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Abstract

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LUMINESCENCE SPECTRA OF COORDINATION COMPOUNDS OF URANYL NITRATE

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The photoluminescence of uranyl salts has now been studied quite thoroughly. In particular, the influence of the number of molecules of water of crystallization on the luminescence spectrum of uranyl nitrate has been examined in detail ([1]). The spectrum is attributed to an electronic transition in the uranyl ion, upon which are superimposed vibrations of the group O—U—O, as well as vibrations of the crystal lattice. However, the presence of the uranyl ion is apparently not a sufficient condition for the appearance of the luminescence-spectrum structure characteristic of uranyl salts. Thus, B. E. Gordon ([2]) pointed out the absence of luminescence in uranyl nitrate completely deprived of water of crystallization. Katz and Gibson ([3]), who obtained especially pure samples of anhydrous uranyl nitrate, noted very weak luminescence of the salt powder, observed only at 90° K, without, however, giving this question special attention. In contrast to them, A. N. Sevchenko, V. M. Vdovenko, and T. V. Kovaleva ([1]), and later L. V. Volodko and A. N. Sevchenko ([4]), give a discrete luminescence spectrum of powdered anhydrous uranyl nitrate, in which the frequency interval characteristic of uranyl salts is preserved between the individual lines. This result, however, raises objections, since the method used in the cited works for preparing anhydrous uranyl nitrate by thermal dehydration of crystalline hydrates in vacuum is not satisfactory. The salt obtained in this way is always strongly contaminated by products of its partial decomposition, as has been pointed out repeatedly earlier ([2,5]). Like anhydrous uranyl nitrate ([2,3]), anhydrous uranyl sulfate ([2,6,7]) and uranyl chloride (according to our data) likewise do not have the discrete luminescence spectrum characteristic of uranyl salts.

On the other hand, according to M. Freymann and Chantrel ([8]), M. Freymann and R. Freymann ([9]), as well as Volodko and Sevchenko ([4]), coordination compounds of uranyl nitrate with acetone, ethyl ether, dioxane, nitromethane, and other molecules luminesce brightly at the temperature of liquid air and have a

Fig. 1. Luminescence spectra of coordination compounds of uranyl nitrate.

Figure 1: Fig. 1. Luminescence spectra of coordination compounds of uranyl nitrate.

structured spectrum, the fine structure of whose bands, caused by the crystal lattice, was studied in the last-mentioned work.

Thus, it may be assumed that the presence of a structured luminescence spectrum is not a specific property of crystalline hydrates of uranyl nitrate, but rather is a consequence of a more general phenomenon—the coordination of addend molecules at the uranyl ion.

In the present work the luminescence was studied both of anhydrous uranyl nitrate and of some of its coordination compounds with various addends, in order to clarify the influence of coordination and of the properties of the addend molecules on the luminescence spectrum. Luminescence spectra were obtained for microcrystalline powders of the following coordination compounds of uranyl nitrate: $UN \cdot 2H_2O$, $UN \cdot 3H_2O$, $UN \cdot 6H_2O$, $UN \cdot nNH_3$, $UN \cdot 2C_5H_5N$, $UN \cdot 2(C_2H_5)_2O$, $UN \cdot 2(C_4H_9)_2O$, $UN \cdot 2(C_2H_4Cl)_2O$, $UN \cdot 2O(CH_2)_4O$, $UN \cdot nC_2H_5OH$, $UN \cdot 2CH_3CN$, $UN \cdot 2C_6H_5NO_2$, $UN \cdot 2CH_3NO$, $UN \cdot 2NO_2$, where

UN denotes, for brevity, $UO_2(NO_3)_2$. Mixed complexes of the composition $UN \cdot 2H_2O \cdot 2(C_2H_5)_2O$ and $UN \cdot 2H_2O \cdot 2NO_2$ were also studied. Anhydrous uranyl nitrate was prepared by the method described by Gibson and Katz ([3]), by the reaction
$UO_3 + 3N_2O_4 \rightarrow UO_2(NO_3)_2 \cdot 2NO_2 + N_2O_3$. The complex compound $UO_2(NO_3)_2 \cdot 2NO_3$ thus obtained was then decomposed in vacuum (10^{-5} mm Hg)

Fig. 1. Luminescence spectra of coordination compounds of uranyl nitrate.
1 —$UN \cdot 2C_5H_5N$; 2 —$UN \cdot 2(C_2H_5)_2O$; 3 —$UN \cdot 2CH_3CN$;
4 —$UN \cdot 2C_6H_5NO_2$; 5 —$UN \cdot 2CH_3NO_2$; 6 —$UN \cdot 2NO_2$; 7 —UN

at 165°C, with formation of $UO_2(NO_3)_2$. The complex compounds listed above were obtained either by condensation of the vapors of the adduct substance onto anhydrous uranyl nitrate in vacuum, or (where this was possible) by saturating the corresponding organic liquids with anhydrous uranyl nitrate and subsequently crystallizing from supersaturated solutions. The mixed complexes $UN \cdot 2H_2O \cdot 2NO_2$ and $UN \cdot 2H_2O \cdot 2(C_2H_5)_2O$ were prepared by the methods described in ([3,10]).

The composition of the complex compounds obtained was checked by determining the uranium and water content. Luminescence was excited by a PRK-4 mercury lamp through a UFS-4 light filter. Both photographic and photoelectric recording of the spectra was used on an ISP-51 spectrograph with an FEP-1 attachment. All luminescence spectra were obtained at a temperature of 77°K. The vibrational structure of the electronic band of the coordinated cation was

studied without resolving the finer structure due to the crystal lattice. The investigated samples of anhydrous uranyl nitrate showed no glow at room temperature and luminesced only very weakly at 90°K in comparison with crystalline hydrates. As is seen from the spectrogram in Fig. 1, the luminescence spectrum of the anhydrous salt obtained by us is a broad band in the region from 4965 to 6100 Å, with a maximum at 5455 Å, against the background of which weakly expressed maxima are observed. In contrast to anhydrous uranyl nitrate, all the complex compounds listed above in which the adducts are electron-donor molecules luminesce brightly at 90°K (and some of them, for example $UN \cdot 2NO_2$, $UN \cdot 2C_5H_5N$, $UN \cdot 2CH_3CN$, also at room temperature) and have a luminescence spectrum characteristic of uranyl salts, with a sharply expressed vibrational structure of the spectrum. Some of them are shown in Fig. 1. The vibrational frequency is determined mainly by the uranyl ion and depends little on the nature of the adduct. An exception is the ammoniate of uranyl nitrate, whose luminescence spectrum is structureless. Upon condensation onto anhydrous uranyl nitrate of NO, SO_2, or vapors of benzene and cyclohexane—substances that do not form

with $UO_2(NO_3)_2$ of complex compounds stable in vacuum, a uniform decrease in the intensity of the glow of anhydrous uranyl nitrate at 90°K was observed, and in some cases luminescence was practically completely absent.

From all that has been said it follows that a necessary condition for the appearance of the luminescence-spectrum structure characteristic of uranyl compounds is the coordination, at the uranyl ion, of electron-donor molecules with the formation of sufficiently strong compounds.

Table 1

Comparison of the intensity maximum in the luminescence spectrum of coordination compounds of uranyl nitrate with quantities characterizing the electron-donor (basic) properties of the addends

Addend	λ_{max}, cm^{-1}	Basicity constant (11)	Infrared absorption $\frac{\Delta\nu}{\nu}$, % (12)	Infrared absorption $\frac{\Delta 3\nu}{3\nu}$, % (13)	Raman scattering $-\frac{\Delta\nu}{\nu}$, % (14)
NH_3	18850	10^{-5}	21.0		
C_5H_5N	18970	$8 \cdot 10^{-8}$	23.0		7.2
C_2H_5OH	19150	10^{-10}			
$(C_2H_5)_2O$	19850	10^{-16}	12.0	7.1	4.2
$O(CH_2)_4O$	19800	$2 \cdot 10^{-18}$			4.2
$(CH_3)_2CO$	19800	$2 \cdot 10^{-18}$	9.5	8.0	3.8
CH_3CN	18950				
$C_6H_5NO_2$	19800	$4 \cdot 10^{-25}$		3.1	
CH_3NO_2	20000			2.7	

Addend	λ_{max}, cm^{-1}	Basicity constant [11]	Infrared absorption $\frac{\Delta\nu}{\nu}$, % [12]	Infrared absorption $\frac{\Delta 3\nu}{3\nu}$, % [13]	Raman scattering $-\frac{\Delta\nu}{\nu}$, % [14]
NO_2	20270				
C_6H_6	–		2.9	2.5	1.7
C_6H_{12}	–				

It should also be noted that in the luminescence spectra of the complex compounds studied (with the exception of $UN \cdot 2C_6H_5NO_2$) a regular shift of the maximum of glow intensity toward lower frequencies is observed as the donor properties of the addend molecules increase. In an analogous manner, the short-wavelength band of the luminescence spectrum is shifted; its position to a certain extent characterizes the magnitude of the purely electronic transition. Table 1 gives the position of the intensity maximum in the structural luminescence spectrum of the complexes. As a characteristic of the donor properties of the addends, the basicity constants of some of them are indicated [11]. The following columns give the relative lowering of the frequency of the valence vibration and of the second overtone of the OH group of hydroxyl-containing molecules (phenol, methanol, surface OH), which is shifted as a result of interaction with the addends under consideration [12–14]. This quantity also characterizes the increase in the donor properties of the addends.

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