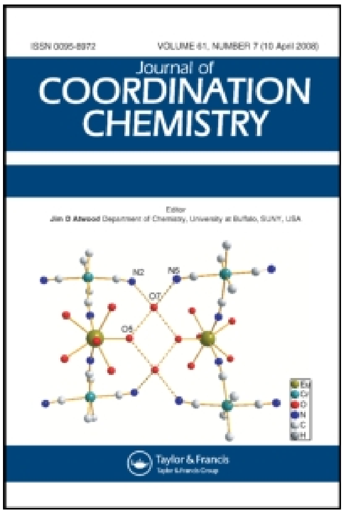

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and properties of a copper(II) complex with the tripod ligand <i>tris</i>(<i>N</i>-methylbenzimidazol-2-ylmethyl)amine and 4-hydroxycinnamate

Hui-Lu Wu[a]; Ji-Gang Liu[a]; Peng Liu[a]; Wei-Bing Lv[a]; Biao Qi[a]; Xing-Ke Ma[b]
[a] School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, China [b] College of Science, Henan University of Technology, Zhenzhou, China

To cite this Article Wu, Hui-Lu , Liu, Ji-Gang , Liu, Peng , Lv, Wei-Bing , Qi, Biao and Ma, Xing-Ke(2008) 'Synthesis, crystal structure and properties of a copper(II) complex with the tripod ligand **<i>tris</i>**(**<i>N</i>**-methylbenzimidazol-2-ylmethyl)amine and 4-hydroxycinnamate', Journal of Coordination Chemistry, 61: 7, 1027 — 1035

To link to this Article: DOI: 10.1080/00958970701481430

URL: http://dx.doi.org/10.1080/00958970701481430

Journal of Coordination Chemistry
Vol. 61, No. 7, 10 April 2008, 1027–1035

Taylor & Francis
Taylor & Francis Group

Synthesis, crystal structure and properties of a copper(II) complex with the tripod ligand *tris*(*N*-methylbenzimidazol-2-ylmethyl)amine and 4-hydroxycinnamate

HUI-LU WU*†, JI-GANG LIU†, PENG LIU†,
WEI-BING LV†, BIAO QI† and XING-KE MA‡

†School of Chemical and Biological Engineering,
Lanzhou Jiaotong University, Lanzhou 730070, China
‡College of Science, Henan University of Technology,
Zhenzhou 450000, China

(*Received 15 March 2007; in final form 18 June 2007*)

A five-coordinate copper complex with the tripod ligand *tris*(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) and 4-hydroxycinnamate, with the composition [Cu(Mentb)(4-hydroxycinnamate)](ClO_4)·0.5DMF, was synthesized and characterized by means of elemental analyses, electrical conductivities, thermal analyses, IR, and UV. The crystal structure of the copper complex has been determined by single-crystal X-ray diffraction, and shows that the Cu^{II} atom is bonded to a *tris*(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) ligand and a 4-hydroxycinnamate through four N atoms and one O atom, giving a distorted trigonal-bipyramidal coordination geometry ($\tau = 0.78$), with approximate C_3 molecular symmetry. Cyclic voltammograms of the copper complex indicate a quasireversible Cu^{+2}/Cu^{+} couple. Electron spin resonance data confirm the trigonal–bipyramidal structure and indicate $g_{\parallel} < g_{\perp}$ with a very small value of $A_{\parallel}$ ($57 \times 10^{-4}\,cm^{-1}$).

Keywords: *Tris*(*N*-methylbenzimidazol-2-ylmethyl)amine; Copper(II) complex; Crystal structure; Trigonal–bipyramidal

1. Introduction

Imidazole is a typical heterocyclic ligand with nitrogen as the donor atom and a component of biologically important molecules [1]. Because of this, the coordination chemistry of related ligands has been the subject of numerous investigations [1]. Amongst them, the coordination of chelating benzimidazolic ligands has been studied by several research groups, some of them with an interest in mimicking biological activities [2–4]. Benzimidazoles exhibit a wide variety of pharmacological activities such as fungicides or anti-helminthics [5]. Tripodal ligands such as tripyridylalkylamine and triazacyclononane have long been used in both copper coordination and bioinorganic

---

*Corresponding author. Email: wuhuilu@163.com

ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701481430

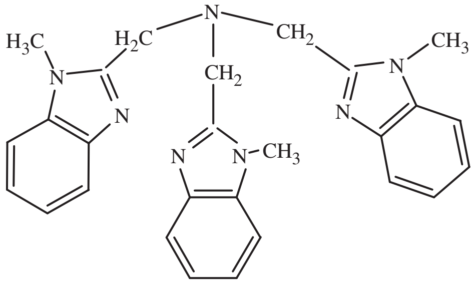

Figure 1. Structure of Mentb.

chemistry [6–8]. The tetradentate tripodal ligand, *tris*(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) (figure 1), is similar to imidazole in its mode of coordination [9]. Since the three arms of this type of ligand can each rotate freely around an N(apical)–C bond, multicomponent complexes or coordination polymeric networks may be expected to form with metal ions of low coordination number. We have been interested in the coordinating ability of benzimidazolic ligands towards transition metal ions [10–13]. In this article, we prepare and investigate the properties and crystal structure of the copper(II) complex with Mentb and 4-hydroxycinnamate as an exogenous ligand. The copper(II) in the complex adopts a distorted trigonal-bipyramidal coordination geometry with the N_4O ligand donor set.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were reagent grade and used without further purification. C, H and N elemental analysis were determined using a Carlo Erba 1106 elemental analyzer. Metal content was determined by EDTA titration. Thermal studies of the complex were made in the 25–800°C range using a ZRY-2P thermal analyzer with a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$. The IR spectra were recorded in the 4000–400 $\mathrm{cm^{-1}}$ region with a Nicolet FI-IR Avatar 360 spectrometer using KBr pellets. Electronic spectra were taken on a TU-Visible spectrophotometer. Electrolytic conductance measurements were made with a DDS-11A type conductivity bridge using a $10^{-3}\,\mathrm{mol\,L^{-1}}$ solution in DMF at room temperature. ^{1}H NMR spectra were recorded on a Bruker AM200A NMR spectrometer with TMS as internal standard and DMSO-d$_6$ as solvent. Electrochemical measurements were performed on a LK98APLUS electrochemical analyzer under nitrogen at 283 K. A glassy carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel electrode (SCE) reference electrode were used in the three-electrode measurements. The electroactive component was at $1.0\times10^{-3}\,\mathrm{mol\,dm^{-3}}$ with tetrabutylammonium perchlorate (TBAP) ($0.1\,\mathrm{mol\,dm^{-3}}$) used as the supporting electrolyte in DMF solution. The EPR spectra were recorded on a Bruker 200D spectrometer with the X-band.

2.2. *Preparation of tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) and the copper complex*

Tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) was synthesized by the literature method [9]. Yield: 4.6 g (51%); m.p.: 215–217°C (m.p.: 215°C in the literature [9]). The infrared and ^1H NMR spectra of Mentb were consistent with the literature [9].

[Cu(Mentb)(4-hydroxycinnamate)](ClO_4) · 0.5DMF. To a stirred solution of Mentb (0.0899 g, 0.2 mmol) in hot MeOH (10 cm^3) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0741 g, 0.2 mmol), followed by a solution of Na(4-hydroxycinnamate) (0.0372 g, 0.2 mmol) in MeOH (5 cm^3). A blue-green crystalline product which formed rapidly was filtered off, washed with MeOH and absolute Et_2O, and dried *in vacuo*. The dried precipitate was dissolved in DMF resulting in a blue-green solution that was allowed to evaporate at room temperature. Blue-green crystals suitable for X-ray diffraction studies were obtained after two weeks. Yield: 0.0683 g (42%). Anal. found: C, 55.70; H, 4.47; N, 12.91; Cu, 7.78. Calcd for $C_{37.5}H_{37.5}ClCuN_{7.5}O_{7.5}$ (MW 812.24): C, 55.45; H, 4.65; N, 12.93; Cu, 7.82%. Λ_M (DMF, 297 K): 68.7 S $cm^2 mol^{-1}$.

2.3. *X-ray structure determination of [Cu(Mentb)(4-hydroxycinnamate)](ClO_4) • 0.5DMF*

All data were obtained using a Bruker Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm) at 293 K. Data reduction and cell refinement were performed using SMART and SAINT programs [14]. The absorption corrections were carried out by the empirical method and the structure solved by direct methods (Bruker SHELXTL) using all unique data [15]. The non-H atoms in the structure were subjected to anisotropic refinement. Hydrogen atoms were located geometrically and treated with the riding model. The crystal data and experimental parameters relevant to the structure determination are listed in table 1 and the final positional and thermal parameters are available as supplementary material.

3. Results and discussion

The copper complex is soluble in DMF and DMSO, but insoluble in water and organic solvents, such as methanol, ethanol, benzene, petroleum ether, trichloromethane, *etc*. The elemental analyses show that the composition is [Cu(Mentb)(4-hydroxycinnamate)](ClO_4) · 0.5DMF. A comparsion of molar conductance value shows 1 : 1 electrolytes in DMF [16].

The TGA curve of the copper(II) complex shows that the initial mass loss within the 159–165°C range is attributed to elimination of the DMF molecules. The DTA curve indicates an endothermic process. The decomposition of the complex starts at 230°C and is completed at *ca*. 605°C, yielding CuO as the final product.

Table 1. Crystal data and structure refinement for [Cu(Mentb)(4-hydroxycinnamate)](ClO_4) · 0.5DMF.

Formula	$C_{37.5}H_{37.5}ClCuN_{7.5}O_{7.5}$
Molecular weight ($g\,mol^{-1}$)	812.24
Crystal system	Monoclinic
Space group	*P*2(1)/c
Unit cell dimensions (Å, °)	
a	15.1645(8)
b	13.1277(7)
c	19.6013(10)
α	90.00
β	96.034(2)
γ	90.00
Vol ($Å^3$)	3880.5(4)
Z	4
T (K)	293(2)
D (calculated) ($g\,cm^{-3}$)	1.390
Absorption coefficient (mm^{-1})	0.691
$F(000)$	1684
Crystal size (mm^3)	0.39 × 0.35 × 0.28
θ range for data collection (°)	1.87–28.33
Index ranges	$-15 \le h \le 20$, $-17 \le k \le 15$, $-23 \le l \le 26$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9619[$R_{int} = 0.0806$]/30/519
Goodness-of-fit on F^2	0.935
Final R_1 and wR_2 [$I > 2\sigma(I)$]	0.0618, 0.1672[a]
R_1 and wR_2 indices (all data)	0.1263, 0.2057
Large diff. peak and hole ($e\,Å^{-3}$)	0.925 and −0.496

[a] $w = 1/[\sigma^2 F_o^2 + (0.1183P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$.

3.1. *Crystal structure of [Cu(Mentb)(4-hydroxycinnamate)](ClO_4) · 0.5DMF*

The molecular structure and crystal packing of the copper(II) complex are shown in figures 2 and 3; selected bond distances and angles are shown in table 2. The crystal structure consists of a discrete [Cu(Mentb)(4-hydroxycinnamate)]$^+$ cation, a perchlorate anion and 0.5 DMF molecule. The perchlorate C(37) and O(8) of the DMF are disordered because of thermal vibration. The Cu^{II} atom is five-coordinate with a CuN_4O chromophore. The Mentb ligand acts as a tetradentate N-donor, and the carboxylate groups of the 4-hydroxycinnamate completes the coordination. The coordination geometry of Cu^{II} is best described as distorted trigonal-bipyramid ($\tau = 0.78$), with approximate molecular symmetry C_3. The parameter τ is defined as (β–α)/60 [where β = N(1)–Cu–O(2), α = N(2)–Cu–N(6)] and its value varies from 0 (in a regular square-based pyramid) to 1 (in a regular trigonal bipyramid) [17]. The coordination geometry around Cu^{II} appears to relieve the steric crowding. The equatorial plane is occupied by three N atoms of three benzimidazolyl groups, while the Cu^{II} atom protrudes towards O(2) and is 0.517(3) Å from the plane of N(2)/N(4)/N(6). The axial positions are occupied by N(1) and O(2), with Cu–N(1) 2.140(3) Å, Cu–O(2) 1.917(3) Å and N(1)–Cu–O(2) is 173.53(11)°. The bond distance between the copper and the apical nitrogen atom is 2.140(3) Å, which is about 0.073 Å longer than the bond distances between the copper ion and the trigonal basal nitrogen atoms (2.046–2.100 Å, average 2.067 Å). This significant elongation has been observed in copper complexes of tripodal tetradentate ligands with benzimidazolylmethyl [18]. The three benzimidazole

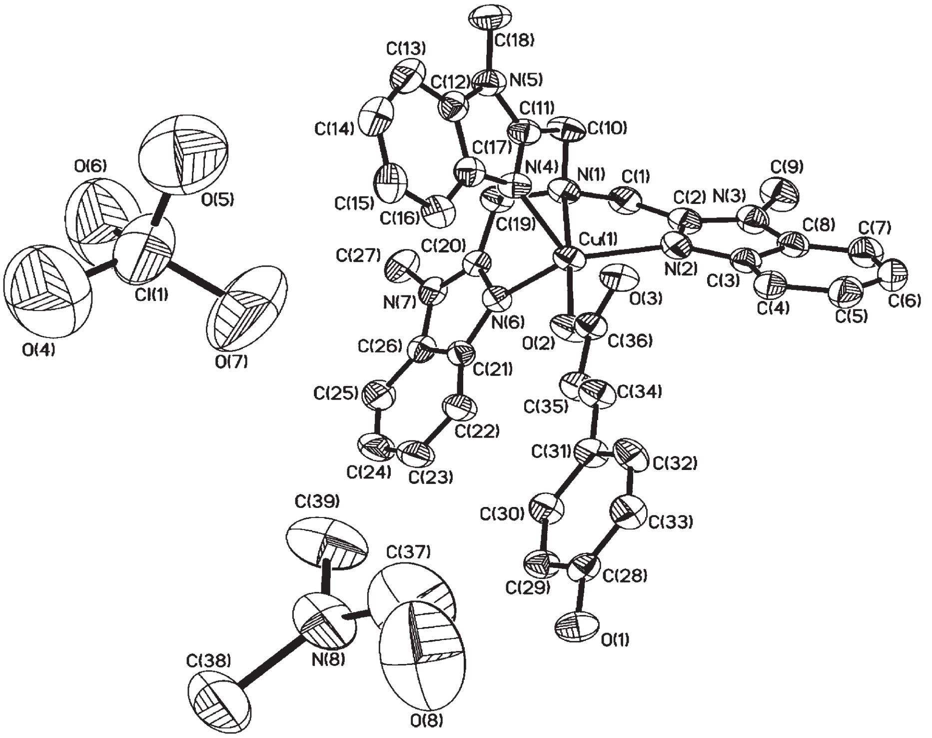

Figure 2. Molecular structure and atom numbering of [Cu(Mentb)(4-hydroxycinnamate)](ClO_4) · 0.5DMF with hydrogen atoms omitted for clarity.

ring arms of the Mentb ligand form a cone-shaped cavity. The angles N(2)–Cu–N(6), N(2)–Cu–N(4) and N(4)–Cu–N(6) are 126.45(12), 116.94(13) and 106.58(13)°, respectively. The N(1)–Cu–N(2) 79.24(13), N(1)–Cu–N(4) 78.86(12) and N(1)–Cu–N(6), 80.19(12)° angles, which are all *ca.* 11° less than the ideal 90°, are imposed by the geometry of the Mentb ligand. The distance between Cu^{II} and O(3) is 3.120(3) Å, so O(3) is not coordinated. The angles and distance in the Mentb and 4-hydroxycinnamate are normally equal.

Weak supramolecular $\pi \cdots \pi$ and strong OH ··· O hydrogen-bonding interactions play important roles in the crystal packing modes in the complex. The planes of benzimidazole and benzene form $\pi \cdots \pi$ stacking interactions along the crystallographic *b* axis. Mononuclear cations form polymers through the O(1) ··· O(3) hydrogen-bond bridges. The whole crystal structure may be regarded as a three-dimensional hydrogen-bonded network joined by the hydrogen-bond bridges. The hydrogen bond parameters are listed in table 3.

3.2. *IR and electronic spectra*

The IR spectral data for the copper complex along with their assignments are given in table 4. In free Mentb, a strong band is found at *ca.* 1475 cm^{-1} together with a weak

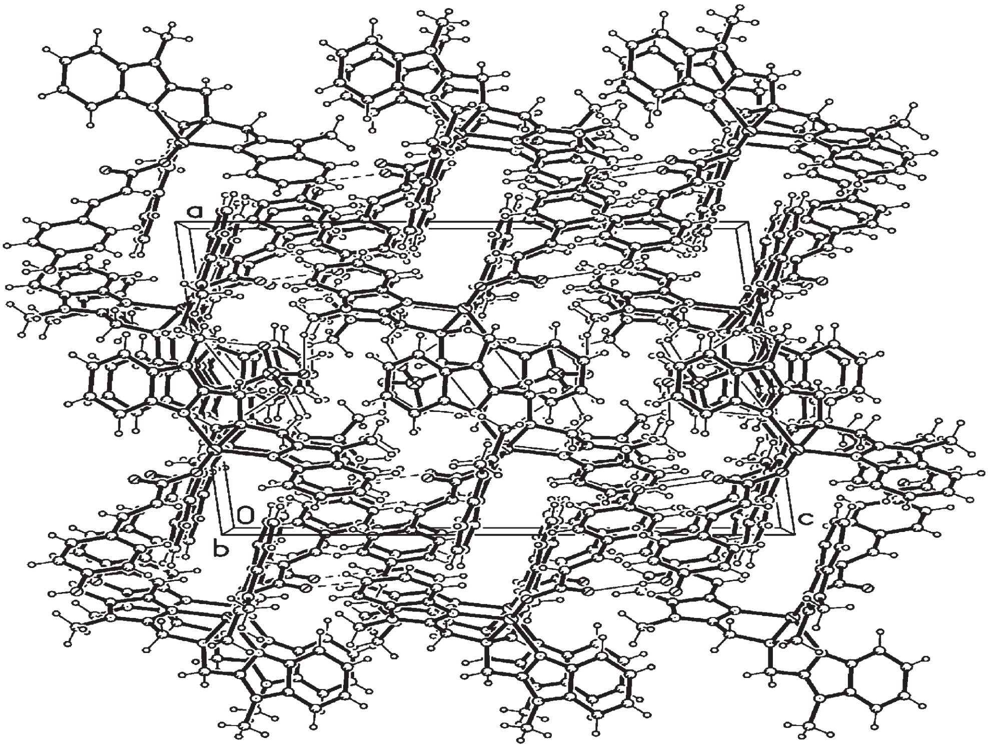

Figure 3. Packing structure along *a* axis of [Cu(Mentb)(4-hydroxycinnamate)](ClO_4) · 0.5DMF.

Table 2. Selected bond distances (Å) and angles (°).

Cu–O(2)	1.917 (3)	O(2)–C(36)	1.279 (4)
Cu–N(2)	2.055 (3)	O(3)–C(36)	1.239 (4)
Cu–N(4)	2.100 (3)	C(34)–C(35)	1.316 (5)
Cu–N(6))	2.046 (3)	O(1)–C(28)	1.364 (4)
Cu–N(1)	2.140 (3)	Cu · · · O(3)	3.120 (3)
O(2)–Cu–N(6)	93.88 (11)	O(3)–C(36)–O(2)	123.5 (3)
O(2)–Cu–N(2)	102.51 (13)	O(3)–C(36)–C(35)	121.5 (3)
O(2)–Cu–N(4)	105.53 (13)	O(2)–C(36)–C(35)	114.9 (3)
O(2)–Cu–N(1)	173.53 (11)	C(34)–C(35)–C(36)	122.8 (4)
N(6)–Cu–N(2)	126.45 (12)	O(1)–C(28)–C(33)	122.8 (3)
N(6)–Cu–N(4)	106.58 (13)	O(1)–C(28)–C(29)	118.3 (3)
N(2)–Cu–N(4)	116.94 (13)	C(1)–N(1)–Cu	107.4 (2)
N(6)–Cu–N(1)	80.19 (12)	C(10)–N(1)–Cu	107.1 (2)
N(2)–Cu–N(1)	79.24 (13)	C(19)–N(1)–Cu	109.6 (2)
N(4)–Cu–N(1)	78.86 (12)	C(36)–O(2)–Cu	125.2 (2)

Table 3. Hydrogen bonding distances (Å) and angles (°).

D–H · · · A	D–H	D · · · A	H · · · A	∠D–H · · · A
O(1)–H(1) · · · O(3)#1	0.82	2.742(4)	1.93	174.1

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $y+1/2$, $-z-1/2$.

Table 4. IR spectral data for the Cu complex and their relative assignments (cm^{-1}).

Compound[a]	$\nu_{as}COO$	ν_sCOO	$\Delta\nu$	$\nu C=C$	$\nu C=N$	$\nu C=N–C=C$	νClO_4^-	νAr–O
NaL	1546s	1414s	132	1639m	–	–	–	1244m
Mentb	–	–	–	–	1515m	1475 s	–	–
Cu complex	1560s	1383s	177	1640m	1509m	1455s	1090bs	1238m

[a] L = 4-hydroxycinnamate; b = broad; s = strong; m = medium.

band at 1515 cm^{-1}. By analogy with the assigned bands of imidazole, the former can be attributed to ν(C = N–C = C), while the latter can be attributed to ν(C = N) [9, 19, 20]. They shift to the higher frequency *ca.* 6–20 cm^{-1} in the complex, which implies direct coordination of all four imine nitrogen atoms to copper(II). This is the preferred nitrogen atom for coordination as found for other metal complexes with benzimidazoles [21]. Information regarding possible bonding modes of the perchlorate may also be obtained from the IR spectra. The strong, fairly broad absorption band at 1090 cm^{-1} indicates that ionic perchlorate (T_d) is present [22]. Since the carboxylate group can coordinate to the metal ion in a bidentate or a monodentate fashion, the 'Δ criterion', which is based on the difference between the ν_{as}(O–C–O) and ν_s(O–C–O) values, compared to the corresponding value in sodium carboxylate, determines the coordination of the carboxylate [22–25]. The data in table 4 suggests that the carboxylate of 4-hydroxycinnamate in the complex is monodentate, confirmed by the crystal structure. The band at 1649 cm^{-1} may originate from the C = C bond vibration of the α,β-unsaturated carboxylate group.

A DMSO solution of Mentb ligand and the copper complex show, as expected, identical UV spectra. The UV band of Mentb (290 nm) is only marginally blue shifted (7 nm) in the complex, which shows clear evidence of C = N coordination to copper. The absorption band is assigned to $\pi \rightarrow \pi^*$ (imidazole). The copper complex exhibits two absorptions in the visible spectra ($\lambda = 725$, 984 nm). The higher-energy band is dxz, dyz → $dx^2–y^2$ transition, while the next lower energy transition is dxy → dx^2-y^2 [26]. This spectral pattern is typical of five-coordinate trigonal bipyramidal copper(II), trigonal bipyramidal systems, e.g., $[Cu(Me_6tren)X]^+$ and $[Cu(tren)L]^{n+}$ (tren = $N(CH_2CH_2NH_2)_3$; Me_6tren = $N[CH_2CH_2N(CH_3)_2]_3$; X = Cl, Br, I, NO_3, ClO_4; L = OH, py, NH_2Ph, NCS, NH_3) exhibit very similar spectra [27, 28].

3.3. *Electrochemistry and EPR spectra*

The electrochemical properties of the copper complex have been studied by cyclic voltammetry (CV) in DMF. The voltammogram of the copper(II) complex shows only a single reduction peak (Cu^{2+}/Cu^+) at 0.122 V (E_{pc}) during the cathodic potential scan. During the return anodic potential scan, just after the reduction peak, an anodic peak is observed at 0.215 V (E_{pa}). The separation between the cathodic and anodic peak potentials ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) of 93 mV indicates a quasi-reversible redox process assignable to the Cu(II)/Cu(I) couple and $E_{1/2}$ [$(E_{pa} + E_{pc})/2$] is equal to 0.168 V [29, 30]. The neutral uncomplexed ligand ntb is not electroactive over the range −1.2 to + 1.2 V.

The X-band EPR spectrum was measured in a single crystal at 285 K. That $g_{\parallel} = g_{zz}$ and $g_{\perp} = g_{xx} = g_{yy}$ shows that the spectral features are of axial symmetry.

Table 5. EPR spectral of the copper complex in single crystal at 285 K.

Compound[a]	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel}$ ($\times 10^{-4}$)	$A1_{\perp}$ ($\times 10^{-4}$)
$[Cu(Mentb)(L)](ClO_4) \cdot 0.5DMF$	2.073	2.249	2.190	57 cm^{-1}	65 cm^{-1}

[a] L = 4-hydroxycinnamate; $g_{av} = (g_{\parallel} + 2g_{\perp})/3$; Spectrometer conditions: microwave frequency, 9.65 GHz; microwave power, 10 mW; gain, 4.0×10^4; mid-range, 3181 G; scan range, 2000 G; time constant, 0.5 s; scan time, 200 s.

Copper complexes of tren, Me_6tren, Et_6tren which have trigonal-bipyramidal structures have $g_{\parallel} < g_{\perp}$ and $A_{\parallel}$ in the range ~65–100 ($10^{-4}\,cm^{-1}$) [26–28]. Spin-Hamiltonian parameters for the copper complex are reported in table 5. $A_{\parallel}$ value is typically low and $g_{\parallel}$ value is greater than g_e. Systems of this type can be interpreted in terms of a dz^2 ground state in a trigonal-bipyramidal structure but the large value of $g_{\parallel}$ implies mixing of dxy and dx^2-y^2 orbitals into the ground state via vibronic coupling. Because of $g_{\parallel} < g_{\perp}$ and the lower $A_{\parallel}$ value, the structure of the copper complex may be best described as distorted trigonal-bipyramid.

Supporting information available

Crystallographic data (excluding structure factors) for the structure in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 627349. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgements

The authors acknowledge the financial support and grant from ‘Qing Lan’ Talent Engineering Funds by Lanzhou Jiaotong University. The grant from the Middle-Young Age Science Foundation of Gansu Province (Grant no. 3YS061-A25-023) is also acknowledged.

References

[1] J. Reedijk. *Comprehensive Coordination Chemistry*, (Chapter 13.2), Vol. 2, Pergamon, Oxford (1987).
[2] R. Rajan, R. Rajaram, B.U. Nair, T. Ramasami, S.K.J. Mandal. *Chem. Soc., Dalton Trans.*, 2019 (1996).
[3] T.J. Cardwell, A.J. Edwards, J.M. Hartshorn, R.J. Holmes, W.D. McFadyen. *Aust. J. Chem.*, **50**, 1009 (1997).
[4] J. García-Lozano, J. Server-Carrió, E. Coret, J.V. Folgado, E. Escrivà, R. Ballesteros. *Inorg. Chim. Acta*, **245**, 75 (1996).
[5] T.M. Aminabhavi, N.S. Biradar, S.B. Patil, D.E. Hoffman. *Inorg. Chim. Acta*, **125**, 125 (1986).
[6] M. Schatz, M. Becker, F. Thaler, F. Hampel, S. Schindler, R.R. Jacobson, Z. Tyeklar, N.N. Nurthy, P. Ghosh, Q. Chen, J. Zubieta, K.D. Karlin. *Inorg. Chem.*, **40**, 2312 (2001).
[7] K. Jitsukawa, M. Harata, H. Arii, H. Sakurai, H. Masuda. *Inorg. Chim. Acta*, **324**, 108 (2001).
[8] Q.X. Li, W. Zhang, Q.H. Luo, Y.Z. Li, Z.L. Wang. *Trans. Met. Chem.*, **28**, 682 (2003).

[9] H.M.J. Hendriks, P.J.M.W.L. Birker, G.C. Verschoor, J. Reedijk. *J. Chem. Soc., Dalton Trans.*, 623 (1982).
[10] Z.X. Su, Y.Q. Wan, H.L. Wu. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **35**, 553 (2005).
[11] H.L. Wu, Y.C. Gao, K.B. Yu. *Trans. Met. Chem.*, **29**, 175 (2004).
[12] H.L. Wu, W. Ying, L. Pen, Y.C. Gao, K.B. Yu. *Synth. React. Inorg. Met.-Org. Chem.*, **34**, 1019 (2004).
[13] H.L. Wu, Y.C. Gao. *J. Coord. Chem.*, **59**, 137 (2006).
[14] Bruker, *Smart Saint and Sadabs,* Bruker Axs, Inc., Madison, Wisconsin, USA (2000).
[15] G.M. Sheldrick. *SHELXTL, Siemens Analytical X-Ray Instruments, Inc.*, Madison, Wisconsin, USA (1996).
[16] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971).
[17] S. Youngme, J. Phatchimkun, U. Sukangpanya, C. Pakawatchai, N. Chaichit, P. Kongsaeree, J. Krzystek, B. Murphy. *Polyhedron*, **26**, 871 (2007).
[18] J. Sletten, H. Grove. *Acta Chem. Scand.*, **51**, 822 (1997).
[19] C.Y. Su, B.S. Kang, C.X. Du, Q.C. Yang, T.C.W. Mak. *Inorg. Chem.*, **39**, 4843 (2000).
[20] T.J. Lane, I. Nakagawa, J.L. Walter, A.J. Kandathil. *Inorg. Chem.*, **1**, 267 (1962).
[21] M. McKee, M. Zvagulis, C.A. Reed. *Inorg. Chem.*, **24**, 2914 (1985).
[22] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn, pp. 200–320, John Wiley and Sons, New York (1978).
[23] J. Catterick, P. Thornton. *Adv. Inorg. Chem.*, **20**, 291 (1977).
[24] S. Musumeci, E. Rizzarelli, S. Sammartano, A. Seminaba. *Z. Anorg. Allg. Chem.*, **433**, 297 (1977).
[25] Y.Y. Wang, Q. Shi, Q.Z. Shi, Y.C. Gao, Z.Y. Zhou. *Polyhedron*, **18**, 2009 (1999).
[26] L.K. Thompson, B.S. Ramaswamy, R.D. Dawe. *Can. J. Chem.*, **56**, 1311 (1978).
[27] M. Ciamolini, N. Nardi. *Inorg. Chem.*, **5**, 41 (1966).
[28] G. Albertin, E. Bordignon, A.A. Orio. *Inorg. Chem.*, **14**, 1411 (1975).
[29] A.W. Addison, H.M.J. Hendriks, J. Reedije, L.K. Thompson. *Inorg. Chem.*, **20**, 103 (1981).
[30] K. Jitsukawa, M. Harata, H. Arii, H. Sakurai, H. Masuda. *Inorg. Chim. Acta.*, **324**, 108 (2001).