$[Pt_2(\mu\text{-SAz})(\mu\text{-S})]^{2+}$ (SAz = Azolium thiolate) Dication as an Unusual Source for Quadruply Bridging Sulfide in $[Ag_2Pt_2(\mu\text{-SAz})(\mu_4\text{-S})]^{3+}$

Jingqiu Li, Fuwei Li, Lip Lin Koh and T. S. Andy Hor*

X-ray Crystal Structure Determination and Refinement

All the crystals were grown in the mixture solvent of CH_2Cl_2 and MeOH. The disorder of imidazole was found in most of the crystal structures. They are very common to be investigated in such structures. The solvent molecules in the voids as these are small molecules (CH_2Cl_2 or MeOH), which tend to be lost after crystals were exposed in air. The diffraction experiments were carried out on a Bruker SMART CCD diffractometer using Mo-Ka radiation (l = 0.71073 A˚). The program SMART[1] was used for collecting frames of data, indexing reflections and determination of lattice parameters, and SHELXTL[2] for space group and structure determination, refinements, graphics, and report of structure. The structures were refined by full-matrix least squares on $F2$ with atomic displacement parameters for non-hydrogen atoms and all hydrogen atoms were placed in idealized positions. The structures of complexes **8, 13, 14, 15, 16** and **17** were refined by full-matrix least squares on F^2 with atomic displacement parameters for non-hydrogen atoms. The selected bonds and angles are summarized in Table 1.

Table 1 Selected Bond Lengths [Å] and Angles [deg] for **8**, **13**, **14**, **15**, **16** and **17**

$[Pt_2(\mu\text{-S})(\mu\text{-SCH}_2\text{CH}_2\text{C}_3\text{H}_3\text{N}_2\text{CH}_3)(PPh_3)_4](PF_6)_2$ **(8)**
Dihedral Angle Pt(1)S(1)S(1A)Pt(1A): 138 º

Pt(1)-P(2)	2.278(3)	Pt(1)-P(1)	2.298(2)	Pt(1)-S(1A)	2.338(2)
Pt(1)-S(1)	2.346(3)	S(1)-Pt(1A)	2.338(2)	S(1)-C(1)	1.84(2)
P(2)-Pt(1)-P(1)	98.9(1)	P(2)-Pt(1)-S(1A)	93.40(9)	P(1)-Pt(1)-S(1A)	167.42(9)
P(2)-Pt(1)-S(1)	174.80(9)	P(1)-Pt(1)-S(1)	86.34(9)	S(1A)-Pt(1)-S(1)	81.4(1)
C(1)-S(1)-Pt(1A)	107.9(7)	C(1)-S(1)-Pt(1)	108.1(6)	Pt(1A)-S(1)-Pt(1)	90.13(9)

$[Pt_2(\mu\text{-S})(\mu\text{-S(CH}_2)_3\text{C}_7\text{H}_5\text{NS})(PPh_3)_4](PF_6)_2$ **(13)**
Dihedral Angle Pt(1)S(1)S(2)Pt(2): 134 º

Pt(1)-P(2)	2.281(3)	Pt(1)-P(1)	2.298(3)	Pt(1)-S(2)	2.346(3)
Pt(1)-S(1)	2.352(3)	Pt(2)-P(4)	2.279(3)	Pt(2)-P(3)	2.319(3)
Pt(2)-S(2)	2.326(3)	Pt(2)-S(1)	2.370(3)	S(1)-C(1)	1.85(1)
P(2)-Pt(1)-P(1)	100.5(1)	P(2)-Pt(1)-S(2)	84.9 (1)	P(1)-Pt(1)-S(2)	173.6(1)
P(2)-Pt(1)-S(1)	165.5 (1)	P(1)-Pt(1)-S(1)	93.6(1)	S(2)-Pt(1)-S(1)	80.83(9)
P(4)-Pt(2)-P(3)	100.4(1)	P(4)-Pt(2)-S(2)	92.2(1)	P(3)-Pt(2)-S(2)	167.3(1)
P(4)-Pt(2)-S(1)	172.8(1)	P(3)-Pt(2)-S(1)	86.6(1)	S(2)-Pt(2)-S(1)	80.87(9)
C(1)-S(1)-Pt(1)	107.3(4)	C(1)-S(1)-Pt(2)	100.4(3)	Pt(1)-S(1)-Pt(2)	88.52(9)

Pt(2)-S(2)-Pt(1)	89.72(8)				

$[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2CH_2C_3H_3N_2CH_3)(dppy)_4](PF_6)_2$ **(14)**

Dihedral Angle Pt(1)S(1)S(2)Pt(2): 141 º

Pt(1)-P(1)	2.273(2)	Pt(1)-P(2)	2.294(2)	Pt(1)-S(2)	2.324(2)
Pt(1)-S(1)	2.362(1)	Pt(2)-P(3)	2.283(2)	Pt(2)-Pt(4)	2.297(2)
Pt(2)-S(2)	2.329(2)	Pt(2)-S(1)	2.355(1)	S(1)-C(1)	1.842(6)
P(1)-Pt(1)-P(2)	100.50(6)	P(1)-Pt(1)-S(2)	91.27(5)	P(2)-Pt(1)-S(2)	167.95(6)
S(2)-Pt(2)-S(1)	81.42(5)	C(1)-S(1)-Pt(2)	107.4(2)	C(1)-S(1)-Pt(1)	98.8(2)

$[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2CH_2C_3H_3N_2CH_3)(dppf)_2](PF_6)_2$ **(15)**

Dihedral Angle Pt(1)S(1)S(2)Pt(2): 145 º

Pt(1)-P(1)	2.271(5)	Pt(1)-P(2)	2.282(5)	Pt(1)-S(2)	2.342(5)
Pt(1)-S(1)	2.353(5)	Pt(2)-P(3)	2.282(5)	Pt(2)-Pt(4)	2.282(6)
Pt(2)-S(1)	2.340(5)	Pt(2)-S(2)	2.349(5)	S(2)-C(1)	1.72(2)
P(1)-Pt(1)-P(2)	100.3(2)	P(1)-Pt(1)-S(2)	167.5(2)	P(2)-Pt(1)-S(2)	90.8(2)
S(2)-Pt(1)-S(1)	81.1(2)	C(1)-S(2)-Pt(2)	113.3(9)	C(1)-S(2)-Pt(1)	111.5(9)

$[Pt_2(\mu\text{-}SCH_3)(\mu\text{-}SCH_2CH_2C_3H_3N_2CH_3)(PPh_3)_4](PF_6)_2$ **(17)**

Dihedral Angle Pt(1)S(1)S(2)Pt(2): 145 º

Pt(1)-P(2)	2.292(5)	Pt(1)-P(1)	2.302(6)	Pt(1)-S(1A)	2.354(5)
Pt(1)-S(1)	2.366(6)	S(1)-C(1X)	1.85(1)	S(1)-C(1)	1.85(1)
S(1)-Pt(1A)	2.354(5)				
P(2)-Pt(1)-P(1)	97.9(2)	P(2)-Pt(1)-S(1A)	168.4(2)	P(1)-Pt(1)-S(1A)	93.2(2)
P(2)-Pt(1)-S(1)	86.4(2)	P(1)-Pt(1)-S(1)	175.2(2)	S(1A)-Pt(1)-S(1)	82.4(2)
C(1X)-S(1)-Pt(1A)	106(2)	C(1)-S(1)-Pt(1A)	110(3)	C(1X)-S(1)-Pt(1)	110(2)
C(1)-S(1)-Pt(1)	102(3)	Pt(1A)-S(1)-Pt(1)	91.8(2)		

$[Pt_2(\mu\text{-}SAgOH_2AgCF_3SO_3)(\mu\text{-}SCH_2CH_2C_3H_3N_2CH_3)(PPh_3)_4](CF_3SO_3)_2$ **(16)**

Dihedral Angle Pt(1)S(1)S(2)Pt(2): 143 º

Pt(1)-P(2)	2.288(2)	Pt(1)-P(1)	2.305(2)	Pt(1)-S(1)	2.345(2)
Pt(1)-S(2)	2.382(2)	Pt(2)-P(3)	2.290(2)	Pt(2)-P(4)	2.294(2)
Pt(2)-S(1)	2.362(2)	Pt(2)-S(2)	2.364(2)	Ag(1)-O(7S)	2.174(5)
Ag(1)-S(1)	2.427(2)	Ag(2)-O(1W)	2.197(5)	Ag(2)-S(1)	2.394(2)
S(2)-C(1)	1.834(7)				
P(2)-Pt(1)-P(1)	98.01(6)	P(2)-Pt(1)-S(1)	166.67(6)	P(1)-Pt(1)-S(1)	91.56(5)
P(2)-Pt(1)-S(2)	90.91(5)	P(1)-Pt(1)-S(2)	170.61(5)	S(1)-Pt(1)-S(2)	80.14(5)
P(3)-Pt(2)-P(4)	97.74(6)	P(3)-Pt(2)-S(1)	171.80(6)	P(4)-Pt(2)-S(1)	89.58(5)
P(3)-Pt(2)-S(2)	92.81(5)	P(4)-Pt(2)-S(2)	168.83(5)	S(1)-Pt(2)-S(2)	80.16(5)
O(7S)-Ag(1)-S(1)	167.0(2)	O(1W)-Ag(2)-S(1)	170.0(1)	Pt(1)-S(1)-Pt(2)	96.80(5)
Pt(1)-S(1)-Ag(2)	107.93(6)	Pt(2)-S(1)-Ag(2)	107.00(6)	Pt(1)-S(1)-Ag(1)	109.83(6)
Pt(2)-S(1)-Ag(1)	114.66(7)	Ag(2)-S(1)-Ag(1)	118.34(6)	C(1)-S(2)-Pt(2)	103.1(2)
C(1)-S(2)-Pt(1)	105.9(2)	Pt(2)-S(2)-Pt(1)	95.73(5)		

1. SMART & SAINT *Software Reference Manuals*, 1996, version 4.0, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI (USA).
2. G. M. Sheldrick, SHELXTL, 1996, version 5.03, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI (USA).