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The chemistry and mechanism of thermal degradation reactions of oxovanadium(IV) complexes of dithiocarbamates containing a thiadiazole ring

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Abstract

The dithiocarbamato complexes of oxovanadium(IV), abbreviated as $VO(L)_2(H_2O)$ where LK are potassium salts of dithiocarbamic acids derived from different substituted aminothiadiazoles, were prepared and characterized by elemental analyses, electrical conductance and magnetic susceptibility measurements, and spectral (electronic and IR) studies. The thermal behaviour of these compounds in non-isothermal conditions was investigated using TG, DTG and DSC techniques. The intermediates obtained at the end of various thermal decomposition steps were identified from elemental analyses and infrared spectral studies. The graphical method of Coats and Redfern was employed to evaluate the kinetic parameters such as the apparent activation energy and order of reaction. The heats of reaction for the different decomposition steps were calculated from the DSC curves.

INTRODUCTION

A number of metal dithiocarbamates have been synthesized and characterized [1–4]. The dithiocarbamate ligand is known to stabilize the higher coordination states of metals due to the low change and relatively small bites (2.8–2.9 Å). However, a literature survey reveals that although considerable research has been carried out investigating the thermal behaviour of metal dithiocarbamates [5, 6], no paper has been published on thermal studies of metal oxycation dithiocarbamate complexes, except one for the titanyl, zirconyl and hafnyl complexes [7]. In the present communication, we report the synthesis, characterization and thermal studies of oxovanadium(IV) complexes with a new series of dithiocarbamate ligands in which one heterocyclic ring (thiadiazole) is attached to the nitrogen. The most important result of this investigation is that these ligands form six-membered chelate rings through N-coordination of the thiadiazole ring and one

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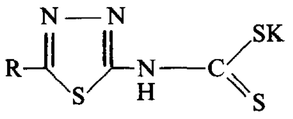
TABLE 1

Analytical data of the oxovanadium(IV) complexes

Compound [a]	Colour	Found (calcd.)/%				
		C	H	N	S	V
$VO(L_1)(H_2O)$	Brown	38.7 (38.9)	2.8 (2.9)	13.4 (13.6)	31.1 (31.1)	8.2 (8.2)
$VO(L_2)(H_2O)$	Brown	31.6 (31.8)	1.6 (1.8)	16.4 (16.5)	28.2 (28.3)	7.5 (7.5)
$VO(L_3)(H_2O)$	Brown	32.7 (32.8)	1.8 (1.8)	12.6 (12.8)	29.0 (29.2)	7.6 (7.7)
$VO(L_4)(H_2O)$	Brown	36.7 (36.9)	2.7 (2.8)	12.9 (12.9)	29.6 (29.6)	7.8 (7.8)

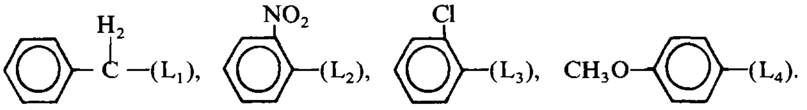
[a] L_1 is $C_{10}H_8N_3S_3$; L_2 is $C_9H_5N_4O_2S_3$; L_3 is $C_9H_5N_3S_3Cl$; L_4 is $C_{10}H_8ON_3S_3$.

sulphur atom coordination of the dithiocarbamato group. The structures of the ligands are given in Formula 1,



where

R is



Formula 1.

EXPERIMENTAL

All reagents used for the preparation of these compounds were either BDH AnalaR or E. Merck Pro analysi grade. The ligands were synthesized by general methods described in the literature [8].

PREPARATION OF THE COMPOUNDS

The following general method was used. A hot methanolic solution (≈20 ml) of the respective ligand (0.1 mol) and a hot water–methanolic solution (≈25 ml) of vanadyl sulphate (0.05 mol) were mixed together and boiled under reflux for approx. 10–12 h. The solution was then concentrated to half its original volume and, on cooling, a brown precipitate separated out, which was filtered, washed with methanol and distilled water, and dried over phosphorus pentoxide under vacuum at room temperature.

The details on the analyses and physical measurements are as reported earlier [9]. The metal content was determined as its oxide using a standard method [10].

RESULTS AND DISCUSSION

The method used for the preparation and isolation of these compounds yields materials of high purity as can be judged by the satisfactory elemental analyses (Table 1) and infrared spectral studies. The elemental analyses correspond to the formula $[VO(L)_2(H_2O)]$. The complexes are soluble in dimethylformamide and dimethylsulphoxide, and partially soluble in methanol, carbon tetrachloride and benzene. Electrical conductance measurements in dimethylformamide indicate the non-electrolytic nature of the complexes.

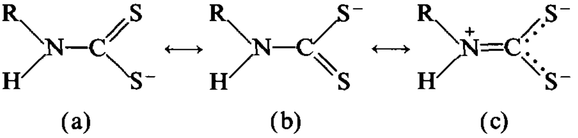
Magnetic moments and electronic spectral studies

The spin-orbit coupling (λ) for the oxovanadium(IV) complexes is positive [11] and magnetically dilute oxovanadium(IV) complexes should exhibit magnetic moments very close to the spin-only magnetic moments of 1.73 BM, as expected for an $S = 1/2$ system. All the dithiocarbamato complexes exhibit magnetic moments in the 1.68-1.74 BM range, corresponding to one unpaired spin.

The interpretation of the electronic spectra of the oxovanadium(IV) complexes is the subject of a continuing investigation and discussion. Three spin-allowed transitions, $b_2 \rightarrow e_\pi^*(^2B_2 \rightarrow E)$, $b_2 \rightarrow b_1(^2B_2 \rightarrow {}^2B_1)$ and $b_2 \rightarrow a_1$ $(^2B_2 \rightarrow {}^2A_1)$ are expected for distorted octahedral oxovanadium(IV) complexes according to the energy level schemes suggested by Ballhausen and Gray [12], Selbin [13] and Lever [14]. The present complexes exhibit all three d-d transitions in the 12200-14500, 15500-17200 and 22800-24800 cm^{-1} regions, assigned [15] to the $b_2 \rightarrow e_\pi^*(^2B_2 \rightarrow E)$, $b_2 \rightarrow b_1(^2B_2 \rightarrow {}^2B_1)$ and $b_2 \rightarrow a_1$ $(^2B_2 \rightarrow {}^2A_1)$ transitions, respectively, according to the above scheme.

Infrared spectral studies

The major interest in the preparation of these complexes is to study the effect of the attachment of dithiocarbamate ligand to vanadium in the presence of the bulky thiadiazole ring. Due to steric factors, this might have some effect on the structure of the complexes. The structure of the dithiocomplexes can be represented as shown in Formula 2.



Formula 2.

The extent to which these resonance forms contribute to the structure and its effect on the physical and chemical properties has been extensively studied [16]. The monodentate and/or bidentate nature of the dithiocarbamato group in the ligand is reflected in the (C–S) stretching frequency. In the case of bidentate behaviour, a single strong band appears in the 1000–970 $\mathrm{cm^{-1}}$ region, while a doublet is expected in the region of 1000 ± 70 $\mathrm{cm^{-1}}$ for monodentate behaviour. The complexes reported in this paper show two bands in the region of 1020–980 $\mathrm{cm^{-1}}$, indicating the presence of one complexed (C–S) group and one uncomplexed (C=S) group, i.e. monodentate bonding. A strong band in the 1600–1585 $\mathrm{cm^{-1}}$ region in the ligands is characteristic of the ν(C=N) group. However, in the complexes, the ν(C=N) band is split into two bands, one almost at the original position at ≈1600 $\mathrm{cm^{-1}}$, due to uncoordinated ν(C=N), and the other shifted to a lower frequency by ≈25–20 $\mathrm{cm^{-1}}$, arising from the coordinated C=N mode. The splitting of the ν(C=N) absorption band suggests that only one of the nitrogens is involved in coordination, the other being free and uncoordinated. The ν(NH) band appears at approx. 3200–3150 $\mathrm{cm^{-1}}$ in the ligands. The persistence of the band at the same position in the complexes indicate non-coordination of the amino nitrogen. The ν(V–S), ν(V–N) and ν(V=O) vibrations appear at approx. 360–340 $\mathrm{cm^{-1}}$, 400–380 $\mathrm{cm^{-1}}$ and ≈950 $\mathrm{cm^{-1}}$, respectively. In addition, all the complexes show a band at around 3400 $\mathrm{cm^{-1}}$ due to ν(O–H) of the coordinated water molecule.

Thus, the infrared spectra suggest that the nitrogen of the thiadiazole ring and one of the sulphur atoms of the dithiocarbamate group are involved in chelation.

Thermal analysis

The thermal behaviour of these compounds under non-isothermal conditions was investigated by TG, DTG and DSC techniques in N_2 and O_2 atmospheres. The thermal stability and decomposition ranges of the complexes are given in Table 2. There is a qualitative correspondence between the DSC and DTG curves for all these complexes, indicating that every thermal effect is accompanied by a corresponding mass loss. All the complexes display a three-stage weight loss, namely dehydration of the complexes, decomposition of the dehydrated complexes to the oxo metal isothiocyanates, and, finally, decomposition of the oxo metal isothiocyanates, in both oxygen and nitrogen atmospheres. The decomposition steps are not significantly influenced by the surrounding gaseous atmosphere employed, except for the last step. The intermediates obtained at the end of the various thermal decomposition steps were identified from analyses and IR spectral studies.

TABLE 2

Temperature range, weight loss, activation energy and heat of reaction of the different decomposition steps

Decomposition	Temp. range (in °C) in N_2 (in O_2)	DSC peak	% weight loss		Heat of reaction in (kcal mol^{-1})	Activation energy in (kcal mol^{-1})	Order of reaction
			Calc.	Found in N_2 (in O_2)			
Decomposition of $VO(L_1)_2(H_2O)$							
Dehydration	160–175 (160–180)	172 (170)	2.91	2.80 (2.78)	11.2	–	–
Decomposition of dehydrated complex	220–240 (220–235)	235 (230)	70.35	70.20 (70.10)	70.2	30.42	1
Decomposition of isothiocyanate	380–410 (350–370)	390 (360)	70.55	70.0 (69.85)	22.80	–	–
Decomposition of $VO(L_2)_2(H_2O)$							
Dehydration	155–180 (160–180)	165 (172)	2.65	2.85 (2.55)	15.60	–	–
Decomposition of dehydrated complex	225–240 (230–250)	238 (240)	73.05	72.85 (72.00)	80.62	40.25	1
Decomposition of isothiocyanate	400–420 (350–370)	410 (365)	73.24	72.50 (73.00)	25.60	–	–
Decomposition of $VO(L_3)_2(H_2O)$							
Dehydration	150–170 (150–175)	162 (165)	2.73	2.70 (2.85)	10.22	–	–
Decomposition of dehydrated complex	220–240 (220–250)	230 (235)	72.20	73.58 (72.00)	48.94 20.50	27.12	1
Decomposition of isothiocyanate	380–400 (390–405)	390 (395)	72.38	71.50 (72.20)	18.95	–	–
Decomposition of $VO(L_4)_2(H_2O)$							
Dehydration	170–180 (165–180)	178 (170)	2.77	2.50 (2.85)	20.50	–	–
Decomposition of dehydrated complex	230–245 (230–250)	240 (242)	71.81	71.00 (70.80)	94.20	35.20	1
Decomposition of isothiocyanate	390–420 (380–400)	405 (395)	72.00	71.50 (71.68)	20.32	–	–

Dehydration of the complexes

The first weight loss occurs in the temperature range 150–180°C and corresponds to the loss of water molecules. The observed weight losses in this temperature range correspond to one water molecule. The expected endothermic behaviour for the dehydration process associated with these compounds was observed in almost the same temperature range in the DTG and DSC curves.

Decomposition of dehydrated complexes

The second weight loss occurs in the range 220–250°C, with formation of the oxovanadium isothiocyanate. This was confirmed by elemental analysis and IR spectra. The IR spectra correspond with those reported for metal isothiocyanate derivatives. The ν(V=O) band appears at a lower frequency, $\approx 900-890\ \mathrm{cm}^{-1}$. It is reported [15] that the ν(V=O) frequency depends on the nature of the substituent present. In isothiocyanate derivatives, the presence of an electron-withdrawing group causes a lowering of the ν(V=O) band frequency.

Decomposition of oxovanadium(IV) isothiocyanate

The third weight loss occurs in the range 350–425°C in both nitrogen and oxygen atmospheres. However, the final product at the end of the third step differs in these two atmospheres. In oxygen atmosphere, the oxovanadium(IV) isothiocyanate decomposes to give vanadium pentoxide, whereas in nitrogen atmosphere, the final products are of indefinite composition. This may be due to the simultaneous decomposition of the oxovanadium(IV) isothiocyanate to the vanadium oxides and sulphides, or to the formation of non-stoichiometric compounds. The vanadium pentoxide formed in oxygen atmosphere looses O_2 above 415°C and non-stoichiometric compounds are formed. The formation of vanadium pentoxide in oxygen atmosphere was confirmed by elemental analysis.

From the above results, the following steps may be proposed for the decompositions of oxovanadium(IV) complexes

Step I

$$[\mathrm{VO(L)_2(H_2O)}] \xrightarrow{150-180^\circ\mathrm{C}} [\mathrm{VO(L)_2}]$$

Step II

$$[\mathrm{VO(L)_2}] \xrightarrow{220-250^\circ\mathrm{C}} \mathrm{VO(NCS)_2}$$

Step III

In oxygen atmosphere

$$\mathrm{VO(NCS)_2} \xrightarrow{350-380^\circ\mathrm{C}} \mathrm{V_2O_5} \xrightarrow[\text{loses } O_2]{415^\circ\mathrm{C}} \text{Non-stoichiometric compound}$$

In nitrogen atmosphere

$$\mathrm{VO(NCS)_2} \xrightarrow{350-425^\circ\mathrm{C}} \text{Indefinite composition}$$

The calculation of the apparent activation energy and order of reaction was performed in nitrogen atmosphere by employing the graphical method of Coats and Redfern [17]. The plot of $\{-\log[-\log(1-\alpha)/T^2]\}$ versus $1/T \times 10^3$ for $n = 1$ (n is the apparent order of reaction) gives a straight line with slope $-E/2.303R$. The heat of reaction was calculated from the DSC curves using the expression $\Delta H = KA/m$, where ΔH is the heat of reaction, K is the calibration constant, A is the area under the peak and m is the mass of reactive compound. The calibration constant K was calculated using the equation

$$K = \frac{\Delta H m C}{A \Delta T_s}$$

where ΔH is the heat of transition in cal g^{-1}, m the mass in mg, C the chart speed in inch min^{-1}, A the peak area in inch^2 and ΔT_s the temperature sensitivity in °C inch^{-1}. With these units, K is expressed in mcal min^{-1} °C^{-1}. To calibrate the DSC instrument, pure indium metal, the ΔH of which is 6.79 cal g^{-1}, was used. The value of K calculated using the above equation was 148.74 mcal min^{-1} °C^{-1}. The apparent activation energy and heat of reaction in nitrogen atmosphere are given in the Table 2.

CONCLUSIONS

The thermal studies show that the decompositions of the oxovanadium(IV) complexes proceed through three major steps: dehydration, decomposition of the dehydrated complex to the intermediate oxovanadium(IV) isothiocyanate, and decomposition of the isothiocyanate either to vanadium pentoxide (in O_2 atmosphere) or to compounds of indefinite composition (in N_2 atmosphere). The second-stage decomposition in N_2 atmosphere in all cases follows first-order kinetics.

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