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## Abstract

## Full Text

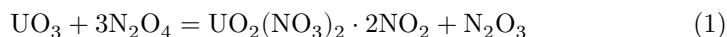
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### CHEMISTRY

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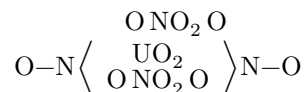
## ON THE STRUCTURE OF $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$

The complex compound of uranyl nitrate with nitrogen dioxide,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ , is obtained by the interaction of liquid nitrogen dioxide with uranium oxides<sup>(1)</sup>, for example:



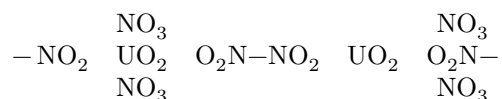
or with  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (in the latter case in a medium of anhydrous nitric acid<sup>(2)</sup>) in the form of small greenish-yellow crystals. This is a very unstable compound: water, ethers, and acetonitrile readily decompose it with evolution of  $\text{NO}_2$  vapors. As Gibson and Katz<sup>(1)</sup> noted, in a dry atmosphere at room temperature  $\text{NO}_2$  is partially split off from the complex; however, when the content of nitrogen dioxide in the compound becomes 10-15% lower than the stoichiometric value, further dissociation of the latter ceases completely.

The question of the structure of the complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$  is of interest, since several variants of the form in which  $2\text{NO}_2$  exists in this compound are conceivable. The investigation carried out in<sup>(3)</sup> of the vibrational spectra of a series of complexes of general composition  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{A}$  (A—addend molecule), including  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ , in the frequency interval 650-1700  $\text{cm}^{-1}$  showed that the positions of the principal frequencies of the coordinated nitrate group in the spectrum depend almost not at all on the nature of the addend. This circumstance speaks in favor of a uniform arrangement of the  $\text{NO}_3^-$  groups in the coordination sphere of uranium and, consequently, of the same structure of the coordination sphere of uranium in such compounds. Thus, at first glance the structure of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$  may be likened to the structure of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ <sup>(4)</sup>, or  $\text{UO}_2(\text{NO}_3)_2 \cdot 2(\text{C}_2\text{H}_5\text{O})_3\text{PO}$ <sup>(5)</sup>—the uranyl ion is surrounded by two  $\text{NO}_3^-$  groups, coordinating bidentately in the trans position, and two  $\text{NO}_2$  molecules:



(I)

However, it is known that nitrogen dioxide molecules, having an electron with uncompensated spin, are prone to dimerization. Thus, in the gas at room temperature about 80% of the  $\text{NO}_2$  molecules are bound in dimers. Sisler et al. <sup>(6)</sup> established that in compounds of ethers with nitrogen dioxide the latter exists only in the form of dimers. Taking this circumstance into account, the structure of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$  may be represented in the form of structures I, “stitched” into chains as a result of dimerization of the  $\text{NO}_2$  molecules:



(II)

Finally, one should point out still another possibility, noted by Addison <sup>(7, 8)</sup>, which consists in the dissociation of  $\text{N}_2\text{O}_4$  into  $\text{NO}^+$  and  $\text{NO}_3^-$  ions in complexes of nitrogen dioxide with metal nitrates. On the basis

synthesis, represented the structure of  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{NO}_2$  in the form  $(\text{NO}^+)_2[\text{Zn}(\text{NO}_3)_4]^{2-}$ , and the volatile complex  $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{NO}_2$  in the form  $[\text{Fe}(\text{NO})(\text{NO}_3)_4]$ , where both the  $\text{NO}$  and  $\text{NO}_3$  groups are covalently bonded to iron, as in  $\text{Fe}(\text{CO})_5$ .

In order to make an unambiguous choice among the possible structures of the complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ , we first measured its magnetic susceptibility. In the presence of monomeric  $\text{NO}_2$  molecules this compound should be paramagnetic with a magnetic susceptibility on the order of  $+2000 \cdot 10^{-6}$  CGSM. The complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$  was obtained by reaction (1). After removal in vacuum at  $30^\circ$  of excess  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{O}_3$ , the compound contained 49.7% uranium (calculated for  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ : 48.97% U), contained no water, and dissolved completely in water.

Measurement of the magnetic susceptibility was carried out by the Gouy method in the temperature range  $5-80^\circ$ . The strength of the magnetic field produced by the electromagnet was 4100 oersted. The apparatus was calibrated with water and benzene. The molar magnetic susceptibility of the complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$  in the indicated temperature range does not depend on temperature and is  $+24 \cdot 10^{-6}$  CGSM. If the diamagnetic contribution of the constituent parts of the substance is subtracted from the value obtained (according to (9), the susceptibility  $\chi_{\text{NO}_3^-} = -20 \cdot 10^{-6}$ , the diamagnetic component  $\chi_{\text{NO}_2} \cong -8 \cdot 10^{-6}$ ,  $\chi_{\text{U(VI)}} = -19 \cdot 10^{-6}$ ,  $\chi_{\text{O}_2^-} = -12 \cdot 10^{-6}$ ), then the paramagnetic component proves to be  $+123 \cdot 10^{-6}$ . This value agrees satisfactorily with the data reported in the literature on the magnetic

Figure 1

Figure 1: Figure 1

susceptibility of the  $\text{UO}_2^{2+}$  ion, which possesses polarization paramagnetism (Nikolau (11) gives the value  $\chi_{\text{UO}_2^{2+}} = +100 \cdot 10^{-6}$ ). Thus it may be concluded that the weak paramagnetism of the complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$  is due to the paramagnetism of the uranyl ion, and the remaining part of the compound is diamagnetic. This thereby rules out structure I, containing monomeric  $\text{NO}_2$  molecules, and subsequently structure II and structures in which the  $\text{N}_2\text{O}_4$  molecule is dissociated into the diamagnetic ions  $\text{NO}^+$  and  $\text{NO}_3^-$ , or, which is also possible,  $\text{NO}_2^+$  and  $\text{NO}_2^-$ , may be discussed.

**Fig. 1.** 1  $-\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ , 2  $-\text{Cs}[\text{UO}_2(\text{NO}_3)_3]$

Since the frequencies of the valence vibrations of  $\text{N}_2\text{O}_4$ ,  $\text{NO}_2^+$ ,  $\text{NO}^+$ , and  $\text{NO}_2^-$  are known, we undertook a search for the corresponding absorption bands in the spectrum of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ . Spectra of a suspension of the complex in paraffin oil were recorded on an IKS-12 spectrophotometer with NaCl and LiF prisms. In the region of  $1700 \text{ cm}^{-1}$ , where the frequency  $\nu_{\text{acc}}^{\text{N}_2\text{O}_4}$  is located, only weak bands at  $1609$ ,  $1730$ , and  $1766 \text{ cm}^{-1}$  were found, analogous to those previously observed in the spectra of uranium nitrate hydrates and  $\text{RbUO}_2(\text{NO}_3)_3$  (12, 13). They are assigned respectively to the overtone  $2\nu_6\text{ONO}_2^-$  and to the combination frequencies  $\nu_3\text{UO}_2^{2+} + \nu_6\text{ONO}_2$  and  $(\nu_2 + \nu_5)\text{ONO}_2^-$ . As was noted in (3), in the frequency region below  $1600 \text{ cm}^{-1}$  there are no other bands except those attributed to vibrations of the uranyl ion and the coordinated  $\text{ONO}_2^-$  group. In particular, in the region of the valence vibrations of the coordinated  $\text{ONO}_2^-$  group, the bands  $\nu_1\text{ONO}_2^-$   $1272$  and  $\nu_4\text{ONO}_2^-$   $1494$ ,  $1528 \text{ cm}^{-1}$  are observed, whereas  $\nu_{\text{acc}}\text{NO}_2^+ \sim$

$\sim 1400 \text{ cm}^{-1}$  (14),  $\nu_{\text{acc}}$  of the coordinated ion  $\text{NO}_2^-$ ,  $1390$ - $1440 \text{ cm}^{-1}$  (15). However, in the region of  $2300 \text{ cm}^{-1}$ , where the frequency of the stretching vibration of  $\text{NO}^+$  is located, a rather intense band at  $2296 \text{ cm}^{-1}$  was found. Figure 1 shows the spectrum of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$  and, for comparison, the spectrum of  $\text{CsUO}_2(\text{NO}_3)_3$  in the interval  $2200$ - $2400 \text{ cm}^{-1}$ , with approximately the same thickness of the absorbing layer. The weak bands at  $2262$  and  $2296 \text{ cm}^{-1}$  in the spectrum of the latter are components of the combination frequency  $(\nu_4 + \nu_5)\text{ONO}_2^-$  (13). It is obvious that the band at  $2296 \text{ cm}^{-1}$  in the spectrum of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$ , being very intense, cannot be assigned only to a combination frequency and most likely belongs to the stretching vibration of the  $\text{NO}^+$  ion, which arises upon ionization of  $\text{N}_2\text{O}_4$ . Table 1 compares the frequencies of  $\text{N} \equiv \text{O}$  in various compounds.

**Table 1**

Compound	$\nu_{\text{NO}}, \text{cm}^{-1}$	Source
solid $\text{NO}^+\text{ClO}_4^-$	2229	( <sup>16</sup> )
$\text{NO}^+$ in solution	2290-2308	( <sup>17</sup> )
$\text{NO}^+[\text{UO}_2(\text{NO}_3)_3]$	2296	Our data
$\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})]$	1939	( <sup>18</sup> )
NO gas	1877	( <sup>19</sup> )

Thus, measurements of the magnetic susceptibility and of the vibrational spectra unambiguously prove that in the complex  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{NO}_2$  nitrogen dioxide is present in the form of the diamagnetic ions  $\text{NO}^+$  and  $\text{NO}_3^-$ .

For uranyl nitrate, the tendency to form the anionic trinitrato complex  $[\text{UO}_2(\text{NO}_3)_3]^-$  is very characteristic. Taking this circumstance into account, we must write the formula of the complex compound of uranyl nitrate with nitrogen dioxide in the following way:  $\text{NO}^+[\text{UO}_2(\text{NO}_3)_3]^-$ . Indeed, the spectrum of this compound in the frequency region of the fundamental vibrations of the coordinated nitrate group (<sup>3</sup>) is in all respects similar to the spectra of  $\text{M}[\text{UO}_2(\text{NO}_3)_3]$  ( $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ ) (<sup>11,12</sup>) (and, of course, similar to the spectra of  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{A}$ , since  $[\text{UO}_2(\text{NO}_3)_3]^-$  is a variety of the latter). We see a serious confirmation of the fact that the compound of uranyl nitrate with nitrogen dioxide is nitrosyluranyl trinitrate in its very bright bluish-green luminescence, which is characteristic of the structure  $[\text{UO}_2(\text{NO}_3)_3]^-$ . In the presence of bridging structures of type II, one would have expected sharply weakened luminescence as a result of migration of the excitation energy throughout the volume of the crystal.

It is very probable that complexes of nitrogen dioxide with nitrates of other metals are built according to the same principle as the complex with uranyl nitrate.

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