

[Cu(*men*)₂(BF₄)₂] (*men* = N-methyl-1,2-diaminoethane): Preparation, crystal structure, spectroscopic and magnetic properties

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ABSTRACT

Single crystals of [Cu(*men*)₂(BF₄)₂] (*men* = N-methyl-1,2-diaminoethane) (**1**) were isolated from an aqueous-ethanolic system Cu²⁺–*men*–BF₄[−]. The crystal structure of **1** consists of [Cu(*men*)₂(BF₄)₂] molecules. Copper ion exhibits usual distorted octahedral coordination; there are two coordinated *men* ligands in the equatorial plane with Cu–N bonds of 2.0451(12) and 2.0035(12) Å, while the axial positions are occupied by fluorine atoms from BF₄[−] anions with Cu–F bond of 2.5091(11) Å. The packing of the [Cu(*men*)₂(BF₄)₂] molecules is governed by N–H...F type hydrogen bonds. The measured ESR spectrum corroborated the presence of Jahn–Teller anisotropy of Cu(II) with $g_{||} = 2.20$ and $g_{\perp} = 2.06$. The magnetic studies in the temperature range 300–2 K reveal that **1** follows the Curie–Weiss law with parameters $g = 2.1612(1)$ and $\theta = -0.233(1)$ K suggesting the presence of weak antiferromagnetic interactions.

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1. Introduction

Hydrogen bonds (HBs) represent an important type of intermolecular interactions and play essential role among others in structural chemistry. It was also shown that HBs can play an important role in magnetic exchange interactions [1–3]. At the same time results of density functional calculations on some dimeric Cu(II) complexes have shown that HBs in mediating magnetic exchange interactions exhibit essentially structural function as they enable to hold the paramagnetic central atoms relatively close to each other [4]. Usually the value of the exchange coupling constant, J through HBs exhibit low or very low values; on the other hand, in [Cu(*diimH*)₂] (*diimH* = C₇H₁₆N₂O₂^{2−}, dianion of the diimine Schiff base) as high value of J as -94 cm^{-1} was reported [5].

The importance of HBs is enhanced also by the fact that they can be responsible for differences in structural and magnetic dimensionalities, at least in the case of some one-dimensional (1D) compounds of Cu(II) ($S = 1/2$) [6–8]. Study of magnetic and thermodynamic properties of structurally 1D compound Cu(*en*)₂·Ni(CN)₄ (*en* = 1,2-diaminoethane) below 0.5 K corroborated its magnetically 2D character (Heisenberg plane); as additional ex-

change paths to the covalent bonds the present HBs of the N–H...N(≡C)...H–N type were suggested [9,10]. In order to modify the bridging species in Cu(*en*)₂Ni(CN)₄ we have decided to use in place of cyano complex anions (5-atomic bridge) tetrafluoroborate anion (3-atomic bridge). Such complex with *en* as ligand was already described but its crystal structure is molecular [11]. As we were successful in preparation of a similar [Cu(*men*)₂(BF₄)₂] (**1**) complex aimed as a model for the study of the exchange interactions between paramagnetic metal ions via hydrogen bonds here we report the results of our study on its preparation, crystal structure, spectroscopic and magnetic properties.

2. Experimental

2.1. Synthesis of N-methyl-1,2-diaminoethane-bis(tetrafluoroborate) copper(II) complex, [Cu(*men*)₂(BF₄)₂] (**1**)

An aqueous solution of Cu(BF₄)₂·xH₂O (0.240 g, 1.0 mmol) was mixed with a solution formed of 10 cm³ of dichloromethane, 10 cm³ of butanol, 10 cm³ of ethanol and 0.18 cm³ (2 mmol) of *men*. A violet solution formed which was filtered in order to avoid any solid impurity. Violet needles separated from the filtrate within 2 days, they were filtered off and dried on air. Yield: 32%.

Anal. [%], calculated for CuC₆H₂₀N₂F₈B₂: C, 18.69; H, 5.23; N, 16.48; found: C, 18.97; H, 5.30; N, 16.55.

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IR (cm⁻¹): 3363m; 3294m; 3242m; 3205; 2931m; 1597s; 1472s; 1316w; 1116sh; 1074s, 846w, 765s; 671s; 523s; 485m.

2.2. Physical measurements

Elemental analyses (C, H, N) were performed on a Flash EA 1112 Elemental Analyser (ThermoFinnigan).

Infrared spectrum was recorded on a FT-IR Avatar 330 Thermo-Nicolet instrument using KBr pellets technique (1:100) in the range of 4000–400 cm⁻¹.

Electronic absorption spectrum was recorded on a Specord 250 spectrometer (Analytik Jena) in Nujol suspension.

Electron-spin resonance (ESR) data were collected at 2.5 K in an X-band Bruker ELEXSYS E500 spectrometer. The ESR measurements have been carried out on powdered sample.

2.3. Magnetic measurements

Susceptibility of **1** was studied on a commercial Quantum Design SQUID magnetometer in the temperature range from 2 to 300 K at 1 kG. The powder specimen (28.2 mg) was fixed in a gelcap and the gelcap was held by a straw. The signal contribution of the gelcap and the straw has been subtracted. The obtained data were corrected to diamagnetic contribution using Pascal's constants [12] and by TIP; a TIP value of $3.8(2) \times 10^{-4}$ emu mol⁻¹ was used.

2.4. X-ray crystallography

X-ray experiments were carried out on a four-circle κ -axis Xcalibur2 diffractometer equipped with a CCD detector Sapphire2 (Oxford Diffraction) at 110(2) K. The CrysAlis software package [13] was used for data collection and reduction. The structures were solved by the SIR97 program incorporated in the WinGX program package [14]. All non-hydrogen atoms of [Cu(men)₂(BF₄)₂] were refined anisotropically by the full-matrix least-squares procedure SHELXL-97 [15] on F^2 . Hydrogen atoms were located from difference Fourier maps and refined using a 'riding' model. Molecular structure of [Cu(men)₂(BF₄)₂] is depicted in Fig. 1. The structural figures were drawn using the Diamond software [16]. Crystal data and final parameters of the structure refinement for **1** are summarized in Table 1, while selected bond lengths and angles are given in Table 2. Possible hydrogen bonds are given in Table 3.

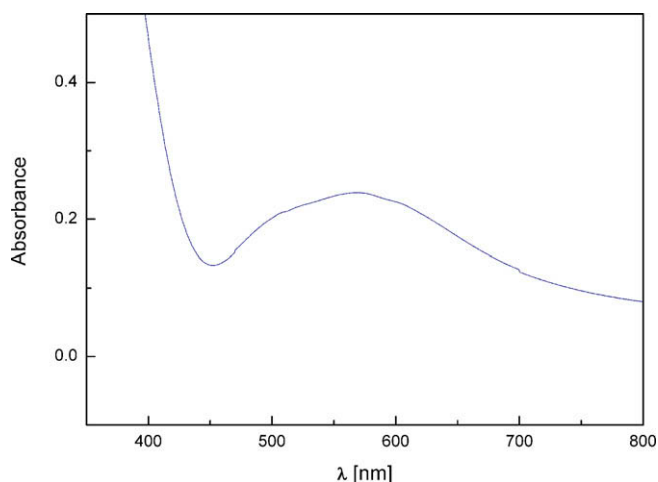


Fig. 1. Electronic absorption spectrum of **1**.

Table 1
Crystal data and structure refinement for [Cu(men)₂(BF₄)₂].

Empirical formula	C ₆ H ₂ O ₂ CuF ₈ N ₄
Formula weight	385.42
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	
<i>a</i> = 8.1540(2) Å	
<i>b</i> = 11.5826(3) Å	<i>β</i> = 113.421(4)°
<i>c</i> = 8.2118(3) Å	
Volume	711.66(4) Å ³
<i>Z</i>	2
Density (calculated)	1.799 g cm ⁻³
Absorption coefficient	1.620 mm ⁻¹
Crystal dimensions	0.20 × 0.20 × 0.10 mm ³
Theta range for data collection	2.72–25.00°
Index ranges	−9 ≤ <i>h</i> ≤ 9, −13 ≤ <i>k</i> ≤ 13, −9 ≤ <i>l</i> ≤ 8
Reflections collected/independent	4803/1252 [<i>R</i> (int)] = 0.0132
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.82071
Data/restraints/parameters	1252/0/98
Goodness-of-fit on F^2	1.066
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0192, <i>wR</i> ₂ = 0.0505
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0240, <i>wR</i> ₂ = 0.0518
Largest diff. peak and hole	0.3(7) and −0.3(4) e Å ⁻³

Table 2
Selected geometric parameters [Å, °] for [Cu(men)₂(BF₄)₂].

Cu(1)–N(2)	2.0035(13)	N(2) ^j 1–Cu(1)–N(1)	84.73(5)
Cu(1)–N(1)	2.0451(12)	Cu(1)–F(1)–B(1)	118.3(7)
Cu(1)–F(1)	2.5091(11)	N(1)–Cu(1)–F(1)	94.70(3)
B(1)–F(2)	1.374(2)	N(2)–Cu(1)–F(1)	90.65(3)
B(1)–F(4)	1.387(2)		
B(1)–F(3)	1.392(2)		
B(1)–F(1)	1.407(2)		

Symmetry transformations used to generate equivalent atoms:
(i) 1 – *x* + 1, –*y* + 1, –*z* + 1.

Table 3
Possible hydrogen bonds [Å, °] for [Cu(men)₂(BF₄)₂] [Å, °].

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	<(DHA)
N(1)–H(1C)···F(3) ⁱ	0.93	2.40	3.2124(17)	145
N(1)–H(1C)···F(3) ⁱⁱ	0.93	2.51	3.1041(16)	122
N(1)–H(1C)···F(2) ^j	0.93	2.58	3.2570(17)	130
N(2)–H(2C)···F(4) ⁱⁱⁱ	0.92	2.28	3.0762(16)	145
N(2)–H(2C)···F(1) ⁱⁱⁱ	0.92	2.57	3.2104(16)	127
N(2)–H(2D)···F(4) ^{iv}	0.92	2.37	3.0745(16)	133
N(2)–H(2D)···F(2) ⁱ	0.92	2.45	3.1957(17)	138

Symmetry transformations used to generate equivalent atoms:
(i) –*x* + 1, –*y* + 1, –*z* + 1; (ii) *x* + 1, *y*, *z*; (iii) *x*, –*y* + 3/2, *z* – 1/2; (iv) *x*, *y*, *z* – 1.

3. Results and discussion

3.1. Synthesis and identification

Single crystals of the title compound **1** were isolated from an aqueous-ethanolic system Cu²⁺–men–BF₄[–]. In order to obtain single crystals of X-ray quality, an addition of dichloromethane and *n*-butanol following the suggestion of [11] was necessary; the lack of these organic solvents led upon slow evaporation of water/ethanol solvents to formation of a gel. The same product was formed also by higher (1:3) Cu:men ratio.

Similar methods were used for the preparation of analogous [Cu(en)₂(BF₄)₂] compound [11]. The results of chemical analyses corroborated the assumed composition of the crystals which was later confirmed by a single crystal X-ray analysis (see below).

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