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SYNTHESES AND THERMAL PROPERTIES OF SOME COMPLEXES WITH 2-MERCAPTONICOTINIC ACID

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Five new complexes M(Hmna)$_2$ [M=Mn(II) (1), Co(II) (2), Ni(II) (3), Cu(II) (4) and Zn(II) (5), H$_2$mna=2-mercaptonicotinic acid] have been synthesized and characterized by elemental analyses, IR spectra, thermogravimetric analyses. In addition, molar specific heat capacities and enthalpy changes of reactions were determined by a microcalorimeter at 298.15 K. All the complexes exhibited similar IR spectra, the sulfur and oxygen atoms from monoanionic Hmna$^-$ ligand coordinated to M^{2+} in a bidentate fashion.

The thermal stability of M(Hmna)$_2$ complexes varied in the sequence **1**>**2**>**3**>**4**>**5**. The complexes were stable up to about 300°C and decomposed to oxides at higher temperatures. The molar specific heat capacities of the complexes were determined in the range between 106.452±0.399 and 145.920±0.423 J mol^{-1} K^{-1}. The enthalpy changes of reactions, $\Delta_r H_m^0$, were determined from 18.28±0.05 to 52.59±0.07 kJ mol^{-1} for complexes **1**–**5**, indicating that the thermodynamic stability of M(Hmna)$_2$ increased in the sequence from Mn^{2+} to Zn^{2+}.

Keywords: *enthalpy changes of reaction, 2-mercaptonicotinic acid, molar specific heat capacity, thermal stability*

Introduction

Metallic complexes of heterocyclic thiones have been widely studied because of their relevance to biological systems and the versatility in their coordination forms [1]. Heterocyclic thiolates are versatile ligands that are capable of involving either the exocyclic sulfur or the endocyclic nitrogen atoms of the thioamide group in monodentade, chelating or bridging coordination [2–7]. 2-Mercaptonicotinic acid has a carboxyl group in the *meta*-position to the pyridyl-N [8, 9]. This polyfunctional ligand exhibited three potential binding sites and may act as a deprotonated ligand through either the carboxylate or the thiolate groups, or as a bidentate ligand through the pyridinic N of the heterocycle and thiolate S atoms coordinated to the same metal ion or bridging two metal ions.

In the last years, several metal complexes containing 2-mercaptonicotinic acid ligand have already been reported [8–18]. Some of them possess well antimicrobial activities [14, 15]. Among them, to our knowledge, 2-mercaptonicotinic acid ligand and their relevant first-row transition metal complexes were less reported [19, 21].

In this paper, we synthesized Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with 2-mercaptonicotinic acid in ethanol solution. The complexes were characterized by elemental analyses, IR spectra, thermogravimetric analyses, molar specific heat capacities and enthalpy changes of reactions. The aim of our paper was to prepare the complexes of first-row transition metals with 2-mercaptonicotinic acid, to determine their properties and to investigate their thermal decomposition in a static air atmosphere.

Experimental

Materials

All chemicals used in the experiments were of analytical grade and commercial available without further purification. Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} were determined with EDTA by complexometric titration and Cu^{2+} was determined by iodimetry.

Syntheses of the complexes

0.3 mmol M(Ac)$_2\cdot n$H$_2$O (when M=Cu, n=1, M=Mn, Zn, n=2, M=Co, Ni, n=4) were added into a clear solution of 2-mercaptonicotinic acid, 0.6 mmol in 30 mL of ethanol, under electromagnetically stirring. After stirring for 40 min, the precipitates were collected by filtration, washed with distilled water and ethanol, respectively, and dried in vacuum and stored in a desiccator over P$_4$O$_{10}$ ready to be used.

Methods

C, H, N contents were determined on a Perkin-Elmer 2400 type elemental analyzer. The IR

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spectra were recorded with a BEQ VZNDX-550 spectrometer using the KBr pellets technique over the range 4000–400 cm^{-1}. All TG-DTG tests were performed with a Perkin-Elmer thermogravimetric instrument. ICP-AES experiment were carried out on a T.E. IRIS advantage inductively coupled plasma atomic emission spectrophotometer. The calorimetric experiments were performed with an RD496- type microcalorimeter [21]. The calorimetric constant at 25.15°C was determined by the Joule effect before experiment, which was 63.901±0.030 $\mu V\ mW^{-1}$. The enthalpy of dissolution of KCl (spectral purity) in deionized water was measured to be 17.238±0.048 kJ mol^{-1}, which was in good agreement with the value of 17.241±0.018 kJ mol^{-1} from reference [22].

Results and discussion

Elemental analyses

The yields, colour and elemental analytical data were summarized in Table 1. From these values, we could find that the experimental data were consistent with the calculated values and the formula $M(Hmna)_2$ were determined.

IR spectra

All the prepared complexes exhibited similar IR spectra in the solid-state.

The bands due to the ν_{NH} (3436 cm^{-1}) or ν_{SH} (2410 cm^{-1}) vibrations, which presented in the free ligand, were not observed in the IR spectra of the complexes, indicating that the deprotonation of the ligand. The IR spectra of the complexes showed distinict vibrational bands at 1573–1564 and 1317–1310 cm^{-1}, which have been assigned as the ν_{CN} vibrations (thioamide I and II bands) and at 1055–1048 and 635–629 cm^{-1}, which were attributed to the ν_{CS} vibrations (thioamide III and IV bands). The corresponding thioamide bands of the free ligand were at 1562, 1310, 1071 and 650 cm^{-1}, respectively. The most significant change have been observed in the thioamide bands III and IV, supporting the sulfur donation of the ligand upon its coordination to the metal ions.

The band of carboxyl group at 1681 cm^{-1}, presented in the ligand, disappeared in the the spectra of the complexes and two bands arised from symmetric and asymmetric stretching vibrations of COO^- at 1473–1464 and 1662–1656 cm^{-1}, respectively. The $\Delta\nu=\nu_{as}-\nu_s=$ $=187–194$ cm^{-1} was more than that of sodium salt of H_2mna ($\Delta\nu$=1603–1438=165 cm^{-1}), indicating that the carboxyl groups of the complexes were coordinated with the metal ions in monodentate coordination mode [23]. Thus, the IR spectra indicated that coordination by the monoanionic $Hman^-$ ligand to the metal center was accomplished with the S and O atoms.

Thermogravimetric analyses

Thermogravimetric analyses (TG-DTG) for the complexes were performed from 40 to 800°C at a heating rate of 10°C min^{-1} under a static air atmosphere (Figs 1 to 5) and the thermal decomposed procedure were deduced as was presented in Scheme 1.

All the complexes were decomposed into the final compounds in one step. The temperature presented in the middle of the temperature enumeration (Scheme 1) was the peak temperature corresponding

$$Mn(Hmna)_2 \xrightarrow[74.49\%\ (74.94\%)]{329\sim402\sim453℃} Mn_2O_3$$

$$Co(Hmna)_2 \xrightarrow[76.74\%\ (77.42\%)]{318\sim398\sim434℃} Co_2O_3$$

$$Ni(Hmna)_2 \xrightarrow[76.89\%\ (77.48\%)]{307\sim369\sim405℃} Ni_2O_3$$

$$Cu(Hmna)_2 \xrightarrow[77.82\%\ (78.61\%)]{297\sim343\sim385℃} CuO$$

$$Zn(Hmna)_2 \xrightarrow[77.28\%\ (78.22\%)]{282\sim338\sim402℃} ZnO$$

Scheme 1 Thermal decomposed procedure for all the complexes

Table 1 Yields (%) from the preparation, colour and composition analytical data of the above complexes

Complex	Yield	Colour	Found(calcd)/%			
			M	C	H	N
$Mn(Hmna)_2$ **1**	85	yellow	15.03 (15.12)	39.75 (39.68)	2.12 (2.22)	7.65 (7.71)
$Co(Hmna)_2$ **2**	90	brown	15.89 (16.05)	39.17 (39.25)	2.14 (2.20)	7.57 (7.63)
$Ni(Hmna)_2$ **3**	90	fawn	15.78 (15.99)	39.22 (39.27)	2.13 (2.20)	7.52 (7.63)
$Cu(Hmna)_2$ **4**	80	yellowgreen	16.84 (17.09)	38.31 (38.76)	2.01 (2.17)	7.34 (7.53)
$Zn(Hmna)_2$ **5**	88	white	17.46 (17.50)	38.52 (38.57)	2.11 (2.16)	7.44 (7.50)

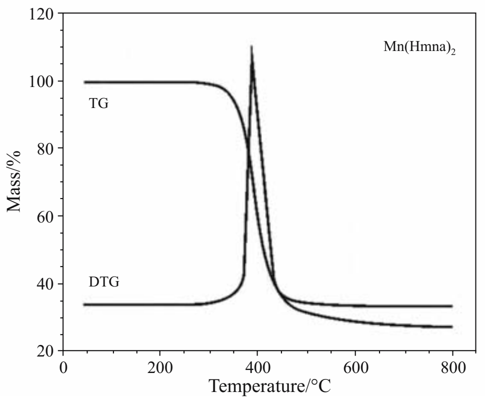

Fig. 1 TG and DTG curves for the complex **1**

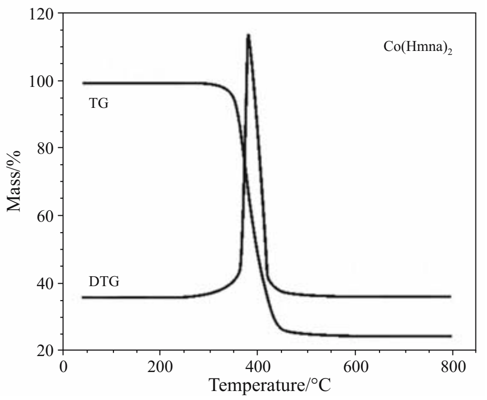

Fig. 2 TG and DTG curves for the complex **2**

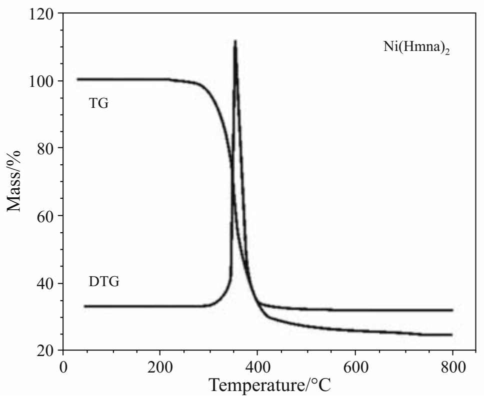

Fig. 3 TG and DTG curves for the complex **3**

to the maximum rate of the thermal decomposition process. The final products of all the complexes were characterized as oxides by X-ray powder diffraction.

The experimental loss percentage masses (74.49% for **1**, 76.74% for **2**, 76.89% for **3**, 77.82% for **4** and 77.28% for **5**) at the end of the decomposition of the complexes were consistent with the calculated values of 74.94% for **1**, 77.42% for **2**, 77.48% for **3**, 78.61% for **4** and 78.22% for **5**.

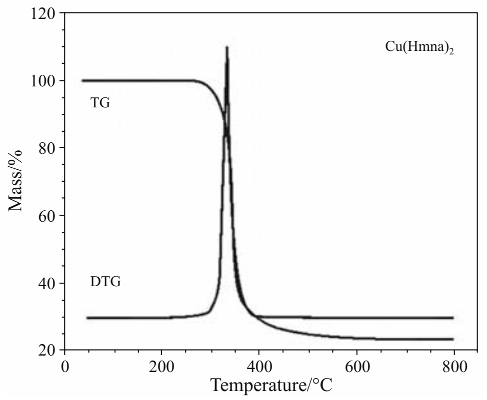

Fig. 4 TG and DTG curves for the complex **4**

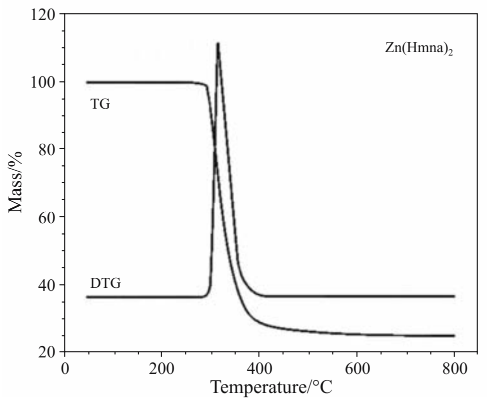

Fig. 5 TG and DTG curves for the complex **5**

Molar specific heat capacities of complexes

The molar specific heat capacities of the complexes were measured according to reference [24] (measuring 6 times for each sample), and their molar specific heat capacities were calculated using the data presented in Table 2 and the results were listed in Table 3.

The results in Table 3 indicated that the data of molar specific heat capacities of complexes existed change irregularly: Co(Hmna)$_2$ had the lowest value and Zn(Hmna)$_2$ had the highest one.

Enthalpy changes of reactions

The crude products of the reactions from the calorimetric experiments were collected and separated by the centrifugal effect. The solid crude products were purified and identified as being the same product as that obtained in the direct synthesis. The concentration of M^{2+} retained in the centrifugal liquid were determined to be $6 \cdot 10^{-3}$ μg mL^{-1} by the ICP-AES experiment, indicating that the starting reactants have been transformed fully to the title products, that was, the reaction proceeds to 100%. Within the range of the experimental temperature, the complexation reactions

Table 2 Data of the heat and heat capability of the empty cell and the standard substances (298.15 K)[a]

Heats of disequilibrium and specific heat capacity	The empty cell	Standard α-Al_2O_3	Sublimed benzoic acid
$q(\mathbf{1})$/mJ	3689.151	3825.725	3909.248
$q(\mathbf{2})$/mJ	3686.060	3827.302	3912.490
$q(\mathbf{3})$/mJ	3687.238	3829.849	3911.858
$q(\mathbf{4})$/mJ	3690.008	3827.946	3908.362
$q(\mathbf{5})$/mJ	3691.445	3830.873	3912.998
$q(\mathbf{6})$/mJ	3691.994	3830.667	3914.650
q(mean±SD)/mJ	3689.316±0.495	3828.727±0.842	3911.601±0.968
The relative standard deviation	$2.578\cdot10^{-4}$	$2.200\cdot10^{-4}$	$2.476\cdot10^{-4}$
Specific heat capacity c/(J mol^{-1} K^{-1})		78.724±1.377 (79.03[25])	145.891±1.003 (145.327[26])

[a] $SD=\sqrt{\frac{\sum(x_1-\bar{x})^2}{n-1}}$

Table 3 Data of the specific heat capacities of the complexes (298.15 K)[b]

Complexes	m/g	q(mean±SD)/mJ	c(mean±SD)/(J mol^{-1} K^{-1})
$Mn(Hmna)_2$	2.6465	3859.054±1.701	117.657±0.405
$Co(Hmna)_2$	2.4656	3832.387±1.477	106.452±0.399
$Ni(Hmna)_2$	3.0276	3907.546±1.010	132.231±0.272
$Cu(Hmna)_2$	2.3356	3853.553±0.830	129.002±0.330
$Zn(Hmna)_2$	2.2137	3865.394±1.349	145.920±0.423

[b] $SD=\sqrt{\frac{\sum(x_1-\bar{x})^2}{n-1}}$

Table 4 Enthalpy changes of reactions at 298.15 K

$M^{2+}(aq)+2Hmna^-(aq) \rightarrow M(Hmna)_2(s)$	Q/mJ						Mean/mJ	$\Delta_r H_m^\theta$/ kJ mol^{-1}
Mn^{2+}	729.518	736.430	729.024	727.893	730.021	743.855	732.790±2.531	18.28±0.05
Co^{2+}	851.540	849.218	843.271	856.008	863.255	851.031	852.387±2.750	21.38±0.06
Ni^{2+}	1011.263	1020.981	1015.969	1026.338	1005.456	1007.169	1014.529±3.318	25.39±0.07
Cu^{2+}	1451.588	1467.070	1468.335	1471.609	1456.105	1468.078	1463.798±3.260	36.65±0.05
Zn^{2+}	2107.577	2116.009	2106.754	2122.010	2111.992	2102.359	2111.117±2.896	52.59±0.07

were endothermic. For each reaction system, Q was measured six times at 298.15 K. Q, mean value of six parallel experiments for each reaction system, was listed in Table 4. As it was observed from Table 4, the calculated values of $\Delta_r H_m^\theta$ increased in terms of the sequence from Mn^{2+} to Zn^{2+}, which indicated the stability of $M(Hmna)_2$ increased gradually in reaction system.

$$M^{2+}(aq)+2Hmna^-(aq)\rightarrow M(Hmna)_2(s)$$
$$(M\text{=Mn, Co, Ni, Cu and Zn})$$

Conclusions

In summary, we have prepared the title complexes, which were characterized by IR spectra to indicate that the sulfur and oxygen atoms from the $Hmna^-$ ligand coordinated to M^{2+} in a bidentate fashion. All the complexes exhibited same coordination pattern. The results of thermogravimetry presented that the thermal stability of $M(Hmna)_2$ complexes varied with the sequence of **1**>**2**>**3**>**4**>**5**. The molar specific heat capacities of the complexes were determined in the range between 106.452±0.399 and

145.920±0.423 J mol^{-1} K^{-1}. The enthalpy changes of reactions, $\Delta_r H_m^\theta$, were determined from 18.28±0.05 to 52.59±0.07 kJ mol^{-1} for complexes **1**–**5**, which indicated that the thermodynamic stability of $M(Hmna)_2$ increased from Mn^{2+} to Zn^{2+}.

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