International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.9, pp 185-189, 2017

Synthesis, Characterization and Pesticidal Potential of Metal Dimethyldithiocarbamates

Anupma Arora[1], J.R.Sharma[2] and B.K.Sharma[3]

[1]Govt. Degree College, Kathua (J & K), India
[2]Retired from Punjab Agricultural University, Ludhiana (Pb.), India
[3]G.G.M. Science College, Jammu (J & K), India

Abstract : A series of transition metal dimethyldithiocarbamates have been synthesized and characterized on the basis of analytical and spectral data. The compounds have been screened for fungicidal potential and insecticidal potential and compared with the standard fungicides Indofil M-45 and Bavistin as well as with standard insecticide Carbaryl. Some of the synthesized complexes exhibited antifungal activity at par with standard fungicide, but none of the complexes could compete with standard insecticide.
Key Words : Organosulphur compounds, dithiocarbamates, fungicide, insecticide.

Introduction

Dithiocarbamates, an important class of Organosulphur compounds are well known for their vast chemical and biological properties[1]. And their activity is further enhanced when they are in the form of metal complexes. Metal dithiocarbamates are known to possess antibacterial[2], antifungal[3, 4] nematicidal[5], insecticidal[6] and antileishmanial[7] properties. In view of the varied pesticidal properties of dithiocarbamates and in continuation of our earlier work, we have synthesized some metal dimethyldithiocarbamates, characterized and screened them for fungicidal and insecticidal properties.

Experimental

Synthesis & Characterization:

Sodium dimethyldithiocarbamate was reacted with metal halide or sulphate in stoichiometric ratio in dichloromethane/water mixture. The reaction was carried by stirring for different time intervals. The organic layer was separated, dried over anhydrous potassium sulphate and the complex was recovered by concentrating the solution[8]. Melting points were determined by capillary method and are uncorrected. Conductance was determined with Elico Conductivity Bridge of type CM82T fitted with platinized platinum electrodes. IR spectra (nujol) were recorded on Perkin Elmer Spectrophotometer. The solubility of various synthesized complexes was checked in different polar and non-polar solvents.

Fungicidal Activity:

The antifungal activity of the synthesized complexes was tested *in vitro* against three phytopathogenic fungi viz. *Alternaria alternata*, *Fusarium oxysporum* and *Colletotrichum capsici* using spore germination inhibition technique[9, 10]. Parent metal salt was also taken and proceeded in the same way as the synthesized metal complex (Table 2). It was done to compare the activity of parent and synthesized compound. The stock

solution/suspension (2000ppm) of the compound / parent salt wee prepared by dissolving 50mg of the compound in 2mL tetrahydrofuran (THF) and making the volume to 25 mL by adding distilled water. The stock solutions were serially diluted to obtain the required concentrations. Cavity slides were used for studying the antifungal activity. The spore suspension of the test fungus (10^6 spores/mL) prepared in sterilized distilled water was mixed separately with the solution / suspension of the compound in the cavity slides. These slides were kept in Petri dishes lined with moist filter paper and incubated for 24 hours at 25 ±1°C. Untreated control was kept along with the treatments under same conditions. The germination of the spores was recorded and the per cent spore germination was calculated by following formula:

$$\text{Per cent Spore Germination Inhibition} = \frac{\text{Spore germination in control} - \text{Spore germination in treatment}}{\text{Spore germination in control}} \times 100$$

The standard fungicides Indofil M-45 (75% manganese ethylene bis dithiocarbamate + 2% zinc) and Bavistin 50WP (methyl-2-benzimidazole carbamate) were used to compare the efficacy of the synthesized compounds. The antifungal activity has been expressed in terms of ED_{50} values (effective dose to inhibit 50% spore germination) calculated by plotting the spore germination inhibition values against different concentrations of the compound on graph paper. The data were analyzed statistically.

Insecticidal Activity:

The insecticidal studies were conducted following CRD (completely randomized design) with three replications to evaluate the efficiency of laboratory prepared metal dimethyldithiocarbamates with standard insecticide carbaryl against the larvae of *Spilosoma obliqua* (Walker) on sunflower by leaf dip method. Laboratory reared fourth instar larvae were used for the experiment. Healthy leaves of sunflower brought from unsprayed field were dipped in solution/suspension of the metal complex of required concentration for one minute and were dried. Ten Larvae of the test insect were released in each jar. Metal dimethyldithiocarbamates were tested at three different concentrations i.e. 300ppm, 500ppm, 1000ppm. These were compared with standard insecticide carbaryl. Untreated control was kept for comparison. The observations were recorded at 24 hours, 48 hours and 72 hours after treatment. At each observation, dead larvae were counted and removed from the jar. The corrected mortality was calculated on the basis of mortality in untreated control by modified Abbot's formula:

$$\text{Per cent Mortality} = \frac{\text{Actual Mortality} - \text{Mortality in Control}}{100 - \text{Mortality in Control}} \times 100$$

The data were statistically analyzed after suitable angular transformations.

Results and Discussion

Synthesis:

The required metal dimethyldithiocarbamates were prepared by displacement reaction of metal sulphate (2a) or halide (2b) with sodium dimethyldithiocarbamate (1) in dichloromethane/water mixture according to the reported procedure (scheme 1). The various synthesized complexes were almost soluble in benzene, tetrahydrofuran, chloroform and dichloromethane, whereas all were insoluble in petroleum ether, ethanol and water. The analytical results indicated 1:2 stoichiometry for 3b, 3d, 3e and 3f complexes and 1:3 stoichiometry for 3a and 3c complexes. All the complexes showed low conductance in dichloromethane indicating non-electrolytic nature. The ir spectra gave intense bands around 1458 cm^{-1}, indicative of CN partial double bond of dithiocarbamate ligand[11]. Asymmetric C-S stretching vibration of metal dithiocarbamate complexes appeared in the 1000-965 cm^{-1} region[12].

The bands in the region 1260-1130 cm^{-1} have been assigned to NC< S grouping[13] (Table 1).

$$6\,[(CH_3)_2NCS_2\text{-}Na] \;+\; Cr_2(SO_4)_3K_2SO_4 \xrightarrow{CH_2Cl_2/H_2O} 2[(CH_3)_2NCS_2]_n\,M \;+\; 3\,Na_2SO_4$$

1 2a 3a

$$n\,[(CH_3)_2NCS_2\text{-}Na] \;+\; MX_n \xrightarrow{CH_2Cl_2/H_2O} [(CH_3)_2NCS_2]_n\,M \;+\; n\,NaX$$

1 2b 3b – 3f

n = 2; M = Mn, Ni, Cu, Zn
n = 3; M = Cr, Fe
3a Cr
3b Mn
3c Fe
3d Ni
3e Cu
3f Zn

Scheme 1

Table 1: Physical. Analytical and Spectral Data of Metal Dimethyldithiocarbamates

S. No.	Compound m.p.	Molecular Formula	Elemental Analysis % age Calculated (Observed)			Specific Conductance (Sm^{-1})	IR Bands (cm^{-1})		
			M	C	N		υ (CN) partial double bond	υ (C-S)	υ (NC< S S)
1	Na DMDTC 136-138^{0}C	$C_3H_6NS_2Na$	-	-	-	-	1430	950	-
3a	Cr $(DMDTC)_3$ 130-132^{0}C	$C_9H_{18}N_3S_6Cr$	12.40 (12.04)	26.72 (27.13)	10.20 (9.54)	2.72 X 10^{-3}	1456	993	1141,1244,1256
3b	Mn $(DMDTC)_2$ 140-142^{0}C	$C_6H_{12}N_2S_4Mn$	18.64 (18.11)	24.41 (25.48)	09.49 (10.50)	3.45 X 10^{-3}	1459	-	1133,1246,1260
3c	Fe $(DMDTC)_3$ >260^{0}C	$C_9H_{18}N_3S_6Fe$	13.41 (12.88)	25.97 (26.53)	10.10 (10.38)	3.20 X 10^{-3}	1462	966	1134,1244
3d	Ni $(DMDTC)_2$ 117-119^{0}C	$C_6H_{12}N_2S_4Ni$	19.62 (19.11)	24.11 (24.78)	09.38 (09.89)	3.49 X 10^{-3}	1459	-	1138,1247,1262
3e	Cu $(DMDTC)_2$ >260^{0}C	$C_6H_{12}N_2S_4Cu$	20.92 (21.91)	23.72 (24.79)	09.23 (09.49)	3.54 X 10^{-3}	1457	975	1156,1253
3f	Zn $(DMDTC)_2$ 138-140^{0}C	$C_6H_{12}N_2S_4Zn$	21.31 (20.49)	23.60 (24.59)	09.18 (10.07)	2.41 X 10^{-3}	1459	966	1151,1250

DMDTC = Dimethyldithiocarbamate

Table 2: Antifungal Potential of Metal Dimethyldithiocarbamates and their parent salts

Metal Compound	Denoted as	ED_{50} Values (ppm) against		
		A. alternata	***F.oxysporum***	***C.capsici***
Na DMDTC	1	67	7	4
$Cr_2(SO_4)_3K_2SO_4$	2a	30	12	70
$Cr(DMDTC)_3$	3a	16	33	16
$MnCl_2$	-	353	360	294
$Mn(DMDTC)_2$	3b	28	34	13
$FeCl_3$	-	17	16	7
$Fe(DMDTC)_3$	3c	13	12	16
$NiCl_2$	-	13	17	14
$Ni(DMDTC)_2$	3d	17	34	16
$CuCl_2$	-	6	5	7
$Cu(DMDTC)_2$	3e	17	32	16
$ZnCl_2$	-	16	29	15
$Zn(DMDTC)_2$	3f	16	35	16
Indofil M-45	-	30	-	17
Bavistin	-	-	7	-

DMDTC = Dimethyldithiocarbamate

Fungicidal Activity:

All the synthesized complexes were screened for their antifungal activity under *in vitro* conditions against three phytopathogenic fungi viz. *Alternaria alternata*, *Fusarium oxysporum* and *Colletotrichum capsici* by spore germination inhibiton technique using Indofil M-45 and Bavistin as standard fungicides. The antifungal potential has been expressed in terms of ED_{50} values (Table 2). All the test compounds exhibited antifungal activity against the three fungi to varying extents. The various synthesized compounds exhibited good antifungal activity against *Alternaria alternata* as well as *Colletotrichum capsici* as compared to standard. Although all the complexes showed promising antifungal activity against *Fusarium oxysporum* but none was comparable to standard fungicide except 2, the parent salt. And most of the synthesized compounds exhibited higher antifungal activity as compared to their parent salts.

Insecticidal Activity:

All the synthesized metal dimethyldithiocarbamates under trial helped to enhance the mortality rate of larvae of *Spilosoma obliqua* (Walker), the test insect, over control, after 48 hours and 72 hours after treatment at 500ppm and 1000ppm (Table 3).

Table 3: Corrected mortality of *S.obliqua* (Bihar hairy caterpillar) larvae with variable doses of metal dimethyldithiocarbamates at different intervals of time

Metal Compound/ Complex	Denoted as	24 Hours			48 Hours			72 Hours		
		300 ppm	500 ppm	1000 ppm	300 ppm	500 ppm	1000 ppm	300 ppm	500 ppm	1000 ppm
Na DMDTC	1	0.0 (4.05)	-	-	1.9(9.00)	-	-	1.9(9.00)	-	-
Cr $(DMDTC)_3$	3a	1.9 (9.00)	1.9(9.00)	13.0 (21.58)	1.9 (9.00)	10.4 (19.24)	19.4 (26.45)	5.3 (13.96)	24.0 (29.63)	51.9 (46.36)
Mn $(DMDTC)_2$	3b	0.0 (4.05)	0.0(4.05)	0.0(4.05)	0.0(4.05)	13.4 (21.91)	33.3 (35.52)	1.9 (9.00)	37.8 (38.20)	51.9 (46.36)
Fe $(DMDTC)_3$	3c	0.0 (4.05)	1.9(9.00)	5.3 (13.96)	0.0(4.05)	5.3 (13.96)	5.3 (13.96)	1.9(9.00)	10.4 (19.24)	24.2 (29.80)
Ni $(DMDTC)_2$	3d	5.3 (13.96)	5.3 (13.96)	-	23.2 (29.12)	30.0 (33.52)	-	23.9 (29.63)	44.8 (42.29)	-
Cu $(DMDTC)_2$	3e	5.3 (13.96)	5.3 (13.96)	10.0 (18.91)	13.0 (21.58)	19.3 (26.45)	26.5 (31.32)	13.4 (21.91)	34.4 (36.20)	44.8 (42.29)
Zn $(DMDTC)_2$	3f	0.0 (4.05)	5.3 (13.96)	5.3 (13.96)	0.0 (4.05)	5.3 (13.96)	13.0 (21.58)	0.0 (4.05)	34.4 (36.20)	51.9 (46.36)
Carbaryl	Standard	33.3 (35.52)	33.3 (35.52)	33.3 (35.52)	46.7 (43.37)	51.9 (46.36)	53.4 (47.21)	59.0 (50.21)	83.9 (66.72)	95.2 (78.03)
LSD (0.05)	-	(9.66)	(14.09)	(10.20)	(17.01)	(10.77)	(10.14)	(12.00)	(7.51)	(10.91)

DMDTC = Dimethyldithiocarbamate

Figures in parenthesis are n + 0.5 angular transformations

At 300ppm, nickel dimethyldithiocarbamate gave 29.63% mortality which was at par with copper dimethyldithiocarbamate showing 21.91% mortality, after 72 hours of treatment. But Carbaryl proved to be significantly better than any of the test compounds. At 500ppm, nickel dimethyldithiocarbamate still remain the best among synthesized complexes after 72 hours of treatment exhibiting 42.29% mortality of the test insect and was at par with the complexes of manganese, copper and zinc showing 38.20%, 36.00% and 36.20% mortality respectively. Complexes of Cr and Fe gave low mortality. None of the complex was at par with carbaryl (66.72%). At 1000ppm, Mn, Zn and Cr dimethyldithiocarbamates proved to be the best exhibiting 46.36% mortality of the larvae of the test insect after carbaryl (78.03%) and were at par with copper dimethyldithiocarbamate showing 42.29% mortality. Ferric dimethyldithiocarbamate gave low mortality (29.80%). Although various test compounds exhibited moderate insecticidal activity, but none of them proved to be at par with standard insecticide.

Recently studies are being carried on organic dithiocarbamates which emerged as potent anticancer drugs and prodrugs[14] in addition to their herbicidal, fungicidal and insecticidal properties.

Acknowledgements

Authors are thankful to Dr. C.L. Arora, Professor (Retired) Deptt. of Chemistry and Dr. Gurdip Singh, Professor (Retired) Deptt. of Entomology, Punjab Agricultural University, Ludhiana for their research guidance and help.

References

1. Thorn G.D. and Ludwig R.A., "The Dithiocarbamates and Related Compounds", Elsevier Publishers, Amsterdam, New York, 1962.
2. Criado J.J., Lopez-Arias J.A., Macias B., Fernandez-Lago L.R. and Salas J.M., *Inorg. Chim. Acta*, 193, 1992, 229.
3. Arora A., Sud D., Sharma J.R. and Arora C.L., *Asian J. Chem.*, 15, 2003, 715.
4. Kamble P.U., Ramiah M. and Patil D.V., *J. Soil Crop*, 10, 2000, 36.
5. Arora C.L., Kaur T. and Kaul V.K., *J. Ind. Coun. Chem.*, 10, 1994, 152.
6. Zorc B. and Sorondo S., *J. Farm. Glas*, 55, 1999, 137.
7. Sankar D.P., Mondal D.K. and Datta, R., *Antimicrob. Agents Chemother.*, 59, 2015, 2144.
8. Arora A., Singh B., Sud, D., Srivastava T. and Arora C.L., *Poll. Res.*, 22, 2003, 349.
9. Nene, Y.L. and Thapliyal, P.N., *Fungicides in Plant Disease Control*, Oxford and IBH Publishing Co. Pvt. Ltd., New Delhi, 1993, 525.
10. Anonymous, *Phytopathology*, 33, 1943, 627.
11. Kumar P., Shukla R.S., Ramrakhyani A.K., Sen Gupta A.K. and Shrivastava O.P., J. Ind. Chem. Soc., 59, 1982, 681.
12. Wu J., Lott P.F. and Droll H.A., *Inorg. Chem.*, 9, 1970, 193.
13. Pantaleo D.C. and Johnson R.C., *Inorg. Chem.*, 9, 1970, 1248.
14. Chaturvedi, D. and Zaidi, S., *Res. & Rev.: J. of Chem.*, 2016, 10.

*****