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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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Energy Transfer from the Uranyl Cation to Phthalocyanine in Solution and in the Adsorbed State

The long lifetime, of the order of 10^{-4} sec, of the excited state of the uranyl cation UO_2^{2+}, manifested in its photochemical reactions and luminescence at low temperatures, should favor intermolecular transfer of excitation energy.

In the experiments described below, metal-free phthalocyanine (H_2Pc) and magnesium phthalocyanine (MgPc) were taken as luminescent energy acceptors, since they possess discrete absorption bands in the red region that do not overlap the uranyl bands, which made possible, to some extent, separate excitation of the components*.

Fig. 1. Luminescence spectrum of a solution of magnesium phthalocyanine and uranyl nitrate in ethanol at 290°K (1) and at 77°K (2)

The investigation was carried out on the same photoelectric spectrophotometer of high dispersion and on the high-intensity monochromator with a diffraction grating that were used in work ([1]), in which intramolecular transfer of excitation in a uranyl complex of phthalocyanine was studied.

Solutions of H_2Pc in dioxane and MgPc in ethanol were used at concentrations 10^{-4}–10^{-5} M; the uranyl nitrate or acetate added to the solution had a concentration in it of 10^{-3}–10^{-4} M. The source of exciting light was an HBO-500 mercury lamp. For excitation with light of 366 mμ, a combined light filter UFS-4 + SZS-10 was used. The spectral width of the slit was 30 cm^{-1} (60 cm^{-1} for the weaker uranyl luminescence).

Addition to solutions of H_2Pc in dioxane or MgPc in ethanol of a uranyl salt (uranyl nitrate or uranyl acetate) substantially changes the luminescence spectrum. A photoelectric recording of the luminescence of an MgPc solution in ethanol with uranyl nitrate at 290 and 77°K is given in Fig. 1. A spectrum is observed with the main maximum of MgPc luminescence at 673 mμ.

Figures 2–4

Figure 2: Figures 2–4

At 290°K only MgPc fluoresces; uranyl nitrate does not luminesce. Lowering the temperature to 77°K reveals in the luminescence spectrum of the MgPc solution, in addition to the maximum at 673 mμ, a strong band at 701 mμ, whose spectral position is close to the luminescence maximum of H_2Pc.

Without uranyl, the luminescence of the pigments upon excitation at 436 mμ is very weak. Addition of a uranyl salt to the pigment solution causes, under the same excitation (436 mμ), a 10–20-fold increase in fluorescence intensity (Fig. 2). The sharp enhancement of pigment fluorescence in the presence of the uranyl ion is accompanied in both cases (H_2Phc and MgPhc), at low temperatures, by the appearance of the main maximum at 701 mμ upon excitation of luminescence in the region of the weak, longest-wavelength absorption band of uranyl (436 mμ). The addition, instead of uranyl salts, of magnesium or vanadium nitrates and acetates causes no changes, which rules out an explanation of the fluorescence enhancement by an ionic effect on the high levels of the pigment molecules. At the same time, along with the enhancement of luminescence in the presence of the uranyl ion, an unusual temperature dependence of the luminescence is also observed; it is most clearly expressed in a solution of H_2Phc with uranyl acetate in dioxane (Fig. 3).

Fig. 2. Luminescence upon excitation at 436 mμ of a solution of H_2Phc in the presence of uranyl acetate in dioxane at 290°K (1) and, under the same conditions, of a solution of H_2Phc in dioxane without uranyl (2)

Fig. 3. Unusual temperature dependence of the luminescence of a solution of H_2Phc and uranyl acetate in dioxane at 290°K (1) and at 77°K (2)

Fig. 4. Dependence of the luminescence spectrum on the wavelength of the exciting light for MgPhc and uranyl nitrate in ethanol. 1 —λ_{ex}436 mμ at 77°K; 2 —λ_{ex}405 mμ at 77°K; 3 —λ_{ex}436 mμ at 290°K; 4 —λ_{ex}405 mμ at 290°K

Lowering the temperature of pigment solutions from 290 to 77°K, in the absence of uranyl, causes a comparatively small increase in the intensity of the fluorescence spectrum (upon excitation at 366 mμ). But in the presence of uranyl, if illuminated at 436 mμ (and also at other wavelengths), such lowering of the temperature with freezing of the solution leads to a sharp decrease in the emis-

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* Preliminary experiments on this subject, carried out several years ago by photographic and spectrophotographic methods of lower dispersion in a limited spectral region, did not give unambiguous results. In addition, in the acetone solution employed, an irreversible photochemical reaction occurred between UO_2^{2+} and MgPc.

sion intensity of both phthalocyanines. As follows from Fig. 4, illumination at 436 mμ in the absorption minimum of MgPhc gives, at 77 and 290°K, spectra comparable in intensity with those excited by light of 405 mμ, i.e., near the absorption maximum (390 mμ) of MgPhc.

The dependence of the spectra on the wavelength of the exciting light (405 and 436 mμ) is given in Fig. 4. At 77°K, alongside the pigment spectrum, weak fluorescence of the uranyl cation appears upon excitation at 366 mμ, with bands at 559, 534, 511, and 490 mμ (Fig. 1), which are considerably stronger in the absence of pigments, in agreement with energy transfer. The conditions for resonance

···of the resonance inductive mechanism of radiationless energy transfer in the system under consideration are not very favorable, since the emission bands of uranyl overlap only weakly with the absorption bands of the phthalocyanines. The situation here is analogous to the recently observed energy transfer from the triplet level of molecules to the excited singlet level of pigment molecules (2).

The fluorescence of the pigments observed under selective absorption of the exciting light by the uranyl cation indicates transfer of excitation energy from the uranyl ion to the pigment molecule; however, the fluorescence spectrum of the energy acceptor is the same for both phthalocyanines, i.e., at low temperature, under selective excitation of the uranyl cation (436 mμ), the most intense maximum at 701 mμ appears in both cases, and the maximum characteristic of metal-containing phthalocyanines (MgPhc) is absent from the spectrum. Excitation at room temperature with wavelengths of 405 and 366 mμ clearly reveals the existence of this maximum (Figs. 1 and 4).

The absence in the MgPhc spectrum of the 673 mμ maximum under selective excitation of the uranyl ion (436 mμ), and the similarity of the spectra observed for solutions of both pigments at low temperatures, indicate the manifestation in both cases of a luminescent carrier of the same nature, with preservation of the system of π-conjugated bonds of the phthalocyanine molecular ring.

To investigate energy transfer with the indicated systems in the adsorbed state, either H_2Phc or MgPhc was first introduced from solution into powdered magnesium oxide gel, and then uranyl nitrate was additionally precipitated from aqueous or ethanol solution.

Table 1

Position of maxima in the luminescence spectrum of MgPhc + uranyl nitrate/magnesium oxide (immersed in nonane). Wave numbers are given in cm^{-1}

MgPhc + uranyl nitrate/magnesium oxide	MgPhc + uranyl nitrate/magnesium oxide	MgPhc + uranyl nitrate/magnesium oxide	MgPhc + uranyl nitrate/magnesium oxide	MgPhc + uranyl nitrate/magnesium oxide	MgPhc + uranyl nitrate/magnesium oxide	MgPhc in ethanol	H_2Phc in dioxane
λ_{ex} 579 mμ	λ_{ex} 579 mμ	λ_{ex} 405 mμ	λ_{ex} 405 mμ	λ_{ex} 436 mμ	λ_{ex} 436 mμ	MgPhc in ethanol	H_2Phc in dioxane
77 °K	290 °K	77 °K	290 °K	77 °K	290 °K	290 °K	290 °K
	15150		15040				
	14730		14730			14840–14800	–
14570	14570	**14600**		**14570**	**14570**	–	14500–14390
	14390	**14400**	**14350**				
13950	14090	13900	14030	13900	14030	14100–14090	–
		13640	13660			–	13790–13720
13210	13250	13260		13200	13260	–	13330–13260

Excitation with 366 mμ light at 77°K of the MgPhc + uranyl adsorbate reveals in the fluorescence spectrum an intense main pigment maximum at 685 mμ and side maxima at 720 and 755 mμ, shifted to the long-wavelength side by 10–20 mμ as compared with the solution, while the frequency intervals are preserved. Immersion of the adsorbate in nonane promotes manifestation of the spectral structure, greatly increasing the intensity of the green luminescence (of the surface crystal) (3), which should probably be explained by weakening of the action of the surface. Washing-out of the pigment is not observed in this case, i.e., the increase in luminescence is not connected with removal of concentration quenching. In addition, the spectrum contains weak maxima at 508 and 487 mμ of the hydrated uranyl cation in the adsorbed state (3), and a broad maximum at 560 mμ, with a half-width of 3000 cm^{-1}, belonging to the dehydrated uranyl cation (4). Upon illumination at 436 mμ of an adsorbate of MgPhc/MgO alone, both at 77°K and at 290°K, no pigment luminescence is observed. In the presence of adsorbed

uranyl, and with the same excitation it appears only at 77°K. Immersion of the combined adsorbate in nonane and its freezing lead, under illumination at 436 mμ, to the appearance of a bright spectrum of adsorbed MgPc with distinct maxima at 685 (principal), 720, and 755 mμ. Their intensity is comparable with that produced by excitation at wavelengths of 579 and 405 mμ, absorbed directly only by MgPc. Bands are also present in the green region of the spectrum of hydrated uranyl. Thus, in the adsorbed state there is a selective spectral action of wavelengths absorbed by the hydrated uranyl cation, as a result of which phenomena are observed that are analogous to those in a binary solution or in a complex.

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