Crystal Structure of Bis(μ_2 -azido)-tetrakis(triphenylphosphine)-di-silver(I)

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The title complex, $[(PPh_3)_2Ag(\mu-N_3)_2Ag(PPh_3)_2]$, has been synthesized and structurally characterized by single-crystal X-ray diffraction. The silver atoms are joined through a double $\mu_{1,3}$ -azido (N_3) bridge. To each silver atom are also coordinated two P atoms from two triphenylphosphine molecules. The coordinated polyhedron around silver is a distorted tetrahedron.

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Silver(I) complexes can show a great variety of coordination chemistry.^{1,2} The structures and spectral properties of many adducts of Ag(I) have been studied in recent years.³⁻⁵ In this context, we examined the nature of the adduct silver complexes formed with an azido ligand. Therefore, the title compound, $[(PPh_3)_2Ag(\mu-N_3)_2Ag(PPh_3)_2]$, was synthesized and structurally investigated (Fig. 1).

The title complex, $[(PPh_3)_2Ag(\mu-N_3)_2Ag(PPh_3)_2]$, was prepared by the reaction of $AgNO_3$ with PPh_3 and NaN_3 (molar ratio 1:2:1) in an acetonitrile solution at 298 K. The precipitate was filtered off and dried under a vacuum. Colorless crystals were obtained by slow diffusion of Et_2O vapor into an acetonitrile-methanol (1:1, v/v) solution of the complex at 273 K. Geometric and intensity data were gathered on an Xcalibur 2 diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å) at 100(1)K. Absorption corrections were calculated numerically on the basis of the crystal morphology.⁶ The structure was solved by direct methods (SHELXS-97).⁷ The final refinement (on F^2) was performed using full-matrix least-squares with anisotropic thermal parameters for the non-hydrogen atoms (SHELXL-97).⁷ The hydrogen atoms were placed at calculated positions and treated as riders with isotropic displacement parameters constrained to 1.2-times the isotropic equivalent displacement parameters of their respective parent atoms. The crystal and experimental data are given in Table 1. Selected bond distances and angles are listed in Table 2, whereas positional parameters and atomic coordinates are given in Table 3.

This complex is dimeric (Fig. 2) and the triphenylphosphine and azide ligands are monodentate. The bond lengths Ag-P

Fig. 1 Chemical structure.

[2.4389(3), 2.4693(3)Å] are in good agreement with the corresponding distances in related complexes.³⁻⁵ The Ag(1)-N(1) and Ag(1)-N(3) bond distances are 2.2937(10) and 2.4508(11)Å, respectively. The coordination geometry around silver could be described as a distorted tetrahedron (average bond angle = 108.13°). Similar distorted silver coordination environments have been observed in related complexes.³⁻⁵

The crystallographic data (excluding structure factors) for the structure of $[(PPh_3)_2Ag(\mu-N_3)_2Ag(PPh_3)_2]$ reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 285593 for $[(PPh_3)_2Ag(\mu-N_3)_2Ag(PPh_3)_2]$. Copies of the data can be obtained free of charge by applying to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Table 1 Crystal and experimental data

Empirical formula	C ₇₂ H ₆₀ Ag ₂ N ₆ P ₄
Formula weight	1348.88
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i>	9.9400(4)Å
<i>b</i>	13.1138(6)Å
<i>c</i>	13.1332(4)Å
α	114.289(4)°
β	90.645(3)°
γ	101.217(4)°
<i>V</i>	1522.59(10)Å ³
<i>Z</i>	1
<i>D_x</i>	1.471 g cm ⁻³
<i>R</i> ₁	0.0211
<i>R</i> _w 2	0.0554
(Δ/σ)	0.001
($\Delta\rho$) _{max-min}	0.519, -0.467 Å ⁻³
No. of reflection used (all data)	18165
2 θ _{max}	67.96°
Measurement	Xcalibur 2
Program system	WINGX
Structure determination	SHELXS-97
Refinement: full matrix least-squares	SHELXL-97

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Table 2 Selected bond distances (Å), and bond angles (°)

Bond distances (Å)			
Ag(1)-N(1)	2.2937(10)	Ag(1)-N(3)	2.4508(11)
Ag(1)-P(1)	2.4389(3)	Ag(1)-P(2)	2.4693(3)
N(1)-N(2)	1.1793(15)	N(2)-N(3)	1.1660(15)
bond angles (°)			
N(1)-Ag(1)-N(3)	90.56(4)	N(1)-Ag(1)-P(1)	115.86(3)
N(1)-Ag(1)-P(2)	113.33(4)	N(3)-Ag(1)-P(1)	106.05(3)
P(1)-Ag(1)-P(2)	123.412(10)	N(3)-Ag(1)-P(2)	99.61(4)
Ag(1)-N(1)-N(2)	121.21(8)	Ag(1)-N(3)-N(2)	139.76(9)
N(1)-N(2)-N(3)	176.95(12)		

Symmetry code: i, (1 - x, -y, 2 - z).

Table 3 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	X	Y	Z	$U_{eq}(\text{\AA}^2)$
Ag(1)	0.361428(8)	-0.062627(7)	0.788973(7)	0.01237(3)
N(1)	0.58474(11)	-0.06386(11)	0.83342(9)	0.02444(2)
N(2)	0.63496(9)	-0.01933(9)	0.92729(8)	0.01523(17)
N(3)	0.69035(12)	0.02436(13)	1.01833(10)	0.0301(3)
P(1)	0.21481(3)	-0.24852(2)	0.66850(2)	0.01075(5)
P(2)	0.33547(3)	0.11911(2)	0.78475(2)	0.01121(5)
C(1)	0.03857(10)	-0.25879(9)	0.70749(9)	0.01214(17)
C(2)	0.01920(12)	-0.21109(11)	0.82182(10)	0.0177(2)
C(3)	-0.11344(12)	-0.21448(12)	0.85515(10)	0.0205(2)
C(4)	-0.22757(12)	-0.26415(11)	0.77517(10)	0.0180(2)
C(5)	-0.20849(11)	-0.31075(10)	0.66157(10)	0.0170(2)
C(6)	-0.07625(11)	-0.30837(10)	0.62751(9)	0.01439(18)
C(7)	0.19647(10)	-0.27775(9)	0.52081(9)	0.01217(17)
C(8)	0.17675(12)	-0.18934(10)	0.49251(10)	0.01610(19)
C(9)	0.16484(12)	-0.20630(11)	0.38071(11)	0.0195(2)
C(10)	0.17482(13)	-0.31163(12)	0.29607(10)	0.0215(2)
C(11)	0.19475(13)	-0.39984(11)	0.32327(10)	0.0210(2)
C(12)	0.20475(12)	-0.38333(10)	0.43528(10)	0.01627(19)
C(13)	0.26218(11)	-0.37735(9)	0.66583(9)	0.01240(17)
C(14)	0.39913(12)	-0.38693(11)	0.65111(11)	0.0180(2)
C(15)	0.43928(13)	-0.48644(11)	0.64105(11)	0.0207(2)
C(16)	0.34387(13)	-0.57626(10)	0.64753(10)	0.0195(2)
C(17)	0.20880(13)	-0.56558(10)	0.66594(10)	0.0179(2)
C(18)	0.16764(11)	-0.46672(10)	0.67454(10)	0.01505(19)
C(19)	0.17393(11)	0.15494(10)	0.83639(9)	0.01347(18)
C(20)	0.15686(13)	0.26761(11)	0.88921(11)	0.0196(2)
C(21)	0.02877(14)	0.28888(13)	0.092219(12)	0.0258(3)
C(22)	-0.08309(13)	0.19846(13)	0.90201(11)	0.0244(3)
C(23)	-0.06703(12)	0.08638(12)	0.84978(11)	0.0227(2)
C(24)	0.06153(12)	0.06470(11)	0.81795(10)	0.0181(2)
C(25)	0.32866(11)	0.12868(9)	0.64997(9)	0.01196(17)
C(26)	0.20452(11)	0.12419(10)	0.59501(9)	0.01499(19)
C(27)	0.20019(12)	0.11883(11)	0.48666(10)	0.0185(2)
C(28)	0.31911(13)	0.11820(11)	0.43170(10)	0.0186(2)
C(29)	0.44297(12)	0.12379(11)	0.48647(10)	0.0184(2)
C(30)	0.44809(11)	0.12805(10)	0.59407(10)	0.01563(19)
C(31)	0.46912(11)	0.24088(9)	0.87643(9)	0.01312(18)
C(32)	0.52423(13)	0.23367(11)	0.97123(11)	0.0185(2)
C(33)	0.62615(14)	0.22310(11)	1.04627(11)	0.0221(2)
C(34)	0.67598(12)	0.41908(11)	1.02639(10)	0.01999(2)
C(35)	0.62262(13)	0.42692(11)	0.93242(10)	0.0201(2)
C(36)	0.51920(12)	0.33805(10)	0.85753(10)	0.0180(2)

Fig. 2 ORTEP structure of the title compound with atom labeling, shown with 50% probability displacement ellipsoids.

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