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Synthesis and Characterization of $Pt(OSNH)_2(S_2N_2H_2)$, (disulfur diimide)bis(thionyl imide-*O*)platinum(II)

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We recently reported the synthesis and X-ray crystal and molecular structure of the first thionyl imide metal complex, *cis*-bis(thionyl imide-*O*)bis(triphenylphosphine)platinum(II), *cis*-$Pt(PPh_3)_2(OSNH)_2$ [1]. The compound was prepared by the reaction of tetrakis(triphenylphosphine)platinum(0), $Pt(PPh_3)_4$, with tetrasulfur tetraimide, $S_4N_4H_4$, in acetone at room temperature. We now report another thionyl imide complex, (disulfur diimide)bis(thionyl imide-*O*)platinum(II), $Pt(OSNH)_2(S_2N_2H_2)$, which is prepared by the reaction of an aqueous solution of potassium tetrachloroplatinate(II), K_2PtCl_4, with $S_4N_4H_4$ in acetone.

Experimental

K_2PtCl_4 was prepared from metallic platinum [2] $S_4N_4H_4$ was prepared by the reduction of tetrasulfur tetranitride, S_4N_4, with $SnCl_2 \cdot 2H_2O$ [3]. S_4N_4 was prepared by using a literature method [4]. The absorption spectra in DMF at ambient temperature were measured using a Cary Model 14 Spectrophotometer. The IR spectra were obtained using a Perkin-Elmer Model 457 Spectrophotometer and the NMR spectra were recorded using a Varian T 60 Spectrometer.

The procedure for the preparation of $Pt(OSNH)_2(S_2N_2H_2)$ is as follows:

An aqueous solution of K_2PtCl_4 (0.41 g, 1.0 mmol) was slowly added to a suspension of $S_4N_4H_4$ (0.20 g, 1.1 mmol) in acetone (10 ml) while stirring. Within five min. the product was precipitated as a red-brown solid. The mixture was cooled in a refrigerator and filtered, washed thoroughly first with water and then with acetone and dried under vacuum over $CaCl_2$. Yield 0.39 g (95% based on K_2PtCl_4), Mp 133–141 °C (dec.). *Anal.* Calcd for $H_4N_4O_2S_4Pt$: S, 30.87; N, 13.49, H, 0.96. Found: S, 31.08; N, 13.28; H, 1.04%.

Results and Discussion

The absorption spectrum of $Pt(OSNH)_2(S_2N_2H_2)$ in DMF shows three absorption bands at 450 nm (ϵ = 939.0 M^{-1} cm^{-1}), 310 nm (ϵ = 3883.5 M^{-1} cm^{-1}), and 300 nm (ϵ = 3982.9 M^{-1} cm^{-1}) possibly due to electronic transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$, and $^1A_{1g} \rightarrow {}^1E_g$, respectively. These three transitions are typical of square-planar d^8 configurations [2].

TABLE I. IR Spectrum of (disulfur diimide)bis(thionyl imide-*O*)platinum(II) in KBr Phase. Absorption Maxima[a] in cm^{-1}.

3300 (br)	420 (m)
1040 (m)	402 (w)
900 (m)	390 (m)
870 (s)	382 (w)
590 (m, br)	370 (m)
510 (w)	360 (vw)
470 (w)	

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

The infrared spectrum of the compound is shown in Table I below. The ν_{N-H} appears [2] at 3300 cm^{-1}. The S = O stretch occurs [5] at 1040 cm^{-1}, indicating the presence of thionyl imide group (OSNH). The previously reported thionyl imide complex, $Pt(PPh_3)_2(OSNH)_2$, also had an absorption in that region [1]. Binary sulfur-nitrogen compounds are known to absorb [6] in the region 900–500 cm^{-1}; while this compound shows absorption bands at 900, 870, 590, and 510 cm^{-1}. The OSNH group is known to coordinate to Pt(II) by the oxygen atom as observed in *cis*-$Pt(PPh_3)_2(OSNH)_2$. A band at 420 cm^{-1} may be assigned to ν_{Pt-O} [7]. In addition to the Pt–O stretch, this material exhibits a band at 360 cm^{-1} indicating Pt–S bonding [8]. The ν_{Pt-N} is also observed [2] at 470 cm^{-1}. The presence of both ν_{Pt-S} and ν_{Pt-N} in this complex indicate that the disulfur diimide ligand is coordinated to the metal by both sulfur and nitrogen atoms (-S-NH-S-NH-).

The proton NMR spectrum of $Pt(OSNH)_2(S_2N_2H_2)$ indicates two singlets at 3.45 ppm and 0.75 ppm with intensity ratio of 1:1. This compound has two thionyl imide protons and two disulfur diimide protons. Since the O = S = NH protons may be more shielded than the -S-NH-S-NH- protons, the peaks at δ 3.45 (S, 1H) and δ 0.75 (S, 1H) may be assigned to the disulfur diimide and thionyl imide protons, respectively.

The ligand $S_2N_2H_2^{2-}$ may have been resulted due to simple fragmentation of the $S_4N_4H_4$ ring. The presence of OSNH is not surprising in this complex.

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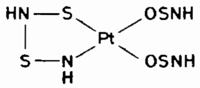
Acetone solutions of $S_4N_4H_4$ are known to introduce the OSNH group in the other platinum(II) complex, $Pt(PPh_3)_2(OSNH)_2$. A proposed structure is shown below:



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