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ )<sup>13</sup>, in which, as in the other trimethylplatinum(IV) compounds, the methyl groups are *cis*-positioned<sup>1</sup>, we suggest for the  $\text{Me}_3\text{Pt-Sal=N-R}$  complexes, the structure shown in Fig. 2.

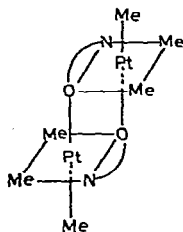


Fig. 2. Suggested structure for  $\text{Me}_3\text{Pt}^{\text{IV}}\text{-Sal=N-R}$  complexes.

Knowledge of the crystal structures of the trimethylplatinum(IV) salicylaldehyde and oxinate strengthens this conclusion. Both these ligands are in many respects similar to the  $\text{H-Sal=N-R}$  ligands used in this work, and their complexes with trimethylplatinum(IV) involve dimeric pseudo-octahedral species with Pt–O–Pt bridges<sup>6–7</sup>. As reported above, many properties of the trimethylplatinum(IV) oxinate are identical to those of our complexes. Confirmation of the suggested structure comes from the existence of a *trans* effect in the NMR spectra of the complexes<sup>26</sup>. In fact they generally exhibit three different signals for the platinum-bonded methyl groups (Table 2) and, in those cases in which the complexes are sufficiently soluble it is possible to measure three different  $^{195}\text{Pt-C-}^1\text{H}$  coupling constants. As previously

shown for the trimethylplatinum(IV) oxinate, this indicates the non-equivalence in solution of the Pt-O-Pt bonds which are equivalent in the solid state<sup>27</sup>. Thus, the salicylaldimines we have studied also give pseudo-octahedrally hexacoordinated complexes, involving dimerization of molecules which are formally pentacoordinated.

The electronic structure of Pt<sup>IV</sup>, the fact that Pt belongs to the third transition series with consequent expansion of the radial functions, and the ability of the ligands to accept electrons from the metal by back-donation, are among the factors favouring the validity of the noble gas rule<sup>28-29</sup>, which is obeyed in the complexes reported by us.

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