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Crystal and Molecular Structure of a 1:1 Complex of Silver Nitrate and Triphenylphosphine, $AgNO_3{\cdot}P(C_6H_5)_3$

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The structure of a 1:1 complex of silver nitrate and triphenylphosphine, $AgNO_3{\cdot}P(C_6H_5)_3$, has been determined from data collected on an automated diffractometer with monochromatized Mo Kα radiation. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.659$ (2) Å, $b = 18.558$ (4) Å, $c = 9.045$ (1) Å, $\beta = 100.393$ (7)°, and $V = 1759.8$ (6) Å^3. The density of 1.631 (1) g cm^{-3} calculated on the basis of four molecules per unit cell agrees with the flotation value of 1.63 (1) g cm^{-3}. The structure was solved by use of Patterson and Fourier summations and refined by use of full-matrix least-squares methods to a conventional R index of 0.049 based on 1949 independent observed reflections. Silver is coordinated to all three nitrate oxygen atoms (to two from one nitrate group and to one from another nitrate group) and to phosphorus. Chains of $AgNO_3$ zigzag along the c axis and occupy layers perpendicular to the a axis. In solution, the nitrate group in this complex is exchanged by Cl^-, Br^-, I^-, and N_3^- to yield the corresponding $(C_6H_5)_3P{\cdot}AgX$ compound.

Introduction

Silver nitrate forms complexes with many phosphorus-containing ligands. In these, the phosphorus-containing ligand:silver (I) ratio can be 1:1, 2:1, 3:1, or 4:1. The ligand tri-*p*-tolylphosphine (L) has been added to $AgNO_3$ to form crystals of L_2AgNO_3, L_3AgNO_3, and L_4AgNO_3.[1] Some 1:1 compounds which are tetramers have been prepared, including $[Et_3PAgI]_4$,[2a] $[Ph_3PAgI]_4$,[2b] and $[Ph_3PAgCl]_4$.[2b] Nitrate coordination has been found to be bidentate, unidentate, or bridging, and M–O distances in the bidentate type can be symmetric or asymmetric. We report here the preparation, some properties, and the crystal structure of a 1:1 complex of silver nitrate and triphenylphosphine, $[Ph_3PAgNO_3]_n$. The bridging nitrate group is doubly bidentate with asymmetric M–O distances.

Experimental Section

Preparation. Silver nitrate (5.02 g, 29.6 mmol) dissolved in a mixture of 5 ml of acetonitrile and 20 ml of methanol was added all at once to triphenylphosphine (5.96 g, 22.7 mmol) in 50 ml of methanol. Crystals of the title compound began to form within a few minutes and were collected after standing at room temperature overnight (yield 15 mmol, 66%). These large tan needles were dissolved in methanol and recrystallized as colorless needle clusters, mp 197 °C dec.

Anal. Calcd for $C_{18}H_{15}PNO_3Ag$: C, 50.02; H, 3.50; N, 3.24. Found: C, 50.29 ± 0.32; H, 3.35 ± 0.04; N, 3.08.

Mass Spectra. At its melting point, nitrato(triphenylphosphine)silver(I) decomposes with effervescence. Mass spectroscopy of the vapors over the melted compound indicated that oxidation of the triphenylphosphine ligand to triphenylphosphine oxide,[3] reduction of nitrate to NO and perhaps N_2,[4] and some oxidation of phenyl groups to CO and CO_2 occur. Major peaks in the small mass range at m/e 28, 30, and 44 appeared in the relative proportions of 1.1:1.2:1.0, respectively. The peak at m/e 28 was found by high-resolution spectrometry to be mostly CO, peak m/e 30 was NO and not formaldehyde or ethane, and m/e 44 was virtually all CO_2 with a very small amount of N_2O apparent at high amplification. Spectra obtained by inserting crystals into the spectrometer on a probe showed, in addition, that some triphenylphosphine escaped from melted nitrato(triphenylphosphine)silver(I) without oxidation.

Anion Exchange. To 1 mmol of $AgNO_3{\cdot}P(C_6H_5)_3$ dissolved in a mixture of 10 ml of methanol and 5 ml of acetonitrile was added 2 mmol of LiCl, NaBr, KI, NaN_3, or KCN in 10 ml of methanol. With the exception of the KCN addition, a white precipitate formed immediately. This precipitate was collected in a porcelain funnel with suction and was washed with methanol. Crystals from the KCN reaction formed at 5 °C and were collected and washed with methanol.

Silver Analysis. Silver was determined by atomic absorption. Silver concentrations were determined by comparison of the atomic absorption measurements of the samples with a standard curve obtained from five concentrations of silver nitrate in 5% (v/v) concentrated NH_4OH in water. Aqueous solutions of the complexes were made as follows. About 3 mg of complex was weighed and transferred to a 250-ml volumetric flask. After the addition of 2 ml of acetonitrile and 1 drop of bromine (ca. 13 mg) the mixture was heated in a warm water bath (70 °C) for 5 min. Then 25 ml of 1:1 concentrated NH_4OH–H_2O was added and the mixture was diluted to volume with H_2O. The melting points and silver analyses are shown in Table I.

Table I. Melting Points and Silver Analyses of $(C_6H_5)_3P{\cdot}AgX$

	Mp, °C		Ag anal., %	
Compd	Found	Lit.	Calcd	Found
$(C_6H_5)_3PAgCl$	296	294[a]	26.6	26.5 ± 0.6
$(C_6H_5)_3PAgBr$	268		24.0	24.0 ± 0.4
$(C_6H_5)_3PAgI$	299	270[a]	21.7	21.9 ± 0.3
$(C_6H_5)_3PAgN_3$	203		26.2	26.3 ± 0.2
$(C_6H_5)_3PAgNO_3$	197		25.0	24.7 ± 0.5
$(C_6H_5)_3PAgCN{\cdot}2CH_3CN$	183		22.6	22.0 ± 0.6

[a] F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 201–205 (1965).

Table II. Crystallographic Data for $AgNO_3{\cdot}P(C_6H_5)_3$

Cell dimensions (25 °C)	
a	10.659 (2) Å[a]
b	18.558 (4) Å
c	9.045 (1) Å
β	100.393 (7)°
V	1759.8 (6) Å^3
λ(Mo Kα)	0.710 73 Å
d_{obsd}(flotation)	1.63 (1) g cm^{-3}
$d_{calcd}(Z = 4)$	1.631 (1) g cm^{-3}
Systematic absences	$0k0$ with $k = 2n + 1$
	$h0l$ with $l = 2n + 1$
Space group	$P2_1/c$, No. 14
Equivalent positions	
A	x, y, z
B	$x, {}^1/_2 - y, {}^1/_2 + z$
C	$1 - x, 1 - y, 1 - z$
D	$1 - x, {}^1/_2 + y, {}^1/_2 - z$

[a] Estimated standard deviations in the least significant digits are given in parentheses in this and following tables.

Crystallographic Data. A crystal of dimensions 0.08 mm × 0.15 mm × 0.33 mm along a, b, and c, respectively, was mounted, on a fiber, with the needle axis along the spindle axis. Oscillation and Weissenberg photographs indicated space group $P2_1/c$. The crystal was transferred to a Syntex $P\bar{1}$ autodiffractometer equipped with a scintillation counter and a graphite monochromator. Lattice parameters were determined using 15 reflections in the range $20° \leq 2\theta \leq 36°$, Mo K$\alpha$ radiation. These parameters are listed with other crystallographic data in Table II.

The intensity data were collected with Mo Kα radiation, a scan rate of 2° min^{-1} and a scan range from 1.25° below the Kα_1 peak to 1.25° above the Kα_2 peak. Background counts were taken for half

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Table III. Atomic Positional Parameters in $AgNO_3 \cdot P(C_6H_5)_3$[a]

Atom	x	y	z
Ag	0.047 45 (7)	0.164 95 (4)	0.098 76 (9)
P	0.221 1 (2)	0.090 1 (1)	0.068 3 (2)
O(1)	−0.097 9 (6)	0.175 1 (4)	0.277 2 (8)
O(2)	−0.086 4 (6)	0.244 0 (4)	0.473 9 (7)
O(3)	0.069 0 (6)	0.238 3 (4)	0.350 6 (8)
N	−0.037 2 (5)	0.218 2 (3)	0.367 5 (8)
C(1)	0.235 6 (8)	0.072 0 (5)	−0.126 5 (9)
C(2)	0.230 4 (11)	0.003 6 (6)	−0.185 4 (10)
C(3)	0.237 7 (14)	−0.006 3 (7)	−0.334 4 (12)
C(4)	0.248 1 (14)	0.053 3 (8)	−0.423 1 (11)
C(5)	0.252 5 (11)	0.122 6 (6)	−0.365 0 (11)
C(6)	0.246 8 (9)	0.130 8 (5)	−0.215 5 (10)
C(7)	0.370 0 (7)	0.134 1 (4)	0.148 4 (9)
C(8)	0.371 1 (9)	0.173 8 (5)	0.279 3 (10)
C(9)	0.483 0 (11)	0.206 6 (6)	0.350 4 (12)
C(10)	0.593 4 (9)	0.201 1 (4)	0.293 4 (13)
C(11)	0.592 5 (8)	0.163 0 (6)	0.162 6 (12)
C(12)	0.481 6 (9)	0.129 1 (5)	0.092 4 (11)
C(13)	0.229 9 (8)	0.002 9 (5)	0.159 9 (9)
C(14)	0.119 9 (9)	−0.029 2 (6)	0.190 8 (11)
C(15)	0.122 1 (10)	−0.094 9 (5)	0.261 5 (11)
C(16)	0.236 4 (11)	−0.130 3 (5)	0.305 4 (12)
C(17)	0.348 8 (10)	−0.099 4 (6)	0.277 9 (13)
C(18)	0.345 2 (9)	−0.033 1 (5)	0.204 2 (11)

[a] The idealized (calculated) positional parameters of the hydrogen atoms are given in Table IV which is available as part of the supplementary material.

the scan time at each end of the scan range. The intensities of three standard reflections (041), (032), and $(11\bar{1})$ were recorded after every 40 intensity measurements. These showed only random variations which were consistent with the $\sigma(I)$ values involved. Reflection data were collected in the range $4° < 2\theta < 50°$. Of the 2353 unique reflections measured, 1949 for which $I > 4.2\sigma(I)$ were considered observed and were used in subsequent calculations. The data were corrected for Lorentz and polarization effects and processed as previously described[5,6] with a value of 0.04 for p. The calculated value of μ for Mo Kα radiation is 12.2 cm^{-1} and the transmission factor is estimated to be 0.86–0.92 for the specimen crystal in the 2θ range involved. A ψ scan of reflections (002), (004), and (006) indicated fluctuations of less than ±5% in I. No corrections for the effects of absorption were made.

Determination and Refinement of the Structure. A trial position for the silver atom was obtained from a three-dimensional Patterson summation. The remaining nonhydrogen atoms were located in a subsequent electron density map. The positional and anisotropic thermal parameters for all nonhydrogen atoms were refined to a conventional R index of 0.049.[7] Each hydrogen atom was assigned a position 1.084 Å from its bonded carbon atom, in a position calculated on the basis of sp^2 C atoms. Each hydrogen atom was assigned a fixed isotropic thermal parameter of 4.0 $Å^2$. The parameters for hydrogen atoms were not refined but they were included in the calculation of structure factors. The "goodness of fit", defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, was 1.879. In this expression, $N_o = 1949$, the number of observed reflections, and $N_v = 217$, the number of variable parameters. The maximum density on a final difference Fourier is 0.5 e $Å^{-3}$ and is located near the silver position. In other areas, the range in electron density is ±0.3 e $Å^{-3}$.

The final atomic positional and thermal parameters are given in Tables III and IV. Table V[8] lists the calculated positional parameters and the assigned isotropic thermal parameters for the hydrogen atoms. A set of structure factors was calculated on the basis of the tabulated parameters and is available as Table VI.[8] The atomic scattering factors for all nonhydrogen atoms were those given in Table 3.3.1A of ref 9. The atomic scattering factors for hydrogen were those given by Stewart et al.[10] The real and imaginary components of anomalous dispersion from Table 3.3.2C of ref 9 were applied to the scattering factors for silver.

Table IV. Atomic Thermal Parameters in $AgNO_3 \cdot P(C_6H_5)_3$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag	91 (1)	34 (1)	153 (1)	30 (1)	58 (1)	−8 (1)
P	65 (2)	20 (1)	85 (3)	2 (2)	32 (4)	−6 (2)
O(1)	99 (6)	44 (3)	183 (10)	−52 (7)	85 (13)	−64 (9)
O(2)	121 (7)	47 (3)	163 (9)	−48 (8)	145 (12)	−47 (9)
O(3)	90 (6)	41 (3)	241 (12)	−39 (7)	122 (13)	−54 (10)
N	81 (5)	25 (2)	139 (9)	−3 (6)	74 (11)	22 (7)
C(1)	74 (7)	27 (3)	82 (10)	−2 (8)	26 (14)	0 (9)
C(2)	196 (14)	26 (3)	101 (11)	−12 (11)	100 (20)	−31 (10)
C(3)	297 (21)	38 (4)	142 (15)	−23 (17)	156 (28)	−66 (13)
C(4)	277 (19)	57 (5)	83 (12)	−14 (18)	130 (24)	−13 (14)
C(5)	191 (14)	41 (4)	113 (13)	0 (13)	82 (22)	38 (13)
C(6)	124 (10)	32 (3)	82 (10)	6 (10)	67 (17)	9 (10)
C(7)	69 (7)	19 (2)	88 (10)	−3 (8)	31 (14)	4 (9)
C(8)	109 (9)	26 (3)	134 (12)	−6 (9)	35 (18)	−5 (11)
C(9)	142 (13)	29 (3)	159 (16)	−10 (12)	−7 (24)	−41 (13)
C(10)	91 (10)	25 (3)	212 (18)	−15 (9)	−29 (23)	14 (13)
C(11)	66 (8)	37 (3)	197 (15)	2 (10)	48 (18)	37 (14)
C(12)	89 (9)	29 (3)	136 (13)	6 (9)	48 (17)	3 (11)
C(13)	93 (8)	19 (2)	77 (10)	−17 (8)	47 (15)	−8 (9)
C(14)	94 (9)	34 (3)	127 (13)	−15 (10)	14 (19)	5 (12)
C(15)	120 (10)	32 (3)	139 (14)	−44 (10)	50 (20)	41 (12)
C(16)	159 (13)	25 (3)	158 (15)	−18 (11)	43 (24)	33 (12)
C(17)	115 (10)	31 (3)	232 (18)	41 (10)	104 (22)	34 (14)
C(18)	86 (9)	28 (3)	176 (14)	12 (9)	72 (18)	15 (12)

[a] All parameters have been multiplied by 10^4. The anisotropic temperature factor expression is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. The hydrogen atoms were assigned the fixed isotropic thermal parameters listed in Table V, which is available as part of the supplementary material.

Table VII. Bond Distances (Å) and Angles (deg) in the Ligands of the Nitrato(triphenylphosphine)silver(I) Complex

	(a) Distances		
P–C(1)	1.828 (11)	N–O(1)	1.238 (9)
P–C(7)	1.816 (11)	N–O(2)	1.270 (9)
P–C(13)	1.813 (11)	N–O(3)	1.227 (9)
C–C(av)	1.382 (14)		
	(b) Bond Angles		
O(1)–N–O(2)	120.3 (5)	P–C(1)–C(6)	116.8 (7)
O(1)–N–O(3)	119.9 (5)	P–C(7)–C(8)	116.7 (7)
O(2)–N–O(3)	119.7 (5)	P–C(7)–C(12)	125.0 (7)
C(1)–P–C(7)	104.3 (5)	P–C(13)–C(14)	120.2 (7)
C(1)–P–C(13)	105.7 (5)	P–C(13)–C(18)	122.0 (7)
C(7)–P–C(13)	104.4 (5)	C–C–C(av)	120.0 (10)
P–C(1)–C(2)	122.6 (7)		

Table VIII. Interatomic Distances (Å) and Angles (deg) around the Silver Atom in $AgNO_3 \cdot P(C_6H_5)_3$

	(a) Distances		
Ag–P	2.369 (6)	Ag–O(3)	2.628 (7)
Ag–O(1)	2.438 (7)	Ag–O(3)′[a]	2.916 (7)
Ag–O(2)′[a]	2.363 (7)		
	(b) Angles		
O(2)′–Ag–P	141.3 (2)	O(1)–Ag–O(3)′	127.6 (2)
O(2)′–Ag–O(1)	82.0 (2)	O(3)–Ag–O(3)′	110.0 (2)
O(2)′–Ag–O(3)	89.7 (2)	Ag–P–C(1)	115.1 (3)
O(2)′–Ag–O(3)′	46.9 (2)	Ag–P–C(7)	109.6 (3)
P–Ag–O(1)	136.5 (2)	Ag–P–C(13)	116.6 (3)
P–Ag–O(3)	117.2 (2)	Ag–O(2)′–N′[a]	109.6 (3)
P–Ag–O(3)′	95.7 (2)	Ag–O(1)–N	99.6 (3)
O(1)–Ag–O(3)	49.7 (2)	Ag–O(3)–N	90.7 (3)

[a] The symbols O(2)′, O(3)′, and N′ represent atoms at symmetry position B (see Table II) 0, 0, $\bar{1}$, i.e., the O(2), O(3), or N atom in position B in the cell located one unit in the negative direction along the c axis.

Description and Discussion of the Structure

The configuration of the ligands about silver in nitrato(triphenylphosphine)silver(I) is illustrated in Figure 1 and a view of the crystal structure down the a axis is shown in Figure 2. Bond distances and angles within the nitrate and triphenylphosphine groups are given in Table VII and the main features of the coordination about the silver atom are presented in Table VIII.

The silver atom is surrounded by two nitrate groups and a triphenylphosphine group. One nitrate group is bonded

Table IX. Results of Least-Squares Planes Calculations [Distances of Atoms from Least-Squares Planes (Å)[a]]

Plane A		Plane B		Plane C		Plane D	
N*	0.014	C(1)*	0.001	C(7)*	0.002	C(13)*	−0.001
O(1)*	−0.005	C(2)*	−0.005	C(8)*	−0.006	C(14)*	0.004
O(2)*	−0.004	C(3)*	0.005	C(9)*	0.001	C(15)*	−0.002
O(3)*	−0.005	C(4)*	0.000	C(10)*	0.006	C(16)*	−0.003
Ag	−0.235	C(5)*	−0.004	C(11)*	−0.010	C(17)*	0.005
		C(6)*	0.004	C(12)*	0.006	C(18)*	−0.004
		P	−0.071	P	0.064	P	0.031
		Rms dev[b]	0.004	Rms dev	0.006	Rms dev	0.003

[a] Atoms used to define least-squares planes are indicated by asterisks. [b] The root-mean-square deviations (in Å) of the asterisked atoms from their respective least-squares planes.

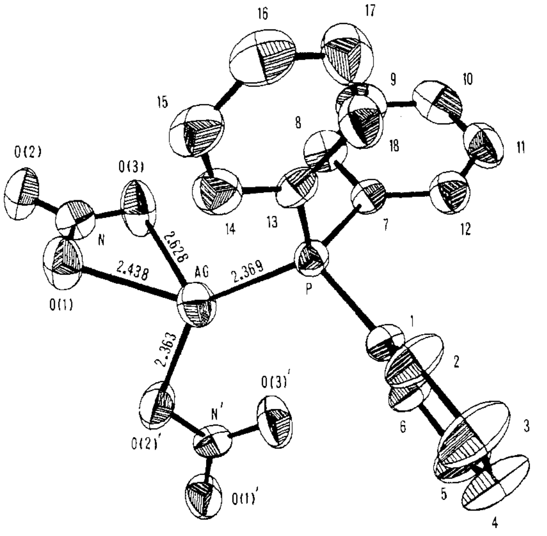

Figure 1. ORTEP plot of the configuration around a silver atom in nitrato(triphenylphosphine)silver(I) showing thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted and carbon atoms are indicated by the numbers 1–18.

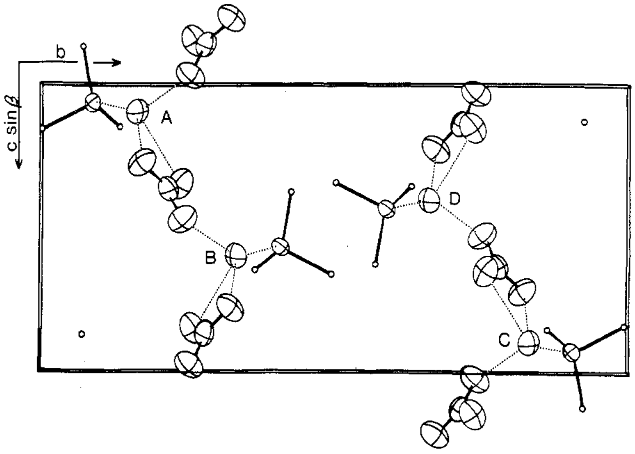

Figure 2. Packing arrangement of nitrato(triphenylphosphine)silver(I) as viewed down the *a* axis of the unit cell. For clarity, only the three carbon atoms attached to each phosphorus atom have been included, and thermal ellipsoids for these carbon atoms are not depicted. The coordinates of the symmetry positions A, B, C, and D are given in Table II.

through two oxygen atoms, O(1) and O(3), to silver. A second nitrate group is bonded through one oxygen atom, O(2), to the silver atom. O(3) on this nitrate group is located 2.916 Å from the silver atom and thus each nitrate group could be considered to be symmetrically and unsymmetrically bidentate.[11] Doubly bidentate nitrate groups bridge silver atoms in $C_{11}H_{15}AsAg_2(NO_3)_2$ with Ag–O distances ranging from 2.35 to 2.85 Å.[12]

If we ignore the Ag–O(3) distance of 2.916 Å, the configuration about silver can be described as a distorted tetrahedron. Chains of $AgNO_3$ zigzag in the direction parallel to *c* and form corrugated sheets sandwiched between layers containing triphenylphosphine. These layers are perpendicular to *a*. This chain and layer arrangement in complexes containing $AgNO_3$ has been found previously.[13]

In coordinated nitrate groups the planarity of NO_3 is preserved and this plane generally includes the metal ion.[11] In the title compound the nitrate group is planar and the silver atom lies 0.235 Å from the least-squares plane through the nitrate atoms. Data derived from least-squares planes calculations are given in Table IX. The N–O bond lengths and O–N–O bond angles in coordinated nitrate groups are often found to be different from the values in the nitrate ion. In the ion, O–N–O = 120° and N–O = 1.245 (10) Å.[11] However, in the title compound, the three O–N–O angles are 120° and the variation in the N–O distances is probably not significant. In nitratosilver(I) complexes the nitrate group is often undistorted,[14,15] although in $[Ag(P(OMe)_3)_2NO_3]_2$ these N–O distances are not equal and O–N–O angles are 116.3 (11), 118.5 (11) and 125.0 (12)°.[16] This dimer contains bridging nitrate groups in which only one oxygen is symmetrically coordinated to two silver atoms; however, this nitrate group bends toward one of the silver atoms and thus there is a second oxygen 3.102 Å from that silver atom.

The Ag–P distance of 2.369 Å is somewhat shorter than the sum of the single-bond covalent radii (2.44 Å)[17] and is shorter than the Ag–P distances found in other triphenylphosphinesilver(I) compounds (2.455 (3) Å,[18] 2.503 (5) Å,[18] and 2.47 Å[19]). The three phenyl rings in triphenylphosphine are each planar and phosphorus is slightly out of the plane of each phenyl group. Within each phenyl group, interatomic distances and angles are within expected values.

The sum of the van der Waals radii for oxygen and hydrogen is 2.6 Å. There are three short contacts between phenyl hydrogens and nitrate oxygens: O(1)–H(11) ($x - 1, y, z$), 2.575 Å; O(2)–H(10) ($x - 1, y, z$), 2.571 Å; O(3)–H(6) ($x, {}^1/_2 - y, {}^1/_2 + z$), 2.447 Å. The only H–H contact less than 2.4 Å is between H(5) and H(8) ($x, y, z - 1$). The title compound can be formulated as $[(C_6H_5)_3PAgNO_3]_n$ in which the links in the infinite chain are the bridging nitrate groups.

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Registry No. $(C_6H_5)_3PAgCl$, 52495-09-7; $(C_6H_5)_3PAgBr$, 47107-31-3; $(C_6H_5)_3PAgI$, 61026-08-2; $(C_6H_5)_3PAgN_3$, 61062-63-3; $(C_6H_5)_3PAgNO_3$, 61026-18-4; $(C_6H_5)_3PAgCN{\cdot}2CH_3CN$, 61026-09-3.

Supplementary Material Available: Table V, the calculated (idealized) positions and assigned isotropic thermal parameters of the hydrogen atoms, and Table VI, the observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

References and Notes

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Structure of Hexaaquairon(III) Nitrate Trihydrate. Comparison of Iron(II) and Iron(III) Bond Lengths in High-Spin Octahedral Environments

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The structure of hexaaquairon(III) nitrate trihydrate, $[Fe(H_2O)_6](NO_3)_3{\cdot}3H_2O$, has been determined from x-ray diffraction data collected by counter methods. The compound crystallizes in space group $P2_1/c$ (C_{2h}^5) with a = 13.989 (1) Å, b = 9.701 (1) Å, c = 11.029 (1) Å, β = 95.52 (1)°, Z = 4, ρ_{measd} = 1.81 (1) g cm^{-3}, and ρ_{calcd} = 1.80 g cm^{-3}. The intensities of 2209 reflections were measured with $I > 1.5\sigma(I)$. The structure was refined by full-matrix least-squares methods to a conventional R index (on F) of 0.042. The structure comprises two crystallographically distinct $Fe(H_2O)_6{}^{3+}$ octahedra, each possessing crystallographic ($\bar{1}$) symmetry, connected by a complex hydrogen-bonded network involving the nitrate anions and lattice water molecules. The mean Fe^{III}–O distance (1.986 (7) Å) is 0.14 Å shorter than the Fe^{II}–O distance in hexaaquairon(II) ions. This substantial difference in the iron–oxygen bond distances between $Fe(H_2O)_6{}^{3+}$ and $Fe(H_2O)_6{}^{2+}$ is interpreted using qualitative ligand field theory.

Introduction

There appears to be little structural information available for aquairon(III) species. A recent survey listed the *trans*-$Fe(H_2O)_4Cl_2{}^+$ structure but no data for penta- or hexaaquairon(III) complexes.[1] A structural analysis of an $Fe(H_2O)_6{}^{3+}$ salt is desirable, not only because of the general importance of this ion in transition metal chemistry but also for the specific analysis of the rates of electron-transfer reactions. The Hush–Marcus model of outer-sphere electron-transfer reactions has successfully accounted for the rate of electron exchange between $Fe(H_2O)_6{}^{3+}$ and $Fe(H_2O)_6{}^{2+}$, using an *estimated* difference of 0.16 Å in iron–oxygen bond distances between the two oxidation states.[2] However, recent crystallographic evidence[3] suggests that, in the absence of spin state changes, there is a much smaller difference in bond distances between oxidation states in octahedral complexes. This would lead to a negligible coordination sphere reorganization energy and the predicted rate would be much faster than the observed rate.

To resolve this conflict we have determined the crystal and molecular structure of $Fe(NO_3)_3{\cdot}9H_2O$, following the report of its unit cell parameters.[4] A subsequent survey of the literature through 1973, accessed through BIDICS,[5] revealed mineralogical examples of aquairon(III) complexes, one of which contains an $Fe(H_2O)_6{}^{3+}$ species.[6] Its structure is consistent with the one reported here.

Experimental Section

Crystals of $[Fe(H_2O)_6](NO_3)_3{\cdot}3H_2O$ can be recrystallized by slow evaporation from dilute nitric acid solutions. Difficulties were experienced in handling the crystals due to their hygroscopic character. Those selected for x-ray examination were first surface dried, coated with silicone grease, and then sealed in glass capillaries. Preliminary precession photography confirmed an earlier assignment of cell dimensions and space group.[4] The space group was uniquely determined as $P2_1/c$. The crystal density was measured as 1.81 (1) g cm^{-3} by flotation in a chloroform/bromoform mixture, the corresponding value calculated for Z = 4 being 1.80 g cm^{-3}. An oval plate of approximate dimensions 0.20 × 0.20 × 0.15 mm was selected for data collection and was mounted on an Enraf-Nonius four-circle CAD-4 diffractometer. Cell parameters were obtained by least-squares refinement of the 2θ values of 25 reflections measured with Mo Kα_1 radiation (λ 0.709 30 Å) in the range 53° < 2θ < 56°. The values obtained were a = 13.989 (1) Å, b = 9.701 (1) Å, c = 11.029 (1) Å, and β = 95.52 (1)°. Data were collected using Mo Kα radiation from a graphite-crystal monochromator. The takeoff angle was 2.8° and the counter was positioned 17.3 cm from the crystal with an aperture 4.0 mm high by 2.0 mm wide. Profile analyses of a few low-angle reflections indicated that an ω–${}^4/_3\theta$ scan method was most appropriate. Scan ranges (SR) were calculated from the formula SR = $M + W \tan\theta$, where M is estimated from the mosaic spread of the crystal and W allows for increasing peak width due to Kα_1 and Kα_2 splitting. M and W were chosen as 1.5° and 0.35°, respectively. Each calculated scan range is extended on either side by 25% to accommodate the moving-background determinations (B_1 and B_2). The net intensity is I = PI − $2(B_1 + B_2)$, where PI is the peak intensity. The scan rate