# TWO NEW VANADYL(IV) COMPLEXES CONTAINING BIURET

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Abstract—Two new biuret/vanadyl(IV) complexes, a normal bis(biuret) oxygen-bonded  $VO(biur)_2Cl_2 \cdot 3H_2O$  and a polymeric one, with bridging-bidentate sulfato groups, VO(biur)-SO<sub>4</sub> · 3H<sub>2</sub>O, have been prepared. They were characterized by their IR and electronic spectra and by TG and DTA measurements. One water molecule is strongly bonded to the cation in both compounds.

Vanadium is an essential trace element in both plants and animals<sup>1-3</sup> with numerous physiological effects. There is ample evidence that in living organisms, vanadium exists primarily as the vanadyl(IV),  $VO^{2+}$ , cation complexed with proteins and other cellular components.

In order to obtain a deeper insight into some basic aspects of the inorganic biochemistry of vanadium, we have begun the study of different model systems, containing this metal, which are relevant for a better understanding of its biochemical properties and effects.<sup>4-6</sup>

In this context we have now investigated the interaction of the  $VO^{2+}$  cation with biuret, which constitutes a good simple model for studies of the coordination properties of amide bonds (cf. for example, Ref. 7). Two new  $VO^{2+}$  complexes,  $VO(biur)_2Cl_2 \cdot 3H_2O$  and  $VO(biur)SO_4 \cdot 3H_2O$ , containing the neutral biuret as ligand, were obtained and thoroughly characterized during these studies.

### **EXPERIMENTAL**

### Preparation of VO(biur)<sub>2</sub>Cl<sub>2</sub>·3H<sub>2</sub>O

A solution of vanadyl chloride was prepared by reacting 0.455 g (2.5 mmol) of  $V_2O_5$  with 5 cm<sup>3</sup> of concentrated HCl in the presence of a few drops of ethanol on a water bath until all the pentoxide dissolved giving a clear blue solution.<sup>8</sup> After a dilution of 30 cm<sup>3</sup> of water, another solution containing 1.031 g (10 mmol) of biuret dissolved in  $80 \text{ cm}^3$  of ethanol was slowly added. The resulting mixture was left to evaporate slowly at room temperature until a greenish-blue precipitate was obtained. The fine crystalline mass was filtered, washed with small portions of absolute ethanol and dried in a vacuum desiccator over P<sub>4</sub>O<sub>10</sub>. Analysis: Found: V, 13.0; N, 21.0%; C, 11.9; H, 3.9%. Calc. for VO(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>N<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>·3H<sub>2</sub>O: V, 12.8; N, 21.1; C, 12.1; H, 4.0%.

### Preparation of VO(biur)SO<sub>4</sub> · 3H<sub>2</sub>O

1.256 g (5 mmol) of  $VOSO_4 \cdot 5H_2O$  were dissolved in a solution of  $35 \text{ cm}^3$  ethanol + 5 cm<sup>3</sup> water. To this solution, 1.031 g (10 mmol) of biuret, dissolved in 80 cm<sup>3</sup> of ethanol, was added dropwise. A fine crystalline clear-blue powder precipitated after a few minutes. It was filtered and handled in the same way as above. *Analysis*: Found: V, 15.8; N, 13.4; C, 7.8; H, 3.3%. Calc. for VO(C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>N<sub>3</sub>) SO<sub>4</sub> · 3H<sub>2</sub>O: V, 15.9; N, 13.1; C, 7.5; H, 3.4%.

### Physicochemical measurements

The electronic spectra of the solid samples were recorded with the reflectance attachment of a Shimadzu UV-600 spectrophotometer, using MgO as a standard. The IR spectra were obtained with a Perkin-Elmer 580 B instrument employing the KBr pellet technique. The thermal behavior was investigated on a Rigaku thermoanalyzer (type YLDG/CN 8002 L2) using a chromel-alumel thermoelement and working under a flowing N<sub>2</sub> stream, at a heating rate of 10°C min<sup>-1</sup>. Al<sub>2</sub>O<sub>3</sub> was used as a DTA standard; sample weight ranged between 25-30 mg.

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Fig. 1. IR spectra of VO(biur)SO<sub>4</sub> · 3H<sub>2</sub>O (A) and VO(biur)<sub>2</sub>Cl<sub>2</sub> · 3H<sub>2</sub>O (B).

#### **RESULTS AND DISCUSSION**

It is known that biuret  $(NH_2CONHCONH_2)$  can form two types of chelate rings,<sup>7,9,10</sup> coordinated to the metal ions through both carbonyl oxygens or to the two, single deprotonated,  $NH_2$  groups.

The stoichiometry found for the two new vanadyl(IV) complexes indicated the formation of C=O coordinated complexes but two different environments, which depend on the starting vanadyl salt, are found. In the case of the sulfate, this anion is incorporated as a bidentate ligand and a polymeric complex (see below) is probably generated. Starting with the chloride, a normal bis(biuret) cationic complex is obtained.

The IR spectra of both complexes in the range  $2000-250 \text{ cm}^{-1}$  (Fig. 1) and their assignment shown in Table 1, support the above suppositions. The spectrum of VO(biur)<sub>2</sub>Cl<sub>2</sub>·3H<sub>2</sub>O is similar to that of Cu(biur)<sub>2</sub>Cl<sub>2</sub><sup>11,12</sup> in which the C=O coordination is supported by a structural<sup>13</sup> as well as by a complete normal coordinate analysis.<sup>11</sup>

The VO(biur)SO<sub>4</sub> ·  $3H_2O$  spectrum is more complex, due to the presence of the coordinated SO<sub>4</sub>ligand. The spectral features and band positions of these SO<sub>4</sub><sup>2-</sup> vibrations indicate the presence of bridging bidentate sulfato groups,<sup>12,14,15</sup> which strongly suggest the presence of a polymeric complex, an assumption which is also supported by the rapid precipitation of this species after mixing the biuret and the vanadyl sulfate solutions.

The symmetric stretching and bending vibrations  $(v_1 \text{ and } v_2)$  of the sulfate groups apparently are too weak in intensity to be detected or they may be overlapped by stronger bands lying in the same spectral range. Also the antisymmetric bending  $(v_4)$ 

is clearly overlapped by a  $\rho(NH_2)$  biuret vibration.

The characteristic V=O stretching vibration lies in the same range for both complexes, although it shows a small shift to higher wavenumbers and also a somewhat higher intensity in the case of the chloro-compound. The V-O stretching mode which originated in the interaction of the cation with the carbonyl oxygens should lie in the lower frequency region of the spectra. We have tentatively assigned this mode to the band found around  $350 \text{ cm}^{-1}$ , although in the bis(biuret) copper(II) dichloride and in the nickel(II) analog it was found below  $300 \text{ cm}^{-1}$ .<sup>11</sup> Notwithstanding, in vanadyl(IV) acetate a band lying at  $442 \text{ cm}^{-1}$  was assigned to this stretching mode.<sup>16</sup>

The electronic reflectance spectra of both compounds are very similar as can be seen from Fig. 2. They show a very strong and broad band and a well-defined shoulder on its higher energy side. The first band is found at 760 nm  $(13,757 \text{ cm}^{-1})$  in the bis(biuret) complex and at 750 nm  $(13,333 \text{ cm}^{-1})$  in the sulfato complex. The shoulder is located at 635 nm  $(15,748 \text{ cm}^{-1})$  in the first case and at ~ 600 nm  $(16,666 \text{ cm}^{-1})$  in the second one.

According to the well known Ballhausen and Gray energy level diagram<sup>17</sup> the main peak can be assigned to the  ${}^{2}E \leftarrow {}^{2}B_{2}$  and the shoulder to the  ${}^{2}B_{1} \leftarrow {}^{2}B_{2}$  transitions, respectively. The value for the crystal field splitting parameter 10Dq is given directly by the last transition. The observed values are in good agreement with those obtained for other vanadyl complexes with a similar VO<sup>2+</sup> environment.<sup>18</sup> The small differences in color arise from the relative displacements of the shoulders and from the different form and extension of the 'window' located between the shoulder and the

$VO(biur)_2Cl_2 \cdot 3H_2O$	VO(biur)SO <sub>4</sub> · 3H <sub>2</sub> O	Assignment
1700 1672	1712	$v(C=O) + \delta(NH_2)$
1640 1605	1665 1630 sh	$\delta(H_2O) + \delta(NH_2)$
1470	1481	v(CN)
1335	1326	δ(N—H)
1132 1118 1102		$\rho_r(\mathrm{NH}_2)$
	1165 1129 1043	$v_3(\mathrm{SO}_4) + \rho_r(\mathrm{NH}_2)$
972	965	v(VO)
952	946	$v(CN) + v(C-NH_2)$
750	760	<b>Ring deformation</b>
678 643		$\rho(\mathrm{NH_2})$
	673 626 591 sh	$\rho(\mathrm{NH}_2) + v_4(\mathrm{SO}_4)$
480	480, 471, 450	<b>Ring deformations</b>
350	370	$v(V - O) + \delta(C - NH_2)$

Table 1. Assignment of the IR spectra of  $VO(biur)_2Cl_2 \cdot 3H_2O$  and  $VO(biur) \\ SO_4 \cdot 3H_2O$  in the 2000-250 cm<sup>-1</sup> region (values in cm<sup>-1</sup>)



Fig. 2. Electronic reflectance spectra of VO(biur) SO<sub>4</sub>·3H<sub>2</sub>O (A) and VO(biur)<sub>2</sub>Cl<sub>2</sub>·3H<sub>2</sub>O (B).

beginning of the strong charge-transfer band, located at higher energies, and not seen in Fig. 2.

The thermal analysis gives more information about the characteristics of the coordination sphere of both complexes. The thermogram of VO(biur)SO<sub>4</sub>  $\cdot$  3H<sub>2</sub>O shows four well-defined endothermic DTA signals, the first of which appears in a doublet form. This doublet (96° and 111°C) corresponds to the loss of two water molecules and the release of the third one occurs at 192°C. After this loss the thermogravimetric curve shows a continuous but irregular weight decrease, related to the other two endothermic peaks. One of them, located at 258°C, is associated with the release of the organic ligand. The last one, at 420°C, corresponds to the generation of SO<sub>3</sub>. Further heating, up to 700°C, gives neither mass changes nor thermal effects. From these results, the thermal degradation can be formulated as follows:

$$VO(biur)SO_4 \cdot 3H_2O \rightarrow VO(biur)SO_4 \cdot H_2O + 2H_2O$$
(1)

$$VO(biur)SO_4 \cdot H_2O \rightarrow VO(biur)SO_4 + H_2O$$
 (2)

$$VO(biur)SO_4 \rightarrow VOSO_4 + biur$$
 (3)

$$VOSO_4 \rightarrow VO_2 + SO_3.$$
 (4)

The theoretical total weight loss [addition of equa-

tions (1)-(4)] gives 74.06% which correlates with the value of 73.8% found experimentally.

In the case of VO(biur)<sub>2</sub>Cl<sub>2</sub>  $\cdot$  3H<sub>2</sub>O the release of the first two water molecules is associated with a strong and well-defined endothermic DTA peak centered at 141°C, whereas the release of the third one corresponds to a second endothermic peak, located at 200°C. After the loss of water a continuous weight decrease is observed. Between 220° and 500°C, the observed weight change corresponds to the release of the two biuret molecules. In this range two not well-defined and weak endothermic DTA signals at 260° and 378°C are observed. At 500°C a clear inflexion is observed in the TG curve, and a further weight loss begins and continues slowly until the maximum temperature (700°C) is reached. In this case, the formation of VOCl<sub>2</sub> as an intermediate can be expected, but pure VOCl<sub>2</sub> decomposes into VOCl and VOCl<sub>3</sub> at temperatures above 380°C.<sup>19</sup> The total conversion of the complex to VOCI requires a weight loss of 74.27% in good agreement with the experimentally found values, which always lie around 75%.

Therefore, the degradation of VO(biur)<sub>2</sub>  $Cl_2 \cdot 3H_2O$  can be formulated as follows:

$$VO(biur)_2Cl_2 \cdot 3H_2O \rightarrow VO(biur)_2Cl_2 \cdot H_2O + 2H_2O$$
(5)

 $VO(biur)_2Cl_2 \cdot H_2O \rightarrow VO(biur)_2Cl_2 + H_2O$  (6)

 $VO(biur)_2Cl_2 \rightarrow VOCl_2 + 2biur$  (7)

$$2\text{VOCl}_2 \rightarrow \text{VOCl}(s) + \text{VOCl}_3(g).$$
 (8)

The most important result obtained from the thermal analysis is the clear evidence of the presence of one strongly bonded water molecule in both complexes. This molecule is probably coordinated directly to the vanadium atom in the *trans* position to the vanadyl oxygen.

The formation of these complexes is another example of the particularly high stability of vanadyl complexes with oxygen donors<sup>21</sup> and suggests a preferential interaction of the  $VO^{2+}$  cation with C=O oxygens in the presence of amide groups in biological environments.

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