

## FLUORESCENT PROPERTIES OF SOME MANGANESE CHLORIDE COMPOUNDS WITH METHYLQUINOLINE HYDROCHLORIDE

I. BURIC, K. VELAŠEVIĆ and K. NIKOLIĆ

*Institute of Physics, Beograd*

Received 10 February 1968; revised manuscript received 8 March 1968

**Abstract:** The luminiscence of complex manganese chloride compounds with methylquinoline hydrochloride has been investigated. These compounds have green or red fluorescence and the emission spectra are given. The spectra of substances with green fluorescence can be represented by a function which is close to the Gaussian distribution. It is found that the  $Mn^{++}$  ion is a luminophor with the transition from the excited state  ${}^4G$  into the ground state  ${}^6S$  giving rise to fluorescence.

### 1. Introduction

The fluorescence of quinoline in acid solutions has been observed by S. Sljivić<sup>1, 2, 3)</sup>, who has systematically investigated heterocyclic compounds with nitrogen atoms. The fluorescent properties of manganese chloride compounds with pyridine and quinoline hydrochloride have also been investigated<sup>4)</sup>.

In many phosphori the  $Mn^{++}$  ion is a part of the luminophor which is active in the luminescent processes of recombination. In complex organic-inorganic compounds the  $Mn^{++}$  ion is included into the electronic system of molecule. Thus changes in molecular structure can affect the electron configuration of the luminophor, and consequently the spectral distribution of the emitted light.

In order to investigate the effect of such changes in complex manganese chloride compounds, we synthesized several compounds with methylquinoline hydrochlorides which differ by the position of the methyl group in the quinoline ring. The fluorescent properties of these compounds were compared with the fluorescent properties of some other compounds of similar structure and so the effect of the molecular configuration on the behaviour of the luminophor was determined.

### 2. Experimental

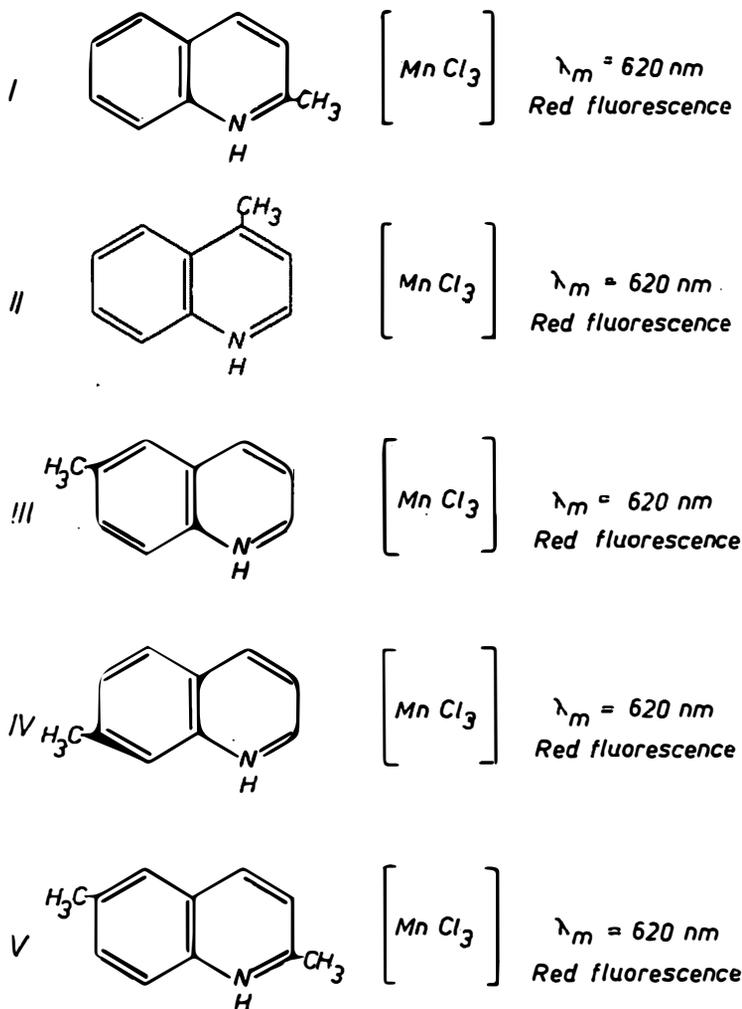
The investigated compounds are given in Fig. 1., while their characteristics are described in ref.<sup>5)</sup>.

Fluorescent spectra were measured by the attachment for the Beckman spectrophotometer DU 2. Some measurements were also performed by a spe-

cially constructed spectrophotometer consisting of a Carl Zeiss Jena monochromator (Type SPM 1) with an aperture ratio of 1 : 6.7, a flint glass prism and a photomultiplier with a recording instrument.

For measurements of red fluorescence a photomultiplier tube M12-35 from Carl Zeiss Jena was used. For the measurement of green fluorescence a 50 AVP photomultiplier from Philips was employed.

The excitation of the sample enclosed in a quartz cell was obtained by the light of a high pressure Philips HPW125 W lamp with a Wood filter for the Hg line of 366 nm. The measurements were performed at room temperature.



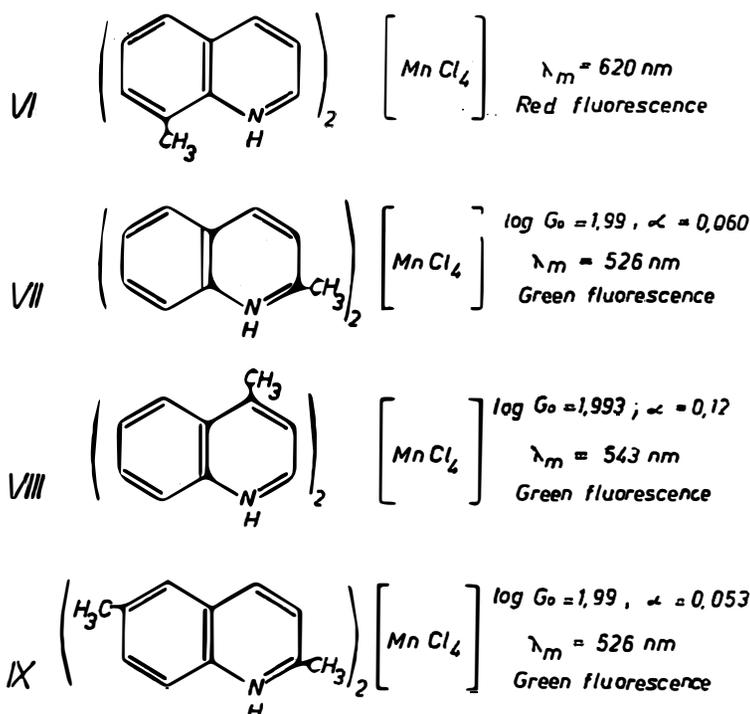


Fig. 1. Formulae of the compounds.

### 3. Results

The emission spectra of the investigated compounds consist of broad bands in the visible region. Typical fluorescent spectra for substances with green or red fluorescence are shown in Fig. 2. The wavelengths of the intensity maxima of the fluorescent spectra are given in Fig. 1.

The positions of the maxima of fluorescent spectra of the compounds with red fluorescence are the same as those found by H. Payen<sup>6)</sup> for the complex compound of manganese chloride with quinoline hydrochloride, while the positions of the maxima for the compounds with green fluorescence differ. For the manganese chloride compound with 4-methylquinoline hydrochloride the maximum occurs at 543 nm, while in the other two compounds it is at 526 nm.

The characteristic shape of fluorescent spectra of substances with green fluorescence makes it possible to represent the emission process by a graph of transition matrix element  $G$  given by

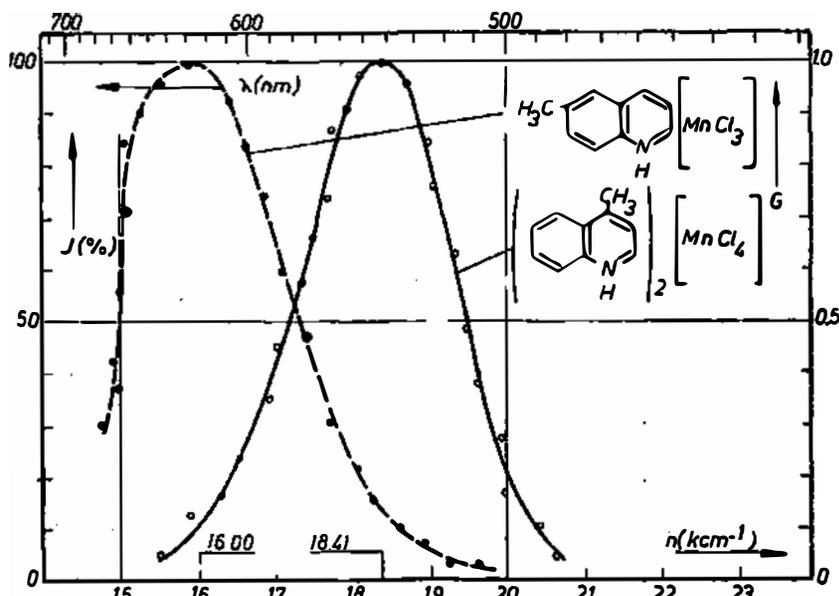


Fig. 2. Typical fluorescent spectra of the substances investigated.

$$G = \frac{I(\lambda)}{n^4}, \quad (1)$$

where  $I(\lambda)$  is the intensity for different wave lengths.

The obtained curve shown in Fig. 3 is close to the Gaussian distribution curve and can be represented by

$$G\left(\frac{1}{\lambda_1}\right) G\left(\frac{1}{\lambda_2}\right) = G_0 \exp\left[-\alpha\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)^2\right]. \quad (2)$$

$\alpha$  and  $G_0$  are constants obtained from the fluorescent spectra for different wavelengths ( $\lambda_1, \lambda_2$ ) and the same intensities. Their values for the complex compounds investigated are given in Fig. 1.

#### 4. Discussion

In the observed manganese-methylquinoline hydrochloride the quinoline ring with one proton attached to the nitrogen atom and  $Mn^{++}$  ion is probably the centre of luminescence. According to Knight<sup>7)</sup>, the absorption in methylquinoline with one proton attached to the nitrogen atom is the result of the  $\pi \rightarrow \pi^*$  transition in the electron system. This transition causes the violet-blue fluorescence in all methylquinoline hydrochlorides in solid state as well as in solutions.

According to Curie<sup>8)</sup>, the ground state of the  $Mn^{++}$  ion is  ${}^6S$  characterized by  $(3d)^5$  electrons with parallel spins. The first excited state is  ${}^4G$  due to the change of spin of an electron. Further excited states are  ${}^4P$ ,  ${}^4D$  and  ${}^4F$ . The energy difference between the ground state and the first excited state is 3.32 eV.

The transition into the quoted states is forbidden in the case of free  $Mn^{++}$  ions. Nevertheless, if the ion is included into a crystal lattice, a change of the spin momentum may occur due to the interaction between the  $Mn^{++}$  ion and the ions of the crystal lattice. In the case of zinc ortho phosphate activated by  $Mn^{++}$  ion, the maximum in the fluorescence spectrum appears at 630 nm,

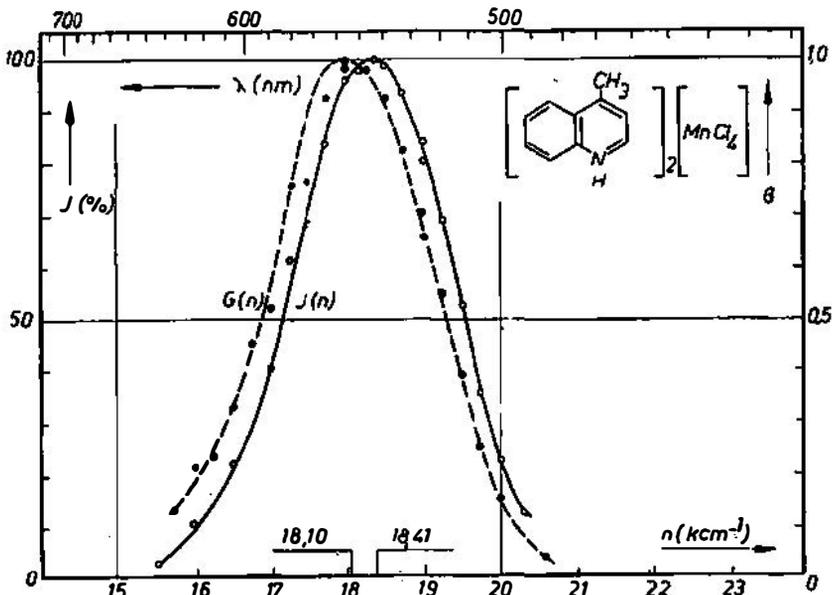


Fig. 3. The graphs of the transition matrix element  $G(n)$  and of the intensity  $I(n)$  as functions of the wave number characteristic of substances with green fluorescence.

while for  $Zn_2SiO_4$  it is at 520 nm. This indicates that such transitions are possible in phosphori. Since the maxima of the examined fluorescence spectra are found in the same spectral region, we assume that the  $Mn^{++}$  ion is a luminiphor and that the fluorescence occurs on account of the transition from the excited state  ${}^4G$  into the ground state  ${}^6S$ . This assumption is supported by the fact that water solutions of these compounds show violet fluorescence, which means that the quinoline ring takes over the role of a luminiphor and that red and green fluorescences are connected with solid state only. This mechanism is plausible for fluorescence, since for the transition of an electron from the term  $(3d)^4 4s$  an energy of 7.2 eV is required and there is little possibility for such a transition.

Green fluorescence occurs mainly in compounds with two molecules of methylquinoline. The only exception is a manganese chloride compound with 8-methylquinoline hydrochloride which shows red fluorescence. The same occurs with  $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$  and  $(\text{C}_2\text{H}_5\text{NH}_3)\text{MnCl}_4$  as found by Payen<sup>6</sup>. These compounds also show red fluorescence though green fluorescence is expected as in the case of most compounds of the same structure. The pre-

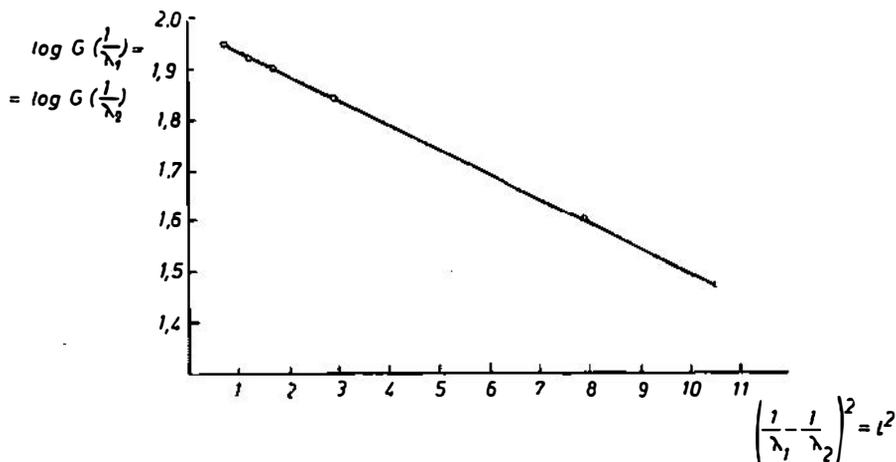


Fig. 4. The function  $\log G(l^2) = \log G_0 - a \log e l^2$  obtained for the manganese chloride compound with 4-methylquinoline hydrochloride.

sence of the methyl group in position 8 in the quinoline ring and in the close proximity of the nitrogen atom is very likely to affect the interaction between the quinoline ring and the  $\text{Mn}^{++}$  ion, leading to the appearance of red fluorescence as it is found in the amines mentioned.

In the manganese chloride compound with 4-methylquinoline hydrochloride there a displacement of the maximum is found towards longer wavelengths, while that is not the case with the other two compounds with green fluorescence. This occurrence could be attributed to the symmetrical position of the methyl group relative to the nitrogen.

The analysis of energy intensity distribution as function of the wave number indicates that the transition matrix element function for the fluorescent spectra of substances with green fluorescence, may be represented by

$$\log G(l^2) = \log G_0 - a \log e l^2$$

$$l^2 = \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)^2 \quad (3)$$

Figure 4 shows this function obtained for the manganese chloride compound with 4-methylquinoline hydrochloride. The constants  $G_0$  and  $\alpha$  may be used for the identification of these compounds as the specific fluorescence is characteristic.

Therefore according to Curie<sup>8)</sup>, it may be expected that the arithmetic mean values of the abscissae for the equal values of the ordinates  $\log G_{(n)}$  lie on a straight line. In Fig. 5 the corresponding curve of  $\log G_{(n)}$  is shown.

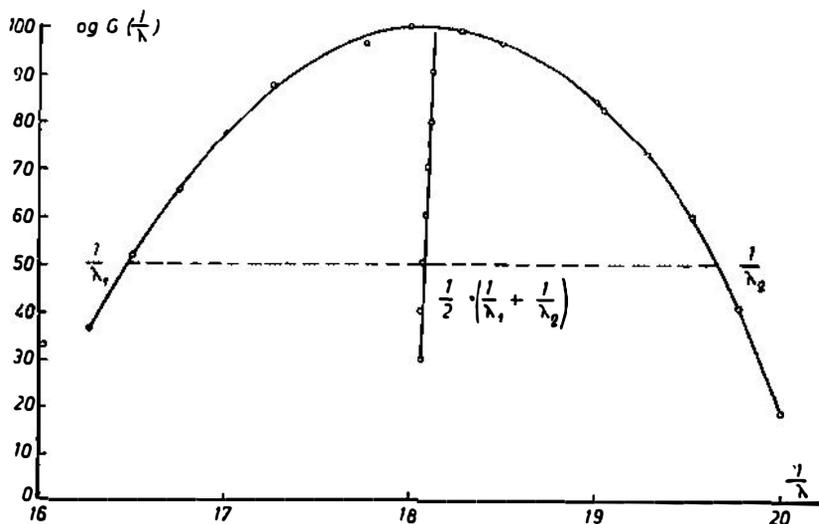


Fig. 5. The curve of  $\log G_{(n)}$  with the arithmetic mean values of the abscissae obtained for the manganese chloride compounds with 4-methylquinoline hydrochloride.

In our case the agreement with this theory is only partial, the reason may be in the fact that the theory based on the diagrams of the configuration curves implies the behaviour on Franck and Condon principles<sup>8)</sup>. The disagreement may be attributed to the change of the position of the chlorine surrounding the  $Mn^{++}$  ion which probably occurs during the emission.

### Literature

- 1) S. Šljivić, Z. Anal. Chem., 143 (1954) 113;
- 2) S. Šljivić, I. Burić, K. Nikolić, Z. Anal. Chem., 145 (1955) 16;
- 3) S. Šljivić, Bull. soc. chim. Beograd, 23, (1959) 239;
- 4) K. Nikolić, H. Payen de la Garanderie, S. Schlivitch, Comptes rendus, 250 (1940), 414;
- 5) K. Nikolić, K. Velašević and A. Djukanović, Bull. soc. chim. Beograd - to be published;
- 6) H. Payen de la Garanderie, Comptes rendus, 254 (1962) 2739;
- 7) S. Knight, Jour. Am. Chem. Soc., 77 (1955) 2577.
- 8) D. Curie, Luminescence cristalline, Dunod, Paris, 1960.

FLUORESCENTNE OSOBINE KOMPLEKSNIH JEDINJENJA  
MANGANOHLORIDA SA METILHINOLINHIDROHLORIDIMA

I. BURIĆ, K. VELAŠEVIĆ i K. NIKOLIĆ

*Institut za fiziku, Beograd*

## S a d r ž a j

Ispitivane su fluorescentne osobine kompleksnih jedinjenja manganohlorida sa metilhinolinhidrochloridima. Proučavana jedinjenja razlikovala su se po položaju metil grupe u hinolinskom prstenu i po broju metilhinolinhidrochlorida vezanih za manganohlorid.

Iz emisionog spektra kod supstanci sa zelenom fluorescencijom, mogla se konstruisati kriva matričnog faktora prelaza u funkciji talasnog broja, koja ima oblik blizak Gauss-ovoj raspodeli.

Konstatovano je da je  $Mn^{++}$  jon luminofor koji prelaskom iz ekscitovanog  $^4G$  stanja u osnovno  $^6S$  stanje daje fluorescenciju.

Kod jedinjenja sa zelenom fluorescencijom dobivena su samo delimična slaganja sa teoriskim računom za izračunavanje modela konfiguracionih krivi iz emisionih spektara. Smatramo da se odstupanja mogu pripisati činjenici, što pri emisiji dolazi do promene položaja hlorovih atoma koji okružuju  $Mn^{++}$  jon.