

## Synthesis and Characterization of Oxovanadium(IV) Urea Compound

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Vanadyl chloride,  $\text{VOCl}_2 \cdot 6\text{H}_2\text{O}$ , reacts with urea at room temperature to form the four coordinated oxovanadium(IV) complex of the type  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$ . The complex is in the mononuclear form where the two urea molecules and two chlorides occupy the four equatorial positions in a plane perpendicular to the vanadyl oxygen forming a distorted square pyramid.

**Key Words:** Vanadyl complexes, Urea, Infrared, Thermal studies.

### INTRODUCTION

Recently, there has been considerable interest in the coordination chemistry of vanadium in view of its biological effects<sup>1-3</sup>. Some vanadium compounds have some potential antifungal, antibacterial and antitumor properties<sup>4</sup>.

Stable complexes are well known to be formed from the reaction of various metal salts with urea<sup>5-9</sup> where the metal to urea ratio varies from 1 : 2, 4 or 6. However, there is no known reported work on any oxovanadium-urea complexes. In the last two decades, our research group focused on the study of metal-urea complexes at elevated temperature<sup>10-14</sup>.

In the present communication, the synthesis and characterization of oxovanadium-urea complexes have been reported. The formed oxovanadium(IV)-urea complexes are very sensitive to heat, decompose rapidly to form vanadium products with no urea. The decomposition products of the complexes at high temperature are also studied.

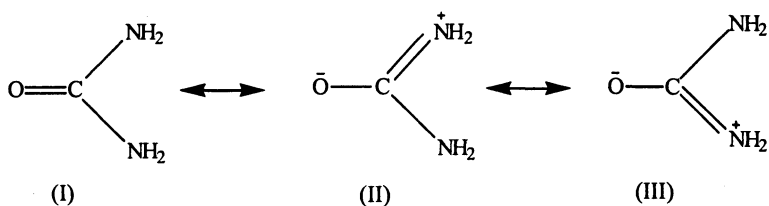
### EXPERIMENTAL

All chemicals were reagent grade and used without further purification. The pale green oxovanadium-urea complex  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  was prepared in aqueous solution by reacting 100 mL of 0.1 M  $\text{VOCl}_2 \cdot 6\text{H}_2\text{O}$  with 100 mL of an aqueous solution of 1 M urea. The reaction mixture was left for 1–2 weeks to precipitate the product complex. Any attempts to concentrate the reaction mixture to speed precipitation lead to a rapid decomposition of the oxovanadium-urea complex forming a new dark-brown product with no urea at all and identified as

$[\text{V}(\text{O})_2(\text{H}_2\text{O})]_2$ . All products were filtered off and dried in vacuum over  $\text{P}_2\text{O}_5$ . The formed complexes were characterized through their elemental and thermal analyses as well as infrared spectra. Analysis (%),  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$ : C, 8.92 (9.30); H, 3.30 (3.10); N, 20.93 (21.71); Cl, 27.10 (27.52); V, 20.34 (19.77);  $[\text{V}(\text{O})_2(\text{H}_2\text{O})]_2$ : H, 1.91% (1.98);  $\text{H}_2\text{O}$ , 18.20 (17.82); V, 51.20 (50.49). The (C, H, N, Cl) analyses were performed at the microanalytical unit, UMIST, England where vanadium was determined gravimetrically. The mid-infrared spectra of urea and the products  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  and  $[\text{V}(\text{O})_2(\text{H}_2\text{O})]_2$  in the  $4000\text{--}500\text{ cm}^{-1}$  region were recorded from KBr discs using a Nicolet FT-IR spectrometer model 670 while the far infrared spectra for the same compounds were recorded in CsI discs using a Nicolet FT-IR spectrometer model 760 Magna. Thermal gravimetric analyses (TG) and (DTG) of the product compounds were carried out using a Perkin-Elmer TGA-7 computerized thermal analysis system. The rate of heating of the samples was kept at  $5^\circ\text{C min}^{-1}$  under  $\text{N}_2$  flow at  $20\text{ mL min}^{-1}$ .  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  was used as the calibrating standard material.

## RESULTS AND DISCUSSION

Urea reacts at room temperature with  $\text{VOCl}_2$  in aqueous media to form the oxovanadium(IV)-urea complex  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  Fig. 1 shows the infrared spectrum of  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  while its infrared band assignments along with those of free urea are given in Table-1. The  $\nu(\text{V}=\text{O})$  bond vibration occurring at  $972\text{ cm}^{-1}$  for the complex agree with presence of mononuclear oxovanadium species<sup>15, 16</sup>. It is well known<sup>9, 17</sup> that the structure of urea involves resonance between the three structures,



However, the urea molecule may coordinate with metal ions through the nitrogen as well as the oxygen atoms. If a nitrogen to metal bond is present in the complex, the spectrum of the complex shows a number of changes in the  $\nu(\text{N—H})$  and  $\nu(\text{C}=\text{O})$  regions<sup>9, 18</sup>. In case of oxygen to metal bonded complexes,  $\nu(\text{N—H})$  vibration should occur at almost the same wavenumber values as those of free urea. Since structures (II) and (III) of urea are dominant in the case of the coordination *via* the oxygen atom, therefore, the  $\nu(\text{CN})$  vibration should occur at higher wavenumber values than those of urea. Furthermore, the CO double bond character will be decreased and hence its vibrational wavenumber value decreases upon coordination. According to the above analysis, the infrared spectrum of  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  indicates that urea coordinates to V(IV) *via* its oxygen atom and not nitrogen atoms.

TABLE-1  
 INFRARED WAVENUMBERS<sup>a</sup> (cm<sup>-1</sup>) AND ASSIGNMENTS FOR  
 UREA AND [V(O)(urea)<sub>2</sub>(Cl)<sub>2</sub>]

Urea	[V(O)(urea) <sub>2</sub> (Cl) <sub>2</sub> ]	Assignments <sup>b</sup>
3445 s	3455 m	v(NH <sub>2</sub> )
3348 ms	3352 m	
3248 mw	3243 mw	v(CO)
1682 s	—	
1628 s	1630 s	δ(NH <sub>2</sub> ), bend
—	1558 m	v(CN)
—	1495 w	v(CO) δ(NH <sub>2</sub> ), bend
1454 s	1455 ms	
1151 m	1150 m	
1061 m	—	δ(NH <sub>2</sub> ), rock
—	1025 w	v(CN)
990 w	—	δ <sub>s</sub> (HCN)
—	972 s	v(V=O)
789 m	780 m	δ <sub>as</sub> (HCN)
601 w	593 w	δ(NCO)
557 s	—	δ(NCN)
—	526 mw	v(V—O), O of urea
—	300 mw	v(V—Cl)

a: s, strong; m, medium; v, very; w, weak.

b: v, stretching; δ, bending.

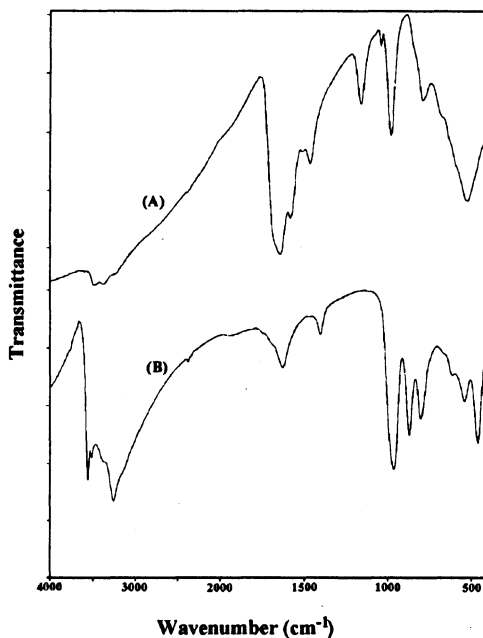


Fig. 1. Infrared spectra of (A) [V(O)(urea)<sub>2</sub>(Cl)<sub>2</sub>] and (B) [V(O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]

The  $\nu(\text{N—H})$  vibrations in the oxovanadium-urea complex are observed at 3455, 3352 and 3248  $\text{cm}^{-1}$ . These values are almost the same for free urea and clearly demonstrate that the nitrogens of urea are not involved in the coordination with vanadium(IV). Furthermore, the different bending and rocking vibrations of  $\text{NH}_2$  groups,  $\delta(\text{NH}_2)$ , are observed almost at the same wavenumber values in both free urea and the complex  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  at 1630, 1455 and 1150  $\text{cm}^{-1}$ . As a result of the formation of the oxygen to metal bond, the CO and CN vibrations in this type of urea complexes are not as separable as in free urea<sup>9</sup>. The infrared band at 1558  $\text{cm}^{-1}$  in the spectrum of  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  should be assigned to  $\nu(\text{CN})$ . This vibration occurs in the free urea<sup>19</sup> at 1061  $\text{cm}^{-1}$ . Such a large increase of  $\nu(\text{CN})$  upon coordination is due to the increase of the CN double bond character which leads to the increase of carbon-nitrogen force constant and hence its vibrational wavenumber value increases. The increase of  $\nu(\text{CN})$  of urea upon coordination represents another support for the formation of V(IV)—O bonds in our oxovanadium complex where structures (II) and (III) of coordinated urea are dominant. The  $\nu(\text{CO})$  in free urea<sup>19</sup> occurs at 1682  $\text{cm}^{-1}$ . This band disappears in the spectrum of  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  while a new band related to this vibration is observed at 1495  $\text{cm}^{-1}$ . Again, the decrease of  $\nu(\text{CO})$  of urea upon coordination to V(IV) *via* its oxygen agrees with structures (II) and (III) of coordinated urea. The above given infrared assignments agree quite well with those known for related urea complexes with other metals where urea coordinates *via* its oxygen atom<sup>9</sup>. Far infrared spectrum of  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  shows two bands at 526 and 300  $\text{cm}^{-1}$ . These two bands do not exist in the spectrum of free urea and are assigned to  $\nu(\text{V—O})$ ; O of urea and  $\nu(\text{V—Cl})$ , respectively. Such assignments agree with those known for related compounds<sup>20</sup>.

Thermal gravimetric analysis (TG and DTG) were carried out to confirm the composition and structure of the formed complex  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$ . The thermograms are shown in Fig. 2. These show that the complex has only two degradation steps. The first step occurs at the maximum of 203°C and is accompanied with a weight loss of 48% corresponding exactly to the loss of the two urea molecules. However, free urea shows its main degradation at 224°C. The second stage of thermal decomposition occurs around 354°C without any measurable weight loss. This step is clearly accompanied by the conversion of the V(IV)-Cl coordinate bonds to ionic bonds forming  $\text{VOCl}_2$  compound. The weight found for the residue after decomposition corresponds to about 52.2% of the complex weight due to the formation of  $\text{VOCl}_2$  very close to the calculated weight of 53.4%.

As explained earlier,  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  in aqueous media is very sensitive to heat forming a dark brown product. Interestingly, the nature of this product is the same upon changing the starting oxovanadium compound from  $\text{V}(\text{O})\text{Cl}_2$  to  $\text{V}(\text{O})\text{SO}_4$ ; so, the counter ions  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  are not a part of its structure. The product was isolated and identified as  $[\text{V}(\text{O})_2(\text{H}_2\text{O})]_2$  based on its elemental analysis, infrared and thermal measurements. The  $\nu(\text{O—H})$  vibrations of coordi-

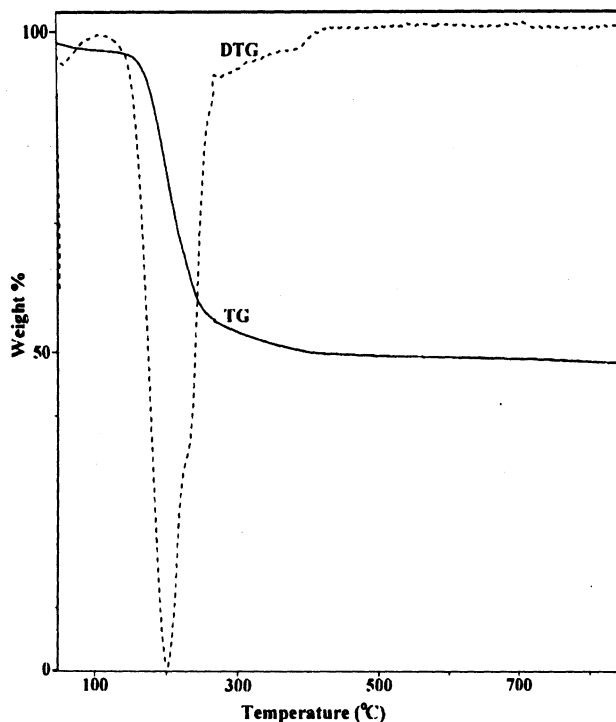


Fig. 2. TG and DTG thermal diagrams for  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$

nated  $\text{H}_2\text{O}$  molecules occur at 3557, 3512, 3364 and 3254  $\text{cm}^{-1}$  while the bending vibrations  $\delta_b(\text{H}_2\text{O})$  occur at 1626 and 1401  $\text{cm}^{-1}$  and the rocking and wagging  $\delta_r(\text{H}_2\text{O})$  and  $\delta_w(\text{H}_2\text{O})$  are observed at 779 and 614  $\text{cm}^{-1}$ , respectively. These vibrational assignments for coordinated water molecules agree with those known for related systems<sup>10</sup>. The  $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$  of  $\text{V}=\text{O}$  vibrations occur at 965 and 869  $\text{cm}^{-1}$  while the  $\nu_{\text{sym}}$  and  $\nu_{\text{asym}}$  of  $\text{V}-\text{O}$  vibrations, O of  $\text{H}_2\text{O}$ , occur at 534 and 459  $\text{cm}^{-1}$ , respectively.

Thermal gravimetric curve for  $[\text{V}(\text{O})_2(\text{H}_2\text{O})_2]_2$  is shown in Fig. 3. The complex shows only one main degradation step around 285°C and is accompanied with a weight loss of 18.20% corresponding to the loss of two  $\text{H}_2\text{O}$  molecules in good agreement with the theoretically calculated weight loss of 17.82% giving a residue of  $\text{VO}_2$  correspond to 82.0% of the complex weight which is very close to the calculated value of 82.18%. Interestingly,  $\text{H}_2\text{O}$  in  $[\text{V}(\text{O})_2(\text{H}_2\text{O})_2]_2$  is lost at about 75 degrees higher than that required for the loss of urea in  $[\text{V}(\text{O})(\text{urea})_2(\text{Cl})_2]$  complex which may infer the involvement of  $\text{H}_2\text{O}$  in  $[\text{V}(\text{O})(\text{H}_2\text{O})_2]$  in strong hydrogen bonding with the vanadyl oxygens. However, the dimeric structure of  $[\text{V}(\text{O})(\text{H}_2\text{O})_2]_2$  could arise from the existence of either  $\text{V}-\text{V}$ , metal-metal bond or/and  $\text{V}=\text{O} \cdots \text{V}=\text{O}$  type of bonding. The thermograms of the complex, Fig. 3, showing two endothermic steps with no weight losses at 365 and 58°C could be related to the cleavage of the above mentioned dimeric bonds, respectively.

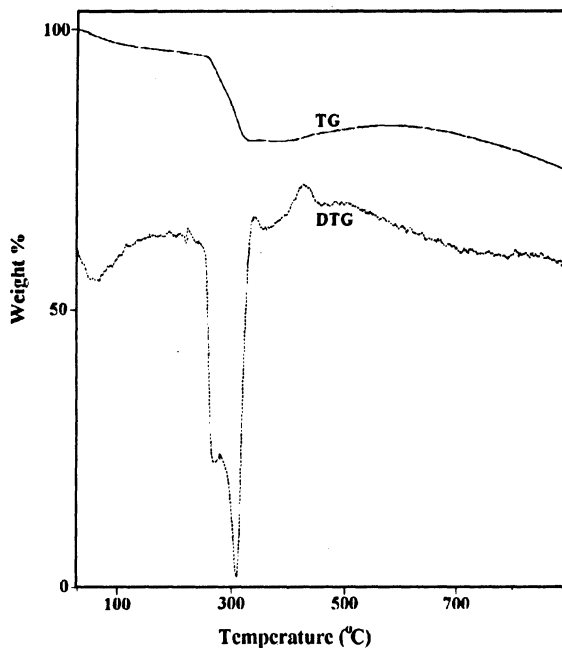
Fig. 3. TG and DTG thermal diagrams for  $[V(O)_2(H_2O)_2]$ 

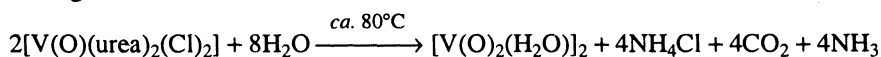
TABLE-2  
 INFRARED WAVENUMBERS<sup>a</sup> ( $cm^{-1}$ ) AND ASSIGNMENTS FOR  $[V(O)_2(H_2O)_2]$

$cm^{-1}$	Assignments <sup>b</sup>
3557 s	
3512 m	$\nu(H_2O)$
3364 w	
3254 s	
1626 m	$\delta_b(H_2O)$
1401 mw	$\delta_b(H_2O)$
965 s	$\nu_{sym}(V=O)$
869 m	$\nu_{asym}(V=O)$
799 m	$\delta_r(H_2O)$
614 wm	$\delta_w(H_2O)$
534 mw	$\nu_{sym}(V-O), O$ of $H_2O$
459 ms	$\nu_{asym}(V-O), O$ of $H_2O$

a: s, strong; m, medium; v, very; w, weak.

b:  $\nu$ , stretching;  $\delta_b$ , bending;  $\delta_r$ , rocking;  $\delta_w$ , wagging.

Finally, at high temperature, the complex  $[V(O)(urea)_2(Cl)_2]$  in aqueous media undergoes the reaction:



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