

SYNTHESIS, CHARACTERIZATION AND FUNGICIDAL ACTIVITY OF ZINC DIETHYLDITHIOCARBAMATE AND PHOSPHATE

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Zinc diethyldithiocarbamate, zinc diethyldithiocarbamate-phosphate and zinc phosphate have been synthesized. They have been characterized using DTA-TG, IR spectra and X-ray. The dithiocarbamate and phosphate contents have been determined spectrophotometrically and volumetrically, respectively. Fungicidal activity of the compounds has been tested by well diffusion method using fungi *Fusarium* sp.

Keywords: fungicide, zinc diethyldithiocarbamate, zinc diethyldithiocarbamate-phosphate, zinc phosphate

Introduction

Literature shows [1] that there are a wide variety of compounds of anions such as dithiocarbamate, dithiocarbonate, dithiocarboxylate, trithiocarbonate, xanthate, thioxanthate, dithiophosphinate and dialkyldithiophosphinate. Each of these ions may have a corresponding monothio analogue that is S, O bound. Dithiocarbamate and dithiophosphinate complexes have important uses. The former are used as fungicides and for solvent extraction and the latter are used as high-pressure lubricants. Dithiocarbamates stabilize high oxidation states in $[\text{Fe}^{\text{IV}}(\text{dthc})_3]$ or $[\text{Ni}^{\text{IV}}(\text{dthc})_3]$. Although dithiocarbamates are usually made from sodium salts such as $\text{NaS}_2\text{CNMe}_2$ or by oxidations using thiuram disulphides, they can also be made by insertion reactions of CS_2 with dialkylamides. Similarly, dithiophosphinate and dialkyldithiophosphates are made from their sodium salts such as NaS_2PR_2 and $\text{NaS}_2\text{P}(\text{OR})_2$.

Many authors investigated organometallic compounds due to their chemical, biological and environmental importance and examined their various properties [2–27]. In our previous papers, we described the thermo-analytical properties of various organometallic compounds [28–53]. Up to our best knowledge, the thermo-analytical and fungicidal properties of zinc diethyldithiocarbamate, zinc diethyldithiocarbamate-phosphate and zinc phosphate were not investigated in details. This fact has prompted us to undertake a systematic study of these newly synthesized organometallic compounds. This

paper describes the synthesis, chemical, physical as well as biological properties of zinc diethyldithiocarbamate, zinc diethyldithiocarbamate-phosphate and zinc phosphate.

Experimental

Materials

Reagents and chemicals

Acetone (Ranbaxy, India); agar-agar (Hi media Laboratories Ltd, India); ammonium molybdate tetrahydrate, copper sulphate pentahydrate, oxalic acid dihydrate, sodium diethyldithiocarbamate trihydrate (CDH, India); benzene (Sarabhai M. Chem., India); citric acid (Indian Drug and Pharmaceuticals Ltd, India); dimethylsulfoxide (DMSO) (Sisco Research Laboratories Pvt Ltd., India); fungi *Fusarium* sp. (Department of Microbiology, A.M.U., India); ethylenediamine tetraacetic acid (EDTA), sodium hydroxide pellets, trisodium phosphate 12-hydrate (Merck, India); glucose, peptone, sodium nitrate (Qualigens Fine Chem., India); zinc sulphate heptahydrate (SD Fine Chem., India).

All other chemicals and reagents used were of AR or LR grades.

Solutions

The solutions of ammonium molybdate (3%), citric acid (25%), copper sulphate (0.2%), EDTA (4%), nitric acid (1 and 16 M), oxalic acid (1 N), sodium

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hydroxide (0.1 M), sodium nitrate (2%), sodium diethyldithiocarbamate (0.1 N), trisodium phosphate (0.1 N) and zinc sulphate were prepared in distilled water (DW). A homogeneous mixture of glucose-peptone-agar (40:10:15) was prepared in demineralized water (DMW) and sterilized by autoclaving at 121°C, 15 lb/cm² for 20 min. The solution of the compounds under study was prepared (1.2–1.8%) in DMSO and their homogeneous suspension (1%) was prepared in distilled water (DW).

Zinc diethyldithiocarbamate (C₁)

Aqueous zinc sulphate solution (500 mL of 0.1 N) was added dropwise with continuous stirring into a solution of sodium diethyldithiocarbamate (500 mL of 0.1 N). The precipitate was left overnight, and then it was filtered on a buckner funnel. The product was washed three times with DW, and dried at 60±5°C. Finally, the precipitate was desiccated over calcium carbonate for a week.

Zinc phosphate (C₂)

Solution of trisodium phosphate (500 mL of 0.1 N) was taken in place of a solution of sodium diethyldithiocarbamate and above procedure was followed.

Zinc diethyldithiocarbamate-phosphate (C₃–C₄)

Solution (500 mL) containing 250 mL of 0.1 N trisodium phosphate and 250 mL of 0.1 N sodium diethyldithiocarbamate was taken in place of a solution of sodium diethyldithiocarbamate and the procedure was followed.

Methods

Apparatus and instruments

Atomic absorption spectrophotometer (GBC 902, Australia), Autoclave (Narang Company, India), Fourier transformed infrared spectrometer (Interspec 2020, India), UV-VIS spectrophotometer (CL 24 Elico Pvt. Ltd, India), magnetic stirrer (Sunvic, U.K.), melting point apparatus (Pooja Scientific Instruments, India), temperature controlled electric oven (Tempo, India), TG-DTA instrument model PerkinElmer (Pyres Diamond, U.S.A.), X-ray (B.V. PW 1710 Philips Analytical, Netherland) were used.

Analysis of samples

X-ray: X-ray diffraction of powder samples was recorded. The results are given in Table 1.

FTIR: the FTIR spectra were taken using KBr disc method in the range of 400–4000 cm⁻¹. The results are shown in Table 2.

TG and DTA: the thermogravimetric analysis of the samples was carried out at a constant heating rate 10°C min⁻¹ up to 1000°C in air atmosphere (300 mL min⁻¹). The results are recorded in Table 3.

Spectrophotometry: copper sulphate solution (10 mL of 0.2%) was taken in a beaker, 5 mL of 25% aqueous citric acid was added into it, the mixture was render slightly alkaline with dilute NH₃ solution, the excess of ammonia was boiled off and then 15 mL of 4% EDTA were added into it. The contents were cooled to room temperature, transferred into a separatory funnel, 0.6 mL of 1% analyte was added to it, the mixture was shaken for 45 s, and then the yellow product was extracted in 10 mL of butyl acetate. The lower layer was discarded and the organic layer was taken to determine the absorbance [54] at 435 nm against a blank. The blank was prepared by treating 10 mL of butyl acetate with the above admixture without the analyte.

Table 1 Powder X-ray data of zinc dithiocarbamates and phosphates

d-values $\alpha^1/\text{\AA}$	Angle/ 2 θ	Rel. int./%	d-values $\alpha^1/\text{\AA}$	Angle/ 2 θ	Rel. int./%
C ₁			C ₂		
8.75	10.10	100	4.13	9.68	74.22
7.30	12.12	72	4.83	18.35	13.40
6.14	14.42	52.30	4.57	19.40	100
5.03	17.62	25.58	4.00	22.18	17.52
4.39	20.19	36.04	3.42	26.03	23.71
4.25	20.86	56.97	2.85	31.39	65.97
3.77	23.56	47.67	2.62	34.18	13.40
3.65	24.38	24.41	2.09	43.13	10.30
2.82	31.64	34.88	1.93	46.90	23.71
2.68	33.42	25.50	1.52	60.70	13.40
C ₃			C ₄		
8.77	10.08	100	8.76	10.08	100
7.29	12.14	62.10	7.30	12.10	70.65
6.14	14.40	49.47	6.14	14.42	52.17
5.02	17.63	25.26	5.03	17.62	27.17
4.40	20.17	37.89	4.40	20.18	36.95
4.25	20.86	52.63	4.25	20.86	59.78
3.77	23.56	45.26	3.77	23.57	47.82
3.65	24.34	23.15	3.65	24.39	26.08
2.82	31.63	32.63	2.82	31.65	35.86
2.67	33.47	24.21	2.67	33.47	26.08

C₁=zinc diethyldithiocarbamate, C₂=zinc phosphate, C₃=zinc diethyldithiocarbamate-phosphate, C₄=zinc diethyldithiocarbamate-phosphate

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Table 2 Selected infrared frequencies of zinc dithiocarbamates and phosphates

IR frequencies/cm ⁻¹	Compound			
	C ₁	C ₂	C ₃	C ₄
ν _{C-N}	1272.10s	–	1264.02s	1273.24s
ν _{C-S}	997.31s	–	996.00s	996.31s
ν _{P=O}	–	1111.60	–	–
ν _{P-O}	–	949.96,634.75	–	–

Table 3 Thermogravimetry of zinc dithiocarbamate and phosphate

Temperature range/°C	Mass loss/%	Temperature range/°C	Mass loss/%
C ₁		C ₂	
18–218	1.36	22–99	7.60
218–292	15.65	99–150	2.30
292–312	20.57	150–258	1.81
312–324	20.79	258–359	4.16
324–347	26.20	359–705	0.29
347–576	2.26	705–1008	–0.02
576–637	1.83		
637–829	0.28		
829–1007	0.09		
C ₃		C ₄	
19–187	1.68	21–221	2.28
187–278	11.31	221–296	19.91
278–315	31.05	296–321	29.26
315–348	34.03	321–348	28.93
348–661	2.70	348–678	2.81
661–1007	0.72	678–1006	0.61

Volumetry: The test sample (0.025 g) was weighted, dissolved in 5 mL of 16 M HNO₃, and then 20 mL of distilled water and 10 g of ammonium nitrate were added into it. This mixture was heated at 55±5°C for 5 min and then it was treated with 50 mL of 3% ammonium molybdate solution. The precipitate thus formed [55], was filtered off, washed with 2% sodium nitrate solution and DMW until the washings become neutral. The un-reacted precipitate was dis-

solved in 50 mL of 0.1 M sodium hydroxide. The un-reacted sodium hydroxide was titrated with 1 N oxalic acid using phenolphthalein as indicator. The results were calculated from the following relation:

$$1 \text{ mL of } 0.1 \text{ N NaOH} = 0.000309 \text{ g P}_2\text{O}_5 \\ = 95 \times 2 \times 0.000309 \text{ g PO}_4/142$$

Volume of 0.1 N NaOH was taken for dissolving the ppt = x mL,

Volume of 0.1 N oxalic acid required for neutralization of the alkali = y mL,

Volume of 0.1 N NaOH used for dissolving the ppt = x – y mL,

% of PO₄ in the sample = $(100 \times (x - y) \times 95 \times 2 \times 0.000309 \text{ g PO}_4/142) / \text{mass of the sample}$.

Atomic absorption spectrophotometry: the dried and powdered sample (100 mg) was dissolved in 10 mL of 1 M HNO₃ and then it was diluted with DW to obtain a solution of the required concentration for analysis.

Melting point: it was determined as usual and the results are given in Table 4.

Solubility: the powdered sample (100 mg) was shaken with 10 mL of solution/solvent in a 250 mL of conical flask. The contents were placed at room temperature for 24 h and then the changes were noted. The results are recorded in Table 5.

Fungal activity test

The synthesized compounds were tested for fungicidal activity by agar well diffusion method [56] using *Fusarium* sp. by the following procedure:

i) Sabourad dextrose agar plates: a homogeneous mixture of glucose-peptone-agar (40:10:15) was sterilized by autoclaving at 121°C and 15 lb/cm² for

Table 4 Melting point and analysis of zinc dithiocarbamates and phosphates

Compound	M.P./°C	Analysis					
		Zn/%		CS ₂ /%		PO ₄ /%	
		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
C ₁	200	23	18.09	52.4	42.6	–	–
C ₂	>300	25	48.47	–	–	16.53	35.20
C ₃	194	17	–	32	–	–	–
C ₄	221	20	–	49.6	–	–	–

Table 5 Solubility of zinc dithiocarbamates and phosphates

Solvent	Compound			
	C ₁	C ₂	C ₃	C ₄
Acetone	Slightly soluble	Slightly soluble	Slightly soluble	Slightly soluble
Benzene	Slightly soluble	Insoluble	Slightly soluble	Slightly soluble
DMSO	Soluble	Soluble	Soluble	Soluble
HCl	Soluble	Soluble	Soluble	Soluble
HNO ₃	Soluble	Soluble	Soluble	Soluble
H ₂ SO ₄	Soluble	Soluble	Soluble	Soluble
Methanol	Insoluble	Insoluble	Insoluble	Insoluble
Distilled water	Insoluble	Insoluble	Insoluble	Insoluble

20 min. The sterilized solution (25 mL) was poured onto each sterilized Petri dish in laminar flow and left for 20 min to form the solidified Sabourad dextrose agar plate. These plates were inverted and kept at 30°C in incubator to remove the moisture and to check any contamination.

Antifungal assay: fungal strain was grown in 5 mL Sabourad dextrose broth (glucose: peptone, 40:10) for 3–4 days to achieve 10⁵ CFU/mL cells. The fungal culture (0.1 mL) was spread out uniformly on the Sabourad dextrose agar plates by sterilized triangular folded glass rod. Plates were left for 5–10 min so that culture is properly adsorbed on the surface of Sabourad dextrose agar plates. Now small wells of size (4.2 mm) were cut into the plates with the help of well cutter and bottom of the wells were sealed with 0.8% soft agar to prevent the flow of test sample at the bottom of the well. The test solution 100 µL of 1.2, 1.4, 1.6 and 1.8% were loaded into the wells of the plates. DMSO also loaded as control. The plates were kept for incubation at 30°C for 3–4 days and then the plates were examined for the formation of zone of inhibition. The results recorded in Table 6.

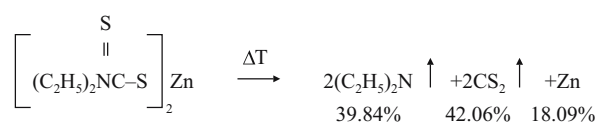
Results and discussion

Diethyldithiocarbamate (C₁) is a well-known compound. It has been prepared for comparison. The product, which has been obtained by the procedure under study, is white to off white crystalline powder (Tables 1 and 5). It is soluble in dilute HCl, HNO₃, H₂SO₄ and DMSO; slightly soluble in acetone and benzene; and insoluble in methanol and DW. It melts at 200°C. IR spectrum shows the presence of C=S (997.31 cm⁻¹) and C–N (1272.10 cm⁻¹) bands (Table 2). The compound shows fungicidal activity

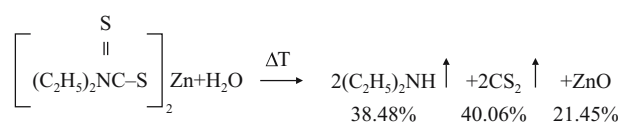
Table 6 Fungicidal activity of zinc dithiocarbamates and phosphates by inhibition zone method

Compound	Zone of inhibition/mm			
	1.2/%	1.4/%	1.6/%	1.8/%
C ₁	12	13	14	15
C ₂	0	0	0	0
C ₃	12	13	14	15
C ₄	11	11	12	13
Control	0	0	0	0

(Table 6) as they inhibit the fungal growth by forming inhibition zones of 12, 13, 14 and 15 mm for *Fusarium* sp. DTA and TG data (Table 3) show only one peak at 330°C and only one main plateau corresponding to 83.18% mass loss. The following chemical equation can be proposed on the basis of above data:



or



This mass loss is due to the decomposition of zinc diethyldithiocarbamate and evaporation of (C₂H₅)₂NH (B.P. 55.5°C) and CS₂ (B.P. 46.3°C). The data given in Table 4 support the above conclusions.

Literature [57] survey shows that several types of zinc phosphates such as (Zn₃(PO₄)₂·4H₂O; Zn₃(PO₄)₂·Zn(OH)₂; Zn₃(PO₄)₂·Zn(OH)₂·3H₂O; 2Zn₃(PO₄)₂·4Zn HPO₄·8H₂O and Zn₃(P₃O₉)₂·9H₂O) have been prepared by using different procedures. The product under study (C₂) is a white crystalline powder (Table 1). It melts at >300°C and is soluble in dilute HCl, HNO₃, H₂SO₄ and DMSO; slightly soluble in acetone and insoluble in benzene methanol and DW. IR analysis shows that it contains P–O (1111.60 cm⁻¹) and P=O (949.96 cm⁻¹) and (1006.83 cm⁻¹) bands. It does not show any fungicidal activity for the fungi under study. DTA and TG of zinc phosphate under study show the first major peak at 92°C (mass loss 7.6%) follows by the first minor peak at 115°C (mass loss 22.33%), second major peak at 286°C (1.81%) and second minor peak at 330°C (4.16%) (Table 3). On the basis of above data the following structure can be proposed:

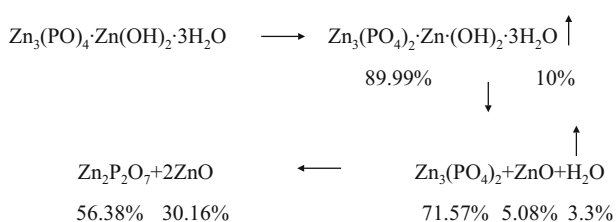


Table 4 supports the above conclusions.

Zinc diethyldithiocarbamate phosphate (C_3) is a white crystalline powder, melts at 194°C, soluble in dilute HCl, HNO₃, H₂SO₄ and DMSO; slightly soluble in acetone and benzene; and insoluble in methanol and DW. IR analysis shows that it contains C=S (996 cm⁻¹) and C-N (1264 cm⁻¹) bands. It shows fungicidal activity as it inhibits the growth of *Fusarium* sp. by inhibition zone of 12, 13, 14, 15 mm. DTA and TG curves are similar to those of zinc diethyldithiocarbamate. Sample C_3 seems to be zinc diethyldithiocarbamate, which contains zinc phosphate as impurities. It may be due to the co-precipitation of the latter. It attributes to the fact that zinc diethyldithiocarbamate is totally insoluble while zinc phosphate is feebly soluble in water.

Zinc diethyldithiocarbamate-phosphate (C_4) is a white crystalline powder, melts at 221°C, soluble in dilute HCl, HNO₃, H₂SO₄ and DMSO; slightly soluble in acetone and benzene; and insoluble in methanol and DW. IR shows that it contains C=S (996 cm⁻¹) and C-N (1273.24 cm⁻¹) bands. It shows fungicidal activity as it inhibits the fungal growth by forming an inhibition zone of 11, 11, 12 and 13 mm for *Fusarium* sp. DTA and TG show almost the similar behavior as shown by zinc diethyldithiocarbamate. Samples C_3 and C_4 seems to be almost similar in nature i.e. they are mixture of zinc diethyldithiocarbamate and zinc phosphate. Table 4 supports the above conclusions and it also shows that concentration of zinc in C_3 and C_4 is less than that in zinc diethyldithiocarbamate (C_1). It may be due to the presence of zinc phosphate in C_3 and C_4 at trace levels.

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