Chem Sci Trans., 2013, **2(2),** 367-374
DOI:10.7598/cst2013.265

Chemical Science Transactions
ISSN/E-ISSN: 2278-3458/2278-3318

RESEARCH ARTICLE

Preparation and Characterization of the Adducts of Bis(*N*,*N*-diethyldithiocarbamato)oxovanadium(IV) and Copper(II) with *n*-Propylamine and Isopropylamine

MOUSAMI SHARMA*, ANJU SHARMA and RENU SACHAR

Department of Chemistry, University of Jammu, Babasaheb Ambedkar Road,
Jammu-180006, India
mousami.sharma@gmail.com

Received 19 June 2012 / Accepted 8 July 2012

Abstract: Two new 1:1 adducts of $VO(dedtc)_2$, two 1:1 and two 1:2 adducts of $Cu(dedtc)_2$ (where dedtc = diethyldithiocarbamate) with *n*-propylamine and isopropylamine have been prepared. The resulting complexes have been characterized by elemental analysis, molar conductance, magnetic susceptibility, IR and UV-Vis spectral and TGA/DTA techniques. Analytical data reveals that VO(IV) complex forms only 1:1 adducts with the formula $[VO(dedtc)_2L]$ while Cu(II) complex forms both 1:1 and 1:2 adducts with 1:1 adducts having general formula $Cu(dedtc)_2.L$ and 1:2 adducts having general formula $Cu(dedtc)_2.L_2$ (L = *n*-propylamine and isopropylamine). Antifungal activity of some complexes has been carried out against the fungal strain *Sclerotium rolfsii*. Electronic and magnetic measurements indicate a square pyramidal geometry for the 1:1 adducts of Cu(II) complex and an octahedral geometry for the 1:1 adducts of VO(IV) complex and for the 1:2 adducts of Cu(II) complex.

Keywords: Diethyldithiocarbamate, *n*-Propylamine, Isopropylamine, Diethylamine, *Sclerotium rolfsii*

Introduction

Dithiocarbamates are a versatile class of monoanionic 1,1-dithiolato systems involving sulfur donor ligands. A large number of transition metal dithiocarbamate complexes have been synthesized and characterized until now[1-3]. These compounds present striking structural features and have diverse applications such as vulcanization accelerators, fungicides, pesticides, floatation agents and high pressure lubricants[4-9]. They are used as curing agents in rubber processing and in photographic films[10,11]. They play an important role as an adjuvant in the chemotherapy of human cancers; treat acquired immune depressive syndrome and drug resistant fungal infection[12-15]. They are also found to be helpful in the treatment of chronic alcoholism as alcohol aversion therapy[16,17]. They have been widely used in solvent extraction and other analytical procedures. In view of the potential biological activity and practical applications of the dithiocarbamates, we have reported the synthesis and characterization of 1:1 and 1:2 adducts of some 3*d*-transition metal dithiocarbamates with *n*-propylamine and isopropylamine.

Experimental

Diethylamine, *n*-propylamine and isopropylamine were used as such. Metal analysis was done by the reported methods[18]. Carbon, hydrogen and nitrogen analysis were performed by micro analytical methods. Molar conductivity in chloroform and DMF (10^{-3} M) at room temperature was measured using a digital conductivity meter "Century CC 601" and a conductivity cell with a cell constant 1. Magnetic susceptibility of the complexes was recorded at room temperature by VSM technique. IR spectra of the complexes over the region 4000-400 cm^{-1} were recorded on Perkin Elemer FTIR spectrophotometer using KBr disc. The electronic spectra of the complexes were recorded in the range 12500-40000 cm^{-1} on Systronics 119 UV-visible spectrophotometer. Thermogravimetric analysis (TGA/DTA) of the complexes was recorded on EXSTAR TG/DTA 6300 thermoanalyzer at the heating rate of 10 ^{o}C/min. The antifungal activity of the complexes was tested by poisoned food technique against the pathogenic fungus, *Sclerotium rolfsii*. All the experiments were carried out at room temperature.

Preparation of sodium salt of diethyldithiocarbamate

Diethylamine (12 mL), ethanol (50 mL) and carbon disulfide (12 mL) were taken in a beaker and the contents were mixed by stirring. To this, a saturated solution of sodium hydroxide (9 g) was added and stirred well. The reaction mixture was allowed to cool in ice. On cooling, white needle like crystals separated out which were filtered, washed several times with rectified spirit and dried in a vacuum desiccator.

Preparation of bis(N,N-diethyldithiocarbamato) complexes of VO(IV) and Cu(II)

Oxovanadium(IV) and Copper(II) diethyldithiocarbamate complexes were prepared by adding an aqueous solution of sodium salt of diethyldithiocarbamate (0.02 mole) to an aqueous solution of $VOSO_4$ (1.63 g, 0.01 mole) and $CuSO_4.5H_2O$ (2.49, 0.01 mole) respectively with stirring in 2:1 molar ratio. The VO(IV) complex formed was greenish-yellow in colour while Cu(II) complex obtained was brown in colour. The complexes were precipitated immediately which were filtered, washed several times with distilled water and dried in a vacuum desiccator.

Preparation of 1:1 adducts of bis(N,N-diethyldithicarbamato)VO(IV)

1:1 Adducts of $VO(dedtc)_2$ with *n*-propylamine and isopropylamine were obtained by dissolving 0.01 mole (3.63 g) of the dithiocarbamate complex with 0.01 mole of ligand (*n*-propylamine, isopropylamine) in chloroform. The green coloured adducts separated out immediately which were filtered and dried *in vacuo*.

Preparation of 1:1 adducts of bis(N,N-diethyldithicarbamato)Cu(II)

The 1:1 adducts of bis(*N*,*N*-diethyldithicarbamato)Cu(II) were prepared by refluxing the complex (0.01 mole, 3.59 g) with the ligand (0.01 mole) in dimethylformamide for about two hours. The contents were kept as such overnight when shining brown crystals of the adducts were obtained which were filtered, washed and dried *in vacuo*.

Preparation of 1:2 adducts of bis(N,N-diethyldithicarbamato)Cu(II)

Bis(*N*,*N*-diethyldithicarbamato) Cu(II) (0.01 mole, 3.59 g) was dissolved in dimethylformamide and the ligand (0.02 mole) was added to it. The contents were refluxed for about two hours. The resulting reaction mixture was kept undisturbed overnight when shining blackish brown crystals of the adducts were formed which were filtered, dried and stored in a vacuum desiccator over calcium chloride.

Results and Discussion

The complexes were analyzed by various analytical and physico-chemical techniques and the results show that VO(dedtc)$_2$ forms 1:1 while Cu(dedtc)$_2$ form both 1:1 and 1:2 adducts. The analytical data (Table 1) reveals that 1:1 adducts have general formulae VO[S$_2$CN (C$_2$H$_5$)$_2$]$_2$.L, Cu[S$_2$CN(C$_2$H$_5$)$_2$]$_2$.L and 1:2 adducts have general formula Cu[S$_2$CN (C$_2$H$_5$)$_2$]$_2$.L$_2$ (where L= *n*-propylamine, isopropylamine). All the complexes are coloured and stable in air. Conductance measurements were done to ascertain the electrolytic/non-electrolytic nature of the metal complexes. The molar conductivity values of 1:1 and 1:2 adducts of Cu(dedtc)$_2$ measured in 10^{-3} M chloroform solution are found to be in the range of 7-27 ohm^{-1} cm^2 mol^{-1} (Table 1). On the other hand the conductivity measurements of the adducts of VO(dedtc)$_2$ were carried out in dimethylformamide and the values of their millimolar solutions are found to be 25 and 41 ohm^{-1} mole^{-1} cm^2 (Table 1). These values suggest non-electrolytic nature of these addition complexes.

Table 1. Analytical and physical data of the adducts

S.No.	Complex	Molar Conductivity, Ohm^{-1}cm^2 mol^{-1}	Magnetic moments (B.M.) (300 K)	Analysis Found (Calculated)				
				C	H	N	S	M
1.	VO(dedtc)$_2$. *n*-propylamine	25	1.82	36.29 (36.96)	6.22 (6.87)	9.43 (9.95)	29.95 (30.32)	11.87 (12.08)
2.	VO(dedtc)$_2$.isopropylamine	41	1.86	36.12 (36.96)	6.19 (6.87)	9.48 (9.95)	30.02 (30.32)	11.76 (12.08)
3.	Cu(dedtc)$_2$. *n*-propylamine	27	1.83	36.52 (37.26)	6.31 (6.93)	9.67 (10.03)	30.12 (30.57)	14.63 (15.18)
4.	Cu(dedtc)$_2$.isopropylamine	13	1.85	36.39 (37.26)	6.47 (6.93)	9.42 (10.03)	30.09 (30.57)	14.49 (15.18)
5.	Cu(dedtc)$_2$. (*n*-propylamine)$_2$	7	1.93	39.47 (40.19)	7.28 (7.95)	11.09 (11.72)	26.37 (26.81)	12.98 (13.30)
6.	Cu(dedtc)$_2$. (isopropylamine)$_2$	27	1.89	39.62 (40.19)	7.54 (7.95)	11.28 (11.72)	26.29 (26.81)	12.86 (13.30)

Magnetic measurements

The magnetic moments of all the complexes are measured at room temperature and presented in Table 1. The 1:1 and 1:2 adducts of bis(*N*,*N*-diethyldithiocarbamato)Cu(II) exhibit magnetic moment values in the range 1.83 to 1.93 B.M. These values are slightly higher than the spin only value and are in accordance with square pyramidal geometry for the 1:1 adducts and octahedral geometry for the 1:2 adducts. The adducts of bis(*N*,*N*-diethyldithiocrbamato)VO(IV) are found to be paramagnetic having magnetic moment values of 1.82 and 1.86 B.M. These results show the existence of monomeric species of oxovanadium(IV)[19]. The higher values of magnetic moment may be attributed to the orbital contribution[20].

Infrared spectra

The most relevant bands in the IR spectra of the adducts of VO(dedtc)$_2$ and Cu(dedtc)$_2$ are shown in Table 2. All the adducts show a strong band in the region 1505-1455 cm^{-1} which can be assigned to the stretching vibration of the C—N bond. This band is found to lie between υ(C═N) (1680-1640 cm^{-1}) and υ(C—N) (1350-1250 cm^{-1}) ranges indicating partial double bond character of the C—N bond[21-23]. One C—S stretching frequency υ(CSS) is observed in the range 1049-1012 cm^{-1} in all the adducts which indicates a symmetrical bidentate binding of the dithiocarbamato moiety[23-25]. A new band of medium to strong intensity observed in the region 420-405 cm^{-1} may be assigned to υ(M—S) stretching mode. The $\upsilon(NH_{sym})$ vibrations of the coordinating amines were observed in the region 3269-3302 cm^{-1} while $\upsilon(NH_{asym})$ vibrations were found to be in the range 3292-3320 cm^{-1} showing a negative shift of 160-150 cm^{-1} upon coordination with the metal. In the infrared spectra of the adducts of $VO(dedtc)_2$ a strong band at 986-991 cm^{-1} is observed which can be attributed to the terminal V=O bond. The V=O band in the parent complex observed at 1000 cm^{-1} is displaced to lower frequencies in the adducts which is due to the electronic donation of the base to the vanadium (N→V)[19].

Table 2. Important IR spectral bands (cm^{-1}) and their assignment

S.No.	Complex	υ(N—H) asym.	υ(N—H) sym.	υ(C—N)	υ(C—S)	υ(M—S)
1.	$VO(dedtc)_2$.*n*-propylamine	3320	3298	1461	1045	411
2.	$VO(dedtc)_2$.isopropylamine	3313	3302	1455	1049	405
3.	$Cu(dedtc)_2$.*n*-propylamine	3298	3269	1504	1012	420
4.	$Cu(dedtc)_2$.isopropylamine	3312	3295	1466	1019	418
5.	$Cu(dedtc)_2$.(*n*-propylamine)$_2$	3292	3275	1505	1015	413
6.	$Cu(morphdtc)_2$.(isopropylamine)$_2$	3305	3284	1458	1022	415

Electronic spectra

The electronic spectral data of adducts are given in Table 3. The spectra of the 1:1 adducts of $VO(dedtc)_2$ were recorded in dimethylformamide while those of the 1:1 and 1:2 adducts of $Cu(dedtc)_2$ were recorded in chloroform in the range 12500-40000 cm^{-1}. The adducts of bis(diethyldithiocarbamato) oxovanadium(IV) show electronic transitions of e ← b_2 (υ_1) in the range 13349-13837 cm^{-1}, b_1 ← b_2 (υ_2) in the range 18021-18426 cm^{-1} and a_1 ← b_2 (υ_3) in the range 25027-25386 cm^{-1}. Above transitions have major contribution for distorted octahedral geometry of oxovanadium(IV) complexes which is also supported by the reported literature[19,20].

Table 3. Electronic spectra of the adducts

S.No.	Complex	υ_1	υ_2	υ_3
1.	$VO(dedtc)_2$.*n*-propylamine	13837	18426	25386
2.	$VO(dedtc)_2$.isopropylamine	13349	18021	25027
3.	$Cu(dedtc)_2$.*n*-propylamine	16842	-	-
4.	$Cu(dedtc)_2$.isopropylamine	16892	-	-
5.	$Cu(dedtc)_2$.(*n*-propylamine)$_2$	15462	-	-
6.	$Cu(dedtc)_2$.(isopropylamine)$_2$	15532	-	-

1:1 Addition complexes of $Cu(dedtc)_2$ show a broad band with maximum intensity centered around 16000 cm^{-1} which can be assigned to $^2B_1 \rightarrow {}^2E$ (υ_1), suggesting a square pyramidal geometry around Cu(II) ion. A weak shoulder at around 11000 cm^{-1} is also shown by these complexes[26]. On the other hand 1:2 adducts of $Cu(dedtc)_2$ with n-propylamine and isopropylamine show a broad absorption band at 15462 cm^{-1} and 15532 cm^{-1} respectively. This band is an average of two transitions $^2B_1 \rightarrow {}^2B_2$ and $^2B_1 \rightarrow {}^2E$ and is regarded as "copper band"[27]. These transitions suggest an octahedral geometry for these Cu(II) adducts.

Thermal studies

The thermal analysis was studied for selected compounds. The data on thermal decomposition of adducts are given in Table 4. The thermogram of the adduct [VO(dedtc)$_2$. *n*-propylamine] (Figure 1) shows multistep decomposition starting at 155 °C. The initial weight loss corresponds to the loss of one *n*-propylamine molecule which is followed by the loss of two diethyldithiocarbamato moieties. The final residue as analyzed for VO(IV) complex at a temperature of 988 °C is VO$_2$.

Table 4. Thermal degradation of the adducts

S.No.	Complex	Decomposition Temp. °C	% Weight loss obs. (calc.)	Residue compd.	% Weight obs. (calc.)
1.	[VO(dedtc)$_2$. *n*-propylamine]	988	80.79 (80.34)	VO$_2$	18.92 (19.66)
2.	Cu(dedtc)$_2$. *n*-propylamine	964	76.60 (77.18)	CuS	23.40 (22.82)
3.	Cu(dedtc)$_2$. (*n*-propylamine)$_2$	963	79.10 (80.00)	CuS	20.90 (20.00)

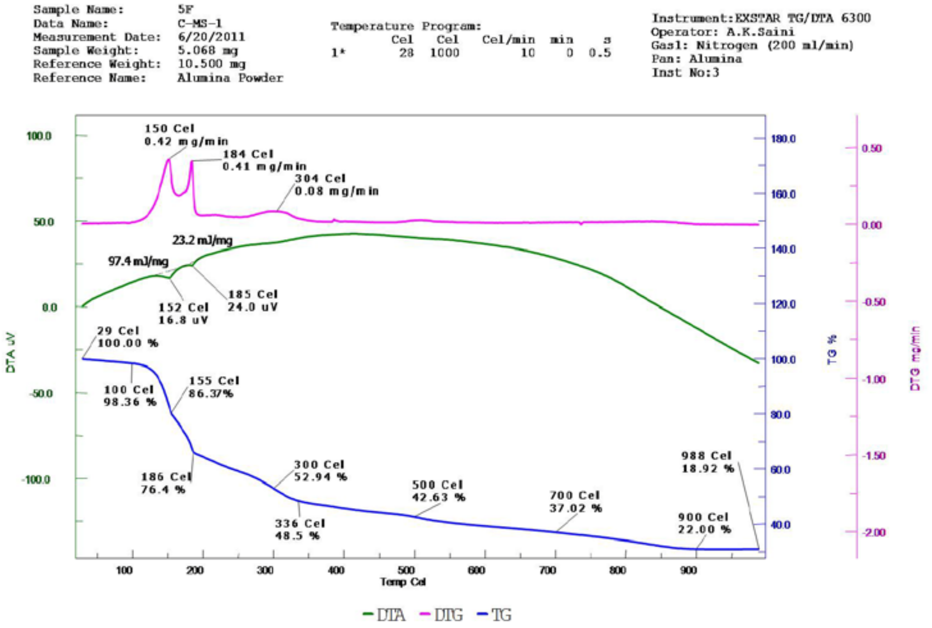
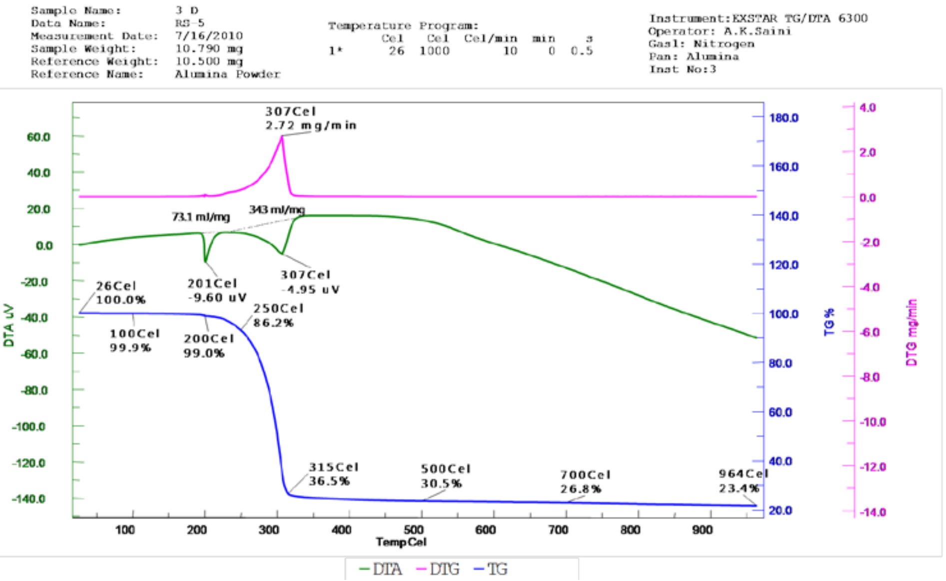


Figure 1. Thermogram of the adduct [VO(dedtc)$_2$. *n*-propylamine]

The TG curve of 1:1 adduct, [Cu(dedtc)$_2$.*n*-propylamine], shows an initial loss of one *n*-propylamine molecule at 250 °C and then a continuous weight loss is observed due to the loss of $C_{10}H_{20}N_2S_3$ moiety till a stable sulphide, CuS, is obtained at 964 °C (Figure 2). Thermal decomposition of the 1:2 adduct, [Cu(dedtc)$_2$.(*n*-propylamine)$_2$] starts at 251 °C showing the loss of two *n*-propylamine molecules. Then a continuous weight loss is observed due to the loss of $C_{10}H_{20}N_2S_3$ moiety and the resultant weight corresponds to the formation of a stable sulphide CuS at 963 °C (Figure 3).

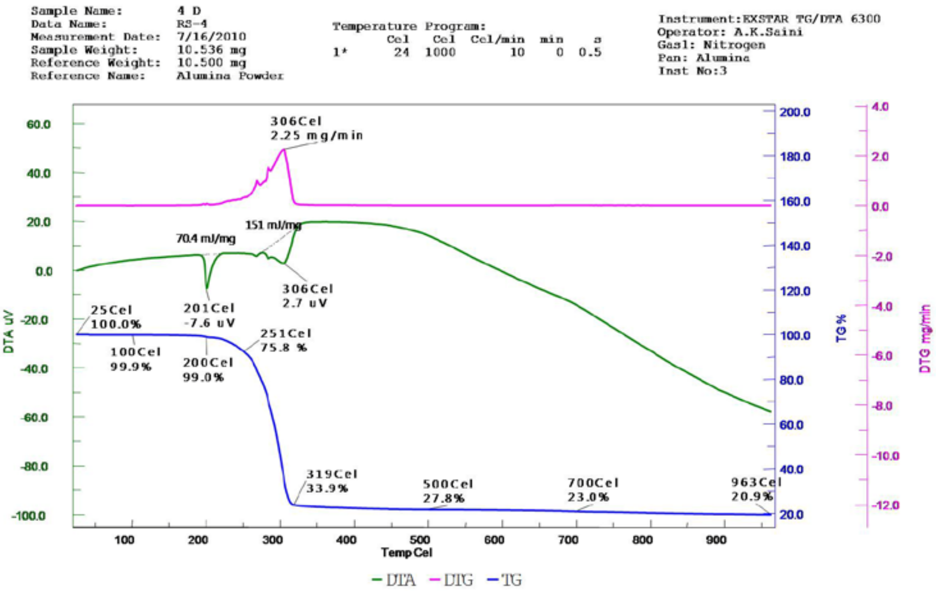


Sample Name: 3 D
Data Name: RS-5
Measurement Date: 7/16/2010
Sample Weight: 10.790 mg
Reference Weight: 10.500 mg
Reference Name: Alumina Powder

Temperature Program:
Cel Cel Cel/min min s
1* 26 1000 10 0 0.5

Instrument:EXSTAR TG/DTA 6300
Operator: A.K.Saini
Gas1: Nitrogen
Pan: Alumina
Inst No:3

Figure 2. Thermogram of the adduct [Cu(dedtc)2. *n*-propylamine]



Sample Name: 4 D
Data Name: RS-4
Measurement Date: 7/16/2010
Sample Weight: 10.536 mg
Reference Weight: 10.500 mg
Reference Name: Alumina Powder

Temperature Program:
Cel Cel Cel/min min s
1* 24 1000 10 0 0.5

Instrument:EXSTAR TG/DTA 6300
Operator: A.K.Saini
Gas1: Nitrogen
Pan: Alumina
Inst No:3

Figure 3. Thermogram of the adduct [Cu(dedtc)2. (*n*-propylamine)$_2$]

Biological studies

The *in vitro* biological screening effects of three complexes were tested against the pathogenic fungus, *Sclerotium rolfsii* by Poisoned Food Technique[28]. The linear growth of the fungus in controlled manner was recorded at different concentrations of the complexes. The growth inhibition of *Sclerotium rolfsii* over control was calculated (Table 5).

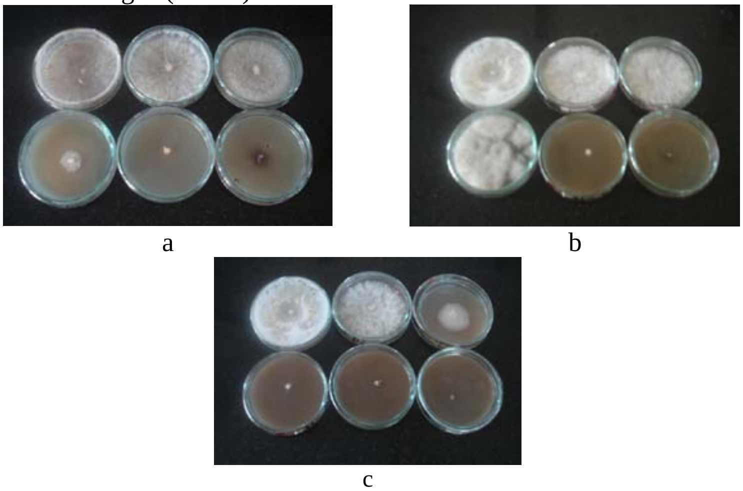
Table 5. Antifungal activities of some adducts mean colony diameter in the control = 91 mm

S.No.	Complex	Concenteration, ppm	Colony Diameter, mm	% Inhibition $I = [(C-T)/C]\times100$
1.	$VO(dedtc)_2$. *n*-propylamine	100	90	1.09
		200	78	14.28
		300	21	76.92
		400	8	91.20
		500	5	94.50
2.	$Cu(dedtc)_2$. *n*-propylamine	100	91	0
		200	90	1.09
		300	80	12.08
		400	5	94.50
		500	5	94.50
3.	$Cu(dedtc)_2$. (*n*-propylamine)$_2$	100	88.5	2.74
		200	44	51.64
		300	5	94.50
		400	5	94.50
		500	5	94.50

It is found that on increasing the concentration of the complexes, the colony diameter of the fungus decreases and hence percent inhibition increases (Figure 4). The growth inhibition of *Sclerotium rolfsii* over control was calculated as:

$$\% \text{ Inhibition (I)} = \frac{C - T}{C} \times 100$$

Where, I= percent inhibition, C= mean growth of fungus (in mm) in control and T= mean growth of fungus (in mm) in treatment.



a b

c

Figure 4. Antifungal activity of the adducts (a) $VO(dedtc)_2$(*n*-propylamine), (b) $Cu(dedtc)_2$ (*n*-propylamine) and (c) $Cu(morphdtc)_2$(*n*-propylamine)$_2$

Conclusion

On the basis of above studies it is found that 1:1 adducts of $VO(dedtc)_2$ and 1:2 adducts of $Cu(dedtc)_2$ have octahedral geometry while 1:1 adducts of $Cu(dedtc)_2$ have square pyramidal geometry. The complexes analyzed for the antifungal activity show considerable activity.

References

1. Ondrusova D, Jona E and Simon P, *J Therm Anal Cal.*, 2002, **67**, 147.
2. Daniel K G, Chen D, Orlu S, Cui Q C, Miller F R and Dou Q P, *Breast Cancer Res.*, 2005, **7(6)**, 897-908.
3. Sarwar M, Ahmad S, Ahmad S, Ali S and Awan S A, *Trans Met Chem.*, 2007, **32(2)**, 199-203.
4. Kalia S B, Kaushal G, Sharma D K and Verma B C, *Synth React Inorg Met-Org Nano-Met Chem.*, 2005, **35**, 181.
5. Cervantes G, Moreno V, Molins E and Miravitlles C, *Metal Based Drugs*, 1997, **4(6)**, 317-325.
6. Mauclaire, Laurent and Berthommier, *Eric FR Appl.*, 2000, **15**, 57; *Chem Abstr*., 2002, **137**, 14843m.
7. Neves A, Rossi L M, Bortoluzzi A J, Mangrich A S, Haase W and Werner R, *J Brazil Chem Soc*., 2001, **12**, 747; *Chem Abstr*., 2002, **136**, 144232b.
8. Arora C L and Kaur J, *Asian J Chem.*, 1993, **5**, 473.
9. Coucouvanis D, *Prog Inorg Chem.*, 1970, **11,** 233-371.
10. Datta R N, Das P K and Basu D K, *Rubber Chem Technol.*, 1984, **57**, 879.
11. Cavalheiro E T G, Ionashiro M, Marino G, Berviglieri S T and Chierice G O, *J Braz Chem Soc.*, 1999, **10**, 65.
12. Reisinger E C, Kern P, Ernst M, Bock P, Flad H D and Dietrich M, *Lancet*, 1990, **335**, 679-882.
13. Gandara D R, Perez E A, Weibe V and De Gregorio M W, *Semin Oncol.*, 1991, **18**, 49-55.
14. Kim C H, Kim J H, Xu J, Hsu C Y and Ahn Y S, *Blackwell Synergy: J Neurochem.*, 1999, **72(4)**, 1586-1592.
15. Sauna Z E, Shukla S and Ambudkar S V, *Mol BioSyst Royal Soc Chem.*, 2005, **1(2)**, 127-134.
16. Fischer C M, *Arch Neurol.*, 1989, **46(7)**, 798-804.
17. Thorn G D and Ludwig R A, The Dithiocarbamates and Related Compounds, New York, 1962.
18. Jeffery G H, Bassett J, Mehdham J and Denny R C, Vogel's Text Book of Quantitative Chemical Analysis, 5th Edition Longman Group UK Ltd., 1989, **455**, 472.
19. Doadrio A L, Sotelo J and Ruano A F, *Quim Nova.*, 2002, **25**.
20. Aswar A S, Bansod A D, Aswale S R and Mamdlik P R, *Indian J Chem.*, 2004, **43(A)**, 1892.
21. Bradley D C and Gitlitz M H, *J Chem Soc (A)*, 1969, 1152.
22. Criado J J, Carrasco A, Macias B, Salas J M, Medarde M, Castillo M, *Inorg Chim Acta*, 1989, **160,** 37.
23. Fabretti A C, Forghieri F, Giusti A, Preti C and Tosi G, *Inorg Chim Acta.*, 1984, **86(2)**, 127-131.
24. Golding R M, Harris C M, Jessop K J and Tennant W, *Aust J Chem.*, 1972, **25**, 2567.
25. Bonati F and Ugo R, *J Organometallic Chem.*, 1967, **10**, 257-268.
26. Duggan M, Ray N and Hathaway B J, *J Chem Soc Dalton*, 1980, 1342.
27. Hathaway B J, Billing D E, Nicholls P and Procter I M, *J Chem Soc (A)*, 1969, 319.
28. Nene Y L and Thapliyal P N, Fungicides in Plant Disease Control III Edn., 1993, 691.