

Preparation and Structural Characterization of [Ag₂(NO₃)₂(P(OPh)₃)₄]

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Di- μ -nitrate-bis[bis(triphenylphosphite)silver(I)] has been synthesized and characterized by ³¹P and ¹⁰⁹Ag NMR spectroscopy and X-ray diffraction. The crystal structure has been determined by X-ray single crystal analysis. The crystals are orthorhombic, space group *Fdd2*, $a=40.507(15)$, $b=25.917(14)$, $c=13.355(5)$ Å and $Z=8$. The structure was solved by direct and subsequent Fourier methods and refined to an R value of 0.057 for 2032 independent reflections. The dimeric molecule possesses a crystallographic two-fold symmetry with the Ag–Ag distance of 4.055(1) Å. The silver atom is four-coordinated with an O–Ag–O angle of 71.9(3)° and a P–Ag–P angle of 147.9(1)°. The Ag–P bond distances are 2.403(5) and 2.402(5) Å. Only one oxygen of the nitrate group coordinates and forms unsymmetrical bridges between the two silvers with the Ag–O distances of 2.366(8) and 2.641(8) Å. The ³¹P and ¹⁰⁹Ag NMR spectra exhibit a single resonance at room temperature indicating that the compound undergoes a rapid exchange of the phosphite ligands in chloroform solution.

There has been considerable interest recently in the syntheses and structural characterization of mixed metal cluster compounds containing AuPR₃ fragments. These gold derivatives are commonly prepared by the direct reaction of cluster anions with an equivalent amount of trialkyl- or triarylphosphinegold(I) moiety.^{1–4} In some cases, investigations of the structures of the gold derivatives may be more appropriate than studies of the cluster anions or their hydrides themselves, particularly in the cases where the hydrides are unstable or fluxional and the location of the hydrogen atom cannot be determined by X-ray diffraction.⁵ On the contrary, there are few reports of similar heteronuclear metal clusters with silver.^{6–9} Along with R₃PAuX complexes for the preparation of mixed metal clusters, we are interested in silver phosphines and phosphites, too. The results of structural studies on phosphine and phosphite complexes of silver(I)^{10–17} show that the compounds are mostly polymeric and the silver atom is either three- or four-coordinated in solid state. In solutions they may dissociate and/or disproportionate, phosphine complexes being more labile than phosphite ones.¹⁸ Gold complexes show, however, a pronounced tendency to exhibit a linear two-fold coordination and form rather easily AuPR₃ fragments in solution for synthesis of mixed metal clusters.^{19–22} In this paper we report a single crystal X-ray diffraction study of di- μ -nitrate-bis[bis(triphenylphosphite)silver(I)] and results on its NMR measurements in chloroform at room temperature.

EXPERIMENTAL

Synthesis. Di- μ -nitrate-bis[bis(triphenylphosphite)silver(I)] was prepared by adding 0.011 mol of triphenylphosphite to a stirred diethyl ether solution (30 ml) containing 0.011 mol of silver(I) nitrate. After 10 minutes a white solid was filtered off and washed with ether. The precipitate was extracted with acetone and after concentration and cooling of the solution white crystals of the title compound separated. The crystals decompose slowly in air and have a mp of 95–100 °C (dec.).

Crystallography. A single crystal of dimensions 0.25×0.30×0.30 mm was selected for the X-ray investigation and mounted on a glass fiber and coated with epoxy super glue. The lattice parameters were obtained from a least-squares refinement of 23 well centered reflections measured on a Nicolet R3m diffractometer using graphite monochromatized MoK α radiation ($\lambda=0.71069$ Å). Crystal data: $a=40.507(15)$, $b=25.917(14)$, $c=13.355(5)$ Å, $Z=8$, $D_m=1.48$, $D_c=1.498$ g/cm³, space group $Fdd2$, $\mu(\text{MoK}\alpha)=1.75$ cm⁻¹.

Intensity data were collected ($5 < 2\theta < 50^\circ$) at room temperature using ω -scan technique and a scan rate varying from 2.0 to 29.3° min⁻¹ depending upon the peak intensity. The intensities of three check reflections, recorded after every 97 measurements, remained essentially constant throughout the data collection. Out of 3234 independent reflections measured, 2032 had $I > 2.5\sigma(I)$, and were used in the structure determination. The data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct and subsequent Fourier syntheses using the SHELXTL program package.²³ Refinement for a model in which atoms not in the phenyl rings were anisotropic and the carbon atoms of the phenyl rings were isotropic with riding hydrogen atoms ($C-H=0.96$ Å and $U(H)=1.2xU(C)$) gave an R index of 0.057. The weighting scheme was $w^{-1}=\sigma^2(F)+0.0005F^2$. The largest peak on the final difference map was close to O22 and had an electron density of 0.5 eÅ⁻³.

NMR studies. Room temperature ³¹P and ¹⁰⁹Ag NMR spectra were obtained on a Bruker AM-250 spectrometer operating at 101.26 and 11.64 MHz, respectively. The ³¹P chemical shifts are in ppm against the external 85 % H₃PO₄ standard. The ¹⁰⁹Ag chemical shifts are reported in ppm relative to the external AgNO₃ standard.

RESULTS AND DISCUSSION

The atomic coordinates and isotropic temperature factors are given in Table 1. Lists of the structure factors and anisotropic thermal parameters can be obtained from the authors. The dimeric molecular structure of [Ag₂(NO₃)₂(P(OPh)₃)₄] is shown in Fig. 1. Bond distances and angles within the nitrate and phosphite groups are listed in Table 2. Interatomic distances around the silver atom are given in Table 3.

The unit cell contains eight [Ag₂(NO₃)₂(P(OPh)₃)₄] dimers held together by van der Waals' forces. The shortest intermolecular distances are between C224...O3', 3.375 Å, C223...O3', 3.496 Å, C114...O2'', 3.430 Å and C213...C315''', 3.567 Å; the others being longer than 3.6 Å.

The dimeric molecule possesses a crystallographic two-fold symmetry with the Ag–Ag distance of 4.055(1) Å. The silver atom is surrounded by two triphenylphosphite ligands and two bridging nitrate groups. The present structure resembles that of [Ag₂(NO₃)₂(P(OMe)₃)₄].¹¹ The Ag–P distances of 2.403 and 2.402 Å are in good agreement with the distances of 2.411 and 2.412 Å found in the trimethylphosphite complex but they are somewhat longer than the Ag–P distance of 2.369 Å found in [{AgNO₃(PPh)₃}]_n.¹⁰ This is expected as the accepting ability of Ag decreases with the increasing number of coordinated good-donor atoms.^{15,17,20,22}

The main difference between the structures of this and the trimethylphosphite complex is found in the Ag–O bond distances of the nitrate bridges. In the trimethylphosphite complex

Table 1. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3 \text{ \AA}^2$).^a

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U
Ag	12(1)	782(1)	0	75(1)
P1	-239(1)	989(1)	1581(4)	67(1)
P2	137(1)	1046(1)	-1682(3)	72(1)
O11	-49(2)	1385(3)	2302(6)	66(3)
O12	-598(2)	1243(3)	1620(7)	72(3)
O13	-295(2)	490(3)	2244(7)	75(3)
O21	432(2)	728(3)	-2130(7)	88(4)
O22	-126(3)	957(8)	-2575(11)	190(9)
O23	221(5)	1596(4)	-1951(10)	203(9)
O1	362(2)	52(3)	33(13)	85(3)
O2	862(3)	-156(6)	303(11)	177(8)
O3	720(3)	621(6)	97(14)	161(8)
N	656(3)	159(6)	146(10)	89(6)
C111	284(3)	1432(4)	2336(9)	61(3)
C112	482(3)	1048(5)	2461(11)	83(4)
C113	839(4)	1089(6)	2574(13)	102(5)
C114	955(4)	1575(5)	2545(13)	98(4)
C115	761(4)	1980(6)	2381(13)	103(5)
C116	422(3)	1923(5)	2263(11)	85(4)
C121	-659(3)	1688(5)	1113(10)	66(3)
C122	-614(3)	2148(5)	1581(13)	88(4)
C123	-686(4)	2608(6)	1092(12)	99(5)
C124	-797(4)	2602(6)	105(15)	107(5)
C125	-852(3)	2136(5)	-334(12)	93(4)
C126	-781(3)	1679(5)	152(11)	82(4)
C131	-456(3)	486(5)	3171(10)	64(3)
C132	-283(4)	585(6)	4019(14)	110(5)
C133	-436(4)	559(7)	4942(17)	129(6)
C134	-763(4)	409(6)	4968(16)	112(5)
C135	-921(4)	304(6)	4141(15)	111(5)
C136	-775(4)	333(6)	3204(13)	94(5)
C211	630(3)	828(5)	-2966(10)	71(4)
C212	951(4)	900(6)	-2823(13)	100(5)
C213	1155(4)	1001(6)	-3683(14)	110(5)
C214	1034(4)	1014(6)	-4559(14)	109(5)
C215	706(4)	971(7)	-4756(15)	127(6)
C216	491(4)	853(5)	-3878(12)	99(5)
C221	-465(4)	971(6)	-2436(14)	91(5)
C222	-617(3)	1442(6)	-2747(11)	97(5)
C223	-967(4)	1448(6)	-2676(12)	103(5)
C224	-1129(4)	1068(6)	-2330(12)	103(5)
C225	-964(4)	640(6)	-2041(13)	109(5)
C226	-644(4)	580(6)	-2079(11)	92(4)
C231	307(3)	2001(6)	-1295(12)	91(4)
C232	69(4)	2289(6)	-920(13)	106(5)
C233	162(5)	2739(8)	-327(17)	152(8)
C234	515(5)	2812(7)	-239(15)	131(6)
C235	713(6)	2473(8)	-591(20)	152(8)
C236	606(5)	2064(8)	-1128(17)	140(7)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond distances (Å) and angles (°) in the ligands of $[\text{Ag}_2(\text{NO}_3)_2(\text{P}(\text{OPh})_3)_4]$.

Distances			
P1-O11	1.603(9)	O11-C111	1.355(13)
P1-O12	1.597(8)	O12-C121	1.359(15)
P1-O13	1.583(10)	O13-C131	1.400(16)
P2-O21	1.571(10)	O21-C211	1.399(16)
P2-O22	1.615(14)	O22-C221	1.387(18)
P2-O23	1.509(13)	O23-C231	1.412(20)
C-C (av)	1.36(2)	N-O1	1.231(15)
		N-O2	1.184(21)
		N-O3	1.228(22)
Angles			
P1-O11-C111	123.7(7)	O11-P1-O12	98.8(4)
P1-O12-C121	119.9(7)	O11-P1-O13	104.8(5)
P1-O13-C131	124.6(8)	O12-P1-O13	100.8(5)
P2-O21-C211	130.1(8)	O21-P2-O22	98.3(7)
P2-O22-C221	123.3(13)	O21-P2-O23	103.5(9)
P2-O23-C231	127.6(12)	O22-P2-O23	96.2(10)
C-C-C (av)	120.0(16)	O1-N-O2	123.2(15)
O-C-C (av)	119.4(13)	O1-N-O3	114.6(13)
		O2-N-O3	122.2(14)

Table 3. Interatomic distances (Å) and angles (°) around the silver atom in $[\text{Ag}_2(\text{NO}_3)_2(\text{P}(\text{OPh})_3)_4]$.

Distances			
Ag-Ag ⁱ	4.055(1)	Ag-O3	2.901(9)
Ag-P1	2.403(5)	Ag-O2 ⁱ	3.913(9)
Ag-P2	2.402(5)		
Ag-O1	2.366(8)		
Ag-O1 ⁱ	2.641(8)		
Angles			
P1-Ag-P2	147.9(1)	Ag-P1-O11	117.9(3)
P1-Ag-O1	114.6(4)	Ag-P1-O12	120.4(4)
P1-Ag-O1 ⁱ	85.7(4)	Ag-P1-O13	111.7(4)
P2-Ag-O1	96.8(4)	Ag-P2-O21	111.6(4)
P2-Ag-O1 ⁱ	111.7(4)	Ag-P2-O22	120.8(5)
O1-Ag-O1 ⁱ	71.9(3)	Ag-P2-O23	122.6(6)
Ag-O1-N	113.7(9)	Ag-O1-Ag ⁱ	108.1(3)
Ag ⁱ -O1-N	137.8(9)		

both nitrate groups form symmetrical bridges between the silver atoms with the Ag-O and Ag-O' distances of 2.455 and 2.454 Å, respectively.¹¹ In the present compound the Ag-O distances are 2.366 and 2.641 Å. In addition the second nitrate oxygen atom forms a short contact of 2.901 Å with the silver atom thus the nitrate groups can be considered as an unsymmetrically bridging and chelating ligand. The two longer silver-oxygen interactions are facilitated by the bending of the N-O3 bond of the nitrate group. This is evidenced by the small O1-N-O3 angle of 114.6° vs. angles of 123.2 and 122.2° for O1-N-O2 and

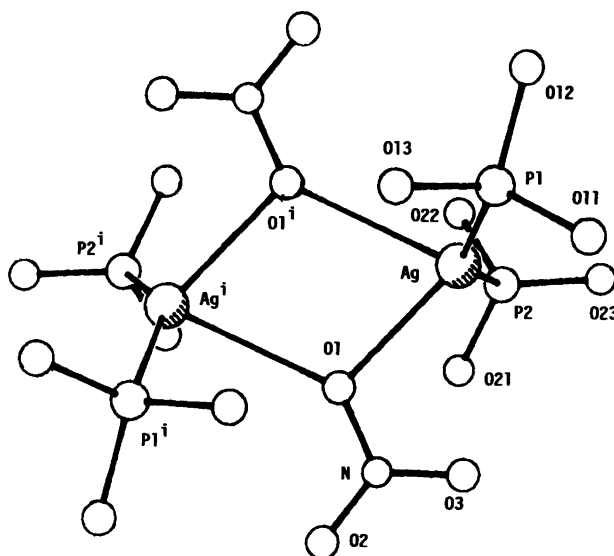


Fig. 1. View of the dimeric array and atom-numbering scheme.

O2–N–O3, respectively. The three nitrogen–oxygen bond distances fit within the uncertainties of the measurement the expected values for two interacting oxygens (N–O1, 1.231 Å; N1–O3, 1.228 Å; N–O2, 1.184 Å). The elongation of the N–O distances of the oxygens O1 and O3 in the present structure is not as great as normally observed. For a large group of symmetrical bidentate nitrates a coordinated N–O distance of 1.27 Å has been observed.²⁴ At the same time the terminal N–O distances are shortened to 1.20 Å due to polarization of the coordinated nitrate group. A similar trend seems to be effective in the present molecule.

The Ag–O distance of 2.901 Å is shorter than the corresponding distance of 3.102 Å in the trimethylphosphite complex where the distance was alleged to be short enough for silver–oxygen orbital overlap.¹¹ The distance may also be due to crystal packing forces since it is appreciably longer than the Ag–O covalent bond length²⁵ and only 0.1 Å shorter than the sum of van der Waals' radii for silver and oxygen.²⁶ Thus the silver atom also in the present compound is best regarded as four-coordinated, the coordination sphere being distorted tetrahedron. The P–Ag–P angle of 147.9° is primarily due to steric effects caused by bulky phenyl rings bound to the phosphorus atoms. The two phosphorus atoms, the closest oxygen O1 and the silver atom are nearly coplanar (Fig. 2), the average deviation of the atoms from the least-squares plane being under 0.08 Å.

The unsymmetric bridging of the nitrate group between the two silver atoms in the solid state reflects the lability of the dimeric structure to break down to AgL_2NO_3 monomers. A bisphosphite complex $\text{Ag}(\text{P}(\text{OEt})_3)_2\text{NO}_3$ has been shown by molecular weight measurements to be monomeric in solution.¹⁸ Based on the observed low conductivity it probably exists in solution as a neutral complex for which a tetrahedral structure with a bidentate nitrate group has been suggested. This triethylphosphite complex has also been observed through analysis of ^{31}P NMR data to undergo ligand exchange at a rate comparable to those of the tetrahedral AgXL_3 complexes.¹⁸ The phosphite ligands of the present complex are also labile on the basis of the ^{31}P and ^{109}Ag NMR. Only a single resonance was observed at

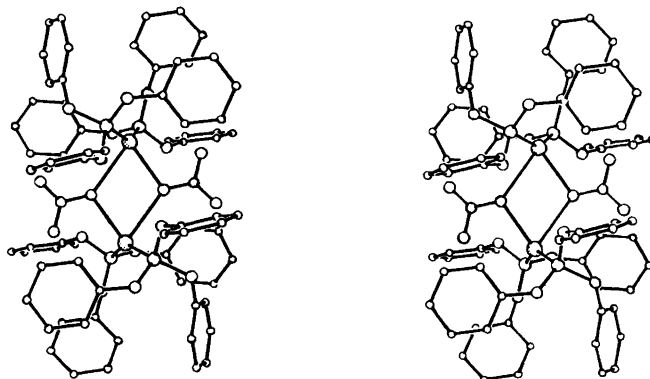


Fig. 2. Stereoview of the molecule of $[\text{Ag}_2(\text{NO}_3)_2(\text{P}(\text{OPh})_3)_4]$.

108.9 ppm for the ^{31}P nuclei and at 409 ppm for the ^{109}Ag nuclei at room temperature (in CDCl_3). The isostructural complex $[\text{Ag}_2(\text{NO}_3)_2(\text{P}(\text{OMe})_3)_4]$ similarly dissociates in solution to give a mixture of species whose identities are unknown.¹¹ The complex nature of ligand dissociation in the silver phosphite and phosphine complexes¹⁸ may be one explanation for the mixed metal clusters containing AgPR_3 or $\text{AgP}(\text{OR})_3$ fragments being less common than those with AuPR_3 groups.

Acknowledgements. This research was supported by a research grant from the University of Joensuu. We are also grateful to Mr. Jouko Vepsäläinen, M.Sc., for measuring the NMR spectra.

REFERENCES

1. Bruce, M.I. and Nicholson, B.K. *Organometallics* 3 (1984) 101.
2. Barrientos-Penna, C.F., Einstein, F.W.B., Jones, T. and Sutton, D. *Inorg. Chem.* 24 (1985) 632.
3. Casalnuovo, A.L., Laska, T., Nilsson, P.V., Olofson, J. and Pignolet, L.H. *Inorg. Chem.* 24 (1985) 233.
4. Casalnuovo, A.L., Laska, T., Nilsson, P.V., Olofson, J., Pignolet, L.H., Bos, W., Bour, J.J. and Steggerda, J.J. *Inorg. Chem.* 24 (1985) 182.
5. Lauher, J.W. and Wald, K. *J. Am. Chem. Soc.* 103 (1981) 7648.
6. Freeman, M.J., Green, M., Orpen, A.G., Salter, I.D. and Stone, F.G.A. *J. Chem. Soc. Chem. Commun.* (1983) 1332.
7. Braunstein, P. and Rose, J. *J. Organomet. Chem.* 262 (1984) 223.
8. Briant, C.E., Smith, R.G. and Mingos, D.M.P. *J. Chem. Soc. Chem. Commun.* (1984) 586.
9. Mayes, M.J., Raithby, P.R. and Taylor, P.L. *J. Chem. Soc. Dalton Trans.* (1984) 959.
10. Stein, R.A. and Knobler, C. *Inorg. Chem.* 16 (1977) 242.
11. Meiners, J.H., Clardy, J.C. and Verkade, J.G. *Inorg. Chem.* 14 (1975) 632.
12. Teo, B.K. and Calabrese, J.C. *Inorg. Chem.* 15 (1976) 2467.
13. Teo, B.K. and Calabrese, J.C. *Inorg. Chem.* 15 (1976) 2474.
14. Cassel, A. *Acta Crystallogr. B* 35 (1979) 174.
15. Cassel, A. *Acta Crystallogr. B* 37 (1981) 229.
16. Alyea, E.C., Ferguson, G. and Somogyvari, A. *Inorg. Chem.* 21 (1982) 1369.
17. Engelhardt, L.M., Pakawatchai, C. and White, A.H. *J. Chem. Soc. Dalton Trans.* (1985) 125.

18. Mutterties, E.L. and Alegranti, W. *J. Am. Chem. Soc.* 84 (1972) 6386.
19. Baenziger, N.C., Dittmore, K.M. and Doyle, J.R. *Inorg. Chem.* 13 (1974) 805.
20. Hitchcock, P.B. and Pye, P.L. *J. Chem. Soc. Dalton Trans.* (1977) 1457.
21. Demartin, F., Manassero, M., Naldini, L., Ruggeri, R. and Sansoni, M. *J. Chem. Soc. Chem. Commun.* (1981) 222.
22. Muir, J.A., Muir, M.M., Arias, S., Jones, P.G. and Sheldrick, G.M. *Inorg. Chim. Acta* 81 (1984) 169.
23. Sheldrick, G.M. *The SHELXTL System, Rev. 3*, Nicolet Co., U.S.A. 1981.
24. Addison, C.C., Logan, N., Wallwork, S.C. and Garner, C.D. *Quart. Rev. Chem. Soc.* 25 (1971) 289.
25. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, N.Y. 1960.
26. Bondi, A. *J. Phys. Chem.* 68 (1964) 441.

Received May 2, 1985.