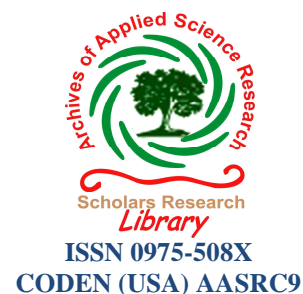




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Synthesis, characterization and antifungal activities of adducts of Bis (S-isopropyltrithiocarbonato)oxovanadium(IV) with nitrogen and oxygen donor ligands

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ABSTRACT

A new series of Adducts of Bis(S-isopropyltrithiocarbonato)oxovanadium(IV) with nitrogen and oxygen donor ligands have been prepared. The resulting adducts have been characterized by elemental analysis, molar conductance, magnetic susceptibility measurement, thermal gravimetric analysis, biological studies, IR, UV-visible spectral studies. Analytical data reveals that VO(IV) complexes forms 1:1 adducts. Antifungal activity of some adducts have been carried out against the fungal strain *Sclerotium rolfsii*. Electronic and magnetic measurements indicate distorted octahedral geometry for the 1:1 adducts of VO(IV) adducts.

Keywords: Bis(S-isopropyltrithiocarbonato)oxovanadium(IV), nitrogen and oxygen donor ligands, *Sclerotium rolfsii*.

INTRODUCTION

Trithiocarbonates belongs to the family of sulphur compounds, the other congener were xanthates, dithiocarbamates, dithiophosphates, etc. Trithiocarbonate complexes closely resembles the xanthates in all aspects in the possession of hetero atom 'S' atom in place of 'O' present in case of xanthate. Transition metal complexes of many mono anionic 1,1- dithiolates have been prepared and studied^[1-8]. The strong metal binding properties of the trithiocarbonates were recognized early by the virtue of the capacity of the molecules to form chelate complexes. Trithiocarbonates can function as unidentate, bidentate, tridentate, chelating as well as bidentate bridging ligands^[9-14]. Reports on trithiocarbonates(thioxanthates) compounds are relatively few compared to their xanthates or dithiocarbamates analogues, and mainly involves the transition metals^[15-17].

MATERIALS AND METHODS

Preparation of Sodium salt of S- isopropyltrithiocarbonates

The sodium salt of S-isopropyltrithiocarbonate was prepared by the dropwise addition of the isopropane thiol (1mol) to a saturated solution of sodium hydroxide at 0°C, followed by the addition of excess carbon disulfide (1.2mol). The yellow precipitate formed immediately was collected by filtration and twice recrystallized from water-acetone mixture. The salt was stored in a vacuum dessicator over phosphorus pentoxide^[18].

Preparation of Bis(S-isopropyltrithiocarbonato)oxovanadium(IV)

The complex was synthesized by mixing aqueous solutions of Vanadyl sulfate(0.01mol) and Sodium salt of S-isopropyltrithiocarbonate(0.02mol) when immediate precipitation occurs and green colored precipitates were formed which were filtered and dried in a vacuum dessicator.

Preparation of 1:1 adduct of Bis(S-isopropyltrithiocarbonato)oxovanadium(IV) with nitrogen and oxygen donor ligands:

1:1 adducts of Bis(S-isopropyltrithiocarbonato)oxovanadium(IV) with nitrogen and oxygen donor ligands were prepared by stirring Bis(S-isopropyltrithiocarbonato) oxovanadium(IV)(0.01mol) with the ligand(2-ethylpyridine, 3-ethylpyridine, 4-ethylpyridine, 2-chloropyridine, 3-chloropyridine, dimethylsulphoxide and hexamethylphosphoramide)(0.01 mol) in chloroform for 5-6 hours. Dark green coloured precipitates of the adducts were obtained. The precipitates were filtered and dried in a vacuum desiccator over anhydrous calcium chloride.

Results and discussion :

The adducts were analyzed by various analytical and physico – chemical techniques and the results shows that Bis(S-isopropyltrithiocarbonato)oxovanadium(IV) forms 1:1 adducts with nitrogen and oxygen donor ligands. The analytical data (**Table 1**) reveals that 1:1 adduct have general formula $VO[S_2CS(C_3H_7)]_2L$ (where L= 2-ethylpyridine, 3-ethylpyridine, 4-ethylpyridine, 2-chloropyridine, 3-chloropyridine, dimethylsulphoxide and hexamethylphosphoramide) . All the adducts 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 adducts of $VO[S_2CS(C_3H_7)]_2L$ measured in 10^{-3} M DMF solution are found to be in the range of 4.57-6.99 $ohm^{-1}cm^2mol^{-1}$ (**table2**). These values suggest non-electrolytic nature of these adducts^[19-22].

Magnetic susceptibility measurement:

The 1:1 adducts of Bis(S-isopropyltrithiocarbonato)oxovanadium(IV) with nitrogen and oxygen donor ligands exhibit magnetic moment values in the range of 1.78-1.84 B.M (**Table2**). These values are slightly higher than the spin only value and are in accordance with octahedral geometry for the 1:1 adducts and monomeric nature of oxovanadium(IV) adducts^[23-24].

Table (1): Analytical data of 1:1 adducts of Bis(S-isopropyltrithiocarbonato) oxovanadium(IV)with nitrogen and oxygen donor ligands

S. No	Name of the adduct	%Yield	%age (Found)				%age (Calculated)			
			C	H	N	S	C	H	N	S
1	Bis(S-isopropyltrithiocarbonato)(2-ethylpyridine)oxovanadium(IV)	74	36.98	3.94	2.18	39.93	37.82	4.83	2.94	40.34
2	Bis(S-isopropyltrithiocarbonato)(3-ethylpyridine)oxovanadium(IV)	84.4	36.89	3.99	2.23	39.87	37.82	4.83	2.94	40.34
3	Bis(S-isopropyltrithiocarbonato)(4-ethylpyridine)oxovanadium(IV)	82.5	36.97	3.87	2.27	39.82	37.82	4.83	2.94	40.34
4	Bis(S-isopropyltrithiocarbonato)(2-chloropyridine)oxovanadium(IV)	76.2	31.63	2.93	2.16	39.16	32.34	3.73	2.90	39.80
5	Bis(S-isopropyltrithiocarbonato)(3-chloropyridine)oxovanadium(IV)	86	31.73	3.13	2.26	39.29	32.34	3.73	2.90	39.80
6	Bis(S-isopropyltrithiocarbonato)(dimethylsulphoxide)oxovanadium(IV)	71.2	26.17	4.03	-	49.76	26.85	4.47	-	50.12
7	Bis(S-isopropyltrithiocarbonato)(hexamethylphosphoramide)oxovanadium(IV)	69.5	30.16	5.34	7.17	34.42	30.66	5.84	7.67	35.04

Table 2: Molar conductance and magnetic susceptibility measurement data of 1:1 adducts of Bis(S-isopropyltrithiocarbonato) oxovanadium(IV) with nitrogen and oxygen donor ligands

S.No	Name of the adduct	Molar conductance ($Ohm^{-1}mol^{-1}cm^2$)	Magnetic data	
			μ_{eff} (B.M)	Temperature(K)
1	Bis(S-isopropyltrithiocarbonato)(2-ethylpyridine)oxovanadium(IV)	6.89	1.79	298
2	Bis(S-isopropyltrithiocarbonato)(3-ethylpyridine)oxovanadium(IV)	6.99	1.84	298
3	Bis(S-isopropyltrithiocarbonato)(4-ethylpyridine)oxovanadium(IV)	6.56	1.80	298
4	Bis(S-isopropyltrithiocarbonato)(2-chloropyridine)oxovanadium(IV)	6.09	1.78	298
5	Bis(S-isopropyltrithiocarbonato)(3-chloropyridine)oxovanadium(IV)	4.67	1.83	298
6	Bis(S-isopropyltrithiocarbonato)(dimethylsulphoxide)oxovanadium(IV)	4.57	1.84	298
7	Bis(S-isopropyltrithiocarbonato)(hexamethylphosphoramide)oxovanadium(IV)	4.87	1.80	298

Infrared spectra:

The most relevant bands in the IR spectra of the adducts of $\text{VO}[\text{S}_2\text{CS}(\text{C}_3\text{H}_7)]_2 \cdot \text{L}$ (where L = 2-ethylpyridine, 3-ethylpyridine, 4-ethylpyridine, 2-chloropyridine, 3-chloropyridine, dimethylsulphoxide and hexamethylphosphoramide) are shown in (Table 3). The IR spectra of the free ligand and the complexes were obtained in the range of $4000\text{-}300\text{cm}^{-1}$. All the bands present in the IR spectra of the free ligand were also observed in the spectra of the complexes. In the present work IR spectra of the adducts of Bis(S-isopropyltrithiocarbonato)oxovanadium(IV) show characteristic bands corresponding to $\nu(\text{C-S-C})_{\text{asym}}$ and $\nu(\text{C-S-C})_{\text{sym}}$ vibrations in the range of $687\text{-}701\text{ cm}^{-1}$ and $653\text{-}676\text{ cm}^{-1}$. An intense band corresponding to $\nu(\text{C-S})$ vibration is also observed in the range of $1035\text{-}1045\text{ cm}^{-1}$ for all the adducts synthesized which suggests that thioxanthate is binding as symmetrical bidentate chelating ligand^[25-26]. On formation of adducts, there is a shift in the stretching frequencies, because of donation of electrons by the Lewis bases which weakens the metal sulfur bond that leads to corresponding weakening of C-S bond. A band of medium to strong intensity observed in the region $406\text{-}416\text{ cm}^{-1}$ may be assigned due to (V-S) stretching mode^[27].

Table 3: Vibrational spectral data of 1:1 adducts of bis(S-isopropyltrithiocarbonato)oxovanadium(IV) with nitrogen and oxygen donor ligands

S.No	Name of the Adduct	$\nu(\text{C-S})$	$\nu(\text{C-S-C})_{\text{asym}}$	$\nu(\text{C-S-C})_{\text{sym}}$	$\nu(\text{V=O})$	$\nu(\text{V-S})$
1	Bis(S-isopropyltrithiocarbonato)(2-ethylpyridine)oxovanadium(IV)	1035	687	653	970	406
2	Bis(S-isopropyltrithiocarbonato)(3-ethylpyridine)oxovanadium(IV)	1036	691	661	980	410
3	Bis(S-isopropyltrithiocarbonato)(4-ethylpyridine)oxovanadium(IV)	1035	690	659	980	416
4	Bis(S-isopropyltrithiocarbonato)(2-chloropyridine)oxovanadium(IV)	1038	701	672	972	408
5	Bis(S-isopropyltrithiocarbonato)(3-chloropyridine)oxovanadium(IV)	1039	700	670	970	410
6	Bis(S-isopropyltrithiocarbonato)(dimethylsulphoxide)oxovanadium(IV)	1045	699	676	969	412
7	Bis(S-isopropyltrithiocarbonato)(hexamethylphosphoramide)oxovanadium(IV)	1040	696	675	967	410

Electronic Spectra:

The electronic spectral data of adducts are given in (table 4). The electronic spectral data of 1:1 adducts of bis(S-isopropyltrithiocarbonato)oxovanadium(IV) show three bands in the range $12259\text{-}14434\text{cm}^{-1}$, $15775\text{-}17830\text{cm}^{-1}$, and $23865\text{-}26420\text{cm}^{-1}$ and are assigned to $b_2 \rightarrow e$, $b_2 \rightarrow b_1$ and $b_2 \rightarrow a_1$ transitions respectively (Table 4). These bands are characteristic of oxovanadium(IV) complexes in an octahedral environment. Beside d-d transitions, bands of very high intensity due to charge transfer transitions are also observed in the region above 30000cm^{-1} ^[28-29].

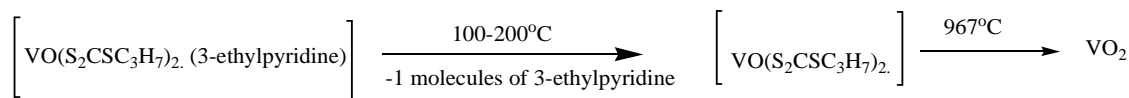
Table 4: Electronic spectral data of 1:1 adducts of bis(S-isopropyltrithiocarbonato)oxovanadium(IV) with nitrogen and oxygen donor ligands

S. No	Name of the adduct	$\nu^1(\text{cm}^{-1})$	$\nu^2(\text{cm}^{-1})$	$\nu^3(\text{cm}^{-1})$	C-T Transitions (cm^{-1})
1	Bis(S-isopropyltrithiocarbonato)(2-ethylpyridine)oxovanadium(IV)	12259	17830	23869	42000
2	Bis(S-isopropyltrithiocarbonato)(3-ethylpyridine)oxovanadium(IV)	12656	17337	23865	39700
3	Bis(S-isopropyltrithiocarbonato)(4-ethylpyridine)oxovanadium(IV)	14277	16963	24799	26295
4	Bis(S-isopropyltrithiocarbonato)(2-chloropyridine)oxovanadium(IV)	13988	17223	26420	25486
5	Bis(S-isopropyltrithiocarbonato)(3-chloropyridine)oxovanadium(IV)	14392	17727	26415	43100
6	Bis(S-isopropyltrithiocarbonato)(dimethylsulphoxide)oxovanadium(IV)	13462	16741	25027	37230
7	Bis(S-isopropyltrithiocarbonato)(hexamethylphosphoramide)oxovanadium(IV)	14434	15775	24884	40360

Thermal gravimetric analysis:

The adducts were subjected to TG analysis from 25°C to 1000°C in nitrogen atmosphere and the results of the novel investigated adducts is as given below. The TG curve of this addition complex show an initial weight loss of 19.6% at 160°C which may be due to the loss of one ethylpyridine molecule (calculated weight loss = 20.59%). Then a continuous weight loss is observed which may be due to the loss of two thioxanthate moiety.

The resultant weight of 18.0% (calculated = 18.90%) corresponds to the formation of a stable oxide^[30] VO₂, at 967°C



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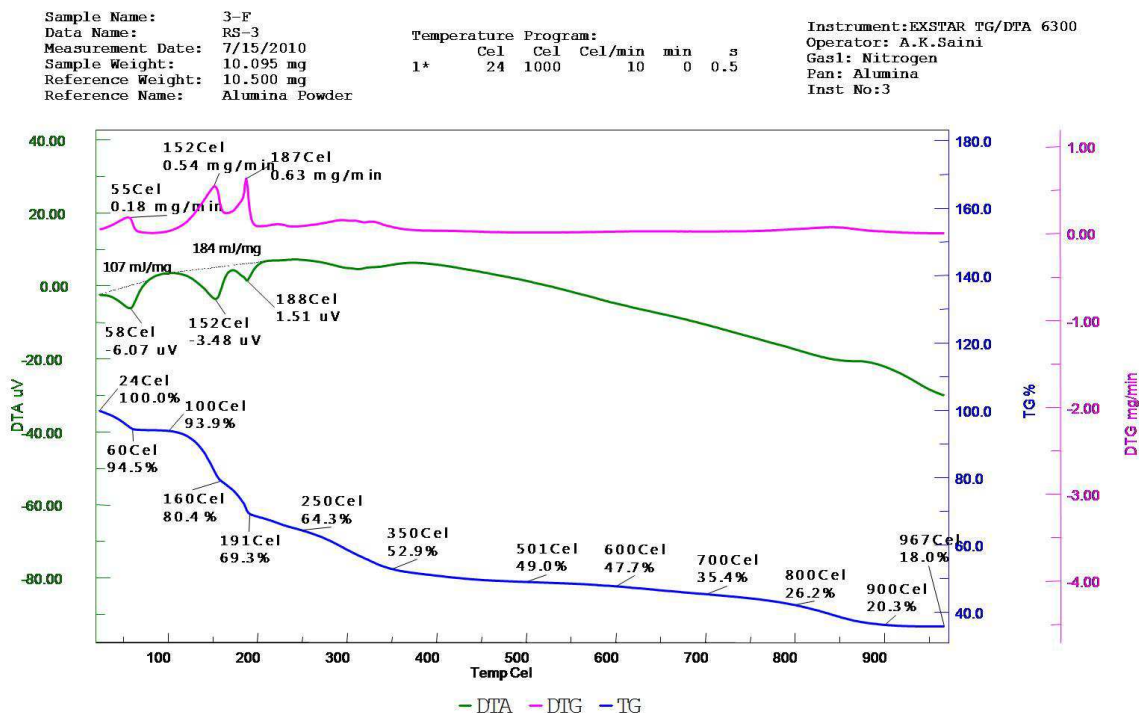


Fig. No. 1 TGA-DTA curve of bis(S-isopropyltrithiocarbonato)(3-ethylpyridine)oxovanadium(IV)

Table 5. Antifungal activities of some adducts mean colony diameter in the control=90 mm

S.No	Name of the Adduct	Colony diameter in control	Concentration in (ppm)	Colony diameter in (mm)	% INHIBITION I = [(C-T)/C]×100
1	Bis(S-isopropyltrithiocarbonato)(3-ethylpyridine)oxovanadium(IV)	90	50	90	0
			100	83	7.77
			150	82	8.88
			200	78.5	12.77
			250	74	17.77
2	Bis(S-isopropyltrithiocarbonato)(2-chloropyridine)oxovanadium(IV)	90	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

Biological studies:

The antifungal activity of the complex was tested by Poisoned Food Technique against the pathogenic fungus, *Sclerotium rolfsii*. The linear growth of fungus in controlled manner was recorded at different concentrations of the complexes. The growth inhibition of fungus 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.2)^[31]. The growth inhibition of *Sclerotium rolfsii* over control was calculated as:

% inhibition (I) = C-T/C×100

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

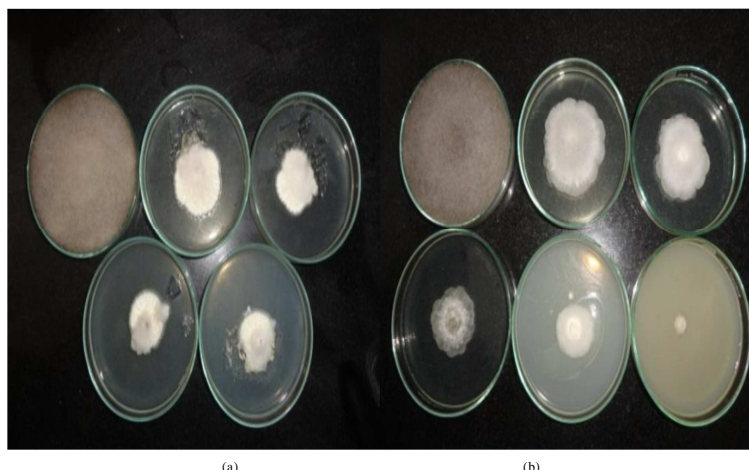


Figure 2: Antifungal activity of the adducts of (a) Bis(S-isopropyltrithiocarbonato)(3-ethylpyridine)oxovanadium(IV) and (b) Bis(S-isopropyltrithiocarbonato)(2-chloropyridine)oxovanadium(IV)

CONCLUSION

On the basis of above studies it is found that 1:1 adducts of Bis(S-isopropyltrithiocarbonato)oxovanadium(IV) with nitrogen and oxygen donor ligands have distorted octahedral geometry.

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