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Some Novel Platinum Complexes Containing Binary Sulfur–Nitrogen Ligands

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A few complexes of platinum are known which involve platinum(0) or platinum(II) bonded directly to a ligand containing only sulfur and nitrogen atoms, which in turn has been derived from a cyclic sulfur nitride. Fluck, Goehring and Weiss reported a compound having the formula $Pt(NS)_4$ [1]. In 1958 Weiss and Goehring [2] determined the correct formula to be $Pt(S_2N_2H)_2$ in analogy to the work of Piper on the corresponding nickel complex [3]. At the same time the structure was established by X-ray diffraction [4, 5]. The compound was synthesized by direct reaction of platinum(II) chloride with tetrasulfur tetranitride in a relatively nonpolar solvent (benzene) or methanol. A compound of the formula $Pd(S_2N_2H)(S_3N)$ results from the reaction of palladium(II) chloride with S_4N_4 in methanol [6], but the analogous platinum compounds have not been reported.

Starting with tetrakis(triphenylphosphine)platinum(0) and tetrasulfur tetranitride or tetrasulfur tetraimide we have synthesized (tetrasulfur tetranitride)bis(triphenylphosphine)platinum(0), $(Ph_3P)_2$-PtS_4N_4; (disulfur dinitride)bis(triphenylphosphine)-platinum(II), $(Ph_3P)_2Pt(N_2S_2)$, and (disulfur diimide)bis(triphenylphosphine)platinum(II), $(Ph_3P)_2$-$PtS_2N_2H_2$. Analogous complexes containing the triphenyl phosphite ligand are reported for the cases of complexes containing disulfur dinitride and tetrasulfur tetranitride.

Experimental

Potassium tetrachloroplatinate(II) was prepared from metallic platinum [7]. Tetrakis(triphenylphosphine)platinum(0) was prepared by the reaction of potassium tetrachloroplatinate(II) in water with triphenylphosphine in methanolic potassium hydroxide [8]. Tetrakis(triphenylphosphite)platinum(0) was prepared from tetrakis(triphenylphosphine)platinum-(0) by a ligand substitution reaction with triphenylphosphite [8].

Tetrasulfur tetranitride [9] and tetrasulfur tetraimide [10] were prepared by standard methods. Electronic spectra were recorded using a Cary-14 recording spectrophotometer. In most cases the solvent used was acetone. All materials used were of reagent grade.

Preparation of (Tetrasulfur tetranitride)bis(triphenylphosphine)platinum(0)

Tetrasulfur tetranitride (0.062 g, 0.32 mmol) was added to a stirred benzene solution of 0.4 g (0.33 mmol) of tetrakis(triphenylphosphine)platinum(0). The solution turned green and a green precipitate was obtained by adding hexane. The precipitate was filtered, washed with hexane and dried in vacuum. Yield 0.26 g (89%), mp 115 C. *Anal.* Calcd for $C_{36}H_{30}P_2S_4N_4Pt$: C, 47.73; H, 3.31; S, 14.14; N, 6.19; Pt, 21.56. Found: C, 47.93; H, 3.29; S, 14.42; N, 3.70, Pt, 21.79%.

Preparation of (Disulfurdinitride)bis(triphenylphosphine)platinum(II)

Tetrakis(triphenylphosphine)platinum(0) in benzene (0.48 g, 0.39 mmol) was mixed with tetrasulfur tetranitride (0.671 g, 0.39 mmol). A green solution was obtained, which on stirring for 10 minutes turned brown. Upon cooling below room temperature brown crystals were formed. Recrystallization of the crude product was carried out by the addition of hexane to the benzene solution of the existing crude product. The brown compound was filtered, washed with hexane and dried in vacuum. Yield 0.23 g (73%), mp 160 °C. *Anal.* Calcd for $C_{36}H_{30}P_2S_2N_2Pt$: C, 53.26; H, 3.70; N, 3.45; S, 7.89; Pt, 24.05. Found: C, 51.74; H, 4.00; N, 2.87; S, 7.66; Pt, 24.44%.

Preparation of (Disulfur diimide)bis(triphenylphosphine)platinum(II)

A solution of 0.7 g (0.58 mmol) of tetrakis(triphenylphosphine)platinum(0) dissolved in a minimum amount of benzene was mixed with 0.106 g (0.54 mmol) of tetrasulfur tetraimide dissolved in a minimum amount of acetone. The mixture was stirred for one hour and upon addition of hexane formed a yellow precipitate. The precipitate was recrystallized by the addition of hexane to an acetone solution of the crude product, filtered, washed with hexane and dried in vacuum. Yield: 0.43 g (94%), mp 220 °C. *Anal.* Calcd for $C_{36}H_{32}P_2S_2N_2Pt$: C, 53.14; H, 3.94; S, 7.87; N, 3.34, Pt, 24.0. Found: C, 51.06; H, 3.48; S, 7.05; N, 2.78; Pt, 24.13%.

Preparation of (Tetrasulfur tetranitride)bis(triphenylphosphite)platinum(0)

A benzene solution of 0.143 g (0.10 mmol) of tetrakis(triphenylphosphite)platinum(0) was added

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TABLE I. Physical Properties.

Compound	Color	Melting Point	UV–Visible Max.
K_2PtCl_4	red-brown		485 nm; 390 nm; 325 nm
$(Ph_3P)_2PtS_2N_2$	brown	160 °C	405 nm; 365 nm; 325 nm
$(Ph_3P)_2PtS_2N_2H_2$	yellow	220 °C	470 nm; 405 nm; 365 nm; 325 nm
$[(PhO)_3P]_2PtS_2N_2$	brown	130 °C	355 nm; 315 nm; 355 nm
$(Ph_3P)_4Pt$	yellow	118 °C	325 nm
$(Ph_3P)_2PtS_4N_4$	green	115 °C	325 nm
$[(PhO)_3P]_4Pt$	white	145 °C	355 nm; 325 nm
$[(PhO)_3P]_2PtS_4N_4$	green-black	78 °C	355 nm; 325 nm

to a benzene solution of 0.0185 g (0.10 mmol) of tetrasulfur tetranitride. A green violet solution formed. Addition of hexane caused a greenish black precipitate to form. It was filtered, washed with hexane and dried in vacuum. Yield: 0.086 g (87%), mp 78 °C. *Anal.* Calcd for $C_{36}H_{30}P_2O_2S_4N_4Pt$: C, 43.16; H, 3.00; N, 5.59; S, 12.76. Found: C, 43.35; H, 3.36; N, 5.23; S, 12.61%.

Preparation of (Disulfur dinitride)bis(triphenylphosphite)platinum(II)

A saturated benzene solution containing 0.09 g (0.1 mmol) tetrasulfur tetranitride was added to a saturated benzene solution of 0.13 g (0.5 mmol) of tetrakis(triphenylphosphite)platinum(0). The solution turned greenish violet. After 10 min of stirring the color changed to brown. Hexane was added. On cooling a brown solid was obtained (0.062 g). The compound was recrystallized by the addition of hexane to the benzene solution of the crude product. Yield: 0.062 g (76%), mp 130 °C. *Anal.* Calcd for $C_{36}H_{30}P_2O_2S_2N_2Pt$: C, 47.52; H, 3.30; N, 3.08; S, 7.04. Found: C, 50.61; H, 3.35; N, 1.78; S, 5.33%.

Results and Discussion

The physical and spectral properties of these compounds are summarized in Table I. The compounds which contain the disulfur dinitride or disulfur diimide ligands appear to be complexes of square planar coordinated platinum(II). The ultra violet spectra show three absorbtion maxima typical of configuration d^8; *e.g.* $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_g$. X-ray studies are in progress to confirm these structures. The tetrasulfur tetranitride bis(triphenylphosphine) complex may represent a four coordinate complex of platinum(0). The spectrum resembles that of the known platinum(0) complex, $Pt(Ph_3P)_4$, exhibiting a single maximum at 325 nm. Tetrakis(triphenylphosphine)platinum(0) also has a single maximum at 325 nm. It is most likely a d^{10} complex of tetrahedral geometry with S_4N_4 occupying two of the four apices.

The bonding can be developed via interaction between the 6p orbitals of platinum [12] with the unshared electron pairs of the nitrogen or sulfur atoms of tetrasulfur tetranitride or interaction of metal 6p orbitals with the π electron system of S_4N_4. Since sulfur is a "soft" base and platinum(0) is a "soft" acid, HSAB theory [11] favors coordination via sulfur. The absence of detailed structural information negates further speculation, but it is possible that (tetrasulfur tetranitride)bis(triphenylphosphine)platinum(0) may possibly involve a heretofore unknown type of coordination between S_4N_4 and a platinum group element. X-ray diffraction studies are in progress, which when completed, will greatly facilitate an analysis of the electronic structure of the complex.

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