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Variety of polymorphic forms contrasted with uniform crystal packing in sparteine ML_2 complexes: Crystal structure, spectroscopic and magnetic properties of (−)-α-isosparteine and (−)-sparteine complexes with $CuBr_2$

Beata Jasiewicz [a,*], Beata Warżajtis [a], Urszula Rychlewska [a], Tomasz Toliński [b]

[a] Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
[b] Institute of Molecular Physics, Polish Academy of Science, Smoluchowskiego 17, 60-179 Poznań, Poland

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ABSTRACT

This paper reports the synthesis, thermogravimetric and magnetic measurements for (−)-α-isosparteine $CuBr_2$ complex (**1**) and the existence of the fourth polymorph (**2**) of (−)-sparteine $CuBr_2$ complex. The two $CuBr_2$ complexes have been structurally characterized by X-ray crystallography. A diverse supramolecular aggregation of (−)-sparteine $CuBr_2$ complex has been contrasted with strong tendency for isostructuralism observed in a series of ML_2 complexes (M = metal, L = halogen or pseudohalogen) with both sparteine (**3**) and α-isosparteine (**4**). The incidence of polymorphism in a group of compounds which readily form the isomorphic series is quite unusual. Moreover, the reported crystal structure of **2** constitutes the first example showing that the organization of metal complexes of sparteine isomers into similar packing architecture is possible, although in general configurational changes within the sparteine ligand differentiate packing of otherwise similar (−)-sparteine-ML_2 or (−)-α-isosparteine-ML_2 molecules.

1. Introduction

Interest in the chemistry of alkaloids with a sparteine (**3**, see Fig. 1) skeleton (i.e. bis-quinolizidine alkaloids) is increasing due to their coordinating ability towards metal ions. Copper complexes with (−)-sparteine (Sp) display interesting physical, chemical and structural behavior. It has been demonstrated that (−)SpCuBr complex plays an important role in synthesis of novel rod-coil block copolymers [1], (−)$SpCuCl_2$ complex is a good chiral catalyst in polymerization reaction [2] and sparteine related compounds are successfully used as structure-directing agents to synthesize the molecular sieves with unique structures [3].

Copper halide compounds have been the subject of many structural and magnetic studies [4–11]. Electronic and magnetic properties of such compounds have been analyzed in order to establish relationship with their structural features [6–11]. Among them there are distorted tetrahedral copper(II) (−)-sparteine complexes. There are reports of weak anti-ferromagnetic behavior characteristic for (−)$SpCuBr_2$ [8], (−)SpCu(PhCOO)Cl [10] and (−)SpCu(PhCOO)Br [12] complexes. In view of the antiferromagnetic interactions in the copper(II)-halide systems, hydrogen bonding and short Cu–X···X–Cu contacts were considered as possible pathways for magnetic exchange [13–16]. The magnetic exchange between adjacent Cu(II) centers, especially in the square-planar copper(II) compounds, could also occur through a Cu–X–Cu bridge by expansion of the coordination number [17].

In this work, we report the synthesis, crystal structure and spectroscopy of (−)-α-isosparteine (**4**, see Fig. 1) (hereafter α-Sp) complex with $CuBr_2$ (**1**) and the fourth polymorphic form of (−)$SpCuBr_2$ complex (**2**). The other three forms that have been previously reported in the literature have been designated by us as **2a** [6,8], **2b** [6] and **2c** [8]. Polymorphism among the crystals of (−)-sparteine metal(II) complexes is quite often encountered. Besides being displayed by in the studied (−)-sparteine $CuBr_2$ complex, it has been found in (−)-sparteine copper(II) dinitrate [18] and dichloride [19–21] and (−)-sparteine zinc(II) bromide [22,23].

In view of the anti-ferromagnetic properties of some of the known polymorphic forms of (−)$SpCuBr_2$ complexes [6,8] magnetic properties of (−)-α-isosparteine complex (**1**) have been also examined. Unfortunately, we could not collect enough quantity of **2** to measure its magnetic susceptibility and thermal stability. However, having in our disposal the other polymorphic form, i.e. **2c**, which was obtained by us from the commercial sparteine sulfate pentahydrate $C_{15}H_{26}N_2 \times H_2SO_4 \times 5H_2O$ and copper(II) bromide, we have measured the powder-diffraction pattern for this polymorph, registered its TG curve and repeated the magnetic measurements. This not only gave us an opportunity to compare

* Corresponding authors. Tel.: +48 61 829 1354; fax: +48 61 829 1505.
E-mail address: beatakoz@amu.edu.pl (B. Jasiewicz).

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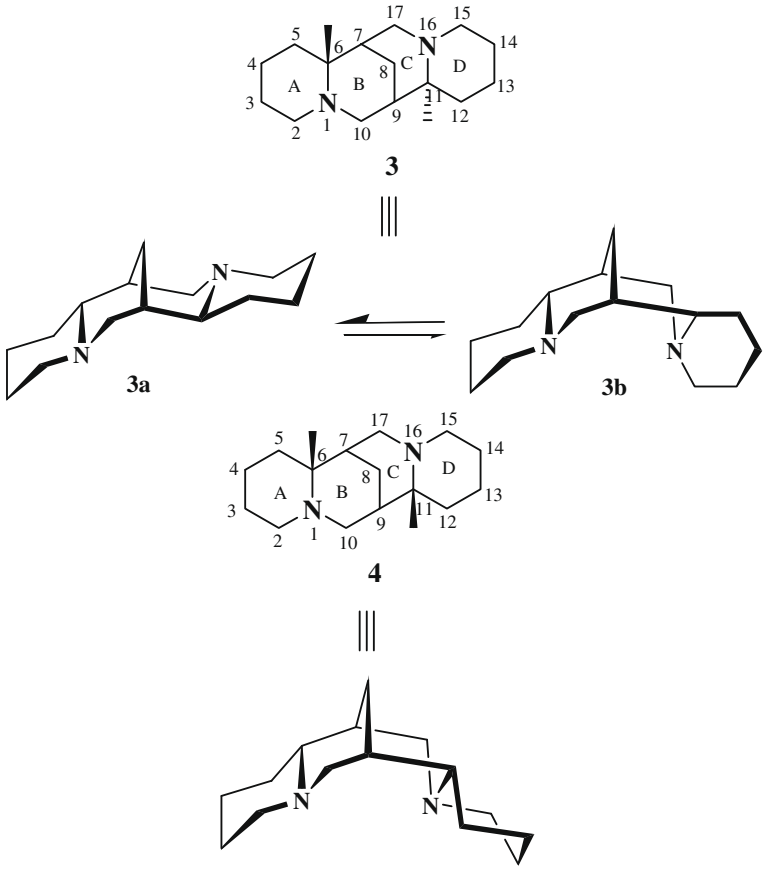

Fig. 1. Sparteine (**3**) and α-isosparteine (**4**), ring labeling and atom numbering.

the obtained results with the analogous data registered for **1** but also allowed to clarify the literature reports concerning the magnetic properties of **2c**. We have also made an attempt to correlate the obtained structural parameters with the available magnetic measurements.

2. Experimental

2.1. General techniques

The IR spectra were recorded by means of a FT-IR Bruker 113v spectrometer (KBr pellets). Electronic spectra were measured on a JASCO V-550 spectrophotometer, in methanol solution. Elemental analysis was carried out by means of a Perkin-Elmer 2400 CHN automatic device. TG and DSC studies were carried out on a SETARAM Instrument Setsys12 TG-DSC 15, in an atmosphere of He at a heating rate of 5 °C min^{-1} from room temperature to 350 °C (TG) or in the temperature range 0–350 °C (DSC). Empty aluminum pans were used as reference. Mass spectra were recorded using a model 402 two-sector mass spectrometer AMD-Intectra GmbH Harpstedt, Germany. Measurements of the magnetic DC susceptibility were carried out on a MagLab 2000 System DC magnetometer/AC susceptometer (Oxford Instruments Ltd.) providing magnetic field up to 9T and temperatures from 300 K down to 2 K. Both the zero field cooling (ZFC) and field cooling (FC) magnetizations have been measured. The ZFC mode means cooling the sample without the presence of the external magnetic field, then switching the field on at low temperatures and carrying out the measurements during warming, keeping the applied field. The FC mode consists in the presence of the field during the whole procedure, i.e. it is switched on before the cooling starts.

2.2. Materials and preparation

Copper(II) bromide was commercially supplied by Aldrich. (−)-Sparteine was obtained from commercial sparteine sulfate pentahydrate $C_{15}H_{26}N_2 \times H_2SO_4 \times 5H_2O$ (Aldrich) [24]. (−)-α-Isosparteine was obtained according to method described previously [25] with the important modification that significantly improves the efficiency of reactions. Modification involves using H_3PO_3 to remove excess of Hg^{+2} ions.

(−)α-Sp$CuBr_2$ (**1**). A solution of $CuBr_2$ (224 mg, 1 mmol) in methanol (20 mL) was added dropwise to a solution of (−)-α-isosparteine (234 mg, 1 mmol) in methanol (15 mL) at room temperature. The resulting reddish-orange precipitate was filtered off and recrystallized from methanol. Yield: 84%. Anal. Calcd. for $C_{15}H_{26}N_2Br_2Cu$: C, 39.36; H, 5.72; N, 6.12. Found: C, 39.65; H, 5.64; N, 6.17.

(−)Sp$CuBr_2$ (**2**) was obtained as a byproduct during the synthesis of the $CuBr_2$ complex of the (−)-sparteine N16-oxide as a result of impurity of the starting material. Anal. Calcd. for $C_{15}H_{26}N_2Br_2Cu$: C, 39.36; H, 5.72; N, 6.12. Found: C, 39.42; H, 5.76; N, 6.10.

In contrast to two (−)Sp$CuBr_2$ polymorphs **2a** and **2b** obtained by Kang and co-workers [6], complexes **1** and **2** are stable to the moisture and we can store them under room temperature conditions.

2.3. X-ray crystallography

2.3.1. Powder diffractometry

In order to identify the (−)Sp$CuBr_2$ polymorph that we have synthesized from the commercial (Aldrich) sparteine sulfate pentahydrate $C_{15}H_{26}N_2 \times H_2SO_4 \times 5H_2O$ we have registered its powder