Inorganica Chimica Acta 406 (2013) 87–94

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

First examples of 3d-uranium compounds derived from single-compartment Schiff base ligands: Syntheses, crystal structures and d–d band correlation

Leena Mandal, Sagarika Bhattacharya, Sasankasekhar Mohanta *

Department of Chemistry, University of Calcutta, 92 A. P. C. Road, Kolkata 700 009, India

ARTICLE INFO

Article history:
Received 13 May 2013
Received in revised form 26 June 2013
Accepted 3 July 2013
Available online 13 July 2013

Keywords:
3d–5f compounds
Spectral correlation
Schiff base
Uranyl
Crystal structure

ABSTRACT

This paper deals with the syntheses, characterization, crystal structures and UV–Vis spectroscopy of three diphenoxo-bridged dinuclear $Cu^{II}(U^{VI}O_2)$ compounds $[Cu^{II}(MeCN)L^1(U^{VI}O_2)(NO_3)_2]$ (**1**), $[Cu^{II}(MeCN)L^2(U^{VI}O_2)(NO_3)_2]$ (**2**) and $[Cu^{II}(MeCN)L^3(U^{VI}O_2)(NO_3)_2]$ (**3**) derived from the single-compartment Schiff base ligands H_2L^1 (2:1 condensation product of salicylaldehyde and 1,3-diaminopropane), H_2L^2 (2:1 condensation product of salicylaldehyde and 1-ethyl-1,3-diaminopropane) and H_2L^3 (2:1 condensation product of 2-hydroxyacetophenone and 1,3-diaminopropane). While copper(II) occupies the N_2O_2 compartment, uranium(VI) center is linked with Schiff base ligand through the two bridging phenoxo oxygen atoms. Copper(II) is pentacoordinated and distorted square pyramidal, while the uranium(VI) center is octacoordinated and distorted hexagonal bipyramidal in which the two uranyl oxygen atoms occupy the apical positions. Electronic spectra of **1**–**3** and the corresponding mononuclear Cu^{II} compounds have been recorded and a previously reported but practically unexplored correlation regarding d–d band position has been highlighted. Although the correlation is not valid for only mononuclear or only dinuclear compounds derived from different ligands, a nice correlation is found out on comparing the spectra of dinuclear compounds with the corresponding mononuclear compounds.

1. Introduction

Studies of spectroscopic properties, both absorption and emission, of metallo-organic systems have been receiving much attention in recent years [1–8]. Some of the important aspects in this area include understanding of reaction kinetics and intermediates, development of metal ion sensors and imaging application in living cells [1–8]. Therefore, enlightenment of spectroscopic correlation [9,10] or determination of a new correlation deserve importance.

In contrast to the numerous 3d–3d and many 3d–4f compounds, the number of 3d–5f compounds is yet significantly smaller. The single-compartment Schiff base ligands obtained on condensation of salicylaldehyde/2-hydroxyacetophenone and a diamine as well as the di-compartment ligands obtained on condensation of 3-methoxysalicylaldehyde/3-ethoxysalicylaldehyde and a diamine have been widely utilized to derive many 3d–3d and 3d–4f compounds [11–48]. On the other hand, Ephritikhine, Salmon and coworkers have utilized 3-hydroxysalicylaldehyde-diamine di-compartment ligands to stabilize a number of dinuclear $M^{II}U^{IV}$, trinuclear $M^{II}U^{IV}M^{II}$, dinuclear $M^{II}(U^{VI}O_2)$ and tetranuclear $\{M^{II}(U^{VI}O_2)\}_2$ compounds, where M = Cu, Ni, Zn [49–55]. Uranium(IV/VI) centers in these compounds are accommodated in the O(phenoxo)$_4$ compartment and each 3d-uranium pair in these compounds is diphenoxo-bridged. Observing the capability of the O_4 compartment in 3-hydroxosalicylaldehyde-diamine Schiff base ligands to accommodate uranium center, one can anticipate that diphenoxo-bridged 3d-uranium compounds would also be stabilized in the 3-methoxy/ethoxysalicylaldehyde-diamine Schiff base ligands. However, in the course of our exploration of structural diversity of 3-methoxy/ethoxysalicylaldehyde-diamine ligands (H_2L^{OMe}/H_2L^{OEt}), we reacted mononuclear Cu^{II}/Ni^{II} compounds with uranyl(VI) nitrate hexahydrate and isolated only cocrystals of mononuclear $[Cu^{II}L^{OMe/OEt}]/[Ni^{II}L^{OMe/OEt}]$ and mononuclear $[U^{VI}O_2(H_2O)_2(NO_3)_2]$ or dinuclear $[(U^{VI}O_2)_2(\mu\text{-}H_2O)_2(NO_3)_4]$ moieties [56–58]. Clearly, contrary to the usual anticipation, the uranium center is not coordinated with the Schiff base ligands in these compounds [56–58]. We have therefore interested to explore whether 3d-uranium compounds will be stabilized in the single-compartment salicylaldehyde/2-hydroxyacetophenone-diamine ligands, and, if so, whether those would contain Schiff base-coordinated uranium or not. Accordingly, we have reacted three mononuclear copper(II) compounds $[Cu^{II}L^1(H_2O)]$, $[Cu^{II}L^2]$, and $[Cu^{II}L^3]$ with uranyl(VI) nitrate hexahydrate and isolated three compounds $[Cu^{II}(MeCN)L^1(U^{VI}O_2)(NO_3)_2]$ (**1**), $[Cu^{II}(MeCN)L^2(U^{VI}O_2)(NO_3)_2]$ (**2**) and $[Cu^{II}(MeCN)L^3(U^{VI}O_2)(NO_3)_2]$ (**3**), where H_2L^1 and H_2L^2 are

---

* Corresponding author. Tel.: +91 9433883751; fax: +91 33 23519755.
E-mail address: sm_cu_chem@yahoo.co.in (S. Mohanta).

0020-1693/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2013.07.012

obtained on condensing salicylaldehyde with, respectively, 1,3-diaminopropane and 1-ethyl-1,3-diaminopropane, H_2L^3 is obtained on condensing 2-hydroxyacetophenone with 1,3-diaminopropane (Scheme 1). Herein, we report the syntheses, characterization, crystal structures and UV–Vis spectroscopy of **1**–**3** along with correlation of d–d band position with a structural parameter.

2. Experimental

2.1. Materials and physical measurements

All the reagents and solvents were purchased from commercial sources and used as received. The mononuclear compounds $[Cu^{II}L^1(H_2O)]$ [59], $[Cu^{II}L^2]$ [60] and $[Cu^{II}L^3]$ [61] were synthesized by the reported procedures. Elemental (C, H and N) analyses were performed on a Perkin–Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm^{-1} on a Bruker-Optics Alpha–T spectrophotometer with samples as KBr disks. UV–Vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer.

2.2. Syntheses

2.2.1. $[Cu^{II}(MeCN)L^1(U^{VI}O_2)(NO_3)_2]$ (**1**), $[Cu^{II}(MeCN)L^2(U^{VI}O_2)(NO_3)_2]$ (**2**) and $[Cu^{II}(MeCN)L^3(U^{VI}O_2)(NO_3)_2]$ (**3**)

These three compounds were prepared by following a general procedure as described below for **1**: To an acetonitrile solution (10 mL) of $[Cu^{II}L^1(H_2O)]$ (0.05 g, 0.138 mmol) was dropwise added an acetonitrile solution (5 mL) of uranyl nitrate hexahydrate (0.069 g, 0.138 mmol) with stirring. The color of the solution changed from green to brown. After one hour stirring, the solution was filtered to remove suspended particles, if any, and the filtrate was kept for slow evaporation at room temperature. After a few days, brown crystalline compound containing diffraction quality single crystals deposited, which was collected by filtration and washed with acetonitrile-methanol (1:1).

Data for **1**: Yield: 0.075 g (70%). *Anal.* Calc. for $C_{19}H_{19}N_5O_{10}CuU$ (FW: 778.96): C, 29.30; H, 2.46; N, 8.99. Found: C, 28.97; H, 2.65; N, 8.75%. FT-IR (cm^{-1}, KBr): ν(C=N), 1634m; ν(nitrate), 1384s and 1278s; ν(uranyl), 937m.

Data for **2**: Yield: 0.068 g (65%). *Anal.* Calc. for $C_{21}H_{23}N_5O_{10}CuU$ (FW: 807.01): C, 31.25; H, 2.87; N, 8.68. Found: C, 31.43; H, 2.70; N, 8.42%. FT-IR (cm^{-1}, KBr): ν(C=N), 1624vs; ν(nitrate), 1384s and 1276vs; ν(uranyl), 927s.

Data for **3**: Yield: 0.078 g (72%). *Anal.* Calc. for $C_{21}H_{23}N_5O_{10}CuU$ (FW: 807.01): C, 31.25; H, 2.87; N, 8.68. Found: C, 31.58; H, 2.64; N, 8.90%. FT-IR (cm^{-1}, KBr): ν(C=N), 1599s; ν(nitrate), 1384vs and 1297s; ν(uranyl), 926s.

2.3. Crystallographic studies

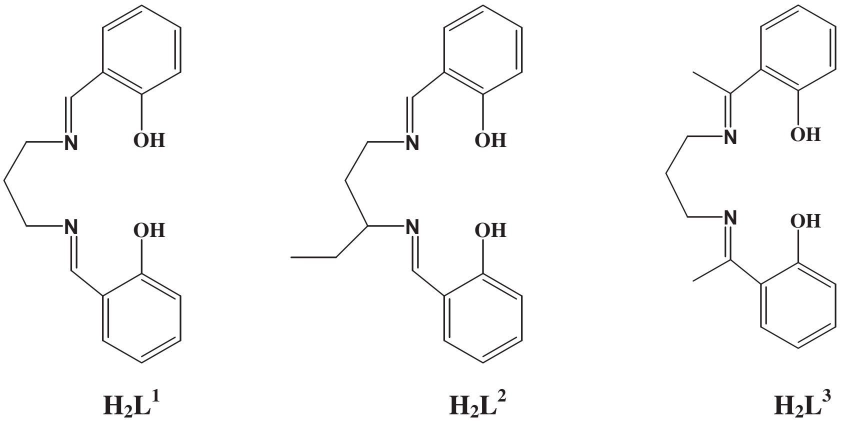
The crystallographic data for **1**, **2** and **3** are summarized in Table 1. X-ray diffraction data were collected on a Bruker-APEX II SMART CCD diffractometer at 296 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). For data processing the packages SAINT [62] were used. All the data were corrected for Lorentz-polarisation effects. Multi-scan absorption corrections were performed for all the three cases using the program SADABS [62]. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXTL [63] and SHELXL-97 packages [64]. All hydrogen atoms in **1**, **2** and **3** were inserted at calculated positions with isotropic thermal parameters and refined. All the nonhydrogen atoms were refined anisotropically. The final refinement converged to R_1 ($I > 2\sigma(I)$) values 0.0257, 0.0335 and 0.0278 for **1**, **2** and **3**, respectively.

3. Results and discussion

3.1. Syntheses and characterization

The dinuclear compounds **1**–**3** are readily formed in good yield on reacting the corresponding mononuclear copper(II) compounds with uranyl(VI) nitrate hexahydrate in acetonitrile. The cyanide stretching in **1**–**3** appear at 1634, 1624 and 1599 cm^{-1}, respectively. One band at 1384 cm^{-1} (for all of **1**–**3**) and one band at 1278 cm^{-1} (for **1**)/1276 cm^{-1} (for **2**)/1297 cm^{-1} (for **3**) can be assigned to vibrations of nitrate moieties. The characteristic stretching of the uranyl moiety in **1**–**3** takes place at 937, 927 and 926 cm^{-1}, respectively.

Before recording UV–Vis spectra of **1**–**3** in acetonitrile solution (*vide infra*), we checked the stability of the dinuclear systems in this solvent by allowing the evaporation of the acetonitrile solution of the isolated compounds. From the solutions in all the three cases, the respective dinuclear compound separated in crystalline form; the FT-IR spectra of these compounds are superimposable with the spectra of the corresponding $Cu^{II}(U^{VI}O_2)$ system. So, the dinuclear compounds are not decomposed in acetonitrile solution. The molar conductance of the three compounds were recorded in acetonitrile solution. The values are 8.5, 15.0 and 9.0 ohm^{-1} cm^{-1} -mol^{-1} l, indicating that the nonelectrolytic nature in the solid state is preserved in acetonitrile solution. Moreover, as the coordinated solvent in the solid state in **1**–**3** is acetonitrile, it is highly likely that this solvent is also coordinated in the solution of the



Scheme 1. Chemical structures of ligands.