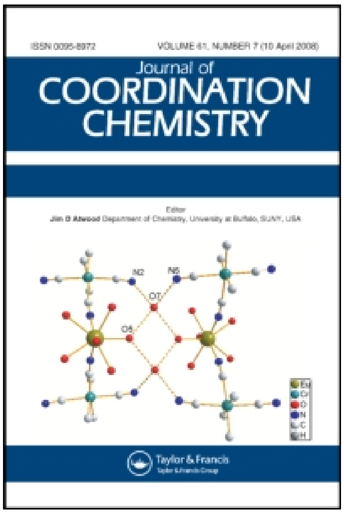

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, Crystal Structure and Properties of a 4,4'-Bipyridine Bridged Trigonal-Bipyramidal Copper Homobinuclear Complex with Tris(2-Aminoethyl)amine

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To cite this Article Xu, Xing-You , Zheng, Tao , Ma, Wei-Xing , Zhang, Ming-Xing , Liu, Qing-Liang , Grguric, Sanja , Dinovic, Vesna , Kaluderovic, Goran and Sabo, Tibor(2002) 'Synthesis, Crystal Structure and Properties of a 4,4'-Bipyridine Bridged Trigonal-Bipyramidal Copper Homobinuclear Complex with Tris(2-Aminoethyl)amine', Journal of Coordination Chemistry, 55: 6, 711 — 716

To link to this Article: DOI: 10.1080/00958970290027589
URL: http://dx.doi.org/10.1080/00958970290027589

J. Coord. Chem., 2002, Vol. 55(6), pp. 711–716

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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF A 4,4′-BIPYRIDINE BRIDGED TRIGONAL-BIPYRAMIDAL COPPER HOMOBINUCLEAR COMPLEX WITH TRIS(2-AMINOETHYL)AMINE

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(Received 18 August 2000; In final form 20 July 2001)

The synthesis of the binuclear complex [(tren)Cu(4,4′-bipy)Cu(tren)] $(ClO_4)_4$ where tren = tris(2-aminoethyl) amine and 4,4′-bipy = 4,4′-bipyridine, is described. Single-crystal X-ray diffraction study of the homobinuclear complex shows that two copper(II) ions are bridged by 4,4′-bipyridine and each copper(II) ion is trigonal-bipyramidally coordinated, with tren occupying four sites [Cu–N = 2.030(2), 2.047(2), 2.078(2), and 2.119(2) Å respectively] and a bridging 4,4′-bipyridine in the apical position. The Cu–Cu distance is 11.11 Å. In variable-temperature ESR spectra, the presence of hyperfine structure suggest that some interaction exists between the two copper(II) ions. Temperature-dependent susceptibility studies indicate that it is a weak ferromagnetic interaction with $2J = 1.23\,cm^{-1}$.

Keywords: Copper(II); Amines; Bipyridyl; Crystal structure; Homobinuclear complex

INTRODUCTION

4,4′-Bipyridine is a very promising ligand in the syntheses and structures of coordination polymers to bridge metal centres to form one-, two-, and three dimensionally connected polymers [1,2]. Syntheses and structural chemistry of one- or two-dimensional polymer systems can provide insight into the role of specific solvents and counter ion effects on the polymerization process [3]. To the best of our knowledge, however, it has been found that in almost all cases, the metal centres connected by 4,4′-bipyridine are four- or six-coordinated and the complexes are chain or layer-type polymers. We report here new five-coordinate copper(II) dimers bridged by 4,4′-bipyridine in which

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ISSN 0095-8972 print: ISSN 1029-0389 online © 2002 Taylor & Francis Ltd
DOI: 10.1080/00958970290027589

each copper(II) ion is trigonal-bipyramidally coordinated by five nitrogen atoms with approximately D_{3h} symmetry. Because the fundamental importance of long-range magnetic interactions in these kinds of complexes [4], we have studied the magnetic properties of the title complex by temperature-dependent ESR and magnetic susceptibility measurements.

EXPERIMENTAL

All reagents were of analytical grade. The compound tris(2-aminoethyl)amine (tren) was prepared according to the literature [5].

[Cu(tren)](ClO_4)$_2$ (1)

A solution containing $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 0.1 mmol) in 10 cm^3 of methanol was added in portions to 15 cm^3 of a methanol solution containing tren (0.0292 g, 0.2 mmol). After stirring for one hour, the resulting blue precipitate was filtered off, washed and dried in vacuum.

[(tren)Cu(4,4′-bpy)Cu(tren)](ClO_4)$_4$ (2)

To a solution containing **1** (0.163 g, 0.4 mmol) in 45 cm^3 of methanol was added a methanol solution of 4,4′-bipyridine dihydrate (0.038 g, 0.2 mmol). After reflux for 1 h, the solution was filtered and the filtrate allowed to evaporate slowly. After a few days, blue single crystals were obtained. Yield: *ca.* 50%. *Anal.* calc. for $C_{22}H_{44}Cl_4Cu_2N_{10}O_{16}$(%): C, 27.15; H, 4.52; N, 14.38; Cu, 13.04. Found: C, 27.84; H, 4.52; N, 14.42; Cu, 12.88.

Caution! Perchlorate salts of compounds containing organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with caution. These complexes have, so far, been found to be safe when used in small quantities.

Physical Measurements

Electronic spectra were measured on a Shimadzu UV-240 spectrophotometer and IR spectra were measured using KBr discs on a Nicolet FT-IR 410 spectrophotometer. The molar conductivity measurement was carried out using a BDS-11A conductometer (Jiangsu, China) with solution concentration of $\sim 10^{-4}$ mol dm^{-3} in acetonitrile. TG-DTA curves were recorded on a Rigaku PIC 10A differential chemical analyzer in a nitrogen atmosphere. X-band ESR spectra of **2** in CH_3CN solution as a function of temperature were recorded on a Bruker ER 200D-SRC spectrometer. Variable-temperature magnetic susceptibility data were obtained with a vibrating-sample magnetometer.

X-ray Crystallography

Table I lists relevant crystallographic data. A single crystal of dimensions 0.30 × 0.26 × 0.20 mm was mounted on a glass fibre. Diffraction measurements were made on a SIMENS P_4 four-circle diffractometer using graphite-monochromated MoK$_a$

TABLE I Crystal and refinement data for complex **2**

Formula	$C_{22}H_{44}Cl_4Cu_2N_{10}O_{16}$
Fw	973.55
Temp (K)	294 (2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a(Å)	9.637 (2)
b(Å)	15.560 (3)
c(Å)	12.945 (3)
β (°)	96.50 (3)
V (Å^3)	1928.7 (7)
Z	2
Dc (g cm^{-3})	1.676

TABLE II Atomic coordinates (10×10^4) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for the complex. $U_{(eq)}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	Y/b	z/c	$U_{(eq)}$
Cu(1)	−3187 (1)	1511 (1)	2823 (1)	65 (1)
Cl(1)	−4240 (1)	928 (1)	7725 (1)	95 (1)
O(1)	−3106 (3)	451 (2)	7502 (2)	212 (1)
O(2)	−3874 (4)	1735 (2)	7798 (4)	240 (2)
O(3)	−5353 (2)	847 (2)	6955 (2)	129 (1)
O(4)	−4707 (3)	667 (3)	8661 (2)	174 (1)
Cl(2)	909 (1)	1563 (1)	5280 (1)	87 (1)
O(5)	2156 (3)	1995 (2)	5535 (2)	175 (1)
O(6)	−109 (3)	2191 (2)	5094 (2)	180 (1)
O(7)	986 (5)	1040 (2)	4462 (2)	221 (2)
O(8)	705 (4)	1080 (2)	6151 (2)	174 (1)
N(1)	−4327 (2)	2061 (1)	3872 (1)	78 (1)
N(2)	−5144 (3)	1492 (2)	1894 (2)	95 (1)
N(3)	−2060 (2)	2629 (1)	2957 (2)	81 (1)
N(4)	−2766 (2)	567 (1)	3950 (1)	81 (1)
N(5)	−2030 (2)	964 (1)	1790 (1)	69 (1)
C(1)	−5688 (3)	2301 (3)	3351 (3)	147 (2)
C(2)	−6215 (3)	1789 (3)	2491 (3)	126 (1)
C(3)	−3479 (4)	2800 (2)	4370 (3)	127 (1)
C(4)	−2712 (3)	3238 (2)	3606 (2)	93 (1)
C(5)	−4447 (4)	1444 (2)	4720 (3)	139 (1)
C(6)	−3337 (3)	835 (2)	4898 (2)	100 (1)
C(7)	−2486 (3)	892 (2)	787 (2)	99 (1)
C(8)	−1737 (3)	529 (2)	80 (2)	98 (1)
C(9)	−428 (2)	203 (1)	370 (1)	61 (1)
C(10)	49 (3)	293 (2)	1423 (2)	91 (1)
C(11)	−764 (3)	656 (2)	2089 (2)	91 (1)

($\lambda = 0.71073$ Å) radiation. Crystal data were collected using a $2\theta \sim \omega$ scan mode with 2θ ranging from 4.10° to 51.12°. A total of 3096 independent reflections collected in the range $-11 \le h \le 11$, $0 \le k \le 18$, $0 \le l \le 15$ were used in the structure determination and refinement after Lp and semi-empirical absorption corrections were applied. The structure was solved by direct methods and refined by full-matrix least-square techniques. All non-hydrogen atoms were located by difference Fourier maps and their positions refined anisotropically. All hydrogen atoms were refined isotropically. The final cycle of least squares gave $R = 0.0614$ and $wR2 = 0.1883$, for data with $I > 2\delta(I)$.

Final coordinates for the non-hydrogen atoms are given in Table II.

RESULTS AND DISCUSSION

Description of Structure

The molecular structure of **2** is shown in Fig. 1 and and selected bond lengths and angles are listed in Table III. The complex consists of a [(tren)Cu(4,4′-bipy)Cu(tren)]$^{4+}$ cation and four ClO_4^- anions. In the cation, two Cu(II) ions are bridged by 4,4′-bipyridine, forming a centro-symmetrical homobinuclear complex. Coordination around each metal ion is described as a rather regular trigonal bipyramid, in which the three primary amine nitrogen atoms, N(2), N(3), N(4) occupy equatorial positions and the tertiary amine nitrogen atom, N(1), the apical position. The structural index parameter, τ, of five-coordinate polyhedron from a perfectly tetragonal ($\tau = 0$) to a perfectly trigonal-bipyramid ($\tau = 1$) has been calculated according to the literature method [6]. In **2**, $\tau = 0.999$, indicating that the geometry is quite regular Cu(1) is displaced by 0.2187 Å from the mean N(2)–N(3)–N(4) plane towards the bridging group and the distance between Cu(1) and Cu(2) is 11.110 Å. Cu–N(tren) is 2.030 Å, whereas the Cu–N(amino) lengths are 2.119, 2.047 and 2.078 Å Cu–N (tertiary nitrogen) is shorter than Cu–N (amino) as observed in previous literature [7]. In **2**, the shortest Cu–N bond length is the distance Cu–N(5), 2.023 Å. The two pyridine rings of the

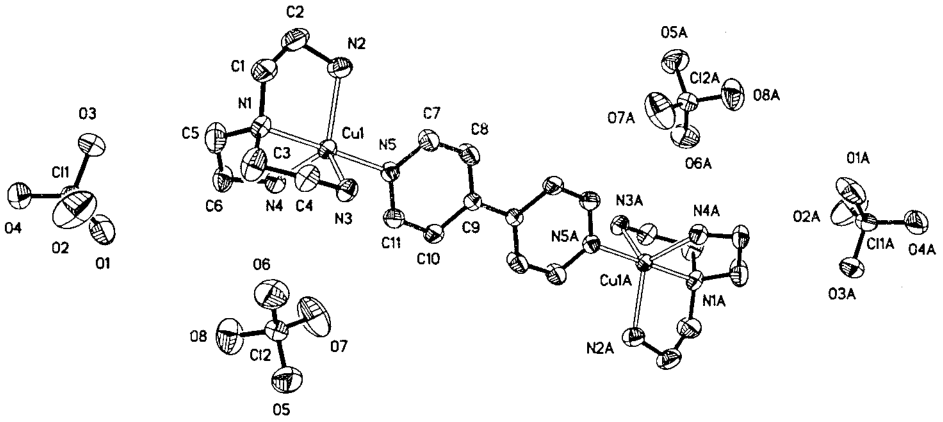

FIGURE 1 Molecular structure of complex **2**.

TABLE III Selected bond lengths(Å) and angles (°) for complex **2**

Cu(1)–N(5)	2.023(2)	Cu(1)–N(1)	2.030(2)
Cu(1)–N(3)	2.047(2)	Cu(1)–N(4)	2.078(2)
Cu(1)–N(2)	2.119(2)	N(1)–C(1)	1.455(4)
N(1)–C(5)	1.472(4)	N(1)–C(3)	1.513(4)
N(2)–C(2)	1.434(5)	N(3)–C(4)	1.456(3)
N(4)–C(6)	1.461(3)	N(5)–C(11)	1.327(3)
N(5)–C(7)	1.328(3)		
N(5)–Cu(1)–N(1)	179.28(7)	N(5)–Cu(1)–N(3)	94.98(8)
N(1)–Cu(1)–N(3)	84.73(8)	N(5)–Cu(1)–N(4)	95.01(8)
N(1)–Cu(1)–N(4)	84.56(8)	N(3)–Cu(1)–N(4)	118.78(8)
N(5)–Cu(1)–N(2)	98.10(9)	N(1)–Cu(1)–N(2)	82.62(9)
N(3)–Cu(1)–N(2)	119.34(9)	N(4)–Cu(1)–N(2)	118.60(9)

4,4′-bipyridine bridge are planar with a dihedral angle of nearly 0°. The molar conductivity of **2** (460 S cm^2 mol^{-1} in CH_3CN solution at room temperature) confirms at the perchlorate ions do not coordinate to the metal ions.

Spectroscopy

In the electronic spectrum, two broad absorption peaks appear at 14,500 cm^{-1} and 11,900 cm^{-1}, with ε values being *ca.* 200 and 300 M^{-1} cm^{-1} respectively, characteristic of *d–d* transitions in trigonal bipyramidal CuN_5 chromophores. In the IR spectrum, two strong absorptions at 3453 and 3496 cm^{-1} arise from symmetrical and antisymmetrical vibration of the primary amine. One strong peak at *ca.* 1100 cm^{-1} may be attributed to uncoordinated ClO_4^- anions, with heating, complex **2** decomposes at 242.2°C abruptly and completely.

X-ray band ESR spectra of **2** measured in CH_3CN solution at various temperatures are shown in Fig. 2. Compared to the spectra of the similar compounds in which no hyperfine structure was detected, the presence of hyperfine structure at room temperature suggests some interaction between the two metal ions. Values of $g_{\parallel} = 2.06$ and $g_{\perp} = 2.12$ show that the local symmetry of the copper(II) ion is trigonal bipyramid

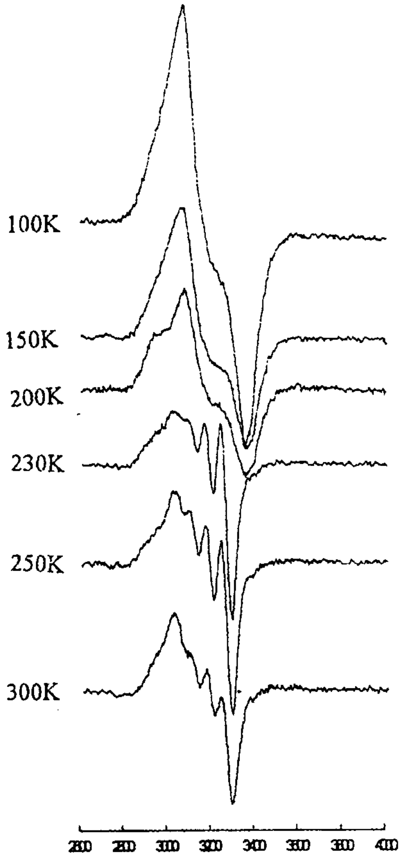

FIGURE 2 ESR spectra of CH_3CN solutions of complex **2** at various temperatures.

with mainly a d_{z^2} ground state. With cooling, hyperfine structure disappears gradually, while g values and signal intensity remain the same. This behaviour is different to that for antiferromagnetic exchange coupling with the spin triplet state as the excited state, in which a T^{-1} intensity dependence with temperature is expected.

Variable-temperature susceptibility data were collected for solid complex **2**. At 290 K, χ^T is equal to 0.840 $\mathrm{cm^3\,mol^{-1}\,K}$, a little higher than for uncoupled copper(II) ions. Upon cooling, χ^T decreases slightly and then increases to a value of 0.5 at *ca.* 50 K. This is characteristic of ferromagnetic interaction between the two copper(II) ions. A very good fit was derived with $2J = 1.23\,\mathrm{cm^{-1}}$, a weak ferromagnetic exchange constant. It is known that the exchange coupling between metal centres sets arises *via* overlap of metal orbitals and those of the bridging atoms [9]. The small exchange constant may be explained by the long distance between the two metal ions and poor overlap of the metal orbitals with the delocalized π electrons of the pyridine rings.

Acknowledgements

This work was supported by the National Science Foundation of Jingsu Province and the State Key Laboratory of Coordination Chemistry of Nanjing University.

Supplementary Material

Full lists of crystallographic and magnetic data are available from the authors upon request.

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