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Sonochemical synthesis and characterization of new seven coordinated zinc, cadmium and mercury nitrate complexes: New precursors for nanostructure metal oxides

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ABSTRACT

The nitrate complexes of group 12 elements with a tridentate Schiff base ligand (L = (E)-N1-((E)-3- phenylallylidene)-N2-(2-((E)-((E)-3-phenylallylidene) amino)ethyl) ethane-1,2-diamine) were synthesized via sonochemical process and characterized by various physical and chemical methods. The structural analysis of the zinc nitrate complex by single crystal X-ray diffraction analysis shows that the central atom is seven-coordinated by three nitrogen atoms from the Schiff base ligand as well as four oxygen atoms from two different nitrate anions. The geometry around the metal center can be described as a distorted pentagonal bipyramid. The crystal packing analysis of zinc nitrate complex indicates that the intermolecular interactions related to nitrate groups plays the essential role in the orientation of supramolecular structure. Hirshfeld surfaces (HS) and their corresponding fingerprint plots (FP) have been also used for further investigation of crystal structure of zinc nitrate complex. Furthermore thermal analyses (TG/DTG) of three nanostructure complexes were carried out and discussed. Finally, direct thermolysis of zinc and cadmium nitrate complexes in air atmosphere led to the production of zinc and cadmium oxide nanoparticles.

1. Introduction

There is a demonstrated interest in the synthesis and structural characterization of metal complexes particularly in areas including catalysis, medicine, agriculture, polymer industries, bioinorganic chemistry, microbiology and optical industries [1–6]. By the combination of different types of ligands and metal ions in varied ratios the synthesis of a range of metal coordination compounds can be achieved providing the opportunity to design various compounds for different scientific purposes [7]. Among the various metal compounds, those with Schiff base ligands are significant [8]. These ligands are readily prepared and coordinate with a broad spectrum of metal ions. Under favourable conditions some Schiff base complexes can form extended supramolecular structures stabilized by non-covalent intermolecular interaction such as hydrogen bonding [9] that extend their applications to include solar cells [10], biological systems [11], magnetic and conducting materials [12], gas storage [13], nano-materials [14], catalytic and pharmaceutical industry [15,16]. The broad scope of structural properties demonstrated by Schiff base complexes underlies their important role in many scientific applications. Synthesis of coordination compounds in nano-meter size is a new trend in inorganic chemistry and has attracted much attention due to their unique properties which arise due to the large number of surface molecules in comparison to the bulk [17,18]. Among the different methods that have been used for the synthesis of nano structures, the sonochemical procedure has become popular due to the rapid synthesis, product quality, environmentally friendly and low cast [19,20]. A literature survey indicates that synthesis of different inorganic Zn, Cd and Hg compounds have been reported [21–24] but the reports for nano structure coordination compound with tridentate Schiff base ligands and their use as precursors for the preparation of nanostructure metal oxide are rarely found. Metal oxides play a key role in many areas of science [25]. In technological applications, oxides are used in the fabrication of microelectronic devises, sensors, catalysts, ceramics, optoelectronic

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devices, anticorrosion coatings and fuel cells [26,27]. Herein, we extend our previous work [28–33], and report the synthesis and characterization of some new Zn, Cd and Hg complexes of a tridentate Schiff base ligand entitled as (E)-N1-((E)-3-phenylallylidene)-N2-(2-((E)-((E)-3-phenylallylidene) amino) ethyl) ethane-1, 2-diamine. The nanostructure and metal oxide of the complexes were also prepared under ultrasonic irradiation and calcination method respectively.

2. Experimental

2.1. Materials and methods

All materials used in the synthetic and analytical procedures were purchased from Merck, Aldrich and/or BDH chemical companies in high purity and were used as received.

For recording of UV–Visible spectra of the compounds in the range of 200–800 nm, a JASCO-V570 spectrophotometer instrument was applied. The FT/IR spectrum of all compounds were carried out on a JASCO-FT/IR680 instrument in the range of 4000–400 cm^{-1} as KBr discs. ^1H and ^{13}C NMR spectra of the ligand and its zinc, cadmium and mercury complexes measured on a Bruker DPX FT/NMR-400 in DMSO-d_6. Melting points or decomposition temperatures were measured by BUCHI B-545 instrument. Molar conductivities of the compounds in chloroform were determined using a Metrohm-712 conductometer with a dip-type conductivity cell made of platinum black at room temperature. Thermal analyses (TG/DTG/DTA) were obtained on a Perkin-Elmer Pyris model instrument. Scanning electron microscopy (SEM) images were taken on a Hitachi S-1460 field emission scanning electron microscope using Ac voltage of 15 kV. X-ray powder diffraction (XRD) spectra were recorded on a STOE type STIDY-MP-Germany X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The high-power ultrasonic cleaning unit Bandelin Super Sonorex RK-100H with ultrasonic peak output 320 W and HF power 80 W_{eff} has been used for ultrasonically synthesis of nano structure complexes. The CrystalExplorer [34] computer software has been used for analysis of molecular Hirshfeld surfaces.

2.2. Crystallography

Single-crystal X-ray data for the $ZnL(NO_3)_2$ complex were collected at 100 K with a ADSC quantum 210r detector (Synchrotron, λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least-squares based on F^2 with SHELX-2014 [35]. Hydrogen atoms treated by a mixture of independent and constrained refinement. The molecular and packing diagrams were generated using the MERCURY [36] software.

2.3. Synthesis of Schiff base ligand

Schiff base ligand (L) was prepared by a condensation reaction between cinnamaldehyde and diethylenetriamine in a 1:2 M ratio in ethanolic solution. The reaction mixture was kept in an ultrasonic bath for 45 min at room temperature under ultrasound irradiation to complete the reaction. Afterward, the yellow viscous oil as product was washed twice with n-hexane to remove impurities

2.4. Sonochemical synthesis of nano-structure complexes

Preparation of $[ZnL(NO_3)_2]$, $[CdL(NO_3)_2]$ and $[HgL(NO_3)_2]$ complexes were carried out by drop wise addition of fresh ligand solution (1 mmol in 20 mL) into zinc, cadmium and mercury nitrate salts in ethanol (1 mmol in 20 mL) respectively, the reaction mixtures were exposed to ultrasound irradiation at room temperature. After complete addition, the solutions were kept in the ultrasonic bath for a period of 60 min. The resulting precipitates were filtered, dried and placed at 80–100 °C under vacuum and then kept in a desiccator over silica gel.

Table 1
Analytical and physical data of the Schiff base ligand and its M (II) complexes.

compounds	Color	M.P (°C)	Yield (%)	Λ°_M ($cm^2\,\Omega^{-1}\,mol^{-1}$)
Ligand	orange	Oil	95	0.007
$ZnL(NO_3)_2$	cream	112	62	0.019
$CdL(NO_3)_2$	white	127	79	0.016
$HgL(NO_3)_2$	white	133	70	0.018

The physical and spectral data (IR and UV visible) of the compounds have been collected in Tables 1 and 2. The ^1H and ^{13}C NMR data of complexes based on Scheme 1 are listed as follow:

Ligand (L); ^{1}HNMR(in DMSO): 7.79(d, 1H_d, J = 10.02 Hz), 7.76(dd, 2H_g, J = 6.80 Hz, J = 3.30 Hz), 7.61(bd, 2$H_{g'}$, J = 7.49 Hz), 7.48(m, 7$H_{h,h',i,i',e'}$), 7.11(d, 1H_f, J = 16.22 Hz), 7.00(d, 1$H_{f'}$, J = 16.21 Hz), 6.87(dd, 1H_e, J = 15.96 Hz, J = 7.59 Hz), 4.05(m, 1$H_{d'}$), 3.98(m, 2$H_{c'}$), 3.89(m, 2$H_{b'}$), 3.82(m, 2H_b), 3.74(bs, 2H_c), 3.19(bs, 1H_a). ^{13}C NMR (in DMSO): 167.02(C_3), 146.79($C_{5,5'}$), 131.22($C_{6,6'}$), 129.07($C_{9,9'}$), 128.72($C_{8,8'}$), 128.49($C_{7,7'}$), 127.47($C_{4,4'}$), 108.37($C_{3'}$) 55.52($C_{1'}$), 49.87(C_1), 43.63(C_2), 42.37($C_{2'}$) ppm.

$[ZnL(NO_3)_2]$: ^{1}HNMR (in DMSO): 8.26 (d, 2$H_{d,d'}$, J = 8.99 Hz), 7.60(d, 4$H_{g,g'}$, J = 6.98 Hz), 7.47(m, 6$H_{h,h',i,i'}$), 7.25(d, 2$H_{f,f'}$, J = 15.67 Hz), 7.78(bs, 2$H_{e,e'}$, J = 15.92 Hz, J = 8.75 Hz), 3.66(bs, 4$H_{c,c'}$), 2.90(bs, 4$H_{b,b'}$ and 1NH) ppm. ^{13}CNMR (in DMSO): 168.26($C_{3,3'}$), 147.06 ($C_{5,5'}$), 134.71 ($C_{6,6'}$), 130.43($C_{9,9'}$), 129.10($C_{8,8'}$), 127.69($C_{7,7'}$), 125.19($C_{4,4'}$), 56.56($C_{2,2'}$) and 46.33 ($C_{1,1'}$) ppm.

$[CdL(NO_3)_2]$: ^{1}HNMR (in DMSO): 8.40(d, 2$H_{d,d'}$, J = 7.70 Hz), 7.60(d, 4$H_{g,g'}$, J = 6.40 Hz), 7.39–7.48(m, 8$H_{f,f',h,h',i,i'}$), 7.20(dd, 2$H_{e,e'}$, J = 15.60 Hz, J = 6.20 Hz), 3.65(s, 4$H_{c,c'}$), 2.87(bs, 4$H_{b,b'}$) and 2.68(s, 1H_a) ppm. ^{13}CNMR (in DMSO): 168.26($C_{3,3'}$), 146.32 ($C_{5,5'}$), 134.80 ($C_{6,6'}$), 130.34($C_{9,9'}$), 129.12($C_{8,8'}$), 127.62 ($C_{7,7'}$), 126.05($C_{4,4'}$), 56.57($C_{2,2'}$) and 47.31 ($C_{1,1'}$) ppm.

$[HgL(NO_3)_2]$: ^{1}HNMR (in DMSO): 8.43(bs, 2$H_{d,d'}$, J = 9.32 Hz), 7.63(d, 4$H_{g,g'}$, J = 7.19 Hz), 7.45(m, 6$H_{h,h',i,i'}$), 7.33(d, 2$H_{f,f'}$, J = 15.41 Hz), 7.08(dd, 2$H_{e,e'}$, J = 16.16 Hz, J = 8.99 Hz), 3.69(bs, 4$H_{c,c'}$), 3.02(bs, 4$H_{b,b'}$ and 1NH) ppm. ^{13}CNMR (in DMSO): 166.60($C_{3,3'}$), 145.22($C_{5,5'}$), 135.01 ($C_{6,6'}$), 130.00($C_{9,9'}$), 128.99($C_{8,8'}$), 127.79 ($C_{7,7'}$), 126.07($C_{4,4'}$), 55.09($C_{2,2'}$), 50.14 ($C_{1,1'}$) ppm.

2.5. Preparation of zinc (II) oxide and cadmium (II) oxide nano-particles

An appropriate quantity of zinc nitrate and cadmium nitrate complexes were used as precursors for synthesis of ZnO and CdO nano particles was transferred into a porcelain crucible and then heated up to 500 °C in a furnace under an air atmosphere. After about 3 h, the obtained powders were washed with a little amount of acetone solvent to remove any organic impurities, and then the product was dried at 80 °C for 1 h to give zinc and cadmium oxide nanoparticles.

3. Results and discussion

3.1. Physical and analytical data

Based on physical and analytical data collected in Table 1, the general formula; $ML(NO_3)_2$ (M = Zn, Cd and Hg) is proposed for the complexes that has been presented in Scheme 1. The X-ray crystallography of $ZnL(NO_3)_2$ proved the suggested structure for the complexes as exhibited in Scheme 1. All compounds are stable at room temperature. Chloroform, dichloromethane, dimethylformamide and dimethylsulfoxide are suitable solvents for the synthesized compounds as the solubility test indicated. Melting points or decomposition temperatures of the complexes are found in the range of 129–208 °C as showed in Table 1. The molar conductivity values of the complexes were measured in dichloromethane (10^{-3} M) at room temperature confirmed the non-electrolytic nature for them.