Some 1:1 adducts of bis(O-ethyldithiocarbonato)Oxovanadium (IV) with substituted heterocyclic amines: Synthesis, characterization and biological activity.

Sanjay Kapoor and Abhishek Dutta

Abstract: A series of 1:1 adducts of Bis(O-ethyldithiocarbonato)Oxovanadium(IV) with substituted heterocyclic amines such as 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 3-cyanopyridine and 4-cyanopyridine have been synthesized. These were characterized on the basis of some physico-chemical parameters like elemental analyses, molar conductance measurement, magnetic moment, IR Spectra and electronic spectral studies. The molar conductance values of these Oxovanadium(IV) complexes in dimethylformamide indicate neutral and non-ionic nature. The magnetic and spectral studies support octahedral coordination of VO(IV) complexes. Some of these complexes were screened for their biological activity against the pathogenic fungi *Sclerotium rolfsii* indicating antifungal activity.

Key words: Adducts; biological activity; bis(O-ethyldithiocarbonato)Oxovanadium(IV); synthesis.

1. Introduction

Xanthates also known as O-alkyldithiocarbonates have been known for a long time [1, 2] and many adducts of metal xanthates with different ligands have been prepared and studied in the last several decades [3,4]. Xanthates have the ability to bind to various metals [5,6]. They are versatile chelating agents for the separation and extraction of metals in analytical chemistry [7, 8]. Xanthates are used in curing and vulcanisation of rubber, as collectors of sulphide ores in froth-floatation process and in the manufacture of synthetic textiles. These are extensively used as fungicides, pesticides in agriculture, as corrosion inhibitors and quite recently in therapy for HIV infections [9-11].

Sanjay Kapoor (✉)
Department of Chemistry,
Govt. Degree College, Paloura,
Jammu, J&K, India.
Email: sanjay151278@yahoo.com

Abhishek Dutta
Department of Botany,
University of Jammu, Jammu
E-mail: abhishekdutta492@gmail.com

To the best of our knowledge, the reaction products of oxovanadium(iv)xanthate with substituted heterocyclic amines (Lewis bases) have been much less extensively studied than other similar compounds. So here we report or present the synthesis, characterization and biological activity of some 1:1 adducts of bis(O-ethyldithiocarbonato)oxovanadium (IV) with substituent heterocyclic amines such as 2-,3- and 4- aminopyridines and 3- and 4- cyanopyridines.

2. Experimental

2.1 Preparation of potassium salt of O-ethyldithiocarbonate

The potassium salt of O-ethyldithiocarbonate was prepared by the standard published method [12]. 42 g (0.75 mol) of KOH pellets were placed in a 500 ml flask and 120g (152 ml, 2.6 mol) of ethanol was added. The resulting solution was heated under reflux for 1 hour and then allowed to cool. From the reaction mixture, liquid portion was carefully decanted off. The residual solid was transferred into a dry 500 ml flask to which 57 g, (45 ml, 0.75 mol) of CS_2 was added slowly with constant shaking. The resulting solid yellow mass was filtered after cooling in ice and it was washed with three 25 ml portions of ether. The potassium O-ethyldithiocarbonate obtained was finally dried.

2.2 Preparation of bis(O-ethyldithiocarbonato) oxovanadium (IV)

The saturated aqueous solutions of hydrated vanadyl sulphate (2.53g, 0.01mol) and potassium salt of O-ethyldithiocarbonate (3.20g, 0.02mol) were prepared separately and then mixed with constant stirring. Dark green precipitates were formed which were filtered immediately and dried in vaccum dessicator over anhydrous calcium chloride. The composition of the complex was established to be $[VO(S_2COC_2H_5)_2]$ by the elemental analysis .(vanadium: found 16.08%,calculated 16.50%)

2.3 Preparation of 1:1 adducts of bis(O-ethyldithiocarbonato)oxovanadium(IV) with substituted heterocyclic amines (substituted pyridines).

2-, 3- and 4- aminopyridine (0.244 g,0.0026 mol) , 3- and 4- cyanopyridine (0.270 g, 0.0026 mol) was added to bis (O-ethyldithiocarbonato)oxovanadium(IV) (0.803 g, 0.0026 mol) dissolved in 60 ml of acetone by stirring. The solution was stirred and then allowed to be kept undisturbed overnight. Green coloured adducts obtained were filtered and dried in a vaccum dessicator over anhydrous calcium chloride. The composition of the adducts was established to be $[VO(S_2COC_2H_5)_2(C_5H_6N_2)]$ & $[VO(S_2COC_2H_5)_2(C_6H_4N_2)]$ by the elemental analysis.

3. Methods

Carbon , hydrogen, nitrogen and sulphur contents of the adducts were determined on elemental analyzer (CHNS-932, LECO Corporation, USA).Molar conductance was determined on the millimolar solution in DMF using Digital Conductivity meter "Century CC 601".Infrared spectra of the complexes over the region 4000-400cm^{-1} were recorded using KBr pellets on Infrared Spectrophotometer (Perkin Elemer FT-IR) . The electronic spectra of adducts were recorded in DMF on systronics 119 UV-visible spectrophotometer. Magnetic moments were determined at room temperature by VSM (Vibrating Sample Magnetometer) method. Antifungal activity of adducts has been studied by poisoned food technique against pathogenic fungi *"Sclerotium rolfsii"*. The analytical data, molar conductance and magnetic moments of adducts isolated are presented in table 1 and 2. Important IR bands and electronic spectral data are cited in Table 3 and 4. Antifungal activities of the addition complexes are shown in Table 5 and Fig. 1(a&b).

4. Results and discussion

The adducts of bis(o-ethyldithiocarbonato) oxovanadium(IV) with heterocyclic nitrogen donors such as 2- ,3- and 4- aminopyridines and 3- and 4-cyanopyridines are microcrystalline solids. These are light green to dark green in colour. Most of the adducts are insoluble in common organic solvents. However, these are soluble in DMF and DMSO. On the basis of elemental analysis (Table 1 and 2), the adducts isolated having 1:1 stoichiometry are assigned the formula $VO(S_2COC_2H_5)_2$ L (where L=2-, 3- and 4-aminopyridines and 3- and 4-cyanopyridines).

Table 1. Analytical data of the 1:1 adducts of bis(o-ethyldithiocarbonato)oxovanadium(IV) with amino and cyanopyridines

Name of the adduct	Formula	% Found				% Calculated			
		C	H	N	S	C	H	N	S
Bis(O-ethyldithiocarbonato) (2-aminopyridine) oxovanadium)(IV)	$[VO(S_2COC_2H_5)_2(C_5H_6N_2)]$	32.2	3.4	6.1	31.2	32.7	4.0	6.9	31.8
Bis(O-ethyldithiocarbonato) (3-aminopyridine) oxovanadium(IV)	$[VO(S_2CO\ C_2H_5)_2\ (C_5H_6N_2)]$	32.2	3.5	6.1	31.2	32.7	4.0	6.9	31.8
Bis(O-ethyldithiocarbonato) (4-aminopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)(C_5H_6N_2)]$	32.2	3.6	6.2	31.3	32.7	4.0	6.9	31.8
Bis(O-ethyldithiocarbonato) (3-cyanopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)(C_6H_4N_2)]$	34.3	3.0	6.0	30.5	34.9	3.4	6.8	31.0
Bis(O-ethyldithiocarbonato) (4-cyanopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_6H_4N_2)]$	34.3	3.0	6.2	30.5	34.9	3.4	6.8	31.0

The molar conductivity values calculated (in the range of 3.49-4.93 $ohm^{-1}mol^{-1}cm^2$) from the conductivities measured on millimolar solutions of the adducts in DMF, support the neutral and non-ionic nature of the complexes [13,14]. The 1:1 adducts of bis(o-ethyldithiocarbonato) oxovanadium(IV) with amino and cyanopyridines exhibit magnetic moment in the range of 1.76-2.08 B.M which is in agreement with magnetic moment values observed for octahedral oxovanadium(IV) complexes [15,16].

Table 2. Molar conductance and magnetic data of the 1:1 adducts of Bis(o-ethyldithiocarbonato)oxovanadium)(IV) with amino and cyanopyridines

Name of the adduct	Molar conductance ($Ohm^{-1}mol^{-1}cm^2$)	Magnetic Data	
		μ_{eff}(B.M.)	Temperature (K)
Bis(O-ethyldithiocarbonato)(2-aminopyridine) oxovanadium(IV)	3.52	1.79	298
Bis(O-ethyldithiocarbonato)(3-aminopyridine) oxovanadium(IV)	3.49	1.82	298
Bis(O-ethyldithiocarbonato)(4-aminopyridine) oxovanadium(IV)	4.55	1.74	298
Bis(O-ethyldithiocarbonato)(3-cyanopyridine) oxovanadium(IV)	4.82	1.99	298
Bis(O-ethyldithiocarbonato)(4-cyanopyridine) oxovanadium(IV)	4.93	1.84	298

A comparison of the IR spectra of the present complexes with the corresponding free ligands reveals that most of the absorption bands of the free ligands are shifted in their respective complexes (Tables 3 and 4). Amino and cyanopyridines have two possible coordinating cites. It has been established that N-H and C-N frequencies must show negative shift if the coordination occurs through amino group or cyano group Nitrogen atom [17, 18]. But in the present complexes, they show no appreciable negative shift. Thus the possibility of coordination of 2-, 3- and 4-aminopyridines, 3- and 4-cyanopyridines through their amino and cyano Nitrogen atom with metal is ruled out. This has been further confirmed by examining the C-H out of plane deformation vibration. In amino and cyanopyridine complexes the C-H out of plane bands occur at lower energy position on complexation, indicating negative shifts, which confirm that these ligands interact with the metal ion through their ring nitrogen atom. The electronic spectra of 1:1 adducts has been recorded in DMF .It shows three bands ν_1,ν_2 & ν_3 around 14000, 17000 and 25000 cm^{-1} respectively. Appearance of these three bands shows that adducts are having octahedral geometry around oxovanadium(IV)ion [17].

Table 3. Important infrared spectral bands of the 1:1 adducts of bis(o-ethyldithiocarbonato) oxovanadium(iv) with amino and cyanopyridines

Name of the adduct	Formula	ν(C-S)	ν(C-O)	ν(V=O)	ν(V-S)
Bis(O-ethyldithiocarbonato)(2-aminopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_5H_6N_2)]$	1034	1160	972	415
Bis(O-ethyldithiocarbonato)(3-aminopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_5H_6N_2)]$	1044	1142	962	417
Bis(O-ethyldithiocarbonato)(4-aminopyridine)oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_5H_6N_2)]$	1039	1171	965	420
Bis(O-ethyldithiocarbonato)(3-cyanopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_6H_4N_2)]$	1042	1163	980	414
Bis(O-ethyldithiocarbonato)(4-cyanopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_6H_4N_2)]$	1040	1150	978	415

Table 4. Electronic spectral data of the 1:1 adducts of bis(o-ethylthiocarbonato)oxovanadium(IV) with amino and cyanopyridines

Name of the Adduct	Formula	$\nu_1(cm^{-1})$	$\nu_2(cm^{-1})$	$\nu_3(cm^{-1})$
Bis(O-ethyldithiocarbonato)(2-aminopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_5H_6N_2)]$	12876	16855	24062
Bis(O-ethyldithiocarbonato)(3-aminopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_5H_6N_2)]$	12771	16920	25126
Bis(O-ethyldithiocarbonato)(4-aminopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_5H_6N_2)]$	12658	16637	24329
Bis(O-ethyldithiocarbonato)(3-cyanopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_6H_4N_2)]$	13974	17149	24425
Bis(O-ethyldithiocarbonato)(4-cyanopyridine) oxovanadium(IV)	$[VO(S_2COC_2H_5)_2(C_6H_4N_2)]$	14225	17042	24444

Antifungal activity

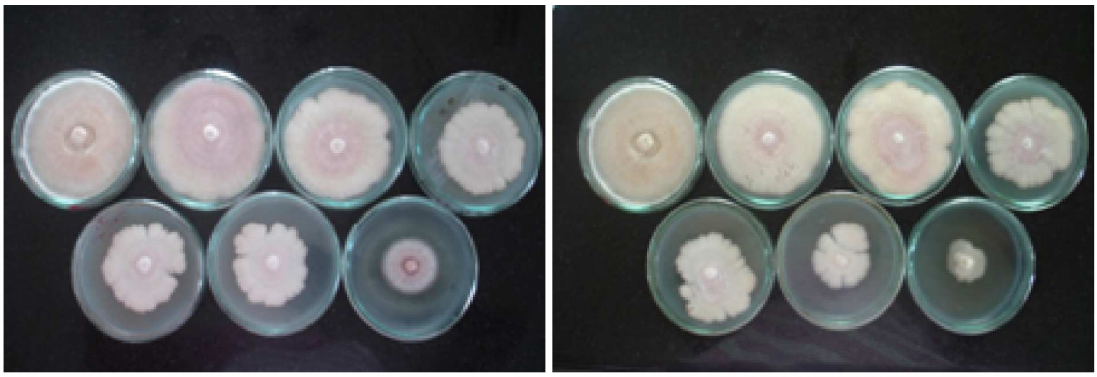
The in-vitro biological screening effects of some of the investigated compounds were tested against the pathogen *"Sclerotium rolfsii"* by the poisoned food method using Potato Dextrose Agar (PDA) nutrient as the medium. The linear growth of the fungus in control and treatment were recorded at different concentrations of the complexes[18].Table 5 and Fig. 1(a&b) shows that on increasing the concentrations of the complexes , the colony diameter of the fungus decreases and hence percent inhibition increases. On doubling the concentration of the complexes the percent inhibition also doubles, which shows linear relationship between concentration and percent inhibition. The increase in antimicrobial 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 [19, 20].

Table 5. Antifungal activity of some 1:1 adducts of Bis(o-ethyldithiocarbonato)oxovanadium(IV) and Bis(o-propyldithiocarbonato)oxovanadium(IV) with amino and cyanopyridines against *Sclerotium rolfsii.* Colony diameter in control = 90 mm

Addition Complex	Colony diameter in control (mm)	Concentration (ppm)	Colony diameter (mm)	% Inhibition I=[(C-T)/C] x 100
Bis(O-ethyldithiocarbonato)-(2-aminopyridine)Oxovanadium(IV)	90	50	80.5	10.55
		100	77.5	13.88
		150	67.5	25.00
		200	57.0	36.66
		250	49.0	45.55
		500	40.0	55.55
Bis(O-ethyldithiocarbonato)-(3-cyanopyridine)Oxovanadium(IV)	90	50	76.5	15.00
		100	68.0	24.44
		150	57.0	36.66
		200	50.0	44.44
		250	42.0	53.33
		500	32.0	64.44

Conclusion

The xanthate synthesised was microcrystalline solid having light or dark green colour. The adducts possess octahedral geometry around oxovanadium (IV) ion. The *in vitro* biological screening effects of the investigated compounds against *Sclerotium rolfsii* showed that on increasing the concentration of the complexes, the colony diameter of the fungus decreases and hence percentage inhibition increases. This showed that the compound used against the pathogen possess good antifungal activity and therefore can be used to control various fungal contaminations (i.e. Southern blight, Stem rot, White mold) caused by *Sclerotium rolfsii.*



(a) [VO(S2COC2H5)2(C5H6N2)] **(b) [VO(S2COC2H5)2(C6H4N2)]**

Fig. 1(a&b): Antifungal activities of some adducts of Bis(o-ethyldithiocarbonato)oxovanadium(IV) against *Sclerotium rolfsii*.

References

1. Coucovanis D (1970) In: Lippard SJ(ed) Progress in inorganic chemistry, Vol 11. Interscience, New York, pp. 233.
2. Eisenberg R (1970) In: Lippard SJ(ed) Progress in inorganic chemistry,Vol 12. Interscience, New York, pp. 295.
3. Cras JA Willemsc J (1987) In: Wilkinson G,Gillard RD,Mc Cleverty JA (eds) Comprehensive coordination chemistry, Vol 2. Pergamon Press, Oxford, pp. 579.
4. Haiduc I (2004) In: Mc Cleverty JA, Mayer TJ, Lever ABP(eds) Comprehensive coordination chemistry II, Vol 1. Elsevier Pergamon, Amsterdam, pp. 349.
5. Formanek J, Holeckova H, Charewicz W, Walkowiak W, Gendolla T (1985) Przem Chem 64:98.
6. Kotlyar DG, Tolley WK (1995) Min Eng 11:1033.
7. Gimeno MC, Jambrina E, Laguna A, Laguna M, Murray HH, Terroba R (1996) Ineog Chim Acta 249:69.
8. Allen FH, Kennard O (1993) Chem Des Autom News 8:31.
9. Victorriano LI, Cortes HB (1996) J Coord Chem 39:231.
10. Rao SR (1971) Xanthates and related compounds, chap. I. Marcel Decker, New York.
11. Ara I, Bahij FE (2003) Trans Met Chem. 28:908.
12. Furniss BS, Hannaford AJ, Smith PWG, Tatchell AR (1989) Vogel's text book of Practical organic chemistry, 5th edition Pearson Education, London.
13. Martin RL, Whitley A (1958) J Chem SOC 1394.
14. Lever ABP (1965) J Inorg Nucl Chem. 27:149.
15. Baslo F, Matousch WR (1953) J Am Chem. SOC 75:5663.
16. Coucouvanis D, Fackler JP (1967) Inorg Chem 6:2047.
17. Lever ABP (1984) Inorganic electronic Spectroscopy. Elsevier, Amsterdam.
18. Mishra L, Singh V.K (1993) Indian J. Chem (A), 32:446.
19. Nene Y.L, Thapliyal P.N. (1993) Fungicides in Plant Disease Control, 3rd edition. Science Publishers, U.S.
20. Dharamraj N, Vishwanathamurthi P, Natarajn K (2001) Trans. Met. Chem, 26:105.