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The Unexpected Formation of the Peroxodisulphato Derivative $[Pt_2(OH)_2(PPh_3)_4][S_2O_8]$ from $Pt(PPh_3)_2(SO_4)$

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It is known that the platinum peroxo complex, $Pt(PPh_3)_2O_2$, reacts with heterocumulenes such as N-sulphinylaniline, ArNSO, leading to the sulphato derivative, $Pt(PPh_3)_2(SO_4)$ [1, 2]. The same compound can be obtained when the reaction is carried out in the presence of oxygen or free triphenylphosphine. However, when both these reagents are present, an entirely different reaction path is observed. $Pt(PPh_3)_2(SO_4)$ is still the first product of the reaction, but it undergoes further reaction with the excess ArNSO (Ar = Ph, p-MeC_6H_4), O_2 and PPh_3, giving the final product (A) (eq. 1):

$$2\,Pt(PPh_3)_2(SO_4) \xrightarrow[\text{wet benzene}]{ArNSO/O_2/PPh_3} \underset{(A)}{[Pt_2(OH)_2(PPh_3)_4][S_2O_8]} \quad (1)$$

$$2\,ArNH_2\cdot H_2SO_4 + n\,O{=}PPh_3$$

The formation of compound (A) and of $ArNH_2\cdot H_2SO_4$ is practically quantitative, according to eq. 1.

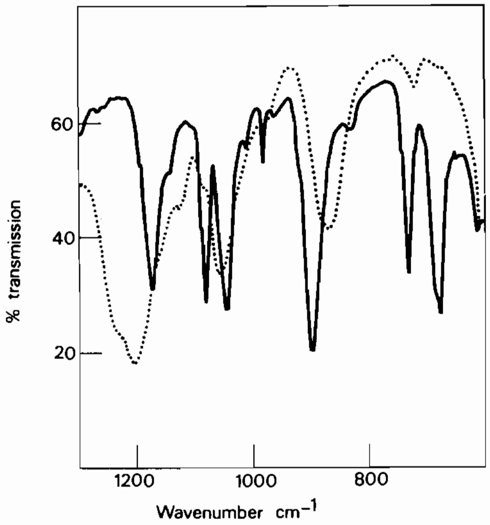
Since N-sulphinylamines are sensitive to moisture giving SO_2 and the corresponding amine, particularly in the presence of transition metal complexes as we observed many times, independent reactions of $Pt(PPh_3)_2(SO_4)$ with O_2, SO_2 and PPh_3 or O_2, $ArNH_2$ and PPh_3 have been carried out. However, no reaction was observed, and thus only the complex association of reagents reported in eq. 1 is able to lead to the ionic peroxodisulphato derivative $[Pt_2(OH)_2(PPh_3)_4][S_2O_8]$ (A).

The nature of this compound was recognised by its elemental analysis (in particular oxygen and sulphur analyses) and by comparing its i.r. spectrum (see Fig. 1) and chemical reactivity with those of an authentic sample prepared according to eq. 2:

$$[Pt_2(OH)_2(PPh_3)_4][BF_4]_2 \underset{\text{excess } NaBF_4}{\overset{\text{excess } (NH_4)_2S_2O_8}{\rightleftharpoons}} \underset{(A)}{[Pt_2(OH)_2(PPh_3)_4][S_2O_8]} + 2\,(NH_4)BF_4 \quad (2)$$

Compound (A) shows i.r. bands in the 900–1200 cm^{-1} region comparable with those of the $S_2O_8^=$ ion (see Fig. 1). Unlike from the tetrafluoroborate derivative [3], compound (A) is a hygroscopic material, unstable in polar solvents such as acetone or ethyl alcohol, in which it readily transforms back into the sulphato complex, $Pt(PPh_3)_2(SO_4)$. This parallels the well known behaviour of the $S_2O_8^=$ ion. The presence of a variable amount of water in compound (A) did not allow to detect the absorption associated with the bridging OH groups in the i.r. spectrum [3]. However, this band was clearly observed at 3550 cm^{-1} when the anion exchange reaction of eq. 2 on the complex prepared according to eq. 1 was carried out. In the mother liquor of this exchange reaction, the usual analytical reactions in order to identify the $S_2O_8^=$ anion were carried out. Moreover, the presence of an ion having oxidising power was proved by reacting compound (A) with acids such as HX (X = Cl, I), *i.e.* having reducing anions. In both cases H_2S evolution was observed, while the metal was recovered as $Pt(PPh_3)_2X_2$; when the same reactions were carried out on $Pt(PPh_3)_2(SO_4)$, $Pt(PPh_3)_2X_2$ were again obtained but no H_2S was detected among the products.

The reaction here reported is rather complex, and no reasonable hypothesis can be proposed about its mechanism. In any case it corresponds to the oxidation of the sulphur atom of ArNSO to sulphur(VI), while it is not clear whether the $S_2O_8^=$ ion originates from ArNSO or from the SO_4 group of the starting complex. However, the observed oxidation is remarkable reaction, which as far as we know has never



IR spectrum of (——) $[Pt_2(OH)_2(PPh_3)_4][S_2O_8]$ and (……) of $(NH_4)_2S_2O_8$

Figure.

been reported to occur under so mild conditions. Moreover, compound (A) appears to be the first example of a complex cation having the S_2O_8 group as the anion. We are currently studying the same reaction on $Pd(PPh_3)_2(SO_4)$; preliminary results indicate the formation of a different type of product which is still under investigation.

Experimental

$[Pt_2(OH)_2(PPh_3)_4][S_2O_8]$ (A)

(i) To a benzene suspension (20 ml) of $Pt(PPh_3)_2O_2$ (0.234 g), *p*-MeC_6H_4NSO (0.355 g) and PPh_3 (0.161 g) were added. The mixture was stirred for 4 h while oxygen was slowly bubbled through. The white insoluble material, after filtration, was treated with $CHCl_3$ and *p*-$MeC_6H_4NH_2 \cdot H_2SO_4$ (0.034 g) was recovered as the chloroform insoluble product. It was identified by comparing its i.r. spectrum with that of an authentic sample.

The $CHCl_3$ solution was evaporated to dryness and the residue treated with n-hexane giving compound (A) (0.239 g, 92% yield). *Anal*: Found, C, 51.12; H, 3.6; O, 10.76; S, 3.73. Calcd., C, 52.0; H, 3.73; O, 9.62; S, 3.85. M.p. (°C), 160 (dec). The high value found for oxygen is due to the marked hygroscopic properties of (A); owing to this fact, anhydrous solvents must be used.

When an acetone suspension of (A) was stirred for 2 h, $Pt(PPh_3)_2(SO_4)$ was recovered as the only reaction product.

(ii) Compound (A) could also be obtained by using $Pt(PPh_3)_2(SO_4)$ as the starting material instead of $Pt(PPh_3)_2O_2$.

(iii) To a CH_2Cl_2 solution (30 ml) of $[Pt_2(OH)_2(PPh_3)_4][BF_4]_2$ (0.1 g), prepared as described in ref. 3b, excess $(NH_4)_2S_2O_8$ was added. The mixture was stirred for 48 h and then filtered; the mother liquor was evaporated to dryness and the residue treated with diethyl ether, filtered off and dried *in vacuo.*

Exchange Reaction between (A) and $NaBF_4$

This reaction has been carried out as described under (iii), by using $CHCl_3$ as solvent. The chloroform solution was evaporated to dryness and the residue was identified as $[Pt_2(OH)_2(PPh_3)_4][BF_4]_2$ by its i.r. spectrum and elemental analysis [3b]. Moreover, its ^1H n.m.r. spectrum showed the expected signal at 7.9τ due to the bridging OH groups. This signal could not be clearly detected in compound (A) owing to the presence of traces of water.

On the $CHCl_3$ insoluble material of this exchange reaction, the usual analytical tests for the $S_2O_8^=$ ion were carried out, giving in any case positive results.

Reactions of (A) with HX (X = Cl, I)

To an aqueous suspension of (A) few drops of aqueous HX were added. After 30 min a white (X = Cl) or yellow (X = I) precipitate was filtered off. They were identified as $Pt(PPh_3)_2X_2$. H_2S was recognised as the evolved gas by the usual analytical reactions.

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