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Sparteine and α-Isosparteine Complexes with Zn(II) and Cu(II): Structure and Spectroscopic Properties

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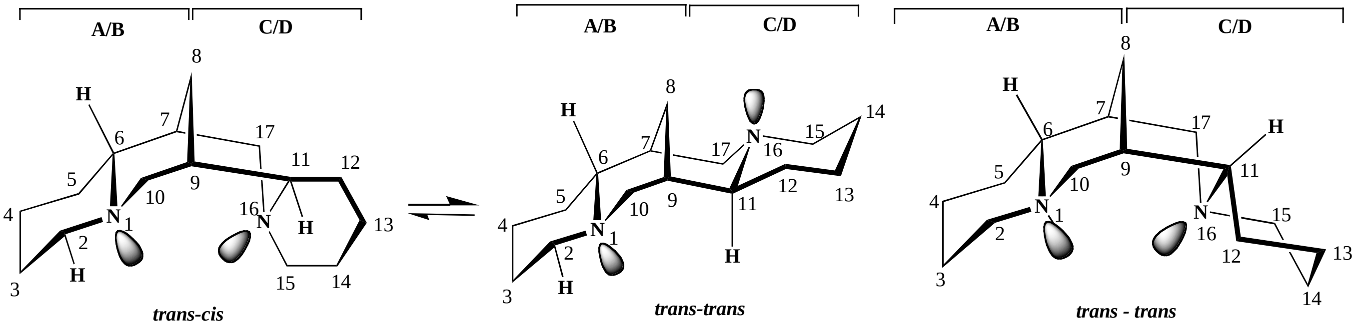
Abstract: Coordination compounds based on bis-quinolizidine alkaloids sparteine and α-isosparteine as ligands with Zn(II) and Cu(II) salts are described from the viewpoint of their spectroscopic and structural properties. In particular the complexes of LMX_2 types where L = alkaloid, X = halides (Cl^-, Br^-, I^-), pseudo-halides (CN^-, SCN^-) and oxy-anions ($C_4H_5OO^-$, CH_3COO^-, NO_3^-).

Keywords: Alkaloids, sparteine, α-isosparteine, Zn(II) and Cu(II) complexes, X-ray structure, spectroscopic properties.

1. INTRODUCTION

Lupine alkaloids have been intensively studied for many decades, mainly for their biological and biochemical significance [1]. The main representative of this group of compounds is bis-quinolizidine alkaloid sparteine (Sp) (**1**). The hitherto studies of bis-quinolizidine complexes concerned mainly sparteine and covered different aspect of possible applications of such complexes, starting from analytical determination of cations [2], identification of amines [3], through the role in living organism [4-9], to the applications in asymmetric synthesis [10-15]. The impact of sparteine as a chiral ligand in asymmetric synthesis, particularly in organolithium chemistry, has been profound and, more recently, its use has been extended to form complexes with other metal ions such as Mg, Pd, Zn and Cu [16]. Moreover, the Cu(II) sparteine complexes have been used as model compounds for type I copper(II) site of blue copper protein [17]. Sparteine was found to exhibit interesting configurational-conformational isomerism. In Sp the A/B rings make the *trans*-quinolizidine system practically unsusceptible to inversion of configuration at the atom N1. The C/D rings make a labile boat-chair *trans*-quinolizidine system that can be transformed into the *cis*-quinolizidine system as a result of inversion at the nitrogen atom N16 (see Fig. **1**). Sp has a strong preference (3.4 kcal/mol) for the conformation of a chair/chair *trans*-quinolizidine A/B system and a boat/chair *trans*-quinolizidine C/D system over the all-chair *trans/cis* conformation [18]. The reason for the dominance of this conformation is the repulsive activity of free electron pairs on the nitrogen atoms N1 and N16 in the all-chair conformer. Moreover, in this conformation, there is a set of van der Waals repulsion effects of pairs of hydrogen atoms situated close to each other in rings C and D: H8α-H12β, H12β-H17β and H14β-H17β which are not present in the conformation with a boat conformation of ring C. When the ring C adopts the boat conformation, only the hydrogen atom at C8 and the lone electron pair at N16 interact. In contrast to sparteine its diastereoisomer α-isosparteine (αSp) (**2**) has an all-chair system of *trans-trans* bis-quinolizidine (see Fig. **1**). This system is preserved in liquid and in solid state. It occurs in all α-isosparteine derivatives and does not change even on double protonation of the molecule, despite a strong repulsion between the positively charged $N1^+$-H and H-$N16^+$ groups in the dication molecule [19-21]. The calculations show that this *trans/trans* conformation has a global minimum, some 6 kcal/mol more stable than that with chair-chair A/B *trans* and B/C *cis* [18].



(1)

(2)

Fig. (1). Conformation and atom numbering in sparteine (**1**) and α-isosparteine (**2**).

In the 1970s, Boschmann, Weinstock and Carmack were the first to study the reactivity and properties of the complexes of sparteine and sparteine isomers with copper(II) chloride [22]. The comparative study of certain properties of Sp and αSp complexes with copper(II) chloride has shown that the differences in the properties are related to small differences in the structure of the complexes. Therefore, it can be supposed that the structural differences will be also reflected by different biological activities of the compounds compared. As shown by Kang and others, for asymmetric allylic alkylation, both Sp and αSp can behave as chiral bidentate ligands, however αSp is preferred [23-26]. Also αSp has stronger complexing power with Grignard Reagents than Sp [27]. Of particular interest to us were the effects of the stereochemical variations in bis-quinolizidine on the properties of copper(II) and zinc(II) complexes. The alkaloids have the terminal A and D rings folded-in over the metal or folded-out or a combination of both. In αSp, rings A and D make a more or less coplanar extension of rings B and C, extending beyond the two coordinating tertiary nitrogen atoms in such a way as to shield the metal atom from the attack by the reagent or solvent from two sides and also to inhibit the possibility for two alkaloid molecules to coordinate simultaneously with one metal

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ion. Sp has ring A folded down over the metal and ring D folded back away from the metal. This review describes our recent works on the synthesis, structures and spectroscopic properties of sparteine and α-isosparteine complexes with zinc(II) and copper(II) salts. The structure and properties of the complexes obtained have been compared with those of the complexes of this type known in literature.

2. SYNTHESIS

The majority of the complexes studied were obtained as a result of direct reaction of the alkaloid with the proper metal salt in a methanol solvent [28-33] or in ethanol-triethyl orthoformate (5:1 v/v) solution [34-38]. The complexes with $M(CN)_2$, $M(SCN)_2$, MI_2 (M = Zn, Cu) and CuN_3 were obtained as a result of the ligand exchange reaction of the salt coordinated. The reaction was based on the lability of nitrate anions(V), which easily undergo ligand exchange with various anions [39]. Depending on the complex obtained, the reaction was conducted either in methanol or in ethanol-triethyl orthoformate solution [40,41]. The type of alkaloid (Sp, αSp) has no significant effect on the course of the reaction. Sparteine complexes with CuX_2 and ZnX_2 (X = Cl, Br) were obtained as a result of the reaction of the natural base (-)-sparteine and elemental metals (Cu and Zn) in a CCl_4/DMSO [42] (or CBr_4/DMSO [43]) solvent system and Lopez and co-workers obtained the sparteine complexes with $CuCl_2$ by first deprotonating CH_3-NO_2 with *n*-BuLi, and than reacting the product with [Me_2SCuBr] followed by the addition of (-)-sparteine [44]. All the compounds analysed are the 1:1 stoichiometry complexes (alkaloid: metal).

3. SPECTROSCOPIC FEATURES

The IR absorption in the spectra of quinolizidine and its derivatives in the 2840-2600 cm^{-1} region (the so-called 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 the above bonds 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 spectrum of *trans-band* of sparteine reveals two absorption maxima at about 2795 and 2760 cm^{-1} [45]. The attachment of a metal atom to N atoms results in the disappearance of the *trans-band*. The absence of this band in the spectrum of the complexes suggests that both nitrogen atoms are involved in coordination. Similarly, the features of the C–N absorptions around 1450 cm^{-1} undergo changes upon complexation. The shifts (by about +20 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–metal bond. The occurrence of the absorption bands in the 420–470 cm^{-1} region has been assigned to ν (M-N) modes. The IR spectra of the complexes exhibit additional bands assigned to coordinated anions (see Table **1**). The type of binding in metal carboxylates has often been distinguished on the basis of their IR spectra. The acetate ion has the symmetric stretching frequency ν_s (COO$^-$) and the asymmetric stretching frequency ν_a (COO$^-$) modes at ~ 1450 and 1570 cm^{-1}, respectively, and these frequencies can vary by ±20 cm^{-1}. According to Deacon and Philips [46], the monodentate complexes exhibit Å values [ν_a (COO$^-$) - ν_s (COO$^-$)] which are greater than in the ionic complexes. Bidentate complexes exhibit Å values which are significantly lower than the ionic values. The Å value for ionic acetate is 164 cm^{-1} [47]. Generally, monodentate complexes exhibit Å value which is much greater than 200 cm^{-1}, and bidentate complexes exhibit Å value which is lower than 120 cm^{-1}. For sparteine and α-isosparteine complexes with zinc and copper acetate, the Å values are in the range of 200-300 cm^{-1} indicating that the acetate ligands in this complexes coordinate to the metal center in a monodentate fashion. In the electronic absorption spectra recorded in methanol, sparteine and α-isosparteine display a intense transitions in the UV region, with the maximum at about 202 nm. The UV-vis spectra of the compounds studied show the ligand-to-metal charge transfer transitions (LMCT) in the range 200-300 nm; and the characteristic band of d-d transition at over 600 nm. All these UV-Vis NIR bands have been reported earlier by Choi *et al.* [48] who deduced for such complexes a tetrahedral distorted structure.

The molecular structures of newly obtained zinc(II) complexes in solution have been inferred from their ^{1}H and ^{13}C NMR spectra. For tetracyclic alkaloids, we can use quite precise criteria of conformation, being the ^{13}C chemical shifts of the atoms C12 and C14 (in ring D). These atoms are exposed to the γ-synclinal effects from the atoms C8 and C17 in the chair conformers but not in the boat ones. The less precise criterion is the ^{1}H-^{1}H coupling constant of the bridgehead proton and the proton at the next carbon atom (between the bridgehead C atom and the nitrogen atom) from the β-side. In the alkaloids with the sparteine skeleton the coupling constant is denoted as $J_{7\text{-}17\beta}$. If ring C is a chair, $J_{7\text{-}17\beta}$ is small (less than 3 Hz in complexes), if it is a boat, $J_{7\text{-}17\beta}$ takes a value from above 10 Hz (10.8 Hz in sparteine [52]). The signals of the protons H9 and the two H10 can indicate the conformation of ring B. The chair conformation (in all investigated compounds) of the ring is connected with the gauche position of H9 and the two H10 and with two small vicinal coupling constants (about 2.0 Hz). Most indicative of the all-chair sparteine skeleton in complexes of sparteine are the large upfield shifts observed on C12, C14 and C17, which in the cis-quinolizidine fragment C/D are subjected to γ-gauche interaction (Table **2**). It results in a diamagnetic shift of the signals assigned to these carbon atoms by 7-11 ppm relative to those for the free base. The γ-gauche effect on C8 is undetectable because in sparteine the interaction of one of the C8 protons with the lone electron pair on N16 through space causes a strong upfield shift of the C8 signal [53]. The lack of this interaction in the all chair conformation of the complexes is compensated by the γ-gauche effect, so the chemical shift at C8 in the spectra of the complexes is close to that in the spectra of the free base. For sparteine the pure complexation effect of Cα to the nitrogen atom can be detected only on C2. The signal assigned to the other carbon atom at α position to the nitrogen atom C15 is shifted towards higher field values mainly because of the conformational changes in the C/D system. The structure of the ligand implies that the coordinated anions are inequivalent and hence give two different signals in the NMR spectra (Table **3**). From the appearance of only eight signals in the spectra of α-isosparteine complexes it is evident that these complexes have symmetric structure. In the NMR spectra of these complexes, the chemical shifts of the carbon atoms are similar to those reported for α-isosparteine (Table **2**). Taking into regard the symmetrical structure of the complexes, the signal of low intensity (slightly over 36 ppm) must be assigned to C8. All the remaining signals are the signals assigned to the two carbon atoms. The most distinct ^{13}C NMR spectroscopic feature of sparteine and its complexes is the bridge carbon signal C8, whose position is diagnostic of the conformation of the two fused B/C rings in the sparteine skeleton. According to the criterion of Bohlmann and Zeisberg for the one carbon bridge in the bicycle [3.3.1] moiety, this resonance is expected to move downfield in the sequence boat/boat, chair/boat, chair/chair [53,54]. For sparteine (chair/boat) this resonance occurs at about 27.5 ppm; for α-isosparteine (chair/chair) at 36.4 ppm [55]. In the spectra of α-isosparteine complexes the complexation causes chemical shifts of carbon atoms in α-position to nitrogen atoms (C2, C6, C10, C11, C15 and C17) and the shifts have the positive sign and range from +1.2 to +3.6 ppm [56]. Thus it can be concluded that the nature of the coordinating anions in sparteine and α-isosparteine complexes has no effect on the chemical shifts of the carbon atoms. Another notable aspect of the NMR spectra of the complexes is the ^{1}H resonance. The formation of the complexes by

Table 1. Selected Spectroscopic Data of Complexes Studied

Complex	IR ν(X-Y) cm^{-1}	Ref.
SpZnCl$_2$	(Zn-N) 460, 438 (Zn-Cl) 330, 305	[48]
SpZnBr$_2$	(Zn-N) 460, 435 (Zn-Br) 230, 210	[48]
SpZnI$_2$	(Zn-N) 460, 424 (Zn-I) 204, 190	[49]
SpZn(CN)$_2$	(C≡N) 2235 (N-Zn) 445	[28]
SpZn(SCN)$_2$	(C≡N) 2195 (N-Zn) 442	this paper
SpZn(CH$_3$COO)$_2$	(COO$^-$) 1624, 1616, 1392, 1327	[50]
SpZn(C$_4$H$_5$O$_2$)$_2$	(C=O) 1644, (C=C) 1602 (Zn-N) 421	[29]
αSpZnCl$_2$	(N-Zn) 465, 432 (Zn-Cl) 335, 310	[30]
αSpZnBr$_2$	(N-Zn) 462, 434 (Zn-Br) 225, 205	[30]
αSpZn(CN)$_2$	(C≡N) 2233 (N-Zn) 464	[30]
αSpZn(SCN)$_2$	(C≡N) 2190 (N-Zn) 440	this paper
αSpZn(CH$_3$COO)$_2$	xxx, 1614, 1393, 1320	[31]
αSpZn(C$_4$H$_5$O$_2$)$_2$	(C=O) 1644, (C=C) 1597 (Zn-N) 428	[29]
SpCuCl$_2$	(Cu-N) 468, 436 (Cu-Cl) 297, 274	[22]
SpCuBr$_2$	(Cu-N) 469, 438 (Cu-Br) 248, 236	[51]
SpCu(CH$_3$COO)$_2$	(COO$^-$) 1606, 1585, 1377, 1325	[50]
SpCu(SCN)$_2$	(C≡N) 2150 (N-Zn) 445	this paper
αSpCuCl$_2$	(Cu-N) 478, 462 (Cu-Cl) 298, 285	[22]
αSpCuBr$_2$	(Cu-N) 475, 464 (Cu-Cl) 246, 242	[32]
αSpCu(SCN)$_2$	(C≡N) 2140 (N-Zn) 440	this paper
αSpCu(CH$_3$COO)$_2$	(COO$^-$) 1632, 1588, 1397, 1327	this paper
Complex	UV-vis [λ_{max} (nm) (log ε)]	Ref.
SpCuCl$_2$	780 (184), 355 (1880), 308 (2180), 245 (2368)	[22]
SpCuBr$_2$	822 (327), 427 (2877), 344 (4109), 277 (2016)	[51]
SpCu(CH$_3$COO)$_2$	786 (174), 932 (80)	[50]
SpCu(SCN)$_2$	468 (14969), 226 (15057), 212 (14924)	this paper
αSpCuCl$_2$	949 (82), 760 (113), 321 (2368), 242 (1684)	[22]
αSpCuBr$_2$	804 (270), 420 (867), 333 (2586), 251 (2477), 204 (7218)	[32]
αSpCu(CH$_3$COO)$_2$	675 (144), 305 (2743), 206 (2515)	this paper
αSpCu(SCN)$_2$	473 (1325), 225 (6684), 208 (14928)	this paper

the way of the metal coordination by two nitrogen atoms is evident for both sparteine and α-isosparteine by changes in the chemical shift of the protons bonded to carbon atoms at α position to the nitrogen atoms (H2, H6, H10, H11, H15 and H17). The chemical shifts of these protons are in the range 1.75-3.95 ppm for sparteine complexes and 1.85-3.70 ppm for α-isosparteine complexes [56].

The mass spectrometry study has demonstrated that the Zn(II) complexes of (-)-sparteine and (-)-α-isosparteine could be differentiated by mass spectrometric analysis, using both their EI and their FAB mass spectra. Analysis of the EI-MS spectra has been based on the dependence of the decomposition of the bis-quinolizidine skeleton on the stereochemistry at the A/B and C/D ring junctions [57-60]. In the EI mass spectra of the complexes investigated, molecular ions were not observed. The principal fragmentation pathways of the complexes of Sp and αSp are similar, but show differences in the relative abundances of important fragment ions. The differences in the EI fragmentation of the isomeric complexes of Sp and αSp have been expressed quantitatively by comparing the calculated values of the μ coefficients, i.e. the abundances of selected fragment ions to that of the fragment ions $C_{15}H_{26}N_2$ (m/z 234). The differences between the calculated values of μ can be sufficient to differentiate the ligands of zinc(II) complexes of Sp and αSp. The spectra of the complexes of Sp are characterised by higher μ values than those of their isomeric αSp complexes [61]. In the FAB spectra of zinc(II) Sp and αSp complexes, the molecular and ($C_{15}H_{25}N_2Zn$+H) ions were absent. The FAB spectra of the complexes studied show differences in the abundances of the fragment ions situated at m/z 233 ($C_{15}H_{25}N_2$), which allowed the differentiation of the ligand (Sp or αSp) in the molecules of these compounds. The data presented assist the structural determination of new complexes of this type [61]. The ESI-mass spectra of complexes with zinc acetate and methacrylate show signals assigned to the proto-

Table 2. **^{13}C NMR Spectra of Selected Carbon Atoms for Sparteine and α-isosparteine Complexes with Zn(II) Salts in CDCl$_3$ (δ in ppm) (*complexation effect* given in italics*)**

Carbon Atom Compound	C8	C12	C14	C17	Literature
Sp	27.4	34.5	25.8	53.4	[55]
SpZnCl$_2$	27.9 *+0.5*	23.8 *-10.7*	17.8 *-8.0*	45.2 *-8.2*	[33]
SpZnI$_2$	27.9 *-1.6*	23.7 *-10.8*	17.5 *-8.3*	45.2 *-8.2*	this paper
SpZn(CN)$_2$	28.2 *+0.8*	23.9 *-10.6*	17.8 *-8.0*	46.3 *-7.1*	[28]
SpZn(SCN)$_2$	27.4 *0.0*	23.8 *-10.7*	17.3 *-8.5*	45.8 *-7.6*	this paper
SpZn(CH$_3$COO)$_2$	28.6 *+1.2*	23.9 *-10.6*	17.7 *-8.1*	45.6 *-7.8*	[56]
SpZn(C$_4$H$_5$O$_2$)$_2$	28.3 *+0.8*	24.0 *-10.5*	17.8 *-8.0*	45.7 *-7.7*	[29]
αSp	36.4	30.0	25.3	55.8	[55]
αSpZnCl$_2$	36.7 *+0.3*	28.3 *-1.7*	24.2 *-1.1*	57.1 *+1.3*	[30]
αSpZnBr$_2$	36.7 *+0.3*	28.5 *-1.5*	23.8 *-1.5*	57.1 *+1.3*	[30]
αSpZnI$_2$	36.7 *+0.3*	29.0 *-1.0*	23.5 *-1.8*	57.1 *+1.3*	this paper
αSpZn(CN)$_2$	36.3 *-0.1*	28.5 *-1.5*	23.9 *-1.4*	57.2 *+1.4*	this paper
αSpZn(SCN)$_2$	36.2 *-0.2*	29.7 *-0.3*	24.5 *-0.8*	57.1 *+1.3*	this paper
αSpZn(CH$_3$COO)$_2$	36.9 *+0.5*	28.2 *-1.8*	24.0 *-1.3*	57.2 *+1.4*	[31]
αSpZn(C$_4$H$_5$O$_2$)$_2$	36.8 *+0.4*	27.8 *-2.2*	24.0 *-1.3*	57.3 *+1.5*	[29]

* Complexation effects were determined by subtracting the chemical shifts of the individual carbon atoms of the free base from those of the corresponding atoms of the complexes.

Table 3. **^{13}C NMR Spectra of Coordinated Anions X for sparteine and α-isosparteine Complexes with Zn(II) salts in CDCl$_3$ (δ in ppm)**

Carbon Atom Compound	-CN	-SCN	Acetate Group		Methacrylate Group				Literature
			>C=O	-CH$_3$	-CH$_3$	=CH$_2$	=C=	=C=O	
SpZn(CN)$_2$	137.0 138.4	-	-	-	-	-	-	-	[28]
SpZn(SCN)$_2$	-	129.2 130.8	-	-	-	-	-	-	this paper
SpZn(CH$_3$COO)$_2$	-	-	176.9 177.3	23.0	-	-	-	-	[56]
SpZn(C$_4$H$_5$O$_2$)$_2$	-	-	-	-	19.6	121.4 121.7	140.5 141.1	172.8 174.3	[29]
αSpZn(CN)$_2$	138.8	-	-	-	-	-	-	-	[30]
αSpZn(SCN)$_2$	-	131.4	-	-	-	-	-	-	this paper
αSpZn(CH$_3$COO)$_2$	-	-	177.0	17.7	-	-	-	-	[31]
αSpZn(C$_4$H$_5$O$_2$)$_2$	-	-	-	-	19.6	121.4	141.2	172.4	[29]

nated ions formed as a result of abstraction of a single methacrylate or acetate group from the complex [29,31].

4. X-RAY STRUCTURE

The tetrahedral Zn(II) and Cu(II) complexes investigated are built of chiral Sp or αSp acting as a bidentate ligand, and monodentate (and the same) chloride, bromide, iodide, cyanide, thiocyanide, acetate, methacrylate, nitrate and azide anions, respectively. Metalcomplexation of Sp induces changes in the conformation of ring C from boat to chair and simultaneous inversion of configuration at the C/D ring junction from *trans* to *cis*. The geometry around the metal centre in all complexes in question can be described by the values of the deformation parameters δ_{tetr} (Eq. 1). It should be noted that 0 value of δ_{tetr} indicates the ideal tetrahedral geometry, as opposed to 44 which signals the square planar arrangement of ligands [62].

$$\delta = \sqrt{\sum_{i=1}^{6} (\alpha_i - 109.5)^2 / 6} \qquad (1)$$

The distortions from the tetrahedral geometry around the metal atom in the complexes investigated concern mainly the two bond angles: the bite angle N1-M-N16 which is limited by the rigidity of the alkaloid ligands, both, Sp and αSp, and the X1-M-X2 angle, influenced by the monodentate ligands and steric hindrance produced by them (see Fig. **2**). The bite angle N1-M-N16 is approximately constant in the Sp and αSp complexes of Zn(II) and Cu(II) investigated and adopts the value of ~90^{o} (Table **4**) [28-32, 34-38, 40-44, 49-51, 63]. As follows, the bite angle is not susceptible to configurational changes connected with the *cis*/*trans* isomerization of the *C*/*D* ring fusion within the alkaloid skeleton. However, the anions coordinated to the metal atom influence the X1-M-X2 angle, where X denotes the anionic ligand atom. In the αSp complexes with zinc chloride, bromide and cyanide the dihedral angles between the planes N1-Zn-N16 and X1-Zn-X2 of 71.3, 71.1 and 71.4^{o}, respectively differ significantly from orthogonality and from the values observed for the analogous complexes containing Sp as a bidentate ligand, i.e. $SpZnCl_2$ (A), $SpZnBr_2$ (B) and $SpZn(CN)_2$ (C) complexes [28, 30, 36, 37, 43]. In the latter series, these angles adopt the values much closer to orthogonal, namely 82.2^{o} in A [37], 82.4 and 83.5^{o} in two polymorphic form of B [36, 43], and 82.8^{o} in C [28], respectively. For the $SpZnI_2$ complex this angle adopts the value of 83.1^{o} [49].

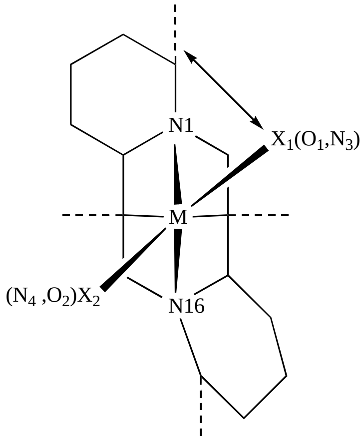

Fig. (2). View showing dihedral angle between N1-M-N16 and X1-M-X2 (or O1-M-O2 or N3-M-N4) planes.

From this comparison it is evident that the steric hindrance in the αSp complexes is greater than in their Sp analogues, although α-isosparteine seems to have a stronger complexing power [27]. In the complexes with zinc acetate and methacrylate, the Zn atom is surrounded by two N atoms of the chelating Sp or αSp ligand (N1 and N16) and by two atoms of two acetate or methacrylate anions. Thus, in these complexes, the coordination of the zinc atom is determined by the steric effects of the anion coordinated being of much greater volume than the earlier considered ones. In complexes with $Zn(CH_3COO)_2$, the acetate ligands whose carbonyl groups are directed inwards, towards the Zn atom, bring about a steric hindrance which leads up to enlargement of the bond angle O1-Zn-O2 to a very high value of over 126^{o}. This angle varies significantly in the zinc methacrylate complexes, being much wider in the αSp complex (122.8^{o}) than in the Sp complex, in which the mean of two observations is 111.6^{o} [29]. The tetrahedral geometry of Zn(II) in $\alpha SpZn(CH_3COO)_2$ complex is almost not distorted, the dihedral angle between the N1-Zn-N16 and O1-Zn-O2 planes is 85.0^{o}, a value close to that of a perfect tetrahedron (90^{o}) [31]. In the Sp complex this angle amounts to 74.0^{o} [50]. This observation is in line with the observations made for the Sp and αSp complexes with zinc methacrylate [29]. In α-isosparteine this angle equals to 84.6^{o}, while in sparteine it amounts to 70.9 and 75.9^{o} [29]. This suggest that the steric hindrance in sparteine zinc acetate and methacrylate complexes is more severe than in analogous α-isosparteine complexes. The majority of four-coordinate copper(II) complexes prefer to adopt a square-planar structure as a natural consequence of the d^9 configuration, and the distortion from this structure is due to the coordination of a bulky bidentate sparteine or α-isosparteine to the Cu(II) atom. The molecules of the $SpCu(NO_3)_2$ complex are mixed four- and five-coordinate in one crystalline phase and only four-coordinate in the other [63]. The situation of the nitrate ligand being sometimes monodentate and sometimes bidentate in Cu(II)Sp is very unusual. In analogous αSp complex nitrate ligands are coordinated to the Cu atom in a monodentate mode, and the coordination geometry around the Cu(II) center is four-coordinate. The dihedral angle between the N1-Cu-N16 and O1-Cu-O2 planes for $\alpha SpCu(NO_3)_2$ is 27.7^{o} [34] and is smaller than the corresponding dihedral angle of 31.7^{o} reported for the four-coordinate $SpCu(NO_3)_2$ [63]. In the two complexes we observe the small O1-Cu-O2 angles slightly above 87.0^{o} In Sp and αSp complexes with copper(II) azide, the Cu atom is surrounded by two N atoms (N1 and N16) of the chelating alkaloid and by two nitrogen atoms (N3 and N4) of the two azide anions, forming a distorted CuN4 tetrahedron. The N1-Cu-N16 plane is twisted from the N3-Cu-N4 plane by 50.0^{o} and 55.3^{o} for $\alpha SpCu(N_3)_2$ [40] and $SpCu(N_3)_2$ [41], respectively. This smaller dihedral angle can be visualized as a balance between the crystal field stabilization effect and the steric effect of alkaloid. The acetate ion, like the nitrate or nitrite ions, can coordinate to a metal in either a mono- or a bidentate fashion. The Cu(II) ion in $SpCu(CH_3COO)_2$ complex is exclusively four-coordinate with a highly distorted tetrahedral geometry and the two acetate ions in it are monodentate [38]. The dihedral angle between the N1-Cu-N16 and O1-Cu-O2 planes is 45.8^{o}, which is much lower than the value obtained for the Sp complex with zinc acetate [50]). This reduced dihedral angle is definitely attributed to electronic effect, since the copper(II) ion favors the square-planar structure around the metal centre over the tetrahedral structure. The O1-Cu-O2 bond angle takes the value of 92.4^{o}, which is much lower than in the complexes of Sp and αSp with zinc acetate [31, 50]. In complexes with the copper(II) chloride and bromide distortions from Cu(II) tetrahedral environment are manifested in much smaller values of the dihedral angle than the value obtained for acetate, nitrate or nitrite complex. The dihedral angles between the N1-Cu-N16 and X1-Cu-X2 planes adopt the values of 75^{o} in sparteine complexes [35, 44, 51] and about 60^{o} in α-isospartiene one [32]. As can be seen from Table **4**, the variations in the ligand bite angle in these complexes are very small, ranging from 89.5 to 90.5^{o}. As follows from this comparison, a change from Sp to αSp ligand in Cu(II) chloride and bromide

Table 4. Selected Crystal Data for Complexes Studied

Complex	δ Parameter	Dihedral Angles (°) Between Planes N1-M-N16 and X1-M-X2	N1-M-N16 Angles (°)	X1-M-X2 Angles (°)	Literature
$SpZnCl_2$	10.6	82.2	88.7	115.9	[37]
$\alpha SpZnCl_2$	15.3	71.3	87.9	110.9	[30]
$SpZnBr_2$ (two polymorphic forms)	10.5/10.6	82.4/83.5	88.9/88.7	114.2/113.7	[36/43]
$\alpha SpZnBr_2$	13.8	71.1	88.1	108.5	[30]
$SpZnI_2$	10.8	83.1	88.3	111.94	[49]
$SpZn(CN)_2$	10.7	82.8	88.5	118.2	[28]
$\alpha SpZn(CN)_2$	13.6	71.4	87.7	113.2	[30]
$SpZn(CH_3COO)_2$	13.9	74.0	87.7	126.8	[50]
$\alpha SpZn(CH_3COO)_2$	12.1	85.0	86.5	126.9	[31]
$SpZn(C_4H_5O_2)_2$	14.4/12.6	70.9/75.9	87.8/88.5	108.9/114.3	[29]
$\alpha SpZn(C_4H_5O_2)_2$	10.8	84.6	87.9	122.8	[29]
$SpCuCl_2$	14.7	76.0	90.5	106.9	[44]
$SpCuBr_2$ (three polymorphic forms)	12.3/12.7/13.4	75.0/73.8/73.6	90.6/89.9/89.5	108.6/107.3/106.9	[35/51]
$\alpha SpCuBr_2$	18.1	60.4	89.8	100.6	[32]
$SpCu(CH_3COO)_2$	25.6	45.8	90.1	92.4	[38]
$SpCu(NO_3)_2$	12.3	31.7	90.2	87.8	[63]
$\alpha SpCu(NO_3)_2$	9.1	27.7	89.7	87.9	[34]
$SpCu(N_3)_2$	20.5	55.3	90.2	101.1	[41]
$\alpha SpCu(N_3)_2$	18.4	50.2	89.0	99.6	[40]

complexes does not affect the geometry determined by the ligand chelation. A comparison of the complexes with zinc and copper has pointed out the Cu(II) tendency towards inducing the change in configuration about the coordination centre from tetrahedral into square-planar. This tendency is manifested by the value of δ parameter much greater for the copper complexes and the angle between the N1-M-N16 and X1-M-X2 planes, (O1-M-O2 or N3-M-N4) much lower for the complexes with copper.

5. MAGNETIC PROPERTIES

Copper(II) halide compounds have been the subject of many polymorphic structural [35, 64, 65] and magnetic studies [51, 66-68]. Electronic and magnetic properties of such compounds have been analyzed in order to establish their relationships with the structural features. Among them there are tetrahedrally distorted copper(II) Sp complexes. There are reports of weak anti-ferromagnetic behavior characteristic of $SpCu(PhCO_2)Cl$ [67] and $SpCu(PhCO_2)Br$ [69] complexes. Lee and co-workers reported that the adduct of sparteine with $CuBr_4$ exhibits weak anti-ferromagnetism but its $CuCl_4^{2-}$ salt lacks such a property, even though the two crystals are isostructural [68]. In view of the anti-ferromagnetic interactions in the Cu(II) halide systems, hydrogen bonding and short Cu-X¨X-Cu contacts were considered as possible pathways for magnetic exchange [70-73]. The magnetic exchange between the 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 [74]. The magnetic data of $SpCuCl_2$ [35], $SpCuBr_2$ [35, 51] and $\alpha SpCuBr_2$ [32] have been analyzed using the theoretical expression (the Hamiltonian being $\hat{H} = -2J \Sigma \hat{S}_i\hat{S}_j$) proposed by Hall [75] for a uniform chain of local spin S = ½ (Eq. 2)

$$\chi_M = \frac{Ng^2\beta^2}{kT} \cdot \frac{A + B\chi + C\chi^2}{D + E\chi + F\chi^2 + G\chi^3} \qquad (2),$$

where N is the Avogadro number, β is the Bohr magneton, g is the spectroscopic splitting factor, $\chi = |J|/k$ and the seven parameters A-G are provided in Ref. [35]. The fitting results are $J = -1.89\ cm^{-1}$, $g = 2.20$ for $SpCuBr_2$ [35] and $J = 1.25\ cm^{-1}$, $g = 2.06$ for $\alpha SpCuBr_2$ [32]. The magnetic super-exchange in $SpCuCl_2$ and $\alpha SpCuBr_2$ either via a Cu-X-Cu bridge or via a Cu-X¨X-Cu contact is not likely to be observed. These compounds exhibit simple paramagnetism as opposed to the anti-ferromagnetic behavior of $SpCuBr_2$ [35]. The observed weak anti-ferromagnetism of sparteine complex with $CuBr_2$ cannot be due to a Cu-Br-Cu bridge between the molecules because the nearest interatomic Cu...Br distance in this compound of 6.012 Å is too long, but the Br...Br distance, 6.680 Å, is long enough for the Cu-Br¨Br-Cu magnetic super-exchange contact [35]. The magnitude of the halide-halide contact interaction depends also on the geometry of the super-exchange pathway. In $SpCuBr_2$, the torsion angle of the Cu-Br...Br-Cu contact pathway is 71.6° and the Cu-Br...Br angle is 101.93° [35].

CONCLUSIONS

Formation of the Sp complexes with Zn(II) and Cu(II) leads to a conversion of configuration at the N16 stereogenic center and the subsequent adoption of a chair conformation by C ring. This conformation ensures suitable conditions for formation of specific chelate-type complexes. αSp acts as a symmetrical bidentate chiral ligand with a privileged binding site for tetrahedral coordination and a tendency to utilize its two-fold symmetry in the crystal. Both alkaloids bind metal centers strongly and predictably. The geometry of all complexes investigated is fundamentally the same. The crystal structure analysis has shown that Sp and αSp force a highly distorted configuration of the MN_2X_2 coordination type.

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