Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 2, 317–321

THERMAL STABILITY OF SOME NEW COMPLEXES BEARING LIGANDS WITH POLYMERIZABLE GROUPS

Mihaela Badea[1*], *Rodica Olar*[1], *Dana Marinescu*[1], *E. Segal*[2] *and A. Rotaru*[2]

[1]University of Bucharest, Faculty of Chemistry, Department of Inorganic Chemistry, 90-92 Panduri St., 050663 Sector 5 Bucharest, Romania
[2]University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, 4-12 Elisabeta blvd, Bucharest, Romania

A series of new complexes with mixed ligands of the type M(4,4'-dipy)($C_3H_3O_2$)$_2$(H_2O)$_y$ ((**1**) *M*=Mn, *y*=2; (**2**) *M*=Ni, *y*=2; 4,4'-dipy: 4,4'-dipyridyl and $C_3H_3O_2$ is acrylate anion) and respectively M_2(4,4'-dipy)($C_3H_3O_2$)$_4$(H_2O)$_y$ ((**3**) *M*=Cu, *y*=0; (**4**) *M*=Zn, *y*=1). The modification evidenced in IR spectra was correlated with the presence of acrylate ion as unidentate in the case of complex (**1**) and as bidentate for others complexes. The electronic reflectance spectra showed the *d–d* transition for complex (**1**) and (**2**) characteristic for the octahedral surrounding while the spectrum for complex (**3**) have the characteristic pattern for square-pyramidal stereochemistry. The thermal behaviour steps were investigated. The thermal transformations are complex processes according to TG and DTG curves including dehydration, acrylate ion oxidative degradation and thermolysis process of aromatic amine. The final products of decomposition are the most stable metal oxides.

Keywords: *acrylate, complexes, 4,4'-dipyridyl, formate, thermal stability*

Introduction

The interest in the coordination compounds having as mixed ligands an aromatic amine and an organic derivative, which possesses a vinyl group, potentially polymerizable (as acrylate ion), was generated by the possibility of their inclusion in polymeric matrix. If the complex compounds are biological active, the polymeric biocompatible material can assure the target delivery and the controlled release of the active compound.

Recently it was also shown that some acrylate complexes present antimicrobial activity [1] and also have an interesting thermal behaviour [1, 2].

In order to modulate biological properties of acrylate complexes, four new complexes with mixed ligands have been synthesized and characterized using IR, and electronic spectroscopy. These compounds were obtained in two steps: first, was obtained metallic acrylate from the reaction of the metal carbonate with acrylic acid in aqueous solution. The second step consists in the reaction between the metallic acrylate with 4,4'-dipyridyl. The obtained compounds have the following formulas: [Mn(4,4'-dipy)(acr)$_2$(H_2O)$_2$], [Ni(4,4'-dipy)(acr)$_2$]·2H_2O, [Cu_2(4,4'-dipy)(acr)$_4$] and [Zn_2(4,4'-dipy)(acr)$_4$]·H_2O. The complexes were formulated on the basis of analytical and spectral data.

The thermal behaviour provided confirmation of the complexes composition as well as the number and the nature of water molecules and the intervals of thermal stability. The thermal transformations are complex processes according to TG and DTG curves including dehydration, acrylate ion oxidative degradation and thermolysis process of aromatic amine. The products of decomposition are the metal oxides.

Experimental

Synthesis of the complexes

All reagents were purchased from Aldrich and Merck, reagent grade and were used without further purification.

Complex [Mn(4,4'-dipy)(acr)$_2$(H_2O)$_2$] (**1**)

To a suspension of 1.15 g of $MnCO_3 \cdot xH_2O$ in 25 mL water was added dropwise under continuous stirring 0.8 mL (ρ=1.05 g cm^{-3}) acrylic acid and the mixture was stirred for 1 h. The reaction mixture was filtered and 10 mL ethanolic solution of 0.35 g 4,4'-dipyridyl was added to solution. The yellow solution obtained after 1 h of stirring was let at room temperature for several days until yellow crystals were formed. The compound was filtered out and washed with cooled ethylic alcohol and air-dried. Analysis, found: Mn, 14.08; C, 49.41; H, 4.72; N, 7.24%; calculated

---

[*] Author for correspondence: e_m_badea@yahoo.com, badea.elena@unibuc.ro

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

for $MnC_{16}H_{18}N_2O_6$: Mn, 14.14; C, 49.36; H, 4.63; N, 7.20%; IR (KBr pellet), cm^{-1}: ν_{H_2O}, 3350m, $\nu_{C=C}$, 1641vs; ν_{asCOO}, 1597vs; $\nu_{C=N}$, 1540m; ν_{sCOO}, 1362m; δ_{COO}, 652m; ν_{Mn-O}, 420w.

Complex [Ni(4,4'-dipy)(acr)$_2$]·2H_2O **(2)**

To a suspension of 1.59 g of $NiCO_3 \cdot Ni(OH)_2 \cdot 6H_2O$ in 25 mL water was added dropwise under continuous stirring 1 mL (ρ=1.05 g cm^{-3}) acrylic acid and the mixture was stirred for 1 h. The reaction mixture was filtered and 10 mL ethanolic solution of 0.5 g 4,4'-dipyridyl was added to solution. The blue solution obtained immediately was let at room temperature for several days until microcrystals were formed. The compound was filtered out and washed with cooled ethylic alcohol and air-dried. Analysis, found: Ni, 14.92; C, 48.69; H, 4.61; N, 7.28%; calculated for $NiC_{16}H_{18}N_2O_6$: Ni, 15.01; C, 48.85; H, 4.58; N, 7.12%; IR (KBr pellet), cm^{-1}: ν_{H_2O}, 3380m; $\nu_{C=C}$, 1637m; ν_{asCOO}, 1540vs; $\nu_{C=N}$, 1530m; δ_{CH}, 1428s; ν_{sCOO}, 1364m; δ_{COO}, 668m.

Complex [Cu_2(4,4'-dipy)(acr)$_4$] **(3)**

To a suspension of 0.44 g of $CuCO_3 \cdot Cu(OH)_2$ in 25 mL water was added dropwise under continuous stirring 0.2 mL (ρ=1.05 g cm^{-3}) acrylic acid and the mixture was stirred for 1 h. The reaction mixture was filtered and 10 mL ethanolic solution of 0.13 g 4,4'-dipyridyl was added to solution. The dark blue solution obtained immediately was let at room temperature for several days until crystals were formed. The compound was filtered out and washed with cooled ethylic alcohol and air-dried. Analysis, found: Cu, 22.35; C, 46.52; H, 3.58; N, 4.96%; calculated for $CuC_{11}H_8NO_4$: Cu, 22.40; C, 46.56; H, 3.53; N, 4.94%; IR (KBr pellet), cm^{-1}: $\nu_{C=C}$, 1648s; ν_{asCOO}, 1560vs; $\nu_{C=N}$, 1542m; δ_{CH}, 1433vs; ν_{sCOO}, 1365vs; δ_{COO}, 680m.

Complex [Zn_2(4,4'-dipy)(acr)$_4$]·H_2O **(4)**

To a suspension of 0.648 g of ZnO in 25 mL water was added dropwise under continuous stirring 0.8 mL (ρ=1.05 g cm^{-3}) acrylic acid and the mixture was stirred for 1 h. The reaction mixture was filtered and 10 mL ethanolic solution of 0.5 g 4,4'-dipyridyl was added to solution. The yellow solution obtained immediately was let at room temperature for several days until microcrystals were formed. The compound was filtered out and washed with cooled ethylic alcohol and air-dried. Analysis, found: Zn, 22.07; C, 44.69; H, 3.71; N, 4.82%; calculated for $ZnC_{11}H_9NO_{4.5}$: Zn, 22.11; C, 44.90; H, 3.74; N, 4.76%; IR (KBr pellet), cm^{-1}: ν_{H_2O}, 3431m, $\nu_{C=C}$, 1644s; ν_{asCOO}, 1556vs; $\nu_{C=N}$, 1556m; δ_{CH}, 1436m; ν_{sCOO}, 1363s; δ_{COO}, 671m.

Methods

IR spectra were recorded in KBr pellets with a Bio-Rad FTIR 135 spectrometer in the range 400–4000 cm^{-1}. Electronic spectra of the solids (380–1200 nm) were obtained by diffuse reflectance technique, using MgO as standard, with a VSU-2P Zeiss Jena instrument.

The heating curves (TG, DTA and DTG) were recorded in a static air atmosphere using a MOM (Hungary) derivatograph, type Erdey–Paulik–Paulik, with a sample mass of 30–80 mg over the temperature range of 20–1000°C, using a heating rate of 10°C min^{-1}.

The chemical analysis and IR spectral data were used in order to confirm the nature of some intermediates and also the final products. Chemical analysis of carbon, nitrogen and hydrogen has been performed using an EA 1110 analyser. Manganese, nickel, copper and zinc were determined gravimetrically (manganese, copper and zinc as oxinates, nickel as dimethylglyoximate) in the laboratories of Inorganic Chemistry Department.

Results and discussion

Physico-chemical characterization of complexes

In this paper, we report the preparation and physico-chemical characterisation of some complexes with acrylate and 4,4'-dipyridyl. The major goal of this paper was to evidence the thermal behaviour of these complexes that could be used as intermediate for obtaining some metal containing polymer (MCP) species. The complexes have been formulated on the basis of chemical analysis, IR and electronic spectra as follows:

$$Mn(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2 \qquad \textbf{(1)}$$

$$Ni(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2 \qquad \textbf{(2)}$$

$$Cu_2(C_{10}H_8N_2)(C_3H_3O_2)_4 \qquad \textbf{(3)}$$

$$Zn_2(C_{10}H_8N_2)(C_3H_3O_2)_4(H_2O) \qquad \textbf{(4)}$$

These compounds were obtained in two steps. First, metallic acrylate from the reaction of a metal derivative (carbonate, basic carbonate or oxide) with acrylic acid in aqueous solution was obtained. Based on the low reactivity of metal carbonate, basic carbonate or oxide, an excess of acrylic acid were used (1:3 molar ratio). The second step consists in 4,4'-dipyridyl reaction with metallic acrylate. In order to maintain the molar ratio metal ion:amine

(1:1), a lower amine quantity was used. These complexes are different as chemical formulae and IR spectra; the complex **(3)** does not contain water even if they were obtained in the similar condition.

It is important to mention that the physico-chemical studies had evidenced for the Cu(II) complex a square pyramidal stereochemistry, while Mn(II) and Ni(II) ions adopt an octahedral stereochemistry. In all complexes the 4,4'-bipyridyl acts as bridge while the acrylate acts as bidentate ligand in complexes except for complex **(1)** where it is found as unidentate.

In the IR spectra of complexes are viewed the characteristic patterns of 4,4'-dipyridyl (experimental part) that generate two strong bands about 1640 and 1540 cm^{-1} assigned to $\nu_{C=C}$ and $\nu_{C=N}$ vibrations. The acrylate fragment can be identified due ν_{asCOO} and ν_{sCOO} bands. According to the literature data [3], $\Delta=\nu_{asCOO}-\nu_{sCOO}$ value higher than the ionic value of 203 cm^{-1} observed for sodium acrylate, indicates a unidentate coordination mode while a $\Delta<203$ cm^{-1} value indicates a bidentate (chelation/bridging) coordination mode. The Δ value of 235 cm^{-1} in the case of compound **(1)** indicates the unidentate coordination mode while a lower difference for other complexes is correlated with the presence of this ligand as bidentate. The small Δ value for nickel complex may indicate chelation rather than bridging.

The presence of water molecule in complexes could be responsible for the appearance of a large band about 3400 cm^{-1} assigned to ν_{OH} stretching vibrations [4].

The solid-state *d–d* spectrum of **(1)** shows the characteristic bands of Mn(II) in a pseudooctahedral environment. The assignment of the absorptions at 22730 and 15385 cm^{-1} to the spin forbidden $^6A_1\rightarrow^4A_1$, $^4E(G)$ and $^6A_1\rightarrow^4T_1$ transitions are based on literature data [5]. In the spectrum of complex **(2)** (Fig. 1) the bands at 9524 and 15625 cm^{-1} are assigned to spin allowed transitions $^3A_2\rightarrow^3T_2$ and $^3A_2\rightarrow^3T_1$. The position of the absorption maxims is in agreement with an octahedral stereochemistry for a $[NiN_2O_4]$ chromophore. The diffuse-reflectance spectrum of Cu(II) complex (Fig. 2) in the Vis-near-IR region show a single broad band at 13333 cm^{-1}, as is usually observed for this ion in complexes bearing ligands with oxygen and nitrogen donor atoms and displaying a square-pyramidal stereochemistry [5].

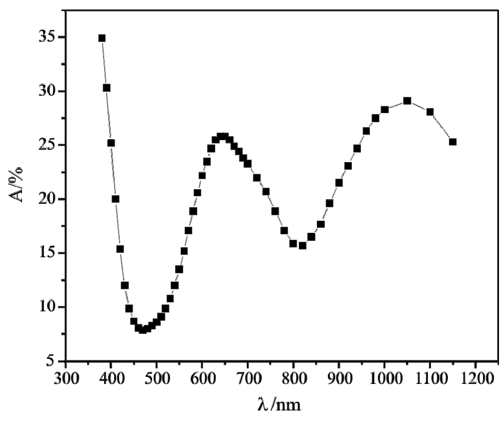

Fig. 1 Electronic spectrum of $[Ni(4,4'\text{-dipy})(acr)_2]\cdot 2H_2O$

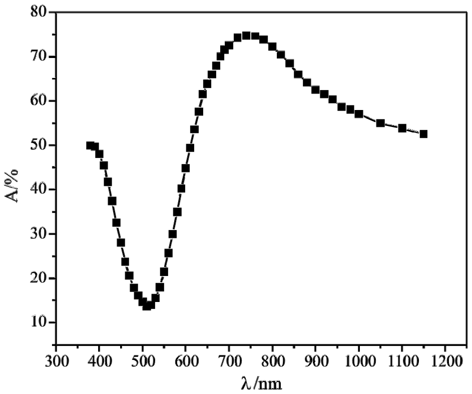

Fig. 2 Electronic spectrum of $[Cu_2(4,4'\text{-dipy})(acr)_4]$

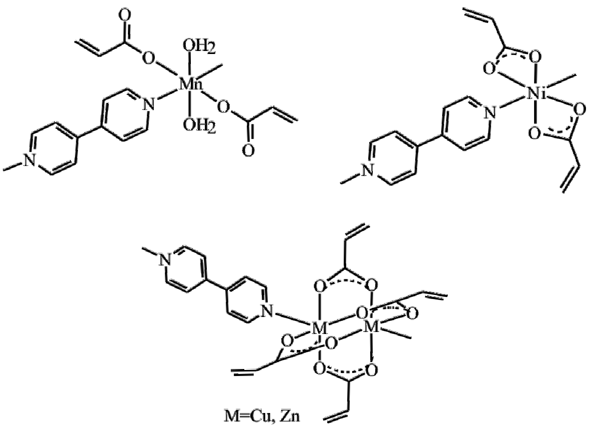

Fig. 3 The proposed coordination for complexes

On the basis of the above data the proposed coordination for the complexes is shown in Fig. 3.

Thermal behavior of complexes

The main objective of this paper was to analyse the thermal behaviour of the complexes in order to acquire a polymeric fashion for them.

The results concerning the thermal decomposition/degradation of the new complexes are presented as it follows.

Thermal decomposition of $Mn(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$

Thermal analysis for **(1)** has confirmed the first step of compound transformation as an endothermic elimination of water molecules. The reaction

Table 1 Thermal behaviour data (in static air atmosphere) for the acrylate complexes

Complex	Step	Thermal effect	Temp. interval/°C	Δm_{exp}/%	Δm_{calc}/%
$Mn(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$	1	endothermic	125–160	9.40	9.25
	2	exothermic	210–250	13.20	13.37
	3	exothermic	250–270	57.00	57.07
		residue (Mn_2O_3)		20.40	20.31
$Ni(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$	1	endothermic	120–155	9.39	9.25
	2	exothermic	220–480	70.95	71.46
		residue (NiO)		19.65	19.28
$Cu_2(C_{10}H_8N_2)(C_3H_3O_2)_4$	1	exothermic	170–460	71.97	71.96
		residue (CuO)		28.03	28.04
$Zn_2(C_{10}H_8N_2)(C_3H_3O_2)_4(H_2O)$	1	endothermic	160–200	3.28	3.06
	2	exothermic	200–270	17.75	17.69
	3	exothermic	270–310	10.52	10.20
	4	exothermic	310–560	40.76	41.50
		residue (ZnO)		27.69	27.55

proceeds with a maximum rate at 140°C. Based on the higher temperature corresponding to the dehydration process, it could be assumed that the water molecule is coordinated [6–8]. The second step, which is exothermic, corresponds to oxidative transformation of acrylate ion into formate anion (Table 1).

The third step corresponds to the oxidative degradation of the intermediate and Mn_2O_3 formation as the final product.

Thermal decomposition of $Ni(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$

The TG and DTA curves corresponding to the complex **(2)** heated in the 20–800°C temperature range are presented in Fig. 4.

The thermal decomposition of $Ni(C_{10}H_8N_2)(C_3H_3O_2)_2(H_2O)_2$ **(2)** occurs in two, well-defined steps. The first step, which is endothermic, corresponds to the loss of water molecules. Considering that the IR spectrum indicates clearly the bidentate nature of acrylate the water molecules are uncoordinated. On this basis it is surprising that they are eliminated at so high temperatures. This behaviour could indicate that these molecules are involved in strong hydrogen interactions with the acrylate. The resulted anhydrous compound is stable in a wide range of temperature. The second step, an exothermic one, corresponds to an oxidative degradation of organic components. This step is complex being an overlap of at least three oxidative processes.

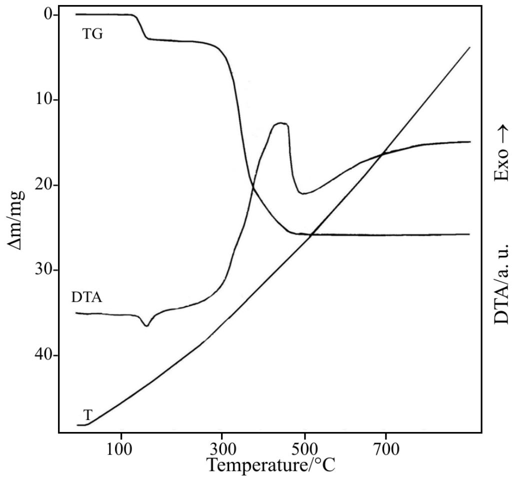

Fig. 4 TG and DTA curves of [Ni(4,4’-dipy)(acr)$_2$]·2H_2O

Thermal decomposition of $Cu_2(C_{10}H_8N_2)(C_3H_3O_2)_4$

The TG and DTA curves corresponding to the complex **(3)** heated in the 20–1000°C temperature range are presented in Fig. 5.

The oxidative degradation of this anhydrous compound starts simultaneous with the melting. The two processes are not well delimitated. The organic part degradation occurs in at least two processes as DTA and TG curves indicate. Probably a basic carbonate is obtained as intermediate at 280°C. This assumption is based on the fact that such species occur in nature and was observed as products of thermal degradation of some complexes [9, 10]. The final product at 460°C is copper(II) oxide.

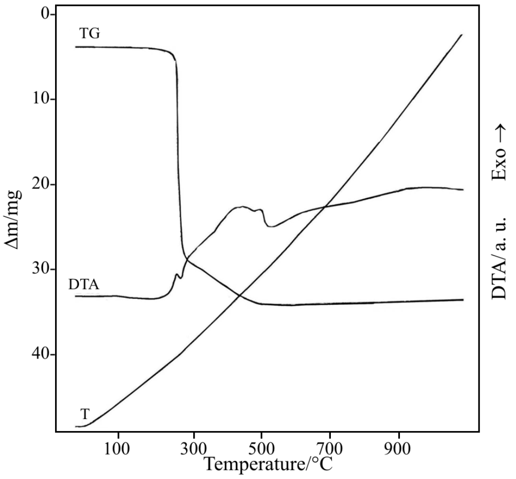

Fig. 5 TG and DTA curves of [Cu_2(4,4'-dipy)(acr)$_4$]

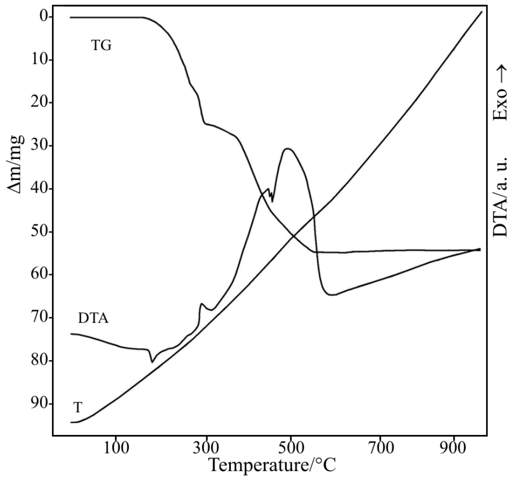

Fig. 6 TG and DTA curves of [Zn_2(4,4'-dipy)(acr)$_4$]·H_2O

Thermal decomposition of $Zn_2(C_{10}H_8N_2)(C_3H_3O_2)_4(H_2O)$

In the case of complex **(4)** the thermal decomposition (Fig. 6) starts with the complex dehydration followed by the oxidative degradation of acrylate. This second step leads to formate stabilisation. The third step, exothermic one, corresponds to formate transformation into carbonate. This intermediate is stable and was identified by IR spectroscopy. The last step, strong exothermic, consists in oxidative degradation of 4,4'-dipyridyl and decomposition of carbonate. The final residue obtained at 560°C is zinc oxide.

Conclusions

The new complex compounds of Mn(II), Ni(II), Cu(II) and Zn(II) with mixed ligands (4,4'-dipyridyl and acrylate) belong to a class of coordination compounds of current interest having into its composition a ligand which allows inclusion of the metallic ions into a polymeric matrix.

Thermal analysis (TG, DTA) of these complexes elucidated the composition and also the number and nature of the water molecules. It was also evidenced for manganese and zinc complexes the existence of an intermediate step corresponds to the formation of metallic formates.

Acknowledgements

The MATNANTECH National Romanian Research Program 204(403)/2004 financially supported this study.

References

1 M. Badea, R. Olar, D. Marinescu and G. Vasile, J. Therm. Anal. Cal., 80 (2005) 273.
2 M. Badea, R. Olar, D. Marinescu and G. Vasile, J. Therm. Anal. Cal., 85 (2006) 285.
3 C. Oldham, Comprehensive Coordination Chemistry, G. Wilkinson, R. D. Gillard and J. A. McCleverty, Eds, Pergamon Press: Oxford, UK 1987, Vol. 2, p. 435.
4 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York 1986, p. 228.
5 A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, London, New York 1986, pp. 440, 507 and 544.
6 T. Premkumar, S. Govindarajan, W.-P. Pan and R. Xie, J. Therm. Anal. Cal., 74 (2003) 325.
7 I. Labadi, L. Horvath, G. Kenessey and G. Liptay, J. Therm. Anal. Cal., 80 (2005) 1.
8 T. Premkumar and S. Govindarajan, J. Therm. Anal. Cal., 79 (2005) 685.
9 M. Badea, R. Olar, D. Marinescu, G. Vasile and S. Stoleriu, J. Therm. Anal. Cal., 80 (2005) 679.
10 R. Olar, M. Badea, E. Cristurean, D. Marinescu and C. Parnau, J. Therm. Anal. Cal., 84 (2006) 53.

DOI: 10.1007/s10973-006-8031-2