in the half-wave potential as a function of the ionic strength can be described by eq. 1. Because of this agreement, one must conclude that hydration is more important than complexation in these systems.

The plot of log $(i/i_d - i)$ vs. $E_{d.e.}$ for the zinc systems yielded a linear curve with a slope of approximately 33 mv., a reversible two-electron reduction; the values approached the theoretical value of 30 mv. as the concentration of $LiNO_3$ was increased. The same plot for the nickel systems yielded a nonlinear curve with slope values in the vicinity of 120 mv. indicating a nonreversible reduction.

The use of hydration parameters for these ions in the vicinity of 10–15 appear to be the most probable.[4]

(4) R. A. Robinson and R. H. Stokes, ref. 3, pp. 62, 246.

The hydration parameters chosen for these systems were 12 for zinc and 10 or 20 for nickel. Since nickel shows a nonreversible reduction, either a one- or two-electron mechanism might be proposed for the primary electrode reaction. Calculations were made using a hydration parameter of 10 when a one-electron reduction was considered, and a hydration of 20 when a two-electron mechanism was proposed. In the case of nickel, a better experimental–theoretical fit of the data was obtained when the hydration parameter of 10 and a one-electron mechanism was used (see Table II).

Binding of Silver Ion by Adenine and Substituted Adenines

By Keith Gillen, Ronald Jensen, and Norman Davidson

Potentiometric, pH-Stat titrations reveal that silver ion forms insoluble compounds at pH values around 7 with 6-dimethylaminopurine, adenine, deoxyadenosine, and 9-methyladenine; and a soluble polymeric species with deoxyadenosine 5'-monophosphate. The binding by 9-methyl-6-dimethylaminopurine is much weaker. In the reaction with 6-dimethylaminopurine, a 1:1 compound is formed and the N-9 proton is displaced according to the reaction: $Ag^+ + BH \rightleftharpoons (AgB)_{ppt} + H^+$, $K = 5.0 \times 10^3$ M^{-1}. With 9-methyladenine and deoxyadenosine, the reaction is: $3Ag^+ + 2BH + ClO_4^- \rightleftharpoons [Ag_3B_2\cdot ClO_4]_{ppt} + 2H^+$, $K = [H^+]^2/[BH]^2[Ag^+]^3 = 1.37 \times 10^4$ M^{-3} and 6.08×10^2 M^{-3}, respectively. The novel and unexpected result of this investigation is that with substances like adenosine and 9-methyladenine, the very weakly acidic amino hydrogens can be displaced by silver ions. With adenine, the reaction is complex; both N-9 and amino hydrogens are displaced. There is 1.5–2.0 Ag^+ bound per adenine and slightly less proton displacement. With deoxyadenosine 5'-monophosphate at pH ≥ 7, a soluble polymeric species is formed according to a reaction of the type: $2Ag^+ + BHP^{-2} \rightleftharpoons (1/n)[Ag_2BP]_n^{-n} + H^+$.

Introduction

Silver ion and mercuric ion form complexes with the nucleic acids and with polynucleotides which undoubtedly involve covalent bond formation with the purine and pyrimidine moieties, and most probably electron-pair bonds to σ-electron pairs of nitrogen atoms (although the possibility of π-bonding or some other exotic type of interaction is not absolutely excluded).[1-3] In order to understand these complexes more fully, we have investigated the reactions between silver ion and some monomeric adenine derivatives.

It is well known that silver ion forms precipitates with purines but not with pyrimidines in fairly acid solution.[4] (Although, so far as we know, the first measurement of a solubility product constant is that reported here.) A simple hypothesis as to the structure of the insoluble silver–purine complex is that it is a 1:1 compound, and a linear neutral polymer formed by replacement of the N-9 hydrogen atom of purine by silver, and then the formation of a second silver–nitrogen bond with one of the several basic nitrogen atoms of another purine molecule. In the sketch in Fig. 1, the polymerization involves the N-9 and N-7

nitrogen atoms. It will be shown that the reaction to form a 1:1 compound does occur, but it is not the only possible reaction for adenine derivatives.

If the N-9 hydrogen were the only replaceable hydrogen, adenine derivatives which are blocked in the N-9 position, such as 9-methyladenine or adenosine, would be unable to form such neutral linear polymers, and would either form conventional, soluble 2:1 complexes (analogous to $H_3N:Ag:NH_3^+$), or, conceivably, charged linear polymers, $-Ads-Ag^+-Ads-Ag^+-$ (Ads being the neutral adenosine molecule).

The investigations reported here reveal that the predictions described in the previous paragraph are wrong. Silver ion can react with 9-methyladenine and with adenosine by displacement of one of the weakly acidic amino protons to form fairly insoluble compounds.

Experimental

Materials.—The adenine derivatives studied were the highest grade available from the sources indicated below. No further purification was attempted. The disodium salt of deoxyadenylic acid (5') (A grade), deoxyadenosine (A grade), adenine (A grade), and 6-dimethylaminopurine (A grade) were from Calbiochem. 9-Methyladenine was supplied by the Cyclo Chemical Co.[5]; and 9-methyl 6-dimethylaminopurine was kindly furnished by Prof. Roland K. Robbins of the University of Arizona.[6]

(1) T. Yamane and N. Davidson, J. Am. Chem. Soc., **83**, 2599 (1961).
(2) T. Yamane and N. Davidson, Biochim. Biophys. Acta, **55**, 609 (1962).
(3) S. Katz, ibid., **68**, 240 (1963).
(4) A. Bendich, "The Nucleic Acids," Vol. I, E. Chargaff and J. N. Davidson, Ed., Academic Press, New York, N. Y., 1955, p. 124.

(5) Los Angeles 1, Calif.
(6) R. K. Robbins and H. H. Lin, J. Am. Chem. Soc., **79**, 490 (1957).
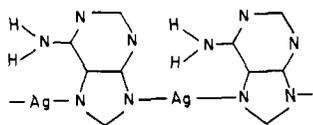
Fig. 1.—A possible neutral linear 1:1 polymer of silver ion and purine.

Physical constants from the literature or as determined by us for some of these compounds are: 6-dimethylaminopurine, λ_{max} 277 mμ (ϵ 1.56 × 10^4) at pH 2 (data from Calbiochem and ref. 7), pK_a = 3.87 in H$_2$O,[7] pK_a = 4.53 in 0.1 M NaClO$_4$ (this work); 9-methyladenine, λ_{max} 262 mμ (ϵ 1.32 × 10^4) at pH 7[8]; 9-methyl 6-dimethylaminopurine, λ_{max} 277 mμ (ϵ 1.64 × 10^4) at pH 6, pK_a = 4.25 in 0.1 M NaClO$_4$ (this work).

Potentiometric pH-Stat Titrations.—This is the basic experimental measurement in this work, and makes it possible to measure the amount of silver ion bound and the number of protons released upon binding. Thus the equilibrium silver concentration and the unknown stoichiometric ratio m/β in the equation

$$\beta Ag^+ + H_n Pu \rightleftharpoons [Ag_\beta{}^+H_{n-m}Pu]^{\beta-m} + mH^+ \quad (1)$$
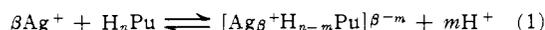
are measured. The coefficient β has been determined by direct analysis of the precipitates, and by the shape of the titration curves. The method used in the titrations is essentially the same as used previously[2] but some important technical improvements have been introduced. The electrodes for measuring the free silver ion concentration are a silver wire and a Beckman saturated calomel electrode (s.c.e.). To prevent AgCl precipitation, the s.c.e. is separated from the solution being titrated by a salt bridge (a tube with a Beckman fiber junction) containing only the supporting electrolyte being used in the experiment. Since there should be no junction potential between the experimental solution and the salt bridge solution, the potential measured is as accurate as a s.c.e. allows.

The pH is measured using this same s.c.e. and salt bridge vs. a Beckman general purpose glass electrode. However, in standardizing the pH meter against a standard buffer, the salt bridge is not used. The ionic composition of the buffer and the salt bridge solution will in general be different, and a junction potential of several tenths of a pH unit can be generated.

The silver wire vs. s.c.e. potential was measured with a Leeds and Northrup K-2 potentiometer, using a Keithley Model 200B vacuum tube voltmeter as a null detector. This instrument has an input impedance of ca. 10^{14} ohms and worked well even with a shunt of 10^9 ohms (which was not however normally used). pH was measured with a Beckman Model 76 expanded-scale pH meter. In order to eliminate pickup in measurements like this it is essential to disconnect the potentiometer completely when measuring pH and to disconnect the pH meter completely when measuring the potential of the silver wire. A high impedance switch to do this was constructed. As an additional precaution, everything except the pH meter was enclosed in a Faraday cage. Potentials were reproducible to about 1 mv. (corresponding to an error of ±10% in [Ag$^+$]); pH could be read to 0.01 unit. The potential of the silver wire relative to the s.c.e. was given by

$$E \text{ (mv.)} = 550 + 58.5 \log [Ag^+] \quad (2)$$

All solutions which were to be titrated were flushed with water-saturated argon for at least 30 min. before the titration and were kept under flowing argon during the titration. This expelled CO$_2$ to such an extent that the pH of an unbuffered solution would remain constant at 7 ± 0.05 for at least 3 hr. All pH-Stat titrations were done at 25 ± 1°.

Generally speaking, after each addition of silver, when precipitates were present, the pH and silver electrode potential become constant in about 30–60 min.

(7) S. F. Mason, J. Chem. Soc., 2071 (1954).

(8) S. F. Mason, "CIBA Foundation Symposium on the Chemistry and Biology of Purines," G. E. W. Wolstenholme and C. M. O'Connor, Ed., J. and A. Churchill, Ltd., London, 1957, p. 66.
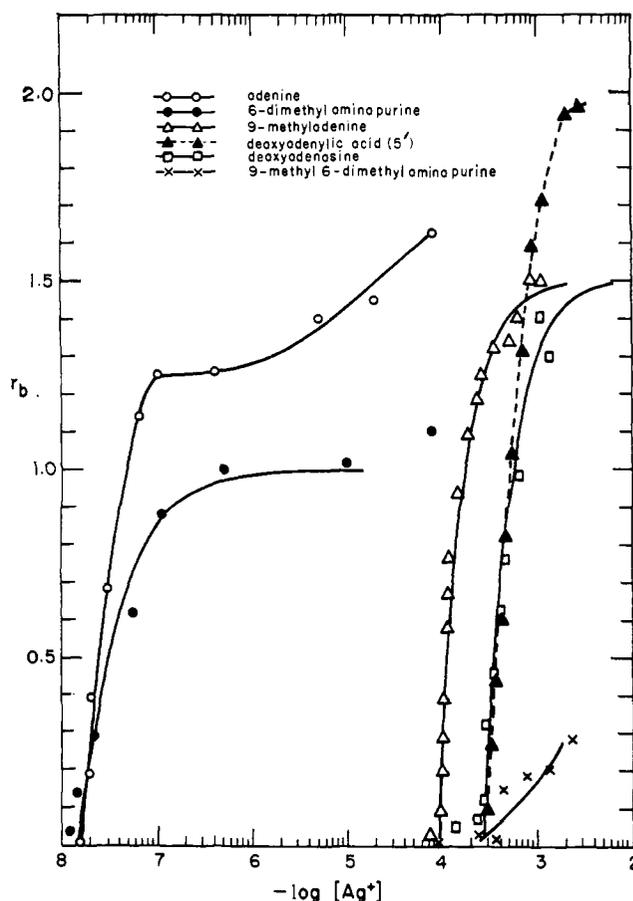
Fig. 2.—Binding curves for adenine derivatives and silver ion at pH 7 in 0.1 M NaClO$_4$ at 25 ± 1°. The initial purine concentration is always 10^{-3} M. The quantity r_b is defined as the moles of silver bound per mole of purine. For 9-methyladenine and deoxyadenosine the curves are theoretical curves for eq. 4 with K = [H$^+$]^2/[Ag$^+$]^3[BH]^2 = 1.37 × 10^4 M^{-3} and 6.08 × 10^2 M^{-3}, respectively. For 6-dimethylaminopyrine the curve is the theoretical curve for eq. 3 with K = [H$^+$]/[Ag$^+$][BH] = 5.0 × 10^3 M^{-1}.

Precipitate Analyses.—The ratio of protons displaced to silver ions bound is best measured by the titration method just described. The ratio of silver to purine in the precipitates formed is best measured by direct analysis. These analyses were done in the following manner. A deoxyadenosine or 9-methyladenine solution was buffered at the desired pH with cacodylate buffer (10^{-2} F). A specified amount of silver nitrate solution was added, whereupon a precipitate formed. At least 4 hr. was allowed for the system to equilibrate, after which the precipitate was separated from the supernatant either by centrifugation or filtration through a sintered glass filter. The precipitate was dissolved with 0.1 F HClO$_4$ and the ultraviolet spectra of the two solutions were taken. Assuming there was no soluble complex in either of these solutions, this immediately gave the amount of purine in the precipitate and free in the equilibrium solution. The sum of these always added to within 2% of the total purine present. The amount of silver in each solution was measured either by a direct potential reading using the silver wire electrode, or (in later, improved experiments) by titration with KSCN using the potential to determine the equivalence point. Using direct measurement of potential, the sum of the moles of silver in the two solutions was usually within about 10% of the total moles put into the system. By titrating with KSCN, the sum was within 1% of the moles of Ag$^+$ originally added.

Results

The results are displayed in the figures and tables which are, we hope, largely self-explanatory.

Figure 2 shows that the strongest binding is by the two purines, adenine and 6-dimethylaminopurine,
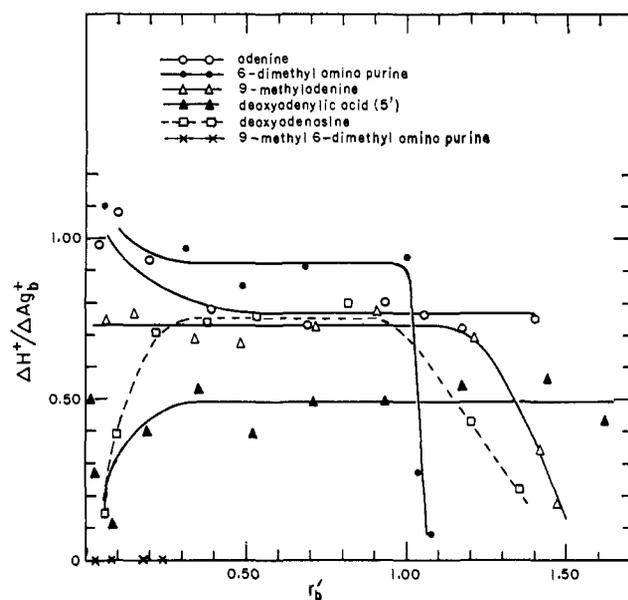
Fig. 3.—Proton release data at pH 7 with an initial purine concentration of 10^{-3} M. The quantity $\Delta H^+/\Delta Ag^+_b$ is the number of protons released per silver ion bound when a small amount of silver (usually corresponding to $\Delta r_b \approx 0.1$) is added to the solution under the given conditions. The horizontal coordinate ($r_b{}'$) is the quantity r_b at the center of each increment in r_b.

which have an N-9 hydrogen atom. The three substances, 9-methyladenine, deoxyadenosine, and deoxyadenosine 5'-monophosphate (deoxy-AMP), which are N-9 blocked but have amino hydrogens, bind less strongly, but still very markedly. The binding by 9-methyl 6-dimethylaminopurine, with no N–H bonds, is weaker and just barely perceptible under the conditions used. In all cases where binding occurs, except with deoxy-AMP, a precipitate appears to form as soon as a significant amount of silver has been bound. The titration curves are quite sharp which is qualitatively more consistent with the formation of an insoluble precipitate or a soluble polymer than with the formation of a soluble low molecular weight complex.

It may be mentioned incidentally that the binding of Ag^+ by DNA and by poly-A at this pH is weaker than the binding by the N-9 unblocked purines but stronger than the binding by the other derivatives studied.[9]

The proton release data (Fig. 3) show that for 6-dimethylaminopurine, one proton is released per silver bound; Fig. 2 and 3 both indicate that the reaction stops with one silver ion bound per purine. The reaction is therefore

$$Ag^+ + (CH_3)_2N\text{-}C_5H_2N_4H \rightleftharpoons$$
$$[(CH_3)_2N\text{-}C_5H_2N_4Ag]_{ppt} + H^+ \quad (3)$$
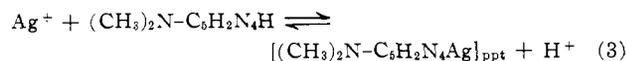
For 9-methyladenine and deoxyadenosine, there is about $0.75H^+$ released per Ag^+ bound. This is true at all pH values where reasonably accurate measurements can be made. (The binding of Ag^+ by deoxyadenosine is too weak at pH 6 for accurate measurements.) The proton release is approximately constant until $r_b > 1$ and then decreases toward zero at $r_b \approx 1.5$ (where r_b is the moles of silver bound per mole of purine). There is a fair amount of experimental error in these differential measurements.

(9) R. Jensen and N. Davidson, unpublished work.

The binding curves (Fig. 2) appear to level off at $r_b = 1.5$. We therefore propose as an idealized interpretation of the data that the reaction taking place throughout the range $0 \leq r_b \leq 1.5$ is

$$3Ag^+ + 2BH + ClO_4^- \rightleftharpoons [(Ag_3B_2)ClO_4]_{ppt} + 2H^+ \quad (4)$$
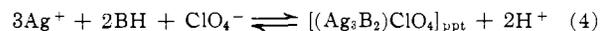
where BH is the neutral purine with H being an amino hydrogen. This predicts a constant displacement of 0.67 proton per Ag^+ bound up to $r_b = 1.5$. Reaction 4 conceivably could occur in stages, with a $1:1$ precipitate and one proton displaced in the early states of the reaction, and an additional $0.5AgClO_4$ being bound later. The constancy of the proton release argues against this possibility. Furthermore, the precipitate analyses in Table I confirm the silver

TABLE I

PRECIPITATE ANALYSES FOR SILVER ADENOSINE AND SILVER 9-METHYLADENINE PRECIPITATES

Purine[a]	pH[b]	r_b	Ratio[c]	Method[d]	Silver lost, %[e]
dA	6.60	0.87	1.54	AgSCN	<1
dA	7.80	0.87	1.46	AgSCN	<1
9-MA	6.87	0.82	1.49	AgSCN	<1
9-MA	6.85	0.80	1.46	AgSCN	<1
dA	6.7	0.10	1.45	Pot.	15
dA	6.7	0.20	1.4	Pot.	25
dA	6.8	1.10	1.53	Pot.	4
dA	6.7	1.16	1.91	Pot.	2

[a] Deoxyadenosine (dA) or 9-methyladenine (9-MA). [b] pH of precipitation. All solutions 0.1 M in $NaClO_4$ and buffered with 0.01 F cacodylate. [c] Silver to purine ratio in precipitate. [d] Thiocyanate titration or direct potentiometric determination of silver concentration. [e] Silver found in precipitate and supernatant compared to silver added. The amount of purine found was always within 1% of that expected.

to purine ratio of $1.5:1$ even at low r_b values; thus, reaction 4 is the main reaction occurring. (The most accurate silver determinations on the precipitate are done by the thiocyanate method. Unfortunately, due to an oversight, these were all done at fairly high r_b. However, we believe the analyses by the direct potential method are sufficiently accurate to justify the statements made above.)

The variation of the log of the equilibrium silver concentration with pH at fixed r_b may be represented by a straight line with slope 0.7 ± 0.1 (Fig. 4) in approximate agreement with the predictions of eq. 4. The predicted variation of the silver concentration with r_b at a fixed pH from eq. 4 is plotted in Fig. 2 for average values of the equilibrium constants. The results are in approximate agreement with the theoretical curves. The values of K computed from individual points along the curve however vary by more than 50%; hence, the agreement between theory and experiment displayed in Fig. 2 is not sufficiently good to be a strong argument for the correctness of eq. 4. The same remark applies to eq. 3 and the theoretical curve for 6-dimethylaminopurine.

The results with adenine (which has been less intensively studied) suggest that silver is bound by two consecutive but overlapping reactions

$$Ag^+ + BH_2 \rightleftharpoons [AgBH]_{ppt} + H^+ \qquad (5a)$$

$$[AgBH]_{ppt} + xAg^+ + (x - y)ClO_4^- \rightleftharpoons$$
$$[Ag_{1+z}BH_{1-y}(ClO_4)_{x-y}] + yH^+ \quad (5b)$$
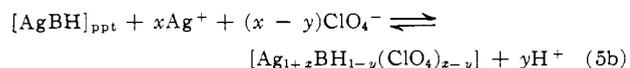
where BH_2 is neutral adenine and $1 \geq x > y \geq 0.5$. The N-9 hydrogen is displaced in (5a) and the amino hydrogen from some of the purines in (5b). The proton release starts at unity and decreases with r_b; this is the principal evidence that the two reactions overlap. The subsequent binding reaction that follows (5a) has not been carefully studied because the results at high r_b are not very precise.

The integrated proton release data for the various substances (Table II) support the interpretations offered. When an excess of silver ion is added, one proton is displaced from deoxyadenosine, 9-methyladenine, and 6-dimethylaminopurine in agreement with eq. 3 and 4. From adenine 1.5 protons are displaced in approximate agreement with eq. 5.

TABLE II

TOTAL PROTON RELEASE IN THE pH-STAT TITRATIONS[a]

Purine	pH	Final r_b	Total H⁻ released / Total purine present
6-Dimethylaminopurine	7	1.1	0.90
	7	1.0	0.93
Deoxyadenosine	7	1.6	1.0
	7	1.4	0.85
	8	1.6	1.1
9-Methyladenine	7	1.6	0.94
	7	1.5	1.0
	8	1.5	1.1
Adenine	7	1.6	1.5
Deoxyadenylic acid	7	2.8	1.0
	7	2.1	0.91
	8	2.3	0.96
	8	2.7	1.1

[a] The conditions of the titrations are as described in the legends to Fig. 2 and 3.

With deoxyadenosine 5'-monophosphate, a precipitate is not observed until about $r_b = 2.3$ at pH ≥ 7 and $r_b = 0.3$ at pH 6. The proton release data are probably somewhat complicated by the fact that the phosphate group protonates with a pK of about 6.2. The indications are that above pH 7 a soluble polymeric species is formed according to a reaction of the type

$$2Ag^+ + BHP^{-2} \rightleftharpoons (1/n)[Ag_2BP]_n^{-n} + H^+ \quad (6)$$
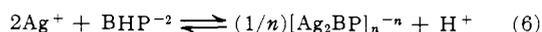
where BHP^{-2} is the dinegative deoxyadenosine monophosphate anion. The precipitate at lower pH is presumably due to protonation of the phosphate groups.

Discussion

For the soluble monomeric complexes of a series of monofunctional nitrogen bases with silver ion, the equilibrium constants for the reactions

$$Ag^+ + B \rightleftharpoons BAg^+ \quad K_{BAg} \qquad (7a)$$

$$H^+ + B \rightleftharpoons BH^+ \quad K_{BH} \qquad (7b)$$
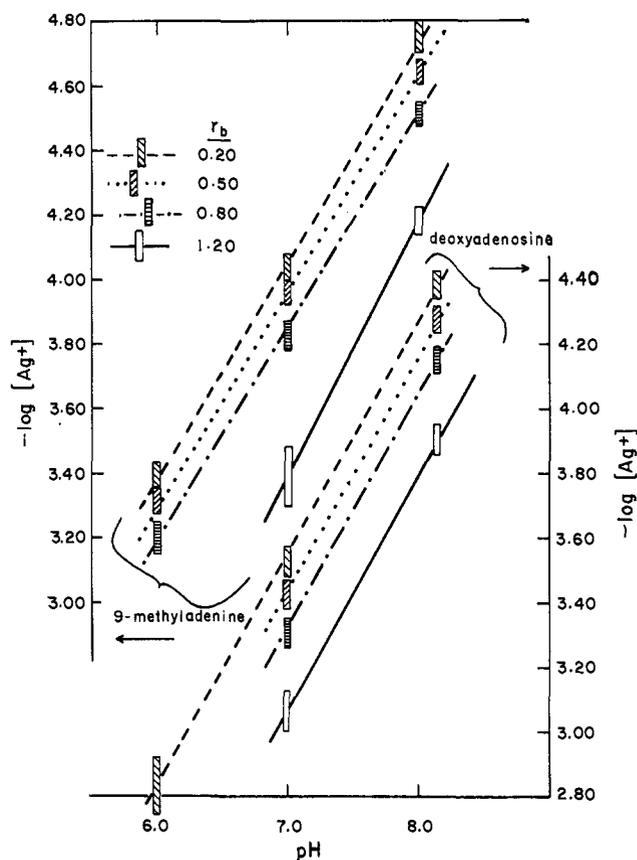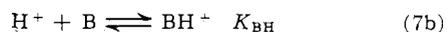
Fig. 4.—Variation of log [Ag⁺] with pH at several r_b values for deoxyadenosine and 9-methyladenine. The slopes of the straight lines are shown.

r_b	Slope (9-methyladenine)	Slope (deoxyadenosine)
0.20	0.68 ± 0.04	0.72 ± 0.06
0.50	0.66 ± 0.04	0.74 ± 0.07
0.80	0.65 ± 0.05	0.73 ± 0.07
1.20	0.79 ± 0.13	0.72 ± 0.09

fit the linear free energy equation[10]

$$\log K_{BAg} \approx 0.3 \log K_{BH} + constant \qquad (8)$$

That is, for a series of acids BH, the equilibrium constant K_9, for the breaking of a nitrogen to hydrogen bond and the formation of a nitrogen to silver bond

$$Ag^+ + BH \rightleftharpoons BAg^+ + H^+ \quad K_9 = K_{BAg}/K_{BH} \qquad (9)$$

is predicted to follow the equation

$$\log K_9 \approx -0.7 \log K_{BH} + constant \qquad (10)$$

The weaker the acid, BH, the more is reaction 9 displaced to the left at a given pH and silver ion concentration.

The pK values of the N-9 hydrogens of adenine and 6-dimethylaminopurine are 9.8 and 10.5.[7] The amino hydrogens of adenine, adenosine, and 9-methyladenine are much less acidic. Thus, at first sight, it appears plausible that the N-9 hydrogen should be replaceable by silver at a moderate pH such as 7 but surprising that the amino protons can be displaced.

(10) R. J. Bruehlman and F. H. Verhoek, J. Am. Chem. Soc., 70, 1401 (1948).
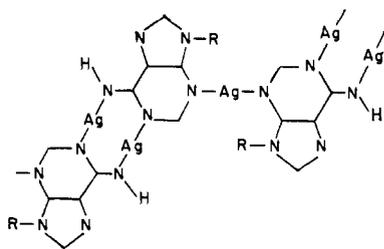
Fig. 5.—A speculation as to the structure of the silver 9-methyl-adenine (or silver adenosine) precipitate.

On reconsideration, however, this result may not be so surprising. Equation 10 is not expected to apply accurately to the substances studied here. They are not structurally very similar to the nitrogen bases which were correlated by eq. 8 in the original paper.[10] The formation of a precipitate and the necessity of comparing different reaction types (eq. 3 and 4) is an additional complicating factor. However, eq. 10 might be approximately applicable. Figure 2 shows that at pH 7 and at any fixed r_b around 0.5, the equilibrium silver ion concentration for displacing an N-9 hydrogen is about 10^{-4} of that for displacing an amino hydrogen. Take 10 for the pK_a of an N-9 NH bond; eq. 10 then predicts a pK_a of $10 + (4/0.7) \approx$ 16 for an amino hydrogen. There are no measurements available, but our chemical intuition is not repelled by this estimate.

In part, the driving force of the reactions studied here is the formation of polymeric species, either soluble or as precipitates, due to the presence of several basic nitrogen atoms in a purine ring system. This is not a decisive factor however in making a displacement of an amino hydrogen possible. Simpson has observed proton displacement of amino hydrogens of purines and pyrimidines by the monofunctional methylmercury cation to give soluble complexes.[11] Eichorn and Clark[12] have presented evidence that mercuric ion can replace a proton from the amino group of adenosine on cytidine.

There remains the perplexing question of why the silver to purine ratio for amino binding (deoxyadenosine and 9-methyladenine) is $3:2$ rather than $1:1$. A number of speculations can be put forth but, in the absence of further evidence, it is not profitable to do so. However, we wish to record the suggestion displayed in Fig. 5. Here, two silvers are used in the way that hydrogens are used in the hydrogen-bonded base pairs of nucleic acids. This type of ring formation would provide an additional driving force for the displacement of the amino hydrogens. The uptake of an additional silver per base pair (by N-3 in the figure but it could just as well be N-7) is necessary in order to get an insoluble, polymeric species.

(11) R. B. Simpson, *J. Am. Chem. Soc.*, **86**, 2059 (1964).
(12) G. L. Eichorn and P. Clark, *ibid.*, **85**, 4020 (1963).

Alkyliridium and Alkylrhodium Dihalocarbonylbis(trialkyl- or triarylphosphines)

BY R. F. HECK

Rhodium and iridium halocarbonylbis(trialkyl- or triarylphosphines) react readily with active organic halides producing alkylrhodium and alkyliridium dihalocarbonylbis(trialkyl- or triarylphosphines) in good yields. Methylrhodium chloroiodocarbonylbis(tri-n-butylphosphine) absorbs carbon monoxide at atmospheric pressure and 30° to form the corresponding acetyl derivative. Carbon tetrachloride oxidizes $RhCl(CO)[P(C_2H_5)_3]_2$ to $RhCl_3(CO)[P(C_2H_5)_3]_2$. Bromine and iodine add to $RhCl(CO)[P(n-C_4H_9)_3]_2$ to form the mixed trihalides, $RhClBr_2(CO)[P(n-C_4H_9)_3]_2$ and $RhClI_2(CO)[P(n-C_4H_9)_3]_2$, respectively.

Introduction

Only two examples of σ-bonded organorhodium compounds have been reported. Chatt[1] in 1963 found that bis(1-naphthyl)rhodium bromobis(tri-n-propylphosphine) could be prepared in 3% yield by the reaction of 1-naphthylmagnesium bromide with rhodium tribromotris(tri-n-propylphosphine). A similar compound was also prepared with diethylphenylphosphine in place of the tri-n-propylphosphine. No σ-bonded organoiridium compounds have been described in the literature although Chatt has referred to unpublished

$$1\text{-}C_{10}H_7MgBr + RhBr_3[P(n\text{-}C_3H_7)_3]_3 \longrightarrow$$

$$(1\text{-}C_{10}H_7)_2RhBr[P(n\text{-}C_3H_7)_3]_2$$

work on such compounds.[1] Both iridium and rhodium form stable π-bonded organometallic derivatives.

The report of Vaska[2] that $IrCl(CO)[P(C_6H_5)_3]_2$ has a great tendency to add covalent molecules, such as halogens, halogen halides, and hydrogen, suggested that it might be possible to add alkyl halides to this complex also and form alkyliridium derivatives.[2] The addition of alkyl halides to electron-deficient metals or metal compounds is well known with nontransition metals but there are only a few reported examples of transition metals undergoing the reaction. Two pertinent examples are the platinum tris(triphenylphosphine) reaction with methyl iodide, giving methylplatinum iodobis(triphenylphosphine),[3] and the reaction

(1) J. Chatt and A. E. Underhill, *J. Chem. Soc.*, 2088 (1963).

(2) L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **84**, 679 (1962); **83**, 2784 (1961).
(3) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).