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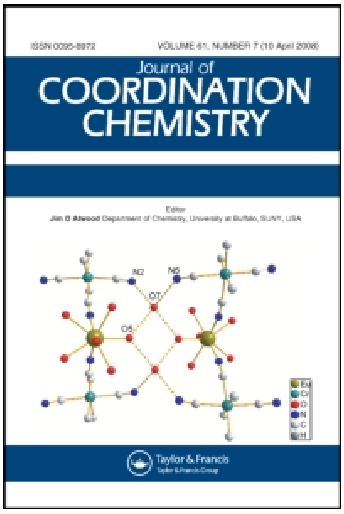

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The Crystal and Molecular Structure of *bis* [1,2-bis(Diphenylphosphino)Ethane] Silver(I) Nitrate

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To cite this Article Harker, Cameron S. W. and Tiekink, Edward R. T.(1990) 'The Crystal and Molecular Structure of *bis* [1,2-bis(Diphenylphosphino)Ethane] Silver(I) Nitrate', Journal of Coordination Chemistry, 21: 4, 287 — 293
To link to this Article: DOI: 10.1080/00958979009408190
URL: http://dx.doi.org/10.1080/00958979009408190

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J. Coord. Chem. 1990, Vol. 21, pp. 287–293
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THE CRYSTAL AND MOLECULAR STRUCTURE OF *BIS* [1,2-*BIS*(DIPHENYLPHOSPHINO)ETHANE] SILVER(I) NITRATE

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(Received January 7, 1990; in final form February 17, 1990)

The title compound, $[Ag(dppe)_2]NO_3$, is shown to be *bis*-chelated by two dppe ligands so that the silver atom is four-coordinate; Ag–P 2.488(3), 2 × 2.523(3) and 2.527(3) Å. Distortions from ideal tetrahedral geometry are related to the restricted bite distances of the dppe ligands such that the P(1)–Ag–P(2) and P(3)–Ag–P(4) angles are 84.5(1) and 83.8(1)°, respectively. The compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 14.834(2)$, $b = 19.795(2)$, $c = 15.856(3)$ Å, $\beta = 93.09(1)°$ and $Z = 4$. The structure was refined by a full-matrix least-squares procedure to final $R = 0.063$ for 3776 reflections with $I \geq 2.5\,\sigma(I)$.

Keywords: Silver(I), diphosphine, dppe, X-ray structure

INTRODUCTION

Recently, it has been demonstrated that certain gold(I) phosphine complexes display potentially useful pharmaceutical properties.[1] Thus the linear gold(I) phosphine thiolate complex, (1-thio)-β-D-glucopyranose 2,3,4,6-tetraacetato-*S*)(triethylphosphine)gold(I), (Auranofin) is widely used in the treatment of rheumatoid arthritis.[2] It has also been shown that the bis chelated gold(I) complex, $[Au(dppe)_2]NO_3$ [where dppe is 1,2-bis(diphenylphosphino)ethane], is cytotoxic towards certain tumorous cells.[3,4] Subsequently the silver(I) analogue, $[Ag(dppe)_2]NO_3$, was also shown to be anti-tumour active.[5] This paper reports the solid state structure of the latter compound, $[Ag(dppe)_2]NO_3$, as determined by X-ray crystallography, which was investigated in order to compare the structural characteristics of this compound with the gold(I) analogue.

EXPERIMENTAL

Preparation

The complex, $[Ag(dppe)_2]NO_3$, was prepared according to the literature method.[6] Colourless crystals were grown by the slow evaporation of an ethanol solution of the compound; m.p. 228–234°C (lit.[6] 225–230°C). The fast atom bombardment mass spectrum of the compound (recorded on a VG ZAB-2HF instrument in a 3-nitrobenzyl alcohol matrix) gave rise to characteristic isotopic peak ratios for ^{107}Ag and ^{109}Ag having natural abundance of 52 and 48% respectively. Major fragments

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(for the ^{107}Ag isotope) were found at m/z 903, corresponding to the complex cation, m/z 505 $[Ag(dppe)]^+$, m/z 291 $[AgPPh_2]^+$, and m/z 184 $[PPh_2]^+$.

Crystallography

The crystal chosen for X-ray analysis was a well-formed needle with faces (and distances from centroid) $\pm(0\ 1\ 0)$ 0.09, $\pm(1\ 0\ 1)$ 0.44 and $\pm(1\ 0\ \bar{1})$ 0.04 mm. Intensity data for 6828 reflections were measured on an Enraf-Nonius CAD4F diffractometer with the use of graphite monochromatized Mo$K\alpha$ radiation and the $\omega:2\theta$ scan technique such that θ_{max} was 25°. The data were corrected for Lorentz and polarization effects and for absorption.[7] There were 6315 unique reflections (R_{amal} 0.027) and of these 3776 satisfied the $I \geq 2.5\,\sigma(I)$ criterion of observability. Crystal data and refinement details are given in Table I.

TABLE I

Crystal and refinement details for $[Ag(dppe)_2]NO_3$.

Formula	$C_{52}H_{48}AgNO_3P_4$
M_r	966.7
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	14.834(2)
b, Å	19.795(2)
c, Å	15.856(3)
β (°)	93.09(1)
Vol. (Å^3)	4649.2
Z	4
D_c (g cm^{-3})	1.381
F(000)	1992
μ, cm^{-1} (Mo$K\alpha$)	5.70
Transmission factors (max; min.)	0.958; 0.897
θ limits (°)	1.5–25.0
No. of data collected	6828
No. of unique data	6315
No. of unique reflections used, $I \geq 2.5\sigma(I)$	3776
R	0.063
k	1.55
g	0.001
R_w	0.065
ρ_{max} (e Å^{-3})	1.02

The structure was solved from the interpretation of the Patterson synthesis and refined by a full-matrix least-squares procedure based on F.[7] Non-phenyl, non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions. Phenyl rings were refined as hexagonal rigid groups. Refinement with a weighting scheme of the form $w = k/[\sigma^2(F) + g(F)^2]$ converged with final R 0.063, R_w 0.065, $k = 1.55$, and g 0.001.

Fractional atomic coordinates are listed in Table II and the numbering scheme employed is shown in Figure 1 (drawn at 25% probability ellipsoids with ORTEP[8]). The refinement was performed with the SHELX76[7] program system installed on a SUN 4/280 computer system. Scattering factors for Ag$^+$ (corrected for f' and f'')

were from the *International Tables for X-ray Crystallography*[9] and those for the remaining atoms were those incorporated in SHELX76.[7] Listings of thermal parameters, hydrogen atom parameters, all bond distances and angles, and the observed and calculated structure factors are available on request from the Editor.

TABLE II

Fractional atomic coordinates ($\times 10^5$ for Ag, $\times 10^4$ for other atoms) for [Ag(dppe)$_2$]NO$_3$.

Atom	*x/a*	*y/b*	*z/c*
Ag	22363(5)	1852(4)	24386(5)
P(1)	3048(2)	−576(1)	1488(2)
P(2)	1169(2)	−799(1)	2559(2)
P(3)	1512(2)	1320(1)	2129(2)
P(4)	2820(2)	753(1)	3784(2)
C(1)	2214(6)	−1243(5)	1224(6)
C(2)	1755(6)	−1486(5)	2020(6)
C(3)	1780(6)	1802(5)	3102(6)
C(4)	1926(6)	1370(5)	3921(6)
C(111)	3432(4)	−302(3)	471(3)
C(112)	3769(4)	355(3)	436(3)
C(113)	4082(4)	604(3)	−318(3)
C(114)	4059(4)	195(3)	−1036(3)
C(115)	3722(4)	−461(3)	−1000(3)
C(116)	3408(4)	−710(3)	−247(3)
C(121)	4021(4)	−1030(3)	1959(3)
C(122)	4431(4)	−1567(3)	1557(3)
C(123)	5199(4)	−1872(3)	1934(3)
C(124)	5557(4)	−1641(3)	2713(3)
C(125)	5147(4)	−1105(3)	3115(3)
C(126)	4379(4)	−799(3)	2738(3)
C(211)	67(4)	−733(3)	1992(4)
C(212)	15(4)	−304(3)	1293(4)
C(213)	−811(4)	−203(3)	848(4)
C(214)	−1584(4)	−529(3)	1102(4)
C(215)	−1531(4)	−958(3)	1802(4)
C(216)	−706(4)	−1060(3)	2247(4)
C(221)	916(5)	−1166(3)	3569(5)
C(222)	898(5)	−718(3)	4248(5)
C(223)	638(5)	−945(3)	5031(5)
C(224)	395(5)	−1620(3)	5136(5)
C(225)	413(5)	−2067(3)	4457(5)
C(226)	673(5)	−1840(3)	3674(5)
C(311)	1817(5)	1917(3)	1319(4)
C(312)	2196(5)	1668(3)	595(4)
C(313)	2414(5)	2110(3)	−48(4)
C(314)	2254(5)	2801(3)	32(4)
C(315)	1875(5)	3050(3)	756(4)
C(316)	1657(5)	2608(3)	1399(4)
C(321)	287(5)	1337(4)	2030(4)
C(322)	−174(5)	1640(4)	1340(4)
C(323)	−1116(5)	1656(4)	1293(4)
C(324)	−1596(5)	1369(4)	1935(4)
C(325)	−1134(5)	1066(4)	2625(4)
C(326)	−193(5)	1049(4)	2673(4)

TABLE II cont.

Atom	*x/a*	*y/b*	*z/c*
C(411)	3001(4)	368(3)	4828(5)
C(412)	2471(4)	516(3)	5504(5)
C(413)	2619(4)	178(3)	6271(5)
C(414)	3297(4)	−309(3)	6362(5)
C(415)	3828(4)	−457(3)	5685(5)
C(416)	3679(4)	−119(3)	4918(5)
C(421)	3804(5)	1294(3)	3690(4)
C(422)	4260(5)	1281(3)	2943(4)
C(423)	4991(5)	1711(3)	2844(4)
C(424)	5266(5)	2155(3)	3491(4)
C(425)	4810(5)	2168(3)	4238(4)
C(426)	4079(5)	1738(3)	4337(4)
N(1)	6823(8)	2530(6)	995(9)
O(1)	6883(9)	2395(5)	247(8)
O(2)	7175(11)	3020(7)	1262(10)
O(3)	6392(7)	2148(6)	1426(7)

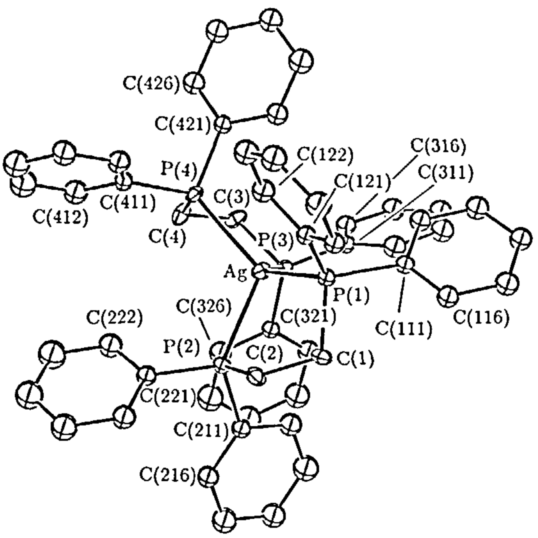

FIGURE 1 Molecular structure and crystallographic numbering scheme for $[Ag(dppe)_2]NO_3$.

RESULTS AND DISCUSSION

The molecular structure of $[Ag(dppe)_2]NO_3$ is shown in Figure 1 and selected interatomic parameters are listed in Table III. The Ag atom is chelated by two dppe ligands and exists in a distorted tetrahedral geometry. The Ag–P bond distances fall in two distinct groups with Ag–P of 2.488(3) Å in one set and 2 × 2.523(3) and 2.527(3) Å in the other. This distribution is consistent with a slightly flattened

TABLE III

Selected bond distances (Å) and angles (°) for [Ag(dppe)$_2$]NO$_3$.

Distances			
Ag-P(1)	2.488(3)	Ag-P(2)	2.523(3)
Ag-P(3)	2.527(3)	Ag-P(4)	2.523(3)
P(1)-C(1)	1.842(9)	P(2)-C(2)	1.848(9)
P(3)-C(3)	1.840(9)	P(4)-C(4)	1.825(9)
P(1)-C(111)	1.822(6)	P(1)-C(121)	1.826(6)
P(2)-C(211)	1.827(7)	P(2)-C(221)	1.817(7)
P(3)-C(311)	1.821(7)	P(3)-C(321)	1.815(7)
P(4)-C(411)	1.829(7)	P(4)-C(421)	1.823(7)
C(1)-C(2)	1.54(1)	C(3)-C(4)	1.56(1)
N(1)-O(1)	1.22(2)	N(1)-O(2)	1.17(2)
N(1)-O(3)	1.22(1)		
Angles			
P(1)-Ag-P(2)	84.5(1)	P(1)-Ag-P(3)	129.5(1)
P(1)-Ag-P(4)	128.8(1)	P(2)-Ag-P(3)	116.0(1)
P(2)-Ag-P(4)	117.9(1)	P(3)-Ag-P(4)	83.8(1)
Ag-P(1)-C(1)	103.4(3)	Ag-P(1)-C(111)	122.7(2)
Ag-P(1)-C(121)	116.6(2)	C(1)-P(1)-C(111)	104.5(4)
C(1)-P(1)-C(121)	104.3(4)	C(111)-P(1)-C(121)	103.4(3)
Ag-P(2)-C(2)	102.8(3)	Ag-P(2)-C(211)	117.1(2)
Ag-P(2)-C(221)	122.4(2)	C(2)-P(2)-C(211)	104.8(4)
C(2)-P(2)-C(221)	103.8(4)	C(211)-P(2)-C(221)	103.9(3)
Ag-P(3)-C(3)	103.2(3)	Ag-P(3)-C(311)	126.5(2)
Ag-P(3)-C(321)	116.5(2)	C(3)-P(3)-C(311)	101.8(4)
C(3)-P(3)-C(321)	103.5(4)	C(311)-P(3)-C(321)	102.3(3)
Ag-P(4)-C(4)	100.4(3)	Ag-P(4)-C(411)	127.3(3)
Ag-P(4)-C(421)	115.6(2)	C(4)-P(4)-C(411)	104.1(4)
C(4)-P(4)-C(421)	101.9(4)	C(411)-P(4)-C(421)	103.9(3)

tetrahedral geometry about the Ag atom; the dihedral angle between the AgP(1)P(2) and AgP(3)P(4) planes is calculated to be 88.7°. The Ag–P bond distances reported here for [Ag(dppe)$_2$]NO$_3$ may be compared to those found in the closely related [Ag(PPh$_3$)$_4$]$^+$ complexes for which there are four separate crystal structure determinations. The Ag–P bond distances in the latter compounds are all longer than the Ag–P bond distances in [Ag(dppe)$_2$]NO$_3$. In [Ag(PPh$_3$)$_4$]X, with the cation situated on a crystallographic 3-fold axis (*i.e.*, two unique Ag–P bond distances), a similar trend is observed as for [Ag(dppe)$_2$]NO$_3$, there being one short Ag–P bond and three longer Ag–P bonds: X = ClO$_4^-$ 1 × 2.650(2), 3 × 2.668(5)[10]; X = NO$_3^-$ 1 × 2.643(3), 3 × 2.671(4)[11]; and X = PF$_6^-$ 1 × 2.639(2), 3 × 2.674(1) Å[12]. In the X = [SnPh$_2$(NO$_3$)$_2$(Cl,NO$_3$)]$^-$ salt,[13] the above trend is reserved, with one longer Ag–P bond distance of 2.746(5) Å and three shorter Ag–P bond distances of 2.615(6), 2.631(5) and 2.645(5) Å. The increased steric pressure arising from the presence of four bulky triphenylphosphine ligands in the [Ag(PPh$_3$)$_4$]$^+$ complexes has the result that the Ag–P distances are longer compared to those observed in [Ag(dppe)$_2$]NO$_3$. The elongation of the Ag–P bond distance in the [Ag(PPh$_3$)$_4$]$^+$ compounds enables the central Ag atom to attain a more regular tetrahedral geometry as manifested by the P–Ag–P angles of *ca* 109° in the X = ClO$_4^-$, NO$_3^-$ and PF$_6^-$ salts and angles that lie in the narrow range 105.9(2)–113.0(2)° in the X = $[SnPh_2(NO_3)_2(Cl, NO_3)]^-$ salt. In contrast, while the Ag–P bond distances are shorter in $[Ag(dppe)_2]NO_3$ owing to comparatively less steric pressure due to the phenyl groups, there are significant distortions away from ideal tetrahedral geometry which can be related to the restricted bite distances of the dppe ligands. The P–Ag–P chelate angles are 84.5(1) and 83.8(1)° and as a consequence the remaining P–Ag–P angles are significantly greater than the ideal tetrahedral angle being 116.0(1), 117.9(1), 128.8(1) and 129.5(1)° to compensate for the acute chelate angles. Bond distances and angles associated with the dppe ligands and with the nitrate groups are as expected.

The structure of $[Ag(dppe)_2]NO_3$ may also be compared to that found for $[Au(dppe)_2]^+$ isolated as the Cl^- salt[14] and as the SbF_6^- salt.[15] Both compounds exhibit distorted tetrahedral geometries about the central atom owing to the presence of two chelating diphosphine ligands. In the $[Au(dppe)_2]^+$ compounds the Au–P bond distances range from 2.384(2) to 2.412(2) Å in the Cl^- salt[14] and 2.389(3)–2.416(3) Å in the SbF_6^- salt.[15] These distances are significantly less than the Ag–P distances in $[Ag(dppe)_2]NO_3$ even though the Au(I) atom is larger. This anomaly can be explained, however, in terms of the reduced steric pressure exerted by the phosphine ligands about the larger Au(I) atom, compared to that about Ag(I) in $[Ag(dppe)_2]NO_3$, thereby enabling the close approach of the P atoms to the Au(I) centre.

This study demonstrates that the solid state structure of $[Ag(dppe)_2]^+$ and those of $[Au(dppe)_2]^+$ [14,15] are similar thus providing supporting evidence that their mechanism of action, at least to a first approximation, is also similar. It has been proposed that the antitumor activity of these complexes arises from the fact that the metal ion, in the complex, 'delivers' the cytotoxic phosphine ligands to the target cells at which stage M–P bond cleavage occurs.[16] The role of the metal ion is to protect the phosphine ligand from chemical reactions on route to the cancerous cells.

ACKNOWLEDGEMENTS

Support from the Australian Research Council is acknowledged.

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