Available online at www.sciencedirect.com

Thermochimica Acta 417 (2004) 43–45

thermochimica acta

www.elsevier.com/locate/tca

The preparation and thermo-analytical characterization of heavy metal complexes of *O*,*O*′-dinonyldithiophosphate

Nermin Biricik*, Bahattin Gümgüm

Department of Chemistry, Faculty of Art and Science, Dicle University, 21280 Diyarbakır, Turkey

Received 25 March 2003; received in revised form 7 January 2004; accepted 7 January 2004

Abstract

O,*O*′-dinonyldithiophosphoric acid was synthesized from the reaction of phosphorus pentasulphide and nonyl alcohol by heating with microwave radiation, and its metal complexes ($M[S_2P(OC_9H_{19})_2]_2$) (M: Cd(II), Co(II), Cu(II), Hg(II), Ni(II), and Pb(II)) were prepared in ethanol. The complexes were characterized by elemental analysis, IR, UV-Vis, AAS and TGA.

Keywords: Dialkyldithiophosphate; Dinonyldithiophosphoric acid; Heavy metal; TGA; Thermo-analytical methods

1. Introduction

Dialkyldithiophosphates are versatile compounds, and have gained interest for analytical as well as industrial applications [1–3]. The use of dialkyldithiophosphate as extractant for metal ions is well known [4–6]. The other important application of dialkyldithiophosphates is related to their antioxidant, anticorrosion and antiwear properties [2,7,8]. Zinc dialkyldithiophosphate is an important commercial additive and widely used as antioxidant and antiwear agent in lubricating oils [2].

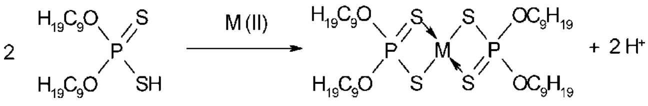
Thermal and lubricant additive properties of the zinc dialkyldithiophosphate (alkyl $= C_4$, C_6 and C_{10}) have been extensively investigated [9], but a few articles have been published on the thermo-analytic properties of the other transition metal dialkyldithiophosphates, and no on dinonyldithiophosphates derivatives: Cu(II) dioctyldithiophosphate [10], Cu(II) and Ni(II) dinaphthyldithiophosphates [11], Pt(II) dialkyldithiophosphates (alkyl: methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, dodecyl, and octadecyl) [12] have been investigated.

In the present work, *O*,*O*′-dinonyldithiophosphate complexes of Cd(II), Co(II), Cu(II), Hg(II), Ni(II), and Pb(II) were prepared and characterized by elemental analysis, IR, UV-Vis, AAS, and TGA under nitrogen atmosphere.

2. Experimental

2.1. Preparation of dinonyldithiophosphoric acid and its metal complexes

Dinonyldithiophosphoric acid was prepared by addition of phosphorus pentasulphide to nonyl alcohol using a CEM-MDS 2000 model microwave oven, according to previous procedure [1]. The complexes (ML_2) were prepared by mixing 2×10^{-2} M solution of dinonyldithiophosphoric acid and 1×10^{-2} M solution of the metals in ethanol with stirring at room temperature.



2.2. Characterization

The complexes were characterized by elemental analysis using a Carlo-Erba EA 1108 CHNS-O Analyzer, and after decomposition and solving processes the metal concentrations were determined by Unicam-929 atomic absorption spectrophotometer (Table 1). IR and UV-Vis spectra

---

* Corresponding author. Tel.: +90-412-2488550; fax: +90-412-2488039.
E-mail address: nbiricik@dicle.edu.tr (N. Biricik).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.01.005

Table 1
The elemental analysis of metal dinonyldithiophosphates

Compounds	Calculated (%)				Found (%)			
	C	H	S	Metal	C	H	S	Metal
$Cd[S_2P(OC_9H_{19})_2]_2$	49.4	8.7	14.6	12.8	49.9	9.0	13.1	11.7
$Co[S_2P(OC_9H_{19})_2]_2$	52.6	9.3	15.6	7.2	51.9	9.7	16.0	7.1
$Cu[S_2P(OC_9H_{19})_2]_2$	52.3	9.2	15.5	7.7	49.6	9.1	14.3	6.9
$Hg[S_2P(OC_9H_{19})_2]_2$	45.0	7.9	13.3	20.8	46.9	8.7	12.1	ND[a]
$Ni[S_2P(OC_9H_{19})_2]_2$	52.7	9.8	15.5	7.2	53.0	10.1	14.3	6.9
$Pb[S_2P(OC_9H_{19})_2]_2$	44.6	7.8	13.0	21.4	44.6	8.1	12.5	21.1

[a] Not determined.

Table 2
The physical and spectral properties of metal dinonyldithiphosphates (ML_2)

ML_2	Color	MP (°C)	Yield (%)	IR (cm^{-1})		UV-Vis
				ν(P=S)	ν(P–S)	λ_{max} (nm)
CdL_2	Colorless solid	28.5 ± 0.5	67	677–649	570	302
CoL_2	Brown oil	–	79	651–632	558	410
CuL_2	Brown oil	–	78	721–647	543	421
HgL_2	Colorless solid	33.5 ± 0.5	60	648	497	316
NiL_2	Violet solid	27.5 ± 0.5	76	658–645	564	486
PbL_2	Colorless solid	47.5 ± 0.5	75	650	551	296

were recorded on Midac 1700 M FT-IR in CCl_4 and Unicam UV2-100 UV-Vis spectrophotometer. Melting points were measured using a Gallenkamp apparatus and are uncorrected (Table 2).

2.3. Thermal analysis

Approximately 5 mg of the samples were used in the TG experiments. The TG measurements were performed using a Schimadzu TGA-50 thermo-gravimetric analyzer over a temperature range from ambient to about 800 °C at the rate of 20 °C min^{-1} under nitrogen (20 ml min^{-1}) atmosphere (Fig. 1).

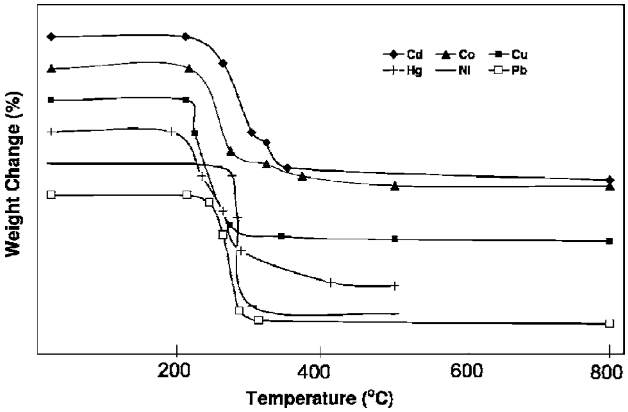


Fig. 1. TG curves of metal dinonyldithiophosphates.

3. Results and discussion

Dinonyldithiophosphate complexes of Cd(II), Co(II), Cu(II), Hg(II), Ni(II), and Pb(II) were prepared and analyzed for C, H, S and heavy metal concentrations. In all the samples, concentrations of the metals were found to be lower than the calculated values, and the results are in agreement with each other (Table 1). The differences between the found/calculated ratios for carbons are changeable up to ~5%, and for a few of the other elements and metals are changeable up to 10%, but generally the results are an acceptable range. The complexes of cobalt and copper are liquid (oil), while the others are solid.

IR studies show that upon complexation the peaks corresponding to S–H bond (2600–2500 cm^{-1}) is diminished, and P=S (740–660 cm^{-1}) and P–S (540 cm^{-1}) values were significantly shifted: P=S peak is shifted down while P–S peak is shifted up (Table 2). Thus, P=S double bonds strength are decreased, while P–S single bond strength is increased.

Electronic spectra, λ_{max} (nm), values of the complexes were found to be in the order of $NiL_2 > CuL_2 > CoL_2 > HgL_2 > CdL_2 > PbL_2$. The first three complexes are colored having λ_{max} values longer than 400 nm, while the last three are colorless having λ_{max} values shorter than 400 nm (Table 2).

The TGA curves of metal dinonyldithiophosphates are shown in Fig. 1. It shows that HgL_2 has the lowest “to start weight loss temperature” (188 °C). On the other hand, the weight loss temperatures for the other samples were found in the range of 208–211 °C. The higher weight loss temperatures can be related to the thermal stability of the complexes. The results can be explained by assuming that, the complexes do not contain water. The shape of TG curves obtained for NiL_2 and PbL_2 are nearly the same, and the mass loss begin at the ∼210 °C. The weight loss percentage of the complexes NiL_2, CoL_2, CuL_2, CdL_2, and PbL_2 are 79, 71, 70, 68, and 61 up to the temperatures 295, 373, 342, 330, and 310 °C, respectively. The weight changes are lower than 3% over these temperatures. It appears that the curve of HgL_2 is different, and the weight loss is 75% up to 285 °C, and the sample was completely vaporized at 500 °C.

4. Conclusion

Dinonyldithiophosphate complexes of Cd(II), Co(II), Cu(II), Hg(II), Ni(II), and Pb(II) have interesting properties, such as CoL_2 and CuL_2 are liquid (oil) at room temperature, the others are solid. The CdL_2 and NiL_2 are viscose liquids at slightly over room temperature (∼28 °C). HgL_2 and PbL_2 melt at 33–34 and 47–48 °C, respectively. The complexes do not involve water, and insoluble in water, but very soluble in organic solvents. They are stable (except HgL_2) up to over 200 °C temperatures.

References

[1] B. Gümgüm, N. Biricik, A. Baysal, Phosphorus Sulfur Silicon 177 (2002) 2507 (and references there in).
[2] A.M. Barnes, K.D. Bartle, V.R.A. Thibon, Tribol. Int. 34 (2001) 389.
[3] I. Haiduc, J. Organomet. Chem. 623 (2001) 29.
[4] T.H. Handley, J.A. Dean, Anal. Chem. 34 (1962) 1312.
[5] R.H. Zucal, J.A. Dean, T.H. Handley, Anal. Chem. 35 (1963) 988.
[6] V.F. Toropova, A.R. Garifzyanov, I.E. Panfilova, Talanta 34 (1987) 211.
[7] S. Al-Malaika, M. Coker, G. Scott, Polym. Degrad. Stab. 22 (1988) 147.
[8] D.R. Amstrong, E.S. Ferrari, K.J. Roberts, D. Adams, Wear 208 (1997) 138.
[9] K.-H. Ohrbach, G. Matuschek, A. Kettrup, A. Joachim, Thermochim. Acta 166 (1990) 277.
[10] J.Y. Zhang, W.M. Liu, Q.J. Xue, Q.H. Wang, Wear 216 (1998) 35.
[11] S.Y. Wu, B. Xie, Chin. J. Inorg. Chem. 15 (1999) 267.
[12] M. Gianini, W.R. Caseri, V. Gramlich, U.W. Suter, Inorg. Chim. Acta 299 (2000) 199.