

FLUORESCENT PROPERTIES OF SOME MANGANESE CHLORIDE COMPOUNDS WITH DIMETHYLQUINOLINE HYDROCHLORIDES

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Abstract: Photoluminescent properties of manganese chloride compounds with hydrochlorides of some dimethylquinoline bases are investigated. On the basis of the behaviour of luminescence spectra and some other properties, the conclusion on fluorescence mechanism is made. The change of fluorescence intensity with temperature is found by the compounds with green fluorescence which may be expressed by Mott-Seitz law.

1. Introduction

Great number of energy states in the quinoline ring cause various chemical and physical interactions. It was found by S. Šljivić¹⁾ that the interaction between electromagnetic energy and protonized quinoline base leads to luminescence. Energy distribution in the fluorescence spectrum of protonized base, differs considerably from the distribution in the case of manganese chloride compounds with quinoline hydrochloride, as found by H. Payen²⁾. By the interaction of manganese chloride with pyridine and quinoline hydrochloride, two types of organometallic compounds are produced. They differ in the number of molecules of quinoline hydrochloride. The compound in which quinoline hydrochloride and manganese hydrochloride are in the ratio 2 : 1, shows green fluorescence, and the compound where this ratio is 1 : 1 shows red fluorescence. By systematic investigation of photoluminescent properties of manganese chloride with hydrochlorides of other N-heterocyclic bases, it was found by S. Šljivić^{3, 4, 5)} that in these compounds approximately the same spectral energy distribution exists which depends on the ratio of N-heterocyclic base to manganese chloride. H. Payen⁶⁾ discovered that manganese chloride compounds with hydrochloride of some aliphatic amines show red fluorescence with spectral distribution similar to that of N-heterocyclic bases. Therefore these photoluminescent properties are not in connection with the presence of N-heterocyclic base only.

Earlier investigations show that in the presence of hydrochloric acid, manganese chloride with different isomers of dimethylquinoline bases, as well as with 2-phenylquinoline, yields luminescent compounds. Therefore our intention was to separate those substances whose luminescence we have discovered, and to investigate their structure. Having in mind a very complex nature of the emission centres and the variety of influences on which the transition of the absorbed energy quanta depends, the luminescence spectra of these substances were investigated under different conditions. On the basis of the structure of luminescence spectra, we have tried to draw theoretical conclusions concerning the nature of luminescence spectra and character of the kinetics of emission processes.

In order to investigate the connection between fluorescent properties and the structure of these compounds, we chose dimethylquinoline bases with one methyl group always in position 2, and the other methyl group in different positions of the quinoline ring. The methyl group has a marked electropositive effect upon the quinoline ring, which leads to the change of the charge density on nitrogen atom. Since the phenyl group exerts electronegative influence, it was of interest to investigate also fluorescent properties of manganese chloride compounds with hydrochloride 2-phenylquinoline.

The synthesis of manganese chloride compounds with hydrochloride 2-phenylquinoline and that of the isomeric dimethylquinoline bases has not yet been described in literature. Therefore in the present work a description of the synthesis of the following compounds is given: manganese chloride compounds with hydrochlorides of 2-phenylquinoline, 2,3-, 2,4- and 2,5-dimethylquinoline.

2. Experimental

Hydrochlorides of 2,3-, 2,4- and 2,5-dimethylquinoline yield two types of compounds. By the compound which shows green fluorescence, hydrochloride of the quinoline base and manganese chloride are in the ratio 2 : 1, while by the compounds with red fluorescence this ratio is 1 : 1. 2-Phenylquinoline give only one type of the compounds which shows red fluorescence.

The process of synthesis of these compounds is as follows. The weight parts of manganese chloride and quinoline base are equal to the molecular ratio of the synthesized compound. Manganese chloride crystals are pulverized and diluted in water to which the excess of hydrochloric acid is added. The obtained solution is mixed with the aethanol solution of the quinoline base after which the mixture is left to evaporate in water bath until the crystals appear. In the case of the quinoline bases by which two types of manganese compounds are produced, the crystals of the compound with green fluorescence appear first, and afterwards the crystals of the compound with red fluorescence.

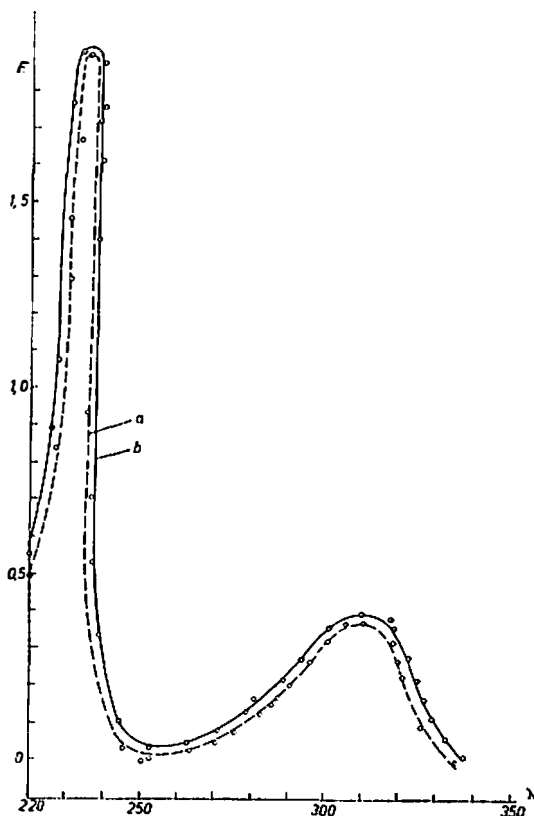


Fig. 1. a) Absorption spectra of 2,4-dimethylquinoline in 0.1 NHCl, b) Absorption spectra of manganese chloride compounds with 2,4-dimethylquinoline hydrochloride in water solution.

The compounds with green fluorescence are thermally unstable so that by temperature elevation up to 150 °C one molecule of the quinoline base is lost, and they turn into the compounds with red fluorescence which are stable even on higher temperatures.

3. Apparatus for optical measurements

For the measurement of absorption spectra a Beckman DU-2 spectrophotometer was used.

The measurements of photoluminescence spectra were performed by the Aminco Bowman spectrofluorimeter. The measurements were performed in a quartz cell on room temperature. During the measurements, photochemical reactions were not observed, what was checked by successive measurements of fluorescence spectra. The obtained measurement results are corrected and the spectral distribution is given relative to the maximum of fluorescence spectra whose intensity is taken as 100.

Table

Compound	Ratio	nm	Maxima of fluor. spec. nm	α	$\log G_s$
2,3-Dimethylquinoline hydrochloride + $MnCl_2$	2 : 1	330	540	0,08	1.990
2,3-Dimethylquinoline hydrochloride + $MnCl_2$	1 : 1	370	622		
2,4-Dimethylquinoline hydrochloride + $MnCl_2$	2 : 1	330	545	0,11	1.990
2,4-Dimethylquinoline hydrochloride + $MnCl_2$	1 : 1	330	670		
2,5-Dimethylquinoline hydrochloride + $MnCl_2$	2 : 1	350	550	0,08	1.992
2,5-Dimethylquinoline hydrochloride + $MnCl_2$	1 : 1	360	665		
2 -Phenylquinoline hydrochloride + $MnCl_2$	1 : 1	366	637		

Infrared spectra were taken by the apparatus Perkin Elmer, model 237 with optical grating.

4. Results

The absorption spectra of water solution of manganese compounds are identical with spectra of dimethylquinoline in 0.1 N solution of hydrochloric acid as given in Fig. 1.

Fluorescence spectra of manganese compounds in water solution and in solid state are not the same. Energy distribution observed by fluorescence spectra of water solutions is similar to that found by dimethylquinoline hydrochloride in solid state. In both cases violet-blue fluorescence appears. Manganese chloride compounds in solid state show red or green fluorescence what depends on molecular relation of hydrochloride quinoline base and $MnCl_2$. Photoluminescent properties of manganese compounds in solid state are given in the Table.

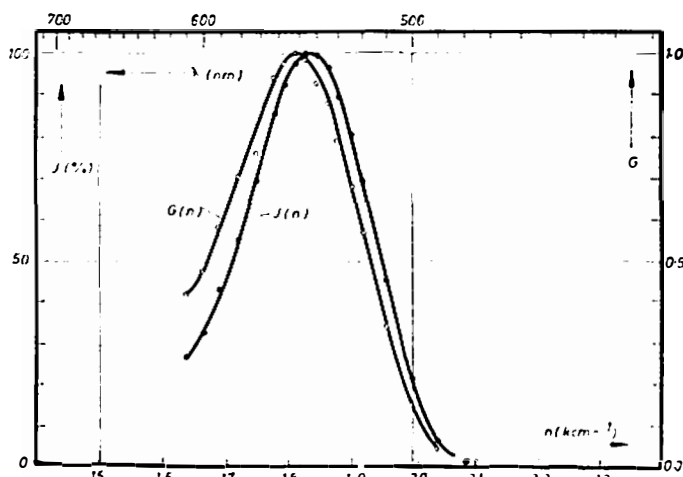


Fig. 2. Graph of the transition matrix element in function of the wave number $G_{(n)}$ and energy intensity in function of the wave number $J_{(n)}$ characteristic for green fluorescence.

Fluorescence spectra of compounds with green fluorescence are characteristic, so that from the experimentally determined function of energy distribution according to the wave number, a graph of transition matrix element in function of the wave number may be plotted. This graph is obtained by dividing the ordinate with the corresponding fourth power of the wave number. In Fig. 2 a curve of energy distribution function and a curve of transition matrix factor according to the wave number is presented.

The obtained form of the function of transition matrix factor is very close to the Gauss distribution curve by which the analytical approximations of the experimental curves are justified. This function may be presented by the following formula

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

This formula may be given in the logarithmic form also

$$\log G_{(\mu)} = \log G_0 - \alpha \mu^2 \log e,$$

which enables the $\log G$ to be presented as a linear function of $\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)^2 = \mu^2$ and may be used for the calculation of constants G_0 and α . Together with the maxima of fluorescence spectra they may be used as analytical characteristics of photoluminescent compounds. The value of these constants are given in the Table. In Fig. 3 the graph of this function is presented.

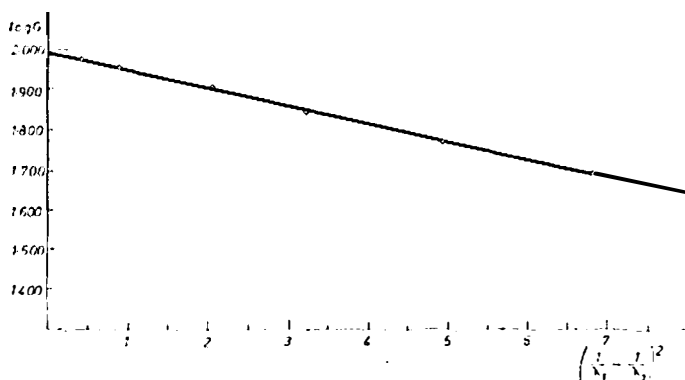


Fig. 3. Graphic presentation of the linear function $\log G_{(\mu)} = \log G_0 - \alpha \mu^2 \log e$ obtained for manganese chloride compound with 2,4-dimethylquinoline hydrochloride (molecular ratio 1 : 2).

By the compounds with red fluorescence the change of fluorescence intensity within temperature interval $0^\circ - 140^\circ \text{C}$ is not observed. By the compounds with green fluorescence this change of fluorescence intensity within

the mentioned temperature interval is observed and may be represented by the linear function of the reciprocal values of absolute temperature according to Mott-Seitz law (Fig. 4).

Infrared spectra of these manganese compounds in KBr pellets show characteristic band which come from the quinoline ring. Nevertheless, characteristic band which comes from the $-C = NH^+$ group does not appear here but is present in UV spectra of water solution of manganese compounds and dimethylquinoline dissolved in 0.1 N solution of hydrochloric acid. By infrared spectra of dimethylquinoline hydrochloride in KBr pellets, this band exists.

5. Discussion

Different behaviour of optical properties of the investigated compounds in solid state and solutions, indicate to the changes of their structure which are due to the solvolytic effects. The presence of the protonized base in water solution is proved in UV and fluorescence spectra. The blueviolet fluorescence of the solution comes from the quinolinium ion which is the lumino-phor, while the manganese ion can not be the fluorophor in water solution since all the transitions in it are forbidden. All the effects of fluorescence

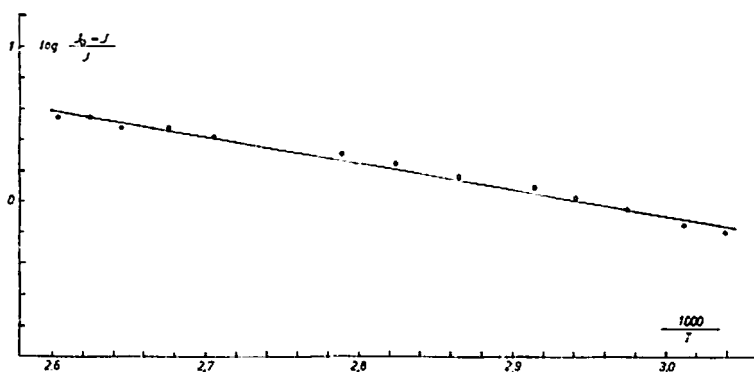


Fig. 4. Temperature quenching of fluorescence of manganese chloride compounds with 2,4-dimethylquinoline hydrochloride (molecular ratio 1 : 2).

quenching observed by dimethylquinoline dissolved in 0.1 N solution of HCl, are also observed in water solutions of manganese compounds. The presence of quinolinium ion in manganese compounds is proved also by potentiometric titration with NaOH and by electrolysis. The steepness of the potentiometric curve lies in the region of pH which corresponds to the dissociation constant of the quinoline base.

By investigating the structure of manganese chloride compounds with quinoline hydrochloride, Taylor⁷⁾ concluded that the compounds in which the ratio of quinoline base and MnCl_2 is 2 : 1, have the following structural formula $(\text{C}_9\text{H}_7\text{NH})_2\text{MnCl}_4$. The compounds in which this ratio is 1 : 1, have the structural formula $\text{C}_9\text{H}_7\text{NHMnCl}_3$. These compounds having similar optical properties in solutions and in solid state as those which are investigated in the present paper, we made analysis with the purpose to prove the same structure in these compounds also. In our case the existence of quinolinium ion is proved, while MnCl_3^- and MnCl_4^- ions are not discovered in the solutions of the investigated concentrations. According to some authors, hydrolysis of these compounds into Mn^{++} and Cl^- ions is possible.

On the basis of potentiometric analysis of concentrated solutions of manganese chloride compounds with pyridine hydrochloride, Fyfe⁸⁾ proposed the following structural formula for the compounds in which the ratio of pyridinehydrochloride and MnCl_2 is 2 : 1 — $\text{H}_2\text{Mn}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_4$ and $\text{H}_2\text{MnC}_5\text{H}_5\text{NCl}_3\text{OH}$ for the compounds in which this ratio is 1 : 1. The structural formulae of these compounds proposed by Taylor are the result of hydrolytic processes whose final products are pyridinium, Mn^{++} and Cl^- ions. Since pyridine hydrochloride with manganese chloride⁹⁾ yields compounds with red and green fluorescence when in solid state, as it is the case with quinoline and dimethylquinoline hydrochlorides, we suppose that the compounds in solid state may have the same structural formula proposed by Fyfe. This is indicated by the fact that infrared spectra of these substances in KBr pellets do not show characteristic band of $-\text{C} = \text{NH}^+$ ion. Therefore the compounds in which the ratio of dimethylquinoline base and MnCl_2 is 2 : 1 have the structural formula $\text{H}_2\text{Mn}(\text{dQN})_2\text{Cl}_4$, while the compounds in which this ratio is 1 : 1 have the structural formula $\text{H}_2\text{MndQNCl}_3\text{OH}$. In the case of the compounds which do not possess a water molecule this structural formula is $\text{HMndQNCl}_3(\text{dQN-dimethylquinoline})$. The protonized quinoline base in water solution, Mn^{++} and Cl^- ions could be explained by hydrolysis. Nevertheless, there is a possibility for the existence of MnCl_4^{--} and MnCl_3^{--} ions which may appear in one of the phases of hydrolysis.

In this way the differences of fluorescent properties of manganese compounds in water solution and in solid state could be also explained. Quinolinium ion is the fluorophor in water solution, while in solid state this role is played by the Mn^{++} ion. In crystal lattice the manganese ion has the properties of a fluorophor, since there is a possibility for transitions into different energy states. It is also proved for the case of ZnS with one Mn^{++} ion incorporated into the lattice, what leads to fluorescence with maxima at 5850 Å. Approximately the same positions were observed in other crystal lattices with one Mn^{++} ion⁹⁾.

According to Curie⁹⁾, by the absorption of electromagnetic energy quanta, the manganese ion changes from the ground state ^6S into the ^4G state through the change of the position of one out of five parallel spins. From the mea-

sured fluorescence spectra it was possible to conclude that by the investigated compounds the energy yields are approximately the same as those found in crystal phosphoruses. Therefore we conclude that in this case also the mechanism of fluorescence is the same.

The decrease of energy intensity with elevated temperature of substances with green fluorescence, is given by Mott-Seitz law

$$\log \frac{I_0 - I}{I} = \log C - \frac{W}{kT} \log e,$$

where

W and C = constant,
 k = Boltzman constant,
 T = absolute temperature.

The explanation of temperature quenching comes from the fact that by lower temperatures the energy of the excitation state of luminescence centres is considerably lower than W , and that is the reason for the existence of emission processes during the transition from the exciting into the ground state. On the contrary, if the oscillation energy of these centres is greater than W , what happens on certain temperatures, nonradiative processes occur by the transition into the ground state. The released energy is transformed into phonons which are transferred through all the parts of crystal lattice.

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FLUORESCENTNE OSOBINE JEDINJENJA MANGANOHKLORIDA SA DIMETILHINOLINHIDROHLORIDIMA

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Ispitivane su fotoluminiscentne osobine jedinjenja manganohlorida sa 2,3-, 2,4- i 2,5-dimetilhinolinhidrohloridom. U čvrstom stanju, fluoesciraju zeleno jedinjenja u kojima je odnos između dimetilhinolinhidrohlorida i $MnCl_2$ 2 : 1 a u kojima je ovaj odnos 1 : 1 imaju crvenu fluorescenciju. Vodeni i etanolni rastvor ovih jedinjenja imaju ljubičasto-plavu fluorescenciju, koja se javlja kao posledica solvolize.

Spektralna raspodela fluorescencije zavisi i od položaja metil grupa u hinolinskom prstenu. Iz fluorescentnih spektara jedinjenja sa zelenom fluorescencijom može se konstruisati kriva matričnog faktora prelaza u funkciji talasnog broja, koja ima oblik blizak Gauss-ovoj raspodeli.

U čvrstom stanju Mn^{++} jon je luminofor u kome se vrši prelaz iz osnovnog 6S stanja u pobuđeno 4G stanje. U vodenom i etanolnom rastvoru luminofor je hinolinijum jon od koga potiče ljubičasto-plava fluorescencija.

Gašenje fluorescencije nastalo povišenjem temperature, koje je zapaženo kod jedinjenja sa zelenom fluorescencijom, ponaša se po Mott-Seitz-ovoj formuli. Ova pojava nije zapažena kod jedinjenja sa crvenom fluorescencijom.