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Intercalative Stacking Interactions and Interligand Hydrogen Bonding in Metal–Purine Complexes. Crystal and Molecular Structure of (*N*-Salicylidene-*N*′-methylethylenediamine)(aquo)(9-methyladenine)copper(II) Nitrate Dihydrate

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This report relates the synthesis and crystal structure of [(*N*-salicylidene-*N*′-methylethylenediamine)(aquo)(9-methyladenine)copper(II)] nitrate, $[(N_2OC_{10}H_{13})(H_2O)(N_5C_6H_7)Cu]NO_3$. The complex crystallizes from water as the dihydrate in the monoclinic system, space group $P2_1/n$, with $a = 12.765$ (4) Å, $b = 21.999$ (19) Å, $c = 7.776$ (4) Å, $\beta = 98.48$ (3)°, $Z = 4$, $d_{\text{measd}} = 1.55$ (1) g cm^{-3}, $d_{\text{calcd}} = 1.56$ g cm^{-3}. Intensities for 4617 symmetry-averaged reflections were collected by diffractometer methods in the θ–2θ scan mode. Standard heavy-atom Patterson and Fourier techniques were used to solve the structure. Full-matrix least squares has led to a final *R* value of 0.075, a weighted *R* value of 0.055, and a goodness-of-fit value of 1.9. The primary coordination sphere about the copper center is approximately square pyramidal with the tridentate Schiff base chelate and N(7) of the 9-methyladenine ligand occupying the four equatorial coordination sites and a water molecule in the axial position, Cu–OH$_2$ distance = 2.353 (2) Å. The most unusual aspect of the structure is the interligand hydrogen bond which exists between the exocyclic amine at C(6) of the 9-methyladenine ligand and the equatorial oxygen atom, O(10), of the salicylidene portion of the Schiff base chelate. Typically, in related copper complexes, the exocyclic amino group forms a hydrogen bond to an axial substituent. The relationship between the Cu–N(7) bond length and the interligand interaction is discussed. The complex cations form columnar stacks along the short *c* axis via the n-glide symmetry operation. The intercalative stacking modes observed in the columnar stacks are compared to other known cases.

Introduction

Stereoselective metal–ligand and ligand–ligand interactions can determine the binding site and stereochemistry of chelate–metal systems with purine and pyrimidine ligands. For example, the copper(II) complex of the tridentate ligand *N*-salicylidene-*N*′-methylethylenediamine has one equatorial site available for ligand attachment and presents to an incoming ligand both the exocyclic oxygen atom of the salicylidene ring and the *N*-methyl terminus of the ethylenediamine chain. The salicylidene oxygen is a potential hydrogen-bond acceptor site, while the *N*-methyl terminus is a potential hydrogen-bond donor group. In the complex (*N*-salicylidene-*N*′-methylethylenediamine)(theophyllinato)copper(II) [where theophyllinato is the monoanion of 1,3-dimethyl-2,6-dioxopurine] the metal binding site is N(7) of the imidazole ring.[1] The complex shows a strong interligand hydrogen bond between the exocyclic carbonyl oxygen at C(6) of the purine ring and the terminal secondary amine of the ethylenediamine group. In the related complex (*N*-salicylidene-*N*′-methylethylenediamine)(cytosine)copper(II) nitrate the heterocyclic ring nitrogen, N(3), of the pyrimidine was bound to the metal.[2] Furthermore, the exocyclic carbonyl oxygen atom at C(2) of the pyrimidine ring formed a weak, but apparently specific, interaction with the copper center via one of the open axial positions of the basic square-planar coordination sphere. The complex cation also exhibits a weak interligand hydrogen bond to the *N*-methylethylenediamine terminus of the Schiff base chelate via the same carbonyl oxygen at C(2).

As a continuation of our studies of specificity associated with exocyclic groups, we have prepared and studied the complex formed between 9-methyladenine and the (*N*-salicylidene-*N*′-methylethylenediamine)copper(II) moiety. This particular complex was chosen for several reasons. We wished to obtain a set of complexes of one multidentate chelate moiety which would afford bonding models for the three common nucleosides (adenosine, guanosine, cytidine) which are expected to interact with copper complexes in the nucleic acids. (The binding of uridine and thymidine is much less important.[3]) The theophyllinato and the cytosine complexes are models for guanosine and cytidine, respectively. The 9-methyladenine complex would then provide information concerning the binding mode of adenosine as both molecules have substituents at N(9). It was of additional interest to us that the complex precursor,

Table I. Crystal Data for (*N*-Salicylidene-*N*'-methylethylenediamine)(aquo)(9-Methyladenine)copper(II) Nitrate Dihydrate

$a = 12.765\ (4)$ Å
$b = 21.999\ (19)$ Å
$c = 7.776\ (4)$ Å
$\beta = 98.48\ (3)°$
$V = 2159.8$ Å^3
$Z = 4$

$[(N_2OC_{10}H_{13})(H_2O)(N_5C_6H_7)Cu]NO_3 \cdot 2H_2O$
Mol wt 506.0
Space group $P2_1/n$
$d_{measd} = 1.55\ (1)$ g cm^{-3}
$d_{calcd} = 1.56$ g cm^{-3}
$\mu = 11.1$ cm^{-1}

(chloro)(*N*-salicylidene-*N*'-methylethylenediamine)copper(II), appeared to prefer N(1) binding to adenosine to a larger extent than did Cu^{2+} ion (DMSO solvent).[4] However, binding at both N(1) and at N(7) is usually important. No structures of copper–N(1)-bound adenine derivative complexes have thus far been reported.

Experimental Section

Preparation of (*N*-Salicylidene-*N*'-methylethylenediamine)(aquo)(9-methyladenine)copper(II) Nitrate Dihydrate. The complex (chloro)(*N*-salicylidene-*N*'-methylethylenediamine)copper(II) was prepared by the method of Sacconi and Bertini.[5] A solution of the aquated cation was obtained by the addition of $AgNO_3$ (1.8 ml of a 0.5 *M* solution, 0.91 mmol) to an aqueous solution (10 ml) of the chloro complex (0.25 g, 0.91 mmol). The solution was filtered to remove the precipitated AgCl, and 0.07 g (0.45 mmol) of 9-methyladenine was added to the filtrate. The resulting solution was then heated on a steam bath for approximately $^1/_2$ hr.

Deep green crystals of the desired product were collected after very slow evaporation of the solvent (approximately 1 month). The crystals are unstable and lose 1 mol of water/mol of complex with the eventual complete loss of crystallinity. All further manipulations were carried out with the crystals coated with a film of low molecular weight petroleum grease and sealed in thin-walled Lindemann capillaries. The magnetic moment, 1.8 BM, was measured using a Faraday balance and is typical for square-pyramidal complexes of copper(II).[6,7]

Collection and Reduction of the X-Ray Diffraction Data. The deep green complex (*N*-salicylidene-*N*'-methylethylenediamine)(aquo)(9-methyladenine)copper(II) nitrate crystallizes as monoclinic prisms with [101] as the prism axis. Preliminary diffraction photographs showed the crystal system to be monoclinic with systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$) consistent with the space group $P2_1/n$. Unit-cell dimensions and their associated standard deviations were derived on the basis of a least-squares fit to the 2θ, ω, and χ angle settings for 14 carefully centered reflections measured on a Syntex $P\bar{1}$ automated diffractometer. The crystal density was measured by neutral buoyancy methods in a mixture of carbon tetrachloride and bromoform; the measured density indicated one formula unit plus two water molecules per asymmetric volume. Complete crystal data are given in Table I.

A total of 11,693 reflections (the $+h$-hemisphere to $2\theta = 55°$) were measured on the diffractometer; molybdenum graphite-monochromatized radiation was employed. The crystal used in data collection was a monoclinic prism with dimensions 0.20 × 0.25 × 0.30 mm; the prism axis was tilted by about 13° relative to the ϕ axis of the spectrometer. Intensity data were collected in the θ–2θ scan mode; individual scan speeds were determined by a rapid scan at the calculated Bragg peak, and the rate of scanning (2θ) varied from 1.5° min^{-1} (less than 100 counts during the rapid scan) to 24.0° min^{-1} (more than 1000 counts during the rapid scan). Four reflections were monitored after every 100 reflections during the course of the experiment; their intensities showed no systematic trends. The 11,693 reflections were reduced to a set of 10,857 values by the exclusion of standards and systematic absences; 9161 of these remaining reflections had $I \geq 0.5\sigma(I)$ [counting statistics] and this set of data was used in all further calculations. The reflections were assigned observational variances based on the equation

$$\sigma^2(I) = S + (B_1 + B_2)(T_S/2T_B)^2 + (pI)^2$$

where S, B_1, and B_2 are the scan and background extremum counts, T_S and T_B are the scan and individual background counting times ($T_B = {}^1/_4 T_S$ for all reflections), and p was taken to be 0.04 and represents the expected error proportional to the diffracted intensity.[8] Intensities and their standard deviations were corrected for Lorentz and polarization effects; no correction for absorption effects was applied [$\mu = 11.1$ cm^{-1}, maximum and minimum transmission factors equal to 0.80 and 0.76, respectively]. The 9161 squared structure factors were placed on an approximate absolute scale by the method of Wilson[9] and subsequently combined to yield a set of 4617 symmetry-independent values.

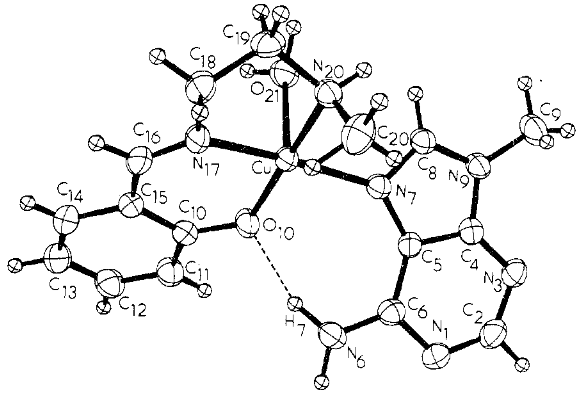

Figure 1. Perspective view of the (*N*-salicylidene-*N*'-methylethylenediamine)(aquo)(9-methyladenine)copper(II) complex cation. The dashed line indicates the interligand hydrogen bond involving the exocyclic amine $N(6)H_2$ on 9-methyladenine and the equatorial salicylidene oxygen O(10) of the Schiff base chelate. The view direction was chosen to show the partial blocking of the sixth coordination site about the copper by the methyl group at the *N*-methylethylenediamine terminus of the Schiff base chelate. The thermal ellipsoids are drawn at the 40% probability level.

Solution and Refinement of the Structure. The position of the copper atom was determined from a three-dimensional Patterson synthesis. A structure factor Fourier calculation based on the copper allowed the positioning of the remaining 31 nonhydrogen atoms ($R = \sum||F_o| - |F_c||/\sum|F_o| = 0.24$). Three cycles of isotropic least-squares refinement, minimizing the quantity $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, plus one cycle of anisotropic refinement on all the nonhydrogen atoms reduced the R value to 0.09. A difference Fourier map was then computed and positional parameters for the 26 hydrogen atoms in the asymmetric unit were derived from this map. The hydrogen atoms were assigned the same isotropic temperature factor as the atom to which they were bonded. Two further cycles of anisotropic refinement led to convergence and a final R value of 0.075. The final weighted R value [$Rw = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$] and goodness of fit [$(\sum w(|F_o| - |F_c|)^2/(NO - NV))^{1/2}$, where NO = 4617 observations and NV = 289 variables] were 0.055 and 1.9, respectively.

Neutral scattering curves for all the nonhydrogen atoms were taken from the compilation of Hanson, Herman, Lea, and Skillman;[10] the scattering curve for H was that of Stewart, Davidson, and Simpson.[11] The real part of the scattering curve for copper was corrected for anomalous dispersion effects.[12] Final heavy-atom parameters are collected in Table II; hydrogen atom parameters are given in Table III. A complete list of calculated and observed structure factor amplitudes is available.[13]

The crystallographic computations were performed with the following programs: structure factor Fourier, X-RAY 67;[14] least-squares refinements, ORFLS;[15] best planes, MEAN PLANE;[16] illustrations, ORTEP.[17] Calculations not cited were performed with locally written programs.

Results and Discussion

Description of the Molecular Structure. The (*N*-salicylidene-*N*'-methylethylenediamine)(aquo)(9-methyladenine)copper(II)(1+) complex cation exists in the crystal in a slightly distorted square-pyramidal geometry, Figure 1. The four equatorial positions are occupied by the tridentate Schiff base chelate and N(7) of the 9-methyladenine ligand. The primary coordination sphere is completed by the occupation of one axial position by a water molecule, $O(21)H_2$, Figure 1. The resulting molecular conformation can be best described as the (4 + 1), Jahn–Teller-distorted coordination geometry.[18] The most interesting aspect of the structure is that an interligand hydrogen bond is formed between the

Table II. Final Heavy-Atom Parameters (×10^4)[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	999 (0.3)	1791 (0.2)	1460 (0.5)	34 (0.2)	13 (0.1)	152 (0.8)	−0 (0.1)	1 (0.3)	2 (0.2)
O(10)	1156 (2)	2621 (1)	2161 (3)	39 (1)	14 (1)	243 (6)	2 (1)	−3 (2)	−3 (1)
O(21)	793 (2)	1382 (1)	4186 (3)	73 (2)	18 (1)	170 (5)	3 (1)	38 (2)	2 (1)
O(22)	2078 (2)	4060 (2)	6930 (4)	100 (2)	51 (1)	225 (7)	−35 (1)	16 (3)	−2 (2)
O(23)	2234 (3)	4982 (1)	4460 (5)	136 (3)	26 (1)	310 (8)	1 (1)	20 (4)	2 (2)
O(24)	3814 (3)	5096 (1)	1472 (5)	131 (3)	26 (1)	328 (8)	−14 (1)	34 (4)	−26 (2)
O(25)	3750 (3)	4301 (1)	−170 (5)	115 (3)	39 (1)	447 (11)	3 (1)	51 (5)	−59 (3)
O(26)	2482 (3)	4522 (2)	1012 (6)	116 (3)	74 (2)	512 (13)	−25 (2)	61 (6)	−83 (4)
N(1)	4676 (2)	2744 (1)	936 (4)	49 (2)	18 (1)	194 (6)	−4 (1)	24 (3)	2 (2)
N(3)	5397 (2)	1821 (1)	2293 (4)	38 (2)	19 (1)	206 (6)	−1 (1)	12 (3)	−3 (2)
N(6)	2876 (2)	2954 (1)	356 (4)	55 (2)	16 (1)	251 (7)	1 (1)	10 (3)	18 (2)
N(7)	2596 (2)	1667 (1)	1968 (4)	41 (2)	12 (1)	174 (6)	−0 (1)	6 (2)	1 (1)
N(9)	4041 (2)	1128 (1)	2933 (4)	45 (2)	13 (1)	164 (6)	3 (1)	−1 (3)	2 (1)
N(17)	−507 (2)	1905 (1)	581 (4)	35 (2)	16 (1)	185 (6)	0 (1)	−3 (2)	1 (2)
N(20)	762 (2)	956 (1)	312 (4)	46 (2)	14 (1)	152 (6)	1 (1)	0 (3)	2 (1)
N(25)	3366 (3)	4673 (2)	709 (5)	69 (2)	28 (1)	214 (8)	3 (1)	8 (3)	−20 (2)
C(2)	5460 (3)	2367 (2)	1569 (5)	44 (2)	22 (1)	219 (8)	−4 (1)	28 (3)	−6 (2)
C(4)	4385 (2)	1663 (1)	2316 (4)	43 (2)	14 (1)	133 (6)	0 (1)	3 (3)	−6 (2)
C(5)	3491 (2)	1999 (1)	1725 (4)	39 (2)	13 (1)	128 (6)	−0 (1)	8 (3)	−4 (2)
C(6)	3658 (2)	2571 (1)	1001 (4)	51 (2)	15 (1)	131 (6)	−3 (1)	16 (3)	−4 (2)
C(8)	2980 (2)	1157 (1)	2712 (5)	43 (2)	13 (1)	191 (7)	−1 (1)	3 (3)	2 (2)
C(9)	4692 (3)	628 (2)	3693 (5)	60 (2)	17 (1)	242 (9)	8 (1)	−9 (4)	9 (2)
C(10)	403 (2)	3024 (1)	2288 (5)	48 (2)	15 (1)	154 (7)	1 (1)	11 (3)	9 (2)
C(11)	684 (3)	3583 (1)	3086 (5)	56 (2)	17 (1)	216 (8)	−0 (1)	1 (4)	−3 (2)
C(12)	−57 (3)	4020 (2)	3293 (5)	81 (3)	15 (1)	219 (9)	2 (1)	33 (4)	−5 (2)
C(13)	−1118 (3)	3924 (2)	2694 (6)	69 (3)	20 (1)	284 (10)	9 (1)	61 (4)	5 (2)
C(14)	−1424 (3)	3385 (2)	1871 (5)	50 (2)	21 (1)	228 (9)	5 (1)	34 (4)	8 (2)
C(15)	−686 (2)	2923 (1)	1670 (5)	45 (2)	16 (1)	156 (7)	3 (1)	17 (3)	11 (2)
C(16)	−1065 (2)	2373 (2)	810 (5)	37 (2)	20 (1)	170 (7)	0 (1)	3 (3)	11 (2)
C(18)	−1007 (2)	1369 (2)	−348 (5)	41 (2)	20 (1)	219 (8)	−4 (1)	−9 (3)	−6 (2)
C(19)	−379 (3)	821 (1)	292 (5)	55 (2)	16 (1)	177 (7)	−9 (1)	3 (3)	−3 (2)
C(20)	1063 (3)	953 (2)	−1446 (5)	67 (3)	30 (1)	195 (8)	2 (1)	33 (4)	−14 (3)

[a] Estimated standard deviations are enclosed in parentheses. The form of the anisotropic ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

Table III. Hydrogen Atom Positional (×10^3) and Isotropic Thermal Parameters

Atom	x	y	z	B,[a] Å^2
H(2)[C(2)]	617	250	150	4.2
H(3)[C(9)]	427	32	418	5.0
H(4)[C(9)]	496	42	300	5.0
H(5)[C(9)]	529	75	465	5.0
H(6)[N(6)]	308	337	4	4.5
H(7)[N(6)]	223	293	89	4.5
H(8)[C(8)]	254	83	306	3.5
H(11)[C(11)]	143	366	348	4.0
H(12)[C(12)]	17	440	390	4.8
H(13)[C(13)]	−164	423	286	5.0
H(14)[C(14)]	−215	333	138	4.4
H(16)[C(16)]	−181	236	40	3.5
H(17)[C(18)]	−174	133	−13	4.8
H(18)[C(18)]	−103	142	−158	4.8
H(19)[C(19)]	−57	48	−45	4.0
H(20)[C(19)]	−51	72	144	4.0
H(21)[C(20)]	92	57	−207	5.0
H(22)[C(20)]	62	132	−207	5.0
H(23)[C(20)]	171	100	−136	5.0
H(24)[O(21)]	58	97	446	4.5
H(25)[O(21)]	36	160	482	4.5
H(26)[O(22)]	150	384	721	7.0
H(27)[O(22)]	242	425	811	7.0
H(28)[O(23)]	212	465	529	7.1
H(29)[O(23)]	227	478	332	7.1
H(30)[N(20)]	116	68	93	3.4

[a] The hydrogen atom isotropic temperature parameters were set about equal to those of the atoms to which they are attached [enclosed in brackets].

exocyclic amine, N(6)H$_2$, of the 9-methyladenine and the equatorial oxygen atom, O(10), of the salicylidene ring. The parameters in this interligand hydrogen-bond system [N(6)···O(10) = 2.870 (4) Å, H(7)···O(10) = 1.93 Å, N(6)–H(7)···O(10) = 161°] are consistent with a strong hydrogen bond.[19]

Several recent studies of the binding of Cu(II)[20,21] and chelated-Cu(II)[22] systems to 9-methyladenine have been directed toward establishing the binding site of the metal and the possible relationship of such model systems to the binding of Cu(II) to adenosine residues in polynucleotides. Solution studies[4,23] have indicated that the purine ring nitrogen atoms N(1) and N(7) are about equally important in the binding of Cu(II) to adenosine. In all of the crystalline Cu(II) complexes[20–22] studied thus far, the metal binding site has been the imidazole ring nitrogen atom N(7). For other metals, Co(II) and Zn(II), binding to N(1) of 9-methyladenine has been established.[24,25]

An important feature, besides the binding at N(7), found in the studies on copper(II)–9-methyladenine complexes is that the exocyclic amine N(6)H$_2$ forms interligand hydrogen bonds to acceptor atoms on axial ligands. For example, in the CuSO$_4$ complex of 9-methyladenine,[20] the exocyclic amine donates a hydrogen bond to an oxygen atom of a weakly bonded sulfate dianion, Cu–O = 2.551 (2) Å. It should be noted that other potential hydrogen-bond acceptor groups are available in the primary coordination sphere of this complex,[20] e.g., three water ligands with Cu–O distances of 1.944 (2), 1.959 (2), and 2.355 (2) Å, but the hydrogen bond involves the oxygen atom with the weakest Cu–O interaction. In the CuCl$_2$ complex,[21] the exocyclic amine group forms a bifurcated hydrogen bond system with two water ligands. All of the water ligands in this complex are symmetry equivalent with Cu–O distances of 2.162 (2) Å. Last, the glycylglycinatocopper(II) complex of 9-methyladenine[22] has been synthesized and its structure determined. In this complex, the exocyclic amine group of the 9-methyladenine ligand participates in an interligand hydrogen bond with an axial water molecule, Cu–O = 2.347 (4) Å. Again, the hydrogen bond is to the oxygen atom with the weakest Cu–O interaction.

The reasons for the atypical hydrogen bonding found in the

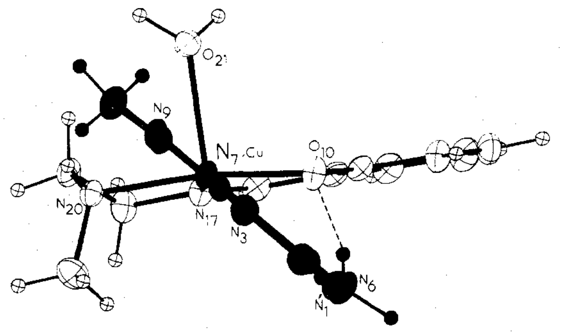

Figure 2. Projection view of the complex cation down the N(7)–Cu bond. The dashed line denotes the interligand hydrogen bond. The thermal ellipsoids are drawn at the 25% probability level. Note in particular the disposition of the 9-methyladenine plane relative to that of the Schiff base chelate.

present system can be understood by comparing the conformational properties and interligand hydrogen-bonding schemes in the Schiff base compound and those of the (glycylglycinato)(9-methyladenine)copper(II) complex.[22] Each tridentate chelate has a coordinated oxygen atom [the salicylidene oxygen atom of the Schiff base, Cu–O = 1.908 (2) Å, and the coordinated carboxylate oxygen of the dipeptide ligand, Cu–O = 1.963 (4) Å] and a coordinated amine nitrogen atom [the terminal amine of the dipeptide, Cu–N = 2.023 (4) Å, and the *N*-methylamine terminus of the Schiff base, Cu–N = 2.045 (2) Å]. In each case, the nitrogen and oxygen atoms are in trans positions in the equatorial plane. Furthermore, each complex has an axial water molecule with very similar Cu–O distances of 2.347 (4) Å in the dipeptide complex[22] and 2.353 (2) Å in the Schiff base complex.

The major difference between the complexes is the presence of the methyl substituent on the terminal amine nitrogen of the Schiff base chelate. The role of this methyl substituent in determining the molecular properties and the interligand hydrogen-bond acceptor site appears to be twofold. (1) As can be seen in Figures 1 and 2, the methyl group appears to hinder strong "on axis" coordination at one of the axial positions of the copper coordination sphere. It is likely then that a strongly bound axial ligand and the methyl group will be trans to each other relative to the equatorial plane; see Figure 2. (2) Accepting this trans positioning of the methyl group and the axial water ligand in this case, space-filling models indicate that severe nonbonded contacts between the *N*-methylethylenediamine group and the 9-methyladenine framework would occur in an attempt to produce a molecular geometry which leads to an N(6)–H···O (axial water) hydrogen-bond system. Such considerations are absent in the glycylglycinatocopper(II)[22] complex and in the $CuSO_4$[20] and $CuCl_2$[21] complexes of 9-methyladenine discussed above.

In conclusion, it would seem that the addition of the axial water ligand is more important to the overall stability of the complex than the formation of the most sterically favorable interligand hydrogen-bond scheme. Qualitatively this is in accord with the expected order of magnitude of the energetics involved in each of the interactions. In the present complex, the positioning of the axial water and the methyl substituent trans to the equatorial plane precludes the formation of the exocyclic amine to axial water hydrogen bond. The equatorial salicylidene oxygen in the coordination sphere provides a secondary hydrogen-bond acceptor position. The net result would seem to be an energetically favorable situation with both the axial ligand interaction and the interligand hydrogen bond contributing to the stability of the complex cation.

Table IV. Heavy-Atom Interatomic Distances (Å) and Angles (deg)[a]

(a) Primary Coordination Sphere about the Copper Atom

Bond Lengths

Cu-N(7)	2.037 (2)	Cu-O(10)	1.908 (2)
Cu-N(17)	1.959 (3)	Cu-O(21)	2.353 (2)
Cu-N(20)	2.045 (2)		

Bond Angles

N(7)-Cu-N(17)	171.9 (1)	N(17)-Cu-O(10)	91.9 (1)
N(7)-Cu-N(20)	92.5 (1)	N(17)-Cu-O(21)	97.4 (1)
N(7)-Cu-O(10)	90.7 (1)	N(20)-Cu-O(10)	170.7 (1)
N(7)-Cu-O(21)	90.9 (1)	N(20)-Cu-O(21)	91.2 (1)
N(17)-Cu-N(20)	83.6 (1)	O(10)-Cu-O(21)	97.4 (1)

(b) *N*-Salicylidene-*N'*-methylethylenediamine Chelate Ligand

Bond Lengths

O(10)-C(10)	1.322 (4)	C(15)-C(16)	1.432 (5)
C(10)-C(11)	1.400 (5)	C(16)-N(17)	1.279 (4)
C(11)-C(12)	1.375 (5)	N(17)-C(18)	1.478 (4)
C(12)-C(13)	1.382 (5)	C(18)-C(19)	1.492 (5)
C(13)-C(14)	1.376 (5)	C(19)-N(20)	1.484 (4)
C(14)-C(15)	1.410 (5)	N(20)-C(20)	1.474 (5)
C(15)-C(10)	1.420 (5)		

Bond Angles

Cu-O(10)-C(10)	128.0 (2)	C(14)-C(15)-C(16)	118.4 (3)
O(10)-C(10)-C(11)	118.7 (3)	C(15)-C(16)-N(17)	126.0 (3)
O(10)-C(10)-C(15)	123.8 (3)	C(16)-N(17)-C(18)	120.1 (3)
C(11)-C(10)-C(15)	117.5 (3)	Cu-N(17)-C(16)	126.3 (2)
C(10)-C(11)-C(12)	122.0 (4)	Cu-N(17)-C(18)	113.5 (2)
C(11)-C(12)-C(13)	120.7 (4)	N(17)-C(18)-C(19)	108.0 (3)
C(12)-C(13)-C(14)	119.0 (4)	C(18)-C(19)-N(20)	108.7 (3)
C(13)-C(14)-C(15)	121.6 (4)	Cu-N(20)-C(19)	105.4 (2)
C(10)-C(15)-C(14)	119.1 (4)	Cu-N(20)-C(20)	111.5 (2)
C(10)-C(15)-C(16)	122.5 (3)	C(19)-N(20)-C(20)	112.3 (3)

(c) 9-Methyladenine Ligand

Bond Lengths

N(1)-C(2)	1.337 (4)	N(7)-C(8)	1.323 (4)
N(1)-C(6)	1.362 (4)	N(9)-C(4)	1.368 (4)
N(3)-C(2)	1.334 (5)	N(9)-C(8)	1.341 (4)
N(3)-C(4)	1.340 (4)	N(9)-C(9)	1.451 (5)
N(6)-C(6)	1.345 (4)	C(4)-C(5)	1.380 (4)
N(7)-C(5)	1.392 (4)	C(5)-C(6)	1.408 (4)

Bond Angles

C(2)-N(1)-C(6)	118.7 (3)	N(3)-C(4)-C(5)	127.4 (3)
C(2)-N(3)-C(4)	110.9 (3)	N(9)-C(4)-C(5)	106.6 (3)
C(5)-N(7)-C(8)	104.2 (3)	N(7)-C(5)-C(4)	109.2 (3)
Cu-N(7)-C(5)	136.2 (2)	N(7)-C(5)-C(6)	134.4 (3)
Cu-N(7)-C(8)	119.6 (2)	C(4)-C(5)-C(6)	116.4 (3)
C(4)-N(9)-C(8)	106.5 (3)	N(1)-C(6)-N(6)	118.1 (3)
C(4)-N(9)-C(9)	127.0 (3)	N(1)-C(6)-C(5)	117.8 (3)
C(8)-N(9)-C(9)	126.5 (3)	N(6)-C(6)-C(5)	124.1 (3)
N(1)-C(2)-N(3)	128.7 (3)	N(7)-C(8)-N(9)	113.5 (3)
N(3)-C(4)-N(9)	126.0 (3)		

(d) Nitrate Anion

Bond Lengths

N(25)-O(24)	1.202 (5)	N(25)-O(26)	1.232 (6)
N(25)-O(25)	1.215 (5)		

Bond Angles

O(24)-N(25)-O(25)	126.7 (4)	O(25)-N(25)-O(26)	112.5 (3)
O(24)-N(25)-O(26)	119.8 (4)		

[a] Estimated standard deviations in the least significant figure are contained in parentheses.

Bond Lengths and Bond Angles. The bond lengths and angles in the primary coordination sphere are given in part (a) of Table IV. The Cu–N(7) bond length, 2.037 (2) Å, is the largest yet observed and can be compared to those found in several recent copper(II) complexes of 9-methyladenine: 1.995 (2) Å in the $CuSO_4$[20] structure; 2.008 (2) Å in the $CuCl_2$[21] complex; 2.021 (4) Å in the glycylglycinatocopper(II) complex of 9-methyladenine.[22] We note that the lengthening of the Cu–N(7) bond length from the $CuSO_4$ complex to the glycylglycine complex to the present study parallels the decrease in the copper–acceptor distance from 2.551 (2) to 2.347 (4) to 1.908 (2) Å in the interligand hydrogen-bond system.

Table V. Least-Squares Planes and the Deviations (Å) of Individual Atoms from These Planes[a]

(a) Primary Coordination Sphere about the Copper Atom			
$(0.2967X + 0.3251Y - 0.8980Z = 0.7476$ Å)			
O(10)	−0.002	N(20)	−0.002
N(7)	0.001	Cu	−0.146*
N(17)	0.002	O(21)	−2.492*
(b) Salicylidene Ring			
$(0.2580X + 0.3924Y - 0.8829Z = 1.1200$ Å)			
C(10)	0.002	C(16)	0.004
C(11)	0.012	O(10)	−0.008
C(12)	−0.002	Cu	−0.279*
C(13)	−0.010	N(17)	−0.054*
C(14)	0.007	C(18)	−0.023*
C(15)	−0.006		
(c) 9-Methyladenine Planes			
(1) 9-Atom Framework			
$(0.0992X - 0.4184Y - 0.9028Z = -2.6030$ Å)			
N(1)	0.009	C(5)	−0.012
N(3)	−0.008	C(6)	−0.007
N(7)	0.008	C(8)	0.002
N(9)	0.006	Cu	0.051*
C(2)	0.008	N(6)	−0.003*
C(4)	−0.007	C(9)	0.013*
(2) Imidazole Ring			
$(0.1037X - 0.4125Y - 0.9051Z = -2.5689$ Å)			
N(7)	0.007	C(8)	−0.007
N(9)	0.004	Cu	0.042*
C(4)	0.001	C(9)	0.005*
C(5)	−0.004		
(3) Pyrimidine Ring			
$(0.0937X - 0.4238Y - 0.9009Z = -2.6603$ Å)			
N(1)	0.002	C(5)	0.000
N(3)	−0.006	C(6)	−0.004
C(2)	0.002	N(6)	−0.000*
C(4)	0.004		

[a] In each of the equations of the planes, X, Y, and Z are coordinates (Å) referred to the orthogonal axes a, b, and c^*. Atoms designated by an asterisk were given zero weight in calculating the planes; all other atoms were equally weighted.

There are some differences in the Cu–N or –O [salicylidene] distances in the theophylline,[1] cytosine,[2] and 9-methyladenine Schiff base complexes. The Cu–N(20) bond length, for example, is very similar, 2.045 (2) and 2.048 (3) Å, in the 9-methyladenine and cytosine complexes, while the value in the theophylline complex is significantly shorter at 2.020 (1) Å. This may be related to the fact that the theophylline complex is essentially four-coordinate while the 9-methyladenine and cytosine complexes are formally (4 + 1) and (4 + 2) coordinated, respectively. An increase in coordinated bond lengths with an increase in coordination number is not unexpected.

The bond angles in the primary coordination sphere are in good agreement with those in the theophylline complex,[1] while both the 9-methyladenine and the theophylline complex parameters are significantly different from those found in the cytosine complex.[2] This can possibly be related to the fact that both of the purine complexes show interligand hydrogen bonds with equatorial sites (the *N*-methyl terminus in the theophylline complex and the salicylidene oxygen in the 9-methyladenine complex), whereas the cytosine complex is semichelated through one of the open axial positions and only forms a weak interaction with the equatorial *N*-methyl terminus. This difference in the interactions of the coordinated purine or pyrimidine ligands shows up most clearly in the exocyclic chelate bond angle N(20)–Cu–O(10): 170.7 (1)° in the theophylline complex; 171.9 (1)° in the 9-methyladenine structure; 175.5 (2)° in the cytosine complex. As expected, however, the chelate bite angles, N(17)–Cu–N(20) and N(17)–Cu–O(10), remain consistent over the three structures.

The primary coordination sphere about the copper atom is quite planar, Table V. The copper atom lies 0.146 Å out of the plane toward the axially coordinated water molecule. This parallels the other known square-pyramidal complexes of copper(II).[7,18,22]

In general, the bond lengths and angles in the salicylidene portion of the Schiff base chelate are very similar in the three complexes we have studied, including the present one. However, the *N*-methylethylenediamine ring can exhibit some variability in response to intracomplex steric factors. In particular, the bond lengths C(18)–C(19), C(19)–N(20), and N(20)–C(20) are markedly different in the theophylline[1] and the cytosine[2] complexes. The parameters found here in the 9-methyladenine complex are in good agreement with those in the theophylline complex, and this is reasonable in light of their very similar molecular conformations and interligand hydrogen-bonding schemes. As expected, the salicylidene ring is reasonably planar, Table V.

We have noted several instances now where interligand hydrogen bonding or chelation in metal–purine[1,22,26–28] and metal–pyrimidine[2,29,30] complexes leads to a significant dissymmetry in the exocyclic bond angles at the coordinated nitrogen site. This structural feature is evident in this Schiff base 9-methyladenine complex with Cu–N(7)–C(5) and Cu–N(7)–C(8) bond angles of 136.2 (2) and 119.6 (2)°, respectively. These angles are in close agreement with those found for the theophylline Schiff base complex,[1] 135.0 (2) and 120.4 (2)°, and the glycylglycinatocopper(II) complex of 9-methyladenine,[22] 137.7 (3) and 116.2 (3)°. In all three of these complexes, interligand hydrogen bonding of one type or another is observed.

The bond lengths in the coordinated 9-methyladenine ligand are not remarkably different from those found in other recent determinations.[20–22] It appears on comparison of these structures that the bond lengths N(3)–C(2), N(9)–C(4), and N(6)–C(6) are responsive to the strength of the copper(II)–base interaction. Consistent with this, the bond angles involving the heteroatoms N(3), N(6), and N(9) show some variability.

The nine-atom framework of the 9-methyladenine ligand is reasonably planar, Table V, with the Cu lying 0.051 Å out of the plane. The other exocyclic substituents, N(6) and C(9), are nominally in the plane of the purine framework. A point of some interest is that the amine hydrogen, H(7), involved in the interligand hydrogen bond lies about 0.4 Å out of the purine plane toward the acceptor oxygen O(10). The imidazole and pyrimidine portions of the coordinated purine are quite planar and fold about the C(4)–C(5) bond with a dihedral angle of 0.6 (3)°. This small dihedral angle is consistent with the pseudoaromatic character of the purine system and the lack of any unusual exocyclic substituent interactions or crystal packing forces.[21,22,31,32]

The bond lengths and angles in the nitrate anion are given in Table IV. The temperature factors of the nitrate oxygen atoms are moderately large, Table II, but no evidence of disorder was observed. The average N–O distance, 1.22 (1) Å, is slightly but not significantly shorter than that quoted for the uncoordinated nitrate anion, 1.24 (1) Å.[33] The average O–N–O angle is 119.7°, but the individual bond angles range from 112.5 (3) to 126.7 (3)°. The central nitrogen atom is slightly pyramidal, lying 0.07 Å out of the plane of the three oxygen atoms. The nitrate oxygen atoms are involved in numerous hydrogen bonds and other interactions, Table VI, and presumedly the nonplanarity and angular dissymmetry are a result of the local environment about the nitrate anion in the crystal.

Crystal Packing and Hydrogen Bonding. The principal feature of the crystal packing in this structure is the formation of columns of stacked complexes along the short c axis. A view

Table VI. Distances and Angles in the Interactions of the Type D-H· · ·A

D	H	A	D-H, Å	D· · ·A, Å	H· · ·A, Å	D-H· · ·A, deg
		Strong Hydrogen Bonds				
N(6)	H(7)	O(10)^a	0.98	2.870	1.93	161
O(21)	H(25)	N(1)^b	0.92	2.856	1.96	164
O(22)	H(26)	N(3)^b	0.94	2.936	2.03	162
O(22)	H(27)	O(25)^c	1.04	2.916	2.00	145
O(23)	H(28)	O(22)^a	1.00	2.821	1.83	172
O(23)	H(29)	O(26)^a	1.00	2.926	1.94	169
		Weak Hydrogen Bonds and a C-H· · ·O Interaction				
N(6)	H(6)	O(25)^a	0.99	3.214	2.24	168
N(20)	H(30)	O(24)^d	0.89	3.119	2.39	139
O(21)	H(24)	O(24)^d	0.98	2.931	2.24	127
O(21)	H(24)	O(25)^b	0.98	3.114	2.46	123
O(22)	H(27)	O(26)^c	1.04	3.300	2.33	155
C(8)	H(8)	O(24)^d	0.97	3.395	2.43	169

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

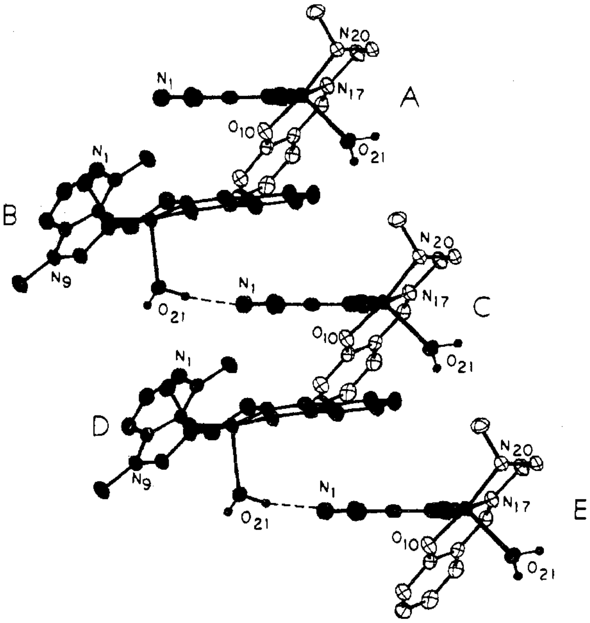

Figure 3. View normal to the stacking direction of the columns of complex cations. The dashed lines denote the axial water, O(21)H_2, to N(1)[9-methyladenine] intracolumn hydrogen bonds. The symmetry transforms of the labeled complexes relative to Table II are as follows: (A) x, y, z; (B) ${}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; (C) $x, y, 1 + z$; (D) ${}^1/_2 + x, {}^1/_2 - y, {}^3/_2 + z$; (E) $x, y, 2 + z$.

normal to the stacking direction is presented in Figure 3. The 9-methyladenine ligand is sandwiched between the salicylidene rings of n-glide related complexes [${}^1/2 + x, {}^1/2 - y, {}^1/2 + z$; ${}^1/2 + x, {}^1/2 - y, -{}^1/2 + z$]; the same is obviously true for the salicylidene rings in these columns, Figure 3. There is a moderately large tilt, 9.3 (4)°, between the plane of the 9-methyladenine and the salicylidene ring of the Schiff base chelate, Figure 3.

These columns contain two markedly different modes of molecular overlap, Figure 4. As can be seen in Figure 4A, the molecular stacking of the 9-methyladenine ring with one of the salicylidene rings is dominated by a high degree of overlap of the pyrimidine ring of the 9-methyladenine ligand and the benzenoid portion of the Schiff base chelate. Close contacts in this stacking interaction are as follows: N(3)···C(11), 3.461 (4) Å; C(2)···C(10), 3.429 (5) Å; C(2)···C(11), 3.466 (5) Å. The stability of this pair is further enhanced by a hydrogen bond from the axial water, O(21)H_2, of one complex cation to the heterocyclic ring nitrogen atom N(1) of the second complex, Figures 3 and 4A and Table VI.

The second type of molecular overlap in these columns is shown in Figure 4B. Here the pyrimidine ring of the 9-methyladenine ligand forms a moderate overlap with the six-membered chelate ring of the Schiff base, while the heterobond N(9)–C(9)H_3 lies approximately over the centroid of the benzenoid portion of the salicylidene ring. Short contacts observed in this stacking interaction are as follows: N(9)···C(14), 3.378 (4) Å; C(5)···C(16), 3.434 (5) Å; C(8)···C(14), 3.366 (5) Å.

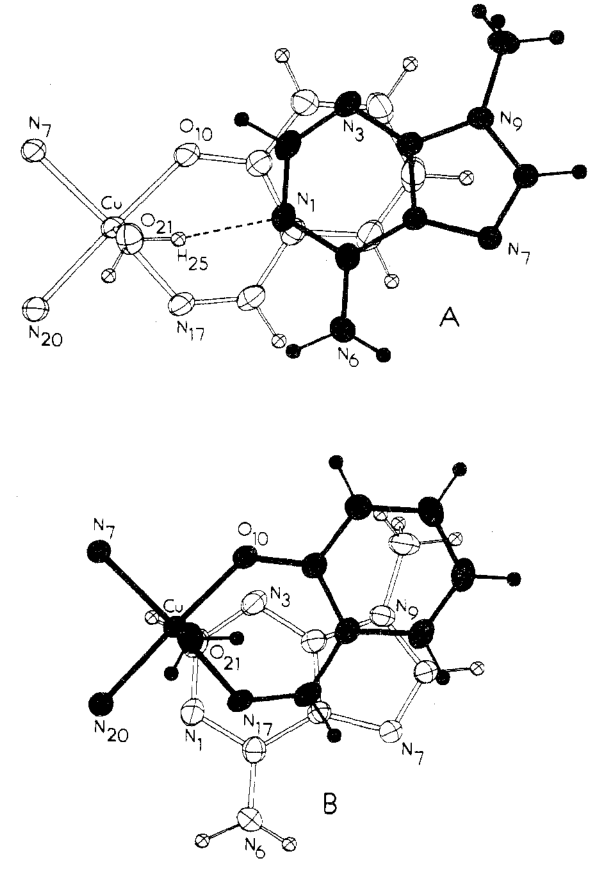

Figure 4. Molecular overlapping in the columns of complex cations. (A) The dashed line indicates the O(21)H_2- - -N(1) hydrogen bond. The 9-methyladenine ligand is at x, y, z and the copper–salicylidene portion of the complex cation is at ${}^1/_2 + x, {}^1/_2 - y, -{}^1/_2 + z$ relative to Table II. (B) The 9-methyladenine ligand is at x, y, z and the copper–salicylidene portion is at ${}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$ relative to Table II.

The intercalative stacking of complexes as found here and in the theophylline complex[1] of this tridentate Schiff base–copper(II) system is consistent with the recent observation that a metal–ligand system with an extensive π network can competitively inhibit the binding of ethidium bromide to calf

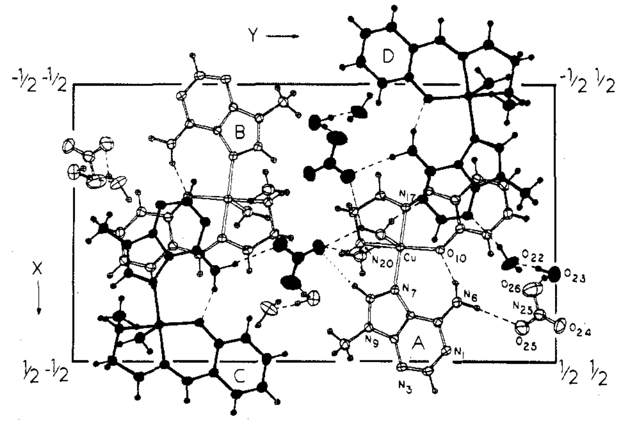

Figure 5. Projection of the unit-cell contents down the c^* axis. Dashed lines denote hydrogen bonds, while the dotted line indicates the C(8)–H· · ·O(24)[nitrate] interaction. The lettered complexes have the following symmetry transforms relative to Table II: (A) x, y, z; (B) $-x, -y, -z$; (C) $^1/_2 - x, -^1/_2 + y, ^1/_2 - z$; (D) $-^1/_2 + x, ^1/_2 - y, ^1/_2 + z$.

thymus DNA.[34] The mean separation between alternate 9-methyladenine residues is 7.06 Å; this value is measurably larger than that found in the theophylline complex,[1] 6.92 Å, and that found, 6.8 Å, in the intercalated ethidium bromide–5-iodouradylyl-(3'→5')-adenosine structure.[35] The expansion, by approximately 0.2 Å, of the interplanar spacing in the 9-methyladenine stacking is very probably related to the significant noncoplanarity of the Schiff base and purine rings, 9.3 (4)°. The noncoplanarity of the molecular planes may in part be due to crystal packing forces. It is more likely, however, that this noncoplanarity may be a function of the overall planarity of the complex. In the theophylline complex,[1] where the salicylidene and purine planes are roughly coplanar, 3.4 (3)°, the molecular complex has a dihedral angle between the purine and the equatorial plane of 33.8 (3)°. In the 9-methyladenine Schiff base cation, the larger noncoplanarity of the purine and salicylidene rings in the stacked columns is paralleled by a larger dihedral angle between the 9-methyladenine framework and the equatorial plane, 45.2 (3)°. It is suggested then that the overall planarity of the complex may be determinative of the relationship between molecular planes within stacks of complexes.

The complete crystal packing is illustrated in Figure 5, which is a projection of the unit-cell contents down the c^* axis. The nitrate anion and the waters of crystallization provide assorted modes of interactions among the columns of stacked complexes, Figure 5 and Table VI. We also note that the hydrogen atom off the imidazole carbon, C(8), is involved in a short contact with one of the nitrate oxygen atoms. This type of interaction involving the C(8)–H group has now been observed in a number of recent structures.[26,28,31,32,36]

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Registry No. [(N-Salicylidene-N'-methylethylenediamine)(aquo)(9-methyladenine)copper(II)] nitrate dihydrate, 56421-94-4.

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 Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number AIC50455R-11-75.

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