



## Thermal and Spectral Characterization of Co(II) and Cu(II) Dinonyldithiophosphates: Removal of Co(II) and Cu(II) from Aqueous Solutions

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Dinonyldithiophosphoric acid (HDDTP) was prepared by addition of phosphorus pentasulphide to nonyl alcohol. Dinonyldithiophosphate complexes of Co(II) and Cu(II) with general formula  $[M(DDTP)_2]$  [ $M = \text{Co(II)}$  or  $\text{Cu(II)}$ ] were prepared by mixing solutions of M(II) with dinonyldithiophosphoric acid in ethanol at room temperature. The acid and its complexes were characterized by elemental analysis and infrared, ultraviolet-visible and inductively coupled plasma-optical emission spectrometry. The thermal behaviour of  $M(DDTP)_2$  was investigated by thermogravimetric analysis under a nitrogen atmosphere. Removal of Co(II) and Cu(II) from aqueous media by dinonyldithiophosphoric acid solutions were investigated. The optimum conditions for extraction, such as the organic solvent, pH of the aqueous phase, time of equilibration, concentration and effect of anions, were studied. It was found that dinonyldithiophosphoric acid is an effective substance for removing Cu(II) and Co(II) from aqueous solutions.

**Keywords:** Dinonyldithiophosphate, Extraction, Removal of Cu(II) and Co(II), Spectroscopy, Thermogravimetric analysis.

### INTRODUCTION

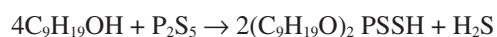
Dialkyldithiophosphoric acids (HDDTP) are versatile compounds have been widely used for analytical and industrial applications<sup>1-3</sup>. Because of preparation and purification problems of long chains dialkyldithiophosphoric acids<sup>2,4</sup>, their use in extraction experiment were rare. Although long chains dialkyldithiophosphoric acids are more easily transferred into the organic phase<sup>5</sup> and more stable against hydrolysis than the short-chain ones<sup>6</sup>. It has been reported that dialkyldithiophosphates (DDTP) having lower alkyl chains such as Me, Et, Pr, i-Pr, Bu, i-Bu, s-Bu, t-Bu, C<sub>5</sub>H<sub>11</sub>, i-C<sub>5</sub>H<sub>11</sub> and 2-ethylhexyl were used for extraction of metal ions from aqueous solutions<sup>2,3,5</sup>. Thermal and lubricant additive properties of the zinc dialkyldithiophosphate (alkyl = C4, C6 and C10) have been extensively investigated<sup>7</sup>, but only a few articles have been published on the thermo-analytic properties of the other heavy metal dialkyldithiophosphates<sup>1-8</sup>. Dialkyldithiophosphates are also used as antioxidants<sup>9</sup>, as anti-wear agents in lubricating oils<sup>10-12</sup>, as pesticides<sup>13-15</sup>, in flotation collectors<sup>17,18</sup> and in the research of heavy metal wastewater treatments<sup>17,18</sup>. Generally, water pollution by heavy metals is a worldwide environmental problem. Thus, removal of heavy metal ions from aqueous solutions or wastes or natural waters has gained importance to solve the industrial or ecological problems<sup>19-21</sup>. Since the heavy

metals copper and cobalt are toxic substances for human health, their removal from aqueous solutions is very important<sup>22-26</sup>.

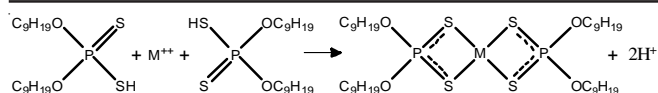
In this work, dinonyldithiophosphoric acid and its dinonyldithiophosphate complexes of Co(II) and Cu(II) were prepared and characterized by spectroscopic techniques and thermal analysis. The removal of Co(II) and Cu(II) from aqueous media using dinonyldithiophosphoric acid solutions were investigated.

### EXPERIMENTAL

**Preparation of dinonyldithiophosphoric acid and its metal complexes:** O, O'-Dinonyldithiophosphoric acid was prepared using a CEM-MDS 2000 model microwave oven (Cem, Matthews, USA) according to a published method<sup>27</sup>. To make a sufficiently pure compound, the method described in the literature<sup>6</sup> had to be modified. Dialkyldithiophosphoric acid was prepared by the reaction of phosphorus pentasulphide and nonyl alcohol by heating with microwave radiation<sup>27</sup>.



The Co(II) and Cu(II) dinonyldithiophosphate complexes  $[M(DDTP)_2]$  were prepared by mixing  $10^{-2}$  M solutions of Co(II) and Cu(II) with an adequate amount of  $10^{-2}$  M solution of dialkyldithiophosphoric acid in ethanol at room temperature.



**Characterization of dinonyldithiophosphoric acid and its metal complexes:** The prepared acid and its metal complexes were characterized by elemental analysis, ultraviolet-visible and infrared spectrophotometers and inductively coupled plasma-optical emission spectrometry (ICP-OES). The thermal behaviour of  $M(DDTP)_2$  was investigated by thermogravimetric analysis (TGA).

Elemental analysis was carried out using a Carlo Erba EA 1108 elemental analyser (CHNS-O, Carlo Erba, Milan, Italy). UV-visible spectra were recorded in the range 200-900 nm by a Unicam-UV2-100 UV/visible spectrophotometer with a quartz cell. The IR spectra were recorded on a Midac Fourier transform IR (FTIR) spectrometer (M Series, Midac Co., Costa Mesa, CA, USA) as neat liquid, using a NaCl cell in the range 4000-400  $\text{cm}^{-1}$ . The concentrations of metal were determined by a Perkin Elmer Optima 2100 DV ICP-OES. The TG measurements were performed using a Schimadzu TGA-50 thermogravimetric analyser over a temperature range from ambient to about 800  $^{\circ}\text{C}$  at the rate of 20  $^{\circ}\text{C min}^{-1}$  under nitrogen (20  $\text{mL min}^{-1}$ ) atmosphere. Approximately 5 mg of the samples were used in the TG experiments.

#### Removal of Co(II) and Cu(II) from aqueous solutions:

Removal of Co(II) and Cu(II) from aqueous solutions into the organic phase were investigated as a function of pH for various anions, solvents, extractant concentrations and extraction times. Solutions of dialkyl dithiophosphoric acid in different solvents, such as kerosene, benzene, *n*-hexane, ethyl acetate, petroleum ether and carbon tetrachloride and  $10^{-3}$  M stock solutions of Co(II) and Cu(II) in distilled water were prepared. All of the chemicals were of analytical reagent grade. Removal of Co(II) and Cu(II) using dialkyl dithiophosphoric acid were carried out from different 0.1 M aqueous solution of  $\text{NaClO}_4$ , NaCl, NaBr,  $\text{NaNO}_3$  and  $\text{CH}_3\text{COONa}$  salts by stirring equal volumes (25 mL) of the organic and aqueous phases at room temperature in a conventional separation funnel at different times (min). The pH values were adjusted by adding sulphuric acid or sodium hydroxide and the pH values were measured with a PCB501 glass electrode Jenway 3010 pH meter (Jenway, London, UK). After separation of the phases, an aliquot of the aqueous part was analysed by an ICP-OES (Table-1) for the particular metal ion concentrations.

The recovery percentage of M(II) can be calculated as follows:

$$R(\%) = \frac{[M^{n+}]_0 - [M^{n+}]}{[M^{n+}]_0} \times 100$$

where  $[M^{n+}]_0$  is initial concentration of the metal ion in the aqueous phase and  $[M^{n+}]$  is the metal ion concentration in the aqueous phase after extraction.

TABLE-1  
OPERATING CONDITIONS OF ICP-OES

RF power (W)	1450
Plasma gas flow rate ( $\text{L min}^{-1}$ )	15
Auxiliary gas flow rate ( $\text{L min}^{-1}$ )	0.2
Nebulizer gas flow rate ( $\text{L min}^{-1}$ )	0.8
Sample flow rate ( $\text{L min}^{-1}$ )	1.5
View mode	Axial
Read	Peak area
Source equilibration time (s)	15
Replicates	3
Detector	CCD
Purge gas	Nitrogen
Shear gas	Air
Gas	Argon
Wavelengths (nm): Co 228.616; Cu 234.754	

## RESULTS AND DISCUSSION

Potentiometric titration of the acid with 0.1 M NaOH showed that the product contained 98 % dialkyl dithiophosphoric acid. Analytical calculated (%) for  $(\text{C}_9\text{H}_{19}\text{O})_2\text{PSSH}$ : C, 56.5; H, 10.2; S, 16.7; found (%): C, 56.8; H, 10.3; S, 16.5 (Table-2).

The recovered metal dinonyldithiophosphates were characterized by elemental analysis. In all the samples, concentrations of the elements in  $\text{Co}(DDTP)_2$  and  $\text{Cu}(DDTP)_2$  were found to be lower than the analytical calculated values and the results are in agreement with each other (Table-2).

The UV-visible spectra of HDDTP dissolved in  $\text{CCl}_4$  using a 1 cm quartz cell shows a peak at 267 nm (Table-3). As shown in the Table-3,  $\text{Co}(DDTP)_2$  and  $\text{Cu}(DDTP)_2$  are viscous liquids (oil). The UV-visible  $\lambda_{\text{max}}$  (nm) of  $\text{Co}(DDTP)_2$  and  $\text{Cu}(DDTP)_2$  were obtained in the same conditions and the relevant results are shown in Table-3. Electronic spectra,  $\lambda_{\text{max}}$  (nm), values of the complexes were found to be in the order of  $\text{Cu}(DDTP)_2 > \text{Co}(DDTP)_2$ . Both complexes are coloured having  $\lambda_{\text{max}}$  values longer than 400 nm.

The IR data of the acid and its metal complexes were recorded at the range 4000-400  $\text{cm}^{-1}$  (Table-3). The results are in agreement with earlier studies carried out on other dialkyl dithiophosphates<sup>1,2</sup>. IR studies show that upon complexation, the peaks (2600-2500  $\text{cm}^{-1}$ ) corresponding to S-H bond of HDDTP is disappeared and P=S (740-660  $\text{cm}^{-1}$ ) and P-S (540  $\text{cm}^{-1}$ ) values were significantly shifted: P=S peak is shifted down while P-S peak is shifted up (Table-3). Thus, P=S double bonds strength are decreased, while P-S single bond strength is increased.

According to the obtained thermograms (Fig. 1),  $\text{Co}(DDTP)_2$  and  $\text{Cu}(DDTP)_2$  are stable at temperatures lower than 210  $^{\circ}\text{C}$  and does not contain water. As shown in Fig. 1,  $\text{Cu}(DDTP)_2$  decomposes in one step and the weight loss of the complex is

TABLE-2  
ELEMENTAL ANALYSIS OF HDDTP AND  $M(DDTP)_2$

Compounds	Calculated (%)				Found (%)			
	C	H	S	M	C	H	S	M
$(\text{C}_9\text{H}_{19}\text{O})_2\text{PSSH}$	56.5	10.2	16.7	-	56.8	10.3	16.5	-
$\text{Co}[\text{S}_2\text{P}(\text{OC}_9\text{H}_{19})_2]_2$	52.6	9.3	15.6	7.2	51.9	9.7	16.0	7.1
$\text{Cu}[\text{S}_2\text{P}(\text{OC}_9\text{H}_{19})_2]_2$	52.3	9.2	15.5	7.7	49.6	9.1	14.3	6.9

TABLE-3  
PHYSICAL AND SPECTRAL PROPERTIES OF HDDTP AND M(DDTP)<sub>2</sub>

M(DDTP) <sub>2</sub>	Colour	Yield (%)	IR (cm <sup>-1</sup> )		UV-visible
			v(P=S)	v(P-S)	λ <sub>max</sub> (nm)
*HDDTP	Yellowish-green oil	89	740-660	540	267
Co(DDTP) <sub>2</sub>	Brown oil	79	651-632	558	410
Cu(DDTP) <sub>2</sub>	Brown oil	78	721-647	543	421

\*HDDTP v(S-H): 2600-2500

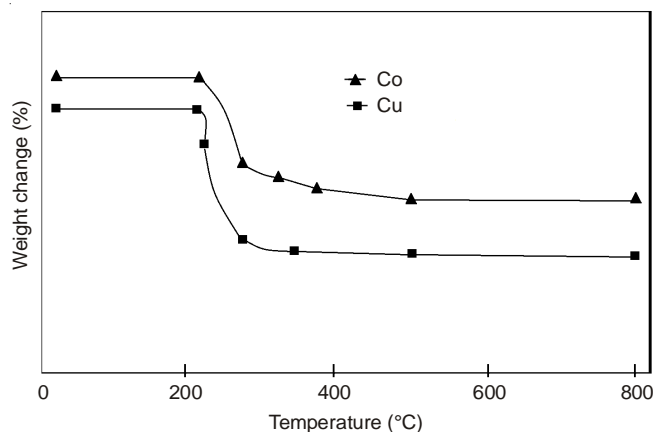


Fig. 1. Thermogravimetric curves of metal dinonyldithiophosphates

because of the organic part, which decomposes from 209 to 342 °C. The weight loss percentage of the complexes Co(DDTP)<sub>2</sub> and Cu(DDTP)<sub>2</sub> are 71 and 70 % up to the temperatures 373 and 342 °C, respectively. The weight changes are lower than 3% over these temperatures. The higher weight loss temperature may be attributed to the thermal stability of Co(DDTP)<sub>2</sub>.

#### Removal of Co(II) and Cu(II) from aqueous solutions:

Our preliminary experiments on removal of the investigated metal ions showed that, Cu(II) can be easily removed from the acidic aqueous media by HDDTP/any organic phase. However, Cu(II) can be easily removed during the extraction procedure, Co(II) cannot be extracted as easily as Cu(II) at the same conditions.

Fig. 2 showed that the extraction time on the removal of Cu(II) and Co(II) were examined and it was found that 1 min

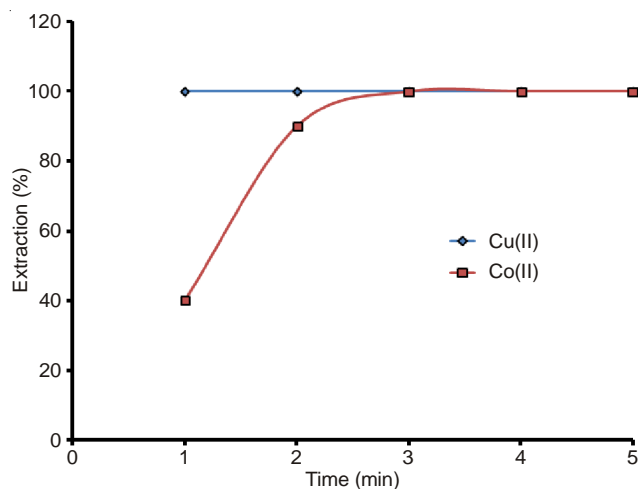


Fig. 2. Effect of time on extraction of Co(II) and Cu(II) from the mixture containing equal concentrations (50 mgL<sup>-1</sup>) of metal ions Co(II) and Cu(II) by 2% HDDTP in CCl<sub>4</sub>

is sufficient for quantitatively extraction of Cu(II), but Co(II) was extracted with percentages 40 and 100 % in 1 and 3 min, respectively.

The pH experiments on the extraction of Cu(II) and Co(II) show that (Fig. 3), it is possible to suggest that Cu(II) can be quantitatively extracted between pH 0.5-6 and Cu(II) was also quantitatively extracted from 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution. Co(II) was extracted with 40 % at pH 0.5 and completely removed at pH 2.5.

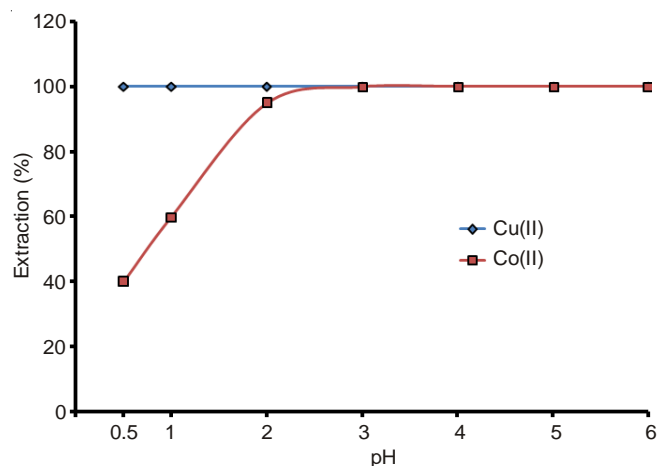


Fig. 3. Effect of pH on extraction of Co(II) and Cu(II) from the mixture containing equal concentrations (50 mgL<sup>-1</sup>) of metal ions Co(II) and Cu(II) by 2% HDDTP in CCl<sub>4</sub>

The experiments on influence of solvents *e.g.*, kerosene, benzene, *n*-hexane, ethyl acetate, petroleum ether and salts like CH<sub>3</sub>COONa, NaCl, NaClO<sub>4</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> are showed there is not important differences between data regarding salts and solvents, except CH<sub>3</sub>COONa. Copper(II) can be extracted quantitatively from all the investigated salt solutions by HDDTP/any organic solvent.

#### Conclusion

O,O'-Dinonyldithiophosphoric acid can react with Cu(II) and Co(II) to form brownish viscous liquid complexes at room temperature and they are insoluble in water, but soluble in organic solvents. The complexes are stable up to 210 °C. Copper(II) and cobalt(II) were quantitatively removed from aqueous solutions in the pH range 0.5 < pH < 6 and 2.5 < pH < 6, respectively. The influence of the investigated common anions on the recovery of Cu(II) and Co(II) were negligible. Copper(II) and cobalt(II) were completely extracted in solvents such as kerosene, benzene, *n*-hexane, petroleum ether and carbon tetrachloride. It can be concluded that HDDTP is an effective substance for removal of Cu(II) and Co(II) from aqueous solution. It is suggested that HDDTP can be used in

order to remove heavy metals from acidic aqueous solutions and wastewater samples.

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