# $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ as a Metalloligand toward Main-Group Lewis Acids. Crystal Structures of Two Complex Adducts of Lead Nitrate, $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)_2]$ and $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)]PF_6$

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*Received February 25, 1993*

## Introduction

The Lewis acidity of $Pt_2(\mu\text{-}S)_2(PPh_3)_4$ is exemplified in its coordination to various transition metal fragments to give heterometallic aggregates of different nuclearities.[1] We have recently shown that its coordination to $Tl(NO_3)$ gives an intriguing "Mexican-hat-like" structure with a two-coordinate Tl(I) suspended on the $\{Pt_2S_2\}$ ring.[2] A coordinatively-exposed Tl(I) with an acute S–Tl–S angle is thus perceived. In view of this unusual Tl(I) geometry, we decided to examine the basicity of the isoelectronic $Pb(NO_3)_2$ toward the sulfido complex for comparison. Since the coordination numbers and geometries of Pb(II) are known to vary sensitively with the ligand requirements,[3] the resultant structure of Pb(II) in an environment comprising a basic but bulky sulfur chelating ligand and a labile but small nitrato group would be a subject of interest. Similar coordination chemistry of $Pb(NO_3)_2$ has recently attracted wide interest, but the ligands used are almost invariably macrocycles of N and O donors.[4]

## Results and Discussion

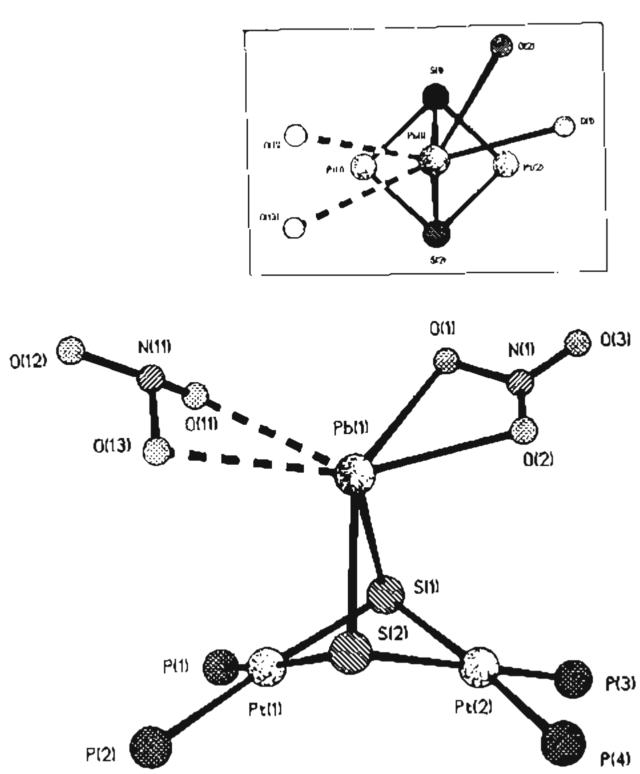

**Figure 1.** Molecular structure of $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)_2]$, **1** (phenyl rings removed for clarity), with the inset showing the neighboring atoms of Pb(II).

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ reacts readily with $Pb(NO_3)_2$ in an 1:1 stoichiometric ratio to give an adduct which can be formulated as $[PbPt_2(NO_3)_2(\mu\text{-}S)_2(PPh_3)_4]$, **1**. Its $^{31}P$-NMR spectrum reveals the chemical equivalence of all the phosphine groups ($\delta$ 17.25). Metathetic exchange with $NH_4PF_6$ in MeOH removes one nitrato ligand to gives a cationic complex, $[PbPt_2(NO_3)(\mu\text{-}S)_2(PPh_3)_4]PF_6$. The retention of a coordinated nitrate which resists displacement is indicated in its IR spectrum ($\nu$ 1263 $cm^{-1}$). The $PF_6^-$ band at 837 $cm^{-1}$ is characteristic of the free ion. The $^{31}P$ resonance at $\delta$ 16.11 suggested some slight changes in the molecular core. As the above information could not reveal the local geometries of Pb(II) in both complexes, an X-ray diffraction study was carried out.

Both complexes show a Pb(II) atom capping symmetrically between the sulfur bridges of the Pt metalloligand (Figures 1 and 2); a similar disposition of the heterometal is also observed in the Pt/Tl complex.[2] But unlike the latter, the Pb(II) in **1** and **2** is further chelated by an asymmetric bidentate nitrate (mean Pb–O = 2.581(12) Å). The coordination-induced distortion of the O–N–O angles is apparent in both complexes. While **1** is also weakly chelated to a second nitrate (mean Pb–O = 2.871(15) Å), the $PF_6^-$ ion in **2** is located outside the bonding distances usually associated with Pb–F bonds (e.g. 2.41–2.69 Å in $PbF_2$[5]) (the closest contacts belonging to Pb–F(5a,b) at 3.031(30) and 3.294(35) Å and Pb–F(1) at 3.384(10) Å). This $PF_6^-$ ion is disordered with the equatorial $F^-$ each showing half-occupancy in two positions. The Pb–O distances for the weakly-bound nitrate in **1** are similar to those found in $Pb(NO_3)_2$ (2.805 Å)[6] and other polar nitrato complexes;[7] the links are thus largely electrostatic. The $\nu(NO_3^-)$ at 1381 $cm^{-1}$ also compares well with that found in $Pb(NO_3)_2$ ($\nu$ 1371 $cm^{-1}$). This is experimentally consistent with its easy removal by $PF_6^-$ to give **2**. On the other hand, the

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(1) (a) Briant, C. E.; Hor, T. S. A.; Howells, N. D.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1118. (b) Briant, C. E.; Gilmour, D. I.; Mingos, D. M. P.; Luke, M. A. *J. Chem. Soc., Dalton Trans.* **1985**, 851. (c) Gilmour, D. I.; Luke, M. A.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1987**, 335. (d) Briant, C. E.; Hor, T. S. A.; Howells, N. D.; Mingos, D. M. P. *J. Organomet. Chem.* **1983**, *256*, C15.

(2) Zhou, M.; Xu, Y.; Koh, L.-L.; Mok, K. F.; Leung, P.-H.; Hor, T. S. A. *Inorg. Chem.* **1993**, *32*, 1875.

(3) (a) Chandler, C. D.; Hampden-Smith, M. J.; Duesler, E. N. *Inorg. Chem.* **1992**, *31*, 4891. (b) Balch, A. L.; Catalano, V. J.; Chatfield, M. A.; Nagel, J. K.; Olmstead, M. M.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1252. (c) Balch, A. L.; Neve, F.; Olmstead, M. M. *Inorg. Chem.* **1991**, *30*, 3395. (d) Veith, M.; Hans, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 878. (e) Tadokoro, M.; Okawa, H.; Matsumoto, N.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1991**, 1657. (f) Bashall, A.; McPartlin, M.; Murphy, B. P.; Fenton, D. E.; Kitchen, S. J.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1990**, 505. (g) Goel, S. C.; Chiang, M. Y.; Buhro, W. E. *Inorg. Chem.* **1990**, *29*, 4640. (h) Engelhardt, L. M.; Furphy, B. M.; Harrowfield, J. McB.; Patrick, J. M.; White, A. H. *Inorg. Chem.* **1989**, *28*, 1410. (i) Engelhardt, L. M.; Furphy, B. M.; Harrowfield, J. McB.; Patrick, J. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1989**, 595. (j) Harrison, P. G.; Begley, M. G.; Kikabhai, T.; Steel, A. T.; Khalil, M. I. *J. Chem. Soc., Dalton Trans.* **1989**, 2443. (k) Kuppers, H. J.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Anorg. Allg. Chem.* **1989**, *577*, 155. (l) Balch, A. L.; Oram, D. E. *Organometallics* **1986**, *5*, 2159. (m) Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Inorg. Chem.* **1984**, *23*, 4232. (n) Canadell, E.; Eisenstein, O.; Hughbanks, T. *Inorg. Chem.* **1984**, *23*, 2435. (o) Barkigia, K. M.; Fajer, J.; Adler, A. D.; Williams, G. J. B. *Inorg. Chem.* **1980**, *19*, 2057. (p) Alcock, N. W.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1979**, *10*, 1486. (q) Alcock, N. W.; Herron, N.; Moore, P. *Inorg. Chim. Acta.* **1979**, *32 (1)*, L25. (r) Freeman, H. C.; Stevens, G. N.; Taylor, I. F., Jr. *J. Chem. Soc., Chem. Commun.* **1974**, 366. (s) Effenberger, H. *Monatsh. Chem.* **1987**, *118 (2)*, 211.

(4) (a) Smith, D. A.; Sucheck, S; Pinkerton, A. A. *J. Chem. Soc., Chem. Commun.* **1992**, *4*, 367. (b) Sakiyama, H.; Tokuyama, K.; Nishio, J.; Matsumoto, N.; Okawa, H. *Chem. Lett.* **1992**, *6*, 1021. (c) Byriel, K.; Dunster, K. R.; Gahan, L. R.; Kennard, C. H. L.; Latten, J. L.; Swann, I. L.; Duckworth, P. A. *Polyhedron* **1992**, *11*, 1205. (d) Rogers, R. D.; Bond, A. H. *Inorg. Chim. Acta* **1992**, *192*, 163.

(5) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1984; p 274.

(6) Hamilton, W. C. *Acta Crystallogr.* **1957**, *10*, 103.

(7) (a) Wieghardt, K.; Klein-Boymann, M.; Nuber, B.; Weiss, J.; Zsolnai, L.; Huttner, G. *Inorg. Chem.* **1986**, *25*, 1647 and references therein. (b) Metz, B.; Weiss, R. *Inorg. Chem.* **1974**, *13*, 2094. (c) Metz, B.; Weiss, R. *Acta Crystallogr., Sect. B* **1973**, *B29*, 1088.

0020-1669/93/1332-4660$04.00/0

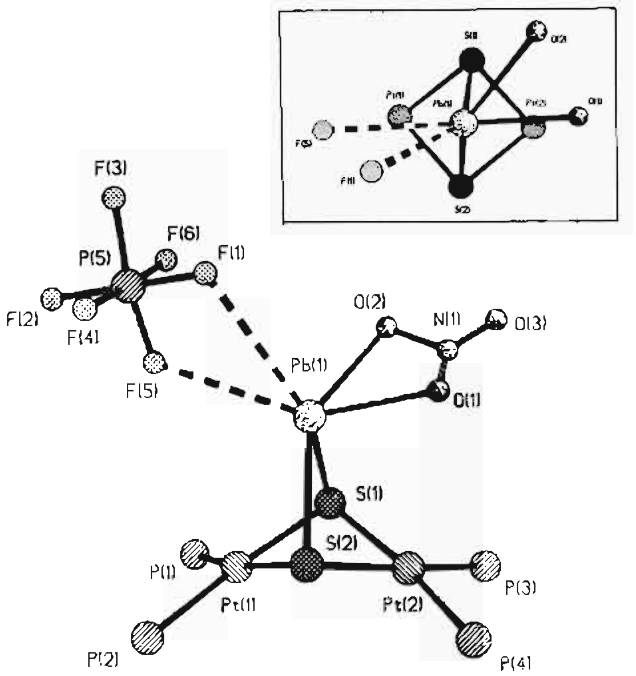

**Figure 2.** Molecular structure of $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)]PF_6$, **2** (phenyl rings removed for clarity), with the inset showing the neighboring atoms of Pb(II).

**Table I.** Crystallographic Data for $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)_2]$, **1**, and $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)]PF_6$, **2**

| | **1** | **2** |
|---|---|---|
| composn | $C_{72}H_{60}N_2O_6P_4PbPt_2S_2$ | $C_{72}H_{60}F_6NO_3P_5PbPt_2S_2$ |
| fw | 1834.6 | 1913.6 |
| space group | $P2_1/c$ | $P2_1/c$ |
| $a$, Å | 23.045(7) | 23.240(8) |
| $b$, Å | 13.326(4) | 13.191(7) |
| $c$, Å | 24.013(10) | 23.650(6) |
| $\beta$, deg | 111.63(3) | 109.63(2) |
| $V$, Å$^3$ | 6855(4) | 6828(5) |
| $Z$ | 4 | 4 |
| $d_{calc}$, g cm$^{-3}$ | 1.778 | 1.861 |
| $T$, K | 298 | 298 |
| λ(Mo Kα), Å | 0.710 73 | 0.710 73 |
| μ, mm$^{-1}$ | 6.728 | 6.788 |
| no. of obsd rflcns | 6460 ($F > 4.0\sigma(F)$) | 7541 ($F > 4.0\sigma(F)$) |
| $R^a$ | 0.042 | 0.031 |
| $R_w{}^b$ | 0.050 | 0.038 |

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

**Table II.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients[a] of Selected Non-Hydrogen Atoms (Å$^2$ × $10^3$)

| atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| | | (a) $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)_2]$, **1** | | |
| Pb | 2814(1) | 641(1) | 4001(1) | 95(1) |
| Pt(1) | 1826(1) | 2107(10) | 4359(1) | 37(1) |
| Pt(2) | 3288(1) | 2121(1) | 5260(1) | 42(1) |
| S(1) | 2758(1) | 2635(3) | 4261(1) | 54(1) |
| S(2) | 2512(1) | 891(2) | 4974(1) | 46(1) |
| P(1) | 1278(1) | 3390(2) | 3767(1) | 43(1) |
| P(2) | 1039(1) | 1352(2) | 4592(1) | 39(1) |
| P(3) | 3972(1) | 3410(3) | 5321(2) | 49(1) |
| P(4) | 3664(1) | 1528(3) | 6220(1) | 47(1) |
| N(1) | 3854(11) | −747(20) | 4723(10) | 128(7) |
| O(1) | 3915(7) | 79(13) | 4687(8) | 153(10) |
| O(2) | 3329(11) | −1168(11) | 4416(11) | 229(15) |
| O(3) | 4252(10) | −1302(20) | 4952(14) | 322(386) |
| N(11) | 1702(19) | 45(34) | 2712(19) | 226(16) |
| O(11) | 1817(10) | 1023(23) | 2828(10) | 238(16) |
| O(12) | 1344(11) | 76(19) | 2186(10) | 246(15) |
| O(13) | 1786(16) | −213(32) | 3105(11) | 343(510) |
| | | (b) $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)]PF_6$, **2** | | |
| Pb | 2146(1) | 5394(1) | 957(1) | 65(1) |
| Pt(1) | 3115(1) | 6951(1) | 627(1) | 29(1) |
| Pt(2) | 1681(1) | 6937(1) | −261(1) | 31(1) |
| S(1) | 2188(1) | 7450(2) | 742(1) | 40(1) |
| S(2) | 2466(1) | 5723(2) | 1(1) | 36(1) |
| P(1) | 3653(1) | 8250(2) | 1212(1) | 34(1) |
| P(2) | 3902(1) | 6187(2) | 396(1) | 32(1) |
| P(3) | 1014(1) | 8251(2) | −308(1) | 39(1) |
| P(4) | 1319(2) | 6311(2) | −1220(1) | 35(1) |
| P(5) | 3170(2) | 4379(4) | 2611(2) | 111(2) |
| N(1) | 1104(5) | 4213(9) | 210(4) | 77(5) |
| O(1) | 1117(4) | 5010(7) | 336(4) | 85(4) |
| O(2) | 1656(5) | 3682(8) | 443(5) | 107(6) |
| O(3) | 719(5) | 3676(9) | −55(5) | 114(6) |
| F(1) | 2460(4) | 4424(6) | 2353(4) | 128(4) |
| F(2) | 3885(5) | 4367(10) | 2891(6) | 207(8) |
| F(3A) | 3105(17) | 3469(41) | 3013(22) | 217(27) |
| F(3B) | 3134(17) | 4401(37) | 3211(11) | 189(18) |
| F(4A) | 3188(10) | 5256(34) | 3053(19) | 163(15) |
| F(4B) | 3144(12) | 5573(20) | 2485(27) | 163(18) |
| F(5A) | 3216(16) | 4994(32) | 2092(14) | 152(16) |
| F(5B) | 3202(21) | 4124(51) | 2000(15) | 225(30) |
| F(6A) | 3113(37) | 3512(33) | 2232(33) | 343(49) |
| F(6B) | 3234(21) | 3240(32) | 2637(30) | 245(35) |

[a] Equivalent isotropic $U_{eq}$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

stronger Pb–$O_2NO$ links in **1** and **2** (2.403(8)–2.710(16)) indicate significant covalency and hence are inert toward anionic replacement. There is ample support in the literature for these observed distances for Pb(II)–O.[8] Compared to the Tl center in $[Pt_2Tl(\mu\text{-}S)_2(PPh_3)_4]PF_6$, which shows no secondary interactions other than the Tl-S links, Pb(II) clearly does not favor a low-coordination geometry.[9]

Especially interesting is the perseverance of the stereogeometry of the $[Pb(S\text{-}S)(NO_3)]$ entity despite exchange of a nitrato ligand with a much weaker coordinating $PF_6^-$ ion. The two complexes can thus be considered as isostructural. The absence of structural reorganization despite the poor coordinating ability of $PF_6^-$ indicates the stereo significance of the remaining coordination sites. With three strong interactions [S(1), S(2), O(1)], and two secondary interactions [O(11) and O(13) in **1** or F(1) and F(5) in **2**], the bonding of Pb(II) can be described as $AX_3Y_3E$ or $AX_4Y_2E$ [10] depending on how one treats the weaker Pb–$O_2NO$ links [Pb–O(2)]. The latter is significantly weaker than the other anchor point [Pb–O(1)], but distances of 2.709(16) Å in **1** and 2.637(10) Å in **2** are similar to those of many $Pb(NO_3)_2$ adducts[4d] and indicate substantial primary interactions. In either case, an active lone pair completes a distorted trigonal prismatic geometry for Pb(II).[11] The weakly-linked nitrate in **1** shows significant deviation from planarity [dihedral angle O(12)–N(11)–O(11)–O(13) = 137.1(5)°]. However, the high thermal motion of these atoms precludes a meaningful discussion.

The nearly identical Pb–S lengths in **1** [mean 2.718(4) Å] and **2** [mean 2.704(3) Å] are typical of covalent Pb(II)–S bonds.[12]

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(8) (a) Leciejewicz, J. *Acta Crystallogr.* **1961**, *14*, 66. (b) Kay, M. I. *Acta Crystallogr.* **1961**, *14*, 80. (c) Spiro, T. G.; Templeton, D. H.; Zalkin, A. *Inorg. Chem.* **1969**, *8*, 856. (d) Spiro, T. G.; Maroni, V. A.; Quicksall, C. O. *Inorg. Chem.* **1969**, *8*, 2524. (e) Garcia-Clavel, M. E.; Martinez-Lope, M. J.; Casais-Alvarez, M. T.; Kilany, A. *Therm. Anal., Proc. Int. Conf., 8th* **1985**, *1*, 547.

(9) Two-coordinate Pb(II) complexes are rare but known in the literature. For example: (a) Brooker, S.; Buijink, J.-K.; Edelmann, F. T. *Organometallics* **1991**, *10*, 25. (b) Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639. (c) Lappert, M. F.; Power, P. P.; Slade, M. J.; Hedberg, L.; Hedberg, K.; Schomaker, V. *J. Chem. Soc., Chem. Commun.* **1979**, 369.

(10) (a) Alcock, N. W. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeléus, H. J., and Sharpe, A. G., Eds.; Academic Press: New York, 1971; p 1. (b) Sawyer, J. F.; Gillespie, R. J. *Prog. Inorg. Chem.* **1986**, *34*, 65.

(11) Note that it is also possible to suggest a [4 + 2] coordination without invoking the lone pair effect when an open face of a Pb(II) complex is blocked by its counteranion (e.g. $[Pb(H_4L)][ClO_4]$ ($H_4L$ = an octadentate macrocycle) in: Tandon, S. S.; McKee, V. *J. Chem. Soc., Dalton Trans.* **1989**, 19). Our distorted structures appear to comply more with the stereo-significant electron pair effect. Refer to the following for an excellent discussion on the lone pair effect of Pb(II): Hancock, R. D.; Shaikjee, M. S.; Dobson, S. M.; Boeyens, J. C. A. *Inorg. Chim. Acta* **1988**, *154*, 229.

**Table III.** Selected Bond Distances (Å) and Angles (deg)

| | | | |
|---|---|---|---|
| (a) $[(PPh_3)Pt_2(\mu_3\text{-}S)_2Pb(NO_3)_2]$, **1** | | | |
| Pb–S(1) | 2.744(4) | Pb–S(2) | 2.692(4) |
| Pb–O(1) | 2.574(14) | Pb–O(2) | 2.709(16) |
| Pb–O(11) | 2.951(15) | Pb–O(13) | 2.790(15) |
| Pt(1)–S(1) | 2.352(4) | Pt(1)–S(2) | 2.362(3) |
| Pt(2)–S(1) | 2.357(3) | Pt(2)–S(2) | 2.334(3) |
| mean Pt–P | 2.296(4) | N(1)–O(1) | 1.117(32) |
| N(1)–O(2) | 1.289(30) | N(1)–O(3) | 1.149(34) |
| N(11)–O(11) | 1.339(53) | N(11)–O(12) | 1.228(43) |
| N(11)–O(13) | 0.955(55) | Pb(1)···Pt(1) | 3.345(2) |
| Pb(1)···Pt(2) | 3.433(2) | Pt(1)···Pt(2) | 3.266(2) |
| S(1)···S(2) | 3.060(4) | | |
| S(1)–Pb–S(2) | 68.5(1) | O(1)–Pb–O(2) | 46.5(6) |
| O(11)–Pb–O(13) | 35.2(30) | S(1)–Pb–O(1) | 104.7(4) |
| S(1)–Pb–O(2) | 146.0(4) | S(2)–Pb–O(1) | 89.4(5) |
| S(2)–Pb–O(2) | 90.5(6) | S(1)–Pt(1)–S(2) | 80.9(1) |
| S(1)–Pt(1)–P(1) | 91.7(1) | S(2)–Pt(1)–P(2) | 87.4(1) |
| P(1)–Pt(1)–P(2) | 100.0(1) | S(1)–Pt(2)–S(2) | 81.4(1) |
| S(1)–Pt(2)–P(3) | 86.2(1) | S(2)–Pt(2)–P(4) | 91.1(1) |
| P(3)–Pt(2)–P(4) | 101.4(1) | O(1)–N(1)–O(2) | 120.2(21) |
| O(1)–N(1)–O(3) | 124.7(6) | O(2)–N(1)–O(3) | 114.2(25) |
| O(11)–N(11)–O(12) | 100.8(33) | O(11)–N(11)–O(13) | 101.1(44) |
| O(12)–N(11)–O(13) | 147.4(52) | | |
| dihedral angle Pt(1)–S(1)–S(2)–Pt(2) | 132.2(1) | | |
| (b) $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)]PF_6$, **2** | | | |
| Pb–S(1) | 2.766(3) | Pb–S(2) | 2.641(3) |
| Pb–O(1) | 2.403(8) | Pb–O(2) | 2.637(10) |
| Pt(1)–S(1) | 2.355(3) | Pt(1)–S(2) | 2.363(2) |
| Pt(2)–S(1) | 2.364(2) | Pt(2)–S(2) | 2.348(2) |
| mean Pt–P | 2.299(2) | N–O(1) | 1.090(15) |
| N–O(2) | 1.400(15) | N–O(3) | 1.149(15) |
| mean P–F(1–2) | 1.563(11) | mean P–F(3–6) | 1.516(42) |
| Pb···F(1) | 3.384(10) | Pb···F(5a) | 3.031(30) |
| Pb···F(5b) | 3.294(35) | Pb(1)···Pt(1) | 3.328(2) |
| Pb(1)···Pt(2) | 3.393(2) | Pt(1)···Pt(2) | 3.290(2) |
| S(1)···S(2) | 3.072(3) | | |
| S(1)–Pb–S(2) | 69.2(1) | O(1)–Pb–O(2) | 49.4(3) |
| S(1)–Pb–O(1) | 100.5(2) | S(1)–Pb–O(2) | 142.3(2) |
| S(2)–Pb–O(1) | 91.1(2) | S(2)–Pb–O(2) | 87.0(3) |
| S(1)–Pt(1)–S(2) | 81.2(1) | S(1)–Pt(1)–P(1) | 93.2(1) |
| S(2)–Pt(1)–P(2) | 86.7(1) | P(1)–Pt(1)–P(2) | 98.9(1) |
| S(1)–Pt(2)–S(2) | 81.3(1) | S(1)–Pt(2)–P(3) | 86.2(1) |
| S(2)–Pt(2)–P(4) | 90.6(1) | P(3)–Pt(2)–P(4) | 101.9(1) |
| O(1)–N(1)–O(2) | 115.9(10) | O(1)–N(1)–O(3) | 133.5(13) |
| O(2)–N(1)–O(3) | 110.4(11) | | |
| dihedral angle Pt(1)–S(1)–S(2)–Pt(2) | 133.5(1) | | |

The S–Pb–S chelate angles [mean 68.9(1)°] are identical to that found in the Tl(I) complex [68.9(1)°] in spite of the different geometries found for the Pb(II) and Tl(I) in these adducts and the smaller size of the former. This implies that the acute angle is determined more by the $\{Pt_2S_2\}$ conformation, including the S···S nonbonding distance, than the local constraints at the p-block metal center. The mean Pt···Pb contacts of 3.375(2) Å in **1** and **2**, which is similar to the heterometal contacts observed in the Tl(I) and Au(I)[13] complexes, are significantly longer than the Pb–Pt bond length [mean 2.781(2) Å] recently found.[14]

Conductivity measurements suggested partial ionization in **1**[15] but full dissociation (of $PF_6^-$) in **2** to give a 1:1 electrolyte. This ionicity difference incurs a slight disparity in their solution structures which is reflected in their $^{31}$P-NMR data. The observed single resonance in their spectra also necessitates a modification from their solid-state structures. A resonance form between the two nitrato groups in **1** and a rapid flipping of the nitrato group across the $\{PbS_2\}$ plane in **2** could equilibrate the phosphines. All the chemical and spectroscopic evidence points to the maintenance of the Pb–S bonds in solution. Neither **1** nor **2** shows any Lewis acidity toward $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$. This supports the observation that **1** is formed as the only isolable species even when the preparation was carried out in molar excess of the metalloligand. This is unexpected on the basis of the known lability of nitrate and the high coordination numbers favored by Pb(II). High steric demand for the Pt–S metalloligand is probably responsible.

## Experimental Section

All manipulations were routinely carried out under dry argon atmosphere using freshly distilled solvents. The instruments used have been previously reported.[2,16] Elemental analyses were performed by the Microanalytical Laboratory in our department.

**Preparations of $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)_2]$, 1, and $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)]PF_6$, 2.** Solid $Pb(NO_3)_2$ (0.044 g, 0.133 mmol) was added to a MeOH suspension (50 mL) of $[Pt_2S_2(PPh_{34})]$ (0.200 g, 0.133 mmol) and the mixture stirred for 48 h. The resultant yellow suspension was filtered, and the solid obtained was purified by crystallization from $CH_2Cl_2$/hexane mixture to give $[(PPh_3)_4Pt_2(\mu_3\text{-}S)_2Pb(NO_3)_2]$, **1**. Yield: 0.195 g (80%). Anal. Calcd: C, 47.14; H, 3.27; N, 1.53; P, 6.76; Pb, 11.29; Pt, 21.28; S, 3.49. Found: C, 46.90; H, 3.11; N, 1.31; P, 7.58; Pb, 10.48; Pt, 18.77; S, 4.06. $^{31}$P NMR ($CDCl_3$): $\delta = 17.25$ ($J$(P–Pt) = 3098, $^3J$(P–Pt) = 16 Hz). $^{31}$P NMR ($CH_2Cl_2$): $\delta = 16.92$ ($J$(P–Pt) = 3105, $^3J$(P–Pt) = 17 Hz). IR ($NO_3^-$, cm$^{-1}$): 1381, 1276. Molar conductivity $\Lambda_m$ ($10^{-3}$ M, $CH_2Cl_2$): 16.5 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. The $PF_6^-$ salt was prepared in nearly quantitative yield by metathesis with $NH_4PF_6$ in MeOH and recrystallized from the $CH_2Cl_2$/hexane mixture. Anal. Calcd: C, 45.09; H, 3.13; N, 0.73; P, 8.09; Pb, 10.80; Pt, 20.35; S, 3.34. Found: C, 45.08; H, 3.16; N, 0.66; P, 7.94; Pb, 9.25; Pt, 18.77; S, 3.75. $^{31}$P NMR ($CDCl_3$): $\delta = 16.11$ ($J$(P–Pt) = 3129, $^3J$(P–Pt) = 15 Hz). $^{31}$P NMR ($CH_2Cl_2$): $\delta = 16.92$ ($J$(P–Pt) = 3105, $^3J$(P–Pt) = 17 Hz). IR (cm$^{-1}$): 1263 ($NO_3^-$), 837 ($PF_6^-$) [for comparison, $Pb(NO_3)_2$ (KBr) 1371 cm$^{-1}$($NO_3^-$)]. Molar conductivity $\Lambda_m$ ($10^{-3}$ M, $CH_2Cl_2$): 57.0 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**X-ray Crystal Structure Determination.** Yellow crystals suitable for a single-crystal X-ray structure determination were grown for complexes **1** and **2** by the slow diffusion of hexane into the sample solutions in $CH_2Cl_2$. The crystals used for analysis is of approximate dimension 0.50 × 0.40 × 0.20 for **1** and 0.50 × 0.30 × 0.20 mm for **2**. The unit cell constants were determined by least-squares fits to the setting parameters of 22 and 20 independent reflections for **1** and **2**. Detailed crystallographic data are listed in Table I. A total of 11 641 for **1** and 12 006 for **2** independent reflections, $3.5° < 2\theta < 50.0°$, were measured by scanning on a Siemens R3M/V2000 diffractometer. The intensity data were reduced and corrected for Lorentz and polarization factors using the applied programs. The crystal structures were solved by direct methods using the XS program of SHELXTL-PLUS[17] and refined by full-matrix least-squares analysis with the XLS program of SHELXS-76. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at calculated positions with fixed isotropic thermal parameters.

**Acknowledgment.** The authors acknowledge the National University of Singapore for financial support (Grant RP850030), the technical staff in our department for supporting services, and Y. P. Leong for assistance in the preparation of this manuscript. Some constructive comments from a reviewer on the lone pair effect of the complexes are much appreciated.

**Supplementary Material Available:** Details of the X-ray structural analyses for **1** and **2** including figures showing structural diagrams and tables of crystallographic data, refined atomic coordinates and isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles (24 pages). Ordering information is given on any masthead page. Listings of structure factors of **1** (26 pages) and **2** (27 pages) can be obtained from the corresponding authors.

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(12) (a) Christou, G.; Folting, K.; Huffman, J. C. *Polyhedron* **1984**, *2*, 1247. (b) Dean, P. A. W.; Vittal, J. J.; Payne, N. C. *Inorg. Chem.* **1984**, *23*, 4232. (c) Dance, I. G.; Guerney, P. J. *Aust. J. Chem.* **1981**, *34*, 57. (d) Hummel, H.-U.; Meske, H. *J. Chem. Soc., Dalton Trans.* **1989**, 627. (e) Holt, E. M.; Nasser, F. A. K.; Wilson, A., Jr.; Zuckerman, J. J. *Organometallics* **1985**, *4*, 2073. (f) Iwasaki, H.; Hagihara, H. *Acta Crystallogr., Sect. B* **1972**, *28*, 507.

(13) Bos, W.; Bour, J. J.; Schlebos, P. P. J.; Hageman, P.; Bosman, W. P.; Smits, J. M. M.; van Wietmarschen, J. A. C.; Beurskens, P. T. *Inorg. Chim. Acta* **1986**, *119*, 141.

(14) Uson, R.; Fornies, J.; Falvello, L. R.; Uson, M. A.; Uson, I. *Inorg. Chem.* **1992**, *31*, 3697.

(15) Its conductivity (16.5 $\Omega^{-1}$cm$^2$mol$^{-1}$) is lower than that of all other similar 1:1 electrolytes such as $[Pt_2Tl(\mu_3\text{-}S)_2(PPh_3)_4]X$ (X = $NO_3$, $PF_6$).

(16) Hor, T. S. A.; Neo, S. P.; Tan, C. S.; Mak, T. C. W.; Leung, K. W. P.; Wang, R.-J. *Inorg. Chem.* **1992**, *31*, 4510.

(17) Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1989.