Polyhedron 61 (2013) 87–93

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Magnetism of novel Schiff-base copper(II) complexes derived from aminoacids

Z. Puterová-Tokárová *, V. Mrázová, R. Boča

Department of Chemistry, FPV, University of SS Cyril and Methodius, Nám. J. Herdu 2, 917 01 Trnava, Slovakia

A R T I C L E I N F O

Article history:
Received 29 April 2013
Accepted 23 May 2013
Available online 1 June 2013

Keywords:
Aminoacids
Schiff base
Cu(II) complex
Magnetism
Magnetic ordering

A B S T R A C T

Magnetic properties of five copper(II) complexes of the formula $[CuL^3(H_2O)_2]$ or $[CuL^4(H_2O)]$ were investigated. These contain a Schiff-base L derived from salicylaldehyde and aminoacids. The ligand L is represented by four bonding isomers (**1** through **4**) and it is either tridentate (L^3) or tetradentate (L^4). The fifth ligand contains sulfonato group instead of the carboxyl one. Structurally, two complexes are monomers (**1** and **4**), one is a dimer (**5**), and two are polymers (**2** and **3**). Their magnetic behaviour is more complex: **1** behaves as an antiferromagnetic Heisenberg diad, **2** and **4** are ferromagnetic chains, **3** is a combined ferromagnetic/antiferromagnetic ladder (ribbon), and **5** exhibits a complex 3D-ordering with unusual temperature evolution of the effective magnetic moment.

1. Introduction

Copper(II) complexes with Schiff base ligands derived from amino acids and salicylaldehyde have been reported in the literature for a long time [1]. The distorted square-pyramidal geometry around Cu(II) ion gives Schiff base copper(II) chelates potential to act as valuable non-enzymatic models for more complicated copper metalloproteins, such as Cu,Zn-superoxide dismutase [2–4] and catechol oxidase [5,6]. The number of reported mononuclear copper(II) *N*-salicylidene aminoacidates [7–12] is superior to those with higher nuclearities [13,14]. This is due to the fact that the majority of ligands are produced by condensation reaction of salicylaldehyde and α-amino acid exhibiting tridentate coordination mode around the metal centre with the most stable five-membered chelate ring. Such arrangement prefers formation of mononuclear copper(II) complexes with one Schiff base ligand and two aqua ligands adopting square-pyramidal geometry [10–12]. The employment of β-aminoacids in the synthesis of *N*-salicylidene-aminoacidato Schiff base ligand offers the possibility of construction of extended networks of higher nuclearity [13] where the six-membered chelate ring is incorporated. Moreover, different coordination behaviour of the carboxylato functional group in a simple β-aminoacids (e.g. β-alanine, β-amino-*iso*-butyric acid) and sulfonato functional group for example in taurine as a part of Schiff base ligand can be observed [14]. Recently, we reported the structure of copper(II) *N*-salicylidene-aminoacidate containing γ-aminobutyric acid which causes coordination via the unique seven-membered ring [15]. Extensive investigations on modelling of active sites of native copper oxidases by copper(II) chelates derived from Schiff base ligands containing amino acids over past decades provided clear insights into the relationship between the structural features and the catalytic activity (superoxide scavenging activity, catechol-oxidase like activity, ascorbic-oxidase like activity) of these complexes [7–21]. Despite of this plethora publications on the structure–activity relationship, studies concerning their magnetostructural correlations are rather rare [13,22]. As an extension of such work, we have chosen five copper(II) *N*-salicylidene-aminoacidates **1**–**5** (Fig. 1) with different coordination modes in order to obtain detailed information about the magnetic exchange mechanism and to identify factors that influence their magnetic properties.

2. Experimental

2.1. Materials

All chemicals were of reagent grade, obtained from commercial sources, and used without further purification. All solvents were dried and distilled by standard methods prior to use. Spectroscopic grade solvents were used for spectral measurements.

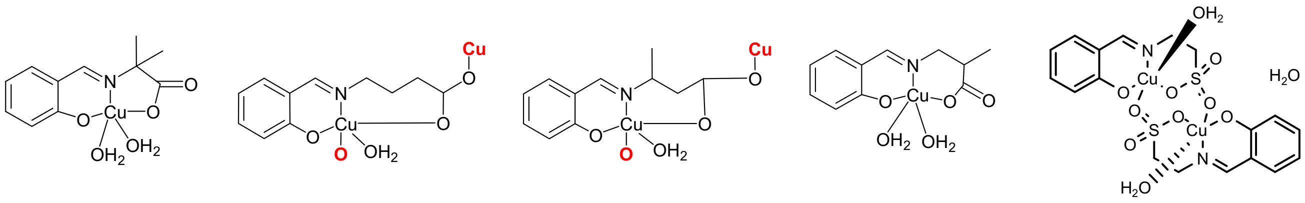
2.2. Physical measurements

IR spectra were measured as KBr pellets (Schimadzu, Impact 400) in the 4000–400 cm^{-1} region. Electronic spectra of DMSO

---

* Corresponding author. Tel.: +421 33 5921408; fax: +421 33 5921 403.
E-mail addresses: zita.tokarova@ucm.sk, zita.puterova@gmail.com (Z. Puterová-Tokárová).

0277-5387/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2013.05.045



1 [Cu(SAIB)(H_2O)$_2$]

2 [Cu(SGABA)(H_2O)]

3 [Cu(DL-SBAIB)(H_2O)]·H_2O

4 Cu(DL-SBAB)(H_2O)$_2$

5 [Cu(STaurine)(H_2O)]·H_2O

Fig. 1. Sketch of complexes under study. Red (bold) atoms are from the neighbouring units. (Colour online.)

solutions of compounds ($c = 4 \times 10^{-3}$ mol dm^{-3}) were measured in the 200–800 nm region (Schimadzu, UV-160). Elemental analysis was performed by FlashEA 1112 (ThermoFinnigan). Content of copper was determined by electrolysis (Pt-cathode, $U = 2$ V, $I = 2$–3 A) after mineralization of the complexes in conc. H_2SO_4.

A SQUID magnetometer (MPMS-XL7, Quantum Design) has been used for magnetic data using the RSO mode of detection. The susceptibility taken at $B = 0.1$ T between $T = 2$–300 K has been corrected for the underlying diamagnetism and converted to the effective magnetic moment. The magnetization has been measured at two temperatures: $T = 2.0$ and 4.6 K.

2.3. Synthesis

2.3.1. Ligands – general procedure

The Schiff-condensation of salicylaldehyde with the corresponding amino acid at a ratio 1:1 in water–alcohol solution for 3 h at room temperature resulted to the tridentate ligands: H_2SAIB, H_2SGABA, H_2SBAIB, H_2SBAB, H_2STaurine. Ligands were subsequently used without further purification.

2.3.2. Complexes – general procedure

To a water/ethanol solution (1:1, 60 cm^3) of appropriate Schiff base ligand (10 mmol), an aqueous solution of copper acetate dihydrate (10 mmol in 60 cm^3 of water) was added and stirred for 1 h at 50 °C accompanied by a colour change to dark green. The resultant reaction mixture was filtered off and the filtrate was left to crystallise spontaneously for several days at room temperature. Final complexes were separated and washed with cold ethanol.

2.3.3. Compound **1** – [Cu(SAIB) (H_2O)$_2$]

Anal. Calc. for $C_{11}H_{15}CuNO_5$ (304.78 g mol^{-1}): C, 43.35; H, 4.96; N, 4.60; Cu, 20.85. Found: C, 45.69; H, 4.52; N, 4.88; Cu, 20.19%. IR(KBr) $\nu = 3446$ (OH, coord. water), 3290, 2984, 1636 (C=N), 1541 (COO$^-_{as}$.), 1340 (COO$^-_{sym}$), 1206, 755, 549, 442 cm^{-1}. UV–Vis (DMSO, $c = 4 \times 10^{-3}$ mol dm^{-3}) $\lambda_{max} = 658$ ($\log\varepsilon = 1.65$), 353 ($\log\varepsilon = 2.39$), 264 nm.

2.3.4. Compound **2** – [Cu(SGABA)(H_2O)]

Anal. Calc. for $C_{11}H_{13}CuNO_4$ (286.76 g mol^{-1}): C, 46.07; H, 4.57; N, 4.88; Cu, 22.16. Found: C, 46.37; H, 4.45; N, 4.70; Cu, 22.54%. IR(KBr) $\nu = 3442$ (OH, coord. water), 3030, 2917, 1635 (C=N), 1540 (COO$^-_{as}$.), 1352 (COO$^-_{sym}$), 1210, 752, 557, 459, 415 cm^{-1}. UV–Vis (DMSO, $c = 4 \times 10^{-3}$ mol dm^{-3}) $\lambda_{max} = 682$ ($\log\varepsilon = 1.48$), 352 ($\log\varepsilon = 2.60$), 282 nm.

2.3.5. Compound **3** – [Cu(DL-SBAIB)(H_2O)]·H_2O

Anal. Calc. for $C_{11}H_{15}CuNO_6$ (320.78 g·mol^{-1}): C, 41.19; H, 4.71; N, 4.37; Cu, 19.81. Found: C, 40.90; H, 4.50; N, 4.76; Cu, 20.11%. IR(KBr) $\nu = 3444$ (OH, coord. water), 3042, 2959, 1627 (C=N), 1540 (COO$^-_{as}$.), 1350 (COO$^-_{sym}$), 1205, 769, 606, 470, 410 cm^{-1}. UV–Vis (DMSO, $c = 4 \times 10^{-3}$ mol dm^{-3}) $\lambda_{max} = 667$ ($\log\varepsilon = 1.28$), 352 ($\log\varepsilon = 2.48$) nm.

2.3.6. Compound **4** – Cu(DL-SBAB)(H_2O)$_2$

Anal. Calc. for $C_{11}H_{15}CuNO_6$ (320.78 g·mol^{-1}): C, 41.19; H, 4.71; N, 4.37; Cu, 19.81. Found: C, 41.52; H, 4.76; N, 4.70; Cu, 20.20%. IR(KBr) $\nu = 3453$ (OH, coord. water), 3050, 2974, 1638 (C=N), 1529 (COO$^-_{as}$.), 1344 (COO$^-_{sym}$), 1211, 753, 564, 454, 412 cm^{-1}. UV–Vis (DMSO, $c = 4 \times 10^{-3}$ mol dm^{-3}) $\lambda_{max} = 670$ ($\log\varepsilon = 1.32$), 352 ($\log\varepsilon = 2.54$) nm.

2.3.7. Compound **5** – [Cu(STaurine)(H_2O)]·H_2O

Anal. Calc. for $C_{18}H_{26}Cu_2N_2O_{12}S_2$ (653.63 g·mol^{-1}): C, 33.10; H, 4.00; N, 4.30; S, 10.00; Cu, 20.00. Found: C, 32.99; H, 3.87; N, 4.28; S, 10.20; Cu, 20.34%. IR(KBr) $\nu = 3418$ (OH, coord. water), 1628 (C=N), 1285 (SOO$^-_{as}$.), 1246 (phenolic O$^-$), 1177 (SOO$^-_{sym}$), 755, 618, 415 cm^{-1}. UV–Vis (DMSO, $c = 4 \times 10^{-3}$ mol dm^{-3}) λ_{max} 716 ($\log\varepsilon = 1.44$), 358 ($\log\varepsilon = 2.40$) nm.

3. Results and discussion

3.1. Synthesis of complexes

All the complexes were synthesized by two step procedure as we had previously described elsewhere [15]. First, by condensation of salicylaldehyde and appropriate amino acid in water–ethanol (1:1) solution Schiff base ligands were formed *in situ*. In the next step, the coordination was performed by the reaction of copper(II) acetate dihydrate with Schiff base ligand leading to final copper(II) complexes **1**–**5** (Fig. 1) in 62–67% yields.

3.2. IR and electronic spectra of the complexes

The electronic spectral data recorded in DMSO ($c = 4 \cdot 10^{-3}$ mol dm^{-3}) of compounds **1**–**5** exhibit a similar absorptions, displaying a d–d transitions in the range 658–716 nm corresponding to the square-pyramidal arrangement of {$CuNO_4$} chromophore. Absorption bands at 350–360 nm are attributed to the ligand-to-metal charge transfer (CT) transitions. IR spectra of all complexes display strong band at 1628–1638 cm^{-1} characteristic for the stretching frequencies of (C=N) group. The asymmetric vibration of the coordinated carboxylato group [ν (COO$^-_{as}$.)] in complexes **1**–**4** are observed at 1529–1540 cm^{-1} region, and a band within the region 1340–1350 cm^{-1} is assigned to symmetric vibration of carboxylato group [ν (COO$^-_{symm}$)] [15]. The frequencies characteristics of the (S–O) stretching modes in compound **5** are observed at 1285 and 1177 cm^{-1}, respectively [14]. The band around 1200–1250 cm^{-1} can be assigned to (C–O) vibrations of the phenolic group in all complexes.

3.3. Description of the structures **1**–**3** and **5**

The crystal structures of complexes [Cu(SAIB)(H_2O)$_2$] (**1**), [Cu(SGABA)(H_2O)] (**2**), [Cu(DL-SBAIB)(H_2O)]·H_2O (**3**), and [Cu(STaurine)(H_2O)]·H_2O (**5**) were already described elsewhere [14,15]. The coordination polyhedron around each copper(II) centre of all