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Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 828 (2007) 181-187

www.elsevier.com/locate/molstruc

A luminescent silver-saccharinato complex with S,S-diphenylsulfimide: Synthesis, spectroscopic, thermal, structural and DFT computational studies

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> Received 17 February 2006; received in revised form 29 May 2006; accepted 31 May 2006 Available online 14 July 2006

Abstract

A new silver(I)-saccharinato (sac) complex with *S*,*S*-diphenylsulfimide, [Ag(sac)(Ph₂SNH)], has been prepared and characterized by elemental analysis, IR spectroscopy, thermal analysis and single crystal X-ray diffraction. X-ray diffraction analyses show that the title complex has a monomeric structure containing linearly coordinated silver(I) ion with an N–Ag–N angle of 173.80(10)°. The individual molecules are linked by strong N–H···O hydrogen bonds and aromatic stacking $\pi \cdots \pi$ interactions and packing of the molecules is further reinforced by C–H··· π interactions. Ph₂SNH and [Ag(sac)(Ph₂SNH)] in solution at room temperature display intense blue luminescence with emission maxima at 380 and 408 nm, respectively. The photoluminescence properties have been investigated by DFT calculations, showing that the luminescence properties of the Ph₂SNH are due to intraligand transitions, while for the silver(I) complex, the luminescence was originated from several transitions including intraligand transitions and metal-to-ligand charge transfer (MLCT). © 2006 Elsevier B.V. All rights reserved.

Keywords: Silver(I); Saccharin; S,S-Diphenylsulfimide; Luminescence, DFT calculations

1. Introduction

The water soluble alkali and Earth-alkali salts of saccharin (also called 2,3-dihydro-3-oxobenzisosulfonazole; 1,2-benzisothiazoline-3-(2H)one 1,1-dioxide or *o*-benzosulfimide) are widely used as a commercially available non-caloric artificial sweetener and food additive. Saccharin, itself, does not coordinate metal ions, but its deprotonated form (saccharinate) interacts with trace elements in human body and readily forms complexes with a large number of metal ions [1].

We have long been interested in the coordination chemistry of the saccharinate anion (sac) since sac acts a polyfunctional ligand and may bond to metals by means of its imino nitrogen, carbonyl oxygen, or sulfonyl oxygen atoms, exhibiting different coordination modes such as monodentate (through the N- or the carbonyl O-atom), bidentate (N, O), tridentate (N, O, O) or bridging forming [2]. Recently, we started a research project to prepare mixed-ligand silver(I) complexes of sac and the studies have generated a wide range of silver(I) complexes with monomeric, dimeric, tetrameric and polymeric structures [3]. Among them, $[Ag_2(sac)_2(aeprd)_2]$ (aeprd = N-(2-aminoethyl)pyrrolidine) was found to be luminescent at room temperature [3i]. As a continuation of this study, in this work, we used a relatively bulky ligand, S,S-diphenylsulfimide (Ph₂SNH), which was shown to form interesting complexes with various metal ions [4], and this paper reports the synthesis of the first example of a S,S-diphenylsulfimide complex of silver(I) with sac, namely [Ag(sac)(Ph₂SNH)]. The crystal structure of this complex was determined by single-crystal X-ray diffraction. It has also been

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characterized by elemental analysis, thermal, and spectroscopic techniques. Furthermore, the spectral and optical properties of $[Ag(sac)(Ph_2SNH)]$ were also studied by DTF calculations.



2. Experimental

2.1. Materials and instrumentation

All reagents were commercially obtained and used without any further purification. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere at a heating rate of $10 \,^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$. Elemental analyses were performed by a Vario EL elemental analyzer for C, H, N and S. FT-IR spectra were measured on a JASCO FT/IR-430 spectrophotometer (KBr pellets) in the $4000-400 \text{ cm}^{-1}$ range. Electronic spectra of 1×10^{-2} M solutions in a 9:1 (v:v) CH₂Cl₂ and acetonitrile mixture were measured with a Unicam UV2 100 spectrophotometer. Excitation and emission spectra were recorded at concentrations of 1×10^{-3} M in a 9:1 (v:v) mixture of dichloromethane and acetonitrile at room temperature with a Perkin Elmer-LS50B spectrophotometer. DFT calculations were performed by using GAUSSIAN 03 program.

2.2. Synthesis of $[Ag(sac)(Ph_2SNH)]$

Solid Na(sac) \cdot 2H₂O (1 mmol, 0.24 g) was mixed with a solution of AgNO₃ (0.17 g, 1 mmol) dissolved in 5 ml distilled water and then, a white polycrystalline precipitate formed. The precipitate was dissolved by adding 20 ml CH₂Cl₂, and Ph₂SNH·H2O (1 mmol, 0.22 g) was added to the solution and stirred for 30 min at room temperature. The resulting solution was allowed to stand in darkness at room temperature. Colorless crystals of [Ag(sac)(Ph₂SNH)] were obtained after two weeks. Yield 89%. Anal. Calcd. for C₁₉H₁₅N₂O₃S₂Ag (%) C, 46.45; H, 3.08; N, 5.70; S, 13.05. Found: C, 46.63; H, 3.24; N, 5.56; S, 13.22%.

2.3. X-ray crystallography

The data collection was performed at 100 K on a Stoe-IPDS-2 diffractometer equipped with a graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71069$ Å). The structures were solved by direct methods using SHELXS-97 [5] and refined by a full-matrix least-squares procedure using the program SHELXL97 [5]. All non-

hydrogen atoms were easily found from the difference Fourier map and refined anisotropically. All CH hydrogen atoms were included using a riding model, while the NH hydrogen atom was refined freely. Molecular graphics were prepared using ORTEP3 [6]. Details of crystal data, data collection, structure solution and refinement are given in Table 1.

2.4. Computational method

DFT calculations are carried out with the GAUSSIAN 03 program [7]. The DFT-B3LYP level was used for both geometry optimization and frequency calculations. The 6- $31G^{**}$ method was used for the Ph₂SNH molecule. The basis set LANL2DZ and the corresponding Los Alamos relativistic effective core potential were employed to consider account scalar relativistic effects, including mass velocity and Darwin corrections for the heavy silver atom, while the 6- $31G^{*}$ basis set was applied to the non-metal atoms in the silver(I) complex.

The ground-state geometries were obtained in the gas phase by full geometry optimization, starting from the structural data without any symmetry constraints. The orbital shapes were visualized using GAUSSIAN VIEW 03 software [8]. The calculated vibrational frequencies are scaled by 0.9614 [9].

Table 1

Cry	vstallogra	phic da	ata and	structure	refinement	for	[Ag((sac)(Ph ₂ SN	√ H)]
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	[Ag(sac)(Ph ₂ SNH)]
Formula	C ₁₉ H ₁₅ N ₂ O ₃ S ₂ Ag
Molecular weight	491.32
Temperature	100(2) K
Wavelength	0.71069 Å
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ /n
Unit cell dimensions	
<i>a</i> (Å)	10.938(2)
b (Å)	14.472(3)
c (Å)	12.119(2)
β (°)	108.27(1)
Volume (Å ³)	1821.7(6)
Z	4
Calculated density (g/cm ³)	1.791
$\mu (mm^{-1})$	1.359
<i>F</i> (000)	984
Crystal size (mm ³)	$0.52 \times 0.39 \times 0.14$
θ range (°)	2.26 to 26.00
Index ranges	$-13\leqslant h\leqslant 13$
	$-17 \leqslant k \leqslant 17$
	$-14 \leqslant l \leqslant 14$
Reflections collected	10889
Independent reflections	3578 $[R_{int} = 0.0401]$
Reflections observed (>2sigma)	3248
Absorption correction	Numerical
Max. and min. transmission	0.756 and 0.593
Data/parameters	3578/248
Goodness-of-fit on F^2	1.035
Final <i>R</i> indices $[I > 2sigma(I)]$	R1 = 0.0292
	wR2 = 0.0672
Largest diff. peak and hole $(e.Å^{-3})$	2.158 and -0.554

3.1. Synthesis

The title silver(I) complex was readily prepared by the direct reaction of equimolar mixture of AgNO₃ and Na(sa-c)·2H₂O in the presence of Ph₂SNH at room temperature and obtained in high yield *ca.* 90%. The analytical data (C, H, N and S) are consistent with the calculated data, and X-ray crystal structure analysis also confirms the chemical formulation of the complex. The title complex is non-hygroscopic and stable in air at ambient temperatures. It is soluble only in CH₂Cl₂ and melts at 207 °C with decomposition.

3.2. Crystal structure

a

The molecular structure of $[Ag(sac)(Ph_2SNH)]$ with the atom labeling is shown in Fig. 1a. The selected bond lengths and angles together with hydrogen bonding geometry are collected in Table 2. The complex crystallizes in the monoclinic space group $P2_1/n$. The silver(I) ion is coordi-

Fig. 1. (a) Molecular structure of $[Ag(sac)(Ph_2SNH)]$ with atom-labeling scheme and thermal ellipsoids at the 50% probability level. (b) View of the crystal packing of $[Ag(sac)(Ph_2SNH)]$. All C–H hydrogen atoms omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for [Ag(sac)(Ph₂SNH)]

	Experimental	Calculated		
Ag1–N1	2.085(2)	2.112		
Ag1–N2	2.069(3)	2.163		
N2-S2	1.586(3)	1.639		
C8–S2	1.794(3)	1.817		
C14–S2	1.795(3)	1.817		
N1–Ag1–N2	173.80(10)	168.20		
N2-S2-C8	107.83(14)	107.33		
N2-S2-C14	108.72(14)	110.54		
C8–S2–C14	99.61(14)	102.20		
Hydrogen bonds				
D–H···A	d(D–H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	<(DHA)
N2–H2A···O3 ^{i}	0.81(4)	2.64(4)	3.426(4)	163(3)

Symmetry transformations used to generate equivalent atoms: (i) = 3/2 - x, 1/2 + y, 1/2 - z.

nated by a sac ligand and a Ph₂SNH ligand, forming a slightly distorted linear AgN₂ motif with an N–Ag–N angle of *ca*. 174°. Both Ag–N bond distances are almost identical. The Ag–N_{sac} bond distance of 2.085(2) Å is also similar to those found in reported silver(I)-sac complexes [3,10], but significantly shorter than the corresponding distances reported for [Ag(sac)(PPh₃)₂] 2.285(8) Å [11] and [Ag₂(sac)₂(µ-aepy)₂] 2.449(2) Å [3f].

The rings of sac (A = C1-C7, N1, S1) and Ph₂SNH (B = C8 - C13 and C = C14 - C19) ligands are essentially planar and the dihedral angles of A/B, A/C, and B/C are 66.82(8), 66.93(8) and 86.80(8)°, respectively. As will be seen in Fig. 1b, the individual molecules of Ag(sac)(Ph₂SNH)] are connected by the N-H···O hydrogen bonds involving the sulfimide N-H group and sulfonyl O atoms. The hydrogen bonded molecules also interact with each other via aromatic $\pi(Ph_2SNH) \cdots \pi(Ph_2SNH)$ $[C_g \cdot C_g^i = 3.831(2)Å; i =$ stacking interactions 1/2 + x, 1/2 - y, 1/2 + z]. The intermolecular interactions are further reinforced by four of C-H··· π interactions involving all phenyl groups.

3.3. FT-IR spectra

Selected spectral data for [Ag(sac)(Ph₂SNH)] are given in Table 3, together with the data obtained from DFT calculations. The absorption band centered at *ca*. 3260 cm^{-1} is assigned to the v(NH) vibration of the N-H group and shifted to the low frequency region by about 75 cm^{-1} , compared to the free Ph₂SNH ligand, due to both the coordination to silver(I) and participation in hydrogen bonding. The relatively weak band around 3050 cm^{-1} is attributed to the absorption of the aromatic CH hydrogens. The sharp band at 1645 cm^{-1} is due to the vibration of the carbonyl group of the sac ligand and well accorded with those of N-coordinated sac complexes (1650 cm⁻¹) [12]. The symmetric (v_s) and asymmetric (v_{as}) stretching modes of the CNS moiety of the sac ligands appeared at approximately 1335 and 960 cm⁻¹, respectively, while the v_{as} and v_s stretchings of the SO₂ group are observed as two strong



Table 3 Experimental IR spectral data^a for [Ag(sac)(Ph₂SNH)], compared with the theoretical IR data obtained from DFT calculations

Assignment	Experimental	Calculated	
v(N–H)	3261sb	3309	
v(C-H)	3053w	3066	
v(C=O)	1645vs	1663	
v(CC)	1585s, 1442s	1583-1429	
$v_{\rm s}({\rm CNS})$	1333m	1328	
$v_{as}(SO_2)$	1290s, 1255vs	1253	
$v_{\rm s}({\rm SO}_2)$	1147vs	1111	
$v_{as}(CNS)$	970vs, 951s	917, 913	
v(S=N)	839m	840	
v(Ag–N)	461w	513, 473	

^a Frequencies in cm⁻¹. b, broad; m, medium; w, weak; vw, very weak; vs, very strong; s, strong; sh, shoulder.

IR bands at *ca*.1255 and 1147 cm⁻¹, respectively. The vibration of the v(S=N) group in the free Ph₂SNH molecule is found at 991 cm⁻¹, but shifted to 839 cm⁻¹ in the silver(I) complex.

3.4. Thermal behavior

Thermal decomposition behavior of both complexes was studied by thermogravimetric (TG) and differential thermal (DTA) analyses in a static atmosphere of air. The TG and DTA curves in Fig. 2 show that the complex decomposes in two distinct stages. The endothermic removal of the Ph₂SNH ligand takes place between 209 and 325 °C with a mass loss of 40.72% (calcd. 40.97%), while the degradation of the sac anion occurs in the temperature range 330-506 °C with two violently exothermic peaks at 460 and 480 °C, which are characteristic for the decomposition of sac complexes [13]. The experimental mass loss of 37.34% is in very good agreement with the calculated mass loss of 37.08%. The decomposition process ends at around 510 °C, giving a final decomposition product of metallic silver (Total mass loss: found 78.06% and calcd. 78.05%).

3.5. Optical properties

The electronic spectra of $[Ag(sac)(Ph_2SNH)]$ and the corresponding ligands are illustrated in Fig. 3. The sac ion in the aqueous solution exhibits two main absorption bands at $\lambda_{\text{max}} = 232 \text{ nm}$ ($\varepsilon = 384 \text{ M}^{-1} \text{ cm}^{-1}$) and 260 nm ($\varepsilon = 263 \text{ M}^{-1} \text{ cm}^{-1}$), similar to the intra-ligand transitions measured in the methanolic solution of Na(sac) · 2H₂O [14], while the Ph₂SNH molecule displays four bands at $\lambda_{\rm max} = 230 \text{ nm}$ $(\varepsilon = 414 \text{ M}^{-1} \text{ cm}^{-1}),$ 240 nm $(\varepsilon =$ 405 M^{-1} cm⁻¹), 250 nm ($\varepsilon = 376 M^{-1}$ cm⁻¹) and 302 nm $(\varepsilon = 300 \text{ M}^{-1} \text{ cm}^{-1})$. The electronic spectra of $[Ag(sac)(Ph_2SNH)]$ show two main absorptions at $\lambda_{max} =$ 278 nm ($\varepsilon = 340 \text{ M}^{-1} \text{ cm}^{-1}$) and 300 nm ($\varepsilon = 325 \text{ M}^{-1} \text{ cm}^{-1}$) for sac and Ph₂SNH species, respectively, and the band at $\lambda_{max} = 242 \text{ nm}$ ($\varepsilon = 422 \text{ M}^{-1} \text{ cm}^{-1}$) is due to both sac and Ph₂SNH absorptions. It may be noted that an approximately 10 nm red-shift occurred for the absorption bands of both ligands centered at around 230 nm, and furthermore, for the sac ligand, the band at 260 nm was shifted to 278 nm in the complex upon coordination.

The sac ion is not luminescent, but the free Ph₂SNH molecule in solution displays a broad emission band at 408 nm followed by a low intensity band at 484 nm upon excitation at 220 nm (see Fig. 4). Both emission bands may be assigned to the $n-\pi^*$ or $\pi-\pi^*$ transitions. Commonly, silver(I) complexes have been found to emit weak photoluminescence at low temperature [15] and only a few silver(I) complexes exhibit luminescence at room temperature [3i,16]. The luminescence spectra of [Ag(sac)(Ph₂SNH)] in solution at room temperature are shown in Fig. 4. The excitation spectrum of the complex shows two maxima at 215 and 284 nm, while the complex exhibits an intense blue photoluminescence with four emission maxima at 380, 420, 487 and 532 nm upon excitation at 215 nm. The emission of the silver



Fig. 2. Thermal analysis curves of [Ag(sac)(Ph₂SNH)].



Fig. 3. Electronic spectra of sac (---), Ph₂SNH (\cdots) , and [Ag(sac)(Ph₂SNH)] (----). Note that the spectra are not in scale.



Fig. 4. Excitation and emission spectra of Ph_2SNH (----) and $[Ag(sac)(Ph_2SNH)]$ (-----) in a 9:1 (v:v) mixture of CH_2Cl_2 and acetonitrile at room temperature.

(I) complex is much more intense and covers a broader spectral range, compared to that of the free Ph₂SNH molecule. The bands at 420 and 487 nm resemble the transition bands observed for the Ph₂SNH molecule, with a slight red-shift, while the low-energy emission band at 532 nm is expected to be the metal-to-ligand charge transfer (MLCT). As will be discussed later, the main high-energy emission band at 380 nm may be originated from a ligand-based $n-\pi^*$ or $\pi-\pi^*$ process, probably induced by the silver(I) ion.

3.6. DFT calculations

The calculated structural parameters are listed in Table 2. The significant number is maintained to be four, which is sufficient for one bond length to be differentiated from the other. It should be noted that the experimental data belong to solid phase, whereas the calculated data correspond to the isolated molecule in gas-phase. However, the experi-

mental and computational data in Table 2 clearly show that both data only slightly differ from each other. For example, the largest difference between experimental and calculated Ag–N length is about 0.09 Å, while the biggest deviation occurs in the N–Ag–N angle by *ca*. 6°. As a result it may be said that the calculated geometrical parameters represent a good approximation.

The computational IR spectral frequencies are listed in Table 3, together with experimentally determined frequencies. The NH and CH groups participate in the hydrogen bonding and therefore, the experimental absorption bands of these groups were found at a lower frequency. The calculated carbonyl frequency of 1663 cm^{-1} well compares with the experimentally determined value of 1645 cm^{-1} , since the carbonyl group of sac does not participate in any intermolecular interaction. As observed earlier [3i], the computational frequencies of the CNS and SO₂ groups of the sac ligand were somewhat low, compared to experimentation. The experimental values of the S=N band of the Ph₂SNH moiety agree very well with the calculated value. Although the experimental frequency value of 461 cm^{-1} seems to be significantly high for such a vibration between silver and the N donor bulky ligands, the assignment of the experimental v(Ag-N) vibration is based on the theoretically calculated frequencies. Both calculated and experimental frequencies are found to be in agreement, and consistent with the frequency value (476 cm^{-1}) of a linear silver complex $[Ag(NH_3)_2]_2SO_4$ [17].

In order to assign the emission bands, molecular orbital (MO) calculations were also performed, and the calculations indicate that Ph_2SNH and $[Ag(sac)(Ph_2SNH)]$ have 53 and 109 occupied MOs, respectively. Fig. 5 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for Ph_2SNH



Fig. 5. Frontier molecular orbitals for Ph₂SNH and [Ag(sac)(Ph₂SNH)].

molecule and the silver(I) complex. As will be seen in Fig. 5, the HOMO of the title complex is principally delocalized among the N atom and three O atoms of the sac ligand and also associated with the silver(I) center (namely the d_{z}^{2} orbital). It may be said that the HOMO is mainly composed of $\sigma(Ag-N_{sac})$ orbital, whereas the LUMO is localized on all the atoms of the Ph₂SNH ligand excluding the silver(I) ion, indicating that the LUMO is mostly the π antibonding type orbital. For Ph₂SNH, the HOMO is associated with the N, S and some C atoms of the phenyl rings, whereas the LUMO is mainly of the π -antibonding character. The values of the energy separation between the HOMO and LUMO in Ph₂SNH and [Ag(sac)(Ph₂SNH)] were found to be identical, and calculated as 0.165 a.u. (4.47 eV), which are much bigger than the experimentally measured emission energy values of 3.04 eV (408 nm) and 3.27 eV (380 nm), respectively. The deviation between experimentation and computation may be due to the ground-state considerations in the DFT calculations, and the intermolecular interactions and solvent effects in the solution.

According to the literature, the emission bands in the reported silver(I) complexes originate from $d\sigma^*$ -p σ or 4d-5s transitions and the excited states of MLCT or MMLCT [18]. The results of the present study show that for the silver(I) complex, the high-energy emission bands can mainly be assigned to intraligand transitions, whereas the low-energy emission transition is expected to be the MLCT and it has been suggested that the photoluminescence of the silver(I) complex is the cooperative association of the intraligand and MLCT transitions.

4. Supplementary data

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary data, CCDC No. CCDC 297772. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors are grateful to the Research Fund of Ondokuz Mayis University (Project No. F365) for financial support of this work. We also thank Prof. Dr. M. Volkan and Research Assistant S. Surdem, for their assistance in obtaining the luminescence spectra.

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