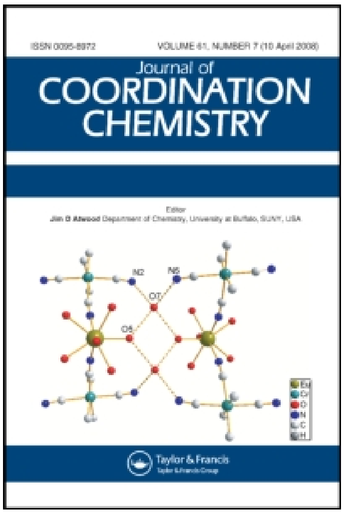

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A five-coordinate copper(II) perchlorate complex with tris(*N*-methylbenzimidazol-2-ylmethyl)amine and salicylate

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A five-coordinate copper(II) perchlorate complex with tris(*N*-methylbenzimidazol-2-ylmethyl)amine and salicylate

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A five-coordinate copper(II) complex with the tripod ligand tris(*N*-methylbenzimidazol-2-ylmethyl)amine (Mentb) and salicylate, with the composition [Cu(Mentb)(salicylate)]$(ClO_4) \cdot 2DMF$, was synthesized and characterized by elemental and thermal analyses, electrical conductivity, IR and UV-Vis spectral measurements. The crystal structure of the complex has been determined by single-crystal X-ray diffraction. The Cu(II) is five-coordinate with four N atoms from the Mentb ligand and an O atom of the monodentate salicylate ligand. The N_4O donors are in a distorted trigonal-bipyramid geometry. Cyclic voltammograms indicate a quasireversible Cu^{2+}/Cu^{+} couple. The X-band EPR spectrum of the complex confirms the trigonal-bipyramidal structure with $g_{\parallel} < g_{\perp}$ and a very small value of $A_{\parallel}$ $(41 \times 10^{-4}\,cm^{-1})$.

Keywords: Tris(*N*-methylbenzimidazol-2-ylmethyl)amine; Crystal structure; EPR; Cyclic voltammetry; Copper(II)complexes

1. Introduction

Tripodal ligands have long been used in both coordination and organometallic chemistry [1, 2], typically polypyrazolylborate and tris(2-pyridyl) tripodal ligands. However, their potential use in supramolecular chemistry for the construction of various cagelike or boxlike complexes has only recently been examined [3–5]. Use of C_3-symmetric tripodal ligands in crystal engineering has been reviewed [6]. Imidazole is a heterocyclic ligand with nitrogen as the donor, common in biologically important molecules [7]. Because of this, the coordination chemistry of related ligands has been the subject of numerous investigations [7], including chelating benzimidazolic ligands, some with an interest in mimicking biological activities [8–10]. Benzimidazoles exhibit a wide variety of pharmacological activities like fungicides or anti-helminthics [11]. The tetradentate tripodal ligand tris(*N*-methylbenzimidazol2-ylmethyl)amine (Mentb) (figure 1) may mimic the histidine imidazole in coordination. 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 from this

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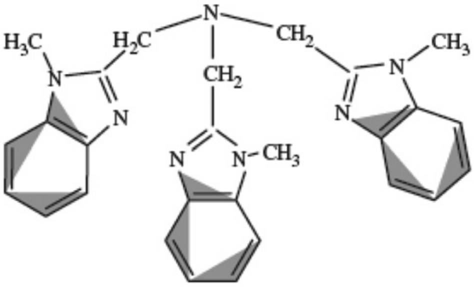

Figure 1. Structure of Mentb.

ligand and metal ions of low coordination number [12–17]. Herein we report the synthesis, crystal structure, and properties of a copper(II) complex with tripodal ligand Mentb and salicylate.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were reagent grade and used without purification. C, H, and N contents were determined using a Carlo Erba 1106 elemental analyzer. Metal contents were determined by EDTA titration. Thermal analyses were carried out under a N_2 flow at a heating rate of 10°C min^{-1} on a ZRY-2P thermal analyzer. IR spectra were recorded from 4000–400 cm^{-1} with a Nicolet FI-IR Avatar 360 spectrometer using KBr pellets. Electronic spectra were taken on a LabTech BlueStarPlus spectrophotometer. Electrolytic conductance measurements were made with a DDS-11A type conductivity bridge using 10^{-3} mol dm^{-3} solution in DMF at room temperature. Electrochemical measurements were performed on a LK2005A electrochemical analyzer under nitrogen at 283 K. A glassy carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel (SCE) reference electrode were used in the three-electrode measurements. The electroactive component was at 1.0×10^{-3} mol dm^{-3} with tetrabutylammonium perchlorate (TBAP) (0.1 mol dm^{-3}) as the supporting electrolyte in DMF. The EPR spectra were recorded on a Bruker 200D spectrometer with the X-band.

2.2. *Preparation of tris(N-methylbenzimidazol-2-ylmethyl)amine and its complexes*

2.2.1. Tris(N-methylbenzimidazol-2-ylmethyl)amine (Mentb). This compound was synthesized by the literature method [18]. Yield: 4.6 g (51%); m.p.: 215–217°C.

2.2.2. [Cu(Mentb)(salicylate](ClO$_4$)·2DMF. To a stirred solution of Mentb (0.0899 g, 0.2 mmol) in hot MeOH (20 mL) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (0.0741 g, 0.2 mmol) followed by a solution of sodium-salicylate (0.0320 g, 0.2 mmol) in MeOH (5 mL).

A blue-green crystalline product formed rapidly. The precipitate was filtered off, washed with MeOH and absolute Et_2O, and dried *in vacuo*. The dried precipitate was dissolved in DMF giving a blue-green solution which was allowed to evaporate at room temperature. After two weeks a mass of blue-green crystals appeared, 0.12 g (67%). Calcd for $C_{40}H_{46}CuClN_9O_9$ (895.85): C 53.45, H 5.15, N 13.95, Cu 7.41%; Anal. found: C 53.45, H 5.18, N 14.07, Cu 7.09%. Λ_M (DMF, 297 K): 60.2 $S\,cm^2\,mol^{-1}$.

2.3. *X-ray structure determination*

All data were collected using a Rigaku R-axis Spider diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm) at 153(2) K. Data reduction and cell refinement were performed using RAPID-AUTO programs [19]. Absorption corrections were carried out by multi-scan. The structure was solved by direct methods (SHELXTL) using all unique data [20]. The aromatic ring of the salicylate ligand was disordered over two sites and from refinement, determined to be of equal occupancy. One DMF is partially disordered over two positions and from refinement, the major component was found to have an occupancy factor = 0.552(15). All H atoms were geometrically positioned and refined using a riding-model approximation with C–H distances ranging from 0.95 to 0.99 Å and O–H distance from 0.83(1), and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $U_{iso}(H) = 0.52U_{eq}(O)$ of the carrier atom. The non-H atoms in the structure were subjected to anisotropic refinement. The crystal data and experimental parameters relevant to the structure determination are listed in table 1.

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. Elemental analyses show that the composition is $[Cu(Mentb)(salicylate](ClO_4) \cdot 2DMF$. Molar conductance shows a 1 : 1 electrolyte similar to previously reported data [21].

Thermogravimetric analysis (TGA) of the copper(II) complex shows that the initial mass loss within the 165–169°C range is attributed to elimination of DMF. Differential thermal analysis (DTA) indicates the dehydration as an endothermic peak. The decomposition of the complex starts at 245°C and is complete at *ca* 593°C, yielding CuO as the final product.

3.1. *Crystal structure of* $[Cu(Mentb)(salicylate](ClO_4) \cdot 2DMF$

The molecular structure and crystal packing of the copper(II) complex are shown in figure 2; selected bond lengths and angles are shown in table 2. The asymmetric unit consists of a $[Cu(Mentb)(salicylate)]^+$ cation, a perchlorate anion and 2 DMF molecules. The Cu^{II} is five-coordinate with a CuN_4O chromophore. The Mentb ligand is tetradentate N-donor, and an oxygen of a monodentate salicylate complete the coordination. The Cu^{II} is a distorted trigonal bipyramid as seen in the value of $\tau = 0.45$, cf. $\tau = 0$ for an ideal square pyramid and $\tau = 1$ for an ideal trigonal bipyramid [22]. The parameter τ is defined as $(\beta - \alpha)/60$ (where $\beta = N(7)–Cu–O(1)$, $\alpha = N(3)–Cu–N(5)$).

Table 1. Crystal data and structure refinement for [Cu(Mentb)(salicylate)](ClO_4)•2DMF.

Formula	$C_{40}H_{46}ClCuN_9O_9$
Molecular weight ($g\,mol^{-1}$)	895.85
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	12.3507(4)
b	12.6632(5)
c	14.4152(4)
α	85.721(1)
β	70.886(1)
γ	76.503(1)
V (Å^3)	2071.40(12)
Z	2
T (K)	153(2)
D (calculated) ($g\,cm^{-3}$)	1.436
Absorption coefficient (mm^{-1})	0.658
$F(000)$	934
Crystal size (mm^3)	$0.54 \times 0.52 \times 0.39$
θ range for data collection (°)	3.2 to 27.5
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 15$, $-16 \le l \le 17$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7660[R(int) = 0.020]/24/603
Goodness-of-fit on F^2	1.05
Final R_1 and wR_2 [$I > 2\sigma(I)$]	0.048, 0.132[a]
R_1 and wR_2 indices (all data)	0.051, 0.134
Largest difference peak and hole (e Å^{-3})	0.88 and −0.86

[a] $w = 1/[\sigma^2 F_o^2 + (0.0705\,P)^2 + 2.6589\,P]$, where $P = (F_o^2 + 2\,F_c^2)/3$.

The coordination geometry around the Cu^{II} appears to relieve steric crowding. The equatorial plane is occupied by three nitrogens of three benzimidazolyl groups, while the Cu^{II} protrudes towards O(1) and is 0.318(2) Å from the plane of atoms N(1)/N(3)/N(5). The axial positions are occupied by N(7) and O(1). The three benzimidazole ring arms of the Mentb ligand form a cone-shaped cavity. The N(7)–Cu–N(1), N(7)–Cu–N(3) and N(7)–Cu–N(5), which are all *ca* 10° less than the ideal 90°, are imposed by the geometry of Mentb. The distance between Cu^{II} and O(2) is 2.961(2) Å, indicating that O(2) is non-coordinating. The angles and distance in Mentb and salicylate are within the normal ranges. Crystal packing and O–H $\cdots$ O hydrogen-bonding interactions play important roles in the crystal packing modes (table 3).

3.2. *IR and UV-Vis spectra*

IR spectra for the copper complex along with their relative assignments are given in table 4. In free Mentb, a strong band is found at 1475 cm^{-1} along with a weak 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) [18, 23, 24]. They shift to higher frequency *ca* 7–20 cm^{-1} in the complex, which implies direct coordination of all four imine nitrogens to copper(II). This is the preferred coordination found for other metal complexes with benzimidazoles [25]. The strong, fairly broad absorption band at 1091 cm^{-1} indicates ionic perchlorate (T_d) is present [26]. Since the carboxylate can coordinate to the metal bidentate or monodentate, the 'Δ criterion',

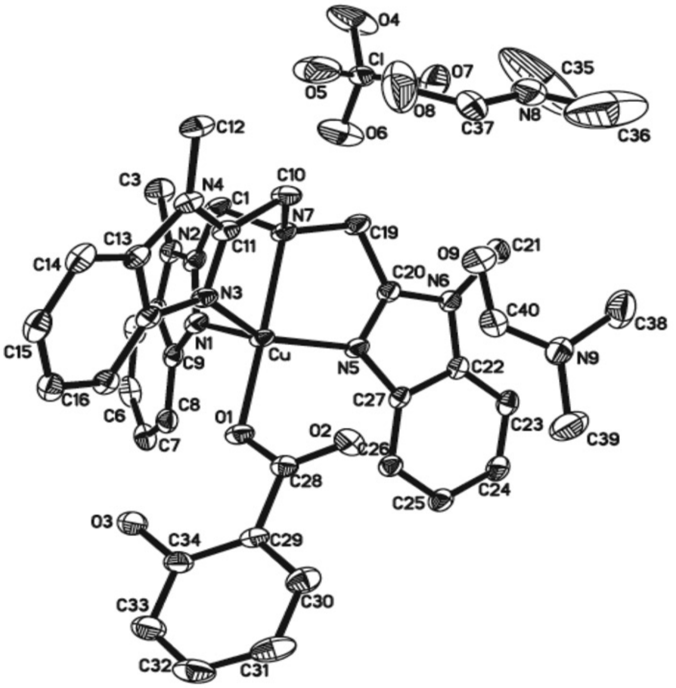

Figure 2. Molecular structure and atom numbering of [Cu(Mentb)(salicylate)](ClO_4) · 2DMF with hydrogens omitted for clarity.

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

Bond lengths			
Cu–N(1)	2.165(2)	Cu–N(7)	2.153(2)
Cu–N(3)	1.983(2)	Cu–O(1)	1.9441(19)
Cu–N(5)	1.983(2)	Cu · · · O(2)	2.961(2)
Bond angles			
N(7)–Cu–N(1)	79.92(9)	N(1)–Cu–N(3)	110.14(8)
N(7)–Cu–N(3)	80.21(9)	N(3)–Cu–N(5)	149.64(10)
N(7)–Cu–N(5)	82.24(9)	N(1)–Cu–N(5)	90.79(9)
N(7)–Cu–O(1)	176.47(8)	C(28)–O(1)–Cu	117.26(16)
N(1)–Cu–O(1)	102.12(9)	O(1)–C(28)–O(2)	124.0(2)
N(3)–Cu–O(1)	96.36(8)	O(1)–C(28)–C(29)	119.7(4)
N(5)–Cu–O(1)	100.54(8)	O(2)–C(28)–C(29)	116.3(4)

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, is employed to determine the coordination of the carboxylate [27, 28]. The data in table 4 suggest that monodentate is confirmed by crystal structure analysis.

DMSO solutions of Mentb and its copper(II) complex show, as expected, almost identical UV spectra. The UV band of Mentb (290 nm) is only marginally blue-shifted (8 nm) in the complex, which is clear evidence of C=N coordination to copper(II). The absorption is assigned to $\pi \rightarrow \pi^*$ (imidazole) transition. The copper complex exhibits two absorptions in the visible spectra ($\lambda = 700$, 931 nm). The higher-energy band is (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$) transition, while the next lower energy transition is ($d_{xy} \rightarrow d_{x^2-y^2}$)

Table 3. Selected hydrogen bonding distances (Å) and angles (°).

D–H···A	D–H	D···A	H···A	D–H···A
O3–H3O···O2	0.83(7)	2.562(7)	1.87(6)	140(4)
O3′–H3O′···O1	0.84(6)	2.493(6)	1.72(6)	152(5)

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

Compound	$\nu_{as}COO$	ν_sCOO	$\Delta\nu$	$\nu C{=}N$	$\nu C{=}N{-}C{=}C$	νClO_4^-	νAr-O
Na(salicylate)	1580s	1485s	95	–	–	–	1247m
Mentb	–	–	–	1515m	1475s	–	–
Cu complex	1561s	1388s	173	1483m	1453s	1091bs	1247m

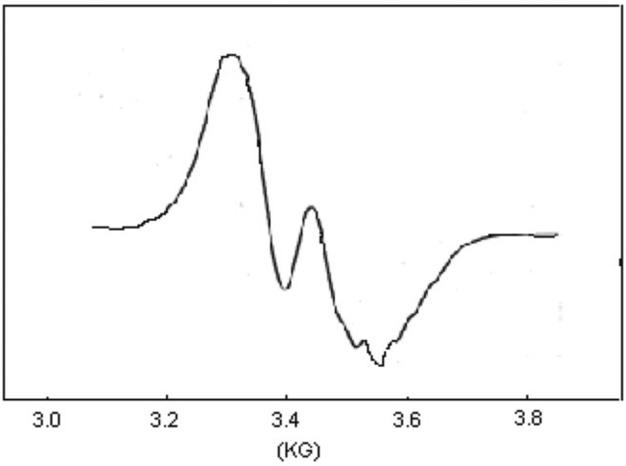

Figure 3. X-band EPR spectrum of the copper complex at 285 K as a single crystal. Spectrometer conditions: microwave frequency, 9.65 GHz; microwave power, 10 mW; gain, 4.0×10^4; mid-range, 3181 G; scan range, 2000 G; time constant, 0.5 s; scan time, 200 s.

transition [29], typical of five-coordinate trigonal bipyramidal copper(II). Known 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 [30, 31].

3.3. *Cyclic voltammogram and EPR spectrum*

Electrochemical properties of the copper complex have been studied by cyclic voltammetry (CV) in DMF showing only a single reduction peak (Cu^{2+}/Cu^+) at 0.131 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 0.236 V (E_{pa}). The separation between the cathodic and anodic peak potentials ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$) of 109 mV indicates a quasi-reversible redox process assignable to the Cu(II)/Cu(I) couple

Table 5. EPR data of the copper complex as a single crystal at 285K.

Compound	$g_{\parallel}$	$g_{\perp}$	g_{av}	$A_{\parallel}(\times 10^{-4})$	$A_{\perp}(\times 10^{-4})$
$[Cu(Mentb)(salicylate)](ClO_4) \cdot 2DMF$	2.052	2.239	2.177	$41\,cm^{-1}$	$53\,cm^{-1}$

$g_{av} = (g_{\parallel} + 2g_{\perp})/3$; 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.

and $E_{1/2}$ $[(E_{pa} + E_{pc})/2]$ is equal to 0.184 V [32, 33]. The uncomplexed Mentb is electroinactive over the range -1.2 to $+1.2$ V.

The X-band EPR spectrum was measured in single crystal at 285 K (figure 3). The fact that $g_{\parallel} = g_{zz}$ and $g_{\perp} = g_{xx} = g_{yy}$ shows axial symmetry. Copper complexes of tren, Me_6tren, Et_6tren which have trigonal-bipyramidal structures have $g_{\parallel} < g_{\perp}$ and $A_{\parallel}$ in the range $\sim$65–100($10^{-4}\,cm^{-1}$) [29–31]. Spin-Hamiltonian parameters for the copper complex are reported in table 5. $A_{\parallel}$ is typically low and $g_{\parallel}$ value is greater than g_e. Systems of this type can be interpreted in terms of a d_{z^2} ground state in a trigonal-bipyramidal structure, but the large value of $g_{\parallel}$ implies mixing of d_{xy} and $d_{x^2-y^2}$ orbitals into the ground state via vibronic coupling. Because $g_{\parallel} < g_{\perp}$ and lower $A_{\parallel}$ value, the structure of the copper complex may be best described as distorted trigonal-bipyramid.

Supplementary material

CCDC 669527 contains supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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