

Synthesis and characterization of the adducts of bis (N,N-diethyldithiocarbamato) oxovanadium(IV) with substituted pyridines

MOUSAMI SHARMA and RENU SACHAR*

Department of Chemistry, University of Jammu,
Babasaheb Ambedkar Road, Jammu-180 006 (India).

(Received: December 15, 2008; Accepted: January 19, 2009)

ABSTRACT

A series of adducts of bis(N,N-diethyldithiocarbamato)oxovanadium(IV) with substituted pyridines have been synthesized by treating bis(N,N-diethyldithiocarbamato) oxovanadium(IV) with substituted pyridines in acetone in equimolar ratios. Analytical results show that the adducts have 1:1 stoichiometry with general formula $VO(dedtc)_2L$ (dedtc = diethyldithiocarbamate, L = 2-, 3-methylpyridines, 2,4-, 2,6-, 3,4-, 3,5-dimethylpyridines and 2,4,6-trimethylpyridine). The addition complexes have been characterized by elemental analysis, conductivity measurements, magnetic susceptibility measurements, infrared and electronic spectral studies. These studies suggest a distorted octahedral structure and paramagnetic nature of the adducts.

Key words: Adducts, oxovanadium derivatives and substituted pyridines.

INTRODUCTION

The chemistry of transition metal-sulfur compounds has attracted much interest for their importance in the field of metalloenzymes, material precursors, and catalysts¹. N,N-disubstituted dithiocarbamates are among the more frequently considered sulfur containing ligands that have been studied from past many years. Dithiocarbamates, the half amides of dithiocarbonic acids, were discovered as a class of chemical compounds in the history of organosulfur chemistry^{2,3}. The structures of the metal dithiocarbamates are being investigated because of (i) the fact that most of their detailed structures are unknown, (ii) the theoretical interests arising from the sulfur containing four membered rings present in these compounds, (iii) their biological (antifungal) activity and (iv) the lack of correlation between structural properties and the known chemical and physical properties of these compounds².

The uses of dithiocarbamates are many from insecticides and fungicides to therapeutic agents for alcoholism and metal intoxication². They have also been reported to treat acquired immune depressive syndrome and cancer⁴⁻⁶. In view of the diverse applications of the dithiocarbamates and various biological aspects of pyridine it is found worthwhile to study complexes containing both sulfur and pyridine^{7,8}. Although the reports on metal complexes containing dithiocarbamates are extensive, the studies on transition metal complexes containing both dithiocarbamate moiety and substituted pyridine ligands are scarce^{9,10}. Moreover, very few dithiocarbamate complexes of vanadium have been reported. In the present communication we have reported the synthesis and characterization of 1:1 adducts of bis(N,N-diethyldithiocarbamato) oxovanadium(IV) with substituted pyridines.

EXPERIMENTAL

Preparation of Sodium Salt of Diethyldithiocarbamate

The dithiocarbamate salts of the general formula $(H_2NR_2^+)(R_2NCSS^-)$ can be prepared by the reaction of carbon disulfide with aliphatic and aromatic primary or secondary amines. The corresponding alkali metal salts are obtained using an alkali metal hydroxide as the proton acceptor. The sodium salt of diethyldithiocarbamate was prepared by the standard published method¹¹. 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)oxovanadium(IV)

The complex bis(N,N-diethyldithiocarbamato)oxovanadium(IV) was prepared by mixing and constant stirring of the aqueous solutions of vanadyl sulfate (1.63 g, 0.01 mole) and sodium diethyldithiocarbamate (5.68 g, 0.02 mole). Greenish-yellow precipitates were formed which were filtered immediately and were dried in a vacuum desiccator over anhydrous calcium chloride. The composition of the complex was established to be $VO[S_2CN(C_2H_5)_2]_2$ by the elemental analysis. (Vanadium: found 13.63%, calculated 14.05%).

Preparation of the adducts of bis(N,N-diethyldithiocarbamato)oxovanadium(IV) with substituted pyridines

Addition complexes of bis(N,N-diethyldithiocarbamato)oxovanadium(IV) with substituted pyridines were prepared by refluxing bis(N,N-diethyldithiocarbamato)oxovanadium(IV) (3.63 g, 0.01 mole) with the ligand (2-, 3-methyl pyridines, 2,4-, 2,6-, 3,4-, 3,5-dimethylpyridines and 2,4,6-trimethylpyridine) in acetone for one hour. Green coloured precipitates of the adducts with low yield were obtained. The solution was concentrated by distillation to obtain the maximum yield. The precipitates were filtered and dried in a vacuum

desiccator over anhydrous calcium chloride.

METHODS

Molar conductance of the adducts was determined on their millimolar solutions in Dimethylformamide by using Digital conductivity meter "Century CC 601". Magnetic measurements were carried out at room temperature by Gouy's method. The infrared spectra of the complexes over the region $4000-400\text{ cm}^{-1}$ have been recorded using KBr pellets on Perkin Elmer FT-IR Spectrophotometer. The electronic spectra of the adducts were recorded in dimethylformamide in the range 12500 cm^{-1} to 40000 cm^{-1} on Systronics 119 UV-Visible spectrophotometer. The analytical data, molar conductance and magnetic moments of the adducts isolated are presented in Table 1. Important IR bands and Electronic spectral data are cited in Table 2.

RESULTS AND DISCUSSION

The dithiocarbamate complex, bis(N,N-diethyldithiocarbamato)oxovanadium(IV) and its addition complexes with the heterocyclic nitrogen donor ligands such as 2-, 3-methylpyridines, 2,4-, 2,6-, 3,4-, 3,5-dimethylpyridines and 2,4,6-trimethylpyridine are microcrystalline solids. The addition complexes are dark green in colour and are insoluble in common organic solvents such as benzene, acetone, toluene, 1,4-dioxane, nitrobenzene, ethanol etc. However, these adducts are soluble in dimethylformamide and dimethylsulfoxide. On the basis of elemental analysis (Table 1) the adducts isolated having 1:1 stoichiometry are assigned the formula $VO[S_2CN(C_2H_5)_2]_2 \cdot L$ (where L = 2-, 3-methylpyridines, 2,4-, 2,6-, 3,4-, 3,5-dimethylpyridines and 2,4,6-trimethylpyridine). The molar conductance values are found in the range of $1.95-7.75\text{ ohm}^{-1}\text{mole}^{-1}\text{cm}^2$ (Table 1). These values are lower than the values which can be expected for uni-univalent electrolytes in the solvent used suggesting that these complexes are neutral and non-ionic in character. VO^{2+} oxyanion, being d^1 ion, possesses a spin only magnetic moment value of 1.73 B.M.¹² corresponding to one unpaired electron. Under the influence of the spin-orbit coupling constant of 250 cm^{-1} , the V^{4+} ion in an octahedral

Table 1: Analytical, molar conductance and magnetic susceptibility data of the adducts of bis(diethyldithiocarbamato)oxovanadium(IV) with substituted pyridines

S. Adducts No.	Formula	% Found				% Calculated				Molar conductance (ohm ⁻¹ cm ²)	μ_{eff} (B.M.)
		C	H	N	S	C	H	N	S		
1	VO(dedtc) ₂ (2- methylpyridine)	41.10	4.63	8.54	27.22	42.11	5.92	9.21	28.07	3.75	1.84
2	VO(dedtc) ₂ (3- methylpyridine)	41.66	5.03	8.72	27.65	42.11	5.92	9.21	28.07	2.5	1.81
3	VO(dedtc) ₂ (2,4-di methylpyridine)	42.84	5.62	8.11	26.54	43.4	6.17	8.94	27.23	2.85	1.92
4	VO(dedtc) ₂ (2,6-di methylpyridine)	42.71	5.59	7.95	26.88	43.4	6.17	8.94	27.23	7.75	1.98
5	VO(dedtc) ₂ (3,4-di methylpyridine)	42.39	5.54	7.89	26.45	43.4	6.17	8.94	27.23	4.75	1.88
6	VO(dedtc) ₂ (3,5-dimethylpyridine)	42.69	5.45	7.96	26.72	43.4	6.17	8.94	27.23	6.95	1.89
7	VO(dedtc) ₂ (2,4,6-trimethylpyridine)	43.82	5.89	7.98	25.63	44.63	6.41	8.68	26.45	1.95	1.99

complex gives rise to a magnetic moment of about 1.7 B.M. at 300 K. For a tetrahedral complex magnetic moment of $1.73(1-2\lambda/10D_q)$ is expected, i.e. slightly below 1.73 B.M.¹³. The adducts of bis(N,N-diethyldithiocarbamato)oxovanadium(IV) with substituted pyridines exhibit magnetic moments in the range 1.81-1.99 B.M. which are in accordance with the distorted octahedral geometry and monomeric nature of oxovanadium(IV) complexes (Table 1)¹⁴. The higher value of magnetic moment may be due to the orbital contribution¹⁵.

The infrared spectra (Table 2) of the adducts of bis(N,N-diethyldithiocarbamato)oxovanadium(IV) exhibit a strong band at 975-960 cm⁻¹ which is attributed to the terminal V=O bond. A comparison of the infrared spectral data of VO(dedtc)₂ with its adducts reveals that V=O band in the parent complex (1000-980 cm⁻¹) gets displaced to lower frequencies (990-970 cm⁻¹) in the adducts¹⁴. 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_p-d_p donation from oxygen atom to vanadium is expected to be reduced. A single sharp band of high intensity has been observed in all the complexes in 1111-1129 cm⁻¹ range. The presence of an only C-S band can be due to the greatest contribution of the resonance form (RN⁺CS₂⁻) in the adducts and the complex thus suggesting symmetrical bidentate binding of the dithiocarbamato moiety¹⁶. A new band of medium to strong intensity, observed in the region 431-416 cm⁻¹, may be assigned to V-S stretching mode. One stretching frequency at 1520-1453 cm⁻¹ is observed in the IR spectra of all the complexes and can be assigned to the stretching vibration of the C-N bond. It is associated with the "thioureide" vibration and indicates a partial double bond character in the C-N bond¹⁷.

Electronic spectra of all the adducts have been recorded in the range 12500 cm⁻¹ to 40000 cm⁻¹. These adducts show three bands in the range 12250-14380 cm⁻¹, 15823-19010 cm⁻¹ and 23420-29200 cm⁻¹ and are assigned to e ← b₂, b₁ ← b₂ and a₁ ← b₂ transitions respectively (Table II). These bands are characteristic of oxovanadium(IV) complexes in an octahedral environment^{14, 15}.

Table 2: Infrared and electronic spectral data of the adducts of is (diethyldithiocarbamate) oxovanadium(IV) with substituted pyridines

S. No.	Adducts	IR Spectral Data				Electronic Spectral Data		
		ν (C–N)	ν (CSS)	V=O	V–S	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)
1.	VO(dedtc) ₂ (2-methylpyridine)	1493	1117	961	428	12250	15823	23420
2.	VO(dedtc) ₂ (3-methylpyridine)	1457	1129	960	418	12658	16015	24308
3.	VO(dedtc) ₂ (2,4-dimethylpyridine)	1499	1111	961	422	13345	17065	24511
4.	VO(dedtc) ₂ (2,6-dimethylpyridine)	1520	1111	969	425	13835	18182	24829
5.	VO(dedtc) ₂ (3,4-dimethylpyridine)	1453	1124	975	431	14310	18262	25024
6.	VO(dedtc) ₂ (3,5-dimethylpyridine)	1499	1113	960	416	14380	18349	25323
7.	VO(dedtc) ₂ (2,4,6-trimethylpyridine)	1491	1120	966	424	13654	19010	29200

REFERENCES

- Kalia S. B., Kaushal G., Sharma D. K. and Verma B. C., *Synth. and React. Inorg., Met.-Org. and Nano-Met. Chemistry*, **35**: 181 (2005).
- Thorn G. D. and Ludwig R. A., *The Dithiocarbamates and Related Compounds*, New York, (1962).
- Schweitzer P. A., Leslie P. E. and Rudnick R., *Lubricant Additive Chemistry and Applications*, 241, (2003).
- Reisinger E. C., Kern P., Ernst M., Bock P., Flad H. D. and Dietrich M., *Inhibition of HIV progression by Dithiocarb. German DTC study Group*, *Lancet*, **335**: 679, (1990).
- Gandara D. R., Perez E. A., Weibe V. and De Gregorio M. W., *Semin. Oncol.*, **18**: 49, (1991).
- Kim C. H., Kim J. H., Xu J., Hsu C. Y. and Ahn Y. S., *Blackwell Synergy: J. Neurochem.*, **72**: 1586, (1999).
- Chaurasia M. R., Sharma A. K. and Sharma S. K., *J. Indian Chem. Soc.*, **LVIII**: 687, (1981).
- Gokhale N. H., Padhye S. B., Billington D. C., Rathbone D. L., Croft S. L., Kendrick H. D., Anson C. E. and A. K. Powell, *Inorg. Chim. Acta*, **349**: 23, (2003).
- Ivanov A. V., Mitrofanova V. I., Kritikos M. and Antzutkin O. N., *Polyhedron*, **18**: 2069, (1999).
- Yusuff K. K. M., Basheer K. M. and Gopalan M., *Polyhedron*, **2**: 839, (1983).
- Coucouvanis D., *Prog. Inorg. Chem.*, **11** (1970).
- Rodgers G. E., *Introduction to Coordination, Solid State and Descriptive Inorganic Chemistry*, McGraw-Hill: New York, 76, (1996).
- Figgis B. N. and Lewis J., *Prog. Inorg. Chem.*, **6**: 37 (1964).
- Doadrio A. L., Sotelo J. and Ruano A. F., *Quim. Nova*, **25** (2002).
- Aswar A. S., Bansod A. D., Aswale S. R. and Mamdlik P. R., *Ind. J. Chem.*, **43(A)**: 1892 (2004).
- Brinkhoff H. C. and Grotens A. M., *Recueil Trav. Chim. Pays-Bas*, **90**, 252, (1971).
- Bradley D. C. and Gitlitz M. H., *J. Chem. Soc.(A)*, 1152 (1969).