Synthesis and Characterization of the Adducts of Morpholinedithiocarbamate Complexes of Oxovanadium (IV), Nickel(II), and Copper(II) with Piperidine and Morpholine

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Received 02 November 2011; Accepted 07 January 2012

Abstract: A series of 1:1 adducts of bis(morpholinedithiocarbamate) complex of VO(IV), 1:1 and 1:2 adducts of bis(morpholinedithiocarbamate) complexes of Ni(II) and Cu(II) with piperidine and morpholine have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility, IR, UV-Vis, and TGA/DTA techniques. Analytical data reveals that VO(IV) complex forms only 1:1 adducts with the formula [VO(morphdte)₂L].H₂O while Ni(II) and Cu(II) complexes form both 1:1 and 1:2 adducts with 1:1 adducts having general formula Ni(morphdte)₂.L and Cu(morphdte)₂.L and 1:2 adducts having general formula Ni(morphdte)₂.L₂ and Cu(morphdte)₂.L₂ (morphdte = morpholinedithiocarbamate, L = morpholine and piperidine). Antifungal activity of some complexes has been carried out against the fungal strain *Fusarium oxysporum*. Thermal studies indicate a continuous weight loss. A square pyramidal geometry has been proposed for the 1:1 adducts of Ni(II) and Cu(II) complexes while an octahedral geometry has been proposed for the 1:1 adducts of VO(IV) and for the 1:2 adducts of Ni(II) and Cu(II) complexes.

Keywords: morpholinedithiocarbamate, piperidine, morpholine.

Introduction

Dithiocarbamates are the half amides of dithiocarbonic acids and can function either as unidentate or bidentate chelating ligands¹⁻⁴. The strong metal binding properties of the dithiocarbamates were recognized early by the virtue of insolubility of the metal salts and the capacity of the molecules to form chelate complexes. They are capable of stabilizing transition metals in a wide range of oxidation states and frequently stabilize the metal centre in an unusually high apparent formal oxidation state. In vast majority of instances, they act merely as non sterically demanding ancillary ligands^{5,6}. These 1,1-dithiolato systems are of current interest due to their potential biological activity and practical applications in the

fields of rubber technology and agriculture, in addition to general considerations of metal-sulfur bonding and electron delocalization in transition metal complexes⁷⁻¹¹. They have been successfully used as fungicides, pesticides, vulcanization accelerators, floatation agents and high pressure lubricants¹². Moreover they act as therapeutic agents for alcoholism and metal intoxication^{13,14}. Now a days they have also been reported to treat acquired immune depressive syndrome and cancer¹⁵⁻¹⁷. In view of the diverse applications of the dithiocarbamates we have reported the synthesis and characterization of 1:1 and 1:2 adducts of some 3d- transition metal dithiocarbamates with morpholine and piperidine.

Experimental

Morpholine (Fluka), and piperidine (SDS) were purified by distillation after keeping the bases over potassium hydroxide overnight. Metal analysis was done by reported methods¹⁸. 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 $4000\text{--}400\text{ cm}^{-1}$ were recorded on Perkin Elemer FTIR spectrophotometer using KBr disc. The electronic spectra of the complexes were recorded in the range $12500\text{--}40000\text{ cm}^{-1}$ on Systronics 119 UV-Visible spectrophotometer. Thermogravimetric analysis (TGA/DTA) of complexes was recorded on EXSTAR TG/DTA 6300 thermoanalyzer at the heating rate of 10 C/min . The antifungal activity of the complex was tested by Poisoned Food Technique against the pathogenic fungus, *Fusarium oxysporum*. All the experiments were carried out at room temperature.

Preparation of Sodium Salt of Morpholine dithiocarbamate

Morpholine (8.7 mL, 0.1 mole) and diethyl ether (150 mL) were taken in a round bottom flask and the contents were stirred for ten minutes. To this carbon disulfide (6 mL, 0.1 mole) was added dropwise with continuous stirring. During the course of the reaction, dithiocarbamic acid was formed to which concentrated solution of sodium hydroxide (4 g, 0.1 mole) was added slowly with continuous vigorous stirring for 4 hours. The sodium salt of morpholinedithiocarbamic acid formed was filtered out and washed with dry ether. The crude product was recrystallized from 2-propanol and dried in a vacuum desiccator.

Preparation of bis(morpholinedithiocarbamate) Complexes of VO(IV), Ni(II) and Cu(II)

Oxovanadium(IV), Nickel(II) and Copper(II) morpholinedithiocarbamate complexes were prepared by adding an aqueous solution of sodium salt of morpholinedithiocarbamate (0.02 mole) to an aqueous solution of VOSO_4 (1.63 g, 0.01 mole), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.3771 g, 0.01 mole) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (2.49, 0.01 mole) respectively with stirring in 2:1 molar ratio. The VO(IV) and Ni(II) complexes formed were green 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(morpholinedithiocarbamate)VO(IV)

The 1:1 adducts were obtained by stirring the ligand (0.01 moles) and $\text{VO}(\text{morphdtc})_2$ (0.01 moles) in acetone for three hours. Green coloured precipitates of the adducts were filtered and dried in a vacuum desiccator over anhydrous calcium chloride.

Preparation of 1:1 Adducts of bis(morpholinedithiocarbamate)Ni(II)

1:1 Addition complexes of bis(morpholinedithiocarbamato)Ni(II) with piperidine and morpholine were prepared by refluxing bis(morpholinedithiocarbamato)Ni(II) (0.01 moles) with the ligand (0.01 moles) in dimethylformamide for one hour. The contents were kept overnight when shining green coloured crystals of the adducts were obtained. The adducts were filtered, washed and dried in vacuo.

Preparation of 1:1 Adducts of bis(morpholinedithiocarbamato)Cu(II)

The 1:1 adducts of bis(morpholinedithiocarbamato)Cu(II) were prepared by refluxing bis(morpholinedithiocarbamato)Cu(II) (0.01 moles) with the ligand 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(morpholinedithiocarbamato)Ni(II)

Bis(morpholinedithiocarbamato)Ni(II) (0.01 moles) was dissolved in dimethylformamide and to it the ligand (0.02 moles) was added. The contents were refluxed for one hour and kept overnight undisturbed when shining dark green crystals of the adducts were obtained which were filtered, dried and stored in a vacuum desiccator.

Preparation of 1:2 Adducts of bis(morpholinedithiocarbamato)Cu(II)

Bis(morpholinedithiocarbamato)Cu(II) (0.01 moles) was dissolved in dimethylformamide and the ligand (0.02 moles) 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 adduct were formed which were filtered, dried and stored in a vacuum desiccator over calcium chloride.

Results and Discussion

The analytical and physico-chemical results show that 1:1 adducts formed have the general formulae $[\text{VO}(\text{S}_2\text{CNC}_4\text{H}_8\text{O})_2\cdot\text{L}]\cdot\text{H}_2\text{O}$, $\text{Ni}(\text{C}_4\text{H}_8\text{ONCS}_2)_2\cdot\text{L}$ and $\text{Cu}(\text{C}_4\text{H}_8\text{ONCS}_2)_2\cdot\text{L}$ and the 1:2 adducts formed have general formulae $\text{Ni}(\text{C}_4\text{H}_8\text{ONCS}_2)_2\cdot\text{L}_2$ and $\text{Cu}(\text{C}_4\text{H}_8\text{ONCS}_2)_2\cdot\text{L}_2$. All the complexes are coloured, stable in air and soluble in some common organic solvents. The molar conductivity of 1:1 and 1:2 adducts of $\text{Ni}(\text{morphdte})_2$ and $\text{Cu}(\text{morphdte})_2$ measured in 10^{-3} M chloroform solution are found to be in the range of $10\text{--}28\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ and $9\text{--}42\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ respectively (Table 1). The molar conductance measurements of the adducts $\text{VO}(\text{morphdte})_2$ were carried out in dimethylformamide and the values of their millimolar solutions were found to be 48 and $56\text{ ohm}^{-1}\text{ mole}^{-1}\text{ cm}^2$ (Table 1). These values observed for all these adducts are lower than the values which can be expected for uni-univalent electrolytes in these solvents suggesting that these complexes are undissociated and non-electrolytic in nature.

Magnetic Measurements

Magnetic susceptibility measurements carried out at room temperature indicate that the 1:1 adducts of bis(morpholinedithiocarbamato)Ni(II) are diamagnetic in nature exhibiting magnetic moments around zero which is in agreement with the magnetic moment values observed for many low spin square pyramidal complexes of Ni(II) while 1:2 adducts of bis(morpholinedithiocarbamato)Ni(II) are paramagnetic exhibiting magnetic moment values of 3.09 and 3.16 B.M. which is in agreement with the magnetic moment values observed for octahedral complexes of Ni(II). The 1:1 and 1:2 adducts of bis(morpholinedithiocarbamato)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 magnetic moments of the adducts of bis(morpholinedithiocarbamato)VO(IV) complex are found to be 1.82 and 1.86 B.M. The values are in accordance with the octahedral geometry and monomeric nature of oxovanadium(IV) complexes¹⁹. The higher value of magnetic moment may be due to the orbital contribution²⁰. The magnetic moments of all the adducts are given in table 1.

Table 1. Analytical and Physical data of the Adducts.

S.No.	Complex	Molar Conductivity (Ohm-1cm2 mol-1)	Magnetic Moments (B.M.) (300 K)	Analysis Found (Calculated)				
				C	H	N	S	M
1	VO(morphdtc) ₂ .morpholine]. H ₂ O	56	1.82	33.15 (33.86)	4.92 (5.44)	8.11 (8.46)	25.01 (25.8)	9.89 (10.28)
2	[VO(morphdtc) ₂ .piperidine]. H ₂ O	48	1.86	36.12 (36.42)	5.25 (5.87)	8.15 (8.49)	25.32 (25.9)	9.92 (10.32)
3	Ni(morphdtc) ₂ .morpholine	15	Diamagnetic	35.11 (35.76)	5.02 (5.32)	8.23 (8.94)	26.94 (27.25)	12.04 (12.48)
4	Ni(morphdtc) ₂ .piperidine	15	Diamagnetic	37.96 (38.48)	5.21 (5.77)	8.32 (8.97)	27.01 (27.36)	12.16 (12.53)
5	Ni(morphdtc) ₂ .(morpholine) ₂	10	3.16	38.27 (38.79)	6.43 (6.79)	10.99 (11.18)	25.11 (25.56)	10.21 (10.52)
6	Ni(morphdtc) ₂ .(piperidine) ₂	28	3.09	42.92 (43.41)	6.49 (6.87)	9.87 (10.13)	22.72 (23.15)	9.98 (10.59)
7	Cu(morphdtc) ₂ .morpholine	11	1.83	34.63 (35.39)	4.86 (5.27)	8.39 (8.85)	29.56 (29.97)	13.02 (13.39)
8	Cu(morphdtc) ₂ .piperidine	42	1.85	37.67 (38.08)	5.21 (5.71)	8.43 (8.89)	26.78 (27.08)	12.95 (13.44)
9	Cu(morphdtc) ₂ .(morpholine) ₂	9	1.93	38.01 (38.45)	5.89 (6.05)	9.97 (9.97)	22.74 (22.78)	11.28 (11.31)
10	Cu(morphdtc) ₂ .(piperidine) ₂	23	1.89	42.86 (43.02)	6.55 (6.81)	9.92 (10.04)	22.63 (22.95)	11.08 (11.39)

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

S.No.	Complex	$\nu(\text{N-H})$	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{M-S})$
1.	$[\text{VO}(\text{morphdte})_2.\text{morpholine}]. \text{H}_2\text{O}$	3292	1462	1114	414
2.	$[\text{VO}(\text{morphdte})_2.\text{piperidine}]. \text{H}_2\text{O}$	3261	1458	1112	412
3.	$\text{Ni}(\text{morphdte})_2.\text{morpholine}$	3274	1491	1011	419
4.	$\text{Ni}(\text{morphdte})_2.\text{piperidine}$	3256	1497	1011	420
5.	$\text{Ni}(\text{morphdte})_2.(\text{morpholine})_2$	3250	1497	1013	420
6.	$\text{Ni}(\text{morphdte})_2.(\text{piperidine})_2$	3245	1495	1025	418
7.	$\text{Cu}(\text{morphdte})_2.\text{morpholine}$	3253	1441	1010	417
8.	$\text{Cu}(\text{morphdte})_2.\text{piperidine}$	3242	1485	1009	420
9.	$\text{Cu}(\text{morphdte})_2.(\text{morpholine})_2$	3250	1485	1009	419
10.	$\text{Cu}(\text{morphdte})_2.(\text{piperidine})_2$	3221	1438	1022	424

Infrared Spectra

The IR spectra of the adducts of $\text{VO}(\text{morphdte})_2$, $\text{Ni}(\text{morphdte})_2$ and $\text{Cu}(\text{morphdte})_2$ exhibit bands characteristic of the presence of coordinated dithiocarbamate group and the ligand molecules. A single band of strong intensity was observed in the range $1025\text{--}1009 \text{ cm}^{-1}$ which may be attributed to $\nu(\text{C-S})$ vibration. A positive shift of $10\text{--}35 \text{ cm}^{-1}$ in comparison to the corresponding band in the free ligand indicates that the dithiocarbamate ligand coordinates with the metal through sulphur atoms. The presence of an only C-S band can be due to the greatest contribution of the resonance form (RN^+CS_2^-) in the adducts and the complex thus suggesting symmetrical bidentate binding of the dithiocarbamate moiety²¹⁻²³. A new band of medium to strong intensity was observed in the region $424\text{--}412 \text{ cm}^{-1}$, which may be assigned to $\nu(\text{M-S})$ stretching mode. A strong band in the region $1497\text{--}1438 \text{ cm}^{-1}$ associated with “thiuride” vibration is attributed to $\nu(\text{C-N})$ vibration and indicates the partial double bond character of the C-N bond²⁴. The NH vibrations of the coordinating secondary amines were observed in the region $3292\text{--}3221 \text{ cm}^{-1}$ showing a negative shift of $160\text{--}150 \text{ cm}^{-1}$ upon coordination with the metal. Apart from this, the infrared spectra of the adducts of $\text{VO}(\text{morphdte})_2$ also exhibit a strong band at $996\text{--}970 \text{ cm}^{-1}$ which is attributed to the terminal V=O bond. A comparison of the infrared spectral data of $\text{VO}(\text{morphdte})_2$ complex with its adducts reveals that V=O band in the parent complex ($1000\text{--}980 \text{ cm}^{-1}$) gets displaced to lower frequencies ($990\text{--}970 \text{ cm}^{-1}$) in the adducts¹⁹. This displacement can be attributed to the electronic donation of the base to the vanadium (N-V), which increases the electron density on the metal d-orbitals, and consequently the $p_\pi\text{--}d_\pi$ donation from oxygen atom to vanadium is expected to be reduced.

Electronic Spectra

The electronic spectra of the 1:1 and 1:2 adducts of $\text{Ni}(\text{morphdte})_2$ and $\text{Cu}(\text{morphdte})_2$ were recorded in chloroform while the electronic spectra of the 1:1 adducts of $\text{VO}(\text{morphdte})_2$ were recorded in dimethylformamide in the range $12500\text{--}40000 \text{ cm}^{-1}$. The adducts of bis(morpholinedithiocarbamato)oxovanadium(IV) show three bands in the range $13870\text{--}14310 \text{ cm}^{-1}$, $16092\text{--}17065 \text{ cm}^{-1}$ and $22080\text{--}22420 \text{ cm}^{-1}$ which are assigned to $e \leftarrow b_2 (\nu_1)$, b_1

$\leftarrow b_2 (v_2)$ and $a_1 \leftarrow b_2 (v_3)$ transitions respectively. These bands are characteristic of oxovanadium(IV) complexes in octahedral environment^{19,20}.

Table 3. Electronic spectra of the adducts.

S.No.	Complex	v_1	v_2	v_3
1.	[VO(morphdte) ₂ .morpholine]. H ₂ O	13870	16092	22080
2.	[VO(morphdte) ₂ .piperidine]. H ₂ O	14310	17065	22420
3.	Ni(morphdte) ₂ .morpholine	16826	24865	-
4.	Ni(morphdte) ₂ .piperidine	16798	24993	-
5.	Ni(morphdte) ₂ .(morpholine) ₂	11245	17844	26990
6.	Ni(morphdte) ₂ .(piperidine) ₂	11321	17242	26998
7.	Cu(morphdte) ₂ .morpholine	16542	-	-
8.	Cu(morphdte) ₂ .piperidine	16748	-	-
9.	Cu(morphdte) ₂ .(morpholine) ₂	15312	-	-
10.	Cu(morphdte) ₂ .(piperidine) ₂	15425	-	-

The 1:1 adducts of Ni(morphdte)₂ show a broad, slightly asymmetric absorption band centred around 24000 cm⁻¹. This transition of very high intensity can be assigned to ¹A₁→¹E transition (v_2). The shoulder around 17000 cm⁻¹ can be assigned to spin allowed orbitally forbidden transition (v_1) i.e., ¹A₁→¹B₁ ($d_{xz}^2 \rightarrow d_{x^2-y^2}^2$)²⁵. The appearance of strong, asymmetric absorption band of very high intensity suggests that square pyramidal geometry can be preferred over trigonal bipyramidal geometry for these adducts. In addition absorption bands observed in the region 33000-41000 cm⁻¹ can be assigned to M→L charge transfer transitions. 1:2 Adducts of Ni(morphdte)₂ show three broad bands in the region 11000, 17000, 27000 cm⁻¹. The band seen around 11,000 cm⁻¹ is assigned to ³A_{2g}(F)→³T_{2g}(F) (v_1) transition while the bands observed around 17000 cm⁻¹ and 28000 cm⁻¹ are assigned to ³A_{2g}→³T_{1g}(F) (v_2) and ³A_{2g}(F)→³T_{1g}(P) (v_3) transitions respectively and are suggestive of octahedral geometry around Ni(II) metal ion²⁶.

1:1 Adducts of Cu(morphdte)₂ show a broad band with maximum intensity appearing around 16000 cm⁻¹ which can be assigned to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}^2$ (v_1), suggesting a square pyramidal geometry around Cu(II) ion. A weak shoulder around 11000 cm⁻¹ is also shown by these adducts²⁷. On the other hand 1:2 adducts of Cu(morphdte)₂ show one broad absorption band in the region 14000-16000 cm⁻¹. The observed band is the average of two transitions $d_{xy} \rightarrow d_{x^2-y^2}^2$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}^2$. The band $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}^2$ is generally regarded as “copper band”²⁸. These transitions correspond to $t_{2g} \rightarrow e_g$ transition in a regular octahedral complex.

Thermal Studies

The TG curves of the complexes (Table 4) were recorded in the temperature range 30–1000°C. The DTA curve of 1:1 adduct of VO(morphdte)₂ with morpholine (Graph 1) shows

a loss of a water molecule at about 149°C which corresponds to a weight loss of 3.62%. In the TG curve a weight loss of 17.36 % at about 151°C is observed which may be due to the loss of one morpholine molecule. Then a continuous weight loss is observed due to the loss of two morphdte ligands and the resultant weight corresponds to the formation of a stable oxide VO_2 at 988°C.

Graph 1

Graph 2

The TG curve of the 1:1 and 1:2 adducts of $\text{Ni}(\text{morphdte})_2$ with piperidine were investigated. The 1:1 adduct shows a weight loss of 18.57% at about 350°C due to the loss of one piperidine molecule. Then a continuous weight loss of 62.63% is observed due to the loss of $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_3$ moiety until a stable sulphide NiS is formed at 996°C (Graph 2). On the other hand 1:2 complex shows the loss of two piperidine molecules at about 350°C corresponding

to the weight loss of 30.43%. Then a continuous weight loss of 52.42% is observed due to the loss of $C_{10}H_{16}N_2O_2S_3$ moiety and the resultant weight corresponds to the formation of stable sulphide NiS at around 966°C (Graph 3)

Table 4. Thermal degradation of the adducts.

S.No.	Complex	Dec. Temp. (°C)	% Weight loss obs. (calc.)	Residue compd.	Weght found (calc.)
1.	$[VO(morphdte)_2.morpholine].H_2O$	988	84.98 (83.27)	VO_2	15.02 (16.72)
2.	$Ni(morphdte)_2.piperidine$	966	81.20 (80.68)	NiS	18.80 (19.32)
3.	$Ni(morphdte)_2.(piperidine)_2$	965	82.85 (83.66)	NiS	17.15 (16.34)
4.	$Cu(morphdte)_2.morpholine$	990	79.96 (79.87)	CuS	20.04 (20.13)
5.	$Cu(morphdte)_2.(morpholine)_2$	989	84.73 (83.04)	CuS	15.27 (16.96)

The TG curve for the complex $Cu(morphdte)_2(morpholine)$ (Graph 4) shows a weight loss of 18.89% at 300°C which may be due to the loss of one morpholine molecule. Then a continuous weight loss of 61.07% is observed which may be due to the loss of $C_{10}H_{16}N_2O_2S_3$ moiety till a stable sulphide (CuS) is formed at about 990°C. On the other hand in the TG curve of the 1:2 complex, $Cu(morphdte)_2(morpholine)_2$, (Graph 5) a weight loss of 31.01% may occur at about 329°C due to the loss of two morpholine molecules. Then a continuous

weight loss of 53.72% is observed which may be due to the loss of $C_{10}H_{16}N_2O_2S_3$ and a stable sulphide (CuS) is formed at about 989°C.

Graph 4

Graph 5

Biological Studies

The antifungal activity of the complex was tested by Poisoned Food Technique against the pathogenic fungus, *Fusarium oxysporium*. The test solutions were prepared by dissolving the compounds in chloroform and dimethylformamide. The test solutions were mixed in the PDA and poured in the petriplates in sterilized conditions inside the Laminar flow. After solidification, the plates were inoculated with seven days old culture of pathogen, *Fusarium*

oxysporium by placing 2 mm bit in the centre of the plates. The inoculated plates were incubated at 27 °C for 4 days. The linear growth of fungus in controlled manner was recorded at different concentrations of the complexes. The growth inhibition of *Fusarium oxysporium* over control was calculated (Table 5) and it shows that on increasing the concentration of the complexes, the colony diameter of the fungus decreases and hence percent inhibition increases (Fig. 1). The increase in antifungal activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to combined activity effect of the metal and the ligand.

Fig.1 .Antifungal activity of the adducts (a) $[\text{VO}(\text{morphdte})_2(\text{morpholine})]\cdot\text{H}_2\text{O}$, (b) $\text{Ni}(\text{morphdte})_2(\text{morpholine})$, (c) $\text{Ni}(\text{morphdte})_2(\text{morpholine})_2$, (d) $\text{Cu}(\text{morphdte})_2(\text{morpholine})$, and (e) $\text{Cu}(\text{morphdte})_2(\text{morpholine})_2$.

Such increased activity of the metal complexes can be explained on the basis of Overtone's concept²⁹ and Tweedy's chelation theory³⁰. The lipid membrane that surrounds the cell favours passage of only lipid soluble materials due to liphophilicity being an important factor which controls the antifungal activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor group.

Table 5. Antifungal activities of some adducts.

S.No.	Complex	Concentration (ppm)	Colony Diameter (mm)	% Inhibition $I = [(C-T)/C] \times 100$
1.	[VO(morphdtc) ₂ .morpholine].H ₂ O	50	81.5	9.44
		100	78.5	12.77
		150	68.5	23.88
		200	58	35.55
		250	42	53.33
		500	40	55.55
2.	Ni(morphdtc) ₂ .piperidine	50	58	4.9
		100	51	16.39
		150	40	34.42
		200	33	45.90
		250	26.5	56.55
		500	15	75.40
3.	Ni(morphdtc) ₂ .(piperidine) ₂	50	54	11.47
		100	42	31.14
		150	39	36.06
		200	35	42.62
		250	25	59.01
		500	24	60.65
4.	Cu(morphdtc) ₂ .morpholine	50	89	1.11
		100	73	18.88
		150	58.5	35
		200	54	40
		250	49	45.55
		500	7	92.22
5.	Cu(morphdtc) ₂ .(morpholine) ₂	50	80	11.11
		100	77	14.44
		150	63	30
		200	54	40
		250	43	52.22
		500	18	80

Conclusions

An octahedral geometry has been proposed for the 1:1 adducts of VO(morphdtc)₂ and for the 1:2 adducts of Ni(morphdtc)₂ and Cu(morphdtc)₂ while a square pyramidal geometry has been suggested for the 1:1 adducts of both Ni(morphdtc)₂ and Cu(morphdtc)₂. Moreover the antifungal activity of the adducts show a linear relationship with the concentration.

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