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X-ray Molecular Structure of $(PPh_3)_2Pt(OSNH)_2$ *Cis* bis(thionylimide-O)bis(triphenylphosphine)platinum(II)

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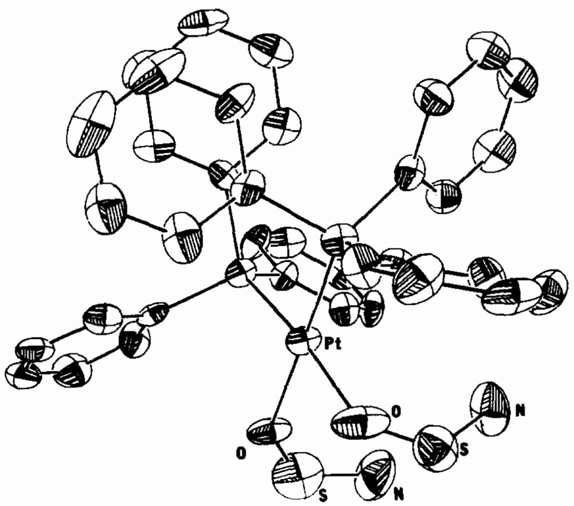

Fig. 1. Structure of *cis* bis(thionyl imide-O)bis(triphenylphosphine)platinum(II).

We recently reported the synthesis of several new coordination compounds of platinum(0) and platinum(II), wherein the ligating groups consisted of various binary sulfur–nitrogen ligands and triphenyl phosphine [1]. One of these was reported to be (disulfurdiimide)bis(triphenylphosphine)platinum(II), $(Ph_3P)_2PtS_2N_2H_2$, which was prepared [1] by the reaction of tetrasulfur tetraimide and tetrakis(triphenylphosphine)platinum(0). An elemental analysis for Pt, C, H, N and S reflected a slight deficiency of C, H, N and S, and accounted for only 88.50 percent of the compound. Analyses were not reported for phosphorus and oxygen. We have now completed an X-ray diffraction study of the same material and found it to in fact be *cis* bis(thionylimide-O)bis(triphenylphosphine)platinum, $(Ph_3P)_2Pt(OSNH)_2$. The new analysis based upon the formula $C_{36}H_{32}P_2S_2N_2O_2Pt\cdot 0.5H_2O$ is: Calcd. C, 50.56; H, 3.87; S, 7.50; N, 3.27; Pt, 22.85; P, 7.25; O, 4.68. Found: C, 51.06; H, 3.48; S, 7.05; N, 2.78; Pt, 24.14; P, 6.71; O, 4.79 (by difference). The structure is illustrated in Fig. 1. It contains platinum(II) in a square planar environment with the ligands in a *cis* arrangement. The two platinum–oxygen distances are 2.088(12) and 2.173(11) Å. The O–S–N–H ligands have sulfur nitrogen distances of 1.452(19) and 1.485(19) Å, respectively. Both of these distances are considerably smaller than that found in S_4N_4 (1.62 Å) [2], S_2N_2 (1.65 Å) [3], or $S_4N_4H_4$ (1.67 Å) [4]. Sulfur–nitrogen bond lengths of 1.485–1.550 Å were observed in the $R_2As_2S_2N_4$ systems [5] (R = phenyl or mesityl); 1.453 Å in $S_5N_5^+AlCl_4^-$ [6], and 1.493 Å in $S_4N_3^+$-NO_3^- [7]. These may be compared with the S–N triple bond distance of 1.45 as it occurs in NSF [8]. A sulfur–oxygen distance of 1.341(17) Å occurs between the sulfur atom and the oxygen atom bonded to the metal in one ligand and a distance of 1.258(11) Å occurs in the other. The S–O bond distance in S–O is about 1.49 while distances around 1.43–1.45 Å occur in sulfur dioxide, sulfur trioxide and the sulfate ion [9]. Shorter S–O distances of 1.22–1.41 Å have been reported in 2-O-(*p*-bromobenzenesulfonyl)-1,4-3,6-dianhydro-D-glucitol-5-nitrate [10] and 1.34–1.39 Å in tosyl-1-propyl-1-hydroxyproline monohydrate [11]. The O–S–N angle is 122 degrees in each ligand. The simple O–S–N–H ligand is presently not known to occur in any previously reported metal complex. The ligand can probably be most simply viewed as $:\underset{\cdot\cdot}{\ddot{O}}-\ddot{S}\equiv N-H$. Such a structure should have a very short S–N distance and bond angle at the sulfur atom in the vicinity of 120 degrees. The X-ray study was unable to locate the position of the hydrogen nuclei and their presence at the terminus of the O–S–N chain is assumed. The infrared spectrum of the material shows absorption peaks at 3050, 3075 and 3150 cm^{-1}, any of which might be indicative of a N–H bond.

The molecule crystallizes in triclinic space group $P\bar{1}$ with unit cell dimensions of a = 10.082(3), b = 10.258(3), c = 17.812(6) Å, α = 86.05(3), β = 81.02(3), γ = 72.45(3). The unit cell contains two molecules. Diffractometer data (3630 independent observations) has been refined by least squares procedure to a final R of 4.8% with anisotropic thermal parameters and corrections for anomalous dispersion and absorption.

TABLE I. IR Spectrum of *Cis*-bis(thionyl imide-O)bis(triphenylphosphine)platinum(II). Absorption maxima[a] in cm^{-1}.

3150 (br)	2330 (w)	1410 (w)	1050	750 (m)
3075 (vw)	1660 (w)	1360 (m)	1030 (w)	690 (s)
3050 (m)	1585 (w)	1350 (vw)	1000 (m)	612 (w)
2925 (w)	1575 (w)	1175 (w)	925 (w)	545 (s)
2850 (w)	1480 (m)	1160 (w)	825 (vw)	525 (s)
2360 (w)	1435 (s)	1100 (s)	850 (vw)	515 (m)
500 (w)				
465 (w)				
445 (w)				
422 (w)				
280 (w)				

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak and br, broad.

The compound is yellow colored, has a melting point of 220 °C and the ultraviolet spectrum shows absorption maxima at 470 nm, 365 nm and 325 nm with a shoulder at 405 nm, typical of square planar d^8 configurations, *e.g.* $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$.

The mass spectrum of the material shows a peak at m/e = 63 in accord with the presence of a O–S–N–H fragment, a peak at 48 (S–O fragment), and a peak at 47 (S–N–H fragment). The compound decomposes in the ion source and we were unable to record a parent peak or Pt–O fragment.

The infrared spectrum of this compound is presented in Table I. In addition to all the characteristic bands due to triphenylphosphine, other main absorption bands occur at 925 cm^{-1} due to ν_{NS} [12], 545 cm^{-1} and 525 cm^{-1} due to ν_{PtO} [12] and 445 cm^{-1} and 422 cm^{-1} due to ν_{PtP} [12].

The spectrum reflects the presence of N–H bands at 3150 cm^{-1} and 1660 cm^{-1}. The structural element S=O is known to absorb at 1018 in the tetramer $(OSNH)_4$ [13] while this material shows a peak at 1030 cm^{-1}.

It is somewhat surprising that the thionyl imide ligand is present in this material. The compound was prepared by mixing a solution of tetrasulfur tetraimide in acetone with a solution of tetrakis(triphenylphosphine)platinum(0) in benzene. E. Fluck and M. Beche Goehring have reported that acetone solutions of thionyl imide tetramer polymerize upon warming above –20 °C [13, 14]. The thionyl imide itself is readily made from the gas phase reaction of $SO{\cdot}Cl_2$ and NH_3 but reports of its synthesis by air oxidation of $S_4N_4H_4$ cannot be found. Nevertheless, such an oxidation must occur in this case. Since the complex was isolated 94% yield it is unquestionably the major product of the reaction. It is possible that tetrakis(triphenylphosphine)platinum(0) is catalyzing the oxidation.

In the absence of a definite location for each hydrogen atom it is difficult to distinguish whether this is a compound of platinum(II) or platinum(0). The visible spectrum is consistent with that of a square planar complex of platinum(II).

Finally, the compound should exist in the form of *cis* and *trans* isomers. Work is continuing in an attempt to produce the *trans* form. A full report of the X-ray study will be published later [15].

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