Thermal Characterization 2-Methoxybenzoate of Bivalent Metal Ion Complexes

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ABSTRACT
Bivalent ion interaction Studying the reactions of Co (II), Ni (II), Cu (II), and Zn (II) with 4,6-dihydroxy-2-mercaptopyrimidine (DHMP) in the presence of oxalic acid (Ox), malonic acid (Mal), o-phenylene diamine (OPDA), 2,2-bipyridyl (Bipy), 1,10-phenanthroline (phen), and ethylene diamine (En). Compounds of the solid form M-2-MeO-Bz have been synthesised; M denotes the bivalent metals Mn, Co, Ni, Cu, and Zn, while 2-MeO-Bz is 2-methoxybenzoate. Differential scanning calorimetry (DSC), X-ray powder diffractometry, thermogravimetry, and derivative thermogravimetry were all utilised to describe and evaluate the thermal behaviour of these substances.
Keywords: Bivalent metals, Thermal behavior, Solid state, Methoxybenzoate, Curves

I. INTRODUCTION

When it comes to the history of coordination chemistry, Schiff base complexes with transition metals take centre stage. There are several industrial and medical uses for Schiff base metal complexes, hence they have been the subject of much research. Intriguing physicochemical features, prominent biological activities, and as models of the metalloenzyme active sites have garnered a lot of attention to metal complexes of N and S chelating ligands. Numerous metallobiomolecules rely on N and S atoms at their active sites for metal coordination, as is well known. Derivatives of the triazole family have been shown to have a variety of therapeutic effects, including those against tuberculosis, bacteria, fungus, hypertension, and low body temperature. The need for novel metal-based antibacterial chemicals has sparked interest in the field of metallo-organic chemistry. The rapid rise of bacterial resistance to antibiotics is a major public health concern. Research initiatives focusing on infectious illnesses must now prioritise the creation of new, highly effective antibacterial medicines with a unique mode of action.

II. EXPERIMENTAL

Carbonates of Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) were prepared by adding slowly with Saturated sodium hydrogen carbonate solution is continuously stirred into solutions of the respective metal chlorides (excluding copper) until complete precipitation of the metal ions occurs. Washing with distilled water until the chloride ions were gone from the precipitates (qualitative test with AgNO3 /HNO3 solution) allowed them to remain in aqueous suspension.

Mixing the appropriate metal carbonates with slightly excess 2-methoxybenzoic acid 99% (2-MeO-HBz) from Aldrich yielded solid state compounds of Mn (II), Co (II), Ni (II), and Zn (II). Slowly, the aqueous suspension was heated to the point of near-ebullition, at which point the carbonates in the solution were completely neutralised. After cooling, the solutions were stored in an ice bath so that

the acid could recrystallize, and then they were filtered using Whatman no. 40 filter paper. Accordingly, the 2-methoxybenzoate metal aqueous solutions were evaporated in a water bath until nearly dry and stored in a desiccator over calcium chloride.

Due to its poor solubility, the copper compound was synthesised by gently adding the aqueous solution of Na-2- MeO-Bz 0.1 mol L-1 to the appropriate metal sulphate solution, while continuously stirring. The precipitate was filtered using Whatman no. 42 filter paper, dried in a desiccator over anhydrous calcium chloride, and stored under continuous pressure until its mass was constant.

Metal ion, water, and 2-methoxybenzoate concentrations in the solids were calculated using the temperature-gradient (TG) plots. Complexometry with standard EDTA solution was also used to detect the metal ions after the compounds were combusted to their respective oxides and dissolved in hydrochloric acid.

X-ray powder patterns were obtained by using a SIEMENS D-5000 X-ray diffractometer using Cu Kα radiation (lλ= 1.541 Å) and setting of 40 kV and 20 mA. Infrared spectra for sodium 2-methoxybenzoate as well as for its metal-ion compounds were run on a Nicolet model Impact 400 FT-IR instrument, within the 4000-400 cm-1 range. The solid samples were pressed into KBr pellets.

Simultaneous TG-DTA and TG/DTG curves were obtained with thermal analysis system model SDT 2960 from TA Instruments. The purge gas was an air flow of 100 mL min-1. A heating rate of 20 ºC min-1 was adopted with samples weighing about 7 mg. Platinum crucibles were used for TG-DTA. DSC curves were obtained with thermal analysis systems model DSC 25 from Mettler Toledo. The purge gas was an air flow of 100 mL min-1. A heating rate of 20 ºC min-1 was adopted with samples weighing about 5 mg. Aluminium crucibles, with perforated cover, were used for DSC.

III. RESULTS AND DISCUSSION

Verification that the generated binary compounds were contaminated with 2-methoxybenzoic acid (2-MeO-HBz) was made possible by analysing their TG-DTA curves, infrared spectra, and chemical composition. The contamination must have arisen from aggregation phenomena, and the method employed to get rid of the surplus of acid probably wasn't very effective because 2-MeO-Bz is more soluble in 2-methoxibenzoate solution and doesn't recrystallize, even in a cold bath. However, the TG-DTA curves revealed that 2-MeO-HBz is eliminated up to 200ºC, prior to the thermal degradation of these compounds, and without a matching thermal event.

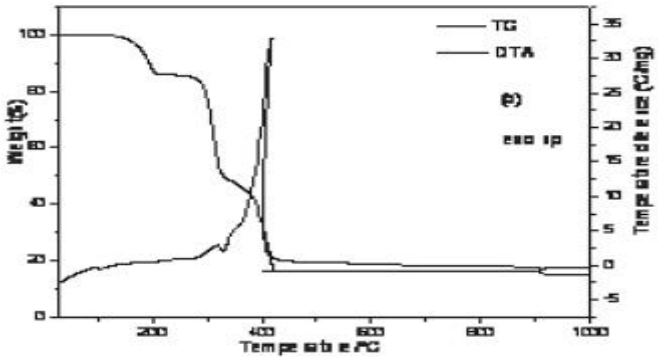

Figure 1: TG-DTA curves of cobalt compound

Fig. 1 displays typical TG-DTA curves for cobalt compounds. To get 2-methoxybenzoate of manganese, cobalt, nickel, and zinc, the aforementioned compounds were heated to 200 oC. Table 1 displays the results of the analytical and thermo analytical (TG) tests performed on the produced substances.

Table 1: Spectroscopic data for sodium 2-metoxybenzoate (2-MeO-Bz) and compounds with some bivalent metal ions a (cm-1)

Compound	$\nu_{(O-H)}H_2O$ [b]	$\nu_{sym\ (COO^-)}$ [c]	$\nu_{asym\ (COO^-)}$ [c]	$\Delta\nu$ [d]
Na(2-MeOBz)	-	1399_s	1595_s	196
$Mn(2\text{-}MeOBz)_2$	-	1380_s	1619_s	239
$Co(2\text{-}MeOBz)_2$	-	1373_m	1619_s	246
$Ni(2\text{-}MeOBz)_2$.	-	1379_s	1625_s	246
$Cu(2\text{-}MeOBz)_2.1H_2O$	3452_{br}	1394_s	1607_s	213
$Zn(2\text{-}MeOBz)_2$	-	1412_s	1618_s	206

[a] br, broad; w, weak; m, medium; s, strong;
[b] $\nu_{(O-H)}$: hydroxyl group stretching frequency;
[c] $\nu_{sym\ (COO^-)}$ and $\nu_{asym\ (COO^-)}$: symmetrical and anti -symmetrical vibrations of the COO^- group, respectively
[d] $\Delta\nu = \nu_{asym\ (COO^-)} - \nu_{sym\ (COO^-)}$

X-ray powder diffraction patterns (Fig. 2) reveal that all the compounds have a propensity to adopt a crystalline structure, with evidence for the creation of isomorphous ones present in all save the copper compound. Table 2 displays the infrared spectroscopy data of 2-methoxybenzoate and its derivatives with the metal ions investigated in this work. The 1700-1400 cm-1 range was the primary focus of the work due to its potential utility in assigning coordination locations. The strong bands at 1595 and 1399 cm-1 in sodium-2-methoxybenzoate are a result of the carboxylate group's anti-symmetrical stretching frequency and its symmetrical stretching frequency, respectively. It has been determined that the anti-symmetrical and symmetrical stretching frequencies for the produced compounds are 1625 cm-1 and 1307 cm-1, respectively. These findings imply that the carboxylate group is behaving as unidentate bound to the metal ion, since the anti-symmetrical and symmetrical stretching vibrations of the carboxylate are moved to higher and somewhat lower frequencies, respectively, compared with the sodium salt.

Table 2: Analytical and thermoanalytical (TG) data of the compounds

Compound	Metal Oxide (%)			Δ (2-MeO-Bz) (%)		H_2O (%)		Final Residue
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	
$Mn(2\text{-}MeO\text{-}Bz)_2$	15.38	15.62	15.50	78.65	78.31	-	-	Mn_3O_4
$Co(2\text{-}MeO\text{-}Bz)_2$	16.31	15.96	16.31	77.78	78.03	-	-	CoO
$Ni(2\text{-}MeO\text{-}Bz)_2$	16.25	16.45	16.17	79.31	78.85	-	-	NiO
$Cu(2\text{-}MeO\text{-}Bz)_2.1H_2O$	16.55	16.57	16.20	79.28	79.26	4.69	4.67	CuO
$Zn(2\text{-}MeO\text{-}Bz)_2$	17.78	17.97	17.45	77.87	77.63	-	-	ZnO

Key: 2-MeO-Bz = 2-methoxybenzoate

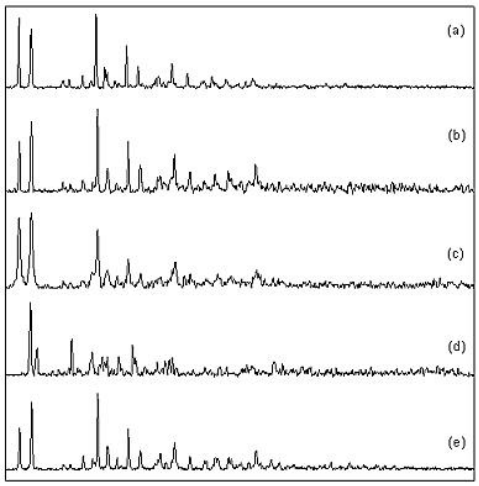

Figure 2: X-ray powder diffraction patterns of the compounds: (a)Mn(2-MeOBz)2 , (b)Co(2-MeO-Bz)2 , (c)Ni(2-MeO-Bz)2 , (d)Cu(2-MeO-Bz).1H2 O and (e)Zn(2- MeO-Bz)2 . 2-MeO-Bz = 2-metoxybenzoate.

IV. CONCLUSIONS

Synthesized binary products from the reaction of metallic carbonate with 2-methoxybenzoic acid were contaminated, as evidenced by TG-DTA curves, infrared spectra, and chemical analyses. It was also demonstrated by DTG-DTA that the 2-MeO-HBz is removed prior to thermal degradation of these compounds. This means that thermosynthesis might be used to produce binary chemicals. Crystalline structures were detected by X-ray powder diffraction in all save the copper compound, suggesting the production of isomorphous compounds.

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