Inorg. Chem. **1996,** *35,* 2253−2258

Synthesis, Characterization, and Crystal Structure of a Novel Copper(II) Complex with an Asymmetric Coordinated 2,2′-Bipyridine Derivative: A Model for the Associative Complex in the Ligand-Substitution Reactions of [Cu(tren)L]$^{2+}$?

Zhong-lin Lu, Chun-ying Duan, Yu-peng Tian, and Xiao-zeng You*

Coordination Chemistry Institute, The State Key Laboratory of Coordination Chemistry,
Nanjing University, and The Center for Advanced Studies in Science and Technology of Microstructure,
Nanjing 210093, P. R. China

Xiao-ying Huang

State Key Laboratory of Structure Chemistry, Fuzhou 350002, P. R. China

Received March 31, 1995[⊗]

The titled compound, (tris(2-aminoethyl)amine)(4,5-diazafluoren-9-one) copper(II) perchlorate, [Cu($C_6H_{18}N_4$)($C_{11}H_6N_2O$)(ClO_4)$_2$], **1**, has been designed, synthesized, and characterized. The electronic and ESR spectra are very different from those of [Cu(tren)L]$^{2+}$ complexes where L is monodentate ligand. The X-ray analysis revealed that the complex crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.726(6)$ Å , $b = 14.921(7)$ Å, $c = 14.649(4)$ Å, $\beta = 95.13(3)°$, and $Z = 4$. The copper(II) ion is coordinated by four nitrogen atoms from tris(2-aminoethyl)amine (tren) and two nitrogen atoms from 4,5-diazafluoren-9-one (dzf) to form an unusual six-coordinate (4 + 1 + 1′) geometry. The structure is very rare, and to our knowledge, it is the first example of an asymmetric bidentate phenanthroline derivative metal complex. The structure could be used as a model of the associative complex in the ligand-exchange and ligand-substitution reactions of [Cu(tren)L]$^{2+}$ and the catalytic mechanisms of enzymes involving copper sites. From the electronic and variable-temperature ESR spectra in solution, the possible mechanism of these reactions has also been proposed. As a comparison, the complex [Cu(tren)(ImH)(ClO$_4$)$_2$], **2**, was also synthesized and characterized, where ImH is imidazole.

Introduction

The rates and mechanism of ligand-exchange and ligand-substitution reactions of the five-coordinated copper complexes [Cu(tren)L]$^{2+}$ (where L is monodentate ligand) have been widely studied[1,2] because of their importance in studying the elementary steps in the catalytic cycles of enzymes such as Cu−Zn SOD involving substitution reactions at the copper sites.[3,4] Although an associative mechanism has been suggested,[5,6] the structure of the associative complex in the reaction has not been determined, and no associative complex has been observed due to its instability. In order to study the associative mechanism further, it is necessary to design a model complex.

In our laboratory, [Cu(tren)(L-L)]$^{2+}$ complexes have been designed and synthesized as models of the associative complex, where L-L is a strongly chelated ligand, such as 2,2′-bipyridine, 1,10-phenanthroline, or one of their derivatives. They have been used because (i) the strongly chelated ligands should cause the [Cu(tren)(L-L)]$^{2+}$ cation to form six-coordinated copper complexes, which have the same coordination number as the associative complex, and (ii) the relatively rigid tripodal construction of tren results in a strong preference to form five-coordinated complexes of copper(II). The two greatly different tendencies should cause the [Cu(tren)(L-L)]$^{2+}$ cation to form an unusual (4 + 1 + 1′) structure, in which the complex has five strongly coordinated atoms and one very weakly semicoordinated atom. This quite distorted (4 + 1 + 1′) six-coordinated structure should be similar to that of the associative complex in the ligand-substitution reactions of [Cu(tren)L]$^{2+}$ complexes.

In this paper, one such complex, [Cu($C_6H_{18}N_4$)($C_{11}H_6N_2O$)](ClO_4)$_2$], **1**, is reported, where $C_6H_{18}N_4$ is tris(2-aminoethyl)amine (tren) and $C_{11}H_6N_2O$ is 4,5-diazafluoren-9-one (dzf). The electronic reflectance and 110 K ESR spectra of **1** are very different from those of the general [Cu(tren)L]$^{2+}$ complexes. The X-ray analysis revealed that the complex has an unusual (4 + 1 + 1′) six-coordinated structure. It is very important to note that dzf is coordinated to the copper(II) ion as an asymmetric bidentate ligand. This structure is very rare, and to our knowledge, it is the first example of a metal complex with an asymmetric bidentate phenanthroline derivative. From the crystal structure and electronic and variable-temperature ESR spectra in solution, the possible mechanism of the ligand-substitution reaction has also been determined to be a three-step process with two kinds of associative complexes.

In order to compare the structures of complex **1** and the general [Cu(tren)L]$^{2+}$ system, the complex [Cu(tren)(ImH)](ClO_4)$_2$, **2**, was also synthesized and characterized, where ImH is imidazole.

Experimental Section

Caution! *Although no problem were encountered in this work, transition metal perchlorate are potentially explosive. They should be prepared in small quantities and handled with care.*

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

(1) Rablen, D. P.; Dodgen, H. W.; Hunt, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 1771.

(2) Cayley, G.; Cross, D.; Knowles, P. F. *J. Chem. Soc., Chem. Commun.* **1976**, 837.

(3) Yadav, K. D. S.; Knowles, P. F. Eur. *J. Biochem.* **1981**, *114*, 139.

(4) Bertini, I.; Banci, L.; Piccioli, M. *Coord. Chem. Rev.* **1990**, *100*, 67.

(5) Cayley, G. R.; Kelly, I. D.; Knowles, P. F.; Yadav, K. D. S. *J. Chem. Soc., Dalton Trans.* **1981**, 2370.

(6) Powell, D. H.; Merbach, A. E.; Fäbiän, I.; Schindler, S.; van Eldik, R. *Inorg. Chem.* **1994**, *33*, 4468−4473.

Table 1. Crystallographic Data for [Cu(tren)(dzf)]$(ClO_4)_2$

formula	$C_{17}H_{24}N_6Cl_2CuO_8$	fw	590.86
a	10.726(6) Å	space group	$P2_1/c$
b	14.921(7) Å	T	23 °C
c	14.649(4) Å	λ	0.710 73 Å
β	95.13(3)°	D_x	1.68 g cm^{-3}
V	2335.17 Å	μ	12.2 cm^{-1}
Z	4	$R(F_o)^a$	0.053
		$R_w((F_o)^b$	0.059

$^a R = \sum|F_o - F_c|/\sum F_o$. $^b R_w = \sum[|F_o - F_c|w^{1/2}]/\sum|F_o|w^{1/2}]$. $w = 1/\sigma^2(F_o)$.

Materials and Reagents. All chemicals were of reagent grade and were used without further purification. 4,5-Diazafluoren-9-one was prepared using the literature method.[7] The complex [Cu(tren)]$(ClO_4)_2$ was synthesized according to the procedure described earlier,[8] however using $Cu(OAc)_2{\cdot}H_2O$ and $NaClO_4$ instead of $CuCl_2{\cdot}2H_2O$ and KSCN. Other complxes were prepared as follows.

[Cu(tren)(dzf)]$(ClO_4)_2$] (1). To a solution of [Cu(tren)]$(ClO_4)_2$ (1 mmol, 0.408 g) in ethanol (30 cm^{-3}) was added 4,5-diazafluoren-9-one (1 mmol, 0.182 g). The mixture was refluxed for 3 h. After cooling of the mixture to room temperature, the precipitate was filtered off by suction and dried in vacuo over silica. Yield: 0.47g, 80%. Anal. Calcd for $C_{17}H_{24}Cl_2CuN_6O_8$: C, 34.55; H, 4.09; N, 14.23. Found: C, 34.28; H, 4.13; N, 14.30.

[Cu(tren)(ImH)]$(ClO_4])_2$[9] (2). The complex was obtained as blue needle-shaped crystals in a similar manner. Yield: 85%. Anal. Calcd for $C_9H_{21}Cl_2CuN_6O_8$: C, 22.27; H, 4.66; N, 17.66. Found: C, 23.08; H, 4.62; N, 17.08.

Physical Measurements. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. Electronic reflectance spectra were recorded on a Shimadzu 240 spectrophotometer, electronic spectra of the complexes in absolute DMF were recorded on a Shimadzu 310 spectrophotometer, and the 110 K ESR and variable-temperature ESR spectra of the complexes in DMF solutions were measured using a Bruker 200D-SRC spectrometer.

Crystallography. Prismatic crystals of complex **1** were obtained by slow evaporation of its ethanol solution at room temperature. A total of 4295 independent reflections were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα (λ = 0.7173 Å) radiation using the $\omega/2\theta$ scan mode in the range 20.50° < θ < 23.94° , and none were corrected. A total of 2824 independent reflections were observed with $I > 3\sigma(I)$. The structure was solved by direct methods and a difference Fourier synthesis and refined by full-matrix least-squares techniques to final $R = 0.052$ and $R_w = 0.059$. All calculations were carried out on a PDP11/44 computer with the SDP program.

Crystallographic data for complex **1** are listed in Table 1.

Results and Discussion

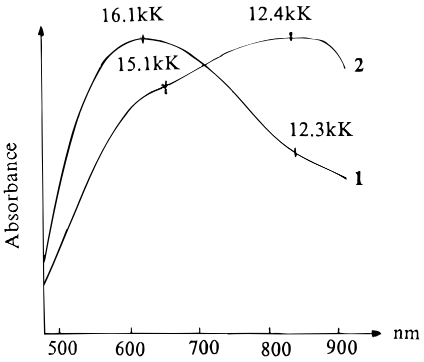


Figure 1. Electronic reflectance spectra of complexes **1** and **2**.

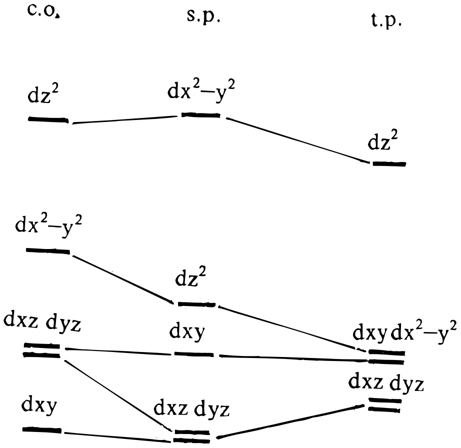


Figure 2. d-Orbital energy sequence of *cis* distorted-octahedral (left) (c.o.), square pyramidal (middle) (s.p.), and trigonal bipyramidal ligand fields (right) (t.p.).

Electronic Reflectance Spectra. Figure 1 shows the electronic reflectance spectra of complexes **1** and **2**. They absorb light in the same region of the visible spectrum; nevertheless their spectra are quite different. Complex **1** has a band maximum at 16 100 cm^{-1} and a lower energy shoulder at 12 300 cm^{-1}; while **2** has a maximum at 12 400 cm^{-1} and a high-energy shoulder at 15 100 cm^{-1}. Both spectra agree with those previously reported for $[Cu(NH_3)_5]]^{2+}$ [10] and $[Cu(tren)(NH_3)]^{2+}$,[11] respectively. This result may demonstrate that complex **1** has a distorted square-based pyramidal geometry, instead of the trigonal bipyramidal stereochemistry which is very common in (tris(2-aminoethyl)amine) copper(II) complexes. The assignment of the electronic reflectance spectra of copper(II) has been extensively discussed in the literature,[12,13] and the orbital sequence of the various stereochemistries is illustrated in Figure 2.[14] It would be reasonable to assign the intense band of complex **1** at 16 100 cm^{-1} as the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition and the shoulder at 12 300 cm^{-1} as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition with the $d_{xy} \rightarrow d_{x^2-y^2}$ transition at 14 000 cm^{-1} in the Gaussian analysis .[11] This assignment is in agreement with that suggested for other square-based pyramidal copper(II) complexes.[12,14,15] A tentative assignment of the electronic reflectance spectra of the $[Cu(tren)L]^{2+}$ cations has been suggested, namely the band maximum at 12 400 cm^{-1} of complex **2** as the d_{xy}, $d_{x^2-y^2} \rightarrow d_{z^2}$ transition, which is allowed in C_3 and D_{3h} symmetries, and the less intense shoulder at 15 100 cm^{-1} as the d_{xz}, $d_{yz} \rightarrow d_{z^2}$ transition, which although allowed in C_3 symmetry is forbidden in D_{3h} symmetry but can occur weakly by a vibrionic mechanism. This shows the characteristics of the trigonal bipyramidal sterochemistry.[12,15,16]

ESR Spectra. The ESR spectra of complexes **1** and **2** in frozen DMF are shown in Figure 3. The spectrum of complex **1** involves an intense $g_{\|}$ signal with clear resolution of the four copper hyperfine lines, $g_{\|} = 2.232$, $A_{\|} = 17.57 \times 10^{-3}$ cm^{-1}, and a very intense $g_{\perp}$ signal with $g_{\perp} = 2.047$, $A_{\perp} = 14.32 \times 10^{-3}$ cm^{-1}. The fact $g_{\|} > g_{\perp}$ confirms a square-based pyramidal stereochemistry in complex **1**.[12,14] The spectrum of complex **2** shows a line shape characteristic of a complex with two different

---

(7) Henderson, L. J.; Frorczek, J. F. R. *J. Am. Chem. Soc.* **1984**, *106*, 5876.

(8) Raymond, K. N.; Basolo, F. *Inorg. Chem.* **1966**, *5*, 1632.

(9) Zhong-lin Lu; Chun-yin Duan; Yu-peng Tian; Xiao-zeng You, *Acta Crystallogr., Sect. C,* in press.

(10) Hathaway, B. J.; Tomlinson, A. A. G. *J. Chem. Soc. A* **1968**, 1695.

(11) Dudley, R. J.; Hathaway, B. J.; Power, P. G.; Loose, D. J. *J. Chem. Soc., Dalton Trans.* **1974**, 1005.

(12) Hathaway, B. J.; Tomlinson, A. A. G. *Coord. Chem. Rev.* **1970**, *5*, 1.

(13) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.

(14) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J. V.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(15) Duggen, M.; Ray, N.; Hathaway, B.; Tomlinson, G.; Brint, P.; Pelin, K. *J. Chem. Soc., Dalton Trans.* **1980**, 1342.

(16) Jain, P. C.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1967**, *89*, 6131.

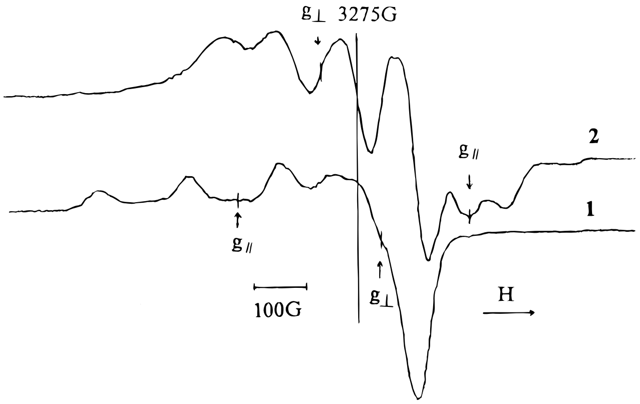


Figure 3. 110 K ESR spectra of complexes **1** and **2** in frozen DMF solutions.

g values but the reverse of that of complex **1**, with $g_{\|} = 2.006$, $A_{\|} = 7.68 \times 10^{-3}$ cm^{-1} and $g_{\perp} = 2.164$, $A_{\perp} = 12.31 \times 10^{-3}$ cm^{-1}. The fact $g_{\perp} > g_{\|}$ agrees with the trigonal bipyramidal stereochemistry established for the [Cu(tren)L]$^{2+}$ system.[14−16]

The differences in the electronic reflectance and 110 K ESR spectra of the two complexes suggest that complexes **1** and **2** have different stereochemistries. Complex **2** should have a trigonal bipyramidal stereochemistry like most five coordinated [Cu(tren)L]$^{2+}$ complexes, while complex **1** may have a distorted square-based pyramidal geometry or a six-coordinated distorted octahedral sterochemistry in the solid state. The results have been confirmed by the crystal structures of complexes **1** and **2**. The structure of complex **2** is reported in another article.[9]

Table 2. Atomic Positional and Thermal Parameters for Complex **1**

atom	x	y	z	B(eq),^{a} Å^2
Cu	0.72776(6)	0.44917(5)	0.74053(5)	2.60(3)
O(1)	1.2038(5)	0.6024(5)	0.5503(4)	8.2(4)
N(1)	0.8877(4)	0.4338(3)	0.6783(3)	3.1(2)
N(2)	0.8201(5)	0.6333(4)	0.6885(4)	3.9(3)
N(3)	0.6249(4)	0.4846(3)	0.6225(3)	3.3(2)
N(4)	0.6688(5)	0.3070(3)	0.7620(3)	3.8(2)
N(5)	0.8185(5)	0.4860(4)	0.8633(3)	3.7(2)
N(6)	0.5690(4)	0.4676(3)	0.8017(3)	2.8(2)
C(1)	0.9352(7)	0.3519(4)	0.6654(4)	4.0(3)
C(2)	1.0490(8)	0.3380(5)	0.6275(5)	5.4(4)
C(3)	1.1140(6)	0.4111(6)	0.6007(5)	5.3(4)
C(4)	1.0648(6)	0.4948(6)	0.6118(4)	4.4(3)
C(5)	1.1113(7)	0.5859(6)	0.5871(5)	5.5(4)
C(6)	1.0123(6)	0.6482(5)	0.6141(5)	4.7(3)
C(7)	0.9968(9)	0.7409(6)	0.6044(5)	6.0(4)
C(8)	0.8942(9)	0.7773(6)	0.6370(6)	5.8(4)
C(9)	0.8113(7)	0.7221(5)	0.6787(5)	4.8(4)
C(10)	0.9210(6)	0.5994(4)	0.6542(4)	3.4(3)
C(11)	0.9527(5)	0.5027(4)	0.6523(4)	3.1(3)
C(12)	0.5006(6)	0.5187(4)	0.6421(4)	4.0(3)
C(13)	0.5051(6)	0.5468(4)	0.7412(4)	3.8(3)
C(14)	0.5761(6)	0.3147(4)	0.8296(4)	3.8(3)
C(15)	0.4919(6)	0.3955(4)	0.8055(4)	3.6(3)
C(16)	0.7333(6)	0.5547(4)	0.8994(4)	3.6(3)
C(17)	0.6049(6)	0.5136(4)	0.8952(4)	3.5(3)
Cl(1)	0.5764(2)	0.7246(1)	0.4573(1)	3.62(7)
O(11)	0.6014(5)	0.8017(3)	0.5121(3)	5.6(3)
O(12)	0.6204(6)	0.7360(3)	0.3696(3)	6.5(3)
O(13)	0.6382(5)	0.6488(3)	0.4991(4)	6.6(3)
O(14)	0.4458(5)	0.7051(4)	0.4491(5)	8.1(4)
Cl(2)	0.8411(2)	0.0903(1)	0.6249(1)	4.55(8)
O(21)	0.8090(7)	0.1371(4)	0.7003(4)	9.0(4)
O(22)	0.876(1)	0.0046(5)	0.6426(6)	13.4(6)
O(23)	0.789(2)	0.124(1)	0.5421(9)	9.3(8)
O(24)	0.969(1)	0.129(1)	0.629(1)	10.1(8)
O(23′)	0.715(1)	0.055(2)	0.597(1)	11(1)
O(24′)	0.892(3)	0.121(2)	0.553(2)	10(2)

[a] $B(\mathrm{eq}) = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ac(\cos\beta)\beta(1,3)]$.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for Complexes **1** and **2**

Distances

1		**2**	
Cu−N(1)	2.027(5)	Cu−N(1)	1.996(7)
Cu−N(3)	2.036(5)	Cu−N(3)	2.091(7)
Cu−N(6)	2.039(5)	Cu−N(6)	2.116(7)
Cu−N(5)	2.042(5)	Cu−N(5)	2.027(5)
Cu−N(4)	2.244(5)	Cu−N(4)	2.124(7)
Cu−N(2)	2.995^a		

Angles

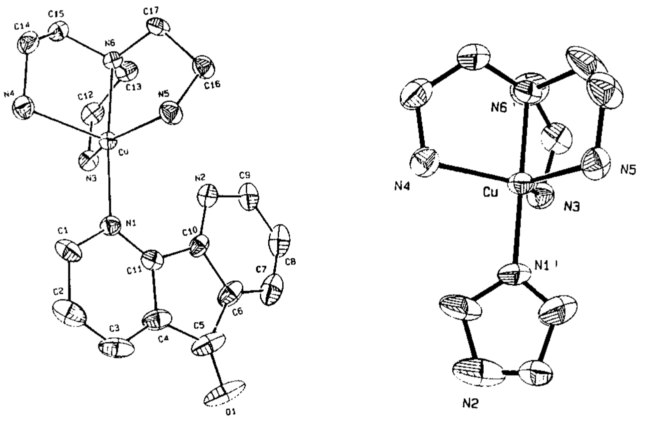
1		**2**	
N(1)−Cu−N(3)	93.72	N(1)−Cu−N(3)	95.4(3)
N(1)−Cu−N(6)	174.52	N(1)−Cu−N(6)	179.1(3)
N(1)−Cu−N(5)	94.02	N(1)−Cu−N(5)	94.9(3)
N(1)−Cu−N(4)	102.52	N(1)−Cu−N(4)	95.8(3)
N(3)−Cu−N(6)	84.82	N(3)−Cu−N(6)	85.3(3)
N(3)−Cu−N(5)	149.02	N(3)−Cu−N(5)	120.0(3)
N(3)−Cu−N(4)	103.12	N(3)−Cu−N(4)	118.5(3)
N(6)−Cu−N(5)	84.72	N(6)−Cu−N(5)	84.3(3)
N(6)−Cu−N(4)	83.02	N(6)−Cu−N(4)	84.3(3)
N(5)−Cu−N(4)	104.42	N(5)−Cu−N(4)	118.9(3)

[a] Value calculated.

Crystal Structure. The coordinates and the thermal parameters of the non-hydrogen atoms of complex **1** are listed in Table 2. As a comparison, the main bond distances and bond angles and labeled views of the molecular cation structures of complexes **1** and **2** are shown in Table 3 and Figure 4, respectively. The copper(II) ion in complex **1** is coordinated by four nitrogen atoms from tren and one nitrogen atom from dzf to form a distorted square-based pyramidal geometry (the geometric τ value is 0.42[14]) with the sixth potentially bonding position occupied by N(2) 2.995 Å from copper(II), a distance that is considered a weak semicoordination. The copper(II) ion in complex **2** is coordinated by four nitrogen atoms from tren and one nitrogen atom from ImH to form a trigonal bipyramidal geometry (the τ value is 1.0). It can be seen that the structure of complex **1** is in agreement with its electronic reflectance and ESR spectra and very different from those of complex **2** and the general [Cu(tren)L]$^{2+}$ complexes (the τ value is often close to 1.0[14]). It is very important to note that dzf coordinates to the copper(II) ion as a very asymmetric bidentate ligand. This structure is very rare, and to our knowledge, it is the first example of a metal complex with an asymmetric bidentate phenanthroline derivative. The strong complexation of dzf and the relative rigid tripodal construction of tren, which often forces five-coordination on a copper(II) ion,[17] make this unusual coordinated structure quite stable. The best evidence for the weak coordination of Cu−N(2) is the unusual trigonally distorted square-based pyramidal stereochemistry, which can be thought as (4 + 1 + 1′) six-coordinate. The atoms N(1), N(3), N(5), and N(6) form the equatorial plane, and the atoms N(4) and N(2) are in the axial positions. This can be supported by the bond length data, which show that the Cu−N(4) is 0.2 Å longer than the other four Cu−N bonds. In fact, the axial bonds of most six-coordinate Cu(II) complexes are often elongated due to the Jahn−Teller effect. Because of the relatively rigid geometry of tren, the Cu−N(4) bond is shorter than the usual axial Cu−N bond of an elongated octahedron, and this may be one of the reasons that another axial Cu−N

---

(17) Laskowski, E. J.; Duggen, D. M.; Henderson, D. N. *Inorg. Chem.* **1975**, *4*, 2449.



$[(C_6H_{18}]N_4)Cu(C_{11}H_6N_2O)]^{2+}$ **1** $[(C6]H_{18}N_4])Cu(C_3H_4N_2)]^{2+}$ **2**

Figure 4. Molecular geometry of the cations of complexes **1** and **2**: $[(C_6H_{18}N_4)Cu(C_{11}H_6N_2O)]^{2+}$, **1**; $[(C_6H_{18}N_4)Cu(C_3H_4N_2)]^{2+}$, **2**.

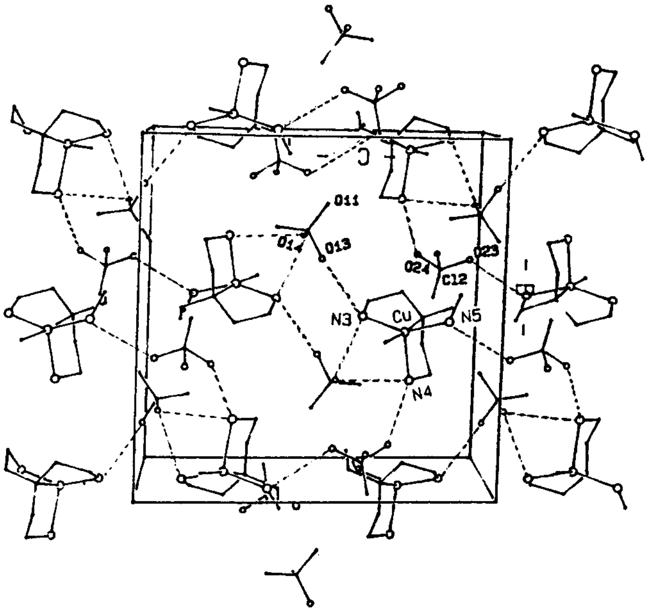


Figure 5. View of hydrogen-bonded layered structure of complex **1** parallel to the $b-c$ plane with hydrogen bonds displayed as dotted lines. The dzf group of the cations has been replaced by a single atom.

Table 4. Geometry of the Hydrogen Bonds of Complex **1**[a]

N(3)−O(13)	3.055(7)	N(3)−H(7)···(13)	135.72
N(3)−O(14)[a]	3.090(8)	N(3)−H(8)···(14)[a]	161.15
N(4)−O(21)	3.123(8)	N(4)−H(14)···(21)	136.19
N(4)−O(14)[a]	3.229(8)	N(4)−H(13)···(14)a	161.15
N(5)−O(23)[b]	3.131	N(5)−H(19)···(23)b	166.30
N(5)−O(24)[c]	3.111	N(5)−H(20)···(24)[c]	139.26

[a] Symmetry codes: (a) $1 - x, 1 - y, 1 - z$; (b) $x, {}^1/_2 - y, {}^1/_2 + z$; (c) $2 - x, {}^1/_2 + y, {}^3/_2 - z$.

bond [Cu−N(2)] is quite a bit longer than the usual axial Cu−N bond.[12,18] In the crystal (Figure 5), the $[Cu(tren)(dzf)]^{2+}$ cation and one of the perchlorate anions are interlinked by an intramolecular hydrogen bond N(3)−H(7)···(13) and intermolecular hydrogen bonds[19,20] N(4)−H(13)···(14)^a and N(3)−H(8)···(14)^a (Table 4) to form a formal dimer unit with the symmetric center of ($^1/_2$, $^1/_2$, $^1/_2$). Each dimer is connected with four such dimers having centers of ($^1/_2$, 1, 0), ($^1/_2$, 0, 1), ($^1/_2$, −1, 0), and ($^1/_2$, 0, −1) in the plane of $x = {}^1/_2$ through another perchlorate anion using the intramolecular hydrogen bond N(4)−H(14)···(21) and the intermolecular hydrogen bond N(5)−H(19)···(23)^b to form a layered network structure. All layers are parallel to the $b-c$ plane. The perchlorate with Cl(2) lies between adjacent layers, connecting the two adjacent layers through the hydrogen bond N(5)−H(5)···(24)^c to form a three-dimensional network structure.

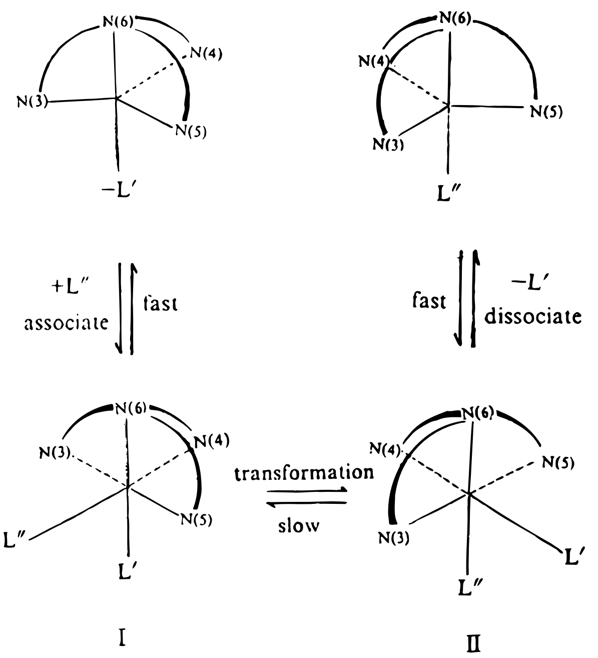


Figure 6. The substitution mechanism of $[Cu(tren)L]^{2+}$.

Mechanism of the Ligand-Substitution Reaction of $[Cu(tren)L]^{2+}$. It is interesting to speculate on the significance of the structure of complex **1** to the model of the associative complex in the associative mechanism of ligand-exchange and ligand-substitution reactions of $[Cu(tren)L]^{2+}$.[1,2] The asymmetric N atoms of dzf could be considered as different ligands L′ and L″ in the associative complex . If the shorter bond Cu−N(1) is considered as the bond of substituted ligand L′ and the longer one Cu−N(2) as the bond of substitutive ligand L″, we can see an associative complex (complex **I**) in the beginning of the ligand-substitution reaction. If the longer bond Cu−N(2) is considered as the bond of substituted ligand L′ and the shorter one Cu−N(1) as the bond of substitutive ligand L″, we can see another associative complex (complex **II**) at the end of the ligand-substitution reaction. In this case, the substitution mechanism could be tentatively explained in Figure 6. In the first step, the substitutive ligand L″ coordinates weakly to Cu(II) (in our complex the bond is about 3.0 Å) and forms a distorted (4 + 1 + 1′) six-coordinated associative complex **I**. This process is faster compared with the following process. In the reaction, the associative complex **I** may be distorted; i.e, the shorter Cu−N bond becomes longer and the longer Cu−N bond becomes shorter, due to the molecular vibration , the solvent effect, and the coordination ability of the substitutive ligand L″. This transformation reaction then gives another associative complex **II**. The only difference between complexes **I** and **II** is that bonds Cu−L″ and Cu−L′ are exchanged. After the substituted ligand L′ in the associative complex **II** is dissociated, the substitution reaction is finished. The dissociative process may be faster, just as the associative process. The axial position of the substitutive ligand L″ and the equatorial character of the substituted ligand L′ in the associative complex make the transformation process rather slow due to the Jahn−Teller effect. This may be the exact reason for the unusual

---

(18) Dister, T.; Vagham, P. A. *Inorg. Chem.* **1967**, *6*, 126.
(19) Eigenbrot, C. W.; Raymond, K. N., Jr. *Inorg. Chem.* **1982**, *21*, 2876.
(20) Duggen, D. M.; Junst, R. G.; Mann, K. R.; Stucky, G. D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3443.

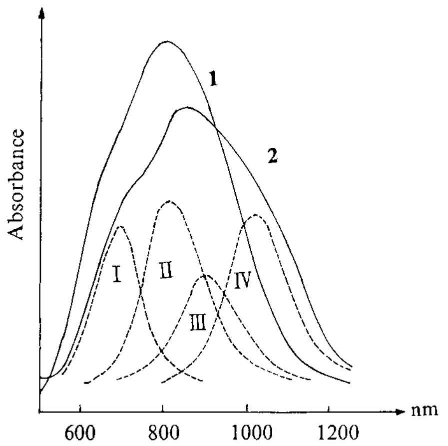


Figure 7. Electronic spectra of complexes **1** and **2** in absolute DMF. The dotted lines represent an approximate Gaussian analysis of the spectrum of **1**.

Table 5. Electronic Spectral Data for Complexes **1** and **2**

	bands, cm^{-1} (ϵ_{max})[a]	
complex **1**		
in dmf	13 800 (130)	11 800 (164)
Gaussian analysis	I, 14 700; II, 12 400	III, 11 000; IV, 9770
reflectance of solid	16 100	12300
complex **2**		
in DMF	14 500 (151)	12 300 (201)
reflectance of solid	15 100	12 300

[a] ϵ_{max} in units of M^{-1} cm^{-1}.

slow rate in the ligand-exchange and ligand-substitution reactions of the $[Cu(tren)L]^{2+}$ system.

Evidence for the Mechanism: Electronic and Variable-Temperature ESR Spectra in Solution. Figure 7 shows the electronic spectra of complexes **1** and **2** in DMF at room temperature. The spectral data are summarized in Table 5. It is obvious that the electronic spectrum of complex **1** is quite different from that of solid state, which indicates that the stereochemistry of complex **1** has changed in the solution. Due to the sparing solubility and some dissociation (after heating) in water, we have not recorded the electronic spectrum of complex **1** in water. Variable-solvent spectra show that the electronic spectrum of complex **1** shows no visible change in different organic solvents, such as acetonitrile and DMF. It is thus validated that the equilibrium

$$\mathrm{Cu(tren)dzf} + \mathrm{S} \rightleftarrows \mathrm{Cu(tren)S} + \mathrm{dzf}$$

(where S represents solvent) does not exist in the solution. Considering the asymmetric coordination of the dzf ligand, the different stereochemistries in the solid state and in solution may be due to the transformation of the two coordinated nitrogen atoms of the dzf in solution. If the sums of Gaussian-shaped bands corresponding to the various types of transition are reproduced with good accuracy, four bands can be observed.[21,22] Bands I and III are quite similar to those of the solid state, which can be assigned as d_{xy}, $d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ of the square-based pyramidal complex, while bands II and IV are quite similar to those of the solid state spectrum of the *cis* distorted-octahedral Cu(II) complex[23] in which two nitrogen atoms of the dzf coordinate to the Cu(II) ion in the dimensional fluxional model and can be assigned as d_{yz}, $d_{x^2-y^2}$, $d_{xz} \rightarrow d_{z^2}$ and $d_{xy} \rightarrow d_{z^2}$. These results may demonstrate that square pyramidal stereochemistries exist which have the lowest potential wells I and II (Figure 8) but also that there are *cis* distorted-octahedral stereochemistries with different Cu−N(1) and Cu−N(2) bond distances which have higher potential energies than wells I and II. The population of the different stereochemistries may be controlled by the temperature and the potential energy of the chromophore CuN_4NN'.

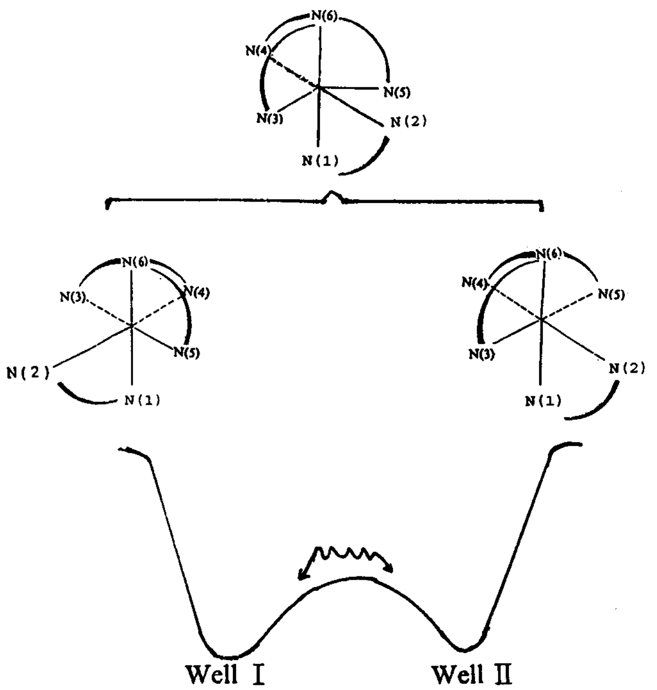


Figure 8. The dimensional fluxional disorder model of the pseudo *cis* distorted-octahedral geometry with a qualitative potential Wells diagram.

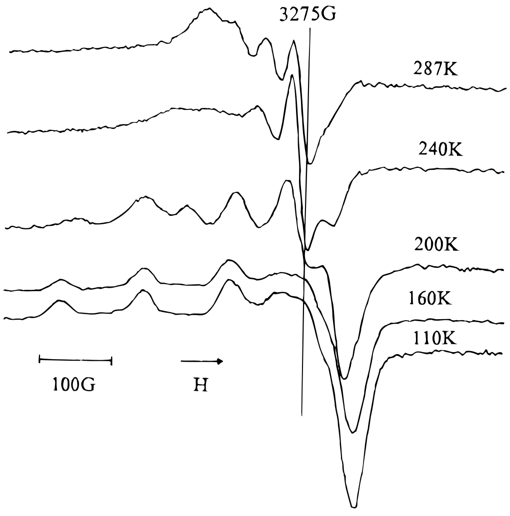


Figure 9. Variable-temperature ESR spectra of complex **1** in absolute DMF.

The variable-temperature ESR spectra (Figure 9) in DMF solution show that the solution coordination of complex **1** is significantly temperature-dependent. The ESR spectral data are summarized in Table 6. The $d_{x^2-y^2}$ ground state in the frozen solution (200 K, 160 K, and 110 K) shows a dominantly tetragonal component in the solution stereochemistries. The

---

(21) All bands in the spectra are assumed to have a Gaussian shape, with the relevant band parameters defined by $f(\nu) = \epsilon_{max} \exp(-[(\nu - \nu_{max})/0.060(\nu_{1/2})]^2)$. The actual spectrum of every single species can be reproduced in the spectra range of interest as a sum of individual bands to a precision of ±5%.

(22) Bignozzi, C. A.; Paradisi, C.; Roffia, S. Scandola, F. *Inorg. Chem.* **1988**, *27*, 408−414.

(23) Hathaway, B. J.; Procter, I. M.; Slade, R. C; Tomlinson, A. A. G. *J. Chem. Soc. A* **1969**, 2219−2224.

Table 6. ESR Spectral Data for Complexes **1** and **2** in Absolute DMF[a]

temp, K	$g_{\|}$	$A\|$	$g_{\perp}$	$A_{\perp}$	g_{iso}
Complex **1**					
287					2.135
240					2.099
200	2.228	18.67	2.042	10.00	2.096
160	2.226	17.94	2.034	11.87	2.094
110	2.226	17.57	2.024	14.42	2.092
Complex **2**					
110	2.006	12.20	2.180	11.46	2.122

[a] *A* values are $\times 10^3$ cm^{-1}.

ESR spectra in solution (287 K and 240 K) show the isotropic spectra of the Cu(II) ion. From the *g* values of the solution stereochemistries which are larger than those of the frozen state, we can suggest that there exist other stereochemistries with larger *g* values except the square-based pyramidal stereochemistry. Considering the asymmetric coordination of dzf and the electronic spectrum in solution, the stereochemistry with the larger *g* value is best referred to as pseudo *cis* distorted-octahedral stereochemistry in which the two nitrogen atoms of dzf coordinate to the copper(II) ion in the dimensional fluxional model .[24,25]

Thus, the electronic and variable-temperature ESR spectra suggest that the structure of complex **1** in solution is not a genuine stereochemistry of the copper(II) ion but arises as a consequence of the pseudo dynamic Jahn–Teller effect[26] generating a dimensional fluxional model involving a static distorted square-based pyramidal $(4 + 1 + 1')$ structure, with nearly equal thermal populations of the two lowest potential wells I and II corresponding to the square-based pyramidal geometries and higher potential barrier corresponding to the *cis* distorted-octahedral stereochemistries with different bond distance ratios of Cu–N(1):Cu–N(2) from 0.677 to 1.478. The highest potential barrier corresponds to the *cis* distorted-octahedral stereochemistry with two equal Cu–N(1) and Cu–N(2) bond distances.

Acknowledgment. This work was supported by a major research project grant from the State Science and Technology Commission and National Natural Science Foundation of China.

Supporting Information Available: Tables of crystallographic experimental data, all bond lengths and angles, all atoms introduced at calculated coordinates, anisotropic thermal parameters as U_{ij}'s, and least-squares planes and deviations therefrom for [Cu(tren)dzf](ClO$_4$)$_2$ (Tables S1–S5) (5 pages). Ordering information is given on any current masthead page.

IC950362L

---

(24) Fitzgerald, W.; Murphy, B.; Tyagi, S.; Walsh, B.; Walsh, B.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1981**, 2271.

(25) Hathaway, B. J.; Duggan, M.; Murphy, A.; Mullane, J.; Power, C.; Walsh, A.; Walsh, B. *Cood. Chem. Rev.* **1981**, *36*, 267.

(26) Bersuker, I. B. *Coord. Chem. Rev.* **1975**, *14*, 375.