Reports of the Academy of Sciences of the USSR

CHEMISTRY

1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1961. Volume 146, No. 5

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR V. M. VDOVENKO, D. N. SUGLOBOV, G. A. ROMANOV

ON THE STRUCTURE OF $UO_2(NO_3)_2 \cdot 2NO_2$

The complex compound of uranyl nitrate with nitrogen dioxide, $UO_2(NO_3)_2 \cdot 2NO_2$, is obtained by the interaction of liquid nitrogen dioxide with uranium oxides ([1]), for example:

$$UO_3 + 3N_2O_4 = UO_2(NO_3)_2 \cdot 2NO_2 + N_2O_3 \qquad (1)$$

or with $UO_2(NO_3)_2 \cdot 2H_2O$ (in the latter case in a medium of anhydrous nitric acid ([2])) in the form of small greenish-yellow crystals. This is a very unstable compound: water, ethers, and acetonitrile readily decompose it with evolution of NO_2 vapors. As Gibson and Katz ([1]) noted, in a dry atmosphere at room temperature 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 $UO_2(NO_3)_2 \cdot 2NO_2$ is of interest, since several variants of the form in which $2NO_2$ exists in this compound are conceivable. The investigation carried out in ([3]) of the vibrational spectra of a series of complexes of general composition $UO_2(NO_3)_2 \cdot 2A$ (A—addend molecule), including $UO_2(NO_3)_2 \cdot 2NO_2$, in the frequency interval 650–1700 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 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 $UO_2(NO_3)_2 \cdot 2NO_2$ may be likened to the structure of $UO_2(NO_3)_2 \cdot 2H_2O$ ([4]), or $UO_2(NO_3)_2 \cdot 2(C_2H_5O)_3PO$ ([5])—the uranyl ion is surrounded by two NO_3^- groups, coordinating bidentately in the trans position, and two NO_2 molecules:

$$O{-}N\left\langle \begin{array}{c} O\,NO_2\,O \\ UO_2 \\ O\,NO_2\,O \end{array} \right\rangle N{-}O$$

(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 NO_2 molecules are bound in dimers. Sisler et al. ([6]) 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 $UO_2(NO_3)_2 \cdot 2NO_2$ may be represented in the form of structures I, "stitched" into chains as a result of dimerization of the NO_2 molecules:

$$-NO_2 \quad \begin{matrix} NO_3 \\ UO_2 \\ NO_3 \end{matrix} \quad O_2N{-}NO_2 \quad UO_2 \quad \begin{matrix} NO_3 \\ O_2N{-} \\ NO_3 \end{matrix}$$

(II)

Finally, one should point out still another possibility, noted by Addison ([7], [8]), which consists in the dissociation of N_2O_4 into NO^+ and NO_3^- ions in complexes of nitrogen dioxide with metal nitrates. On the basis

synthesis, represented the structure of $Zn(NO_3)_2 \cdot 4NO_2$ in the form $(NO^+)_2[Zn(NO_3)_4]^{2-}$, and the volatile complex $Fe(NO_3)_3 \cdot 2NO_2$ in the form $[Fe(NO)(NO_3)_4]$, where both the NO and NO_3 groups are covalently bonded to iron, as in $Fe(CO)_5$.

In order to make an unambiguous choice among the possible structures of the complex $UO_2(NO_3)_2 \cdot 2NO_2$, we first measured its magnetic susceptibility. In the presence of monomeric NO_2 molecules this compound should be paramagnetic with a magnetic susceptibility on the order of $+2000 \cdot 10^{-6}$ CGSM. The complex $UO_2(NO_3)_2 \cdot 2NO_2$ was obtained by reaction (1). After removal in vacuum at 30° of excess N_2O_4 and N_2O_3, the compound contained 49.7% uranium (calculated for $UO_2(NO_3)_2 \cdot 2NO_2$: 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°. 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 $UO_2(NO_3)_2 \cdot 2NO_2$ 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 $\chi_{NO_3^-} = -20 \cdot 10^{-6}$, the diamagnetic component $\chi_{NO_2} \cong -8 \cdot 10^{-6}$, $\chi_{U(VI)} = -19 \cdot 10^{-6}$, $\chi_{O^{2-}} = -12 \cdot 10^{-6}$), 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 UO_2^{2+} ion, which possesses polarization paramagnetism (Nikolau (11) gives the value $\chi_{UO_2^{2+}} = +100 \cdot 10^{-6}$). Thus it may be concluded that the weak paramagnetism of the complex $UO_2(NO_3)_2 \cdot 2NO_2$ 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 NO_2 molecules, and subsequently structure II and structures in which the N_2O_4 molecule is dissociated into the diamagnetic ions NO^+ and NO_3^-, or, which is also possible, NO_2^+ and NO_2^-, may be discussed.

Fig. 1. 1 –$UO_2(NO_3)_2 \cdot 2NO_2$, 2 –$Cs[UO_2(NO_3)_3]$

Since the frequencies of the valence vibrations of N_2O_4, NO_2^+, NO^+, and NO_2^- are known, we undertook a search for the corresponding absorption bands in the spectrum of $UO_2(NO_3)_2 \cdot 2NO_2$. 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 cm^{-1}, where the frequency $\nu_{acc}^{N_2O_4}$ is located, only weak bands at 1609, 1730, and 1766 cm^{-1} were found, analogous to those previously observed in the spectra of uranium nitrate hydrates and $RbUO_2(NO_3)_3$ (12, 13). They are assigned respectively to the overtone $2\nu_6 ONO_2^-$ and to the combination frequencies $\nu_3 UO_2^{2+} + \nu_6 ONO_2$ and $(\nu_2 + \nu_5) ONO_2^-$. As was noted in (3), in the frequency region below 1600 cm^{-1} there are no other bands except those attributed to vibrations of the uranyl ion and the coordinated ONO_2^- group. In particular, in the region of the valence vibrations of the coordinated ONO_2^- group, the bands $\nu_1 ONO_2^-$ 1272 and $\nu_4 ONO_2^-$ 1494, 1528 cm^{-1} are observed, whereas $\nu_{acc} NO_2^+ \sim$

$\sim$ 1400 cm^{-1} (^{14}), ν_{acc} of the coordinated ion NO_2^-, 1390-1440 cm^{-1} (^{15}). However, in the region of 2300 cm^{-1}, where the frequency of the stretching vibration of NO^+ is located, a rather intense band at 2296 cm^{-1} was found. Figure 1 shows the spectrum of $UO_2(NO_3)_2 \cdot 2NO_2$ and, for comparison, the spectrum of $CsUO_2(NO_3)_3$ in the interval 2200-2400 cm^{-1}, with approximately the same thickness of the absorbing layer. The weak bands at 2262 and 2296 cm^{-1} in the spectrum of the latter are components of the combination frequency $(\nu_4 + \nu_5)$ ONO_2^- (^{13}). It is obvious that the band at 2296 cm^{-1} in the spectrum of $UO_2(NO_3)_2 \cdot 2NO_2$, being very intense, cannot be assigned only to a combination frequency and most likely belongs to the stretching vibration of the NO^+ ion, which arises upon ionization of N_2O_4. Table 1 compares the frequencies of $N \equiv O$ in various compounds.

Table 1

Compound	ν_{NO}, cm^{-1}	Source
solid $NO^+ClO_4^-$	2229	([16])
NO^+ in solution	2290-2308	([17])
$NO^+[UO_2(NO_3)_3]$	2296	Our data
$Na_2[Fe(CN)_5(NO)]$	1939	([18])
NO gas	1877	([19])

Thus, measurements of the magnetic susceptibility and of the vibrational spectra unambiguously prove that in the complex $UO_2(NO_3)_2 \cdot 2NO_2$ nitrogen dioxide is present in the form of the diamagnetic ions NO^+ and NO_3^-.

For uranyl nitrate, the tendency to form the anionic trinitrato complex $[UO_2(NO_3)_3]^-$ 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: $NO^+[UO_2(NO_3)_3]^-$. Indeed, the spectrum of this compound in the frequency region of the fundamental vibrations of the coordinated nitrate group ([3]) is in all respects similar to the spectra of $M[UO_2(NO_3)_3]$ (M = K, Rb, Cs) ([11,12]) (and, of course, similar to the spectra of $UO_2(NO_3)_2 \cdot 2A$, since $[UO_2(NO_3)_3]^-$ 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 $[UO_2(NO_3)_3]^-$. 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.

The authors express their gratitude to M. A. Yakimov for the preparation of $CsUO_2(NO_3)_3$.

Received
22 VI 1962

CITED LITERATURE

1. G. Gibson, J. Katz, J. Am. Chem. Soc., **73**, 5436 (1951).

2. E. Späth, Monats h., **505** (1912).

3. D. N. Suglobov, Dissertation, Leningrad Technological Institute, 1961.

4. V. M. Vdovenko, E. V. Stroganov et al., Radiokhimiya, **4**, No. 1, 59 (1962).

5. J. E. Fleming, H. Lynton, Chem. and Ind., **46**, 1415 (1960).

6. B. Rubin, H. H. Sisler, H. Shechter, J. Am. Chem. Soc., **74**, No. 4, 877 (1952).

7. C. C. Addison, Rec. trav. chim., Pays-Bas, **75**, No. 6, 626 (1956).

8. C. C. Addison, B. I. Hathaway, L. Logan, Proc. Chem. Soc., **51** (1958).

9. G. G. Havens, Phys. Rev., **41**, 337 (1932).

10. P. V. Selwood, *Magnetochemistry*, IL, 1958.

11. A. Nicolau, C. R., **205**, 654 (1937).

12. B. M. Gatehouse, A. E. Comyns, J. Chem. Soc., 1958, 3965.

13. J. G. Allpress, A. N. Hambly, Austr. J. Chem., **12**, No. 4, 569 (1959).

14. C. K. Ingold, D. J. Millen, H. G. Poole, J. Chem. Soc., 1950, 2576.

15. B. M. Gatehouse, J. Inorg. and Nucl. Chem., **8**, 79 (1958).

16. W. R. Angus, A. H. Lieckie, Proc. Roy. Soc. (London), **A149**, 327 (1935).

17. D. J. Millen, J. Chem. Soc., 1950, 2600.

18. G. Boz, J. Inorg. and Nucl. Chem., **17**, 174 (1961).

19. T. A. Turney, G. A. Wright, Chem. Rev., **59**, No. 3, 497 (1959).

Note: Figure translations are in progress. See original paper for figures.