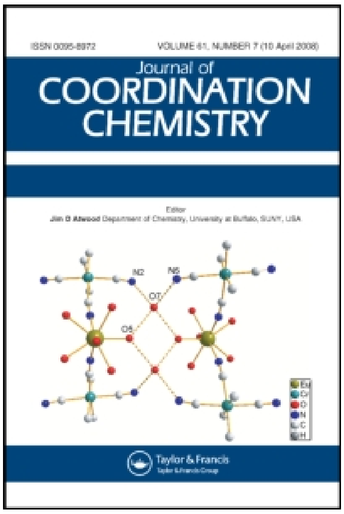

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B. Jasiewicz[a]; W. Ł. Boczoń[a]; A. Kowalczyk[b]
[a] Faculty of Chemistry, A. Mickiewicz University, Poznań 60-780, Poland [b] Polish Academy of Science, Institute of Molecular Physics, Poznań 60-179, Poland

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Synthesis and spectral characterization of sparteine and α-isosparteine complexes with copper(II) sulfate

B. JASIEWICZ*†, W. Ł. BOCZOŃ† and A. KOWALCZYK‡

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

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Complexes of $CuSO_4$ of the general formula $[Cu(C_{15}H_{26}N_2)SO_4]$ where $[C_{15}H_{26}N_2]$ is sparteine or α-isosparteine have been obtained from copper(II) and an appropriate alkaloid. The 1 : 1 (metal : alkaloid) stoichiometry was confirmed by elemental analysis. The compounds have been characterized by mass spectrometry, IR, and UV–Vis spectroscopy. The magnetic properties were also determined; no anti-ferromagnetic behavior was observed. Information on the geometry of newly obtained compounds was obtained using quantum-chemical calculations.

Keywords: Sparteines; Copper(II) complexes; IR and UV–Vis spectroscopy; Magnetic properties; DFT calculations

1. Introduction

(−)-Sparteine and its diastereoisomer α-isosparteine are well-suited as chiral bidentate ligands for many applications, e.g., for metal complexation [1–8] and asymmetric synthesis [9–14]. They are composed of two quinolizidine systems; in sparteine, one forms a double-chair *trans*-quinolizidine system A/B, which is relatively resistant to configurational–conformational changes, the other, of rings C and D, is much more susceptible to inversion at the N16 atom. In consequence, a rearrangement may occur between *trans* boat–chair C/D (a) and *cis* chair–chair C/D (b) configurations and conformations. The α-isosparteine, consisting of two *trans bis*-quinolizidine systems, exists solely in the all chair conformation, which is preserved in both liquid and solid state, and does not change even on double protonation of the molecule [15] (figure 1).

Cu(II) sparteine complexes have been used as model compounds for the type I copper(II) site of blue copper protein. Complexes of this kind have been reported with a pseudo-tetrahedral metal ion environment [16–18]. Owing to our interest in sparteine and α-isosparteine complexes [19–22], we have undertaken a project aimed at characterizing the spectral, analytical and structural properties of copper(II) complexes of (−)-sparteine and α-isosparteine.

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*Corresponding author. Tel.: +48-61-829-1354. Fax: +48-61-865-8008. Email: beatakoz@amu.edu.pl

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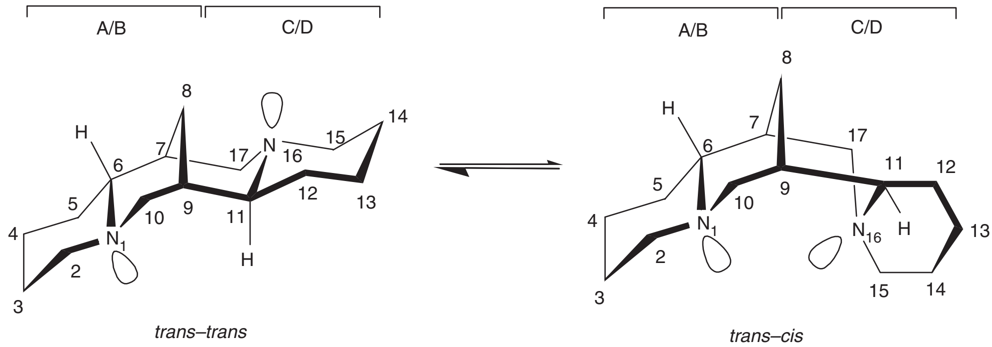
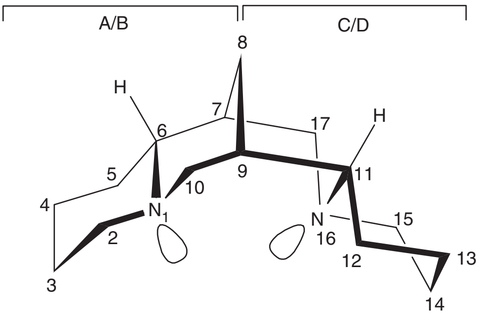


trans–trans

trans–cis

(a) Sparteine (b)



trans–trans

α–Isosparteine

Figure 1. Conformation and atom numbering in sparteine and α-isosparteine.

In the present study, we report the synthesis and properties of complexes formed by (−)-sparteine and α-isosparteine and $CuSO_4$. Magnetic properties of the new compounds have been also determined. The structure of newly obtained complexes was fully optimized by the Gaussian 03 package.

2. Experimental

The IR spectra were recorded on a FT–IR Bruker 113v spectrometer (KBr pellets). Electronic spectra were measured on a JASCO V-550 spectrophotometer, in methanol. ESI mass spectra were obtained on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer. The sample solutions were prepared in methanol. Elemental analyses were carried out by means of a Perkin–Elmer 2400 CHN automatic device. 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 has the magnetic field during the whole procedure, i.e. it is switched on before the cooling starts. Sparteine was obtained from commercial sparteine sulfate $C_{15}H_{26}N_2 \cdot H_2SO_4 \cdot 5H_2O$ [23]. $CuSO_4$ was supplied by Aldrich. α-Isosparteine was obtained according to the method described previously [24].

2.1. *Synthesis of complexes*

A solution of $CuSO_4$ (160 mg, 1 mmol) in methanol (25 mL) was added dropwise to a solution of sparteine (or α-isosparteine) (234 mg, 1 mmol) in methanol (15 mL) at room temperature. The resulting blue-green precipitate was filtered off and recrystallized from methanol.

[CuSO$_4$(sparteine)] (1). Blue-green crystals. Yield: 54%. M.p. >250°C (with decomposition). Anal. Calcd for $C_{15}H_{26}N_2CuSO_4$: C, 45.69; H, 6.60; N, 7.11; S, 8.12. Found: C, 45.58; H, 6.75; N, 7.19; S, 8.15.

[CuSO$_4$(α-isosparteine)] (2). Blue-green crystals. Yield: 47%. M.p. >250°C (with decomposition). Anal. Calcd for $C_{15}H_{26}N_2CuSO_4$: C, 45.69; H, 6.60; N, 7.11; S, 8.12. Found: C, 45.02; H, 6.87; N, 7.07; S, 8.42.

2.2. *DFT calculations*

Information on the geometry of **1** and **2** was obtained using quantum-chemical calculations. The calculations were carried out by the density functional theory method (DFT) at the B3LYP/(6)6-311+G level implemented in the Gaussian 03 program package.

3. Results and discussion

3.1. *Spectroscopic studies*

The ESI–mass spectra of **1** and **2** (figure 2) show peaks corresponding to fragmentation species including: $L{-}H^+$, $L{-}Cu^+$, $L_2CuSO_4^+$. In the mass spectrum of **1** additional ions are observed which can be assigned to the following types of complexes: $L{-}CuSO_4^+$, $L_2(CuSO_4)_2^+$ (L = sparteine).

The IR absorption in the spectra of quinolizidine and its derivatives in the 2840–2600 cm^{-1} region (the so-colled Bohlmann *trans*-band) is assigned to the stretching vibrations of one or more axially oriented C_α–H bonds. The intensity and shape of the band depend on the number of C–H groups and their steric environment in the molecule. In the range 2840–2600 cm^{-1} in the spectrum of α-isosparteine there are three peaks at 2793, 2758 and 2735 cm^{-1}. The *trans*-band of sparteine reveals two absorption maxima at about 2795 and 2760 cm^{-1} [25]. The attachment of copper atom to N results in the disappearance of the *trans*-band. The absence of this band in the spectra of the complexes suggests that both nitrogens are involved in coordination. Similarly, the features of the C–N absorptions around 1450 cm^{-1} undergo changes

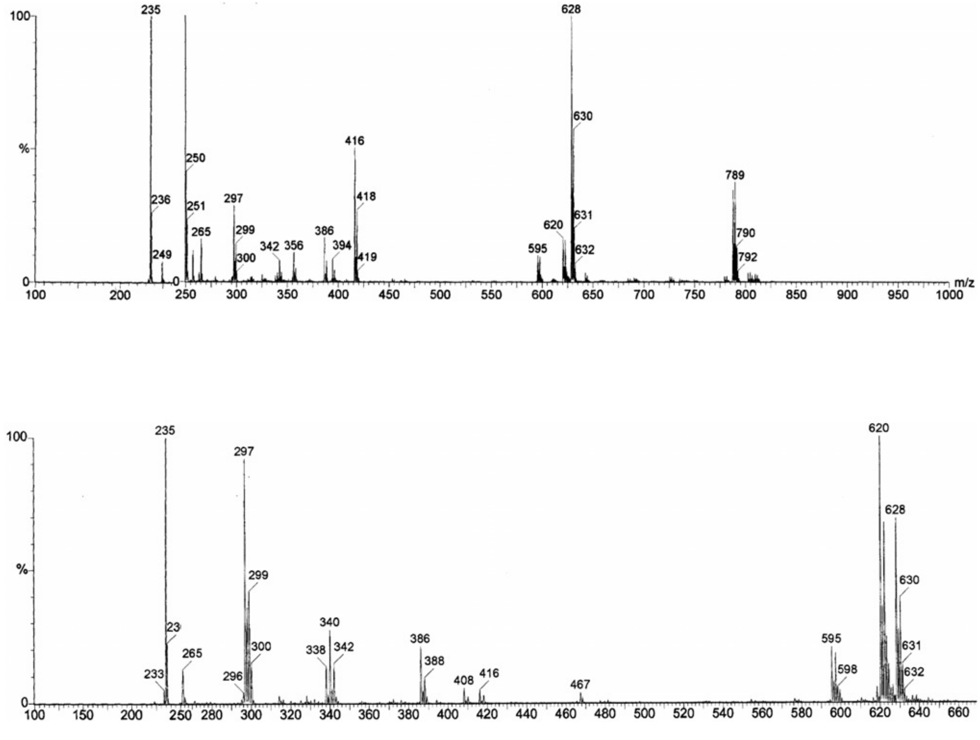


Figure 2. The ESI–mass spectra of sparteine (top) and α-isosparteine (bottom) complexes with $CuSO_4$.

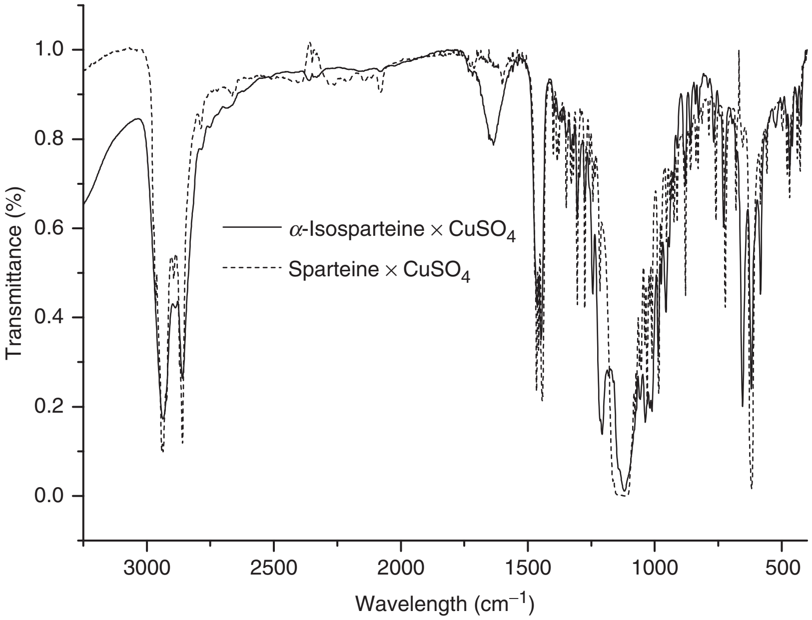


Figure 3. IR spectra of sparteine and α-isosparteine complexes with $CuSO_4$.

upon complexation. Such shifts (about $+20\,\mathrm{cm^{-1}}$) are associated with the fact that in the complexes the lone electron pair on nitrogen is tied up in formation of a fairly rigid nitrogen–copper bond. The IR spectra of new compounds exhibit additional bands at 1442 and $1100\,\mathrm{cm^{-1}}$, as expected for $\nu(\mathrm{SO_4^{2-}})$ [26] (figure 3).

Far-infrared spectra are similar for **1** and **2**, showing at 436 and $467\,\mathrm{cm^{-1}}$ the characteristic vibration due to ν(Cu–N) [27]. In electronic absorption spectra studied in methanol sparteine and α-isosparteine display intense transitions in the UV region, with maxima about 200 nm. The UV–Vis spectra of the studied compounds show ligand-to-metal charge transfer transitions at 273 nm ($\varepsilon = 3038$), and 313 nm ($\varepsilon = 3618$) for **1** and at 270 nm ($\varepsilon = 1961$), and 308 nm ($\varepsilon = 2864$) for **2**; the characteristic d–d transition is at 774 nm ($\varepsilon = 259$) for **1** and 663 nm ($\varepsilon = 138$) for **2** (figure 4). All these UV–Vis and NIR bands have been reported earlier by Choi *et al.* [28] who deduced for such complexes a distorted tetrahedral structure.

3.2. *Magnetic properties*

Copper(II) complexes have been the subject of many magnetic studies, analyzed in order to establish relationships with their structural features [29, 30]. Among them there are tetrahedrally distorted copper(II) (−)-sparteine complexes [16, 31, 32]. Magnetic data for compounds **1** and **2** were collected as a function of temperature (2–300 K).

Figure 5 shows a plot of magnetization, M and magnetic susceptibility in the form $1/\chi$ *versus* temperature in the temperature region 2–300 K. Magnetic susceptibility data for **1** and **2** follow the Curie–Weiss law in the whole temperature range indicating simple paramagnetism of both compounds. In contrast to earlier copper(II) (−)-sparteine complexes no anti-ferromagnetic behavior was observed.

3.3. *DFT calculations*

The structures of **1** and **2** were fully optimized by using the Gaussian 03 package at the B3LYP level with the 6-311+G basis set (see figure 6).

In **1**, the sparteine ligand displays *trans* and *cis* configuration at the A/B and C/D ring-junctions, respectively and all four rings adopt chair conformations, with the A-ring pointing towards the metal center and the D-ring pointing away from the metal center. In **2**, the α-isosparteine skeleton displays *trans*/*trans* configuration at the A/B and C/D ring-junctions and all four rings adopt chair conformations with both terminal rings (A and D) folding inwards towards the metal center. In sparteine–$\mathrm{CuSO_4}$ there is a significant difference in the length of the two N–Cu and Cu–O bonds (1.842 1.856 Å, and 1.848 1.840 Å). The N–Cu and Cu–O bonds in **2** are symmetry related, hence no differentiation in bond length is observed (1.835 Å, and 1.830 Å). The calculated distance between the two coordinating nitrogen atoms is larger in the sparteine complex (2.772 Å) than in α-isosparteine (2.674 Å). The difference in the computed energy, ΔE, between the new complexes is ca $52\,\mathrm{kcal\,mol^{-1}}$.

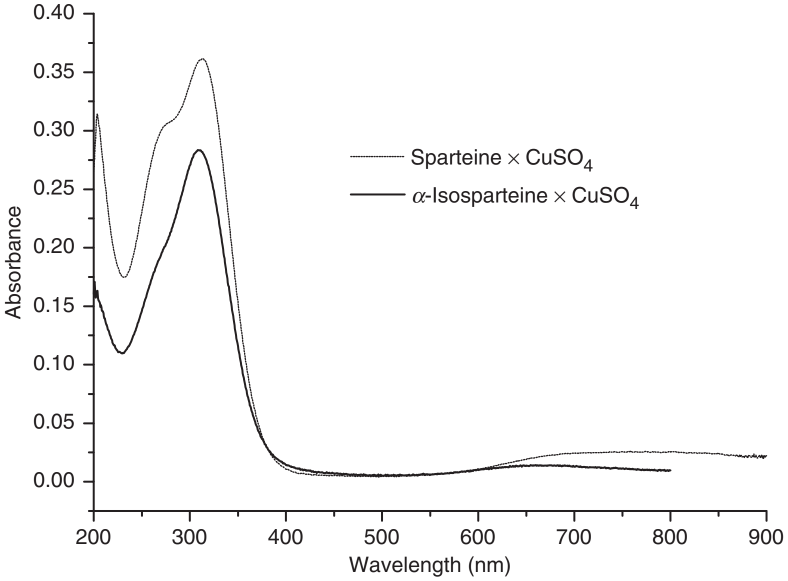


Figure 4. UV–Vis spectra of sparteine and α-isosparteine complexes with $CuSO_4$.

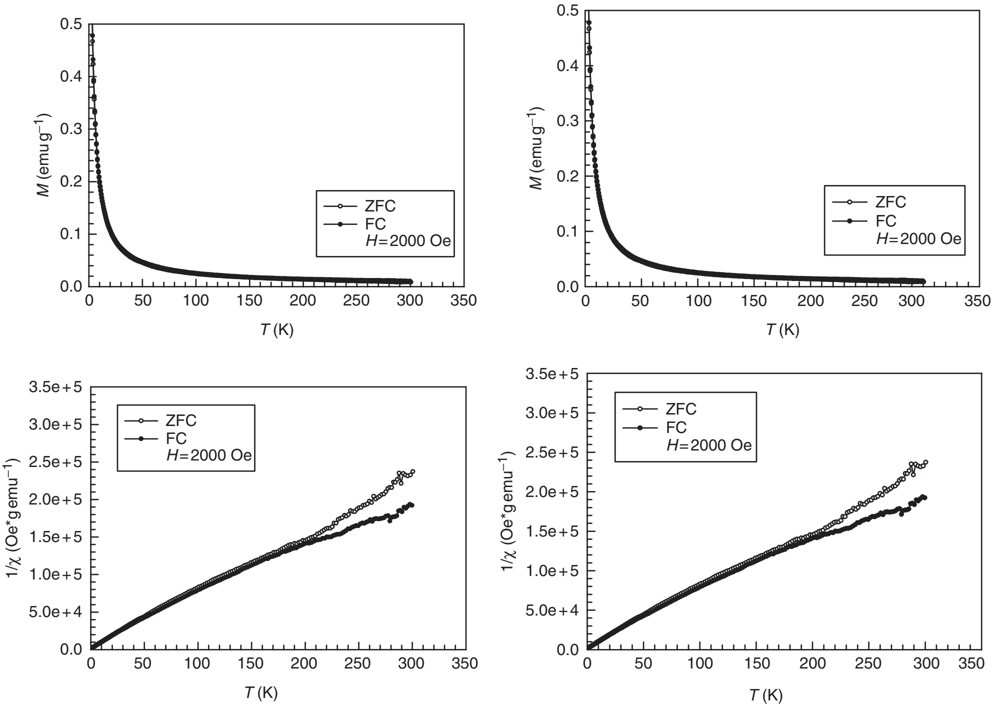
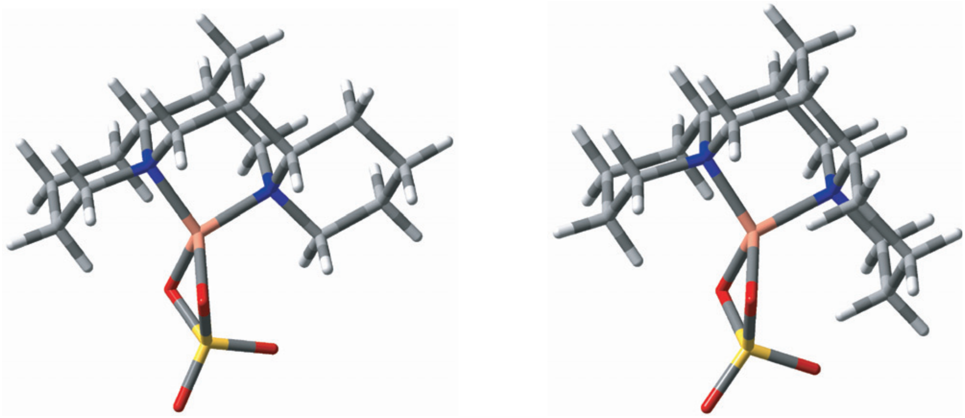


Figure 5. Plots of magnetization, M and magnetic susceptibility in the form $1/\chi$ *vs*. temperature in the temperature region 2–300 K for **1** (left side) and **2** (right side).



Sparteine–$CuSO_4$ α-Isosparteine–$CuSO_4$

Figure 6. The optimized structures of **1** and **2**.

4. Conclusions

New complexes with sparteine and α-isosparteine, prepared by reaction of the alkaloid with $CuSO_4$ were characterised by IR, UV–Vis and MS methods. α-Isosparteine remains structurally unchanged upon complexation whereas for sparteine conversion from the free base to the complex changes the configurational–conformational system from the *trans* C/D boat/chair into the *trans–cis* all-chair configuration. Magnetic susceptibility data for both **1** and **2** follow the Curie–Weiss law in the whole temperature range indicating simple paramagnetism of both.

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