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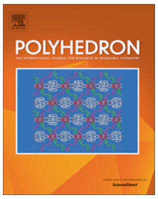

Manganese(II) and zinc(II) complexes of 4-phenyl (2-methoxybenzoyl)-3-thiosemicarbazide: Synthesis, spectral, structural characterization, thermal behavior and DFT study

A. Singh [a], M.K. Bharty [a,*], R.K. Dani [a], Sanjay Singh [b], S.K. Kushawaha [a], N.K. Singh [a,*]

[a] Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India
[b] Department of Chemical Science IISER-Mohali, Knowledge City, Sector 81, S.A.S Nagar, Mohali 140306, Punjab, India

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ABSTRACT

The ligand 4-phenyl(2-methoxybenzoyl)-3-thiosemicarbazide (Hpmt), forms isostructural $[Mn(pmt)_2(o\text{-phen})]$ (**1**) and $[Zn(pmt)_2(o\text{-phen})]$ (**2**) complexes containing *o*-phen as coligand which have been characterized by analytical, spectroscopic (IR, UV–Vis, NMR), magnetic susceptibility, TGA and single crystal X-ray data. Both complexes crystallize in monoclinic systems with the space group *P*2/*n*. The complexes have distorted octahedral geometry around the metal center. The ligand in the complexes is coordinated through the deprotonated hydrazinic nitrogen and carbonyl oxygen. The hydrazinic nitrogen coordinates with a shorter M–N distance than the *o*-phen nitrogen and bond lengths in the chelate ring systems are intermediate between single and double bond distances, suggesting considerable delocalization of charge. There is a good agreement between the geometrical parameters obtained by X-ray crystallography to those generated by DFT method. The thermal degradations of complexes **1** and **2** have been investigated by thermogravimetric analyses which indicate that the final residues left are $Mn(NCO)_2$ and $Zn(NCSNH)_2$. The small HOMO–LUMO energy gap suggests low excitation energy for the complexes.

1. Introduction

Thiosemicarbazide is the simplest representative of the ligands having nitrogen and sulfur as donors. Thiosemicarbazide and substituted thiosemicarbazides are an importantant class of intermediate used for the synthesis of five membered nitrogen–sulfur or nitrogen–oxygen heterocyclic compounds [1–3]. The chemistry of thiosemicarbazide/ substituted thiosemicarbazide complexes has received much attention owing to their significant biological and medicinal properties which are dependent upon the chemical nature of the moiety attached to the C=S carbon atom [4–7]. 1,4-Disubstituted-thiosemicarbazide are biologically versatile compounds displaying a variety of biological effects which include anti-inflammatory [8], antimycobacterial [9,10], antimicrobial [11–13], antifungal [14], antibacterial [15,16] and antiviral [10] activities. Metal complexes containing 1,10-phenanthroline and bipyridine have gained importance because of their versatile roles as building blocks for the synthesis of metallo-dendrimers and as molecular scaffolding for supramolecular assemblies, and in analytical chemistry, catalysis, electrochemistry, ring-opening metathesis polymerization and biochemistry [17–23]. However, most diimine complexes reported are homo ligand compounds of the general formula $[M(N\text{–}N)_3]^{n+}$ or $[M(N\text{–}N)_2(NCS)_2]$ which have shown variable spin transition properties with temperature [24]. Mixed ligand complexes can be a synthetic challenge to tune the various properties of the transition metal complexes. A few papers are available on the transition metal complexes of 1,4-substituted thiosemicarbazide [25,26] but there is no report on the synthesis and structural characterization of the mixed ligand complexes containing bidentate N,N donors and 1,-4-disubstituted thiosemicarbazide. In this paper, we report the synthesis and structural characterization of Mn(II) and Zn(II) complexes of 4-phenyl(2-methoxybenzoyl)-3-thiosemicarbazide and the DFT calculations have been done to corroborate the structural data.

2. Experimental

2.1. Chemical and starting materials

Commercial reagents were used without further purification and all experiments were carried out in open atmosphere. Phenyl isothiocyanate, methyl-2-methoxy benzoate (Sigma Aldrich),

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* Corresponding authors. Tel.: +91 5426702452; fax: +91 5422368127.
E-mail addresses: manoj_vns2005@yahoo.co.in (M.K. Bharty), singhnk_bhu@yahoo.com (N.K. Singh).

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hydrazine hydrate (SD Fine) were used as received. 2-Methoxy benzoic acid hydrazide was prepared by reported method [27]. All the synthetic manipulations were carried out in open atmosphere and at room temperature. The solvents were dried and distilled before use following the standard procedure.

2.2. Physical measurements

Carbon, hydrogen and nitrogen contents were estimated on a CHN Model CE-440 Analyser and on an Elementar Vario EL III Carlo Erba 1108. Magnetic susceptibility measurements were performed at room temperature on a Cahn Faraday balance using $Hg[Co(NCS)_4]$ as the calibrant and electronic spectra were recorded on a SHIMADZU 1700 UV–Vis spectrophotometer. IR spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a JEOL AL300 FT NMR spectrometer using TMS as an internal reference. Thermogravimetric analyses (TG-DTA) of the compounds were performed on a Perkin Elmer-STA 6000 thermal analyzer at a heating rate of 5 °C/min in N_2 atmosphere.

2.3. X-ray crystallography

Crystals suitable for X-ray analyses of complexes **1** and **2** were grown at room temperature. X-ray diffraction data were obtained at 293(2) K on an Oxford Diffraction Gemini diffractometer equipped with CRYSALIS PRO., using a graphite mono-chromated Mo Kα (λ = 0.71073 Å) radiation source. A semi-empirical multi scan absorption correction was applied to the X-ray data of both compounds. The structure was solved by direct methods (SHELXL-13) and refined by full matrix least-square on F^2 (SHELXL) using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in calculated position and refined with a riding model [28]. Figures were drawn using the programs MERCURY and ORTEP-3 [29,30].

2.4. Synthesis

2.4.1. Preparation of 4-phenyl(2-methoxybenzoyl)-3-thiosemicarbazide (Hpmt)

The ligand 4-phenyl(2-methoxybenzoyl)-3-thiosemicarbazide (Hpmt) was prepared as reported in literature [31].

2.4.2. Preparation of [Mn(pmt)$_2$(o-phen)] (**1**)

Methanolic solutions of $Mn(OAc)_2{\cdot}4H_2O$ (0.246 g, 1 mmol) and Hpmt (0.6 g, 2 mmol) were mixed and continuously stirred for 30 min at room temperature. The resulting white precipitate was filtered off, washed with ethanol and air dried. The precipitate was suspended in methanol and stirred with a methanol solution of 1,10-phenanthroline (0.2 g, 1 mmol). The resulting clear yellow solution was filtered off and kept for crystallization, which resulted after slow evaporation of the above solution over a period of 20 days, yellow rod shaped crystals of complex suitable for X-ray analyses. Yield: 70%. M.p: 498 K. *Anal.* Calc. for $C_{42}H_{36}MnN_8O_4S_2$ (835.87): C, 60.29; H, 4.30; N, 13.39; S, 7.65. Found: C, 60.25; H, 4.35; N, 13.28; S, 7.6%. IR data (ν cm^{-1}, KBr): 3272s ν(NH); 1594s thioamide I [β(NH) + ν(CN)]; 1346 thioamide II [ν(CN)+β(NH)]; 1018 ν(N–N) s; 1604 ν(C=O); 928 ν(C=S). UV–Vis [λ_{max}, Nujol mulls, nm]: 280, 310, 648.

2.4.3. Preparation of [Zn(pmt)$_2$(o-phen)] (**2**)

Methanolic solution of $Zn(OAc)_2{\cdot}2H_2O$ (0.218 g, 1 mmol) was added to the methanolic solution of Hpmt (0.6 g, 2 mmol) and the reaction mixture was stirred continuously at room temperature for 30 min. The resulting white precipitate was filtered off, washed with ethanol and air dried. The precipitate was suspended in methanol and stirred with a methanol solution of 1,10-phenanthroline (0.200 g, 1 mmol) at the room temperature which resulted in a clear yellow solution. This was filtered off and kept for crystallization. Yellow needle shaped crystals of the complex suitable for an X-ray analyses were obtained by slow evaporation of the above solution over a period of 10 days. Yield: 70%. M.p: 508 K. *Anal.* Calc for $C_{42}H_{36}ZnN_8O_4S_2$ (711.61): C, 59.52; H, 4.25; N, 13.23; S, 7.56. Found: C, 59.54; H, 4.24; N, 13.23; S, 7.25%. IR data (ν cm^{-1}, KBr): 3259s ν(NH); 1566 thioamide I [β(NH)+ν(CN)] s; 1351 thioamide II [ν(CN)+β(NH)] s; 1018 ν(N–N) s; 1586 ν(C=O); 930 ν (C=S).^1H NMR (300 MHz, DMSO-d_6; δppm): 9.00 (s, 1H, NH); 8.58 (s, 1H, NH); 6.87–8.05 (aromatic protons); 3.87 (m, 3H, $-OCH_3$). The ^{13}C NMR (DMSO-d_6; δ ppm): 177.66 (C=S), 152.66 (C=O), 116.93–130.75 (aromatic ring carbons), 65.39 ($-OCH_3$). UV–Vis [λ_{max}, Nujol mulls, nm]: 325, 350.

3. Results and discussion

The ligand 4-phenyl(2-methoxybenzoyl)-3-thiosemicarbazide react with $Mn(OAC)_2{\cdot}4H_2O$ and $Zn(OAC)_2{\cdot}2H_2O$ and then with *o*-phen in methanol solution yielding [Mn(pmt)$_2$(*o*-phen)] (**1**) and [Zn(pmt)$_2$(*o*-phen)] (**2**), respectively. In both the complexes, the metal is bonded through deprotonated thiohydrazide nitrogen and carbonyl oxygen of the ligand. The six coordination of Mn(II) and Zn(II) is completed by coordination of one molecule of *o*-phen and two molecules of the ligand. These complexes are stable toward air and moisture. Scheme 1 depicts the formation of the ligand and complexes containing *o*-phen as co-ligand. The complexes **1** and **2** are soluble in chloroform and melt at 498 and 508 K, respectively.

3.1. IR spectra

Complexes **1** and **2** show the absence of ν(N–H) band at 3201 cm^{-1} indicating loss of hydrogen from the nitrogen of thiohydrazide group which is supported by a small positive shift of 13 cm^{-1} in ν(N–N). The IR spectra of complexes **1** and **2** show a negative shift of 48–68 cm^{-1} in ν(C=O) indicating bonding of the carbonyl oxygen to the metal ion. Furthermore, complexes **1** and **2** show a very small positive shift in ν(C=S) as compared to the free ligand, showing that the thiohydrazide sulfur is not participating in bonding but the small positive shift can be attributed to the involvement of sulfur in hydrogen bonding with the hydrogen of *o*-phen. Thus, it is clear from the IR data that the ligand acts as uninegative bidentate in complexes **1** and **2** bonding through deprotonated thiohydrazide nitrogen and carbonyl oxygen [32].

3.2. Electronic spectra and magnetic moments

The magnetic moment value of 5.85 B.M. for [Mn(pmt)$_2$(*o*-phen)] (**1**) suggests the presence of high spin Mn(II) with five unpaired electrons. The electronic spectrum of **1** shows a band at 648 nm which may be assigned to the $^6A_{1g} \rightarrow {}^4T_{1g}$ transition in an octahedral geometry [33]. Other high energy bands in complex **1** occurring at 280 and 310 nm are due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. [Zn(pmt)$_2$(*o*-phen)] (**2**) is diamagnetic and shows two high intensity bands at 325 and 350 nm due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively.

3.2.1. ^1H and ^{13}C NMR spectra

The ^1H NMR spectrum of [Zn(pmt)$_2$(*o*-phen)] (**2**) shows two signals at 9.00 (s, 1H) and 8.58 (s, 1H, NH) ppm due to the proton of NH group attached to carbonyl and phenyl group, respectively. The methoxy hydrogens appear at 3.87 ppm. Phenyl and *o*-phen ring