

THE MECHANISM OF LUMINESCENCE PROCESSES AND THE STRUCTURE
OF COMPLEX COMPOUNDS FORMED BY MANGANESE(II) WITH
PAPAVERINE HYDROCHLORIDE IN SOLID STATE *

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Manganese(II) halides combine with the hydrochlorides of some organic bases (pyridine, piperidine, quinoline, isoquinoline and their derivatives) to give complex compounds existing only in solid state^{/1/} and exhibiting photoluminescent properties. The photoluminescence of the complexes formed by manganese(II) chloride with papaverine hydrochloride has already been observed^{/2/} previously. In the present work the luminescent properties have been studied in detail by analyzing the absorption spectra of corresponding solutions and the excitation and emission spectra of the solid state at different temperatures. On the basis of these properties it has been established that two complex species are formed: one with an emission peak in the green region of the spectrum, of a formula $(PAPH)_2MnCl_4$, and another with an emission maximum in the red, of formula $PAPHCl.MnCl_2$. Ethanol solutions of these complexes do not display any luminescence properties, while the absorption spectra of the solutions show that a decomposition of the complex compounds takes place.

The excitation spectra were recorded at the temperature of liquid nitrogen. Corrections for the spectral characteristics of the light source-monochromator system and a resolution of the spectrum into Gaussians were carried out on a computer^{/3/}. They were interpreted in terms of ligand field theory. The values of the Racah parameters B and C (see Tab.) were determined from the positions of the 4A_1 , $^4E(^4G)$ and $^4E(^4D)$ bands whose energy is independent of ligand field strength, while those of the ligand field parameter, $10Dq$, were derived from the Orgel weak field matrix for triplet states of d^5 configuration^{/4/}. The value thus obtained for $10Dq$, as well as the position of the emission peak, show that the central manganese(II) ion in the $(PAPH)_2MnCl_4$ complex is in a field of tetrahedral symmetry. For the compound

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T a b l e .

Compound	B (cm ⁻¹)	G (cm ⁻¹)	10Dq (cm ⁻¹)
(PAPH) ₂ MnCl ₄	530	3 560	4 500
PAPHCl.MnCl ₂	505	3 657	4 800

PAPHCl.MnCl₂ the position of emission band peak is indicative of the existence of an octahedral coordination of manganese(II), whereas the theoretically derived value of 10Dq is inconsistent with the assumption of such a type of binding.

The temperature dependence of the emission spectrum has been studied only for the (PAPH)₂MnCl₄ complex, since the other compound is unstable at higher temperatures. The temperature dependence of the intensity (i.e. of the glow peak and of total glow) was fitted by the Mott-Seitz law, while that of the emission band half-width (L) was fitted by a recently proposed formula^{5/} on a computer. On the basis of values obtained for quenching temperature (T_q), excited state frequency (ν_e) and experimentally determined values of emission spectrum peak (λ_0) and of the constant α/m , equations were derived for the potential energies of the ground state (U_g) and of excited state (U_e) as a function of configurational coordinate (r):

$$U_g = 571 r^2, \quad U_e = 89.7 r^2 - 3.73 r + 2.651;$$

where U and r are expressed in eV and Å, respectively.

From these studies it has been assumed that the complex manganese(II) ion is a luminescence center and that the emission is due to the ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ transition. Since this transition is accompanied by a change in multiplicity, it represents a slow process of low probability, which has experimentally been established by recording with a phosphoroscope.

R e f e r e n c e s

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