A CONTRIBUTION TO THE STUDY OF LUMINESCENCE OF CRYSTALLINE COMPLEXES FORMED BY MANGANESE(II)CHLORIDE

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Manganese(II)chloride combines with 3,5-lutidine (3,5-dimethylpyridine) to give two crystalline complex compounds:(I) a 2:1 complex of $MnCl_2$ with 3,5-lutidine hydrochloride, where the Mn^{2+} ion is in tetrahedral symmetry; (II) a 1:1 complex, where the Mn^{2+} ion is in octahedral symmetry. Both complexes exhibit an intense photoluminescence: the first a green one, and the second a red one. They belonge to the class of complexes having a nitrogen atom in organic ligand (external coordination sphere). The absorption spectra of the complex compounds in ethanol show that the complexes as such do not exist in solution.

The grount term of the free Mn^{2+} ion is ^6S; the process of excitation proceeds to the ^4G, ^4D, ^4P and ^4F quartet terms which, due to the orbital degeneracy caused by a ligand field strength of 10 Dq, are split into ten energy levels, viz. $^4G(^4T_1, ^4T_2, ^4E, ^4A_1)$, $^4D(^4T_2, ^4E)$, $^4P(^4T_1)$ and $^4F(^4A_2, ^4T_1, ^4T_2)$, while the luminescence process is associated with the $^4T_1(G) - {}^6A_1(S)$ transition.

All the transitions were observable in the excitation and emission spectra of both complexes (Table 1).

Table 1.

EXCITATION SPECTRA-MAXIMUMS (nm)										
	$^4T_1$	$^4T_2$	$^4A_1$	^4E	$^4T_2$	^4E	$^4T_1$	$^4A_2$	$^4T_1$	$^4T_2$
(I)	470	452,5 445 442,5	432,5	427,5	382,5 370	357,5	325	280	260	220
(II)	542,5	450	417,5		367,5	350	335	292	243	226
	(G)				(D)		(P)	(F)		
EMISSION SPECTRA-MAXIMUMS (nm)										
(I) 510					(II) 640					

In compound I, the $^4T_2(G)$ and $^4T_2(D)$ levels are split. The Racah parameters B and C (1) were determined experi-

mentally from the condition of independence of $^4A_1(G)$ and $^4E(D)$ terms of ligand field strength, 10Dq:

$$B = 693\ cm^{-1};\ C = 3238\ cm^{-1}.$$

The Racah parameters for compound II are:

$$B = 659{,}8\ cm^{-1};\ C = 3470\ cm^{-1}.$$

A thermal analysis of the emission spectra of comp.I enables the energy scheme of the emission center Mn^{2+} to be presented by single-configurational-coordinate method(2). By fitting to corresponding laws the following equations were obtained:

- for the temperature variation of luminescence intensity:

$$I = 108{,}3./1 + 502\ \exp(-1203/T)/$$

hence the activation energy for quenching is W=0.1037 eV;

- for the temperature variation of band half-Width:

$$1/L^2 = 0{,}268.10^{-2} tgh(201/T) + 0{,}942.10^{-3}$$

whence the excited state frequecy is found to be

$$n_e = 0{,}8379.10^{13} s^{-1}.$$

The ratio of coefficient a to m is constan for any temperature: $a/m = -0{,}38.10^{-4}$ cm.

The potential energies of the ground and excited states are given by the relations :

$$U_g = 110\ R^2 \text{ (in eV)};\ U_e = 7{,}88R^2 - 0.680R + 2{,}650 \text{ (in eV)}.$$

A theoretically determined value for absorbance maximum from a corresponding diagram is $\lambda_{max} = 467{,}7$ A, while the excitation peak of the $^4T_1(G)$ band is $\lambda_{max} = 470$ A, which is in a satisfactory agreement.

In recording the emission spectra use was made of a phosphoroscope, which provides an experimental corroboration to the assumption that the emission process is associated with transitions between states of different multiplicity (phosphorescence).

References

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