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Application of *Bis*(pyrrolidinedithiocarbamato)Cu(II) and *Bis*(diethyldithiocarbamato)Cd(II) as Antioxidant Additives, Precursor for CuS and CdS Nanoparticles and Antibacterial Agent

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Bis(pyrrolidinedithiocarbamato)Cu(II) and *bis*(diethyldithiocarbamato)Cd(II) are studied as a precursor for synthesizing CuS and CdS nanoparticles by thermolysis method and their characterization by SEM. The antioxidant additive behaviour of Cd(II) analogue and its antibacterial studies are reported. Thermal studies indicate that the Cd(II) dithio derivative is more stable than the Cu(II) dithio detrivative.

Keywords: Dithiocarbamate, Thermolysis, Antioxidant, Antibacterial activity.

INTRODUCTION

The metal dithiocarbamates have been widely studied due to their various applications, biological activities as well as for their interesting structure property relationship[1]. The dithiocarbamates can stabilize metal ions with high as well as low oxidation states[2]. They have also industrial applications as floatation agents, high pressure lubricants, antioxidant additives and in rubber vulcanization. Biologically they exhibit antibacterial, cytostatic, antifungal, immunoregulatory activities[3]. The pyrrolidinedithiocarbamate has been shown to exhibit antiviral and anti-inflammatory properties besides its use in chelation therapy for metal intoxication, liver and brain ischemia and in Alzheimer's disease[4]. Now-a-days, large number of dithiocarbamate complexes are being investigated in order to gain insight into the nature of the sulphur-metal bond in many biomolecules and also because of their potential role in cancer disease treatment[5,6]. This area becomes very interesting for researchers and several works have been done in this field[7-11]. In the present study, we report the application of *bis*(pyrrolidinedithiocarbamato)Cu(II) and *bis*(diethyldithiocarbamato)-Cd(II) as precursor for CuS and CdS nanoparticles by thermolysis method, their biological activity against certain bacterium and as antioxidant lubricating additive (Cd(II) analogue).

EXPERIMENTAL

The title complexes were synthesized by reported methods[12,13] and characterized by elemental and spectroscopic analysis.

Preparation of nano CuS and CdS: Place 0.027 g of $Cu(Pyrrodtc)_2$ and $Cd(Et_2dtc)_2$ complexes in 25 mL ethylenediol separately and heating it for 6 h at 100 °C. The products obtained were isolated and characterized by scanning electron microscopy (SEM).

Procedure involved in the antioxidant studies of lubricating oil: A technical grade of white oil of viscosity 21.5 CSt. at 23 °C used for antioxidant investigation. The assembly of apparatus for oxidation test consisted of an oil bath, flowmeter connected to a suction pump to draw air through the oil. The montmorilonite clay was used as a base material in IR spectral analysis.

In oxidation apparatus, the white oil sample (100 mL) was oxidized without additives for 60 h at 120 °C by passing air at a constant rate in presence of 2 g of iron powder as catalyst. After every 15 h, samples were taken out to measure the acidity (acid number = mg KOH/g sample) and viscosity at 23 °C in CSt. Acid number was determined by using reported standared procedure[14]. The samples were also used for recording IR spectra in the carbonyl region (1850-1600 cm^{-1}), TGA/DTA were recorded in air medium with a scanning rate of 10 °C/min. The sample preparation for IR spectra and thermal measurement were done by homogeneously mixing 1-2 drops of the oxidized oil with 500 mg of previously calcined clay of known composition (montmorillonite). Same procedure was followed for additive added (0.25 wt % and 0.5 wt %) oil samples.

Antibacterial studies of Cd(II) complex

(a) Preparation of sample solution: The sample solution is prepared by dissolving 10 mg of the sample in 1 mL of DMSO solvent. The concentration of the solution is 10 mg/mL.

(b) Preparation of media: The media was prepared by taking 38 mL of Mueller Hinton Agar in a 1000 mL distilled water by slight warming and then sterilizing in a autoclave at 120 °C. The petri dishes used in antibacterial test were also sterilized in the autoclave at same temperature.

(c) Antibacterial activity by agar well diffusion method: For carrying out the test, about 30 mL of the media was transferred into sterilized petri plate and left for some minutes for solidification. After solidification of the medium, each of the sterilized dishes were divided into three zones by marking with a marker pen. Each zone on the dish was specified for a certain bacteria against which antibacterial property has to be tested. Then in each plate three wells of 9 mm diameter was made using a sterile borer. Now the four bacteria strains were put one on the petri dishes according to the zones specified for them. After this, 80 μL of the sample was placed in the specified wells. The dishes were then incubated at 37 °C temperature for 18 h. If the sample has any antibacterial activity then the growth of bacteria will be inhibited on the media. By observing the zone where bacteria growth is inhibited the bacteria can be identified against which the sample has its antibacterial activity.

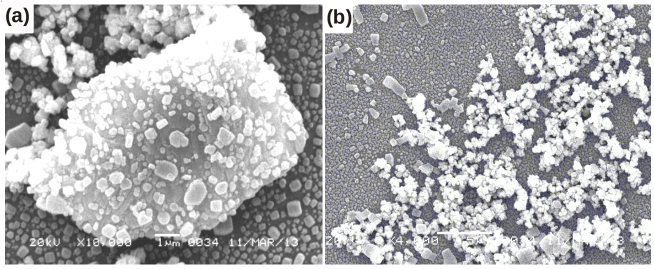

Fig. 1. SEM images (a) and (b) of CuS

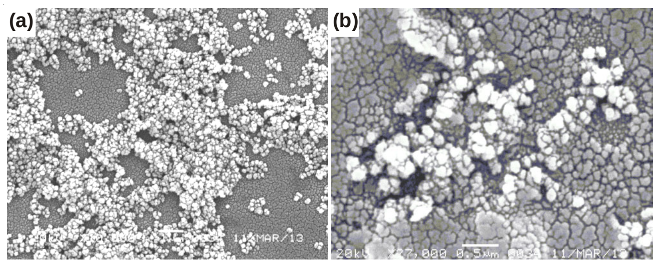

Fig. 2. SEM images (a) and (b) of CdS

RESULTS AND DISCUSSION

The results obtained from SEM study of nano sized CuS and CdS are shown in Figs. 1 and 2. From the SEM patterns, it is observed that there is homogeneous nano sized particle distribution with average sizes in the range of 100 to 50 nm (1-0.5 μm). Therefore, thermolysis of metal dithiocarbamates is a good method for obtaining nano sized CdS and CuS without involving costly other chemical routes. These metal chalcogenides have various opto electronic applications.

Antioxidant behaviour of Cd-complex in lubricating oil: The relatively high temperatures and exposure to moisture oxidizes the lubricating oil, forming sludge, carboxylic acids, alcohols and other polymeric materials. Such oxidized oil is unfit for further use and must be discarded. The effectiveness of the thermally more stable *bis*(diethyldithiocarbamato)Cd(II) is monitored by measuring the acidity, viscosity and such other parameters during the process of oxidation after a definite interval of time, as shown in Table-1.

Table-1 showed that once the oxidation started, which is accelerated by the presence of iron powder, the acid number, viscosity and the carbonyl absorption increases with time for the white oil in the absence of additives. In presence of the additive, the above parameters were observed to decrease indicating the antioxidant property of the compound. With variation of the amount of the additive (*i.e.* 0.25 and 0.50 wt %), there is gradual decrease of acidity, viscosity and carbonyl absorption frequency (Fig. 3). The decrease in the acid number and carbonyl absorption pattern in presence of the additive indicate that the compound hinders the formation of carboxylic acid and carbonyl compound formation. Again, there is a gradual decrease in ν_{co} absorption intensity on addition of the additive. Therefore, it can be concluded that the compound has good antioxidant activity against the lube oil oxidation.

The TGA-DTA data for the lube oil samples are as given in Table-2. In TGA curve of the lube oil samples, observed in calcined clay, the weight loss started around 120 °C and there is a gradual decline till 300 °C in most of the cases. The DTA peaks are centered around 350 °C. This indicates the oxidation of the absorbed lube oil. The DTA peak areas are calculated for the lube oil samples which represent the heat required for total oxidation. The DTA peak areas are observed to be decreased as the time of pre-oxidation increases.

Antibacterial activity of $Cd(Et_2dtc)_2$ complex: The Cd-complex was tested for antibacterial activity test using some

TABLE-1
ACID NUMBER, VISCOSITY AND INTENSITY OF ν_{co} OF WHITE OIL IN PRESENCE OF ADDITIVE AND WITHOUT ADDITIVE

Compound	Wt. % of the additive	Time (h)	Acid number mg KOH/g of oil	Viscosity (at 23 °C)	Intensity of ν_{co} in arbitrary scale
White oil	0	0	0.0025	21.50	2.0
		15	0.0126	22.08	2.8
		30	0.0151	22.42	3.2
		45	0.0214	22.95	3.6
		60	0.0277	23.36	3.9
White oil + $Cd(Et_2dtc)_2$	0.25	15	0.0075	21.92	2.5
		30	0.0101	22.25	2.9
		45	0.0126	22.71	3.3
		60	0.0164	23.12	3.7
	0.50	15	0.0063	21.76	2.2
		30	0.0076	22.11	2.6
		45	0.0101	22.47	3.0
		60	0.0139	22.98	3.4

TABLE-2
TGA-DTA DATA OF THE LUBE OIL SAMPLES

Additive and weight (%)	Oxidation time (h)	Temperature of weight loss (°C)	Maximum (%) weight loss	DTA peak area (cm^2)
White oil (without additives)	0	301.96	27.11	116.62
	15	297.41	36.45	110.67
	30	296.53	37.98	109.27
	45	286.53	32.57	109.02
	60	286.65	33.72	99.87
White oil + $Cd(Et_2dtc)_2$ (0.25 %)	15	295.07	35.33	120.36
	30	299.91	26.98	115.5
	45	294.04	30.19	110.40
	60	293.54	29.04	109.94
White oil + $Cd(Et_2dtc)_2$ (0.5 %)	15	293.76	31.05	134.47
	30	290.29	33.61	124.44
	45	298.61	33.16	121.89
	60	298.05	28.78	113.68

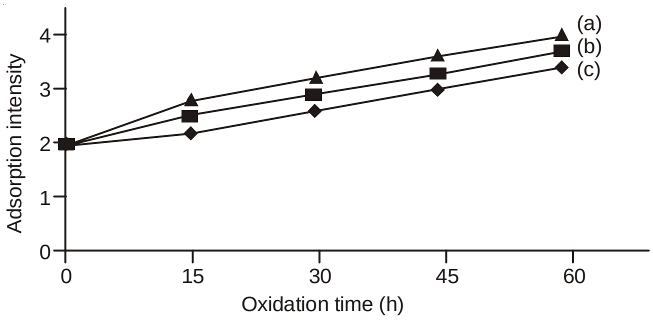

Fig. 3. Plot of carbonyl absorption against oxidation time (a) without additive (b) 0.25 wt % $Cd(Et_2dtc)_2$ and (c) 0.50 wt % $Cd(Et_2dtc)_2$

Gram-positive bacteria and some Gram-negative bacteria. In the test, ciprofloxacin was used as a standard. The antibacterial activity was determined by the presence or absence of the zone of inhibition. It was observed that the complex have anti-bacterial activity against one Gram-positive bacteria, *Bacillus subtilis* and it inhibits the growth of the bacteria.

Conclusion

Both Cu(II) and Cd(II) dithioderivatives are good precursors of CuS and CdS nanoparticles (100-50 nm). The *bis*(diethyldithiocarbamato) Cd(II) derivative exhibit good antioxidant additive action in lubricating oil and also shown to have antibacterial property against *Bacillus subtilis*.

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