

THE EFFECT OF STRUCTURE ON THE FLUORESCENCE AND  
REFLECTANCE SPECTRA OF MANGANESE CHLORIDE COMPOUNDS  
WITH DERIVATIVES OF PYRIDINE AND QUINOLINE  
HYDROCHLORIDES\*

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*Abstract:* The dependence of fluorescence and reflectance spectra on the structure of manganese chloride compounds with hydrochloride derivatives of pyridine and quinoline is investigated. These compounds show red or green fluorescence. It is supposed that green fluorescence is due to  $Mn^{2+}$  in four-fold coordination, and that red fluorescence is due to  $Mn^{2+}$  in six-fold coordination. The character of spectral distribution of fluorescence may be represented by the function

$$\log G(l^2) = \log G_0 - \alpha l^2 \log e l^2 = \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)^2$$

where constants  $G_0$  and  $\alpha$  indicate to the effect the ligand structure has on emittance center of  $Mn^{2+}$  ion.

The reflectance spectra of manganese chloride compounds with derivatives of pyridine hydrochloride, posses pronounced structure in the range 400—500 nm, contrary to the compounds with hydrochloride derivatives of quinoline which do not possess marked peaks in this region. From the reflectance spectra it may also be concluded that the transition  ${}^6S \rightarrow {}^4G$  occurs in the absorption.

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## 1. Introduction

The electronic structure of manganese (II) high spin complexes is the subject of theoretical interest<sup>1-8)</sup> and considerable experimental study. The absorption spectra of these compounds both in crystal form and solution have been also investigated. The mechanism of the formation of absorption spectra was usually accounted for by a simple field theory which has not always been satisfactory but it made possible certain valuable conclusions to be drawn.

Some complex manganese compounds show fluorescent properties which come from the manganese (II) ion whose fluorescence is influenced by ligands by which it is surrounded. Therefore spectral distribution of fluorescence of these compounds is specific. From theoretical postulates<sup>9-14)</sup> based on configuration coordinate curves used to account for the absorption and emission processes in solids, the dependence of fluorescence spectra on the structure of the investigated complex manganese compounds has been investigated. Their reflectance spectra have also been studied. The obtained results contribute to the explanation of the absorption mechanism.

## 2. Experimental

*Apparatus.* Fluorescence spectra were measured at room temperature with the Aminco-Bowman spectrophotofluorimeter. The obtained spectra were corrected according to the method of Lippert et al<sup>15)</sup>. The measurement of reflectance spectra was performed by spectrophotometer Beckman DU-2 with the standard attachment for the measurement of reflectance spectra and magnesium carbonate as the reference sample.

*Preparation of compounds.* 2 pyridine + MnCl<sub>2</sub>, 2 quinoline + MnCl<sub>2</sub>, 2 2-methylquinoline + MnCl<sub>2</sub> and 2 2,6-dimethylquinoline + MnCl<sub>2</sub> were synthesized by mixing ethanol solutions containing equivalent quantities of manganese chloride and the corresponding heterocyclic base.

2 pyridine + 2HCl + MnCl<sub>2</sub>, 2 2-methylpyridine + 2HCl + MnCl<sub>2</sub>, 2 2,6-dimethylpyridine + 2HCl + MnCl<sub>2</sub>, 2 quinoline + 2HCl + 2 2-methylquinoline + 2 HCl + MnCl<sub>2</sub>, 2 2,6-dimethylquinoline + 2 HCl + MnCl<sub>2</sub>, pyridine + HCl + MnCl<sub>2</sub> and quinoline + HCl + MnCl<sub>2</sub> were obtained by mixing the ethanol solution containing equivalent quantities of manganese chloride and the corresponding heterocyclic base. After the solution has been mixed, the hydrochloric acid was added to the excess. By slow evaporation in the water bath the crystals were obtained which were recrystallized from ethanol.

### 3. Results and discussion

Manganese chloride which crystalizes with four molecules of water does not show fluorescence. By removing water, red fluorescence appears whose spectral distribution could not be measured due to its low intensity. The compound with the ratio of pyridine and manganese chloride 2 : 1 does not show fluorescence. The same was observed by the quinoline compounds with manganese chloride. Nevertheless, by manganese chloride compound with 2-methylquinoline and 2,6-dimethylquinoline, green fluorescence appears probably due to the introduction of the methyl group into the quinoline ring.

All the manganese chloride compounds with derivatives of pyridine and quinoline containing also hydrochloric acid in which the ratio of heterocyclic base and manganese chloride is 2 : 1, show green fluorescence, while in the case where this ratio is 1 : 1 the fluorescence is red. Nevertheless the colour of fluorescence does not depend only on this ratio. For example, methylamine hydrochloride and ethylamine hydrochloride make complex compound with manganese chloride which shows red fluorescence. In this case the ratio of amine base and manganese chloride is 2 : 1 so that green fluorescence is expected.

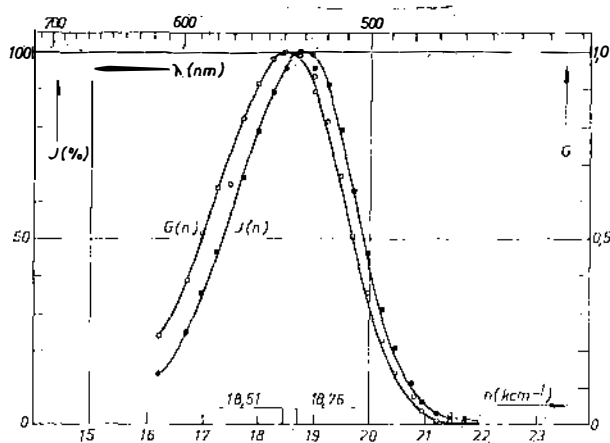


Fig. 1. The graphs of transition matrix element  $G(n)$  and of the intensity  $J(n)$  as functions of the wave number characteristic for substance with green fluorescence.

Investigating the absorption and fluorescence spectra of divalent manganese in different glasses, Bingham and Parke<sup>15)</sup> have found that the silicate glasses in which the manganese ion is tetrahedrally coordinated, show green fluorescence. The phosphate and borate glasses in which  $Mn^{2+}$  has octahedral symmetry, showed red-orange fluorescence. In this way the conclusion of Linwood and Weyl<sup>16)</sup> that green fluorescence is due to  $Mn^{2+}$  in four-fold coordination and that red fluo-

rescence is due to  $Mn^{2+}$  in six-fold coordination, was confirmed. Since the  $Mn^{2+}$  ion was found to be the luminescence center of the investigated complex compounds, it is supposed that in this case also the corresponding colour of fluorescence is caused by the same symmetry.

By the investigated compounds of tetrahedral structure, the pyridinium and quinolinium ions are found to be the cations, while  $[MnCl_4]^{2-}$  is found to be the anion due to which green fluorescence occurs. Robert et al.<sup>17)</sup> found from infrared spectra that the cation of pyridinium is bonded to the anion  $[MnCl_4]^{2-}$  by hydrogen bridge which bond is found to be stronger with chlorine than with bromine. It is interesting to mention here that quinolinium ion in solid state shows violet-blue fluorescence, while in complex compounds with  $MnCl_2$  this fluorescence disappears. The disappearance of fluorescence is probably due to the bond between the quinolinium ion and the complex anion. The presence of the ion of heterocyclic base in the complex compound, in most cases only slightly contributes to the change of the character of fluorescence spectral distribution.

The investigated compounds show green or red fluorescence only when in solid state. In water or ethanol solution they lose this property because electron transitions which cause photoluminescence in solid state are forbidden in the free  $Mn^{2+}$  ion.

The free manganese ion has a  ${}^6S$  ground term and quartet terms  ${}^4G$ ,  ${}^4P$ ,  ${}^4D$  and  ${}^4F$ . Tetrahedral and octahedral symmetries cause the splitting of these levels so that the number of levels from which the transitions into the absorption or energy emission are also possible, is increased. The energy used for the excitation of the investigated complex manganese compounds being of the wavelength 366 nm, the transition  ${}^6S \rightarrow {}^4G$  was possible. According to Cotton and Goodgame<sup>18)</sup>, by the manganese chloride compounds with pyridine hydrochloride the levels due to  ${}^4G$  are:  ${}^4T_1({}^4G)$ ,  ${}^4T_2({}^4G)$  with different energies, and  $E({}^4G)$ ,  ${}^4A_1({}^4G)$  with the same energy. According to Medlin<sup>19)</sup> who has investigated the emission spectra of calcite, dolomite, magnesite and anhydrite activated by  $Mn^{2+}$ , the transition for red fluorescence is  ${}^4T_1({}^4G) \rightarrow {}^6A_1$ , while for green fluorescence is  ${}^4T_2({}^4G) \rightarrow {}^6A_1$ . It is supposed that the same transitions cause the corresponding fluorescence by the investigated complex manganese compounds also.

In the theory of electronic vibrational transitions in crystals and complex molecules, one-coordinate methods are often introduced. With regard to the vibrational energy such systems are analogous to one-dimensional oscillators. Using this method, Von Hippel<sup>20)</sup> and later Seitz<sup>21)</sup> tried to explain qualitatively the absorption and emission processes in inorganic solids. They considered the energy conditions of the luminescence center as function of the configurational coordinate. The potentials of the ground and first excited states have vibrational energy levels. The minima of the potentials give the equilibrium positions which do not coincide except in the case of resonance. Optical transition within this model can be described according to the Franck-Condon principle.

Williams<sup>22)</sup> has applied this model to a Tl ion luminescence center in KCl. Other configuration coordinate curves were compared from experimental data by Klick and Schulman<sup>23)</sup> for a  $Mn^{2+}$  ion center in  $Zn_2SiO_4$ , and by Vlam<sup>24)</sup> for centers in silicates and tungstates. These authors used an approximation by considering the luminescence center a single harmonic oscillator. Thus the potential curves of the ground and excited states are parabolic in shape. Another valuable contribution based also on harmonic oscillator approximation was made by Payen de la Garanderie<sup>10)</sup>, whose method requires less experimental work for the construction of the diagrams. This author proposes an analytical expression for the relative intensity of the luminescence band as a function of the frequency.

The form of the spectral distribution of complex compounds with green fluorescence is such that it was possible to apply the relations which come from the theories based on harmonic oscillator approximation. The characteristic curve of spectral distribution by the compounds with green fluorescence is shown in Fig. 1.

From the experimentally determined function of energy distribution according to the wave number, the graph of the transition matrix factor ( $G$ ) in function of the wave number ( $n$ ) is plotted by dividing the intensity of the fluorescent light ( $\mathcal{J}$ ) with the corresponding wave number involved to the fourth power

$$G = \frac{\mathcal{J}}{n^4}.$$

The obtained function of the transition matrix factor is very close to the Gaussian curve and may be given as

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

where  $G_0$  and  $a$  are the characteristic constants, while  $\frac{1}{\lambda_1}$  and  $\frac{1}{\lambda_2}$  are the wave numbers for the same value of function  $G$ .

The logarithmic form of this function is given in Fig. 2.

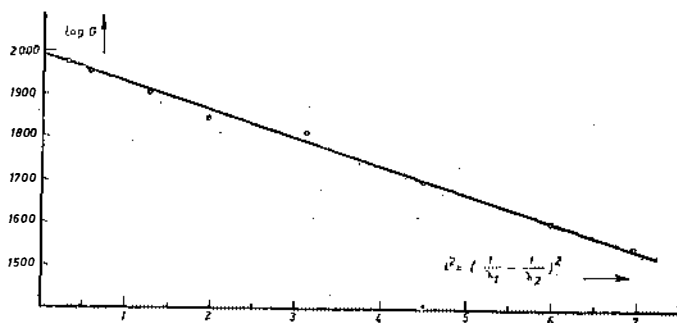


Fig. 2. The function  $\log G (l^2) = \log G_0 - a l^2 \log c$  obtained for the manganese of alkyipyridine and alkyquinoline bases.

In all the cases where spectral distribution could be represented by the linear logarithmic function, the calculation of characteristic constants  $G_0$  and  $\alpha$  was possible which give the insight into the structural dependence of fluorescent properties of complex manganese compounds. By a great many of manganese chloride compounds with hydrochlorides of heterocyclic bases, the fluorescence spectral distribution could be represented in this manner so that constants  $G_0$  and  $\alpha$  are important indicators which give the insight into the fluorescent properties of these compounds, what is not possible to achieve by other procedures.

The reflectance spectra of the complex manganese chloride compounds with derivatives of pyridine are shown in Fig. 3.

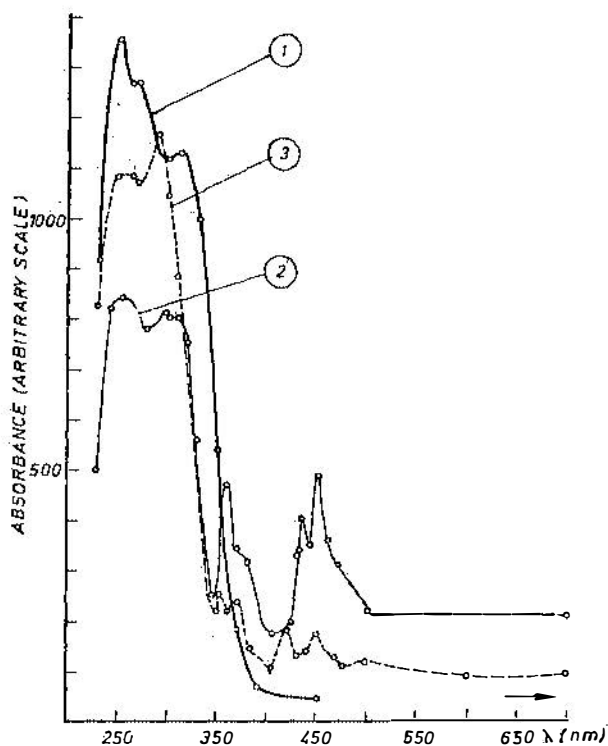


Fig. 3. Reflectance spectra of the complexes manganese chloride with pyridine base and manganese chloride with hydrochlorides of different pyridine bases.

- 1) 2 pyridine +  $MnCl_2$ ,
- 2) 2 pyridine + 2HCl +  $MnCl_2$ ,
- 3) Pyridine + HCl +  $MnCl_2$ .

From the spectra it may be observed that only 2 pyridine +  $MnCl_2$  does not possess the characteristic band in the range 400–500 nm. By all other compounds these bands are present and may be considered to be due to the transition from

the ground state  ${}^6S$  to the excited  ${}^4G$  state. Therefore the compound 2 pyridine + 2 HCl +  $MnCl_2$  has following bands:  ${}^4T_1({}^4G)$  21.050  $cm^{-1}$ ,  ${}^4T_2({}^4G)$  22.000  $cm^{-1}$ . Below 400 nm the bands are:  ${}^4T_2({}^4D)$  26.200  $cm^{-1}$  and  ${}^4E({}^4D)$  27.600  $cm^{-1}$ . Since the compound 2 pyridine +  $MnCl_2$  does not show fluorescence and does not possess the band in the range 400–500 nm, it may be supposed that fluorescent properties of other manganese complexes depend on the transitions in this spectral region. In this way the assumptions on the mechanism of fluorescence are confirmed.

The reflectance spectra of manganese chlorides with quinoline bases shown in Fig. 4, are of different structure as compared to the same spectra of those with pyridine bases.

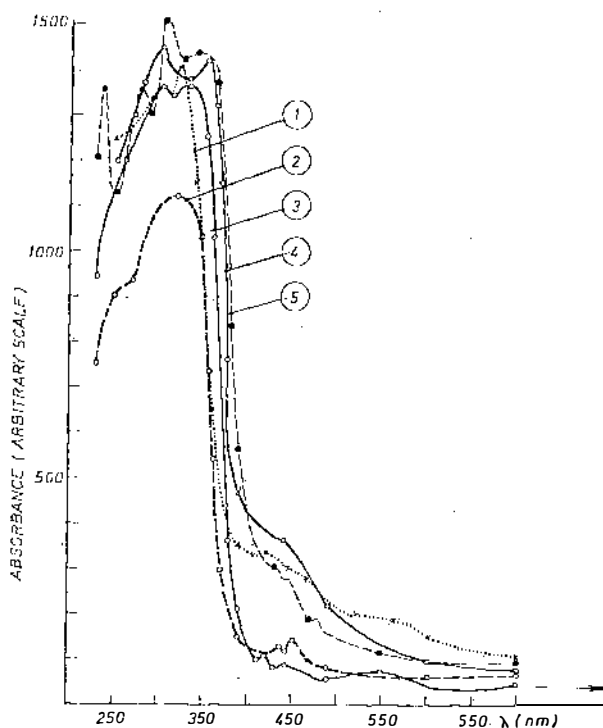


Fig. 4. Reflectance spectra of the complexes manganesechloride with different quinoline base and manganese chloride with hydrochlorides of different quinoline bases,

- 1) 2 quinoline +  $MnCl_2$ ,
- 2) 2 quinoline + 2HCl +  $MnCl_2$ ,
- 3) quinoline + HCl +  $MnCl_2$ ,
- 4) 2 2-methylquinoline + 2HCl +  $MnCl_2$ ,
- 5) 2 2,6-dimethylquinoline + 2HCl +  $MnCl_2$ .

The spectral structure in the range 400–500 nm is not distinct. At any rate, the presence of the quinoline ring affects the disappearance of the structure in this spectral region. Though the spectra of 2 quinoline +  $MnCl_2$  compound are

similar to those of other quinoline compounds, it is the only one among them which does not show fluorescence, and this may be taken to be due to the nonradiative processes inside the molecule.

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## UTICAJI STRUKTURE NA FLUORESCENTNE I REFLEKSIONE SPEKTRE JEDINJENJA MANGANOHLORIDA SA DERIVATIMA PIRIDINA I KINOLINA HIDROHLORIDA

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### Sadržaj

Manganohlorid sa hidrohloridima derivata piridina i kinolina daje jedinjenja sa fluorescentnim osobinama. Jedinjenja u kojima je odnos između heterociklične baze i manganohlorida 2 : 1 fluoresciraju zeleno a ako je taj odnos 1 : 1 imaju crvenu fluorescenciju. Pretpostavljeno je da zelenu odnosno crvenu fluorescenciju uslovljava  $Mn^{2+}$  jon sa koordinacionim brojem 4 odnosno 6.



Spektralna raspodela kod jedinjenja sa zelenom fluorescencijom može se prikazati funkcijom

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

Konstante  $G_0$  i  $\alpha$  ukazuju na uticaj strukture liganda na luminiscentni centar  $Mn^{2+}$  jona.

Refleksioni spektri kod manganohloridnih jedinjenja sa hidrohloridima derivata piridina imaju jasno izraženu strukturu u oblasti 400–500 nm, dok kod jedinjenja sa hidrohloridima derivata hinolina u toj oblasti nemaju izraženih maksimuma. Struktura refleksionih spektara ukazuje da se u apsorpciji vrši prelaz  ${}^6S \rightarrow {}^4G$  koji uslovljava pojavu fluorescencije. Pretpostavljeno je da pojava crvene fluorescencije nastaje prelazom  ${}^4T_1 ({}^4G) \rightarrow {}^6A_1$ . Prelaz  ${}^4T_2 ({}^4G) \rightarrow {}^6A_1$  se javlja kod jedinjenja sa zelenom fluorescencijom.