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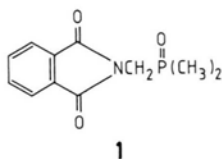
A Platinum(II) Complex with a Phosphine Oxide Adduct of Stannous Chloride

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A platinum(II) complex with an electroneutral adduct of stannous chloride [Pt(Sn(DPPO)Cl₂)₂Cl₂] (DPPO = dimethyl phthalimidomethylphosphine oxide) is synthesized and characterized by infrared and electronic spectra.

The SnCl₃⁻ 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 Sn(DPPO)Cl₂ (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 [Pt(Sn(DPPO)Cl₂)₂Cl₂] 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 Ω⁻¹mol⁻¹cm², indicating its non-ionic character.

The most characteristic infrared frequencies of DPPO, Sn(DPPO)Cl₂ and [Pt(Sn(DPPO)Cl₂)₂Cl₂] 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 O → Sn → Pt. Such lowering of ν_{P=O} in the bimetallic complex as compared to the non-coordinated Sn(DPPO)Cl₂ is indeed observed. Both the frequencies and intensities of Sn–Cl stretching vibrations are known to increase upon coordination of SnCl₃⁻ to transition metals [5, 6]. Bands at 371.8 and 335 cm⁻¹ due to ν_{Sn–Cl} and to ν_{Pt–Cl} at 315.5 and 302 cm⁻¹ have been reported for (PhCH₂NEt₃)₂[*cis*-Pt(SnCl₃)₂Cl₂] [10]. On this basis we assign the very strong and complex band in the 360–280 cm⁻¹ region observed in the spectrum of [Pt(Sn(DPPO)Cl₂)₂Cl₂] to the Sn–Cl and Pt–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 [Pt(SnCl₃)₂Cl₂]²⁻ is known to be thermodynamically more stable [3, 10].

In the electronic absorption spectrum of [Pt(Sn(DPPO)Cl₂)₂Cl₂] (Table I) the bands due to the phthalimide chromophore (215, 238 and 300 nm) remain practically unchanged as compared to Sn(DPPO)Cl₂ 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 250–470 nm was also observed in the diffuse reflectance spectrum of the solid [Pt(Sn(DPPO)Cl₂)₂Cl₂].

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. Sn(DPPO)Cl₂ 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 , $1 \text{ mol}^{-1} \text{cm}^{-1} \cdot 10^3$)
	$\nu_{\text{C}=\text{O}}$	$\nu_{\text{P}=\text{O}}$	$\nu_{\text{Sn}-\text{O}}$	$\delta_{\text{P}=\text{O}}$	$\nu_{\text{Sn}-\text{Cl}}$	$\nu_{\text{Pt}-\text{Cl}}$	
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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