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ON THE LUMINESCENCE OF SOME COORDINATION COMPOUNDS OF MANGANESE (II) IN THE SOLID STATE

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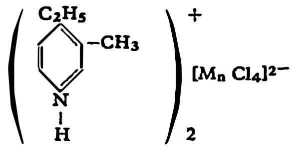
Abstract: The luminescence of the complex formed by manganous chloride with 4-ethyl-3-methylpyridine hydrochloride and of the complex formed by manganous chloride with 2-ethylpiperidine hydrochloride has been investigated. These compounds exhibit green and yellow-green luminescence whose spectral distribution may be represented by a funciton close to the Gaussian distribution, which makes it possible to calculate the characteristic constants a and m for any temperature. From the excitation and reflectance spectra the exsistence of the excitation states $^4T_{1g}$, $^4T_{2g}$ and $^4A_{1g}$, ^4E_g was found. The character of luminescence is determined by the tetrahedral structure of the $[MnCl_4]^{2-}$ ion in the solid state. It was found that the phenomenon of luminescence is due to the $^4T_{2g} \rightarrow {}^6A_1$ transition.

1. Introduction

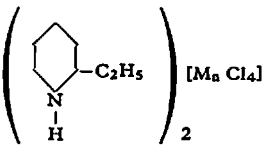
The influence of different factors on the level splitting both in ground and excited states may also affect the luminescence process. Therefore the effect of different ligands on the mechanism of luminescence of the Mn^{2+} ion[1-16] was chosen to be the subject of our investigation. In the course of further investigation of these mechanisms in manganese complex compounds, two new compounds have been synthetized which have not been described in the literature so far. These are the compounds of manganese (II) chloride with 4-ethyl-3-methylpyridine hydrochloride — $(EMPH)_2MnCl_4$ — and of manganese (II) chloride with 2-ethylpiperidine hydrochloride — $(EPPH)_2MnCl_4$. The luminescent properties of these compounds have been investigated by studying the excitation, reflectance, absorption and luminescence spectra, and this helped to gain an insight into the mechanism of luminescence processes.

2. *Experimental*

The compounds $(EMPH)_2MnCl_4$ and $(EPPH)_2MnCl_4$ were synthetized by taking equivalent quantities of manganous chloride and the corresponding pyridine and piperidine bases in ethanolic solution to which hydrochloric acid was added in excess. By slow evaporation on a water bath the yellow-green crystals were obtained. The purification was performed by repeated crystallization from the ethanolic solution, where upon the crystals were dried in vacuum over P_2O_5 at 60°C. By the analysis it was found that this compound in the solid state has the following chemical formula



$(EMPH)_2MnCl_4$



$(EPPH)_2MnCl_4$

The compounds $(EMPH)_2MnCl_4$ and $(EPPH)_2MnCl_4$ are hygroscopic and can be decomposed by heating them above 80°C. They are soluble in water, methanol and ethanol.

The measurement of reflectance spectra was performed at room temperature by the use of a Beckman DU 2 spectrophotometer with the accessory for the measurement of reflectance spectra. Magnesium carbonate was used as reference solid.

The absorption spectra were measured at room temperature with a Unicam SP 800 UV spectrophotometer.

The fluorescence and excitation spectra were measured at different temperatures from —40° to 80°C using an Aminco Bowman spectrofluorimeter. A constant temperature within ±0.1°C was maintained by using a Hopler thermostat. The luminescence spectra were corrected[17–19].

3. *Results and discussion*

The excitation spectrum of the $(EMPH)_2MnCl_4$ crystal has two bands with a shoulder at 21050 cm^{-1} and maxima at 22100 and 22470 cm^{-1} and, further, a shoulder at 28500 cm^{-1} (Fig. 1, curve I). The excitation spectrum at 77K (Fig.

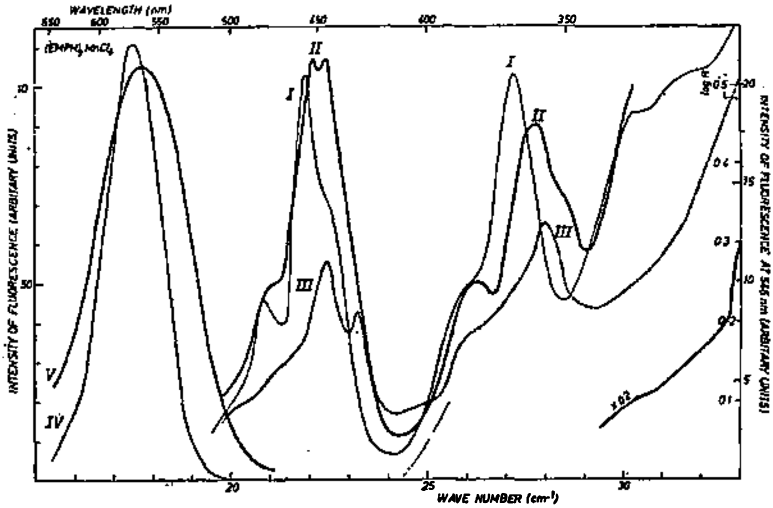


Fig. 1. Spectra of the $(EMPH)_2MnCl_4$ crystal
Curve I: Excitation spectrum at 77 K for $\lambda_{em} = 568$ nm,
Curve II: Excitation spectrum at room temperature for $\lambda_{em} = 546$ nm,
Curve III: Reflectance spectrum at room temperature
(R is the ratio between the intensity of the light reflected from the sample and the intensity of the light reflected from $MgCO_3$),
Curve IV: Luminescence spectrum at 77 K for $\lambda_{ex} = 285$ nm,
Curve V: Luminescence spectrum at room temperature for $\lambda_{ex} = 290$ nm.

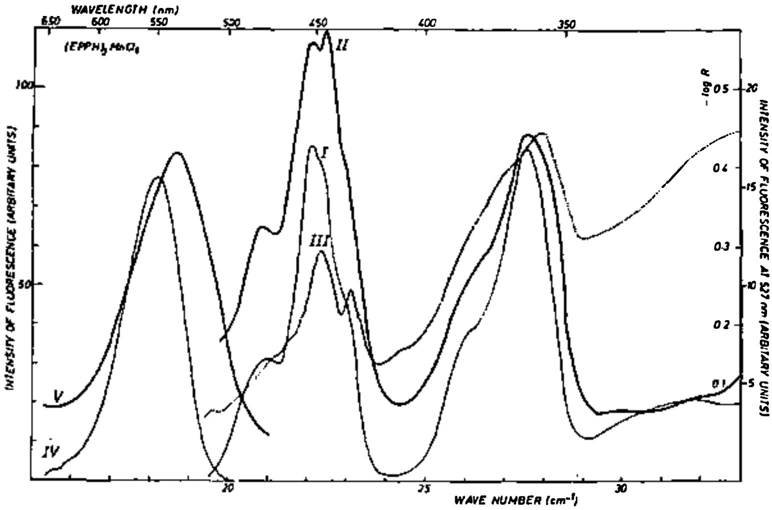


Fig. 2. Spectra of the $(EPPH)_2MnCl_4$ crystal
Curve I: Excitation spectrum at 77 K for $\lambda_{em} = 500$ nm,
Curve II: Excitation spectrum at room temperature for $\lambda_{em} = 527$ nm,
Curve III: Reflectance spectrum at room temperature,
Curve IV: Luminescence spectrum at 77 K for $\lambda_{ex} = 452$ nm,
Curve V: Luminescence spectrum at room temperature for $\lambda_{ex} = 450$ nm.

1, curve II) differs from that recorded at room temperature and has maxima at 20830 cm^{-1} and at 21970 cm^{-1}, and a shoulder at 22470 cm^{-1}. In the second group of bands a shoulder at 25970 cm^{-1} and a maximum at 27200 cm^{-1} are observed. Since these bands do exist in the spectra of a great number of complex compounds of manganese (II) chloride with different heterocyclic bases and are due to the $[MnCl_4]^{2-}$ ion, it may be supposed that this complex ion also exists in the compounds investigated. It is present only in the solid state, since these bands do not appear in the absorption spectra of ethanolic solution in which the solvolysis of the $[MnCl_4]^{2-}$ ion occurs.

Even in the reflectance spectra of the $(EMPH)_2MnCl_4$ crystal in the region abowe 30000 cm^{-1} the characteristic bands appear which arise from the $[MnCl_4]^{2-}$ ion. One group contains bands with a shoulder at 21050 cm^{-1} and with maxima at 22470 and 23260 cm^{-1}. Another group consists of bands with a shoulder at 26320 and a maximum at 27970 cm^{-1} (Fig. 1, curve III). The positions of these bands in the reflectance spectrum are in the same spectral region as in the excitation spectra.

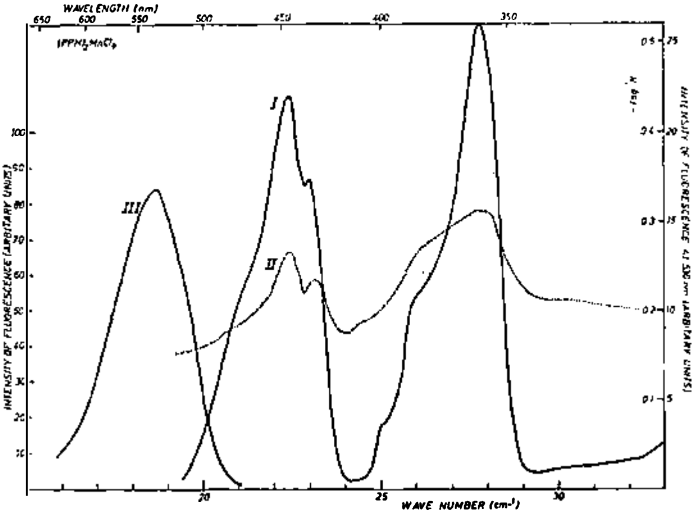


Fig. 3. Spectra of the $(PPH)_2MnCl_4$ crystal at room temperature
Curve I: Excitation spectrum for $\lambda_{em} = 530$ nm,
Curve II: Reflectance spectrum,
Curve III: Luminescence spectrum for $\lambda_{ex} = 450$ nm.

In the excitation spectrum of the $(EPPH)_2MnCl_4$ crystal recorded at room temperature there are two groups of bands. The first group of bands has a shoulder at 21050 cm^{-1}, maxima at 22100 and 22470 cm^{-1} and, further, as houlder at 22850 cm^{-1}. In the second group the shoulder is at 26320 cm^{-1} and the maximum at 27600 cm^{-1} (Fig. 1, curve II). In the excitation spectrum taken at 77K there are also two groups of bands. In the first group, maxima are found at 21050 and 22100

cm^{-1} and a shoulder at 22470 cm^{-1}, while in the second group the shoulder is at 26320 and the maximum at 27 550 cm^{-1} (Fig. 2, curve II).

In the reflectance spectrum of the $(EPPH)_2MnCl_4$ crystal there are also two groups of bands (Fig. 2, curve III). In the first group the shoulder is at 21050 cm^{-1} and the maxima are at 22350 and 23120 cm^{-1}. In the second group a shoulder is found at 27970 cm^{-1}. All these bands in both excitation and reflectance spectra arise from the $MnCl_4]^{2-}$ ion which exists in crystals only. In the absorption spectra of ethanolic solution these bands do not appear due to the solvolysis of the $[MnCl_4]^{2-}$ ion.

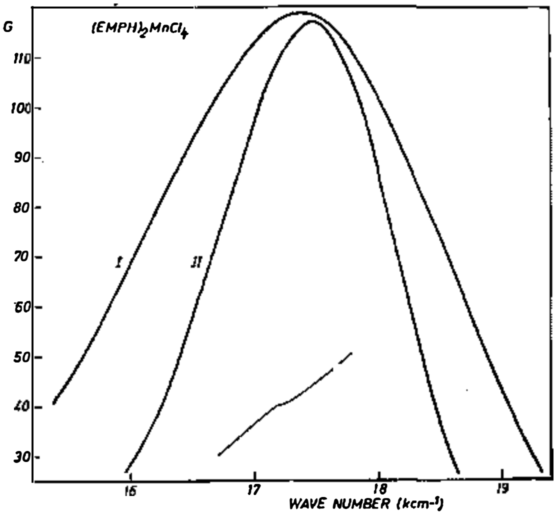


Fig. 4. The curve of G versus $1/\lambda$ for $(EMPH)_2MnCl_4$ at room temperature (I) and at 77 K (II).

Because of the unequal number of maxima and shoulders in the excitation and reflectance spectra of $(EPPH)_2MnCl_4$, the excitation and reflectance spectra of the crystalline compound of manganous chloride with piperidine hydrochloride have been investigated (Fig. 3, curves I and II). In both spectra of this compound the same number of shoulders and maxima appear in the same spectral regions, just as in the spectra of the majority of compounds containing the $[MnCl_4]^{2-}$ ion. Nevertheless, the repeated measurements of the excitation spectrum of $(EPPH)_2$ $MnCl_4$ indicate the existence of two maxima: at 22100 and 22470 cm^{-1}, while in the case of $(PPH)_2MnCl_4$ in the same region there is only one maximum: at 22420 cm^{-1}.

The structure of the reflectance spectra of $(EMPH)_2MnCl_4$ and $(EPPH)_2MnCl_4$ is characteristic of many complexes formed by manganese (II) chloride with different derivatives of pyridine hydrochloride, whose spectra contain bands with closely spaced maxima, like those of the $(EMPH)_2MnCl_4$ and $(EPPH)_2MnCl_4$

compounds. The position and intensity of the bands depend on the specific effect of the ligands surrounding the Mn^{2+} ion is mainly coordinated octahedrally. The considerably greater absorbance in the range 20000 to 25000 cm^{-1} by tetrahedral than octahedral manganese (II) is due to the fairly pronounced yellow to green colours of the tetrahedral tetrahalogene-complexes, whereas octahedral maganese (II) compounds usually have very pale pink tints. Most manganese compounds of tetrahedral structure show green fluorescence. In view of the clearly defined characteristic structure of the reflectance spectra, the yellow-green colour of the crystals and the green fluorescence, it can be considered that the $(EMPH)_2MnCl_4$ and $(EPPH)_2MnCl_4$ compounds have a tetrahedral structure.

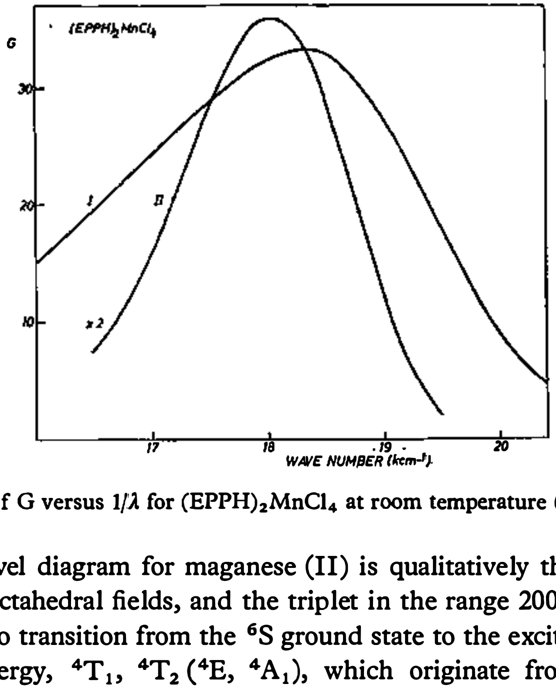


Fig. 5. The curve of G versus $1/\lambda$ for $(EPPH)_2MnCl_4$ at room temperature (I) and at 77 K (II).

The energy level diagram for maganese (II) is qualitatively the same for both tetrahedral and octahedral fields, and the triplet in the range 20000—25000 cm^{-1} can be assigned to transition from the ^6S ground state to the excited state, in order of increasing energy, $^4T_1$, $^4T_2$ (^4E, $^4A_1$), which originate from the ^4G term of the free ion. The separation between these states depends on the ligand field strength, but not linearly, because there are higher-lying T_1 and T_2 states which interact with those considered here. In this presentation of the energy states of the manganese (II) ion the spin-orbit interaction is disregarded. The ^6S ground state is degenerate and has five parallel spins. It gives rise to the $^6A_1$ state [20)].

Since the reflectance spectra of the $(EMPH)_2MnCl_4$ and $(EPPH)_2MnCl_4$ compounds also contain bands in the range 20000 — 25000 cm^{-1}, it can be concluded that in their tetrahedral structure there are the same energy levels. For identification of bands the Heidt et al. diagram (21) was used. Whereas the three peak constituting a triplet are separated by ~ 4000 ($^4T_{2g}$ — $^4T_{1g}$) and ~

$\sim 2000\,({}^4A_{1g}, E_g - {}^4T_{2g})$ wave numbers in the octahedral hexa-aquo ion, the separations observed for the $(EMPH)_2MnCl_4$ compound are $\sim 1420\,({}^4T_{2g} - {}^4T_{1g})$ and $\sim 790\,({}^4A_{1g}, {}^4E_g - {}^4T_{2g})$, while those for the $(EPPH)_2MnCl_4$ compound are $\sim 1300\,({}^4T_{2g} - {}^4T_{1g})$ and $\sim 770\,({}^4A_{1g}, {}^4E_g - {}^4T_{2g})$ wave numbers. Since oxygen, bromide and chloride are all closely placed in the spectrochemical series we should expect 10 Dq in these tetrahedral complexes to be 4/9 of that ($\sim$ 8000) in the hexa-aquo ion. Using the diagram of Heidt et al. we find that for $10\,Dq = 3600\,cm^{-1}$ the expected separations are ~ 1600 $({}^4T_{2g} - {}^4T_{1g})$ and $\sim 500\,({}^4A_{1g}, {}^4E_g - {}^4T_{2g})$ wave numbers. The same value for 10 Dq was used by Cotton et al.[20)] for the $[MnCl_4]^{2-}$ ion and by Goodgame et al.[22)] for complexes formed by manganese salts and triphenylphosphine oxide as ligands. On the basis of fairly good agreement of our results with those of the authors mentioned above the following band assignments were made: ${}^4T_{1g}\,(21050\ cm^{-1})$, ${}^4T_{2g}\ (22470\ cm^{-1})$, ${}^4E_g$, ${}^4A_{1g}\,(23260\,cm^{-1})$ for $(EMPH)_2MnCl_4$, and for $(EPPH)_2MnCl_4$: : ${}^4T_{1g}\,(21050\,cm^{-1})$, ${}^4T_{2g}\,(22350\ cm^{-1})$, ${}^4E_g$, ${}^4A_{1g}\,(23120\ cm^{-1})$. No assignments were given to other bands, since they were not considered in explaining the mechanism of luminescence.

4. Luminescence spectra

The measurement of luminescence spectra was performed at room temperature and at 77 K. The luminescence spectra of $(EMPH)_2MnCl_4$ (Fig. 1, curves IV and V) and of $(EPPH)_2MnCl_4$ (Fig. 1, curves IV and V) consist of one broad band. In the spectrum of $(EMPH)_2MnCl_4$ the maximum at room temperature is found to be at 17700 cm^{-1}, while at 77 K it is found at 17550 cm^{-1}. In the case of $(EPPH)_2MnCl_4$ the maximum at room temperature is at 18690 cm^{-1}, while at 77 K it is at 18180 cm^{-1} (Fig. 2, curves IV and V). The height of the peak depends on the wavelength by which the excitation is brought about, while the halfwidth and the shape of the spectrum remain the same. The excitation was brought about by the wavelength whereby the most intense luminescence is caused. The shape of the luminescence spectrum is such that for its interpretation use can be made of the method of configurational coordinate curves[23)].

According to Payen[23)], the constants a and m may be used to define luminescence spectra at different temperatures. These constanst may be calculated if the appropriate shape of the curve of G versus $1/\lambda$ is obained. The ordinate curve of G versus $1/\lambda$ is calculated as follows

$$G\,(1/\lambda) = I(\lambda)\,\lambda^6,$$

where $I(\lambda)$ is the corrected intensity for the corresponding wavelength (λ). The curve obtained has a maximum at $1/\lambda_0 = 17360\,cm^{-1}$ (Fig. 4, curves I and II) at room temperature for the compound $(EMPH)_2MnCl_4$, while at 77 K the peak is at $1/\lambda_0 = 1748\ \mathrm{cm}^{-1}$. For $(EPPH)_2MnCl_4$ at room temperature the peak of the curve is at $1/\lambda_0 = 18450\ \mathrm{cm}^{-1}$, while at 77 K it is at $1/\lambda_0 = 18020\ \mathrm{cm}^{-1}$. (Fig. 5, curves I and II). Since its shape is similar to the Gaussian distribution it can be represented by the expression

$$G(1/\lambda_1) = G(1/\lambda_2) = G(1/\lambda_0) \exp\left[-a\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)^2\right],$$

where λ_1 and λ_2 are two wavelengths giving the same value of G. The dependence of $\log G$ on $(1/\lambda_1 - 1/\lambda_2)^2$ is represented by a straight line (Fig. 6, curves I and II) for both investigated compounds at room temperature and at 77 K. This shape is in agreement with the theory of the configurational coordinate model. The rectilinear dependance of $\log G$ on $(1/\lambda_1 - 1/\lambda_2)^2$ makes it possible to calculate the constant a whose temperature dependance is shown in the Table.

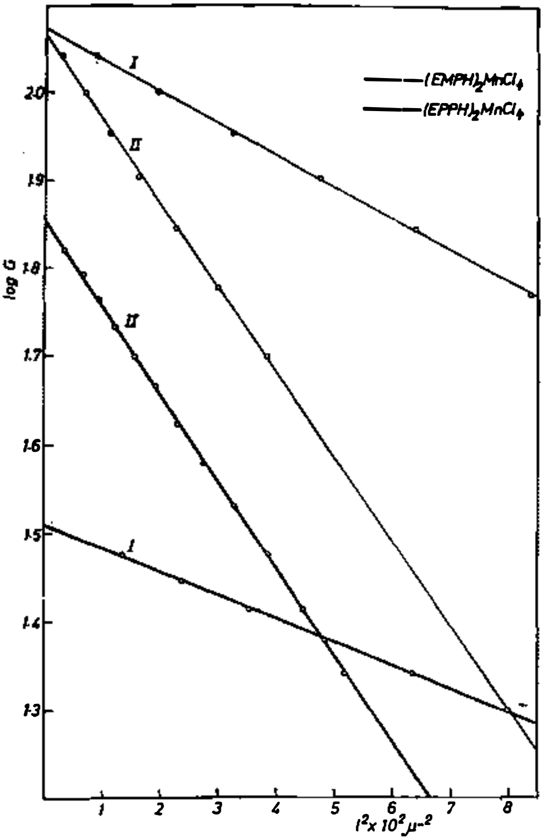


Fig. 6. The dependence of $\log G$ on $(1/\lambda_1 - 1/\lambda_2)^2$ at room temperature (curves I) and at 77 K (curves II) for $(EMPH)_2MnCl_4$ and $(EPPH)_2MnCl_4$, respectively.

$(EPH)_2MnCl_4$

Table

T K	77	243	263	290	298,5	324
$-\alpha\ (\mu^{-2})$	9.91	4.18	3.29	2.77	2.38	1.98
$m\ (\mu^{-1})$	34.0	12.2	9.64	6.25	5.67	3.15
$L^2\ (\mu^2)$	0.0176	0.0718	0.0863	0.1063	0.1102	0.1474

$(EMPH)_2MnCl_4$

T K	77	241.5	258	273.7	305	316	324	333	342
$-\alpha\ (\mu^{-2})$	9.65	3.15	2.78	2.70	3.13	3.32	3.04	2.82	2.2
$m\ (\mu^{-1})$	31.4	12.6	9.87	6.67	3.69	2.43	1.55	1.70	2.65
$L^2\ (\mu^2)$	0.0313	0.0949	0.0999	0.103	0.0936	0.0900	0.119	0.105	0.117

In Fig. 7 we plotted the curve of log G versus $(1/\lambda)$. From the plot it can be seen that the law of rectilinear diameter is valid; the slope m of the line has the following values for different temperatures.

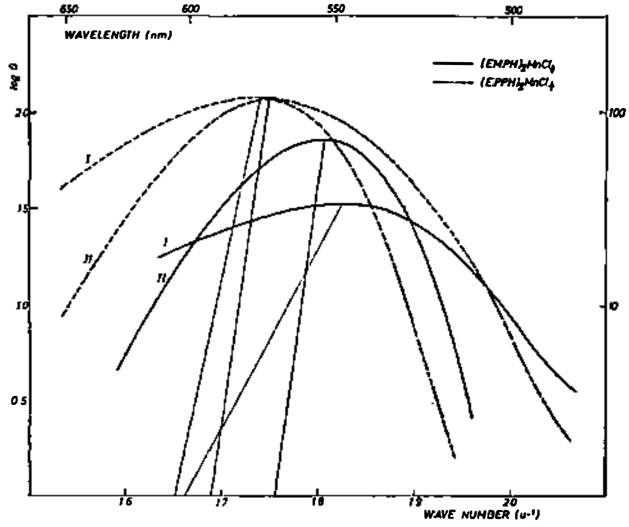


Fig. 7. The curves of log G versus $(1/\lambda)$ at room temperature (curves I and III) and at 77 K (curves II and IV) for $(EMPH)_2MnCl_4$ and $(EPPH)_2MnCl_4$, respectively.

In the temperature range in which the luminescence spectra were measured a slight shift of the maximum towards higher wave numbers with increasing temperature was observed. The halfwidth of luminescence spectra also increases with increasing temperature.

The character of the emission in all the cases is such that it may be attributed to the typical luminescence which is due to the manganese ion. Since in both compounds the $[MnCl_4]^{2-}$ ion is of tetrahedral structure, the character of their luminescence is determined by it. On the basis of the excitation and reflectance spectra of the crystals the following levels are found in both compounds: $^4T_{1g}$, $^4T_{2g}$ and (^4A, $^4E_1$). Therefore the mechanism of luminescence may be accounted for by the $^4T_{2g} \rightarrow {}^6A_1$ transition. The luminescent properties of both compounds disapear when these are dissolved in ethanol and water due to the solvolysis of the $[MnCl_4]^{2-}$ ion and destruction of the lattice. As a result the Mn^{2+} ion is formed, which does not show luminescent properties because of the forbidden transitions.

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O LUMINESCENCIJI NEKIH KOORDINATIVNIH JEDINJENJA MANGANA (II) U ČVRSTOM STANJU

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Sadržaj

Proučavane su, na raznim temperaturama, luminescentne osobine mangano hlorida sa 3-etil-4-metilpiridin hidrohloridom i mangano hlorida sa z-etil peperidin hidrohloridom, preko apsorpcionih, ekscitacionih, refleksionih i luminescentnih spektara. Iz refleksionih i ekscitacionih spektara konstatovano je da kod ovih jedinjenja postoje ekscitirana stanja $^4T_{1g}$, $^4T_{2g}$ i ($^4A_{1g}$, ^4E_g). Za definisanje luminsescentnih spektara na raznim temperaturama upotrebljavane su konstante a i m koje su mogle da se dobiju iz spektralne raspodele, koja je takvog karaktera da se može izračunati $G(1/\lambda)$ pri čemu je dobijena kriva slična Gauss-ovoj raspodeli. Ovaj oblik krive je u skladu sa teorijom konfiguracionog koordinatnog modela što potvrđuje i dobijena pravolinijska zavisnost log G od $(1/\lambda_1 - 1/\lambda_2)^2$.

Zbog pravilnog ponašanja spektralne raspodele na raznim temperaturama važi i zakon pravolinijskog dijametra što omogučuje izračunavanje konstante m. Konstante a i m mogu da posluže za karakterizaciju jedinjenja na određenoj temperaturi.

Postanak luminescencije kod oba jedinjenja može se objasniti prelazom: $^4T_{2g} \rightarrow {}^6A_1$ koji nastaje u $[MnCl_4]^{2-}$ jonu tetreadarske strukture koja postoji samo u čvrstom stanju.