



Zinc(II) halide complexes with 2-methoxyaniline ligand: Synthesis, characterization, thermal analyses, crystal structure determination and luminescent properties



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ABSTRACT

Three new mononuclear zinc(II) complexes, $[\text{Zn}(2\text{-MeO-C}_6\text{H}_4\text{NH}_2)_2\text{X}_2]$ (X is Cl in **1**, Br in **2** and I in **3**), were prepared from the reactions of ZnX_2 with 2-methoxyaniline (2-MeO-C₆H₄NH₂) ligand in methanol. Suitable crystals of these complexes were obtained for X-ray diffraction measurements by slow evaporation of methanol solution at room temperature. The three complexes were thoroughly characterized by thermogravimetric analysis, elemental analysis (CHNO), spectral methods (IR, UV–Vis, ¹³C{¹H}NMR, ¹H NMR and luminescence), and single crystal X-ray diffraction. The X-ray structural analysis indicated that in the structures of these complexes, the zinc(II) cation is four-coordinated in a distorted tetrahedral configuration by two N atoms from two 2-methoxyaniline ligands and two halide anions. Also, in these complexes intermolecular interactions, for example N–H···X hydrogen bonds (in **1–3**), C–H···X hydrogen bonds (in **3**), C–H···π interactions (in **1** and **2**) and π···π interactions (in **3**), are effective in the stabilization of the crystal structures. In addition, the luminescence spectra of all complexes in methanolic solution show that the intensity of their emission bands is stronger than that for free 2-methoxyaniline ligand.

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1. Introduction

In recent years, the rational design and synthesis of d¹⁰ metal complexes with novel structures including N donor ligands quickly developed [1–4]. In this regard, zinc(II) coordination complexes are important due to the good luminescence properties [5–8]. In zinc(II) complexes, due to its closed-shell (3d¹⁰) configuration, the zinc(II) cation has no optical spectroscopic signature, but it can enhance ligand luminescence upon coordination [9,10]. Luminescent zinc(II) complexes are important due to their application in electronic devices and chemical sensors [11–15]. On the other hand, 2-methoxyaniline (o-anisidine or o-methoxyaniline) compound, was first synthesized by Brunck in 1867, from the reaction of hydrochloric acid with 1-methoxy-2-nitrobenzene in the presence of tin metal catalyst [16]. Until now, this compound has been synthesized by numerous methods. The complexes with this ligand have been previously poorly studied. This compound is a bidentate ligand and can be coordinated to metal centers through one nitrogen atom from the –NH₂ group, one oxygen atom from the

methoxy group or both of them. There are only three complexes that the 2-methoxyaniline compound coordinate to metal centers, i.e. $[\text{Cd}(2\text{-MeO-C}_6\text{H}_4\text{NH}_2)_2(\mu\text{-SCN})_2]_n$ [17], $[\text{Y}(2\text{-MeO-C}_6\text{H}_4\text{NH}_2)(2\text{-MeO-C}_6\text{H}_4\text{NH}_2)(\text{OAr})_2]$ (where Ar is 2,6-(^tBu)₂-4-MeC₆H₂) [18] and $[\text{Hf}(2\text{-MeO-C}_6\text{H}_4\text{NH}_2)(\eta^5\text{-C}_5\text{Me}_5\text{Cl}_3)]$ [19]. In complex $[\text{Cd}(2\text{-MeO-C}_6\text{H}_4\text{NH}_2)_2(\mu\text{-SCN})_2]_n$, the 2-methoxyaniline ligand coordinated to Cd(II) ion in monodentate mode from –NH₂, but in the other two complexes, this ligand acts as a bidentate ligand in coordination to metal from –NH₂ and –OCH₃ groups. There are also several proton transfer compounds using 2-methoxyaniline, with proton donor molecules with general formula of $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3]_m[\text{X}]_n$ (where 2-MeO-C₆H₄NH₃ is 2-methoxyanilinium and X are organic anions or anion complexes), such as $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3]_2(\text{SO}_4)$ [20,21], $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3](\text{NO}_3)$ [22], $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3]\text{Cl}$ [23], $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3](\text{H}_2\text{PO}_4)$ [24], $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3][\text{X}]$ (X is 2-carboxy-4,6-dinitrophenolate) [25], $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3][\text{X}]$ (X is 3-hydroxy-2,4,6-trinitrophenolate) [26], $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3]\text{ClO}_4\cdot\text{S}$ (S is 1,4,7,10,13,16-hexaoxacyclooctadecane) [27], $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3][\text{SnCl}_3]\cdot 2\text{H}_2\text{O}$ [28], $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3]_2(\text{SnBr}_6)\cdot 2\text{H}_2\text{O}$ [29], $\text{Li}_2[2\text{-MeO-C}_6\text{H}_4\text{NH}_3]_4[\text{P}_6\text{O}_{18}]\cdot 5\text{H}_2\text{O}$ [30], $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3]_2[\text{BiCl}_5]$ [31] and $[2\text{-MeO-C}_6\text{H}_4\text{NH}_3]_2[\text{BiBr}_5]$

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[32] have been synthesized and characterized by the single crystal X-ray diffraction method. In continuation of these research works, herein we considered three new tetrahedral coordination complexes of zinc(II) including 2-methoxyaniline ligand, formulated as $[Zn(2-MeO-C_6H_4NH_2)_2X_2]$ (X is Cl in **1**, Br in **2** and I in **3**). The structures of these three complexes were studied by elemental and thermogravimetric analysis, X-ray crystallography and luminescence, UV–Vis, IR, 1H and $^{13}C\{^1H\}$ NMR spectroscopic techniques.

2. Experimental

2.1. Materials and physical methods

All materials were purchased from Merck and used without further purification. Melting points were obtained on a Kofler Heizbank Rechart type 7841 melting point apparatus. Elemental analyses were performed using a Heraeus CHN–O Rapid analyzer. Thermal behavior was measured with Mettler Toledo equipment. NMR spectra were recorded on a Bruker AC-300 spectrometer for protons at 300.13 MHz and for $^{13}C\{^1H\}$ NMR at 75.45 MHz in CD_3OD . Infrared spectra (4000 – 250 cm^{-1}) were recorded on a Shimadzu-470 spectrometer in CsI pellets. UV–Vis spectra were recorded on a Perkin Elmer Precisely PTP-1 Peltier System using a 1 cm path length cell in CH_3OH at room temperature, and luminescence spectra were recorded on a FP-6200 spectrofluorometer using a 1 cm path length cell in CH_3OH at room temperature.

2.2. Synthesis of $[Zn(2-MeO-C_6H_4NH_2)_2Cl_2]$ (**1**)

2-Methoxyaniline (0.40 g, 0.36 ml, 3.15 mmol) in 5 ml methanol was added to a solution of $ZnCl_2$ (0.18 g, 1.26 mmol) in methanol (15 ml) at room temperature and the resulting pale yellow solution was stirred for 15 min at $50\text{ }^\circ C$. This solution was left to evaporate slowly at room temperature. After four days, colorless crystals of **1** were isolated (yield 0.37 g, 76.8%, m. p. $166\text{ }^\circ C$). Infrared frequencies (CsI, cm^{-1}) are reported in Table 1. UV–Vis: λ_{max} (CH_3OH , nm): 211, 266. 1H NMR (CD_3OD , ppm): 3.54 (s, 3H, $-OCH_3$), 6.81–6.97 (m, 4H), $^{13}C\{^1H\}$ NMR (CD_3OD , ppm) 55.1(s), 111.1(s), 117.3(s), 120.9(s), 121.4(s), 135.1(s) and 149.2(s). Elemental analysis: $C_{14}H_{18}N_2O_2Cl_2Zn$ (%) (382.59); Anal. Calcd (%): C, 43.95; H, 4.70; N, 7.32; O, 8.36. Found: C, 43.76; H, 4.68; N, 7.28; O, 8.42.

2.3. Synthesis of $[Zn(2-MeO-C_6H_4NH_2)_2Br_2]$ (**2**)

The complex of **2** was prepared according to the procedure of complex **1** except using $ZnBr_2$ instead of $ZnCl_2$ in methanol. Colorless block single crystals of **2** suitable for X-ray analyses were obtained by slow evaporation, at room temperature over five days (yield 0.45 g, 75.7%, m. p. $182\text{ }^\circ C$). Infrared frequencies (CsI, cm^{-1}) are reported in Table 1. UV–Vis: λ_{max} (CH_3OH , nm): 212, 268. 1H NMR (CD_3OD , ppm): 3.51 (s, 3H, $-OCH_3$), 6.76–6.91 (m, 4H), $^{13}C\{^1H\}$ NMR (CD_3OD , ppm) 54.8(s), 110.4(s), 116.9 (s), 120.2(s), 120.6(s), 134.2(s) and 148.6(s). Elemental analysis: $C_{14}H_{18}N_2O_2Br_2Zn$ (%) (471.49); Anal. Calcd (%): C, 35.66; H, 3.82; N, 5.94; O, 6.79. Found: C, 35.52; H, 3.81; N, 5.91; O, 6.84.

2.4. Synthesis of $[Zn(2-MeO-C_6H_4NH_2)_2I_2]$ (**3**)

The complex of **3** was prepared according to the procedure of complexes **1** and **2** except using ZnI_2 instead of $ZnCl_2$ and $ZnBr_2$ in methanol. Colorless block single crystals of **3** suitable for X-ray analyses were obtained by slow evaporation, at room temperature over one week (yield 0.51 g, 71.6%, m. p. $193\text{ }^\circ C$). Infrared frequencies (CsI, cm^{-1}) are reported in Table 1. UV–Vis: λ_{max} (CH_3OH , nm): 214, 272. 1H NMR (CD_3OD , ppm): 3.49 (s, 3H, $-OCH_3$),

Table 1
Infrared frequencies of 2-methoxyaniline and complexes **1–3** (cm^{-1}).

Compound	$\nu(N-H)$	$\nu(C-H)_{ar}$	$\nu(C-H)_{Me}$	$\nu(C=C)$, $\nu(C-N)$, $\delta(N-H)$, $\delta(C-H)$	$\delta(C=C)$, $\delta(C-N)$	$\nu_{as}(COC)$	$\nu_s(COC)$	$\nu(Zn-N)$	$\nu(Zn-X)^a$
2-Methoxyaniline	3462m, 3371m	3047m	2967w, 2865w	1614s, 1506s, 1462s, 1441m, 1343m, 1304m, 1277s, 1228s, 1181m	1142m, 1131m, 1043s, 913m, 846w, 744s, 651m, 578m	1228s	1076m	–	–
1	3316m, 3213m	3015w	2970w, 2832w	1615m, 1567m, 1498s, 1463m, 1448w, 1353m, 1297w, 1256s, 1186m	1045s, 1021s, 933w, 858m, 827m, 745s, 662m, 596m, 520m	1227m	1069s	394m	278s
2	3317m, 3211m	3012w	2966w, 2833w	1613m, 1560m, 1507s, 1461m, 1428m, 1326m, 1278m, 1262s, 1172m	1036s, 1015s, 915w, 839m, 830m, 751s, 665m, 592m, 508m	1224m,	1073s	390m	259m
3	3298m, 3218m	3008w	2926w, 2833w	1600m, 1560m, 1507s, 1461m, 1450m, 1341m, 1305w, 1261s, 1196m	1053s, 1030s, 934m, 862m, 831m, 751s, 632m, 598m, 506m	1226m	1081s	388m	251m

^a X is Cl in **1**, Br in **2** and I in **3**.

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