Crystal structure of (tris(1-pyrazolylethyl)amine-κ^4N,N',N'',N''')-silver(I)] hexafluorophosphate, $[Ag(C_{15}H_{21}N_7](PF_6)$

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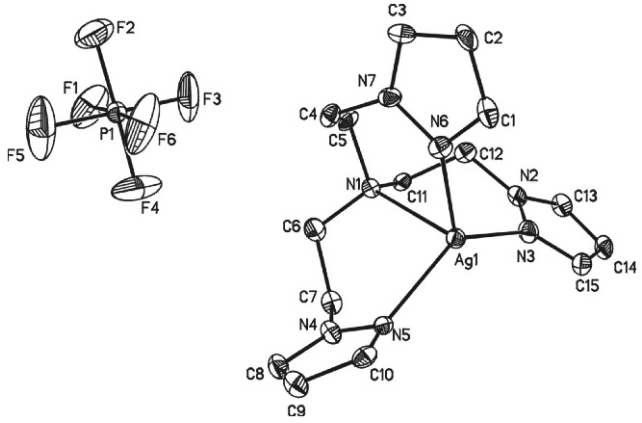
Received May 30, 2011, in revised form September 2, 2011, accepted and available on-line September 20, 2011; CCDC no. 1267/3589



Abstract

$C_{15}H_{21}AgF_6N_7P$, orthorhombic, *Pbca* (no. 61), a = 15.449(3) Å, b = 16.714(3) Å, c = 16.714(3) Å, V = 4315.8 Å^3, Z = 8, $R_{gt}(F)$ = 0.069, $wR_{ref}(F^2)$ = 0.200, T = 123 K.

Source of material

The title complex was prepared as follows. Methanol solution (5 mL) of the ligand tris(1-pyrazolylethyl)amine (TPEA, 60.0 mg, 0.2 mmol) was added into a MeOH and H_2O solution (20 mL, MeOH/H_2O = 9:1 v/v) of $AgPF_6$ (50.4 mg, 0.2 mmol). The mixture was then carefully filtered and the resulting solution was kept at room temperature for about two days, producing needle-shaped brown crystals (yield 50 %).

Elemental analysis — found: C, 32.56 %; H, 3.72 %; N, 17.70 %; calculated for $C_{15}H_{21}AgF_6N_7P$: C, 32.62 %; H, 3.83 %; N, 17.75 %.

Experimental details

All H atoms bound to C atoms were placed using the HFIX commands in SHELXL-97 [1], with d(C—H) = 0.93 Å. All H atoms were allowed for as riding atoms with U_{iso}(H) = 1.2 U_{eq}(C). The structure was checked with PLATON [2], revealing no disordered solvent molecules, but showing that the anion PF_6^- experiences disorder over two positions. The occupancy factors of two sets of disordered atoms were 0.78 and 0.22, respectively. The high R values can be due to the thin needle crystal for X-Ray analysis and the disorder of the anion in the crystal. In the revised manuscript, the R values have been decreased greatly following the treatment on the disorder of the PF_6^- anion.

Discussion

It is well known that multi-nitrogen-containing ligands have been used widely to assemble functional materials such as molecular magnetic, optic and electronic as well as multi-functional materials [3,4]. Among these ligands, tris(2-pyridylmethyl)amine (TPA) ligand and its derivatives containing four nitrogen atoms have been investigated extensively. However, the exploitation of the ligand TPEA, which is very similar to TPA in the structure and can be obtained easily, has been very limited [5].

The molecular structure comprises a $[Ag(I)(TPEA)]^+$ cation and a relatively large PF_6^- anion. The Ag ion is four-coordinated by four nitrogen atoms from the TPEA, yielding a distorted tetrahedral coordination. The TPEA ligand coordinates the Ag ion from one side like a cap. The Ag—$N_{pyrazole}$ bond lengths are very similar and located within the narrow scope 2.268(7) to 2.317(9) Å. The Ag—N_{amine} bond length (2.555(5) Å) is relatively longer than the above Ag—$N_{pyrazole}$ bonds.

Table 1. Data collection and handling.

Crystal:	brown needle, size 0.04 × 0.06 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.75 cm^{-1}
Diffractometer, scan mode:	Bruker APEX II CCD, φ/ω
$2\theta_{max}$:	50.5°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	26576, 3859
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3830
$N(param)_{refined}$:	290
Programs:	SHELXS-97, SHELXL-97 [1], PLATON [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	8*c*	0.7153	–0.1208	0.0836	0.046
H(2)	8*c*	0.5634	–0.1190	0.0345	0.061
H(3)	8*c*	0.5009	0.0098	0.0824	0.051
H(4A)	8*c*	0.5632	0.1354	0.1508	0.040
H(4B)	8*c*	0.6643	0.1387	0.1552	0.040
H(5A)	8*c*	0.5773	0.1540	0.2810	0.039
H(5B)	8*c*	0.5775	0.0603	0.2803	0.039
H(6A)	8*c*	0.7101	0.2206	0.3436	0.043
H(6B)	8*c*	0.7172	0.2140	0.2503	0.043
H(7A)	8*c*	0.8517	0.2410	0.3306	0.038
H(7B)	8*c*	0.8527	0.1478	0.3415	0.038
H(8)	8*c*	0.9054	0.2947	0.1886	0.046
H(9)	8*c*	0.9571	0.2296	0.0625	0.044
H(10)	8*c*	0.9343	0.0842	0.0823	0.036
H(11A)	8*c*	0.6438	0.1130	0.4138	0.035
H(11B)	8*c*	0.7430	0.0944	0.4160	0.035
H(12A)	8*c*	0.6349	–0.0118	0.4491	0.041
H(12B)	8*c*	0.6352	–0.0250	0.3564	0.041
H(13)	8*c*	0.7393	–0.1093	0.5190	0.041
H(14)	8*c*	0.8730	–0.1818	0.4802	0.045
H(15)	8*c*	0.9101	–0.1359	0.3425	0.038

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	8*c*		0.79842(3)	0.00853(3)	0.23369(3)	0.0271(3)	0.0253(3)	0.0283(4)	0.0006(2)	0.0024(2)	0.0015(2)
N(1)	8*c*		0.6971(3)	0.1072(3)	0.3036(3)	0.029(3)	0.022(3)	0.026(3)	–0.001(2)	0.002(2)	0.001(2)
N(2)	8*c*		0.7466(4)	–0.0569(3)	0.4085(3)	0.032(3)	0.030(3)	0.025(3)	–0.004(2)	0.007(2)	0.007(2)
N(3)	8*c*		0.8039(4)	–0.0660(4)	0.3464(4)	0.035(3)	0.033(3)	0.032(3)	0.002(2)	0.001(2)	0.010(3)
N(4)	8*c*		0.8765(4)	0.1818(4)	0.2270(3)	0.031(3)	0.028(3)	0.029(3)	–0.006(2)	–0.003(2)	0.001(2)
N(5)	8*c*		0.8853(3)	0.1091(3)	0.1923(4)	0.023(3)	0.027(3)	0.037(3)	–0.003(2)	0.000(2)	0.000(3)
N(6)	8*c*		0.6944(4)	–0.0136(4)	0.1354(4)	0.031(3)	0.034(3)	0.025(3)	0.003(2)	0.001(2)	0.003(2)
N(7)	8*c*		0.6189(4)	0.0290(4)	0.1341(4)	0.028(3)	0.034(3)	0.029(3)	–0.002(2)	–0.002(2)	0.009(3)
C(1)	8*c*		0.6760(5)	–0.0797(4)	0.0931(5)	0.053(5)	0.026(4)	0.035(4)	–0.002(3)	–0.005(4)	0.002(3)
C(2)	8*c*		0.5908(6)	–0.0797(5)	0.0647(6)	0.054(5)	0.032(4)	0.066(6)	–0.010(4)	–0.034(4)	0.003(4)
C(3)	8*c*		0.5567(5)	–0.0089(5)	0.0917(6)	0.029(4)	0.042(4)	0.057(5)	–0.008(3)	–0.016(4)	0.006(4)
C(4)	8*c*		0.6139(5)	0.1081(4)	0.1713(4)	0.032(4)	0.030(4)	0.038(4)	0.006(3)	–0.001(3)	0.011(3)
C(5)	8*c*		0.6093(4)	0.1073(4)	0.2633(4)	0.021(3)	0.035(4)	0.043(4)	0.009(3)	0.005(3)	0.005(3)
C(6)	8*c*		0.7343(5)	0.1891(4)	0.3003(5)	0.042(4)	0.024(3)	0.041(4)	0.002(3)	0.008(3)	–0.006(3)
C(7)	8*c*		0.8338(5)	0.1907(4)	0.3067(4)	0.042(4)	0.033(4)	0.021(3)	–0.008(3)	–0.001(3)	–0.005(3)
C(8)	8*c*		0.9051(5)	0.2402(4)	0.1775(5)	0.048(4)	0.028(4)	0.040(4)	–0.004(3)	–0.005(3)	0.005(3)
C(9)	8*c*		0.9340(5)	0.2047(5)	0.1074(4)	0.044(4)	0.039(4)	0.027(4)	–0.005(3)	–0.001(3)	0.010(3)
C(10)	8*c*		0.9207(4)	0.1237(4)	0.1195(4)	0.027(3)	0.038(4)	0.026(3)	0.000(3)	0.000(3)	–0.005(3)
C(11)	8*c*		0.6893(4)	0.0818(4)	0.3887(4)	0.027(3)	0.035(4)	0.024(4)	0.003(3)	0.004(3)	0.000(3)
C(12)	8*c*		0.6696(5)	–0.0061(4)	0.4011(5)	0.032(4)	0.040(4)	0.031(4)	–0.002(3)	0.006(3)	0.008(3)
C(13)	8*c*		0.7688(5)	–0.1047(4)	0.4707(4)	0.042(4)	0.036(4)	0.023(3)	–0.002(3)	0.001(3)	0.001(3)
C(14)	8*c*		0.8425(5)	–0.1449(4)	0.4495(5)	0.049(4)	0.029(4)	0.034(4)	0.002(3)	–0.009(3)	0.006(3)
C(15)	8*c*		0.8626(5)	–0.1188(4)	0.3720(4)	0.036(4)	0.031(4)	0.029(4)	0.000(3)	0.006(3)	0.001(3)
P(1)	8*c*	0.780(7)	0.5443(1)	0.3481(1)	0.1234(1)	0.032(1)	0.028(1)	0.031(1)	0.0010(7)	–0.0008(8)	0.0023(7)
F(1)	8*c*	0.780(7)	0.5095(5)	0.4061(4)	0.1947(4)	0.073(5)	0.077(5)	0.041(4)	0.039(4)	–0.011(3)	–0.018(3)
F(2)	8*c*	0.780(7)	0.4460(4)	0.3418(4)	0.0918(5)	0.051(4)	0.052(4)	0.099(6)	0.009(3)	–0.037(4)	–0.013(4)
F(3)	8*c*	0.780(7)	0.5318(5)	0.2756(4)	0.1839(5)	0.069(5)	0.048(4)	0.109(6)	0.012(3)	0.021(4)	0.049(4)
F(4)	8*c*	0.780(7)	0.6400(4)	0.3558(5)	0.1592(5)	0.031(3)	0.089(6)	0.104(6)	0.002(3)	–0.010(4)	–0.030(5)
F(5)	8*c*	0.780(7)	0.5557(7)	0.4254(5)	0.0688(6)	0.133(8)	0.051(4)	0.100(7)	0.010(5)	0.051(6)	0.031(5)
F(6)	8*c*	0.780(7)	0.5800(6)	0.2954(5)	0.0521(4)	0.111(7)	0.083(6)	0.050(5)	0.058(6)	–0.019(4)	–0.035(4)
P(1′)	8*c*	0.220	0.5443(1)	0.3481(1)	0.1234(1)	0.032(1)	0.028(1)	0.031(1)	0.0010(7)	–0.0008(8)	0.0023(7)
F(1′)	8*c*	0.220	0.449(1)	0.355(2)	0.160(1)	0.073(5)	0.077(5)	0.041(4)	0.039(4)	–0.011(3)	–0.018(3)
F(2′)	8*c*	0.220	0.508(2)	0.385(2)	0.041(1)	0.051(4)	0.052(4)	0.099(6)	0.009(3)	–0.037(4)	–0.013(4)
F(3′)	8*c*	0.220	0.506(2)	0.2625(9)	0.090(2)	0.069(5)	0.048(4)	0.109(6)	0.012(3)	0.021(4)	0.049(4)
F(4′)	8*c*	0.220	0.584(2)	0.296(2)	0.195(1)	0.031(3)	0.089(6)	0.104(6)	0.002(3)	–0.010(4)	–0.030(5)
F(5′)	8*c*	0.220	0.591(2)	0.425(1)	0.154(2)	0.133(8)	0.051(4)	0.100(7)	0.010(5)	0.051(6)	0.031(5)
F(6′)	8*c*	0.220	0.627(2)	0.314(2)	0.077(2)	0.111(7)	0.083(6)	0.050(5)	0.058(6)	–0.019(4)	–0.035(4)

Acknowledgment. This work was supported by "The Fundamental Research Funds for the Central Universities (China University of Mining and Technology)".

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