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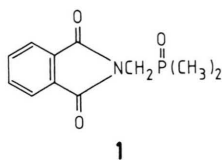
A Platinum(II) Complex with a Phosphine Oxide Adduct of Stannous Chloride

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A platinum(II) complex with an electroneutral adduct of stannous chloride $[\text{Pt}(\text{Sn}(\text{DPPO})\text{Cl}_2)_2\text{Cl}_2]$ (DPPO = dimethyl phthalimidomethylphosphine oxide) is synthesized and characterized by infrared and electronic spectra.

The SnCl_3^- ion is known to form complexes with platinum group metals in which coordination takes place through the lone electron pair on tin [1–13]. However, attempts to isolate such complexes with electroneutral stannous chloride adducts have been unsuccessful [3]. In a previous paper [14] we described a pyramidal complex $\text{Sn}(\text{DPPO})\text{Cl}_2$ (DPPO = dimethyl phthalimidomethylphosphine oxide (**1**)) in which the ligand is coordinated *via* the phosphoryl oxygen atom.



In the present communication the preparation and characterization of the platinum(II) complex of this electroneutral stannous chloride adduct are reported.

According to the elemental analysis, the formula $[\text{Pt}(\text{Sn}(\text{DPPO})\text{Cl}_2)_2\text{Cl}_2]$ was assigned to the new complex. The compound is an orange powder soluble in

methanol, ethanol, and nitromethane; in water it is hydrolyzed to an insoluble dark-brown product. The molar electric conductivity of the complex in nitromethane is $35.2 \Omega^{-1}\text{mol}^{-1}\text{cm}^2$, indicating its non-ionic character.

The most characteristic infrared frequencies of DPPO, $\text{Sn}(\text{DPPO})\text{Cl}_2$ and $[\text{Pt}(\text{Sn}(\text{DPPO})\text{Cl}_2)_2\text{Cl}_2]$ are presented in Table I. As a result of the coordination of the tin atom to the platinum, a lowering of the phosphoryl stretching frequency can be expected due to the shift of the electron density in the direction $\text{O} \rightarrow \text{Sn} \rightarrow \text{Pt}$. Such lowering of $\nu_{\text{P}=\text{O}}$ in the bimetallic complex as compared to the non-coordinated $\text{Sn}(\text{DPPO})\text{Cl}_2$ is indeed observed. Both the frequencies and intensities of $\text{Sn}-\text{Cl}$ stretching vibrations are known to increase upon coordination of SnCl_3^- to transition metals [5, 6]. Bands at 371.8 and 335 cm^{-1} due to $\nu_{\text{Sn}-\text{Cl}}$ and to $\nu_{\text{Pt}-\text{Cl}}$ at 315.5 and 302 cm^{-1} have been reported for $(\text{PhCH}_2\text{NET}_3)_2[\text{cis-Pt}(\text{SnCl}_3)_2\text{Cl}_2]$ [10]. On this basis we assign the very strong and complex band in the $360\text{--}280 \text{ cm}^{-1}$ region observed in the spectrum of $[\text{Pt}(\text{Sn}(\text{DPPO})\text{Cl}_2)_2\text{Cl}_2]$ to the $\text{Sn}-\text{Cl}$ and $\text{Pt}-\text{Cl}$ stretching vibrations. The exact assignment of these bands is complicated due to mutual overlapping with the low frequency bands of DPPO. Because of this, no conclusions regarding the configuration of the complex could be drawn. However, it appears likely that the new complex has a *cis*-configuration, since the *cis*-isomer of the ion $[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$ is known to be thermodynamically more stable [3, 10].

In the electronic absorption spectrum of $[\text{Pt}(\text{Sn}(\text{DPPO})\text{Cl}_2)_2\text{Cl}_2]$ (Table I) the bands due to the phthalimide chromophore (215, 238 and 300 nm) remain practically unchanged as compared to $\text{Sn}(\text{DPPO})\text{Cl}_2$ and DPPO. The additional broad band with its maximum at 279 nm is assignable to charge-transfer transitions taking into account its high extinction coefficient. A similar complex band in the range $250\text{--}470 \text{ nm}$ was also observed in the diffuse reflectance spectrum of the solid $[\text{Pt}(\text{Sn}(\text{DPPO})\text{Cl}_2)_2\text{Cl}_2]$.

Experimental

The molar electric conductivity (10^{-3} M solution) was determined with a Radiometer CDM 83 conductometer. The infrared spectra (nujol mulls) were recorded on a Specord M 80 spectrophotometer, the electronic spectra on a Perkin Elmer 330 apparatus. $\text{Sn}(\text{DPPO})\text{Cl}_2$ was prepared as described in [14].

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Table I. Infrared and electronic spectral data for the compounds.

Compound	Infrared frequencies, cm^{-1}						Electronic spectra ^a λ , nm (ϵ , $1 \text{ mol}^{-1} \text{cm}^{-1} \cdot 10^3$)
	$\nu_{\text{C=O}}$	$\nu_{\text{P=O}}$	$\nu_{\text{Sn-O}}$	$\delta_{\text{P=O}}$	$\nu_{\text{Sn-Cl}}$	$\nu_{\text{Pt-Cl}}$	
DPPO	1774 m 1711 s	1178 s	—	396 m 357 m	—	—	220 (36.9), 240 (9.00) sh, 295 (1.70)
Sn(DPPO)Cl ₂	1768 m 1708 s	1110 s	412 s	400 s	270 s 238 s	—	218 (35.2), 239 (8.50) sh, 296 (1.68)
[Pt(Sn(DPPO)Cl ₂) ₂ Cl ₂]	1776 m 1722 s	1090 s	395 w	387 w	360–280 vs, br		215 (57.4), 238 (24.8) sh, 279 (10.8), 300 (8.66) sh, 346 (3.60) sh, 407 (1.12) sh

^a In methanol.

Bis(benzyltriethylammonium) tetrachloroplatinate,
(PhCH₂NEt₃)₂PtCl₄

Methanol-soluble (PhCH₂NEt₃)₂PtCl₄ was used as a starting platinum reagent for preparing the bimetallic complex. The reagent was obtained as follows: K₂PtCl₄ (1.00 g, 2.41 mmol) and (PhCH₂NEt₃)Cl (1.10 g, 4.82 mmol) are dissolved in 30 ml of hot dimethylformamide. The resulting KCl is filtered off and the filtrate is cooled to 0 °C to give 1.24 g (71%) of beige orange crystals, m.p. 202–204 °C (uncorr.).

C₂₆H₄₄Cl₄N₂Pt (721.55)

Calcd C 43.28 H 6.15 N 3.88 Pt 27.04,
Found C 42.68 H 5.99 N 4.15 Pt 27.66.

Dichloro-bis{dichloro[O-(dimethyl-phthalimidomethyl)phosphineoxide]tin(II)}-platinum(II), [Pt(Sn(DPPO)Cl₂)₂Cl₂]

Solutions of Sn(DPPO)Cl₂ (1.00 g, 2.34 mmol in 45 ml of methanol) and of (PhCH₂NEt₃)₂PtCl₄ (0.34 g, 0.47 mmol in 4 ml of the same solvent) cooled to 15 °C are mixed and allowed to stand at 0 °C for 6 h. The orange precipitate is then filtered, washed with methanol and dried *in vacuo*. Yield 0.38 g (72%), m.p. 240–243 °C (uncorr.).

C₂₂H₂₄Cl₆N₂O₆P₂PtSn₂ (1119.57)

Calcd C 23.60 H 2.16 Cl 19.00 N 2.50,
Found C 23.14 H 2.71 Cl 19.31 N 2.59.

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