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G. N. LYALIN, G. I. KOBYSHEV

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Abstract

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G. N. LYALIN, G. I. KOBYSHEV

LUMINESCENCE OF THE URANYL COMPLEX WITH PHTHALOCYANINE

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The uranyl ion UO_2^{++}, when coordinated with a number of ligands, has a characteristic structured luminescence spectrum ([1,2]). The purpose of the present work was to investigate the luminescence of the complex of the uranyl ion with the tetrapyrrole pigment phthalocyanine (Pc), which, as is known, forms luminescent complexes with many divalent metal cations (Mg^{++}, Zn^{++}, etc.). It was expected that a luminescence spectrum characteristic of such phthalocyanines would be observed and, possibly, the luminescence of the coordinating uranyl cation itself, as well as transfer of excitation energy between them. For complexes with organic ligands, including porphyrins, of rare-earth elements, such a phenomenon has been observed repeatedly ([3–7]). An attempt to detect energy transfer in phthalocyanine complexes with rare-earth cations was recently made without a sufficiently clear result ([8]).

The uranyl complex with phthalocyanine was synthesized by V. F. Borodkin at the Ivanovo Institute of Chemical Technology from uranyl acetate and phthalic anhydride by a method analogous to that used for obtaining metallated phthalocyanines ([9]). The frequencies determined from the infrared absorption spectrum of the synthesized compound are summarized in Table 1, which

Table 1

Frequencies of infrared absorption bands characteristic of metallated phthalocyanines (I) and metal-free phthalocyanine (II), in cm^{-1} ([10])

	MPc	H_2Pc	UO_2Pc
I	888–917	874	878
	1060–1078	–	1055
			1068
	1481–1536	1503	1530
II	–	1304	1310
	–	1321	1325
	–	1007	1006

Table 2

Spectral positions of the maxima of the absorption bands of UO_2Pc, MPc, and H_2Pc, in mμ

UO_2Pc in dioxane	MPc in chloronaphthalene ([14])	H_2Pc in octane ([12])
661	660–670	690–694
632	640–649	652–655
598	600–610	639

also gives the values of the vibrational frequencies recommended in ([10]) for identifying metallated phthalocyanines in the solid phase. Frequencies of 1055, 1068, and 1530 cm^{-1}, which are observed in the spectrum of phthalocyanines containing a metal atom, are distinctly manifested in the spectrum. However, along with this, the presence of frequencies 1310, 1325, and 1006 cm^{-1}, close to the frequencies characteristic of free phthalocyanine (1304, 1321, and 1007 cm^{-1}), should be noted. The relative intensity of the last band in the complex is considerably smaller than in H_2Pc. A similar decrease in the intensity of this band is observed for silver phthalocyanine ([10]). In addition, a frequency of 920 cm^{-1} is observed, corresponding to the antisymmetric valence vibration of the uranyl cation, which in the complex is lowered

by 23 cm^{-1} compared with its value in uranyl acetate, from which the complex was synthesized.

Along with the results obtained in measuring the infrared absorption spectra, the existence of complex formation is indicated by the difference between the electronic absorption and luminescence spectra of a solution of uranyl phthalocyanine in dioxane and the spectra of an analogous solution of metal-free H_2Phc.

From Tables 2 and 3, in which the positions of the maxima of the absorption and luminescence bands of the uranyl phthalocyanine complex are compared with metallated and metal-free phthalocyanines, it follows that the spectral position of the maxima depends little on the solvent (dioxane, acetone, alcohol, etc.), but a substantial difference is observed between the absorption and luminescence spectra of UO_2Phc and those of the metal-free compound. The position of the maxima of the absorption-band spectrum—661, 632, and 598 mμ (290°K) —and of the luminescence spectrum—676, 710, and 748 mμ (77°K)—indicates the presence of a uranyl complex with phthalocyanine, in which the role of the coordinating metal atom is played by the uranyl ion.

Table 3

Spectral position of the maxima of the luminescence bands of UO_2Phc, MPhc, and H_2Phc at 77°K, in mμ

UO_2Phc in dioxane	UO_2Phc in nonane	MgPhc in octane [11]*	H_2Phc in dioxane [15]**	H_2Phc in octane [12]
676	684	674–676	693	690–693
	691			
	701			
709	722	709–710		
	727			725–727
747	751	748–750	733	729
	754			750
				754
	767			761
	776		771	765
				774
				776

* The position of the luminescence maxima of MgPhc is characteristic of metal-containing phthalocyanines.
** For $T = 290°K$.

It was established that the integral intensity of the luminescence of UO_2Phc decreases at 77°K and increases again when the temperature is raised (Fig. 1). The phenomenon is completely reversible and is reproduced many times on the same sample, i.e., an unusual temperature dependence of the luminescence is observed, whereas the luminescence of solutions in dioxane of metal-free H_2Phc and MgPhc has the usual temperature dependence.

To clarify the influence of the uranyl cation on the phthalocyanine component of the complex, and also to investigate the vibrational structure in the luminescence spectrum, the fine-structure spectrum of the UO_2Phc complex dissolved in nonane was obtained by the Shpol' skii method [11] at 77°K (Fig. 2b). In spectral position and in the set of vibrational frequencies it is analogous to the luminescence spectrum of Phc in a frozen octane solution [12]. The spectrum of metal-free H_2Phc reproduced by us (Fig. 2a) completely coincides with the spectrum given in [12]. The luminescence spectrum of the UO_2Phc complex differs substantially from the spectrum of H_2Phc in the distribution of intensity among the "lines" of the spectrum, and also in the considerably greater intensity of the 684 mμ "line." The concentrations of both H_2Phc and UO_2Phc were identical (10^{-5} M).

If a drop of a solution of UO_2Phc in dioxane is introduced into nonane, a short-wavelength maximum appears in the spectrum which is not observed in the spectrum of a solution of metal-free H_2Phc under analogous conditions. The unchanged basic set of vibrational frequencies appearing in the luminescence spectra of UO_2Phc and H_2Phc indicates a weak influence of the uranyl cation on the phthalocyanine skeleton.

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

It was of undoubted interest to elucidate the role, in the emission process, of the central coordinating uranyl cation. In clarifying the nature of the luminescent center in the UO_2Phc complex, a dependence of the luminescence spectrum on the wavelength of the exciting ···

light. The identity of the spectra obtained upon excitation of luminescence in the region of the complex' s own absorption (579 and 405 mμ) is in agreement with the law of independence of the luminescence spectrum of complex molecules in condensed media from the wavelength of the exciting light ([13]), and at the same time indicates the chemical purity of the preparation (Fig. 3). However, if luminescence is excited in the region of the longest-wavelength absorption band of uranyl (436 mμ)*, where the azaporphyrin ring has a minimum of its own absorption, a maximum appears at 692 mμ (at 290°K), characteristic of metal-free Phc (Fig. 3). Thus, the observed deviations from the above-mentioned law

Fig. 1. Photoelectric recording of the luminescence of a solution of uranyl phthalocyanine in dioxane: 1 –at 290°K, 2 –at 77°K

Fig. 2. Luminescence spectra of frozen solutions in nonane ($T = 77^{\circ}K$, $\lambda_{ex} =$ 366 mμ): a –H_2Phc; b –UO_2Phc

indicate the presence of at least two luminescing centers; in the present case it is meaningful to speak of the presence of two luminescent states within a single molecule.

The results of measurements of the luminescence spectra of UO_2Phc and their comparison with data on the positions of maxima in the spectra of H_2Phc and MgPhc are given in Table 3. When luminescence is excited in the absorption region of the uranyl ion, emission occurs mainly from the azaporphyrin skeleton of the molecule. If luminescence is excited in the absorption region of the complex, i.e., within its absorption bands 660-580 mμ, emission occurs from levels characteristic of metallated phthalocyanines. The series of maxima 676, 709, and 747 mμ is the result of luminescence of the elec–

* In the absorption spectrum of the uranyl complex with phthalocyanine, in this region there is a rise on the absorption curve.

of the electronic excitation of the complex as a whole. The series with the main maximum at 692 mμ at 290°K (686 mμ at 77°K), coinciding in spectral position with the luminescence spectrum of H_2Pc, arises upon transfer of energy from the uranyl cation to the system of π-conjugated bonds of the azaporphyrin ring of the UO_2Pc molecule, with emission from the electronic level of the latter.

Fig. 3. Luminescence spectra of a solution of UO_2Pc in dioxane under

Fig. 3. Luminescence spectra of a solution of UO_2Pc in dioxane under monochromatic excitation: a–at 290°K, b–at 77°K; 1–λ_ex = 405 mμ; 2–λ_ex = 579 mμ; 3–λ_ex = 436 mμ

Figure 2: Fig. 3. Luminescence spectra of a solution of UO_2Pc in dioxane under monochromatic excitation: a–at 290°K, b–at 77°K; 1–λ_ex = 405 mμ; 2–λ_ex = 579 mμ; 3–λ_ex = 436 mμ

monochromatic excitation: **a**–at 290°K, **b**–at 77°K; 1–λ_ex = 405 mμ; 2–λ_ex = 579 mμ; 3–λ_ex = 436 mμ.

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Leningrad State University
named after A. A. Zhdanov

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