direct-methods programs, Iber's NUCLS group least-squares refinement program based on Busing and Levy's ORFLS, Busing and Levy's ORFFE, Johnson's ORTEP plotting program, Corfield's RANGER weighting analysis program, and the general absorption program AGNOST.[11] All computations were performed on a CDC 6400 computer.

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Crystal and Molecular Structure of $[Ag(P(OMe)_3)_2NO_3]_2$. A Case of Symmetric Nitrate–Oxygen Bridging

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The crystal and molecular structure of tetrakis(trimethyl phosphite)-di-μ-nitrato-disilver(I), $[Ag(P(OMe)_3)_2NO_3]_2$, has been determined by single-crystal X-ray diffraction methods. The compound crystallizes in the orthorhombic P_{bca} space group with four molecules per unit cell of which the dimensions are $a = 9.146$ (3), $b = 16.769$ (4), and $c = 20.689$ (6) Å. The structure was solved by the heavy-atom method and refined by least-squares calculations to a final R of 0.048 with 1233 independent reflections. While the molecule is a centrosymmetric dimer in the crystalline state with an Ag–Ag bond distance of 4.095 (2) Å, molecular weight determinations indicate the presence of extensive dissociation in solution. The geometry around the silver atom in the solid state is a greatly distorted tetrahedron with an OAgO angle of 67.0 (3)° and a PAgP angle of 133.8 (1)°. The bridging oxygens are equidistant (2.456 (8) and 2.454 (8) Å) from both silvers.

Introduction

In a recent review[2] on nitrate coordination, the authors sort the known structures into three classes: bidentate, unidentate, and bridging nitrate systems. The bidentate class is subdivided into a symmetric group, wherein both metal–oxygen distances are the same, and an unsymmetric group, in which they differ by 0.2–0.7 Å. If this difference is greater than 0.7 Å, the nitrate is considered to be unidentate. Unidentate coordination may also be subclassified as symmetrical if the two metal to noncoordinated oxygen distances are equal or unsymmetrical if these distances are not equal. Many crystal structures of coordinated nitrate complexes have been reported. Classification is not unambiguous inasmuch as some nitrates fall into more than one category[3] and some of the complexes have more than one type of coordinated nitrate.[4,5]

Of the more than 50 compounds containing coordinated nitrate whose structures are known,[2,5-8] about half possess one or more symmetrical bidentate nitrate groups, about 20% have a unidentate nitrate, and approximately 15% have an unsymmetrical bidentate nitrate, leaving almost 15% containing bridging nitrates. The preferred coordination mode of a bridging nitrate utilizes two oxygens, one bound to each metal. The cases in which one nitrate oxygen is coordinated to more than one metal are limited. There is evidence for one oxygen being coordinated to three metal atoms[9] in $Cu_4(NO_3)_2(OH)_6$ although further refinement would be desirable in view of the high R factor (0.30). To our knowledge there are only two cases in which only one oxygen is coordinated to two metal atoms[3,4] and in both cases the two metal–oxygen distances are significantly different. Here we report the first example of a bridged nitrate complex in which the bridging occurs *via* one oxygen which is equidistant from both metal atoms.

Experimental Section

The silver complex was prepared as previously described.[10a] Crystals were grown by dissolving about 2 g in 20 ml of acetone, adding 20 ml of ether, and then adding pentane until slightly cloudy. Slowly cooling the solution to −78° produced clear, colorless, nearly cubic crystals. Inasmuch as they are sensitive to prolonged exposure to atmospheric conditions, one of them was mounted in a 0.3-mm sealed Lindemann capillary tube. Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory. The upper full circle was purchased from STOE and is equipped with encoders (Baldwin Optical) and drive motors. The design of the base allows the encoders to be directly connected to the main θ and 2θ shafts, using solid and hollow shaft encoders, respectively. The diffractometer is interfaced to a PDP-15 computer in a real-time mode and is equipped with a scintillation counter. The χ, ω, and 2θ angles of 13 reflections were tuned and these values were used to calculate[10b] the reduced cell. This cell was

Table I. Final Positional and Anisotropic Parameters for $[Ag(P(OMe)_3)_2NO_3]_2$

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag1	0.00755 (9)	0.01212 (4)	0.09839 (4)	0.0135 (1)	0.00553 (4)	0.00278 (2)	0.0013 (7)	0.00035 (5)	−0.00021 (2)
P1	0.1722 (3)	0.1153 (2)	0.1340 (1)	0.0119 (4)	0.0046 (1)	0.00324 (9)	−0.0006 (2)	−0.0006 (2)	0.00009 (9)
P2	−0.1503 (3)	−0.0806 (1)	0.1537 (1)	0.0155 (5)	0.0044 (1)	0.00341 (9)	−0.0009 (2)	0.0015 (2)	−0.00025 (9)
O1	0.1022 (10)	−0.0583 (5)	0.0031 (3)	0.020 (1)	0.0079 (5)	0.0029 (2)	0.0056 (7)	0.00005 (48)	−0.00003 (26)
N1	0.2221 (12)	−0.0962 (6)	0.0110 (5)	0.01557 (18)	0.0050 (5)	0.0039 (4)	0.0008 (8)	−0.0007 (7)	−0.00036 (35)
O2	0.2746 (11)	−0.0941 (7)	0.0649 (5)	0.0236 (19)	0.0132 (7)	0.0050 (3)	0.0053 (9)	−0.0041 (7)	−0.00005 (40)
O3	0.2700 (10)	−0.1345 (6)	−0.0336 (5)	0.0185 (16)	0.0096 (6)	0.0075 (4)	0.0023 (8)	0.0021 (7)	−0.0038 (4)
O11	0.1156 (12)	0.2004 (5)	0.1466 (6)	0.0325 (21)	0.0051 (4)	0.0101 (5)	0.0019 (8)	−0.0095 (9)	−0.0018 (4)
O12	0.2303 (9)	0.0951 (4)	0.2031 (3)	0.0248 (16)	0.0072 (4)	0.0037 (2)	0.0030 (7)	−0.0037 (2)	0.0009 (2)
O13	0.3158 (10)	0.1319 (7)	0.0950 (5)	0.0227 (16)	0.0149 (8)	0.0053 (3)	−0.0116 (10)	0.0012 (7)	−0.0015 (4)
O21	−0.3201 (10)	−0.0809 (6)	0.1395 (4)	0.0188 (15)	0.0110 (7)	0.0046 (3)	−0.0070 (9)	−0.0005 (5)	0.0006 (3)
O22	−0.1368 (8)	−0.0691 (4)	0.2284 (3)	0.0137 (11)	0.0076 (4)	0.0034 (2)	−0.0015 (5)	−0.00004 (44)	0.0008 (2)
O23	−0.1271 (17)	−0.1715 (5)	0.1461 (6)	0.0609 (38)	0.0051 (4)	0.0093 (5)	−0.0012 (11)	0.0151 (12)	−0.0009 (4)
C11	0.0082 (16)	0.2408 (8)	0.1066 (7)	0.0205 (23)	0.0070 (6)	0.0065 (6)	0.0020 (12)	−0.0017 (11)	0.0009 (5)
C12	0.3312 (20)	0.1450 (9)	0.2394 (7)	0.0329 (33)	0.0091 (8)	0.0052 (5)	−0.0027 (14)	−0.0061 (12)	−0.0003 (5)
C13	0.3387 (18)	0.1210 (10)	0.0295 (6)	0.0310 (31)	0.0120 (10)	0.0031 (4)	−0.0052 (15)	0.0024 (10)	−0.00002 (58)
C21	−0.4006 (17)	−0.0063 (11)	0.1396 (9)	0.0196 (26)	0.0111 (11)	0.0072 (7)	0.0035 (15)	0.0002 (34)	0.0011 (7)′
C22	−0.0547 (16)	−0.0063 (11)	0.1038 (8)	0.0246 (27)	0.0059 (7)	0.0077 (7)	0.0031 (11)	0.0027 (12)	−0.0011 (6)
C23	−0.2182 (17)	−0.1150 (8)	0.2760 (6)	0.0292 (31)	0.0086 (8)	0.0039 (4)	−0.0027 (13)	0.0016 (10)	0.0020 (5)

[a] Standard deviations of the least significant number are in parentheses. [b] The anisotropic thermal ellipsoid is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

monoclinic with cell constants $a = 11.341$ Å, $b = 16.767$ Å, $c = 9.185$ Å, $\beta = 113.90°$, and a volume of 1596.8 Å^3. This cell was transformed to an orthorhombic cell with the matrix: $T(1, 1) = 0$, $T(1, 2) = 0$, $T(1, 3) = 1$, $T(2, 1) = -2$, $T(2, 2) = 0$, $T(2, 3) = -1$, $T(3, 1) = 0$, $T(1, 3) = 1$, $T(3, 3) = 0$. This orthorhombic cell measured $a = 9.146$, $b = 20.689$, and $c = 16.769$ Å and was used to collect data. From systematic extinctions $0kl$ ($l = 2n$) $h0l$ ($h = 2n$), $hk0$ ($k = 2n$), $h00$ ($h = 2n$), $0k0$ ($k = 2n$), and $00l$ ($l = 2n$) occurring in the 2399 data points taken, the space group P_{cab} was assigned. When the data were reindexed by switching the values of k and l and by interchanging the crystallographic axes b and c, the cell became $a = 9.146$ (3), $b = 16.769$ (4), and $c = 20.689$ (6) Å. The systematic extinctions in the data were then $0kl$ ($k = 2n$), $h0l$ ($l = 2n$), $hk0$ ($h = 2n$), $h00$ ($h = 2n$), $0k0$ ($k = 2n$), and $00l$ ($l = 2n$) and the space group was P_{bca}. This assignment was confirmed by subsequent solution and refinement of the structure. The density of 1.76 g/cm^3 computed from the unit cell volume of 3174.8 Å^3 on the basis of four $[Ag(P(OMe)_3)_2NO_3]_2$ molecules per unit cell agrees well with the measured density of 1.75 g/cm^3 determined by the flotation method in CCl_4 and 1,2-dibromoethane. The crystal used to collect data measured approximately 0.18 × 0.10 × 0.10 mm.

Data were taken using a peak height data collection mode which maximizes in ω. The data were collected within a 2θ sphere of 45° ($(\sin\theta)/\lambda = 0.537$ Å^{-1}) using unfiltered pyrolytic graphite-monochromatized Mo Kα radiation (0.7107 Å) at a takeoff angle of 5°. The peak heights were measured for 10 sec and background readings were taken for 5 sec after which the background values were scaled up by a factor of 2. During data collection at 21°, the intensities of three standards ((600), (0,10,0), and (008)) were monitored after every 50 reflections. Crystal decomposition was less than 10% and the intensity data were left uncorrected. The observed intensities were corrected for Lorentz and polarization effects and 1293 reflections which had intensities greater than 3σ above background were used in subsequent calculations. The linear absorption coefficient was 14.1 cm^{-1} and no correction was made for absorption. The maximum and minimum transmission factors were 0.869 and 0.775, respectively.

Using a Hewlett-Packard Model 301A vapor pressure osmometer, a molecular weight of 320 in methylene chloride was obtained. Benzil solutions (0.2–0.8 M in methylene chloride) were used to provide a calibration plot. Molecular weight determinations were also obtained by Schwarzkopf Microanalytical Laboratory of Woodside, N.Y. Cryoscopic values obtained by them in acetone and benzene were 351 and 460, respectively. A second cryoscopic benzene determination gave a value of 381 while an osmometric determination in benzene gave a value of 579.

Structure Determination and Refinement

The position of the silver atom was determined from a three-dimensional Patterson function. After three cycles of least-squares refinement of the positional parameters with the isotropic thermal parameters held at 3.0 and a single scale factor, the discrepancy factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ were 0.293 and 0.343, respectively. The set of phased structure factors from the silver contribution was then used to calculate[11] a difference Fourier map which revealed the positions of all the other atoms except hydrogen. Three cycles of refinement[12] on the positional and isotropic thermal parameters of all atoms followed by an additional three cycles with anisotropic thermal parameters assumed for the silver and two phosphorus atoms gave R_1 and R_2 values of 0.082 and 0.079, respectively. Positional and anisotropic thermal parameters of all atoms were then refined producing R_1 and R_2 values of 0.054 and 0.063, respectively. One final refinement of three cycles in which 60 of the 1293 reflections were omitted for which $|F_o - F_c|/|F_c| > 0.25$ and in which the weights, w, were assigned $1/\sigma(F^2)$ gave discrepancy factors of $R_1 = 0.048$ and $R_2 = 0.057$. The ratio of the largest shift in the last refinement cycle to standard deviation was 0.09. The hydrogen atoms were not located.

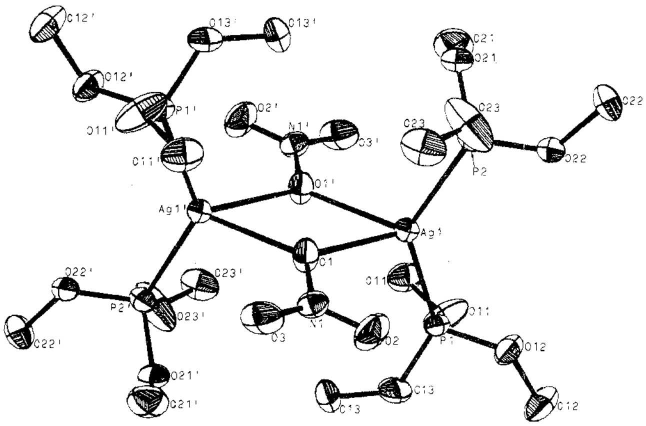

Figure 1. Computer drawing of the structure of $[Ag(P(OMe)_3)_2NO_3]_2$.

The atomic scattering factors used in the refinement were those of Hanson, *et al.*,[13] and the real and imaginary corrections[14] for anomalous dispersion for silver and phosphorus were also included in the calculations.

Results and Discussion

The final positional and anisotropic thermal parameters of the atoms are given in Table I. The unit cell used placed the inversion center of the molecule at the origin; thus the positions of the other atoms needed to complete the dimer structure are symmetry related to those in the table. The final F_o and F_c values (in electrons × 10) for the 1293 reflections used in the refinements have been tabulated.[15] The dimeric molecule revealed by the structure solution is shown in Figure 1.[16] The bridging oxygen (O1) is equidistant from both silver atoms (2.455 (8) Å). Two other crystal structures in which a single

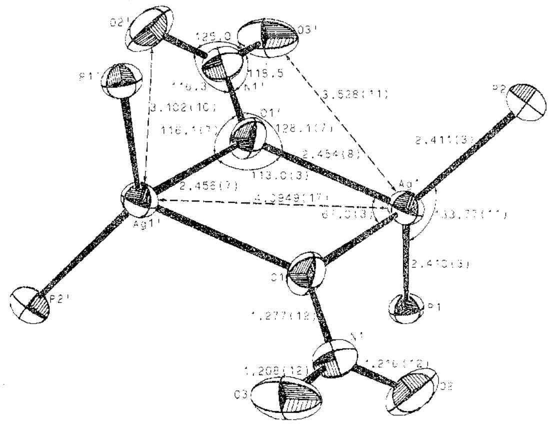

Figure 2. Computer drawing showing the bending of the nitrate groups toward a silver atom in $[Ag(P(OMe)_3)_2NO_3]_2$.

Table II. Interatomic Distances (Å) and Angles (deg) with Standard Deviations in Parentheses

(a) Bonded Distances

Ag1–P1	2.411 (3)	P2–O21	1.580 (10)
Ag1–P2	2.412 (3)	P2–O22	1.562 (8)
Ag1–O1	2.455 (8)	P2–O23	1.547 (10)
Ag1–O1′	2.454 (8)	O11–C11	1.452 (15)
O1–N1	1.277 (12)	O12–C12	1.455 (15)
N1–O2	1.216 (11)	O13–C13	1.384 (15)
N1–O3	1.208 (12)	O21–C21	1.451 (18)
P1–O11	1.539 (9)	O22–C22	1.455 (13)
P1–O12	1.560 (8)	O23–C23	1.299 (16)
P1–O13	1.567 (9)		

(b) Interbond Angles

O1–Ag1–O1′	67.0 (3)	Ag1–P1–O21	120.1 (4)
O1–Ag1–P1	111.7 (2)	Ag1–P2–O22	110.0 (3)
O1–Ag1–P2	106.4 (2)	Ag1–P2–O23	120.3 (5)
O1′–Ag1–P1	111.4 (2)	P1–O11–C11	124.3 (9)
O1′–Ag1–P2	106.9 (2)	P1–O12–C12	124.3 (8)
O1–Ag1–P2	133.77 (11)	P1–O13–C13	127.5 (9)
Ag1–O1–Ag1′	113.0 (3)	P2–O21–C21	131.9 (11)
Ag1–O1–N1	116.1 (7)	P2–O22–C23	124.2 (7)
Ag1′–O1–N1	128.1 (7)	P2–O23–C22	119.6 (9)
O1–N1–O2	116.3 (11)	O11–P1–O12	99.3 (6)
O1–N1–O3	118.5 (11)	O11–P1–O13	101.7 (7)
O2–N1–O3	125.0 (12)	O12–P1–O13	102.9 (5)
Ag1–P1–O11	120.5 (4)	O21–P2–O22	105.2 (4)
Ag1–P1–O12	109.6 (3)	O21–P2–O23	96.4 (7)
Ag1–P1–O13	119.5 (4)	O22–P2–O23	102.2 (6)

(c) Intramolecular Nonbonded Distances

Ag1–Ag1′	4.0949 (17)	O1′–P1	3.908 (9)
O1–O1	2.719 (18)	O1′–P2	4.023 (9)
O1–O2	2.117 (12)	O2–Ag1	3.102 (10)
O1–O3	2.136 (12)	O3–Ag1′	3.528 (11)
O2–O3	2.150 (15)	N1–Ag1	3.228 (12)
O1–P1	4.025 (10)	N1–Ag1′	3.395 (11)
O1–P2	3.897 (8)	P1–P2	4.437 (5)

nitrate oxygen bridges two metal atoms are the α form of copper(II) nitrate[3] and $[Cu(NO_3)_2(py)_2]_2$[4]. Neither compound is symmetrically bridged however, since in the former metal–oxygen distances of 2.43 and 2.68 Å are present and in the latter structure the distances are 2.042 (6) and 2.542 (8) Å. In both cases there is also interaction of a second nitrate oxygen with one of the metals. In the α-$Cu(NO_3)_2$ structure this is unequivocal as the second oxygen–copper distance is only 2.02 Å. In the pyridine complex the distance is 2.906 (7) Å but the authors have proposed[4] that significant interaction is present nonetheless. In our case the closest approach of a second oxygen is 3.102 (10) Å. While this distance is 0.20 Å longer than in $[Cu(NO_3)_2(py)_2]_2$, the covalent radius of silver is 0.17 Å larger than that of copper (1.52 *vs.* 1.35 Å).[17] Thus the 3.102-Å distance may be close enough for silver–oxygen orbital overlap. As can be seen in Figure 2[16] this possible silver–oxygen interaction is occasioned by the bending of the nitrate toward one of the silver atoms. Comparing the Ag–O–N angles of 116 *vs.* 128° as well as the O–N–O angles of 116 *vs.* 119° reveals this distortion. The nitrate plane also seems to be twisted to place the oxygen closer to the silver. Two observations do, however, militate against appreciable interaction between the silver and a second oxygen. First of all, it might have been expected that the bridging oxygens would not be so symmetrical in the presence of the unsymmetrical nonbridging Ag–O bond. Second, both nonbridging O–N distances (N1–O2 and N1–O3) are equal and shorter than the 1.245 (10) Å[18] in free nitrate. It is well known[2,19] that in the nitrate moiety the N–O distance of coordinated oxygens is greater than 1.245 Å. Indeed this distance has been shown to be 1.27 (2) Å for a large group of symmetrical bidentate nitrates[2] while the terminal nitrogen–oxygen lengths in the same group are shortened to 1.20 (2) Å. Both effects have been explained as a result of the high degree of polarization to which coordinated nitrate groups are subjected.[19a] The three nitrogen–oxygen bond lengths found in the present structure fit very well the expected values for only one oxygen being coordinated (N1–O1, 1.277 (12) Å; N1–O2, 1.216 (11) Å; N1–O3, 1.208 (12) Å). Thus a recent crystal structure determination[19b] of the copper(I) complex $(Ph_2MeP)_3CuNO_3$ reveals a unidentate nonbridging nitrate group in which the coordinated oxygen–nitrogen bond (1.166 (8) Å) is shorter than the uncoordinated oxygen–nitrogen distances (1.247 (8) and 1.209 (8) Å). The unsymmetrical angles around the coordinated oxygens in the present structure may be due to packing forces.

Very recently it was shown from an X-ray diffraction study that the silver atoms in polymeric $C_{11}H_{15}AsAg_2(NO_3)_2$ are bridged by two different unique nitrate bridges.[19c] In neither case is assignment regarding bridge type unambiguous, although both nitrates possess one oxygen which is within bonding distance of two metals. In one case these distances are 2.85 (3) and 2.81 (3) Å. The other two oxygens in this instance are 2.45 (3) and 2.35 (3) Å from the two bridged metal atoms, however, which may allow better classification of this nitrate as a two-oxygen bridging system. The second nitrate reveals the unique oxygen to be 2.54 (3) and 2.63 (3) Å from two silver atoms while the other two oxygens are 2.68 (4) and 2.73 (4) Å from their respective metal atoms. Since all these distances are within 0.2 Å, this nitrate could be considered to be bidentate to each metal.

Table II lists the important interatomic distances, angles, and their deviations[20] which were calculated from the final parameters and the correlation matrix. All intermolecular distances are equal to or greater than the sum of van der Waals radii, the shortest being 3.347 (18) Å. The average P–O and C–O distances are 1.560 and 1.416 Å, respectively. These agree well with the P–O and C–O lengths of 1.579 and 1.433 Å found in the trigonal-bipyramidal complex $NiI_2(P(OMe)_3)_3$,[21] the 1.58 and 1.48 Å found for these bonds in $Ni(CN)_2[C_6H_5P(OC_2H_5)_2]_2$,[22] and the average distances of 1.59 and 1.44 Å for the same bonds in $Rh(P(OMe)_3)_2B(C_6H_5)_4$.[23] These values also fall within the range of 1.59 (5) and 1.44 (4) Å tabulated for a number of P–O and CO links, respectively, in orthophosphate esters.[24] The average P–O–C and O–P–O angles are 125.3 and 100.8°, respectively, which lie close to the values of 125.5 and 102.1° found[21] in the nickel iodide complex mentioned above and they are also similar to the 123.6° P–O–C and 101.7° O–P–O angles in the rhodium complex[23] mentioned earlier. Although two other structural studies on complexes containing the trimethyl phosphite ligand have been reported,[25,26a] the interatomic phosphite distances and angles were not given. The O23–C23 distance of 1.299 (16) Å is surprisingly short; however, only P2 at 2.59 (1) Å is within 3.4 Å of C23. Thus there are no obvious packing forces to account for this distance. Nolte and Gafner also

Table III. Least-Squares Best Planes through the Molecule[a]

(a) Planes and Coefficients of the Plane Equation

Plane	Atoms	*a*	*b*	*c*	*d*
1	N1, O1, O2, O3	0.5283	0.8013	−0.2808	+0.3040
2	N1, O1′, O2′, O3′	0.5283	0.8013	−0.2808	−0.3040
3	Ag1, N1, O1, O2, O3	0.5185	0.8127	−0.2657	0.3395
4	Ag1, O1′, O2′, O3′, N1′	0.6442	0.7553	−0.1201	−0.0453
5	Ag1′, O1′, O2′, O3′, N1′	0.5185	0.8127	−0.2657	−0.3395
6	Ag1, Ag1′, O1, O1′	0.7236	0.6839	−0.0930	0.0000

(b) Distances (Å) of Atoms from Planes

Plane	Ag1	Ag1′	O1	O1′	N1	N1′	O2	O2′	O3	O3
1	−0.0681	0.6761	−0.0040	0.6120	0.0164	0.5916	−0.0081	0.6161	−0.0084	0.6164
2	−0.6761	−0.0681	−0.6120	0.0040	−0.5916	−0.0164	−0.6161	0.0081	−0.6164	0.0084
3	−0.0001	0.6791	0.01222	0.6668	0.0171	0.6619	0.0054	0.6737	−0.0332	0.7122
4	−0.0008	0.0914	−0.0977	0.1884	0.1041	−0.0135	0.3136	−0.2229	0.0109	0.0798
5	−0.6791	0.0001	−0.6668	−0.0122	−0.6619	−0.0171	−0.6737	−0.0054	−0.7122	0.0332
6	0.0000	0.0000	0.0032	−0.0003	0.3417	−0.3417	0.6171	−0.6171	0.3036	−0.3036

(c) Dihedral Angles (deg) between Planes

Planes 1–2	0	Planes 2–6	16
Planes 1–3	2	Planes 3–4	15
Planes 1–4	12	Planes 3–5	0
Planes 1–5	2	Planes 3–6	18
Planes 1–6	16	Planes 4–5	15
Planes 2–3	3	Planes 4–6	7
Planes 2–4	12	Planes 5–6	18

(d) Distances (Å) between Parallel Planes

Planes 1–2	0.608	Planes 3–5	0.678

[a] The equations are in the form $ax + by + cz + d = 0$ where x, y, and z are coordinates in Å. All atoms are weighted equally.

found one short O–C distance of 1.32 Å in $Rh(P(OMe)_3)_2B(C_6H_5)_4$.[23] Their average O–C distance was 1.44 Å.

The P–Ag–P angle of 133.8 (1)° is suprisingly large. However for a series of $((C_6H_5)_3P)_2CuX$ compounds,[26b] where X is a bidentate monoanion, the P–Cu–P angles range from 120 to 131°. The "increase" in this angle from the idealized value of 109.5° has been attributed[26b] primarily to steric factors involved in packing ligands of unequal bulk around the spherical d^{10} atom. The angles are largest for planar X ligands and decrease as the nonplanarity and the general crowding of the X ligand increases. In our case the nitrate ligands are planar (Table III, planes 1 and 2) and thus the large P–Ag–P angle is consistent with the trend.

Table III shows that the nitrate atoms are coplanar (plane 1) and that the two silvers and two bridging oxygens form a plane (plane 6). In both cases the average distance of the planar atoms from the plane is under 0.01 Å. The dihedral angle between these planes is 16°, which is about halfway between the 0° expected if O1 were sp^2 hybridized and the 36° if it were sp^3. From Table IIIb it can be seen that O3 is closer to plane 6 than N1 or O2. This illustrates the twisting discussed earlier which places O2 3.102 (10) Å from Ag1. This twisting can also be understood by noticing that Ag1 is nearly in plane 1 which shows that the nitrate plane is oriented toward the silver. The two nitrate planes are coparallel with a 0.608-Å separation between the planes. Figure 2 shows the O2–Ni–O3 angle to be 125° which has opened up from the free nitrate angle of 120°. This result is also in accord with the polarization model discussed earlier[16] and the angle is identical with that found in the $[Cu(NO_3)_2(py)_2]_2$ complex.[4] The O1–O1′ separation of 2.719 (18) Å is nearly the same as the 2.76 Å found for this distance in the copper complex.

In view of the many instances of the bidentate behavior of nitrate, it is curious that the present complex is a dimer bridged by one oxygen on each nitrate. Sterically there appears to be sufficient space for a bidentate nitrate to form a monomer or for two nitrates to bridge *via* two oxygens in the dimeric form. It has been argued[2] that because of the electronegative nature of oxygen, the donation of electronic charge to a metal from a single oxygen would be less favorable than the donation of less charge by each of two oxygens. Hence the reason for the single-oxygen bridging configuration is presently obscure.

Previously, a solution molecular weight of 436 was reported which was consistent with the presence of $[Ag(P(OMe)_3)_2NO_3]$[10a] (mol wt 418). Additional molecular weight measurements reported here made by both the cryoscopic and osmometric method, however, reveal a molecular weight range from 320 to 580 depending on the solvent and concentration. Equilibria involving ligand dissociation of the monomeric complexes are facile in silver nitrate–phosphite systems as has recently been shown with triethyl phosphite.[27]

Complex solution equilibria persisting at low temperatures have been found for other discrete d^{10} crystalline complexes in nmr studies of monovalent copper–, silver–, and gold–phosphine complexes.[28] We conclude, therefore, that the dimer $[Ag(P(OMe)_3)_2NO_3]_2$ also dissociates in solution to give a mixture of species whose stoichiometries are not presently known.

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Registry No. $[Ag(P(OMe)_3)_2NO_3]_2$, 53516-68-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40545G.

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Structure of *trans*-Chlorobis(triethylphosphine)(*p*-fluorophenylhydrazine)platinum(II) Tetrafluoroborate

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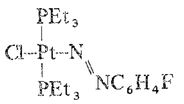
The title compound $[Pt(P(C_2H_5)_3)_2(H_2NNHC_6H_4F)Cl][BF_4]$ is part of a system proposed as a model for the reduction of dinitrogen to ammonia. The structure of the complex has been determined at room temperature from three-dimensional X-ray data collected by counter methods. The structure has been refined by full-matrix least-squares techniques to a final R index (on F) of 0.045 based on 3015 reflections above background. The material crystallizes in the orthorhombic space group $D_{2h}{}^{16}$-$Pnma$ with four molecules in a cell of dimensions a = 16.062 (7), b = 13.625 (6), and c = 12.085 (5) Å. The ions have crystallographically imposed mirror symmetry and the platinum atom has square-planar coordination with Pt–P = 2.328 (2) Å, Pt–Cl = 2.303 (2) Å, and Pt–N(1) = 2.081 (7) Å. The hydrazine ligand, including the phenyl group, lies in a plane approximately perpendicular to the coordination plane. The N(1)–N(2) bond is 1.436 (11) Å and the Pt–N(1)–N(2) angle is 113.2 (5)°. There is an extensive hydrogen-bonding system connecting the anions and cations. The structure of this reduced species is compared with structures of other complexes in the same model system.

Introduction

Not only may unstable or unisolable molecules be stabilized on transition metals, but these coordinated molecules may undergo reactions to produce products not attainable in the absence of the metals. In truly catalytic systems the stabilized intermediates are not isolable because of their short lifetimes, but in other systems they often can be isolated.

One area of research in which there is currently considerable interest is the biological fixation of nitrogen. A wide variety of model systems has been proposed, but one difficulty is that in the systems which are better models for the actual biological process[1] the intermediate species cannot be isolated or characterized. The model system proposed by Parshall[2] in 1965 is still one of the more complete cycles in that each of the intermediate species I–III can be isolated and characterized. These species are being studied structurally because of the paucity of information on such metal–nitrogen systems and on their structural relationships. Compound II, the subject of an earlier structural investigation,[3] is an example of a very unstable molecule, an aryldiazene, stabilized by coordination to a transition metal. The cationic complex II can be deprotonated to yield a neutral aryldiazenido complex I which is currently being investigated structurally.[4] The σ-bonded aryldiazene can also be hydrogenated under mild conditions to give the cationic arylhydrazine complex III the structure of which is reported here. Continued hydrogenation of the arylhydrazine complex results in the formation of ammonia and aniline. Although it has been shown[5] that the diaryl-



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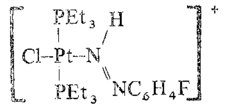
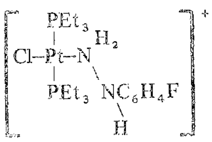


II



III