The Crystal Structure of Diammine Silver Nitrate, Ag(NH$_3$)$_2$NO$_3$, at 223 K

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The structure of diammine silver nitrate has been determined from diffractometer data collected at 223 K. The space group is *Pnnm* with cell dimensions, $a=8.088(3)$, $b=10.416(5)$, $c=6.261(2)$ Å, [$a=8.122(2)$, $b=10.596(2)$, $c=6.292(2)$ at 294 K] and $Z=4$. The structure has been refined by a block-diagonal least-squares method to R$=0.054$ based on 338 independent reflections. The diammine silver ions have a complete linear structure with an Ag−N bond length of 2.12(1) Å. The N−O distances in the nitrate group are 1.23(1) Å.

Linear diammine complexes have been of considerable interest in understanding the molecular motions of the NH$_3$ group in metal ammine complexes.[1,2] Structural investigations of diammine silver complexes reported so far are only [Ag(NH$_3$)$_2$]$_2$SO$_4$,[3] and Ag(NH$_3$)$_2$ · Ag(NO$_2$)$_2$.[4] These investigations confirmed the linear structure of the complex but the Ag−N bond lengths in the two cases are quite different, 1.90 Å and 2.11 Å, respectively. A recent solution X-ray diffraction study[5] has also indicated the presence of the linear Ag(NH$_3$)$_2^+$ ion in aqueous solution however, with a somewhat longer Ag−N distance (2.22 Å).

The crystal structure of the diammine silver nitrate was first investigated in 1934[6] but the structure determination was not successful. In our attempt to solve the structure from diffractometer data collected at room temperature, it was not possible to locate the nitrate oxygen atoms,

which is probably due to a dynamic disorder of the nitrate ion. Hence, intensity data were collected at 223 K, from which the structure could be determined.

EXPERIMENTAL

Ag(NH$_3$)$_2$NO$_3$ was crystallized from a concentrated ammoniacal aqueous solution of AgNO$_3$ with the NH$_3$/Ag mole ratio$=2$ over KOH pellets in a deccicator. The crystals are not stable but decompose in air with loss of ammonia in a few hours.

Preliminary Weissenberg photographs showed orthorhombic symmetry with systematic absences of reflections: $0kl$, $k+l=2n+1$; $h0l$, $h+l=2n+1$ and hence possible space groups are *Pnnm* and *Pnn*2$_1$.

It was found that the structure was subjected to a phase transition, cracking the crystals below 220 K. A single crystal was sealed in a 0.2 mm glass capillary and mounted on a syntex P2$_1$ four-circle diffractometer. Three-dimensional X-ray data were collected at 223 K using the Syntex LT1 low temperature equipment. Cell dimensions at both 223 and 294 K were obtained by refinement of setting angles of 15 reflections. Reflections with h, k and $l>0$ were collected and a standard reflection, monitored after every fiftieth reflection, showed that the crystal was stable in the capillary during data collection. Diffracted data were measured in 96 step profiles on each reflection and the Lehmann-Larsen method[7,8] was applied to calculate the net intensities. Reflections with $I>3\sigma(I)$ were considered as significant and corrected for the Lorentz and polarization effects. Corrections for absorption and extinction effects were not made. Experimental details are summarized in Table 1.

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Table 1. Crystal data, the collection and reduction of intensities and the least-squares refinement.

Formula	$Ag(NH_3)_2NO_3$
F.W.	203.9
D_x(g cm^{-3})	2.57
$F(000)$	392
Crystal habit	Colourless and rectangular
Crystal size (mm)	$0.12 \times 0.21 \times 0.28$ mm
Radiation	Mo$K\alpha$ ($\lambda = 0.71069$ Å)
μ(Mo$K\alpha$) (cm^{-1})	36.4
Monochromator	Graphite crystal
Scan. mode	$\theta - 2\theta$
Maximum 2θ (°)	54
Scan speed (°min^{-1})	Variable, 3.0−20.0
Scan interval, $\Delta 2\theta$ (°)	$[(MoK\alpha_2)+1.00]-[(MoK\alpha_1)-1.00]$
Reflections recorded	650
Significant reflections	338 ($I/\sigma(I) > 3.0$)
Parameters refined	43
$R \equiv \Sigma|F_o-|F_c||/\Sigma F_o$	0.054 ($R = 0.076$ including unobserved reflections)

Table 2. Atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\times 10^4$) with *e.s.d.*'s in parentheses. The form of the temperature factors are exp ($h^2\beta_{11}+\cdots+hk\beta_{12}+\cdots$).

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag(1)	0	0	0	105(2)	94(1)	217(3)	7(2)	0	0
Ag(2)	0	0	5000	103(2)	125(1)	228(4)	−11(2)	0	0
N(1)	7606(12)	5182(9)	5000	112(17)	163(14)	222(30)	4(24)	0	0
N(2)	6359(11)	6742(9)	0	124(16)	112(9)	261(29)	−29(21)	0	0
N(3)	5753(11)	8410(8)	5000	111(13)	60(7)	290(29)	10(18)	0	0
O(1)	7254(10)	8204(9)	5000	85(11)	153(11)	710(51)	−34(21)	0	0
O(2)	4998(8)	8549(12)	6687(16)	197(16)	363(23)	229(24)	183(24)	95(32)	211(46)

STRUCTURE DETERMINATION AND REFINEMENT

The positions of the silver atoms were deduced from three-dimensional Patterson maps to occupy special positions. All other non-hydrogen atoms were located from difference Fourier syntheses. The positional and isotropic thermal parameters as well as an overall scale factor were refined in the two space groups $Pnn2_1$ and $Pnnm$. The R-value was better in the space group $Pnnm$ and in addition one of the N−O distances in the nitrate group did not refine well in $Pnn2_1$. Therefore, we concluded the correct space group to be $Pnnm$. Having introduced anisotropic thermal parameters for all atoms, a block-diagonal least-squares[9] refinement gave a final R-value of 0.054.

Weights according to $w = 1/(12.0+F_o+0.10F_o{}^2)$ gave an acceptable weight analysis. Scattering factors for neutral atoms were taken from International Tables.[10] The final atomic coordinates and thermal parameters are listed in Table 2. A final difference syntheses showed no anomalies. It was not possible to find the ammonia hydrogen atoms. Disregarding diffraction reasons, it is possible that the ammonia molecule rotates around the Ag−N bond to much lower temperatures.[2] All calculations were carried out on an Hp 2100 computer.[11,12]

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

A stereoscopic view of the unit cell is shown in Fig. 1. Significant interatomic distances and bond angles are given in Table 3. There are two
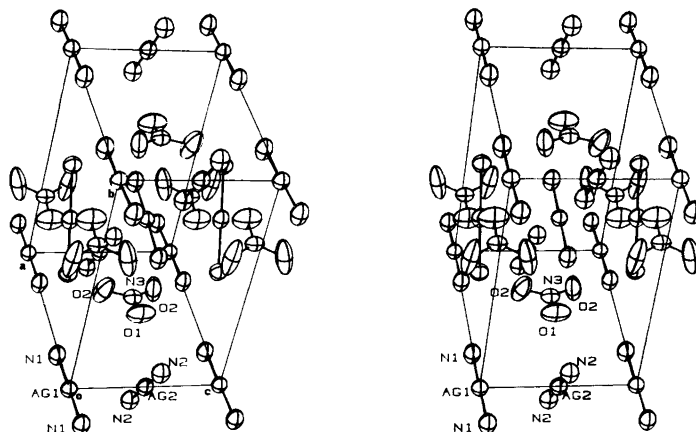
Fig. 1. Stereoscopic view of the $Ag(NH_3)_2NO_3$ structure.

Table 3. Significant interatomic distances (Å) and angles (°) with *e.s.d.*'s in parentheses. The values in brackets are those corrected for thermal motion.[22]

(a) The Ag-coordination	
$Ag(1)-N(1)$	2.116(10)[2.125(10)]
$Ag(2)-N(2)$	2.121(10)[2.122(10)]
$Ag(2)-O(1^{ii})$	2.904(9)
$Ag(2)-O(1^{iii})$	2.904(9)
$N(1)-Ag(1)-N(1^i)$	180
$N(2)-Ag(2)-N(2^i)$	180
(b) The nitrate ion	
$N(3)-O(1)$	1.233(12)
$N(3)-O(2)$	1.229(10)
$O(1)-N(3)-O(2)$	120.7(5)
$O(1)-N(3)-O(2^{iv})$	120.7(5)
$O(2)-N(3)-O(2^{iv})$	118.6(10)
(c) Possible hydrogen bonds	
$N(1)-O(2^v)$	3.13(1)
$N(1)-O(2^{vi})$	3.13(1)
$N(1)-O(1)$	3.16(1)
$N(2)-O(2^{vii})$	3.01(1)
$N(2)-O(2^{iv})$	3.01(1)
$N(2)-O(2^{vi})$	3.14(1)
$N(2)-O(2^{vii})$	3.14(1)

Symmetry codes

(i)	$-x,$	$-y,$	z		(v)	$1/2-x,$	$3/2-y,$	$3/2-z$
(ii)	$1-x,$	$-1+y,$	z		(vi)	$1/2+x,$	$3/2-y,$	$-1/2+z$
(iii)	$-1+x,$	$1-y,$	z		(vii)	$x,$	$y,$	$-1+z$
(iv)	$x,$	$y,$	$1-z$		(viii)	$1/2+x,$	$3/2-y,$	$1/2-z$

Table 4. Comparison of Ag$-$N distances (Å) and N$-$Ag$-$N angles (°) in some linear and tetrahedral silver(I) complexes in the solid state and in solution.

Compound	d(Ag$-$N)	(N$-$Ag$-$N)	Configuration	Ref.
Ag(NH$_3$)$_2$.Ag(NO$_2$)$_2$	2.112(6) 2.117(6)	178.3(3)	Linear	4
Ag(NH$_3$)$_2$NO$_3$	2×2.116(10) 2×2.121(10)	180 180	Linear Linear	This study
[Ag(NH$_3$)$_2$]SO$_4$	2×1.90	180	Linear	3
Ag(C$_3$H$_4$N$_2$)$_2$NO$_3$	2.120(8) 2.132(8)	172.0(3)	Linear	14
Ag(NC$_5$H$_5$)$_2$.H$_2$O	2×2.16(2)	172.7(2)	Linear	15
(CH$_3$)$_4$NAg(NCO)$_2$	2.015(13) 2.068(12)	177.2(5)	Linear	16
AgNCO	2×2.115(8)	180	Linear	17
AgNO$_3$.N$_2$C$_4$H$_4$	2×2.213(14)	159.2(9)	Bent	19
Hg(CN)$_2$.AgNO$_3$	2×2.13(4) 2×2.57(6) Ag$-$O	162(3)	Distorted tetrahedral	18
	2.02(5) 2.18(6) 2.56(5) Ag$-$O 2.55(6) Ag$-$O	163(2)	Distorted tetrahedral	
Ag(NC$_5$H$_5$)$_2$ClO$_4$	4×2.322(3)	110.2(2)	Tetrahedral	20
Solution: Ag(NH$_3$)$_2$$^+$(in H$_2$O)	2.22(2)		Linear	5
Ag(NC$_5$H$_5$)$_4$$^+$(in NC$_5H_5$)	2.30(3)		Tetrahedral	21

independent diammine silver ions in the cell. Both are linear and arranged so that they cross each other along the *c* axis.

The nitrate ion is planar and triangular within the standard deviatons, and the N$-$O distances are in accordance with the literature data. The structural packing of the nitrate ion is ordered but large temperature factors indicate a trace of dynamic motion of the ion also at 223 K. The closest Ag$-$O distance is 2.90 Å (Table 3).

The hydrogen bonding between the ammonia molecules and the nitrate oxygen atoms is rather weak (Table 3), compared to the normal range of N$-$H$\cdots$O distances of 2.78$-$3.13 Å.[13]

Table 4 gives Ag$-$N distances in nitrogen coordinated silver compounds in different solids and in solution. The Ag$-$N bond length in the present compound is in good agreement with those in Ag(NH$_3$)$_2$ · Ag(NO$_2$)$_2$, while the value reported in [Ag(NH$_3$)$_2$]$_2$SO$_4$ is probably too short. In general, the two-fold linear nitrogen coordination at silver is characterized by an

Ag$-$N distance close to 2.12 Å, except the shorter values in cyanato complex found in (CH$_3$)$_4$NAg(NCO)$_2$. The N-Ag-N angles are generally close to 180°, except in Hg(CN)$_2$ ·$\cdot$ AgNO$_3$ · 2H$_2$O and AgNO$_3$ · N$_2$C$_4$H$_4$, in which there are additional short Ag$-$O contacts (2.55$-$2.72 Å). In the other structures the Ag$-$O distances are>2.9 Å.

A previous X-ray investigation of ammoniacal aqueous solution of AgNO$_3$[26] could not definitely prove the linearity of the Ag(NH$_3$)$_2$$^+$ ion in aqueous solution. However, it was found that no water molecule coordinated closer than 2.8 Å, indicating that the diamminesilver ion is linear also in aqueous solution. The Ag$-$N distance found in solution is somewhat longer than those found in the solid state. Bond elongation is normal for solvated complexes compared to the solid state when the ligands are hydrogen bonded to the solvent molecules. The Ag$-$N bond distance of 2.22 Å obtained in solution may be an upper limit for the Ag$-$N two-fold coordination

distance.

Tetrahedral N-coordinated Ag^+ ions have recently been studied in silver pyridine compounds both in the solid state and in solution, in which the Ag–N distances were found to be 2.322(3) Å and 2.30(3) Å, respectively.

The silver coordination has also been studied in liquid ammonia by Raman spectroscopic measurements by Gans and Gill[23] and by Lundeen and Tobias.[24] The former authors assign a tetrahedral Ag–N coordination, while the latter ascribe their spectra to a distorted octahedron. In order to clarify the coordination geometry of the silver ion in liquid ammonia, an X-ray investigation on liquid ammonia solution of $AgNO_3$ is planned.

In the case of the aqua silver ion, an X-ray reinvestigation of aqueous $AgClO_4$ solutions showed that four water molecules are bonded to the silver ion.[25] Therefore, silver ammine complex formation can be interpreted in such a way that tetra-aqua Ag^+ ion, $Ag(OH_2)_4^+$, is converted to a stable linear diammine silver ion, $Ag(NH_3)_2^+$, without any additional bonds in aqueous solution. Higher ammine silver ions can be formed at extreme conditions such as in liquid ammonia.

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