this reaction is largely inhibited for ortho substituents.

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Registry No. **6a**, 63731-74-8; **6b**, 63731-79-3; **6c**, 63731-81-7; **6d**, 63731-72-6; **7a**, 63731-70-4; **7b**, 63731-68-0; **7c**, 63731-65-7; **7d**, 63731-63-5; **8**, 63731-82-8; $[Ir(NHNC_6H_3F)(FBF_3)(CO)(PPh_3)_2]BF_4$, 63731-61-3; $[Ir\{(C_6H_4F)_2N_4\}(CO)(PPh_3)_2]BF_4$, 49732-06-1; $IrH(CO)(PPh_3)_3$, 17250-25-8; o-$NO_2C_6H_4N_2BF_4$, 365-33-3; o-$CF_3C_6H_4N_2BF_4$, 447-59-6; o-$FC_6H_4N_2BF_4$, 446-46-8; p-$FC_6H_4N_2BF_4$, 19578-37-1; p-$NO_2C_6H_4N_2BF_4$, 456-27-9.

Supplementary Material Available: Tables IV and VII, observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Di-μ-adeninium-disilver(I) Perchlorate Monohydrate

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Crystals of the title compound belong to space group $P2_1/c$, with $a = 15.533$ (12) Å, $b = 7.356$ (6) Å, $c = 13.019$ (8) Å, $\beta = 117.43$ (5)°, and $Z = 4$ monomeric units. They contain planar centrosymmetric $[(\text{adeninium})_2Ag_2]^{4+}$ cations in which two adjacent silver atoms are bridged by two N(3),N(9)-bidentate adeninium cations. N(1) is protonated and the acidic proton originally attached to N(9) in adenine is displaced to N(7) in the complex. Each silver atom is coordinated to N(3) of one ligand (Ag–N(3) = 2.194 (10) Å) and N(9) of the other (Ag–N(9) = 2.155 (10) Å). The distortion at Ag (N(3)–Ag–N(9) = 164.1 (2)°) is ascribed to the arrangement of donor atoms in the ligand. No silver–silver bonding is assumed to exist in spite of the lack of intervening ligand and the relatively short Ag–Ag separation (3.002 (1) Å). Perchlorate ions of one type are involved in tridentate interactions with silver atoms: one oxygen in the molecular plane forms a weak ionic bond to silver (Ag–O = 2.635 (6) Å), whereas two more oxygens interact very weakly by bridging a pair of silver atoms on another complex ion (Ag–O = 2.903 (5) and 3.009 (4) Å). The water molecule is strongly hydrogen bonded to N(7)–H(7), but all other hydrogen bonds are rather weak. Complex cations and the latter set of perchlorate ions form layers between which another set of weakly hydrogen-bonded perchlorate ions is inserted.

Introduction

As part of a program of crystallographic studies on silver and mercury complexes with heterocyclic bases of nucleic acids, we recently reported the crystal structure of a silver nitrate complex with 9-methyladenine.[1] Those crystals contain infinite chains of digonally coordinated silver ions and bridging N(1),N(7)-bidentate ligands. The title compound was prepared from adenine and silver perchlorate in 2 M $HClO_4$. At that acidity, N(1) and N(9) would be occupied by protons in the free ligand, which would leave N(7) and N(3) as potential binding sites for silver. However, in multidentate ligands, protons are often transferred to other acceptors by entering metal ions. The crystal structure was investigated in order to determine unambiguously the distribution of silver and hydrogen ions on the various basic sites available on the ligand.

Experimental Section

Preparation. Adenine (0.70 g) was dissolved in 500 mL of warm water and 54 mL of a 2% $AgClO_4$ solution (from Ag_2O and $HClO_4$) was added, followed by 125 mL of concentrated $HClO_4$. On standing in the dark at room temperature, the mixture yielded 0.20 g of well-formed colorless crystals.

Crystal data: formula $C_5H_8AgCl_2N_5O_9$; fw 460.95; monoclinic; space group $P2_1/c$; $a = 15.533$ (12) Å; $b = 7.356$ (6) Å; $c = 13.019$ (8) Å; $\beta = 117.43$ (5)°; $V = 1320.3$ Å^3; $d_{\text{calcd}} = 2.32$ g/cm^3; $d_{\text{obsd}} = 2.30$ g/cm^3 (flotation in bromoform–bromobenzene); $Z = 4$; μ(Mo Kα) = 19.55 cm^{-1}; $T = 23$ °C; λ(Mo Kα) = 0.710 69 Å (graphite monochromator).

Crystallographic Measurements. A drawing showing the shape and dimensions of the crystal used is part of the supplementary material.

Space group $P2_1/c$ was indicated from a set of precession photographs. Accurate cell parameters were obtained by refining the setting angles of 15 reflections automatically centered and indexed on a Syntex $P\bar{1}$ diffractometer.

Intensities of 2340 independent hkl and $hk\bar{l}$ reflections within a sphere $2\theta \leq 50°$ were measured with the $P\bar{1}$ diffractometer using the $2\theta/\theta$ scan technique. The peaks were scanned from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$. The scan rate was 1° (2θ)/min for most reflections, but higher rates (up to 24°/min) were automatically selected by the autocollection program for strong reflections. Stationary-background counts were taken at each limit of the scan. Counting time was selected to make the background time-to-scan time ratio equal to 0.40. Three standard reflections (310, 040, 014) measured every 50 reflections showed maximum fluctuations of ±3% from average during data collection.

Net intensities I were obtained from $I = (I_t - B/0.40)S$, where I_t is the total scan count, B is the total background count, and S is the scan rate. $\sigma(I)$ was calculated from $\sigma^2(I) = (I_t + B/0.16)S^2 + (0.02I)^2$. A total of 476 reflections (including the systematic absences) with $I/\sigma(I) < 2.5$ were considered as "unobserved". Lorentz and polarization corrections were applied. An absorption correction based on the crystal geometry was applied at a later stage (Program NRC-3,

Table I. Refined Atomic Coordinates (×10^4; for Ag ×10^5) and Temperature Factors (×10^3; for Ag and Cl ×10^4)[a]

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag	104570 (2)	37440 (6)	44820 (3)	300 (2)	378 (2)	495 (2)	−96 (2)	206 (2)	−90 (2)
Cl(1)	4624 (1)	−2842 (2)	3975 (1)	318 (5)	271 (6)	388 (6)	−15 (5)	192 (5)	−8 (5)
Cl(2)	11393 (1)	572 (2)	3078 (1)	397 (6)	355 (6)	377 (6)	31 (5)	201 (5)	0 (5)
N(1)	6872 (2)	3100 (6)	4591 (3)	33 (2)	39 (2)	43 (2)	1 (2)	25 (2)	−1 (2)
N(3)	8382 (2)	4218 (5)	4900 (3)	28 (2)	35 (2)	39 (2)	−3 (2)	19 (2)	−3 (2)
N(7)	8080 (2)	−28 (5)	3505 (3)	37 (2)	27 (2)	42 (2)	1 (2)	19 (2)	−7 (2)
N(9)	9200 (2)	2151 (5)	4186 (3)	30 (2)	33 (2)	37 (2)	−3 (2)	17 (2)	−2 (2)
N(10)	6223 (3)	264 (6)	3800 (4)	35 (2)	45 (3)	59 (3)	−14 (2)	24 (2)	−0 (2)
C(2)	7573 (3)	4364 (7)	4970 (4)	32 (2)	37 (3)	42 (3)	−2 (2)	21 (2)	−4 (2)
C(4)	8453 (3)	2660 (6)	4388 (3)	28 (2)	33 (3)	27 (2)	−5 (2)	9 (2)	0 (2)
C(5)	7749 (3)	1314 (7)	3963 (4)	32 (2)	32 (2)	31 (2)	−1 (2)	13 (2)	0 (2)
C(6)	6910 (3)	1477 (7)	4089 (4)	30 (2)	37 (3)	35 (2)	−3 (2)	13 (2)	0 (2)
C(8)	8943 (3)	541 (7)	3653 (4)	33 (2)	37 (3)	41 (3)	0 (2)	15 (2)	−4 (2)
O(11)	4321 (2)	−1358 (5)	3178 (3)	53 (2)	40 (2)	57 (2)	2 (2)	24 (2)	15 (2)
O(12)	5432 (3)	−3721 (6)	3963 (4)	51 (2)	60 (3)	75 (2)	15 (2)	41 (2)	6 (2)
O(13)	3836 (2)	−4088 (5)	3663 (3)	48 (2)	43 (2)	55 (2)	−17 (2)	26 (2)	−7 (2)
O(14)	4887 (3)	−2190 (5)	5129 (3)	54 (2)	51 (2)	39 (2)	−2 (2)	18 (2)	−9 (2)
O(21)	12175 (3)	−568 (6)	3258 (4)	66 (3)	63 (3)	71 (3)	30 (2)	26 (2)	1 (2)
O(22)	11112 (3)	1564 (6)	2040 (3)	90 (3)	60 (3)	56 (2)	14 (2)	28 (2)	21 (2)
O(23)	11666 (3)	1777 (7)	4041 (4)	72 (3)	70 (3)	65 (3)	2 (2)	25 (2)	−24 (2)
O(24)	10599 (3)	−501 (8)	2980 (4)	80 (3)	88 (4)	101 (4)	−28 (3)	61 (3)	−17 (3)
O(W)	6621 (3)	−2608 (5)	2410 (3)	49 (2)	42 (2)	65 (2)	−10 (2)	12 (2)	−3 (2)

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

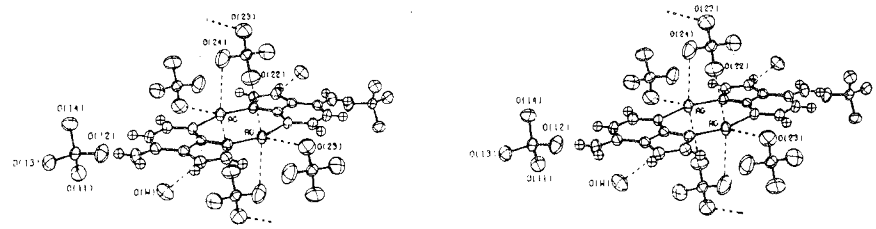

Figure 1. Stereoview of $[(\text{adeninium})_2\text{Ag}_2]^{4+}$ and its environment. A center of symmetry sits halfway between the silver atoms. All atoms of adenine can be identified by comparison with Figure 2. The formula includes four perchlorate ions: two of type 1, two of type 2. Type 1 ions interact only through hydrogen bonding. Tridentate type 2 anions interact intramolecularly and a total of four anions are required to obtain a complete view of silver environment.

Ahmed and Singh). A grid of 10 × 10 × 10 was used and the transmission factor ranged from 0.55 to 0.87. The set of 1864 nonzero reflections was used to solve and refine the structure.

Solution and Refinement of Structure. The structure was solved by the heavy-atom method and refined by full-matrix least squares initially and by block-diagonal least squares in the later stages. The function minimized was $\sum w(|F_o| - |F_c|)^2$.

The silver atom was located from a Patterson map. A subsequent Fourier map revealed the positions of all other nonhydrogen atoms. Isotropic refinement proceeded normally, using unit weights and full-matrix least squares. Silver and chlorine were then refined anisotropically and the R factor ($=\sum||F_o| - |F_c||/\sum|F_o|$) was 0.064. At this stage, the data were corrected for absorption and R was reduced to 0.049. All hydrogen atoms, except those of water, were visible in the difference Fourier map. They were fixed at their calculated positions (C–H = 0.95 Å, N–H = 0.85 Å) and were assigned isotropic temperature factors $B = 6.0$ Å^2. Individual weights $w = 1/\sigma(F)^2$[2] and block-diagonal least squares were subsequently used. Refinement of the scale factor, secondary extinction coefficient,[3] coordinates, and anisotropic temperature factors for all nonhydrogen atoms converged to $R = 0.031$ and $R_w = (\sum w(|F_o| - |F_c|)^2/w|F_o|^2)^{1/2} = 0.041$. The standard deviation of an observation of unit weight was 1.60. No attempts were made to refine hydrogen parameters. Their positions were recalculated at the end and the new positions were introduced into least-squares calculations. Additional refinement produced no significant changes in the parameters of nonhydrogen atoms.

The general background in the final difference Fourier map was lower than ±0.5 e/Å^3, except for two peaks of 0.7 e/Å^3 near silver.

The form factors for nonhydrogen atoms were those of Cromer and Waber.[4] The scattering curve of hydrogen was taken from Stewart et al.[5] Anomalous dispersion factors for silver and chlorine[6] were included in the calculations. The computer programs used are listed elsewhere.[7]

The refined parameters of nonhydrogen atoms are listed in Table I. Hydrogen coordinates are part of the supplementary material.

Description of the Structure

Two centrosymmetrically related units joined together form a planar $[(\text{adeninium})_2\text{Ag}_2]^{4+}$ cation in which silver is bonded to N(3) and N(9) of bridging bidentate adeninium ligands. (Figure 1). [Ligand atoms are numbered as in Figure 2. Cl(1) and O(1*j*) with *j* = 1–4 belong to type 1 perchlorate ions. Atoms of type 2 ions are similarly labeled Cl(2) and O(2*j*). O(W) is water oxygen.] Interatomic distances and bond angles around silver are listed in Table II. The unit cell contains two nonequivalent sets of perchlorate anions. Type 1 anions are remote from silver, and interactions with complex cations are restricted to hydrogen bonding. The pair of silver atoms makes contact with four type 2 anions: two of them form intramolecular bridges above and below the plane of the cation, and two more are found at the ends of the Ag–Ag axis. As noticed for other silver compounds,[8-10] two contiguous silver atoms are nested in a large cavity created by donor atoms of perchlorate ions and adeninium ligands.

Coordination of Silver. Each silver atom is surrounded by six neighbors (two nitrogens, three oxygens, and one silver) within 3 Å (Table II) but strong bonds are established only with N(9) (2.16 (1) Å) and N(3) (2.20 (1) Å). Similar bond lengths have been reported for complexes with imidazole,[11] pyrazine,[12] 9-methyladenine,[1] and other nitrogen donors.[13] Therefore, silver is basically two-coordinated with an N(3)–Ag–N(9) angle of 164.1 (1)°. Packing is responsible for large departure from linearity in a number of silver

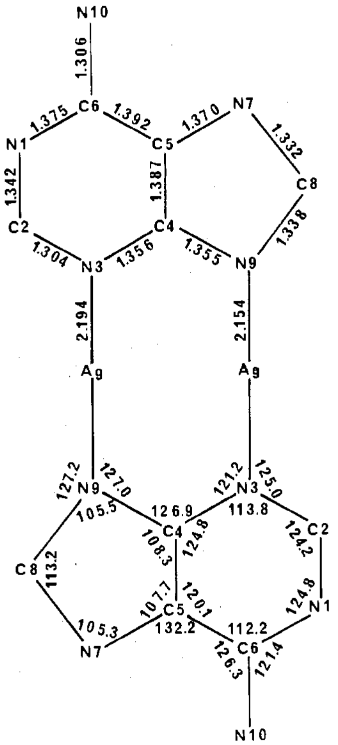

Figure 2. Interatomic distances and bond angles in [(adeninium)$_2$Ag$_2$]$^{4+}$. Unless otherwise stated, esd's are 0.3–0.5° on angles and 0.006–0.007 Å on distances.

Table II. Interatomic Distances and Bond Angles in the Coordination Sphere of Silver and in the Perchlorate Ions

Atoms	Dist, Å	Atoms	Angle, deg
Ag-N(9)	2.155 (10)	N(9)-Ag-N(3)^a	164.1 (2)
Ag-N(3)^a	2.195 (10)	N(9)-Ag-O(22)^b	88.5 (1)
Ag-Ag^a	3.002 (1)	N(9)-Ag-O(23)	109.9 (2)
Ag-O(22)^b	3.009 (4)	N(9)-Ag-O(24)^c	84.4 (2)
Ag-O(23)	2.635 (5)	N(3)^a-Ag-O(22)^b	81.0 (1)
Ag-O(24)^c	2.903 (5)	N(3)^a-Ag-O(23)	84.7 (2)
		N(3)^a-Ag-O(24)^c	103.0 (2)
		O(22)^b-Ag-O(23)	106.8 (1)
		O(22)^b-Ag-O(24)^c	165.3 (1)
		O(23)-Ag-O(24)^c	87.8 (2)
Cl(1)-O(11)	1.429 (4)	O(11)-Cl(1)-O(12)	109.7 (2)
Cl(1)-O(12)	1.418 (5)	O(11)-Cl(1)-O(13)	109.3 (2)
Cl(1)-O(13)	1.430 (4)	O(11)-Cl(1)-O(14)	110.0 (2)
Cl(1)-O(14)	1.445 (4)	O(12)-Cl(1)-O(13)	110.5 (2)
		O(12)-Cl(1)-O(14)	109.6 (2)
		O(13)-Cl(1)-O(14)	107.6 (2)
Cl(2)-O(21)	1.405 (5)	O(21)-Cl(2)-O(22)	109.2 (3)
Cl(2)-O(22)	1.417 (4)	O(21)-Cl(2)-O(23)	109.9 (3)
Cl(2)-O(23)	1.430 (5)	O(21)-Cl(2)-O(24)	109.3 (3)
Cl(2)-O(24)	1.419 (6)	O(22)-Cl(2)-O(23)	110.7 (3)
		O(22)-Cl(2)-O(24)	109.1 (3)
		O(23)-Cl(2)-O(24)	108.6 (3)

^{a} $2-x, 1-y, 1-z$. ^{b} $x, {}^1/_2-y, {}^1/_2+z$. ^{c} $2-x, {}^1/_2+y, {}^1/_2-z$.

complexes.[1,11,12] However, in the present case, distortion is most likely due to the ligand geometry and the nearby silver atom.

The overall coordination sphere also includes three perchlorate oxygens. The closest to silver is O(23) at 2.635 (5) Å in the molecular plane. Inasmuch as short distances of 2.45 Å are attained in ionic salts with other oxyanions (nitrate,[8] chlorite[14]), the Ag–O(23) distance probably corresponds to rather weak ionic bonding. With silver–oxygen distances of 2.903 (5) and 3.009 (5) Å, respectively, O(22) and O(24) are just at the 3-Å limit where Ag···O interactions are considered to become vanishingly small.[8] Strictly speaking, they are not bonded to silver, but their particular location with respect to silver and the complex cation suggests nonnegligible Ag···O interactions. The perchlorate ions themselves have the expected tetrahedral structure with only minor distortion.

Table III. Effect of Protonation and Metalation on Bond Angles (deg) in the Six-Membered Ring^a

	Neutral	N(1)-H$^+$	N(3)-Cu^{2+}	N(1)-H$^+$, N(3)-Ag$^+$
C(5)-C(6)-N(1)	117.5	113.6 (−3.9)	116.8 (−0.7)	112.2 (−5.3)
C(6)-N(1)-C(2)	118.8	123.8 (+5.0)	119.6 (+0.8)	124.8 (+6.0)
N(1)-C(2)-N(3)	128.8	125.2 (−3.6)	127.0 (−1.8)	124.2 (−4.6)
C(2)-N(3)-C(4)	111.0	112.0 (+1.0)	113.5 (+2.5)	113.8 (+2.8)
N(3)-C(4)-C(5)	126.6	127.3 (+0.7)	123.4 (−3.2)	124.8 (−1.8)
C(4)-C(5)-C(6)	117.2	118.0 (+0.8)	119.5 (+2.3)	120.1 (+2.9)
σ	0.6	0.6	0.5	0.4
Source	Ref 1	Ref 1	Ref 17	This work

^{a} Numbers in parentheses represent differences from the neutral form.

The sixth neighbor of silver is the adjacent silver atom in the dimer at 3.002 (1) Å. The Ag–Ag separation is only 0.11 Å greater than in metallic silver,[15] but shorter distances have been observed (e.g., 2.88 Å in glycine–silver nitrate[10]). As will be discussed hereafter, metal–metal bonding is not assumed to take place in the present compound.

The Ligand. Interatomic distances and bond angles in the ligand are shown in Figure 2. They agree well with the results obtained by de Meester and Skapski[16] for (adeninium)$_2$Cu$_3$Cl$_8$, the only complex reported so far in which complexation takes place at N(3) and N(9) and protonation at N(1) and N(7).

Protonation and complexation result in considerable changes in the six-membered ring geometry. As shown in Table III, N(1) protonation increases the internal angle at N(1) by 5° and decreases the adjacent angles at C(2) and C(6) by 3.5–4.0°. Copper complexation at N(3) in [Cu$_2$(adenine)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$·2H$_2$O[17] affects nearby angles similarly but to a lesser extent. Hence, the angle at N(3) undergoes a 2.5° increase, while those at C(2) and C(4) are reduced by 1.8 and 3.2°, respectively. The latter effect is also found in the present silver complex and the overall changes (Table III) correspond approximately to the combined contributions from N(1) protonation and N(3) complexation. Surprisingly, in [(9-methyladenine)Ag]NO$_3$·H$_2$O,[1] ligand geometry was not affected by attachment of silver to N(1).

Differences are observed in the five-membered ring geometry with respect to the free ligand, but individual contributions from N(9) complexation and N(7) protonation cannot be sorted out as above. It is interesting to note, however, that the N(7)–C(8) and C(8)–N(9) bond lengths are different in free adenine rings (1.310, 1.370 Å) but equal in the silver complex (1.332 (4), 1.338 (4) Å). This was also noted for copper complexes[17] and indicates a redistribution of π-electron density and bond order in the N(7)–C(8)–N(9) section of the molecule.

The two-ring system is roughly planar and the distances from the silver atoms to that plane are 0.19 and 0.41 Å.

Packing. A packing diagram is shown in Figure 3. Packing is frequently controlled by ligand stacking and hydrogen bonding in DNA bases and their metal complexes. In this structure, adjacent dimers are not parallel and stacking effects are totally absent because of the lack of contact between purine rings. On the other hand, Table IV shows only one strong hydrogen bond between water oxygen O(W) and N(7)–H(7) (N···O = 2.791 (6) Å). All remaining distances are much greater than those suggested by Hamilton and Ibers[18] for N–H···O (2.9 Å) and O–H···O (2.8 Å) hydrogen bonds, and there is no one-to-one correspondence between donors and acceptors. Indeed, in most cases, N–H bonds are directed

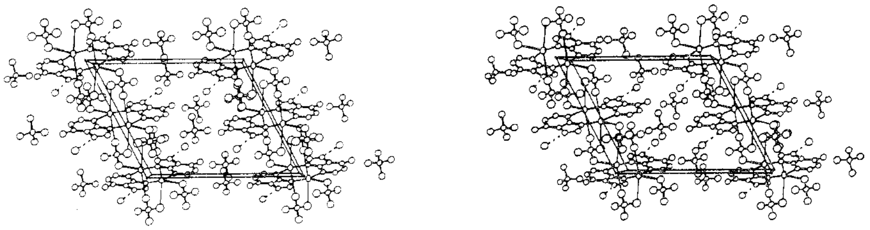

Figure 3. Projection of the structure down the *b* axis. *a* runs from left to right and *c* points toward the top of the drawing. $[(\text{adeninium})_2\text{Ag}_2]^{4+}$ ions and type 2 bridging ClO_4^- ions form layers parallel to the *bc* plane at $a \approx 0$ and 1, whereas type 2 ClO_4^- ions are close to a similar plane at $a \approx {}^1/_2$.

Table IV. Hydrogen Bond Lengths and Angles

Atoms	Angle, deg	Length, Å	Length from H, Å
N(7)-H(7)···O(W)	153.4	2.791 (6)	2.01
N(10)-H(11)···O(W)	157.7	3.026 (6)	2.22
N(10)-H(2)···O(11)	124.0	2.933 (6)	2.37
N(10)-H(2)···O(14)	146.5	3.024 (6)	2.28
N(1)-H(1)···O(14)[a]	147.3	2.994 (6)	2.24
N(1)-H(1)···O(13)[a]	131.4	3.034 (6)	2.40
N(1)-H(1)···O(12)[d]	121.7	3.074 (6)	2.54
O(W)-H···O(14)[b]		2.954 (5)	
O(W)-H···O(13)[c]		2.871 (5)	
O(W)-H···O(12)[e]		3.051 (6)	

[a] $1-x, \bar{y}, 1-z$. [b] $x, -{}^1/_2-y, -{}^1/_2+z$. [c] $-x, {}^1/_2+y, {}^1/_2-z$. [d] $x, 1+y, z$. [e] $1-x, -{}^1/_2+y, {}^1/_2-z$.

between two potential oxygen acceptors at equal distances and, conversely, acceptors are equally close to more than one hydrogen atom. Thus, type 1 perchlorates and dimers are not hooked together by well-defined hydrogen bonds. Instead, the edge of the complex ion (including the strongly H-bonded water molecule) looks like a continuous cushion of positively charged hydrogens in contact with negatively charged oxygens of type 1 perchlorate anions. Type 2 perchlorates probably affect packing to a greater extent. Each type 2 ion has two of its oxygens bridging a pair of silver atoms in a dimer, while a third oxygen is bonded to silver atoms in another dimer. Although Ag···O interactions are not particularly strong, the tridentate character of the ion may force a preferred orientation of complex cations in order to place the three silver atoms at positions consistent with its own tetrahedral structure.

Discussion

Silver was found to react with N(1) and N(7) in $[(9\text{-methyladenine})\text{Ag}]\text{NO}_3\cdot\text{H}_2\text{O}$.[1] However, none of those sites are occupied by silver in the adenine complex described here. Inasmuch as reaction takes place at N(9), a site blocked by a ribose group in DNA, this complex affords little information concerning silver–DNA interactions. However, it raises interesting questions about the distribution of silver and hydrogen ions on the various basic sites available.

The amino "lone pair" on N(6) is always involved in the aromatic π system of adenine rings and shows no basic properties. When N(9) is blocked by a ribose (adenosine, AMP, DNA, etc.) or an alkyl group, three potential coordination sites are available. Complexation takes place preferentially on N(7),[19] and in several compounds, N(1) is simultaneously occupied by a proton[20] or a second metal ion.[1,21] Reaction with N(1) only is known for one zinc complex,[22] but no examples of N(3)-coordinated compounds have been reported so far. In adenine, the blocking group is replaced by an acidic hydrogen attached to N(9). Hydrogen remains at that position in $(\text{adeninium})\text{ZnCl}_3$,[23] where zinc binds to N(7), N(1) is protonated, and N(3) is free. However, hydrogen displacement from N(9) to N(7), and vice versa, is possible in such ligands. For instance, a hydrogen is attached to N(7) in 6-mercaptopurine[24] and transferred to N(9) on binding of mercury to sulfur in *the other ring*.[25] Similarly, in some complexes including ours, metal ions bind to N(9) with displacement of hydrogen to N(7).[16,17,26,27] Cu(II) and now Ag(I) are the only metal ions known to react with N(3), and for both, reaction takes place at N(9) as well.

With copper, adenine bridging via N(3) and N(9) leads to infinite chains in $(\text{adeninium})_2\text{Cu}_3\text{Cl}_8$[16] and to dimers in three other compounds.[17,27,28] The copper dimers have much in common with the silver dimer described here. For copper, strongly bonded N(3),N(9)-bridging adenine ligands are repeated every 90° around the Cu–Cu axis. With silver, bridging pairs of donors also repeat every 90° around the Ag–Ag axis, but strongly bonded adenines alternate with very weakly interacting perchlorate ions. Both ends of the metal–metal axis are closed by ligands: perchlorate oxygens in this case, Cl^- ions or water molecules in the copper dimers. The coordinating portion N(3)–C(4)–N(9) of adenine is structurally similar to a carboxylate group, but with a wider "bite". Dimers as discussed above are formed by copper acetate,[29] silver trifluoroacetate,[30] and carboxylates of other metals.[31]

Metal atoms side by side without intervening ligands raise the problem of metal–metal bonding. The Cu–Cu separation in copper dimers is 0.45 Å greater than in metallic copper and metal–metal bonding is believed to be vanishingly small.[17] However, the Ag–Ag distance observed here is only 0.11 Å greater than in metallic silver (2.89 Å).[15] Silver–silver bonding in thiocarbamates and other compounds has been discussed by Jennische and Hesse,[32] who concluded that metal–metal separation (even when shorter than 3.0 Å) is probably determined by ligand geometry rather than Ag–Ag bonding. It is noteworthy that the Ag–Ag distance (3.009 (1) Å) and the N(3)–Ag–N(9) angle (164.1 (2)°) observed here are close to the expected values (3.08 Å, 166°), assuming that the lone pairs on N(3) and N(9) are oriented symmetrically with respect to the adjacent N–C bonds. Therefore, we do not believe that silver–silver bonding is a determining factor in the structure of the present complex.

This particular distribution of H and Ag atoms on nitrogens could not be predicted. Here are some factors which may contribute to the stabilization of the structure observed here: (i) the tautomerization energy for hydrogen transfer from N(9) to N(7) is small; (ii) silver atoms bonded to N(3) and N(9) in the direction of the lone pairs are separated by a distance greater than in metallic silver; (iii) when pairs of adenine ligands are oriented as observed here, the normal linear two-coordination of silver is achieved with only minor distortion (20° distortions due to packing forces are not unusual); (iv) two-coordination is achieved by nitrogen atoms, for which silver shows a much greater affinity than for oxygen; (v) when linearly coordinated silver interacts more weakly with extra donor atoms (in the solid state), there are no rigid rules concerning the number and distribution in space of such interactions. For instance, in the present compound, two nitrogens and three oxygens define an octahedron with one apex missing. The absence of this sixth donor (which would take the place of the other silver) does not break a rigid rule in the coordination chemistry of silver and produces no appreciable instability in the compound.

All these factors may contribute to various degrees to the stability of the structure observed here.

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Registry No. $[(adeninium)_2Ag_2](ClO_4)_4 \cdot H_2O$, 63301-89-3.

Supplementary Material Available: Listings of structure factor amplitudes and H atom coordinates and a drawing showing the shape and dimensions of the crystal used (12 pages). Ordering information is given on any current masthead page.

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Novel Sulfur Dioxide Coordination in Nitrosyl(sulfur dioxide)bis(triphenylphosphine)rhodium and an Oxygen-18 Study of Its Reaction with Molecular Oxygen[1]

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Crystals of $Rh(NO)(SO_2)(PPh_3)_2$ have been obtained from SO_2-saturated solutions of $Rh(NO)(PPh_3)_3$, and the structure has been determined at 25 °C. The compound crystallizes in the orthorhombic space group *Pbca* with $a = 10.338$ (2) Å, $b = 18.500$ (4) Å, $c = 33.933$ (7) Å, $d_c = 1.48$ g cm^{-3}, $d_m = 1.47$ g cm^{-3}, and $Z = 8$ (Cu $K\alpha_1$ radiation, λ 1.54051 Å). The structure refined to an unweighted R value of 0.038 for 2615 reflections with $I > 2\sigma(I)$. The SO_2 binds to the metal both through the sulfur atom and through one oxygen atom with a Rh–S distance of 2.326 (2) Å and a Rh–O(2) distance of 2.342 (5) Å. The S–O(2) distance of 1.493 (5) Å is considerably longer than the S–O(1) distance of 1.430 (5) Å, while the O(1)–S–O(2) angle is 115.1 (4)°. The RhNO unit in this structure is clearly bent with a Rh–NO angle of 140.4 (6)°. The factors influencing the bending of the nitrosyl are discussed in terms of the metal coordination geometry and number of d electrons. The mechanism of the reaction of this S,O-bonded SO_2 with molecular oxygen to form coordinated sulfate has been studied utilizing oxgen-18 substitution and infrared analysis. This study has revealed a distribution of the labeled oxygen in the resulting $Rh(NO)(SO_4)(PPh_3)_2$ different from that observed for S-bonded SO_2 reactions with molecular oxygen.

Introduction

It is well established that terminally bound SO_2 can possess both coplanar and pyramidal MSO_2 geometry when binding to transition metals through the sulfur atom. Likewise, the O-bonded geometry has been observed in a complex of SO_2 with SbF_5.[2] However, the ability of SO_2 to bind to transition metals through both the sulfur atom and an oxygen atom simultaneously was not recognized prior to our preliminary communication of the structure of $Rh(NO)(SO_2)(PPh_3)_2$.[1] It is interesting to note that this type of geometry does appear to be common for both CO_2 and CS_2 and has been structurally established in $Ni(CO_2)(PCy_3)_2$ (Cy = cyclohexyl)[3] and $Pt(CS_2)(PPh_3)_2$.[4] The extreme lability of the SO_2 in $Rh(NO)(SO_2)(PPh_3)_2$ had been observed previously and had hindered its isolation and characterization. Similarly its reaction with molecular oxygen to form a coordinated sulfate had been reported.[5] The significance of these data, however, could only be recognized after the structural features of this