Crystal Structure of a Copper(II) Complex of *N*-Anthracen-9-ylmethyl-*N,N',N'*-tris-pyridin-2-ylmethyl-ethane-1,2-diamine

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The crystal structure of a five-coordinate copper(II) complex of *N*-anthracen-9-ylmethyl-*N,N',N'*-tris-pyridin-2-ylmethyl-ethane-1,2-diamine (AT5N) has been determined by X-ray diffraction. In this complex, the copper atom has a distorted square-pyramidal geometry. An intermolecular aromatic-aromatic face-to-face interaction was also observed in the crystals.

(Received April 8, 2004; Accepted May 26, 2004; Published on Web July 30, 2004)

The physicochemical properties, stereochemistry and electronic states of copper(II) complexes with polyamines have been extensively studied in attempts to develop agents to cleave DNA.¹ Our research has focused on the synthesis of metal complexes capable of cleaving DNA strand specifically.

We prepared a pentadentate ligand, AT5N, based on 1,2-ethanediamine attaching three pyridylmethyl groups and an anthrylmethyl group; the latter was chosen as an intercalator for DNA-binding. An X-ray crystal diffraction study of a copper(II) complex of AT5N ([Cu(AT5N)](ClO₄)₂, **1**, Fig. 1) was carried out in order to clarify the coordination mode. We report here on the X-ray crystal structure of **1**.

The ligand AT5N was prepared according to a procedure reported by Bernal *et al.*² using *N*-anthracen-9-ylmethyl-ethane-1,2-diamine and 3 equimolar amounts of 2-cholomethylpyridine. A copper(II) complex **1** was prepared in 70% yield by reacting AT5N with an equimolar amount of Cu(ClO₄)₂·6H₂O in methanol for 15 h at room temperature. The precipitated powder was collected and dried under vacuum. Recrystallization from methanol gave single crystals of **1** suitable for an X-ray diffraction study. Data collections were performed at 293 K with graphite-monochromated Mo *K*_α radiation on a Rigaku AFC7R diffractometer ($\lambda = 0.71069$ Å). The structure was solved by the heavy atom Patterson method, expanded using Fourier techniques. All non-hydrogen atoms

were refined with anisotropically by full-matrix least-squares based on *F*². All hydrogen atoms were located by geometrical calculations and were not refined. All calculations were performed using the teXsan crystallographic software package.³ The crystal and experimental data are given in Table 1. The ($\Delta\rho$)_{max} value of 0.96 eÅ⁻³ is rather high; the residual peaks were observed around a perchlorate ion (Cl(2)O₄⁻). The atomic coordinates and temperature factors for non-H atoms are given in Table 2, and selected bond lengths and bond angles are listed in Table 3. An ORTEP drawing of the cation of **1** with the atomic labeling scheme is shown in Fig. 2. The crystal structure of **1** consists of a discrete [Cu(AT5N)]²⁺ cation and two perchlorate anions. The copper atom is coordinated to tertiary amine nitrogens (N1 and N2) and the two pyridines (N3 and N5) from AT5N in the equatorial plane and to the pyridine nitrogen (N4) in the axial position. The geometry around the copper atom is described as distorted square-pyramidal with a

Fig. 1 Chemical structure of [Cu(AT5N)](ClO₄)₂, **1**.

Table 1 Crystal and experimental data

Formula: C ₃₅ H ₃₃ N ₅ O ₈ Cl ₂ Cu	
Formula weight = 786.13	
Crystal system: triclinic	
Space group: <i>P</i> 1	<i>Z</i> = 2
<i>a</i> = 9.013(2) Å	α = 96.93(5)°
<i>b</i> = 10.465(3)	β = 93.49(5)
<i>c</i> = 18.71(3)	γ = 105.21(2)
<i>V</i> = 1682(2) Å ³	
<i>D</i> _{calc} = 1.552 g/cm ³	
No. measured reflections = 8190 (unique: 8186 (<i>R</i> _{int} = 0.032))	
No. reflection used in refinement of reflections = 2992 (<i>I</i> > 2σ(<i>I</i>), 2θ < 54.99°)	
2θ _{max} = 55° with Mo <i>K</i> _α	
<i>R</i> 1 = 0.080	
<i>R</i> _w = 0.080	
Goodness-of-fit = 1.42	
(Δσ) _{max} = 0.001	
(Δρ) _{max} = 0.96 eÅ ⁻³	
(Δρ) _{min} = -0.51 eÅ ⁻³	
Measurement: Rigaku AFC7R	
Program system: Rigaku teXsan	
Structure determination: DIRDIF94 PATTY	
Refinement: full-matrix least-squares	

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Table 2 Atomic coordinates and equivalent isotropic thermal parameters (B_{eq})

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Cu(1)	0.2078(1)	0.6004(1)	0.83091(5)	3.00(2)
Cl(1)	0.2334(3)	0.2350(3)	0.0669(1)	5.29(6)
Cl(2)	0.3868(3)	0.1395(3)	0.6942(1)	5.55(6)
O(1)	0.1161(8)	0.2929(8)	0.0505(5)	9.5(2)
O(2)	0.303(1)	0.196(1)	0.0105(4)	12.2(3)
O(3)	0.2044(9)	0.1488(7)	0.1177(4)	9.1(2)
O(4)	0.353(1)	0.346(1)	0.1048(7)	16.7(4)
O(5)	0.240(1)	0.159(1)	0.6880(6)	18.1(5)
O(6)	0.383(1)	0.0127(8)	0.6619(4)	12.8(3)
O(7)	0.419(1)	0.1544(10)	0.7644(4)	15.0(3)
O(8)	0.470(1)	0.2372(8)	0.6584(5)	12.8(3)
N(1)	0.0313(6)	0.5795(6)	0.7480(3)	2.6(1)
N(2)	0.2543(7)	0.7986(6)	0.8289(3)	2.8(1)
N(3)	0.2637(7)	0.6591(6)	0.9381(3)	3.2(1)
N(4)	0.4055(7)	0.6226(6)	0.7700(3)	3.3(2)
N(5)	0.1097(8)	0.4065(6)	0.8278(3)	3.6(2)
C(1)	0.0032(9)	0.7131(7)	0.7576(4)	3.0(2)
C(2)	0.1543(9)	0.8204(7)	0.7672(4)	3.2(2)
C(3)	0.2252(9)	0.8608(8)	0.9006(4)	3.6(2)
C(4)	0.2760(8)	0.7902(8)	0.9578(4)	3.0(2)
C(6)	0.374(1)	0.7831(9)	1.0772(4)	4.6(2)
C(7)	0.356(1)	0.6490(9)	1.0587(4)	4.8(2)
C(8)	0.3014(10)	0.5908(9)	0.9892(4)	4.3(2)
C(9)	0.4207(9)	0.8480(8)	0.8161(4)	3.4(2)
C(10)	0.4663(9)	0.7498(8)	0.7632(4)	3.4(2)
C(11)	0.5696(9)	0.7897(9)	0.7142(4)	3.6(2)
C(12)	0.6140(9)	0.6948(10)	0.6704(4)	4.5(2)
C(13)	0.5581(9)	0.5619(9)	0.6791(4)	4.3(2)
C(14)	0.4517(9)	0.5295(8)	0.7279(4)	3.8(2)
C(15)	-0.0964(9)	0.4743(8)	0.7705(4)	3.4(2)
C(16)	-0.0379(10)	0.3668(8)	0.7973(4)	3.6(2)
C(17)	-0.128(1)	0.2368(10)	0.7957(5)	5.3(2)
C(18)	-0.068(1)	0.1474(10)	0.8262(5)	6.5(3)
C(19)	0.085(1)	0.1857(9)	0.8565(5)	6.0(3)
C(20)	0.170(1)	0.3164(9)	0.8560(5)	5.4(2)
C(21)	0.0771(8)	0.5382(7)	0.6748(4)	2.9(2)
C(22)	-0.0505(8)	0.4994(8)	0.6127(4)	2.8(2)
C(23)	-0.1302(9)	0.3625(8)	0.5925(4)	3.7(2)
C(24)	-0.0927(9)	0.2556(9)	0.6229(4)	4.4(2)
C(25)	-0.174(1)	0.1235(9)	0.6014(5)	5.6(3)
C(26)	-0.298(1)	0.092(1)	0.5453(6)	6.7(3)
C(27)	-0.337(1)	0.189(1)	0.5158(6)	6.2(3)
C(28)	-0.2574(9)	0.3264(9)	0.5365(4)	4.1(2)
C(29)	-0.2938(9)	0.425(1)	0.5029(4)	4.5(2)
C(30)	-0.2166(9)	0.5566(9)	0.5185(4)	3.7(2)
C(31)	-0.2535(10)	0.658(1)	0.4815(4)	4.8(2)
C(32)	-0.171(1)	0.786(1)	0.4942(5)	5.6(3)
C(33)	-0.0385(10)	0.8236(8)	0.5466(4)	4.0(2)
C(34)	-0.0021(9)	0.7320(8)	0.5835(4)	3.5(2)
C(35)	-0.0855(8)	0.5936(8)	0.5731(4)	3.0(2)

$$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$$

Table 3 Selected bond distances (Å) and angles(°)

Cu(1)-N(1)	2.102(6)	Cu(1)-N(2)	2.011(6)
Cu(1)-N(3)	2.018(6)	Cu(1)-N(4)	2.150(6)
Cu(1)-N(5)	1.981(6)		
N(1)-Cu(1)-N(2)	86.6(2)	N(1)-Cu(1)-N(3)	142.2(2)
N(1)-Cu(1)-N(4)	100.8(2)	N(1)-Cu(1)-N(5)	82.1(2)
N(2)-Cu(1)-N(3)	82.6(2)	N(2)-Cu(1)-N(4)	82.1(2)
N(2)-Cu(1)-N(5)	166.1(3)	N(3)-Cu(1)-N(4)	113.4(2)
N(3)-Cu(1)-N(5)	101.5(3)	N(4)-Cu(1)-N(5)	107.9(3)

Fig. 2 ORTEP drawing of the cation part of **1** with thermal ellipsoids drawn at the 50% probability level. Fig. 3 Crystal packing diagram of **1**.

trigonal component, as revealed by the geometrical parameter τ of 0.40 [$\tau = (\beta - \alpha)/60$, where $\alpha = \text{N}(2)\text{-Cu}(1)\text{-N}(5) = 166.1(3)^\circ$ and $\beta = \text{N}(1)\text{-Cu}(1)\text{-N}(3) = 142.2(2)^\circ$; for perfect square-pyramidal and trigonal bipyramidal geometries the values of τ are zero and unity, respectively]. The copper center is displaced by 0.434(3) Å out of the mean plane, defined by the N(1), N(2), N(3), and N(5) atoms towards the apical nitrogen atom N(4). The Cu-N(1) and -N(2) bond distances are in the normal range for the Cu-N(amine) distances (1.99 – 2.08 Å).⁴ The equatorial Cu-N(3) and -N(5) bond distances are 2.018(6) and 1.981(6) Å, respectively, which are slightly shorter than those of five-coordinate copper(II)-pyridine complexes (average 2.070(3) Å).⁵ The apical Cu-N(4) bond distance of 2.150(6) Å reflects a weak apical interaction due to the Jahn-Teller effect. The anthrylmethyl group takes a pseudo-axial orientation with respect to the five-membered chelate ring formed by Cu(1)-N(1)-C(1)-C(2)-N(2), and situates in a region far from the metal center to avoid any steric repulsion between the anthrylmethyl and pyridylmethyl groups. The five-membered ring of the ethanediamine segment adopts a *gauche* conformation with a torsion angle at a central C(1)-C(2) bond of $-55.3(7)^\circ$.

The crystal packing is shown in Fig. 3. Complex **1** exhibits face-to-face intermolecular stacking between the complex cation along the *a* axis; the interatomic distances found for C(24)···C(32)ⁱ, C(24)···C(33)ⁱ, C(25)···C(33)ⁱ, C(26)···C(33)ⁱ, C(28)···C(34)ⁱ are 3.40(1), 3.53(1), 3.48(1), 3.54(1), and 3.46(1) Å; symmetry code: $-x, -y + 1, -z + 1$.

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