[Chem. Pharm. Bull. 26(8)2465—2474(1978)]

UDC 547.857.7'546.562.02 : 548.737

Crystal Structure of *facial*-[Bis-(adeninato)(diethylenetriamine)-copper(II)] Monohydrate[1]

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(Received February 18, 1978)

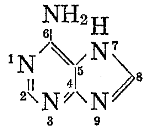
The crystal structure of *fac*-[bis-(adeninato)(dien)copper(II)] monohydrate has been determined from three-dimensional X-ray diffractometer data by heavy atom Fourier methods. Crystals of *fac*-$[Cu(Ade)_2(dien)] \cdot H_2O$ are monoclinic with unit cell dimensions $a=16.015(2)$, $b=14.577(2)$, $c=7.959(1)$ Å, $\beta=90.11(1)°$, space group $P2_1/n$, and $Z=4$. Block-diagonal least-squares refinement using 2695 independent reflexions yielded the R value of 0.068. The copper ion assumes a distorted square pyramidal coordination with five coordination sites of which four square planar sites are occupied by the nitrogen N(9) atoms of two unidentate adenine monoanions and the two (terminal and central) nitrogen atoms of tridentate dien, and the axial site (apical position) is occupied by another terminal nitrogen atom of dien. Therefore, the present dien-copper(II) complex takes a bent form (facial coordination). The propensity of adenine to occupy the *cis* position in equatorial plane of the copper(II) coordination is much stronger than that of dien to take a planar coordination form.

Keywords——adenine; diethylenetriamine; copper(II) complex; mixed ligand complex; crystal structure; bent form; facial coordination; selectivity in adenine coordination; base selectivity for dien-copper complex; *cis*-adeninato-copper(II) complex

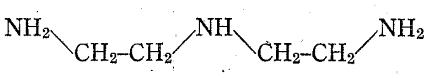
Introduction

Despite the considerable interest in the interaction of metal ion with nucleic acids and nucleotides (for example, deoxyribonucleic acid (DNA) polymerase I,[3] a metalloenzyme from *Escherichia coli*), there have been only a few reports of crystal structures of mixed ligand complexes involving nucleic acid bases.

Of the four commonly occurring nucleic acid bases, adenine has the largest number of unprotonated, heterocyclic donor nitrogen atoms available for metal coordination.



adenine
(denoted by AdeH)



diethylenetriamine
(denoted by dien)

Chart 1

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[1] Presented at the 23rd Annual Meeting of the Japan Society for Analytical Chemistry, Yamaguchi, Oct. 1977. This paper constitutes Part IV of a series entitled "Studies on Metal Complexes of Amino acids and Nucleotide Bases." Part III: H. Sakaguchi, H. Anzai, K. Furuhata, H. Ogura, and Y. Iitaka, *Chem. Pharm. Bull.* (Tokyo), **25**, 2267 (1977).

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Before the establishment of X-ray structure determination of adenine-copper(II) complex by Sletten,[4] the most probable chelating sites in the adenine-copper(II) complex were considered to be the nitrogen atom N(7) and the amino group substituted on C(6).[5,6]

Weiss and Venner[7] on the other hand, showed on the basis of extensive synthetic work on transition metal complexes of purine derivatives that the chelating sites of adenine-copper(II) complexes are probably the nitrogen atoms N(3) and N(9).

Sletten[4] first determined the structure of adenine-copper(II) complex $[Cu_2(Ade)_4(H_2O)_2]\cdot 6H_2O$ by X-ray method and found that the adenine molecule acts as a bridging bidentate ligand *via* N(3) and N(9). For the adenine-copper(II) complexes, there have been a vast amount of reports pointing to the similar bridging system; for example, in $[Cu_2(Ade)_4Cl_2]Cl_2\cdot 6H_2O$,[8] $[Cu_3Cl_8(AdeH)_2]\cdot 4H_2O$,[9] and $[Cu_2(AdeH)_4(H_2O)_2](ClO_4)_4\cdot 2H_2O$,[10] adenine acts as a bridging ligand coordinating its N(3) and N(9) to the copper(II) atom.

On the other hand, there have been a few reports concerning unidentate adenine-copper(II) complexes; only examples are *cis*-$[Cu(AdeH)_2Br_2]Br_2$[11] and Cu(AdeH)(GlyGly)(H_2O)[12] of mixed complex. In these complexes, the binding site of adenine residues has been assigned to ring nitrogen atom N(9). However, masking of the nitrogen atom N(9) by a methyl group such as in 9-methyladenine or by a ribose group as in adenosine leaves three possible metal coordination sites N(1), N(3), and N(7). In [Cu(GlyGly)(9-methyladenine)$(H_2O)]\cdot 4H_2O$, the binding site was found to be N(7).[13]

It is well known that diethylenetriamine (hereafter referred to dien) acts as tridentate ligand and coordinates to the metal ion with either a bent(facial) or planar(meridional) form[14-27] (ref. Fig.1 and Table VI) in which the plannar form is more common in nickel and copper(II) complexes.[16-22] No X-ray crystal structure study of the dien-copper(II) complex showing the bent form (facial coordination) has been presented.

For other metal ions, the bent (facial) form is often observed; such as in Mo(dien)O_3,[27] *cis*-Mo(dien)$(CO)_3$,[28] *cis*-Cr(dien)$(CO)_3$[29] *s-fac*-$[Co(dien)_2]Br_3$,[30] and $(-)_{589}$-*u-fac*-$[Co(dien)_2][Co(CN)_6]\cdot 2H_2O$.[31]

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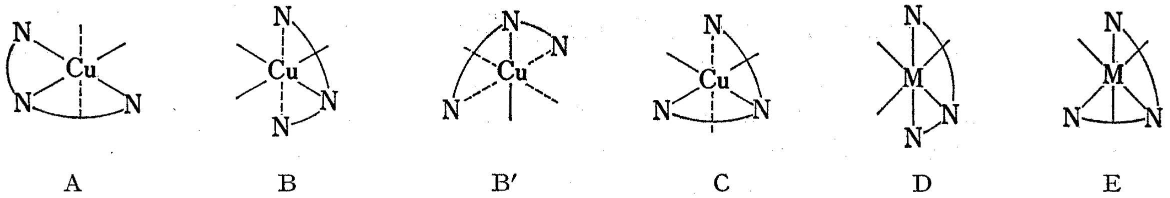

Fig. 1. Coordination Types of Diethylenetriamine-copper (II) Complex

A, B, B′, D: planar form (meridional coordination).
C, E: bent form (facial coordination).
---------, apical bond suggested.
M is metal ion other than copper (II) ion.

The dien mixed copper(II) complexes containing nucleic acid bases have been reported for theophyllinato and thyminato complexes.[17,18] In these mixed copper(II) complexes, all the three nitrogen atoms of dien occupy three of the four corners of equatorial square (planar form). The remaining corner of the square is occupied by the nitrogen of one nucleic acid base. The axial sites (apical positions) of [Cu(Thym)(dien)(H_2O)]Br·2H_2O and [Cu(Theophy)$_2$(dien)]·2H_2O are occupied by the water oxygen and the nitrogen atom N(7) of another theophylline base, respectively.

Stereoselective metal-ligand and ligand-ligand interactions can determine the ligand binding site and stereochemistry of purine complexes[32]. Inter ligand interactions play an important role in determining the selectivity of chelate complexes. Therefore, it is interesting to know the stereochemistry of the present mixed ligand complex.

Experimental

Preparation of *fac*-[Cu(Ade)$_2$(dien)]·H_2O——Method I: A mixture of $Cu(OH)_2$, freshly prepared from $Cu(NO_3)_2 \cdot 3H_2O$ (2.4 g) and NaOH (2.0 g) in H_2O, diethylenetriamine (1.04 g) and adenine (0.27 g) in hot water was heated on a water-bath until no more $Cu(OH)_2$ dissolved. After filtration of the solution, the filtrate was evaporated and blue fine crystals were obtained. These were collected by filtration and recrystallized from water and dried under reduced pressure.

Method II: The adenine mixed complex of copper(II) was prepared by combining 50% methanol solution of [Cu_2(Ade)$_4$(H_2O)$_2$]·6H_2O (0.40 g) and diethylenetriamine (0.21 g). Slow evaporation of the solution yielded blue crystals which were recrystallized from water and dried under reduced pressure.[33]

The crystals of the complex are blue prisms. The specimen employed for the data collection had dimensions of (0.2×0.3×0.4) mm which was mounted on a glass fiber. The crystal data are given in Table I.

Table I. Crystal Data of *fac*-[Cu(Ade)$_2$(dien)]·H_2O

$C_{14}H_{23}N_{13}OCu$	F.W.=452.97	
Crystal system	Monoclinic	
Cell constants	a=16.015(2) Å	β=90.11(1)°
	b=14.577(2) Å	
	c= 7.959(1) Å	V=1858.2(3) Å^3
Space group	$P2_1/n$	
Z	4	
Density (obsd)	D_m=1.619 g·cm^{-3}	
(calcd)	D_x=1.629 g·cm^{-3}	

The intensities were measured on a Rigaku four-circle automatic diffractometer using monochromated Cu–K_α radiation by a graphite plate. Intensities of reflexions with 2θ values up 150° were collected by the θ-2θ scan method with a 2θ scan rate of 2° min^{-1}. The background was measured at each end of the scan range for 10 s. The intensities were collected for Lorentz and polarization factors but not for absorption factors. The total number of independent observed reflexions above the $2\sigma(F)$ level was 2694 out of 3827 theoretically possible reflexions.

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Determination and Refinement of the Structure

From an isolated strong peak at $u=0.414$, $v=0.175$, $w=0.0$ on the three-dimensional Patterson map, the copper(II) ion was placed at (0.207, 0.0875, 0.0). The resulting Fourier map showed all atoms with the exception of hydrogen atoms. Refinement of the structure was carried out by the block-diagonal least-squares method (Program by Okaya and Ashida, 1967).[34] Finally, five cycles of least-squares refinement gave the R index of 0.068. In this calculation, anisotropic thermal motions were assumed for all 29 atoms and the following weight system was applied: $\sqrt{w}=30/F_0$, when $F_0 \geq 30$ and $\sqrt{w}=1$ otherwise. The atomic scattering factors for the Cu(II), C, N, and O were those cited in International Tables for X-ray Crystallography[35] as SX-67, SX-6, 7 and 8, respectively. The real part of the anomalous dispersion correction term, $f'=-2.1$ was taken into consideration for the Cu(II) ion.[36] The final atomic coordinates are listed in Table II. Calculations were carried out on HITAC 8800/8700 computers at the University of Tokyo.

TABLE II. Atomic Parameters

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	2079(1)	878(1)	−8(2)	14(0)	12(0)	63(2)	−1(0)	−2(1)	3(1)
C (2)	416(5)	−1013(6)	−3639(12)	27(3)	28(4)	99(19)	−10(3)	−4(7)	0(7)
C (4)	892(4)	−641(5)	−1083(11)	15(3)	16(3)	64(16)	−3(2)	1(6)	−4(6)
C (5)	550(5)	−1431(5)	−388(11)	17(3)	19(3)	55(16)	−2(2)	7(6)	3(6)
C (6)	143(5)	−2040(5)	−1464(11)	18(3)	18(3)	67(17)	0(2)	1(6)	3(6)
C (8)	1133(5)	−676(5)	1587(11)	20(3)	20(3)	86(18)	−9(3)	−8(6)	10(6)
C (10)	1793(5)	2391(6)	−2444(13)	24(3)	26(4)	107(20)	2(3)	0(7)	23(7)
C (11)	2727(5)	2322(6)	−2126(12)	22(3)	26(4)	95(19)	−1(3)	10(6)	23(7)
C (12)	2703(6)	2666(5)	950(12)	37(4)	17(3)	72(18)	−4(3)	2(7)	−4(6)
C (13)	2633(6)	2157(6)	2643(13)	29(4)	27(4)	91(19)	−3(3)	−2(7)	0(7)
C (2′)	4253(5)	−273(6)	−3453(12)	24(3)	31(4)	83(19)	10(3)	2(7)	10(7)
C (4′)	3642(4)	−181(5)	−927(11)	13(3)	15(3)	56(16)	1(2)	7(5)	4(5)
C (5′)	4190(5)	−842(5)	−278(11)	16(3)	17(3)	54(16)	1(2)	5(5)	2(6)
C (6′)	4752(4)	−1245(5)	−1403(11)	13(2)	18(3)	59(16)	−1(2)	3(5)	−4(6)
C (8′)	3331(5)	−467(5)	1681(12)	25(3)	19(3)	103(19)	8(3)	−6(7)	8(6)
N (1)	59(4)	−1785(5)	−3098(10)	26(3)	27(3)	68(14)	−8(3)	−4(5)	2(6)
N (3)	852(4)	−401(5)	−2742(9)	26(3)	24(3)	55(14)	−9(2)	6(5)	1(5)
N (6)	−199(5)	−2850(5)	−999(10)	32(3)	22(3)	77(15)	−15(3)	−1(6)	0(5)
N (7)	703(4)	−1457(4)	1336(9)	23(3)	18(3)	75(14)	−7(2)	−5(5)	0(5)
N (9)	1274(4)	−164(4)	190(9)	19(2)	19(3)	63(14)	−6(2)	−2(5)	6(5)
N (10)	1391(4)	1524(4)	−1881(9)	20(3)	24(3)	77(14)	2(2)	−12(5)	13(5)
N (11)	2858(4)	1971(4)	−381(9)	16(2)	16(3)	72(14)	−3(2)	1(5)	−2(5)
N (12)	1940(4)	1496(5)	2529(10)	22(3)	27(3)	74(15)	−4(2)	12(5)	−15(6)
N (1′)	4791(4)	−929(5)	−2976(10)	20(3)	24(3)	79(15)	4(2)	7(5)	4(6)
N (3′)	3653(4)	117(5)	−2524(9)	21(3)	29(3)	61(15)	5(2)	10(5)	9(6)
N (6′)	5254(4)	−1981(5)	−956(10)	19(3)	27(3)	79(15)	10(2)	−2(5)	3(6)
N (7′)	3989(4)	−1028(5)	1380(9)	24(3)	25(3)	57(14)	12(2)	−3(5)	5(5)
N (9′)	3093(4)	52(4)	307(9)	18(2)	17(3)	75(15)	4(2)	−1(5)	13(5)
O (w)	2246(4)	164(5)	5301(9)	31(3)	57(4)	74(14)	−3(3)	3(5)	10(6)

Non-Hydrogen atoms. Values are $\times 10^4$. Anisotropic temperature factors are of the form:
$T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

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34) Y. Okaya and T. Ashida, HBLS 4. The Universal Crystallographic Computing System (I), p. 65. Tokyo: The Crystallographic Society of Japan.

35) International Tables for X-ray Crystallography, Vol. III. Birmingham: Kynoch Press (1962).

36) A list of structure factors may be obtained from the author (H.S.) on request.

Description of the Structure and Discussion

The molecular conformation of the *fac*-[bis-(adeninato)(dien)copper(II)] is illustrated in Fig. 2. The coordination about the copper(II) ion is distorted square pyramidal with five coordination sites occupied by the nitrogen atoms of the two adenine monoanions and three nitrogen atoms of dien. The four square planar coordination sites are formed by the nitrogen atoms N(9) and N(9′) of the two adenine monoanions, and terminal and central nitrogen atoms N(10) and N(11) of dien. The apical coordination site is occupied by another terminal nitrogen atom N(12) of dien, and the coordination of water molecule with Cu(II) ion was not observed. Therefore, the present dien-copper(II) complex takes a bent (facial) form (Fig. 1-C and Table VI).

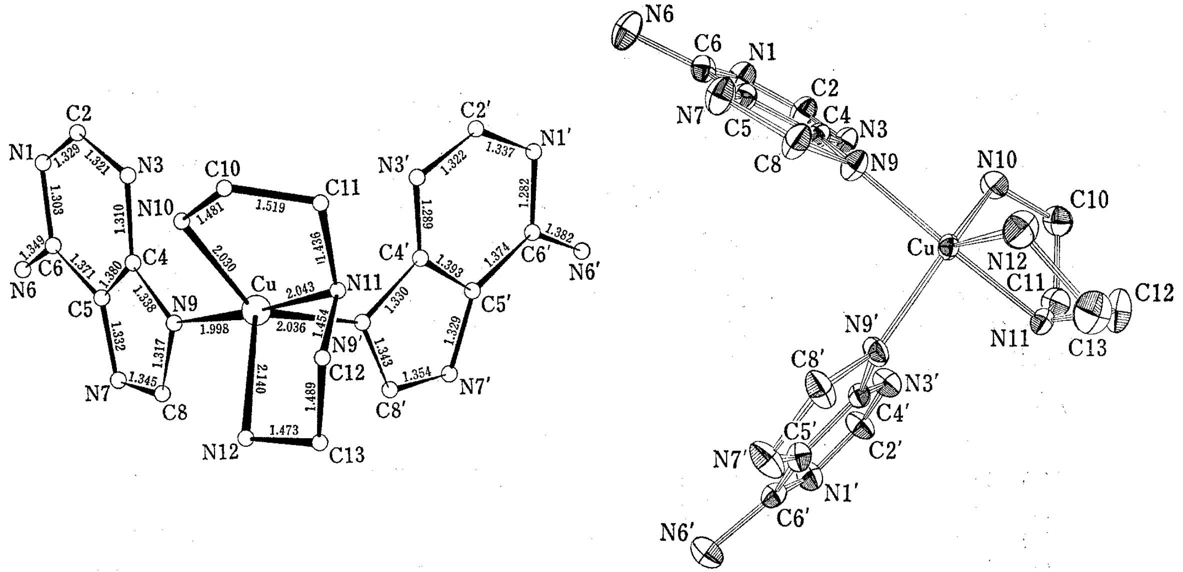

Fig. 2. The Bond Lengths and the Perspective View of the Complex Molecule

In Table III, all the bond lengths and angles found in the complex are listed. Two adenine residues are coordinated at the *cis* position and the angle N(9)–Cu–N(9′) is 93.2°. The four equatorial bond lengths, Cu–N(9), Cu–N(9′), Cu–N(10), and Cu–N(11) are ranged in 2.021±0.023 Å with the average of 2.027 Å. The apical bond of the length 2.140(7) Å which is shorter than the normal, is seriously distorted in conformation from a regular square pyramid. It is also noted that the Cu–N(10) equatorial bond is seriously distorted and the distortions are predominantly seen in the coordination of the dien molecule. It is conceivable that the facial coordination of dien in square pyramidal coordination of Cu(II) may impose such a distortion to the liganded dien molecule. The situation is clearly seen in Table VI. The torsion angles found in the two five-membered chelate rings formed by dien are listed in Table IV.

The *c* axis projection of the crystal structure is shown in Fig. 3. The nitrogen atoms N(3) and N(3′) of the two adenine monoanions in a complex molecule and the terminal nitrogen atom N(12) of dien in the neighbouring complex molecule are connected by hydrogen bonds through the water molecule. Two adenine rings of adjacent complex are arranged anti-parallel to each other across the centre of symmetry and they are stacked along the *c* axis. The rings separated with perpendicular distances of 3.643 and 3.628 Å.

The mixed copper(II) complexes containing dien with other ligands are reported for theophyllinato, thyminato, oxalato, and formato complexes.[17,18,21,22] In these mixed complexes, all the three nitrogen atoms of dien occupy three of the four corners of equatorial

TABLE III. Interatomic Distances (Å) and Bond Angles (°) with Standard Deviations in Parentheses

a) Primary coordination sphere about the Copper Atom			
	Bond lengths		
Cu–N (9)	1.998(6)	Cu–N (9′)	2.036(6)
Cu–N (10)	2.030(7)	Cu–N (11)	2.043(6)
Cu–N (12)	2.140(7)		
	Bond angles		
N (9)–Cu–N (10)	93.2(3)	N (9′)–Cu–N (11)	89.4(3)
N (9)–Cu–N (11)	175.7(3)	N (9′)–Cu–N (10)	142.1(3)
N (9)–Cu–N (12)	100.6(3)	N (9′)–Cu–N (12)	103.1(3)
N (9)–Cu–N (9′)	93.6(3)	N (10)–Cu–N (11)	82.6(3)
N (10)–Cu–N (12)	112.3(3)	N (11)–Cu–N (12)	82.0(3)
b) Diethylenetriamine ligand			
	Bond lengths		
N (10)–C (10)	1.481(11)	N (12)–C (13)	1.473(11)
C (10)–C (11)	1.519(12)	C (13)–C (12)	1.489(13)
C (11)–N (11)	1.436(11)	C (12)–N (11)	1.454(11)
	Bond angles		
Cu–N (10)–C (10)	111.3(5)	Cu–N (12)–C (13)	104.4(5)
N (10)–C (10)–C (11)	109.0(7)	N (12)–C (13)–C (12)	109.4(7)
C (10)–C (11)–N (11)	108.3(7)	C (13)–C (12)–N (11)	105.5(7)
Cu–N (11)–C (11)	108.5(5)	Cu–N (11)–C (12)	110.0(5)
C (11)–N (11)–C (12)	111.6(6)		
c) Adenine monoanion ligands			
	Bond lengths		
N (1)–C (2)	1.329(11)	N (1′)–C (2′)	1.337(11)
N (1)–C (6)	1.303(11)	N (1′)–C (6′)	1.282(11)
C (2)–N (3)	1.321(11)	C (2′)–N (3′)	1.322(11)
N (3)–C (4)	1.310(11)	N (3′)–C (4′)	1.289(11)
C (4)–C (5)	1.380(10)	C (4′)–C (5′)	1.393(10)
C (4)–N (9)	1.338(10)	C (4′)–N (9′)	1.330(10)
C (5)–C (6)	1.371(11)	C (5′)–C (6′)	1.374(11)
C (5)–N (7)	1.332(11)	C (5′)–N (7′)	1.329(11)
C (6)–N (6)	1.349(10)	C (6′)–N (6′)	1.382(10)
N (7)–C (8)	1.345(10)	N (7′)–C (8′)	1.354(11)
C (8)–N (9)	1.317(11)	C (8′)–N (9′)	1.343(11)
	Bond angles		
C (2)–N (1)–C (6)	119.5(7)	C (2′)–N (1′)–C (6′)	118.5(7)
N (1)–C (2)–N (3)	129.8(8)	N (1′)–C (2′)–N (3′)	129.1(8)
C (2)–N (3)–C (4)	109.9(7)	C (2′)–N (3′)–C (4′)	111.7(7)
N (3)–C (4)–C (5)	124.9(7)	N (3′)–C (4′)–C (5′)	123.8(7)
N (3)–C (4)–N (9)	125.3(7)	N (3′)–C (4′)–N (9′)	126.0(7)
C (5)–C (4)–N (9)	109.8(7)	C (5′)–C (4′)–N (9′)	110.1(7)
C (4)–C (5)–C (6)	120.0(7)	C (4′)–C (5′)–C (6′)	119.3(7)
C (4)–C (5)–N (7)	109.1(7)	C (4′)–C (5′)–N (7′)	108.8(7)
C (6)–C (5)–N (7)	130.9(7)	C (6′)–C (5′)–N (7′)	131.5(7)
N (1)–C (6)–C (5)	115.6(7)	N (1′)–C (6′)–C (5′)	117.3(7)
N (1)–C (6)–N (6)	117.2(7)	N (1′)–C (6′)–N (6′)	118.6(7)
C (5)–C (6)–N (6)	127.1(7)	C (5′)–C (6′)–N (6′)	124.1(7)
C (5)–N (7)–C (8)	102.1(6)	C (5′)–N (7′)–C (8′)	103.1(7)
N (7)–C (8)–N (9)	116.9(7)	N (7′)–C (8′)–N (9′)	115.3(7)
Cu–N (9)–C (4)	129.4(5)	Cu–N (9′)–C (4′)	126.6(5)
Cu–N (9)–C (8)	127.0(5)	Cu–N (9′)–C (8′)	130.4(5)
C (4)–N (9)–C (8)	102.1(6)	C (4′)–N (9′)–C (8′)	102.6(6)

TABLE IV. Torsion Angles (°) of Diethylenetriamine Chelate Rings

N (10)-Cu-N (11)-C (11)	−25	C (12)-N (11)-Cu-N (12)	−17
Cu-N (11)-C (11)-C (10)	46	C (13)-C (12)-N (11)-Cu	45
N (11)-C (11)-C (10)-N (10)	−47	N (12)-C (13)-C (12)-N (11)	−60
C (11)-C (10)-N (10)-Cu	26	Cu-N (12)-C (13)-C (12)	44
C (10)-N (10)-Cu-N (11)	−1	N (11)-Cu-N (12)-C (13)	−15
N (10)-Cu-N (11)-C (12)	97	C (11)-N (11)-Cu-N (12)	−139
C (10)-N (10)-Cu-N (12)	77	N (10) Cu-N (12)-C (13)	−93
C (12)-N (11)-C (11)-C (10)	−76	C (13)-C (12)-N (11)-C (11)	165

TABLE V. Deviations of Atoms from the Least-squares Planes[a]

a) Equatorial plane about the copper atom

$(0.6832X+0.3509Y+0.8991Z=-0.77825\ \text{Å})$

N (9)	0.286	N (11)	0.320
N (9′)	−0.219	Cu	0.344*
N (10)	−0.315	N (12)	2.452*

b) Two adenine monoanion planes

(1) Nine-atom base planes

$(0.8518X-0.4897Y-0.1863Z=1.8217\ \text{Å})$		$(0.6429X+0.7100Y+0.2874Z=3.3295\ \text{Å})$	
N (1)	−0.029	N (1′)	−0.013
N (3)	0.016	N (3′)	−0.003
N (7)	−0.011	N (7′)	0.011
N (9)	0.008	N (9′)	−0.027
C (2)	−0.016	C (2′)	0.008
C (4)	0.006	C (4′)	0.028
C (5)	0.005	C (5′)	0.049
C (6)	0.038	C (6′)	−0.036
C (8)	−0.018	C (8′)	−0.019
Cu	0.390*	Cu	−0.284*
N (6)	0.083*	N (6′)	−0.184*

(2) Imidazole rings

$(0.8528X-0.4921Y-0.1749Z=1.8274\ \text{Å})$		$(0.6183X+0.7226Y+0.3093Z=3.1920\ \text{Å})$	
N (7)	0.002	N (7′)	−0.005
N (9)	0.006	N (9′)	−0.005
C (4)	−0.005	C (4′)	0.002
C (5)	0.002	C (5′)	0.001
C (8)	−0.005	C (8′)	0.006
Cu	0.385*	Cu	−0.213*

(3) Pyrimidine rings

$(0.8490X-0.4895Y-0.1992Z=1.8428\ \text{Å})$		$(0.6554X+0.7042Y+0.2729Z=3.4460\ \text{Å})$	
N (1)	−0.021	N (1′)	0.008
N (3)	0.018	N (3′)	−0.019
C (2)	−0.004	C (2′)	0.018
C (4)	−0.008	C (4′)	−0.004
C (5)	−0.015	C (5′)	0.027
C (6)	0.030	C (6′)	−0.030
N (6)	0.072*	N (6′)	−0.167*

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[a] In each of the equations of the planes, the X, Y, and Z are coordinates (Å) refered 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.

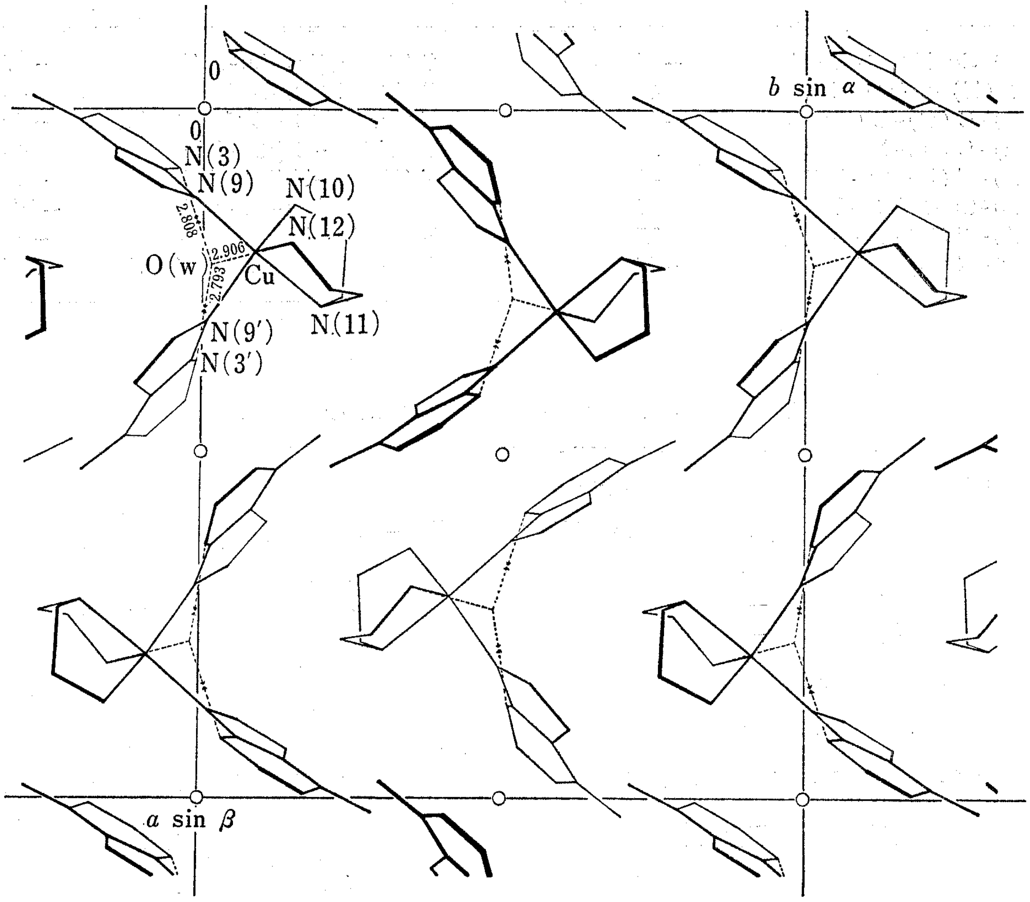

Fig. 3. The Projection of the Crystal Structure Along the c Axis

Centres of symmetry are denoted by ○. Hydrogen bonds are shown by broken lines.

TABLE VI. Comparison of the Angle (N_{term}-Metal-N_{term}) and Distances (N_{term}-Metal) for dien-metal Complexes

Complex	Angle (°)	Distances (Å)		Coordination type (see Fig. 1)	Ref.
fac-$[Cu(Ade)_2(dien)]\cdot H_2O$	112.3	2.030	2.140[a]	C	Present paper
$[Cu(Theophy)_2(dien)]\cdot 2H_2O$	153.7	2.040	2.047	A	17)
$[Cu(Thym)(dien)(H_2O)]Br\cdot 2H_2O$	162.7	2.002	2.040	A	18)
$[Cu(C_2O_4)(dien)]\cdot 4H_2O$	155.0	1.996	2.009	A	21)
$[Cu(HCO_2)(dien)](HCO_2)$	168.8	2.009	2.009	A	22)
$[Cu(dien)_2](NO_3)_2$	159.1	2.203[a]	2.265[a]	B′	19)
	158.6	2.170[a]	2.236[a]	B′	
$[Cu(dien)_2]Br_2\cdot H_2O$	157.3	2.350[a]	2.459[a]	B	20)
	162.9	2.066	2.131	A	
$[Ni(dien)_2]Cl_2\cdot H_2O$	—	2.16	2.16	D	16)
$[Co(Ox)(NH_3)(dien)]NO_3$	170.0	1.95	1.98	D	23)
mer-$[Co(dien)_2](NO_3)_3\cdot H_2O$	171.1	1.969	1.971	D	24)
	170.7	1.957	1.980	D	
$[Pd(dien)(NO_2)]NO_3$	167.2	2.041	2.048	D	25)
$[Pt(dien)Br]Br$	168.2	1.958	1.982	D	26)
$Mo(dien)O_3$	80.0	2.320	2.320	E	27)
cis-$Mo(dien)(CO)_3$	87.5	2.311	2.348	E	28)
cis-$Cr(dien)(CO)_3$	87.6	2.183	2.185	E	29)
s-*fac*-$[Co(dien)_2]Br_3$	89.5	1.97	1.97	E	30)

a) Apical bond suggested.

square (planar form). The remaining corner of the square, is occupied by the nitrogen or oxygen atom of the other ligand molecule and the apical position is occupied by either the water oxygen or the other ligand atom. Thus in $[Cu(Theophy)_2(dien)]\cdot 2H_2O$, the four square planar coordination sites are occupied by the three nitrogen atom of tridentate dien and nitrogen atom N(7) of the purine residue and the axial site(apical position) is occupied by the nitrogen atom N(7) of another purine residue.

Kistenmacher and his associates[37] reported the reaction which exhibits interesting steric dependence:

$$trans\text{-}[Co(en)_2Cl_2]^+ + \text{base} \longrightarrow cis\text{-}[Co(en)_2Cl(\text{base})]^+ + Cl^-$$

Of the four nucleic acid bases tested, only adenine gave the reaction. Thus, the above reaction of adenine with *trans*-$[Co(en)_2Cl_2]^+$ shows a great tendency of adenine bases to occupy an equatorial coordination site. Later, they also found that theophylline gives the similar reaction, but in this case, *trans*-$[Co(en)_2Cl(Theophy)]^+$ complex[38] is obtained mainly, giving only small amount of *cis*-$[Co(en)_2Cl(Theophy)]^+$ complex.[39] For a production of small amount of *cis*-isomer, similar unique structure of coordination is suggested although the base selectivity of theophylline is not so strong as adenine.

TABLE VII. Distances of Hydrogen Bonds (Å)

No.	From[a]	To	Distance
1	N (12)	O (w)[a]	2.906(10)
2	O (w)	N (3)[b]	2.808(10)
3	O (w)	N (3)[b]	2.793(10)

Key to the symmetry operation: *a*) *x*, *y*, *z*; *b*) *x*, *y*, 1+*z*.

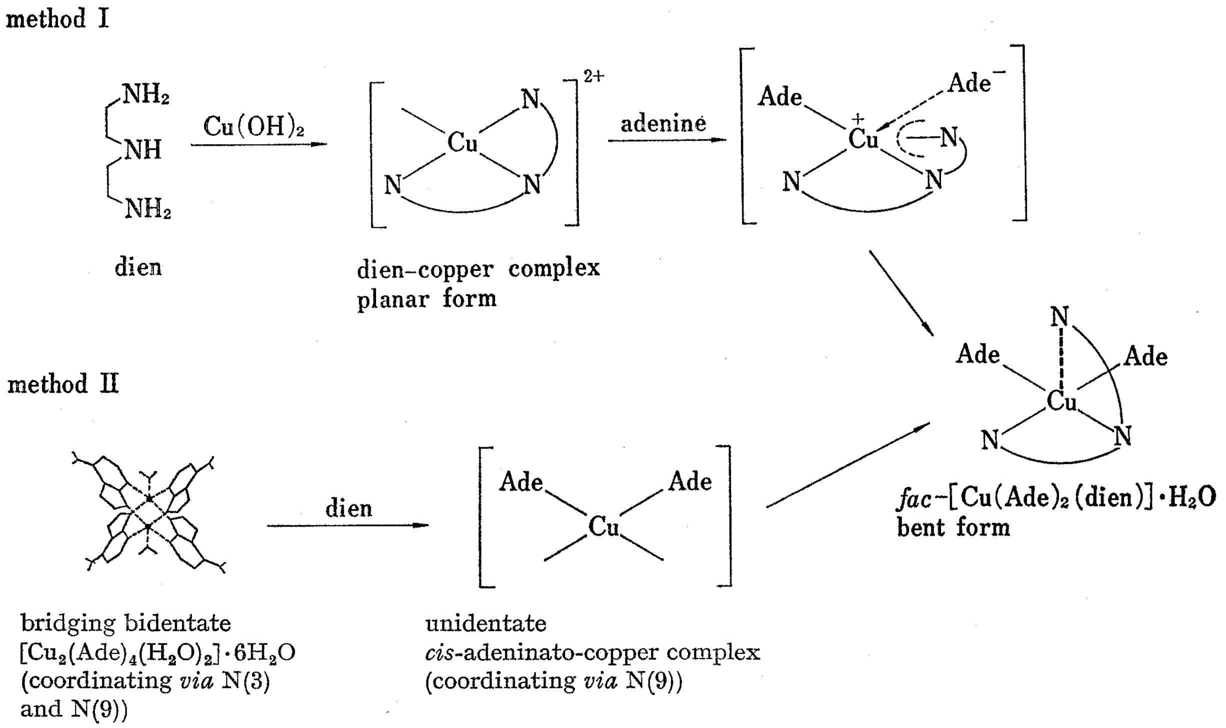

Chart 2

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[37] T.J. Kistenmacher, L.G. Marzilli, and C.H. Chang, *J. Amer. Chem. Soc.*, **95**, 5817 (1973).

[38] L.G. Marzilli, T.J. Kistenmacher, and C.H. Chang, *J. Amer. Chem. Soc.*, **95**, 7507 (1973).

[39] L.G. Marzilli, T.J. Kistenmacher, P.E. Darcy, D.J. Szalda, and M. Beer, *J. Amer. Chem. Soc.*, **96**, 4686 (1974).

The present structure of [Cu(Ade)$_2$(dien)]·H_2O differs from that of [Cu(Theophy)$_2$(dien)]·2H_2O,[17] although both complexes are composed of two unidentate purine residues and one dien molecule. The structure of the present complex is unusual in the point that only two of the three nitrogen atoms of dien are on the equatorial plane and the dien molecule adopts the facial(bent) form of coordination. This shows a tendency to have two adenine bases coordinated to the equatorial plane which results in one of the three nitrogen atoms of dien, terminal nitrogen atom N(12), to be coordinated to the apical position. This tendency is explained by the strong base selectivity of adenine residues to bind at the equatorial site.

The stereochemistry of the reaction of dien-copper(II) complex with adenine (Method I of the preparation of the present adenine complex) and that of bis-adeninato-copper(II) complex with dien (Method II) are illustrated in Chart 2.

The propensity of adenine to occupy the *cis* position in equatorial square of present copper(II) ion (adenine base selectivity for dien-copper(II) complex) is much stronger than that of dien to take a planar coordination form. In dien-copper(II) complexes, the order of the base selectivity may be expressed as follows, Ade>Theophy>Thym.