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

Pooja Sharma, Deepshikha Khajuria and Renu Sachar

Department of Chemistry, University of Jammu, Babasaheb Ambedkar Road, Jammu, India

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. Transisition metal complexes of many mono anionic 1,1- dithiolates have been prepared and studied\textsuperscript{[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\textsuperscript{[9-14]}. Reports on trithiocarbonates(thioxanthates) compounds are relatively few compared to their xanthates or dithiocarbamates analogues, and mainly involves the transition metals\textsuperscript{[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\degree 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\textsuperscript{[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) (0.01 mol) with the ligands (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 show 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[S₂CS(CH₃)₃]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[S₂CS(CH₃)₃]₂L measured in 10⁻³ M DMF solution are found to be in the range of 4.57-6.99 ohm⁻¹ cm² mol⁻¹ (Table 2). 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 (Table 2). These values are slightly higher than the spin only values 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

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

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

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of the adduct</th>
<th>Molar conductance (Ohm⁻¹ mol⁻¹ cm²)</th>
<th>Magnetic data</th>
<th>Temperature(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bis(S-isopropyltrithiocarbonato) (2-ethylpyridine) oxovanadium(IV)</td>
<td>6.89</td>
<td>1.79</td>
<td>298</td>
</tr>
<tr>
<td>2</td>
<td>Bis(S-isopropyltrithiocarbonato) (3-ethylpyridine) oxovanadium(IV)</td>
<td>6.99</td>
<td>1.84</td>
<td>298</td>
</tr>
<tr>
<td>3</td>
<td>Bis(S-isopropyltrithiocarbonato) (4-ethylpyridine) oxovanadium(IV)</td>
<td>6.56</td>
<td>1.80</td>
<td>298</td>
</tr>
<tr>
<td>4</td>
<td>Bis(S-isopropyltrithiocarbonato) (2-chloropyridine) oxovanadium(IV)</td>
<td>6.09</td>
<td>1.78</td>
<td>298</td>
</tr>
<tr>
<td>5</td>
<td>Bis(S-isopropyltrithiocarbonato) (3-chloropyridine) oxovanadium(IV)</td>
<td>4.67</td>
<td>1.83</td>
<td>298</td>
</tr>
<tr>
<td>6</td>
<td>Bis(S-isopropyltrithiocarbonato) (dimethylsulphoxide) oxovanadium(IV)</td>
<td>4.57</td>
<td>1.84</td>
<td>298</td>
</tr>
<tr>
<td>7</td>
<td>Bis(S-isopropyltrithiocarbonato) (hexamethylphosphoramide) oxovanadium(IV)</td>
<td>4.87</td>
<td>1.80</td>
<td>298</td>
</tr>
</tbody>
</table>
Infrared spectra:
The most relevant bands in the IR spectra of the adducts of VO\[S_2CS(C_3H_7)₂L\] (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 4000-3000 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 \(\nu(C-S-C)\) asym and \(\nu(C-S-C)\) sym vibrations in the range of 687-701 cm\(^{-1}\) and 653-676 cm\(^{-1}\). An intense band corresponding to \(\nu(C-S)\) vibration is also observed in the range of 1035-1045 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- 416 cm\(^{-1}\) may be assigned due to (V-S) stretching mode\(^{[27]}\).

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 12259-14434 cm\(^{-1}\), 15775-17830 cm\(^{-1}\), and 23865-26420 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 30000 cm\(^{-1}\)\(^{[28-29]}\).

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

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

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

<table>
<thead>
<tr>
<th>S. No</th>
<th>Name of the adduct</th>
<th>(\nu_1) (cm(^{-1}))</th>
<th>(\nu_2) (cm(^{-1}))</th>
<th>(\nu_3) (cm(^{-1}))</th>
<th>C-T Transitions (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bis(S-isopropyltrithiocarbonato) (2-ethylpyridine)oxovanadium(IV)</td>
<td>12259</td>
<td>17830</td>
<td>23869</td>
<td>42000</td>
</tr>
<tr>
<td>2</td>
<td>Bis(S-isopropyltrithiocarbonato) (3-ethylpyridine)oxovanadium(IV)</td>
<td>12656</td>
<td>17337</td>
<td>23865</td>
<td>39700</td>
</tr>
<tr>
<td>3</td>
<td>Bis(S-isopropyltrithiocarbonato) (4-ethylpyridine)oxovanadium(IV)</td>
<td>14277</td>
<td>16963</td>
<td>24799</td>
<td>26295</td>
</tr>
<tr>
<td>4</td>
<td>Bis(S-isopropyltrithiocarbonato) (2-chloropyridine)oxovanadium(IV)</td>
<td>13988</td>
<td>17223</td>
<td>26420</td>
<td>25486</td>
</tr>
<tr>
<td>5</td>
<td>Bis(S-isopropyltrithiocarbonato) (3-chloropyridine)oxovanadium(IV)</td>
<td>14392</td>
<td>17727</td>
<td>26415</td>
<td>43100</td>
</tr>
<tr>
<td>6</td>
<td>Bis(S-isopropyltrithiocarbonato) (dimethylsulphoxide)oxovanadium(IV)</td>
<td>13462</td>
<td>16741</td>
<td>25027</td>
<td>37230</td>
</tr>
<tr>
<td>7</td>
<td>Bis(S-isopropyltrithiocarbonato) (hexamethylphosphoramide)oxovanadium(IV)</td>
<td>14434</td>
<td>15775</td>
<td>24884</td>
<td>40360</td>
</tr>
</tbody>
</table>

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.

Scholars Research Library
The resultant weight of 18.0% (calculated = 18.90%) corresponds to the formation of a stable oxide $^{[30]} VO_2$, at 967°C.

\[
\text{VO(S}_2\text{CSC}_3\text{H}_7)_2 \quad \text{(3-ethylpyridine)} \quad \xrightarrow{100-200^\circ C} \quad \text{-1 molecules of 3-ethylpyridine} \quad \xrightarrow{967^\circ C} \quad \text{VO}_2
\]

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

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

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of the Adduct</th>
<th>Colony diameter in control</th>
<th>Concentration in (ppm)</th>
<th>Colony diameter in (mm)</th>
<th>% INHIBITION I = [(C-T)/C]×100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bis(S-isopropylthiocarbonato)(3-ethylpyridine)oxovanadium(IV)</td>
<td>90</td>
<td>50</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>83</td>
<td>7.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>150</td>
<td>82</td>
<td>8.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>200</td>
<td>78.5</td>
<td>12.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>250</td>
<td>74</td>
<td>17.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>41</td>
<td>54.44</td>
</tr>
<tr>
<td>2</td>
<td>Bis(S-isopropylthiocarbonato)(2-chloropyridine)oxovanadium(IV)</td>
<td>90</td>
<td>50</td>
<td>81.5</td>
<td>9.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>78.5</td>
<td>12.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>150</td>
<td>68.5</td>
<td>23.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>200</td>
<td>58</td>
<td>35.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>250</td>
<td>42</td>
<td>53.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>40</td>
<td>55.55</td>
</tr>
</tbody>
</table>

**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:

\[
\% \text{ inhibition (I)} = \frac{C-T}{C} \times 100
\]
Where I = percent inhibition, C = mean growth of fungus (in mm) in control and T = mean growth of fungus (in mm) in treatment.

**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.

**REFERENCES**