Asian Journal of Chemistry Vol. 15, No. 2 (2003), 715–719

Transition Metal Dialkyldithiocarbamates and Their Antifungal Activity

ANUPMA ARORA*, DHEERAJ SUD†, J.R. SHARMA‡ and C.L. ARORA
Department of Chemistry, Punjab Agricultural University, Ludhiana-141 004, India

Transition metal dialkyldithiocarbamates [$\{(R_2NCS_2)_nM\}$; $R_2 = Me_2$ or Et_2 and M = V, Mo, W and Pt] complexes were prepared by the reaction of metal chloride {MCl_n; n = 3, M = V, W and n = 4, M = Mo, Pt} with sodium dialkyldithiocarbamate, [$\{R_2NCS_2Na\}$; $R_2 = Me_2$ or Et_2] in dichloromethane/water (1 : 1) mixture. The metal complexes were characterized by elemental analysis, solubility, conductance and infrared spectral studies. The various synthesized complexes along with their parent salts were screened for their fungitoxicity under *in vitro* conditions against the three phytopathogenic fungi *viz. Alternaria alternata, Fusarium oxysporum* and *Colletotrichum capsici* by spore germination inhibition technique. All the complexes exhibit antifungal activity to varying extents.

Key words: Transition metal, Dialkyldithiocarbamates, Antifungal activity.

INTRODUCTION

Dithiocarbamates, the important, organosulphur compounds, are well known for their vast chemical and biological properties[1]. They have strong metal binding properties and the utility of metal dithiocarbamates in various fields of agriculture has been reported[2–8]. We have already reported the preparation of some metal diethyldithiocarbamates, their herbicidal[9] and nematicidal[10] properties. In continuation of our earlier work, we present here the synthesis of series of complexes of transition metals, *i.e.*, vanadium (V), molybdenum (Mo), tungsten (W) and platinum (Pt), with dimethyldithiocarbamate DMDTC, **(1a–1d)** and dialkyldithiocarbamate DEDTC, **(2a–2d)**, ligands, by the reported method[9, 10], their characterization and antifungal activity[11].

EXPERIMENTAL

The metal dimethyldithiocarbamates, [$\{(Me_2NCS_2)_nM\}$; M = V, Mo, W and Pt] and metal diethyldithiocarbamates, [$\{(Et_2NCS_2)_nM\}$; M = V, Mo, W and Pt] complexes were prepared by stirring metal chloride {MCl_n; n = 3, M = V, W and

---

†Lecturer, Department of Chemistry, SLIET, Longowal, India.

‡Senior Plant Pathologist, Department of Chemistry, PAU, Ludhiana, India.

n = 4, M = Mo, Pt} with sodium dialkyldithiocarbamate, [{R_2NCS_2Na}; $R_2 = Me_2$ or Et_2] for different time intervals in dichloromethane-water (1 : 1) mixture. The organic layer was separated from the aqueous layer, dried over anhydrous potassium sulphate and concentrated to get the crystals of the corresponding complex. These were finally dried *in vacuum*, to remove any left over trace of solvent.

$$n[R_2NCS_2Na] + MCl_n \xrightarrow{CH_2Cl_2/H_2O} [R_2NCS_2]_nM + nNaCl$$

Vanadium, molybdenum, tungsten and platinum were estimated in the respective complexes on ICAP (inductively coupled atomic plasma) Emission Spectrophotometer[12]. Analysis of carbon and nitrogen was done on Elemental Analysensteme GmbH Vario EL from Niper, Mohali.

Conductance Studies: Elico conductivity Bridge of type CM 82 T fitted with platinized platinum electrodes was used for conductivity measurements. The solutions of the complexes were made in dichloromethane at 5×10^{-3} M concentration. Cell constant of the cell used was 10 m^{-1}. Specific conductance and molar conductance were calculated. Specific conductance has been expressed in terms of S m^{-1} and molar conductance in terms of S m^2 mol^{-1}.

Specific conductance (K) = cell constant × observed conductance

Molar conductance (Λ_m) = 1000 × K/C

where C = concentration of solution in mol/m^3.

The spectra of the complexes were recorded in 4000–600 cm^{-1} on Perkin-Elmer infrared spectrophotometer in nujol mull using sodium chloride optics.

Antifungal Activity of Metal Dialkyldithiocarbamates

The antifungal activity of complexes was assayed under the supervision of a senior plant pathologist. It was tested in *in vitro* against three phytopathogenic fungi, *viz., Alternaria alternata, Fusarium oxysporum* and *Colletotrichum capsici* by spore germination inhibition technique[11]. The stock solutions/suspensions (2000 ppm) of the complexes were prepared by dissolving 50 mg of the complex in 2 mL of tetrahydrofuran (THF) and making the volume to 25 mL by adding sterilized 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 complexes in the cavities of the slides. These slides were kept in petri dishes lined with moist filter paper and incubated for 24 h at 25 ± 1°C. Untreated control was kept along with the treatments. The germination of spores was recorded and the per cent spore germination inhibition was calculated by the following formula:

Per cent spore germination inhibition

$$= \frac{\text{Spore germination in control} - \text{Spore germination in treatment}}{\text{Spore germination of control}} \times 100$$

Original metal salts were also taken and proceeded in the same way as the metal complexes. It was done to compare their activity with the synthesized complexes. The standard fungicides Indofil M-45 (75% manganese ethylene bis dithiocarbamate + 2% zinc) and Bavistin 50 WP (methyl-2-benzimidazole carbamate) were also used to compare the efficacy of the synthesized complexes. The antifungal activity has been expressed in terms of ED_{50} values (effective dose to inhibit 50 per cent spore germination), calculated by plotting the spore germination inhibition values against different concentrations of the complexes on the graph paper.

RESULTS AND DISCUSSION

All the complexes are stable in air. They are completely soluble in benzene, chloroform and tetrahydrofuran. The analytical results indicate a 1 : 3 stoichiometry for **1a, 1b, 2a** and **2b** complexes and 1 : 4 stoichiometry for **1c, 1d, 2c** and **2d** complexes. All the complexes show low molar conductance in the range of (320–2036) × 10^{-6} $S^{-1}m^{2}\ mol^{-1}$ in dichloromethane indicating non-electrolytic nature (Table-1).

TABLE-1
PHYSICAL AND ANALYTICAL AND INFRARED SPECTRAL DATA
OF COMPLEXES (**1a–1d**) and (**2a–2d**)

S. No.	Complex (% yields), m.p. (°C), colour	% Found (Calculated)			Λ_m $S^{-1}m^{2}mol^{-1}$ ($\times 10^{-6}$)	IR Bands (cm^{-1})		
		M	C	N		ν(C—S)	ν(C—N)	$\nu(\mathrm{NC}{<}^{S}_{S})$
1a	$V(DMDTC)_3$ (25.31), 68–70, Faun	11.59 (12.39)	25.41 (26.28)	9.65 (10.22)	432	997	1470	1129, 1197, 1263
1b	$W(DMDTC)_3$ (50.23), 120–122, Black	32.92 (33.82)	20.73 (19.85)	8.33 (7.72)	572	990	1471	1128, 1197, 1265
1c	$Mo(DMDTC)_4$ (53.34), 115–117, Yellowish green	15.59 (16.67)	26.02 (25.00)	10.36 (9.72)	580	975	1468	1157, 1197, 1261
1d	$Pt(DMDTC)_4$ (46.59), 125–127, Light yellow	– (28.89)	20.30 (21.33)	9.25 (8.30)	1794	970	1469	1159, 1198, 1259
2a	$V(DEDTC)_3$ (58.20), 61–63, Yellowish brown	9.09 (10.28)	37.41 (36.37)	8.90 (8.49)	320	976	1466	1138, 1196, 1263
2b	$W(DEDTC)_3$ (55.76), 65–67, Faun	28.83 (29.30)	29.71 (28.67)	7.64 (6.69)	500	988	1467	1137, 1196, 1265
2c	$Mo(DEDTC)_4$ (59.86), 78–80, Brown	13.40 (13.95)	35.92 (34.88)	9.19 (8.14)	626	970	1462	1150, 1195, 1263
2d	$Pt(DEDTC)_4$ (59.70), 110–112, Dark yellow	– (24.78)	31.42 (30.49)	8.16 (7.11)	2036	987	1466	1152, 1197, 1264

The intense bands in the region 1475–1460 cm^{-1} are indicative of $C=N$ bond of dithiocarbamate ligand. Sodium salts of dialkyldithiocarbamic acids (alkyl = $—CH_3$ or $—C_2H_5$) give CN vibration in 1470–1460 cm^{-1}, whereas CN absorption comes around 1490 cm^{-1} for transition metal dialkyldithiocarbamates[13]. The CN vibration occurs as a strong band at 1440 cm^{-1} and a broad band in the range 1510–1452 cm^{-1} with a peak at 1468 cm^{-1} for tellurium tetrakis(tetramethylenedithiocarbamate)[14]. The CN bond especially upon coordination of carbamate ligand is intermediate between a double bond and a single bond. The frequency of the $C=N$ bond decreases with increasing length of alkyl chain bonded to the nitrogen[15]. Asymmetric C—S stretching vibrations of metal dithiocarbamate complexes appear in the 1000–970 cm^{-1} region. Although the C—S asymmetric stretching absorption usually occurs at low frequency in more stable complexes, even then the position of these bands cannot be used as a measure of stability because the position of absorption is influenced by some other factors[13]. The three bands in 1290–1130 cm^{-1} region have been associated with $NC{<}^{S}_{S}$ grouping[15].

Antifungal activity: Metal complexes of DMDTC and DEDTC ligands, and their parent salts, *i.e.*, sodium dimethyldithiocarbamate and sodium diethyldithiocarbamate and metal halides, were tested for antifungal activity. The results in Table-2 reveal that the activity of all the synthesized complexes under trial was either more than or comparable to standard fungicide indofil M-45 against *A. alternata*. The trend was again same for *C. capsici* except the complexes of platinum whereas none of the complexes could prove as good as

TABLE-2
ANTIFUNGAL ACTIVITY OF METAL COMPLEXES AND THEIR PARENT SALTS

Metal salts/ complexes	ED_{50} values (ppm) against		
	A. alternata	*F. oxysporum*	*C. capsici*
NaDMDTC	66.5	7.0	4.0
NaDEDTC	76.8	31.2	6.1
VCl_3	7.0	6.0	4.0
$V(DMDTC)_3$	27.0	35.0	16.5
$V(DEDTC)_3$	12.2	620.0	14.7
$Mo(DMDTC)_4$	18.5	33.4	16.4
WCl_3	*	*	*
$W(DMDTC)_3$	16.0	16.4	16.4
$W(DEDTC)_3$	27.6	35.6	6.4
$PtCl_4$	54.5	64.0	66.2
$Pt(DMDTC)_4$	17.0	36.0	30.5
$Pt(DEDTC)_4$	13.5	160.0	65.7
Indofil M-45	30.0	—	17.0
Bavistin	—	7.0	—

* denotes more than 1000 ppm.

standard fungicide Bavistin against *F. oxysporum*. However, two of the parent salts, *i.e.*, NaDMDTC and VCl_3 prove the activity comparable to Bavistin and the activity of either complex of vanadium was much lower than vanadium halide against any of the three fungi.

ACKNOWLEDGEMENT

The authors are thankful to Head, Department of Chemistry, for providing necessary research facilities.

REFERENCES

1. G.D. Thom and R.A. Ludwig, The Dithiocarbamates and Related Compounds, Elsevier, Amsterdam-New York (1962).
2. W.H. Tisdale and I. Williams, *U.S.P.I.*, **972**, 961 (1934).
3. A.J. Overman and D.S. Burgis, *Proc. Flo. St. Hort. Soc.*, **69**, 250 (1956).
4. R.D. McMullen, *Nature*, **184**, 1338 (1959).
5. V.K. Ahluwalia, K.K. Arora and G. Kaur, *Synth. React. Inorg. Met.-Org. Chem.*, **16**, 127 (1986).
6. H. Singh, V.K. Srivastava, S.N. Shukla and M.K. Upadhyaya, *Indian J. Chem.*, **31A**, 472 (1992).
7. P.U. Kamble, M. Ramiah and D.V. Patil, *J. Soil Crop*, **10**, 36 (2000).
8. L.G. Bundy and J.M. Bremner, *Soil Sci. Soc. Am. Proc.*, **37**, 396 (1973).
9. C.L. Arora, A. Arora and R. Kaur, *Pestic. Res. J.*, **10**, 228 (1998).
10. C.L. Arora, J.R. Sharma and T. Kaur, *Pestic. Res. J.*, **6**, 34 (1994).
11. Anonymous, *Phytopathology*, **33**, 627 (1943).
12. M.L. Jackson, Soil Plant Analysis, Prentice-Hall of India, New Delhi (1967).
13. F.W. Moore and M.L. Larson, *Inorg. Chem.*, **6**, 998 (1967).
14. J. Wu, P.F. Lott and H.A. Droll, *Inorg. Chem.*, **9**, 193 (1970).
15. D.C. Pantaleo and R.C. Johnson, *Inorg. Chem.*, **9**, 1248 (1970).

(*Received*: 27 August 2002 ; *Accepted*: 15 November 2002) AJC-2916