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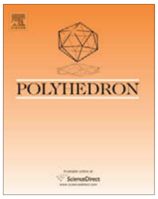

Crystal structures and spectroscopic properties of copper(II) pseudohalide complexes with two sparteine epimers, having a CuN_4 chromophore

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ABSTRACT

Tetrahedrally distorted copper(II) sparteine pseudohalide complexes having a CuN_4 chromophore were prepared and characterized by various spectroscopic techniques and X-ray crystallography. Among them, the crystal structures of copper(II) isothiocyanate complexes with two sparteine epimers, (−)-*l*-sparteine (Sp) and (−)-α-isosparteine (α-Sp), were determined. The N_{Sp}–Cu–N_{Sp} plane in copper(II) (−)-*l*-sparteine isothiocyanate [Cu(Sp)$(NCS)_2$] and copper(II) (−)-α-isosparteine isothiocyanate [Cu(α-Sp)$(NCS)_2$] is twisted by 58.2(6)° and 52.2(9)°, respectively, from the N_{NCS}–Cu–N_{NCS} plane. Based on the values of the dihedral angles and tilted distances of these two complexes, the geometry around Cu(II) in Cu(α-Sp)$(NCS)_2$ is more distorted from the perfect tetrahedron than that in Cu(Sp)$(NCS)_2$. For copper(II) sparteine pseudohalide (NCS^- and N_3^-) complexes having a CuN_4 chromophore, the EPR and the optical spectral data were collected. The results of X-ray crystallography and ESR spectroscopy are in a good agreement with the assumption that the degree of distortion from planarity to tetrahedron will reduce the $A_{||}$ value of four-coordinate copper(II) sparteine pseudohalide complexes.

1. Introduction

There has been considerable interest in the coordination chemistry of four- or five-coordinate copper(II) compounds that mimic the aspects of the properties of copper in protein for more than three decades [1,2]. Among the properties that have drawn the attraction of bio-inorganic chemists, have been the low energy charge transfer transitions (about 600 nm), the unusually positive reduction potentials and the small hyperfine coupling constants $A_{||}$ (less than $90 \times 10^{-4}\,cm^{-1}$) in the ESR spectrum of type I copper(II) protein [1–7]. These extraordinary properties are well known to be related to the copper coordination sphere in the metalloproteins and complexes with biomolecules and/or systems with small organic ligands.

The neutral alkaloid (−)-sparteine ligand has been of much of interest due to its steric requirements imposed by the configurational bulky system since the [(−)-sparteine](maleonitrile-dithiolato)copper(II) complex, as a potential model for distorted-tetrahedral environments of type 1 copper(II) active sites, was reported in 2001 [8]. There exist three diastereomers of (−)-sparteine, (6R,7S,8S,14S)-(−)-sparteine (Sp; $C_{15}H_{26}N_2$), (6R,7S,8S,14R)-(−)-α-isosparteine (α-Sp; α-$C_{15}H_{26}N_2$) and (6S,7S,8S,14S)-(−)-β-isosparteine (β-Sp; β-$C_{15}H_{26}N_2$) (see Scheme 1). These sparteine ligands have attracted research attention and have been intensively utilized in medicinal chemistry [9] and asymmetric synthesis of chiral compounds [10–12]. Crystal structures of copper(II) complexes with the neutral alkaloid sparteine diastereomers have been reported [13–23]. The sparteine copper(II) complexes that have been reported [13–22], with one exception [23], are four-coordinate and tetrahedrally distorted from the ligand-field favorable square–planar geometry [24]. The pseudo-tetrahedral geometry around the Cu(II) center of these complexes is due to the steric requirements imposed by the bulky sparteine ligand. Of course, the role of anionic ligand, L, in these complexes of the type [Cu(Sp)L_2] or [Cu(α-Sp)L_2] is also important in the ultimate molecular structure.

In this study, copper(II) sparteine pseudohalide complexes having a CuN_4 chromophore were prepared and characterized. The crystal structures of these complexes were determined in order to evaluate the extent of distortion imposed by the (−)-sparteine ligand compared with that imposed by the (−)-α-isosparteine ligand. We also attempted to investigate the relationships between the structure and spectroscopic properties in tetrahedrally distorted copper(II) sparteine complexes having a CuN_4 chromophore.

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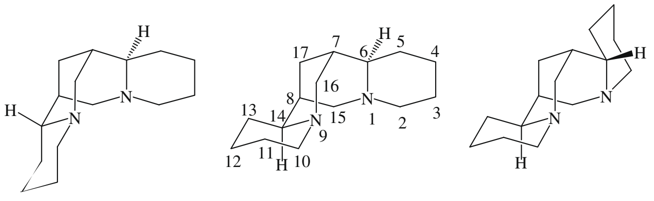

(a) (α-Sp) (b) (Sp) (c) (β-Sp)

Scheme 1. Three diastereomers of (−)-sparteine.

2. Experimental

2.1. Materials and preparation

All reagents and solvents were obtained commercially either from Fisher Scientific Co. or Aldrich Chemical Co. and were used without further purification, except where noted. Anhydrous ethanol was distilled from calcium hydride and stored under argon. (−)-Sparteine (Sp; $C_{15}H_{26}N_2$) was purchased from Sigma Chemical Company. The (−)-α-isosparteine (α-Sp; α-$C_{15}H_{26}N_2$) was derived from commercially available (−)-sparteine by a method in the literature [25].

2.1.1. Cu(Sp)(NCS)$_2$ (**1**) and Cu(Sp)(N$_3$)$_2$ (**2**)

The precursor copper(II) complex, [Cu(Sp)(NO$_3$)$_2$], was prepared by mixing an ethanol-triethylorthoformate (5:1 v/v) solution of copper(II) nitrate hemipentahydrate (3.00 g, 12.42 mmol) with a stoichiometric amount of (−)-sparteine at room temperature for 2 h. The resulting blue precipitate was filtered off, washed with triethylorthoformate, and then dried in a vacuum. Complex **1**, [Cu(Sp)(NCS)$_2$], was prepared from the substitution reaction of [Cu(Sp)(NO$_3$)$_2$] (1.00 g, 2.37 mmol) with a stoichiometric amount of NaNCS in 50 ml ethanol-triethylorthoformate (5:1 v/v) solution. The reddish brown precipitate was filtered off, washed with cold absolute ethanol, and then dried in a vacuum. The yield of the product was 78.5%. Dark reddish brown single crystals were obtained by recrystallization at about 278 K from a dichloromethane–triethylorthoformate (5:1 v/v) solution under carbon tetrachloride vapor. *Anal.* Calc. for $CuC_{17}H_{26}N_4S_2$: C, 49.31; H, 6.33; N, 13.53. Found: C, 49.08; H, 6.35; N, 13.63%. IR (in cm^{-1}, KBr): 2934 (s, ν_s(C–H)), 2856 (s, ν_s(C–H)), 2077 (vs, ν_a(NCS)), 2058 (vs, ν_a(NCS)), 1467 (m, ν_a(C–H)), 1434 (s, ν_a(C–H)), 1304 (s, ν_s(NCS)), 1292 (m, ν_s(NCS)), 432 (w, ν(Cu–N$_{Sp}$)). Complex **2**, [Cu(Sp)(N$_3$)$_2$], was prepared from the substitution reaction of [Cu(Sp)(NO$_3$)$_2$] (1.00 g, 2.37 mmol) with a stoichiometric amount of NaN$_3$ in 50 ml ethanol-triethylorthoformate (5:1 v/v) solution as reported [21]. The yield of the dark yellowish brown precipitate obtained was 85.3%. *Anal.* Calc. for $CuC_{15}H_{26}N_8$: C, 47.17; H, 6.86; N, 29.34. Found: C, 47.83; H, 6.91; N, 29.59%. IR (in cm^{-1}, KBr): 2929 (s, ν_s(C–H)), 2861 (s, ν_s(C–H)), 2048 (vs, ν_a(N$_3$)), 2058 (vs, ν_a(N$_3$)), 1466 (m, ν_a(C–H)), 1447 (s, ν_a(C–H)), 1283 (s, ν_s(N$_3$)), 468 (w, ν(Cu–N$_{Sp}$)).

2.1.2. Cu(α-Sp)(NCS)$_2$ (**3**) and Cu(α-Sp)(N$_3$)$_2$ (**4**)

The precursor copper(II) complex, [Cu(α-Sp)(NO$_3$)$_2$], was prepared in a glove box by mixing an ethanol-triethylorthoformate (5:1 v/v) solution of copper(II) nitrate hemipentahydrate (1.20 g, 5.16 mmol) with a stoichiometric amount of (−)-α-isosparteine. The resulting blue precipitate was filtered off, washed with triethylorthoformate, and then dried in a vacuum. Complex **3**, [Cu(α-Sp)(NCS)$_2$], was prepared from the substitution reaction of [Cu(α-Sp)(NO$_3$)$_2$] (1.00 g, 2.37 mmol) with a stoichiometric amount of NaNCS in 60 ml ethanol-triethylorthoformate (5:1 v/v) solution. The reddish brown precipitate was filtered off, washed with cold absolute ethanol, and then dried in a vacuum. The yield of the product was 79.6%. Dark reddish brown single crystals were obtained by recrystallization at about 278 K from a dichloromethane–triethylorthoformate (5:1 v/v) solution under carbon tetrachloride vapor. *Anal.* Calc. for $CuC_{17}H_{26}N_4S_2$: C, 49.31; H, 6.33; N, 13.53. Found: C, 49.01; H, 6.42; N, 13.39%. Complex **4**, [Cu(α-Sp)(N$_3$)$_2$], was prepared from the substitution reaction of [Cu(α-Sp)(NO$_3$)$_2$] (1.00 g, 2.37 mmol) with a stoichiometric amount of NaN$_3$ in 50 ml ethanol-triethylorthoformate (5:1 v/v) solution as reported [22]. The yield of the dark yellowish brown precipitate obtained was 77.4%. *Anal.* Calc. for $CuC_{15}H_{26}N_8$: C, 47.17; H, 6.86; N, 29.34. Found: C, 47.47; H, 6.89; N, 29.67%.

2.2. Physical measurements

Elemental analyses were carried out using a Profile HV-3 Elemental Analyzer System (Germany) at the Korean Basic Science Institute (Busan Branch). Infrared spectra were obtained using standard KBr pellet techniques with a Mattson Polaris FT-IR spectrometer. The resolution was 4 cm^{-1}. X-band (9.44 GHz) ESR spectra were acquired at room temperature and 77 K using a Bruker Instruments ESP-300S ESR spectrometer at the Korean Basic Science Institute (Seoul Branch).

2.3. X-ray crystal structure determination

Crystals of complexes **1** and **3** for X-ray analysis were obtained by slow evaporation from dichloromethane–triethylorthoformate solutions. The dark reddish brown crystals of **1** and **3** were mounted and aligned on a CAD-4 diffractometer [26]. Accurate cell parameters were refined from setting angles of 40 reflections with $4.87° \leqslant \theta \leqslant 12.54°$ for **1** and 51 reflections with $5.20° \leqslant \theta \leqslant 11.99°$ for **3**. 2508 independent reflections for **1** in an asymmetric unit in range $-11 \leqslant h \leqslant 1$, $-1 \leqslant k \leqslant 17$, $-11 \leqslant l \leqslant 11$ and 2717 independent reflections for **3** in an asymmetric unit in range $-1 \leqslant h \leqslant 10$, $-15 \leqslant k \leqslant 1$, $-1 \leqslant l \leqslant 20$ were collected using graphite-monochromated Mo Kα radiation and the $2\theta/\omega$ scan mode.

All non-H atoms were found by direct methods and their parameters were refined successfully with a full matrix least-squares procedure. The function minimized during least-squares refinement was $\omega^{-1} = [\sigma^2(F_o)^2 + (0.0467P)^2 + 1.7583P]$ for **1** and $\omega^{-1} = [\sigma^2(F_o)^2 + (0.0237P)^2]$ for **3**. H atoms were geometrically positioned and fixed. Empirical absorption corrections by using psi-scan for crystals **1** and **3** were applied to the intensity data (T_{max} and T_{min} are 0.9814 and 0.8493 for **1**, and 0.2699 and 0.2370 for **3**, respectively). Data collection and cell refinement: Bruker XSCANS [27]. Data reduction: SHELXTL [28]. Program used to solve and refine the structures: SHELXS97 and SHELXL97 [29]. Molecular graphics: ORTEP-3 for windows [30].

3. Results and discussion

3.1. Characterization of the compounds

Among the three diastereomers of sparteine, (−)-sparteine was commercially available and (−)-α-isosparteine was derived from (−)-sparteine according to the literature method [25]. The copper(II) sparteine pseudohalide complexes, Cu(Sp)(NCS)$_2$ **1**, Cu(Sp)(N$_3$)$_2$ **2**, Cu(α-Sp)(NCS)$_2$ **3** and Cu(α-Sp)(N$_3$)$_2$ **4**, were prepared from the substitution reaction of copper(II) sparteine dinitrate complexes with stoichiometric amounts of the corresponding sodium salts (NaNCS and NaN$_3$) in ethanol solution. Characterization of these complexes and the precursor complexes, Cu(Sp)(NO$_3$)$_2$ and Cu(α-Sp)(NO$_3$)$_2$, was conducted by IR spectros-