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Short communication

A thermoanalytical study of zinc methanesulfonate urea, imidazole and 2,2-dithiobis(pyridine-*N*-oxide) complexes

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Abstract

Complexes of composition $Zn(MS)_2(UR)_6$, $Zn(MS)_2(IMI)_6$, $Zn(MS)_2(DITHIO)_4$ (where MS: methanesulfonate; UR: urea; IMI: imidazole; DITHIO: 2,2-dithiobis(pyridine-*N*-oxide)) were prepared by reaction of hydrated zinc methanesulfonate with the ligands and characterized by CHN microanalysis, atomic absorption and IR absorption spectra. The complexes were also studied by thermogravimetric analysis and differential scanning calorimetry. Infrared spectroscopy data reveal that methanesulfonate is monodentate in the complexes. Thermogravimetric curves indicate that the decomposition of the complexes occurs in the range 395–1170 K and that ZnO is the final residue.

Keywords: Urea; Imidazole; 2,2-Dithiobis(pyridine-*N*-oxide); Methanesulfonate

1. Introduction

The coordination properties of several zinc complexes have been described in the literature and were found to exist in a variety of structures [1–3]. The methanesulfonate anion has tetrahedral geometry with C_{3v} symmetry and coordinates more strongly than perchlorate and tetrafiuoroborate, but less strongly than chloride and bromide. Methanesulfonate exhibits multi-dentate characteristics and can also act as a bridge between two metal ions [4,5]. Although complexes containing urea [6–9], imidazole [10–13] and 2,2-dithiobis(pyridine-*N*-oxide) [14–17] have been described in the literature data on zinc methanesulfonate complexes with such ligand not have been studied previously.

The aim of the present study was synthesize, characterize and evaluate the effect of different ligands on the thermal stability of zinc methanesulfonate complexes. Urea has nitrogen bonded to the carbonyl group improving the donor ability of oxygen [18]. Urea complexes have been used successfully in the antimony treatment of a kala-azar epidemic in the past. Imidazole is a ligand common in biologically important systems. Coordination complexes containing imidazole are suitable models to study different aspects of biological systems because many etalloproteins are coordinated by the imidazole chains [19]. Amine-*N*-oxides have commercial importance as fungicides and preservatives and their biological activity is attributed to the presence of the *N*-oxide group adjacent to the carbon the sulfur atom neighbor [14,15].

2. Experimental

The complexes were prepared by reaction of hydrated zinc methanesulfonate (MS) in the presence of urea (UR), imidazole (IMI) and 2,2-dithiobis(pyridine-*N*-oxide) (DITHIO) ligands in methanol (molar ratio 1:6).

The complexes were characterized by carbon, hydrogen and nitrogen microanalysis using a CHN Perkin-Elmer instrument model 240. Metal content was determined by atomic absorption using a VARIAN 10 analyzer. IR spectra were performed on FT-IR ABB BOMER model MB104, using KBr pellets over the range of 4000–500 cm^{-1}. Electrolytic conductance measurements were performed at 25 °C, in methanol using a QUIMIS Q45 instrument. X-ray diffractograms were obtained on a Shimadzu XRD-6000 diffractometer using Cu Kα radiation. Thermogravimetric

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curves were obtained on a SHIMADZU TGA-50H instrument at a heating rate 10 °C min^{-1} in nitrogen (50 ml min^{-1} flow), using a platinum crucible and 3.6 mg of sample. DSC curves were obtained on a SHIMADZU DSC-50H thermobalance at a heating rate of 10 °C min^{-1} in nitrogen (50 ml min^{-1} flow), using an aluminum crucible and 1.2 mg of sample.

3. Results and discussion

The analytical results summarized in Table 1 are in agreement with the composition: $Zn(MS)_2(UR)_6$, $Zn(MS)_2(IMI)_6$ and $Zn(MS)_2(DITHIO)_4$. Conductance measurements of millimolar methanol solutions of the complexes indicate non-electrolyte behavior. This suggests that the methanesulfonate anions are coordinated [20].

The IR data are given in Table 2. The C_{3v} symmetry of the free ion ($CH_3SO_3^-$) is changed for C_s when they are coordinated through an oxygen (as in H_3C–SO_2–O*), where O* represents the coordinating oxygen. The number of bands increases in the IR and Raman spectra due to the splitting of E and A species. In the present study, the measurements were carried out up to 500 cm^{-1} and hence the discussions have been restricted the high frequency bands in the IR spectrum. In these complexes, four bands were identified indicating such symmetry lowering and comparing with the data of [5] it is possible to suggest the existence of monodentate methanesulfonates. In all zinc complexes, the methanesulfonate group is considered to be only weakly coordinated. The IR spectra of UR ligands display strong bands at about 1669 cm^{-1}, which can be assigned to the stretching mode of CO. Upon coordination, this band was shifted to 1643 cm^{-1} indicating that the UR ligands are coordinated to zinc ions through the carbonyl oxygen in the $Zn(MS)_2(UR)_6$ complex. The imidazole NH stretching appears as broad bands in a wide range from ∼3500 to 3000 cm^{-1}. The IR spectra of $Zn(MS)_2(IMI)_6$ complex confirmed that the imidazole ligands were coordinated through a broad intense band at 3300 cm^{-1}. The NO stretching band appears at 1248 cm^{-1} in the DITHIO ligand. From the IR spectra of $Zn(MS)_2(DITHIO)_4$ complex it is not possible to distinguish the NO stretching band from SO_2 stretching band of MS, since they appear approximately in the same region, but it is certain that NO stretching is shifted to lower frequencies [4].

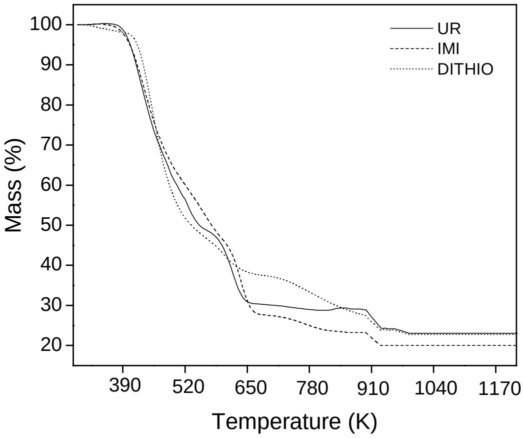

Fig. 1. Thermogravimetric curves of $Zn(MS)_2(UR)_6$, $Zn(MS)_2(IMI)_6$ and $Zn(MS)_2(DITHIO)_4$ complexes.

Fig. 1 shows thermogravimetric curves of $Zn(MS)_2(UR)_6$, $Zn(MS)_2(IMI)_6$ and $Zn(MS)_2(DITHIO)_4$ complexes. Thermogravimetric curves were recorded to evaluate the thermal stability of the complexes. The heating rate and atmosphere were chosen according to preliminary investigations [17]. Thermogravimetric data of these complexes are summarized in Table 3.

The complexation of different ligands can have distinct effects on the thermal stability of the complexes as result of the different chemical environments created. Thermal sta-

Table 1
Summary of analytical results of the complexes of $Zn(MS)_2(L)_x$ (where L = UR and IMI when $x = 6$; L = DITHIO when $x = 4$)

Ligands	Zn (%)		C (%)		H (%)		N (%)	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
UR	10.6	10.5	15.7	15.8	4.9	4.9	27.6	27.2
IMI	9.8	9.6	36.1	35.5	4.5	4.6	25.3	25.3
DITHIO	5.1	5.0	39.8	39.9	3.0	3.1	8.9	9.0

Table 2
Vibrational frequencies (cm^{-1}) of the complexes

Complexes	Assignment						
	$\nu asSO_2$	νsSO_2	νS–O	νS–CH_3	νCO	νNH	νNO
$Zn(MS)_2(UR)_6$	1245	1187	1041	781	1643	–	–
$Zn(MS)_2(IMI)_6$	1243	1187	1052	781	–	3300	–
$Zn(MS)_2(DITHIO)_4$	1230	1187	1052	770	–	–	**

** to add to $\nu asSO_2$.

Table 3
Summary of thermal decomposition of the complexes of $Zn(MS)_2(L)_x$ (where L = UR and IMI when $x = 6$; L = DITHIO when $x = 4$)

Ligands	Temperature range (K)				Mass loss (%)			
	I	II	II	Residue	I	II	III	Residue
UR	423–531	531–640	640–951	1173	39.7	21.6	23.5	15.2
IMI	387–579	579–690	690–980	1173	44.2	16.2	24.3	15.3
DITHIO	319–422	422–617	617–771	1171	3.1	64.6	12.9	19.4

bility depends on the ligand type, the structure and character of the bonds between ligands and central atom. In these zinc complexes, the thermogravimetric curves show three-step decomposition. In first and second stages, the complexes decompose to give zinc methanesulfonates, which further decompose at higher temperatures to yield zinc oxide. The observed mass loss coincides with the values calculated for the intermediate and the final product. As all these complexes decompose at the metal–ligand bond, the more stable compounds would be expected to have a stronger metal–ligand bond. In accordance with data showed in Table 3 and Fig. 1, the thermal stability decreases as follows: $Zn(MS)_2(UR)_6 > Zn(MS)_2(IMI)_6 > Zn(MS)_2(DITHIO)_4$. This difference in thermal behavior also may be attributed to the steric restrictions imposed by the ligands in these complexes. The 2,2-dithiobis(pyridine-*N*-oxide) ligand has a Lewis structure with more bulk than imidazole and urea, this can result in a weaker interaction with zinc ions in relation to the other ligands, consequently a small thermal stability.

Fig. 2 shows DSC curves of $Zn(MS)_2(UR)_6$, $Zn(MS)_2(IMI)_6$ and $Zn(MS)_2(DITHIO)_4$ complexes and Table 4 summarizes the enthalpy change and temperature range of decomposition of the complexes. DSC curves show that the decomposition of the urea and imidazole ligands are both exothermic for the $Zn(MS)_2(UR)_6$ and $Zn(MS)_2(IMI)_6$ complexes, respectively. On the other hand, in the $Zn(MS)_2(DITHIO)_4$ complex, the dithio ligand decomposed both exothermically and endothermically. The experimental ΔH value depends on the bonds between ligands and central atom and of Lewis structure of ligands. DSC measurements (Table 4) also suggested a weaker metal–ligand bond in the $Zn(MS)_2(DITHIO)_4$ complex than in the $Zn(MS)_2(IMI)_6$ and $Zn(MS)_2(UR)_6$ complexes.

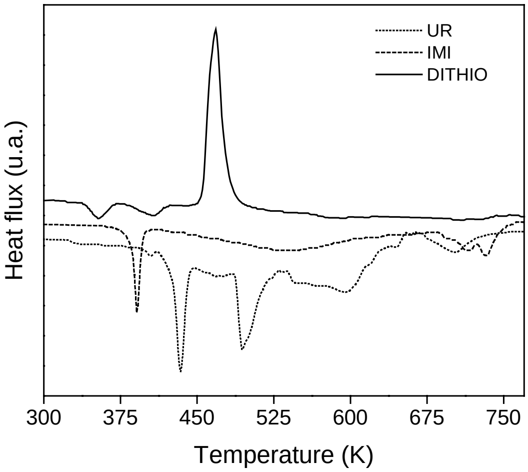

Fig. 2. DSC curves of $Zn(MS)_2(UR)_6$, $Zn(MS)_2(IMI)_6$ and $Zn(MS)_2(DITHIO)_4$ complexes.

4. Conclusions

Zinc methanesulfonate complexes with urea, imidazole and 2,2-dithiobis(pyridine-*N*-oxide) have been prepared. IR spectra contain four bands attributed to methanesulfonate ions indicating monodentate coordination. All ligands studied in this work are bound to the zinc ions as monodentate. The thermal decomposition of zinc methanesulfonate complexes with urea, imidazole and 2,2-dithiobis(pyridine-*N*-oxide) occurs in the range 319–1173 K and resulted in ZnO as final residue. The thermal stability decreases as a function of the steric restrictions of the ligands interacting with the central atom: $Zn(MS)_2(UR)_6 > Zn(MS)_2(IMI)_6 > Zn(MS)_2(DITHIO)_4$. The decompositions of the urea and imidazole ligands are both exothermic in the $Zn(MS)_2(UR)_6$ and $Zn(MS)_2(IMI)_6$ complexes; already the dithio lig-

Table 4
Thermodynamic parameters of thermal decomposition of the complexes of $Zn(MS)_2(L)_x$ (where L = UR and IMI when $x = 6$; L = DITHIO when $x = 4$)

Ligands	Stage of decomposition					
	I		II		III	
	Peak (K)	ΔH ($kJ\,mol^{-1}$)	Peak (K)	ΔH ($kJ\,mol^{-1}$)	Peak (K)	ΔH ($kJ\,mol^{-1}$)
UR	421	−125.9	482	−181.7	587	−47.2
IMI	389	−70.8	562	−264.8	712	−109.1
DITHIO	329	−56.3	400	−46.3	446	625.0

and decomposed exothermic and endothermic in the $Zn(MS)_2(DITHIO)_4$ complex.

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