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DIAGRAM OF CONFIGURATIONAL CURVES OF TETRAHEDRAL COMPLEX COMPOUND OF MANGANESE(II) BROMIDE WITH 2-METHYLPIPERIDINE

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The tetrahedral complex compound of manganese(II) bromide with 2-methylpiperidine, as other manganese amine complex compounds of green colour investigated up to now, exhibits a single band in its emission spectrum. The laws defining the shape of spectra and the established formulae are applicable to this compound and enable a diagram of configurational curves to be plotted.

1. Introduction

In the theory of electronic vibrational transitions in crystals and complex molecules one-coordinate methods are often introduced. Von Hippel$^{1)}$, and later Seitz$^{2)}$, tried to explain qualitatively the absorption and emission processes in inorganic solids. They considered the energy conditions of the luminescence centre as function of the configurational coordinate. Other configuration coordinate curves were computed from experimental data by Klick and Schulman$^{3,4)}$ for an Mn^{2+}ion centre in Zn_2SiO_4 and by Vlam$^{5)}$ for centers in silicates and tungstates. These authors used an approximation by considering the luminescence centre as a single harmonic oscillator which means that the potential curves of the ground and excited states are parabolic in shape.

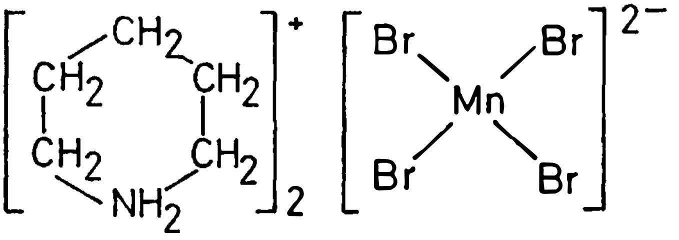
In our previous works$^{6,7)}$ the photoluminescent properties of complex compounds of manganese(II) chloride and bromide with the hydrochlorides and hydrobromides of pyridine bases were investigated. The luminescence spectra of these compounds display some regularities which enable one to give a mathematical interpretation of their spectral distribution.

Continuing the investigation of the luminescence of the complex compounds of manganese(II) we synthetized 2-methylpiperidine tetrabromomanganate and studied its photoluminescent properties in order to explain the mechanism of photoluminescence and examine possibilities of applying the theoretical model.

2. *Experimental*

2-methylpiperidine tetrabromomanganate was synthetized by using equivalent amounts of 2-methylpiperidine and manganese(II) bromide dissolved in methanol to which hydrobromic acid was added in an excess.

The structural formula of this compound is:



The luminescence excitation and emission spectra were measured on an AMINCO-BOWMAN spectrophotofluorimeter and a SAFAS spectrofluorimeter.

3. *Results and discussion*

A. Laws verified by the shape of emission spectra

Spectra were measured at different temperatures over the range 77—333 K. Figure 1 shows spectra recorded at four temperatures within the range observed. At all temperatures they represent a broad band the shape of which obeys the law rectilinear diameter. The validity of this law was confirmed by determining the constants a and m at different temperatures[8].

Figures 2—4 show the curves: $G(\tilde{\nu}) = I_\lambda \lambda^6 = f(\tilde{\nu})$, $\log G(\tilde{\nu}_1) = \log G(\tilde{\nu}_2) = f(l^2)$, where $l = (\tilde{\nu}_1 - \tilde{\nu}_2)$, and $\log G(\tilde{\nu}_1) = f(\tilde{\nu})$ for the complex compound investigated at a temperature of 77 K.

B. Verification of formulae defining the shape of emission spectra at different temperatures

One of us[9] has shown that luminescence intensity per unit wavelength I_λ at all temperatures may be expressed in the form

$$I_\lambda = I_{\lambda M}(\lambda_M/\lambda)^6 \exp\,[-(\beta - C_2)(r - r_M)^2] \qquad (1)$$

where C_2 is a constant, while $I_{\lambda M}$ and λ_M are the values of I_λ and λ when $r = r_M$ (r is the configurational coordinate). The coefficient β is dependent on temperature.

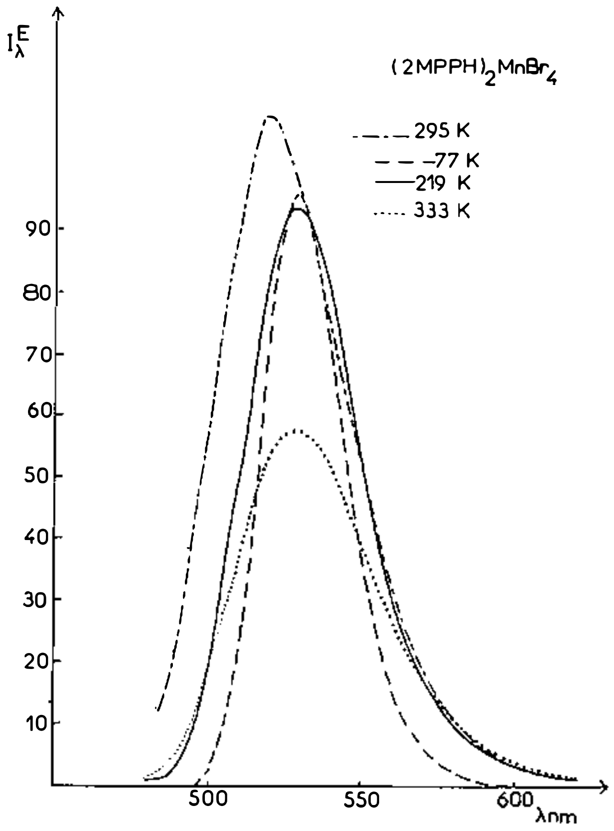


Fig. 1 Emission spectra of the $(2\,MPPH)_2MnBr_4$ complex compound at *77*, *219*, *295*, and *333* K. The radiation energy per unit wavelength is plotted on ordinate in arbitrary units, while wavelength is plotted on abscissa in nanometers.

We have classical relation:

$$\beta = (k_e/h\nu_e)\,\mathrm{th}\,(h\nu_e/2kT) \tag{2}$$

where $h\nu_e$ is the vibrational energy quantum of luminescence centers in excited state, k_e is corresponding Hook's constant, and T is the absolute temperature. Wave number ($\tilde{\nu}$) is related to r by the classical formula:

$$hc\,(\tilde{\nu} - \tilde{\nu}_0) = -\,k_f\, r_0\,(r - r_0) + \frac{1}{2}\,(k_e - k_f)\,(r - r_0)^2, \tag{3}$$

while r_M is connected with r_0 by the relation:

$$r_M = r_0 - (C_1/2\,(\beta - C_2)), \tag{4}$$

in which C_1 is a constant.

Finally, $\tilde{\nu}$ is connected with r by the relation:

$$hc(\tilde{\nu} - \tilde{\nu}_M) = \frac{1}{2}(k_c - k_f)(r - r_M)^2 + [-k_f r_0 + (k_e - k_f)(r_M - r_0)](r - r_M). \quad (5)$$

According to this theory the slope m of the rectilinear diametar of the curve $\ln G(\tilde{\nu})$ is:

$$m = -2(\beta - C_2)/(k_e - k_f). \quad (6)$$

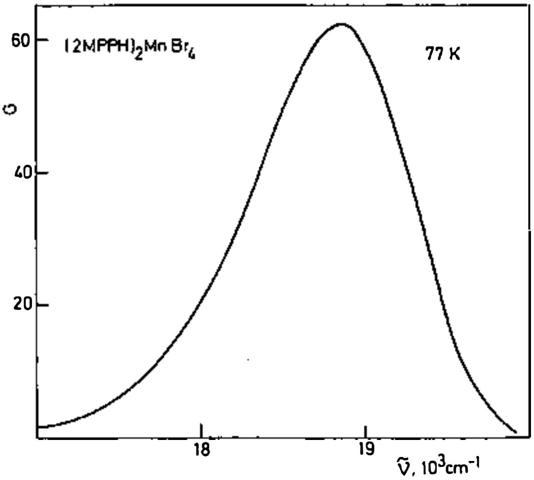


Fig. 2. The $G = f(\tilde{\nu})$ curve (where G is $I_\lambda \lambda^6$, and $\tilde{\nu} = 1/\lambda$) for the $(2MPPH)_2 MnBr_4$ compound at 77 K.

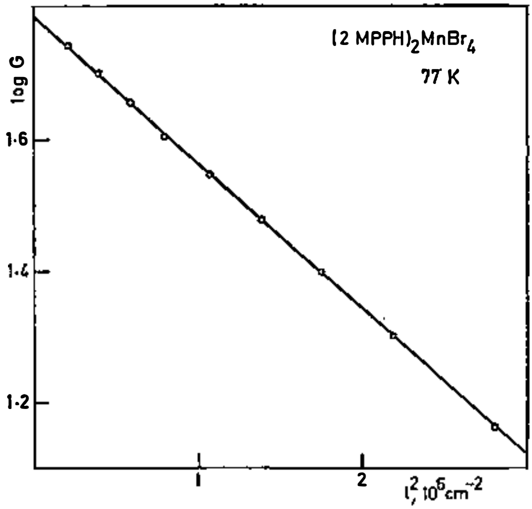


Fig. 3. Dependence of log G on l^2 for the compound investigated at 77 K. The slope of this straight line is the constant α.

On the curve given in Fig. 4 this slope is not infinite.

Likewise the slope a of the straight line representing the variation of the curve $\ln G(\tilde{\nu}_1) = \ln G(\tilde{\nu}_2)$ as a function of l^2 is expressed in the form:

$$a = h^2 c^2 (\beta - C_2)/4 [k_f r_0 - (k_e - k_f)(r_M - r_0)]^2 \tag{7}$$

from which the ratio a/m is derived to be:

$$a/m = hc(k_e - k_f)/8 [k_f r_0 - (k_e - k_f)(r_M - r_0)]^2. \tag{8}$$

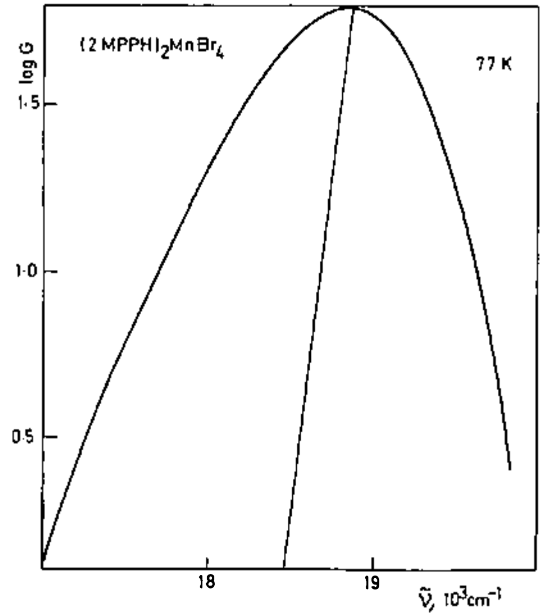


Fig. 4. The curve of log G as a function of $\tilde{\nu}$ for the compound investigated at 77 K. The slope of the straight line joining is m.

The ratio a/m varies slightly with temperature, since r_M depends on temperature.

The complex compound 2-methylpiperidine tetrabromomanganate exhibits spectra which verify this theory. The shape of the spectra is in accordance with formula (1) defining I_λ at any temperature. Namely, it is verified that variations of half-width (L) of the curve $G(\tilde{\nu})$ with temperature satisfy the formula:

$$1/L^2 = A\,\mathrm{th}(h\nu_e/2kT) + B. \tag{9}$$

This relation is derived in the first approximation of formula (7) giving a when r_M is close to r_0, i.e. when the constant C_1 is small. We then have:

$$a = h^2 c^2 (\beta - C_2)/4k_f^2 r_0^2. \tag{10}$$

It should be recalled that $1/K = a/\ln 2$. The value of r_M is close to that of r_0, since the wave number of the maximum of the function $G(\tilde{\nu})$ is little shifted as temperature varies. In fact one gets[9]:

$$hc\,(\tilde{\nu}_M - \tilde{\nu}_0) = -\,k_f\, r_0\,(r_M - r_0) + \frac{1}{2}\,(k_e - k_f)\,(r_M - r_0)^2. \qquad (11)$$

Since $\tilde{\nu}_M$ is close to $\tilde{\nu}_0$, the difference $(r_M - r_0)$ is small and, consequently, the constant C_2 is small, too. Formula (8) defining a is simplified and turns over into formula (10).

In Fig. 5 the variation of $1/L^2$ as a function of $1/T$ is shown. The curve remains close to that derived from the formula (9).

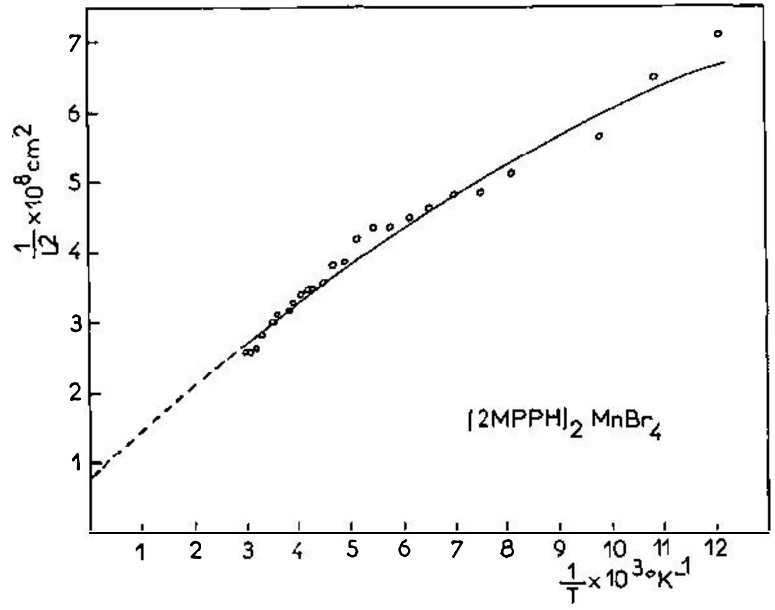


Fig. 5. The curve of the dependence of band half-width (L) on temperature (T) for the $(2\mathrm{MPPH})_2\mathrm{MnBr}_4$ compound. Open circles refer to experimental values, while the line is defined by formula (12).

The constants $h\,\nu_c/2k$, A and B are found to have values of 82.96 K, $7.65 \cdot 10^{-12}\,\mathrm{m}^2$ and $8.12 \cdot 10^{-5}\,\mathrm{m}^2$, respectively.

The following results were obtained on the variation of a/m with temperature:

It is noted that above a temperature of 219 K the value of the ratio a/m remains very close to $-3.42 \cdot 10^{-7}\,\mathrm{m}^{-1}$. Below 219 K the ratio a/m increases, on the average, slightly as the temperature decreases, but the icrease is not monotonous.

TABLE 1

$T\,(K)$	$-a/\mathrm{m}\ (10^{-7}\ \mathrm{m}^{-1})$	$T\,(K)$	$-a/\mathrm{m}\ (10^{-7}\ \mathrm{m}^{-1})$
82	3.89	213	2.90
92	3.69	219	3.43
102	4.20	232	3.51
114	3.80	246	3.54
123	3.44	255	3.47
133	3.26	263	3.50
143	3.16	273	3.55
153	4.00	283	3.48
163	3.41	301	3.45
173	2.85	313	3.52
183	3.85	323	3.43
193	3.04	333	3.52
203	2.30		

C. Thermal quenching

2-methylpiperidine tetrabromomanganate entres thermal quenching band at a temperature above 200 K, approximately. Above 360 K the compound decomposes.

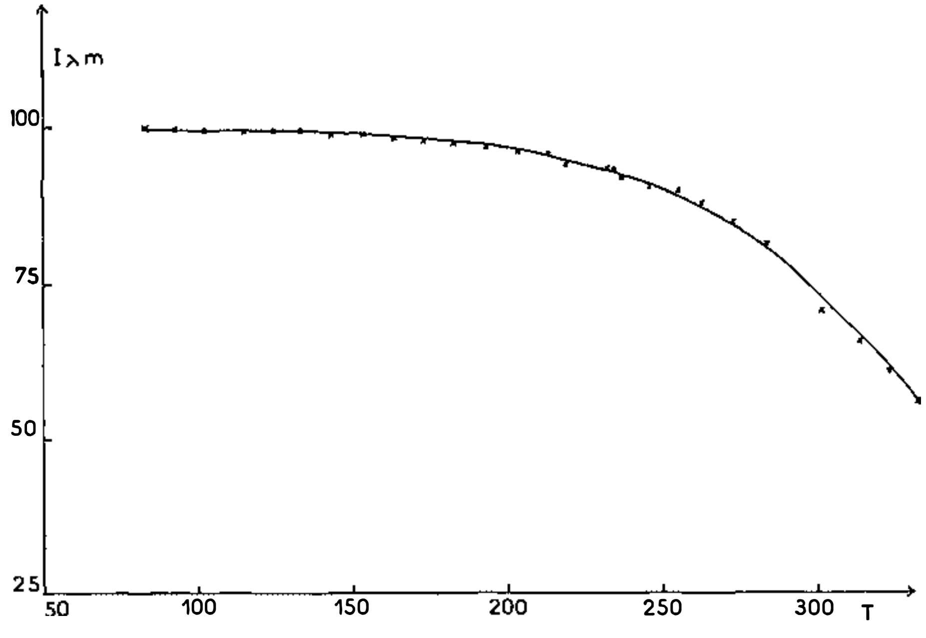


Fig. 6. Temperature dependence of luminescence intensity. $I_{\lambda M}$ is the peak glow of the emission spectrum of the compound investigated.

In Fig. 6 the curve of variation of its total light emitted is presented as a function of absolute temperature.

The Mott-Seitz formula is applicable here. It reads

$$I = I_0/(1 + C \, \mathrm{cxp}\,(- W/kT)).$$

One finds: $W = 2.965 \cdot 10^{-20}$J and $C = 472$.

D. Construction of configurational curves

On the basis of the above presented results it is possible to plot a diagram of configurational curves of 2-methylpiperidine tetrabromomanganate.

The equations of configurational curves are:

$$U_f(r) = \frac{1}{2} k_f r^2$$

$$U_e(r - r_0) = U_0 + \frac{1}{2} k_e (r - r_0)^2$$

where $U_f(r)$ is the potential energy of emitting centers in ground state, $U_e(r - r_0) - U_0$ is that of the centers in excited state and U_0 is the electron energy of emitting centers in excited state.

The two curves $U_f(r)$ and $U_e(r - r_0)$ intersect at abscissa r_1.

The theory of thermal quenching indicates that:

$$W = \frac{1}{2} k_e (r_1 - r_0)^2 = \frac{1}{2} k_f r_1^2 - U_0 = 2.965 \cdot 10^{-20}\mathrm{J}. \qquad (12)$$

Moreover, since the wavelength (λ_M) of the maximum of the function G($\tilde{\nu}$) varies slightly with temperature, we have

$$a/m = hc\,(k_e - k_f)/8\,k_f^2 r_0^2 = -3.42 \cdot 10^{-7}\mathrm{m}^{-1}. \qquad (13)$$

For the same reason it can be written that

$$hc\,\tilde{\nu}_M = hc\,\tilde{\nu}_0 = U_0 - \frac{1}{2} k_f r_0^2 = 3.764 \cdot 10^{-19}\mathrm{J}. \qquad (14)$$

In fact, r_M is very close to r_0, $\tilde{\nu}_M$ is close to $\tilde{\nu}_0$ and the constant C_1 is small.

The variation of band width has made it possible to determine $h\nu_e$:

$$h\nu_e = (h/2\pi)\,(k_e/M)^{1/2} = 2.291 \cdot 10^{-21}\mathrm{J}.$$

Finally, the mass of luminescence centers (M) has been assumed to be that of the Mn^{2+} ion.

From this the value of k_e is found to be 43.06 Nm^{-1}.

Equations (12), (13) and (14) enable one to calculate r_1/r_0, k_e/k_f, U_0 and $k_f\, r_0^2/2$.

Setting $r_1/r_0 = X$, X being the solution of the equation

$$- h\nu_0 X^2 + 2WX - (16a/mhc)(W + h\nu_0)^2 + 2W + h\nu_0 = 0,$$

one has: $h\nu_0 = 3.764 \cdot 10^{-19}J$,

$$2W = 5.930 \cdot 10^{-20}J \text{ and}$$

$$- (16a/mhc)(W + h\nu_0)^2 + 2W + h\nu_0 = 4.975 \cdot 10^{-18}J.$$

Whence one derives: $X = 3.716$

$$U_0 = 4.079 \cdot 10^{-19}J,$$

$$k_e/k_f = 0.1257 \text{ and}$$

$$\frac{1}{2} k_f r_0^2 = 3.172 \cdot 10^{-20}J.$$

The value of $h\nu_e$ is $2.291 \cdot 10^{-20}J$, hence

$$\nu_e = 3.459 \cdot 10^{12}Hz,$$

$$\nu_f = 9.755 \cdot 10^{12}Hz,$$

$$k_e = 43.06\, Nm^{-1},$$

$$k_f = 342.6\, Nm^{-1},$$

$$r_0 = 1.36 \cdot 10^{-11}m \text{ and}$$

$$r_1 = 5.057 \cdot 10^{-11}m.$$

Since the unit of energy is Joule (J) and the unit of length (for r) is meter (m), the equations of configurational curves are:

$$U_f = 171.3\, r^2,$$

$$U_e = 21.53\, r^2 - 5.930 \cdot 10^{-10} r + 4.119 \cdot 10^{-19}.$$

These curves are shown in Fig. 7.

In these curves it is seen that the theoretical wavelength (λ_a) of excitation maximum is $4.820 \cdot 10^{-7}$m. Experimentally it is found that λ_a has a value of $4.810 \cdot 10^{-7}$m. Consequently, there is a very good agreement with theory.

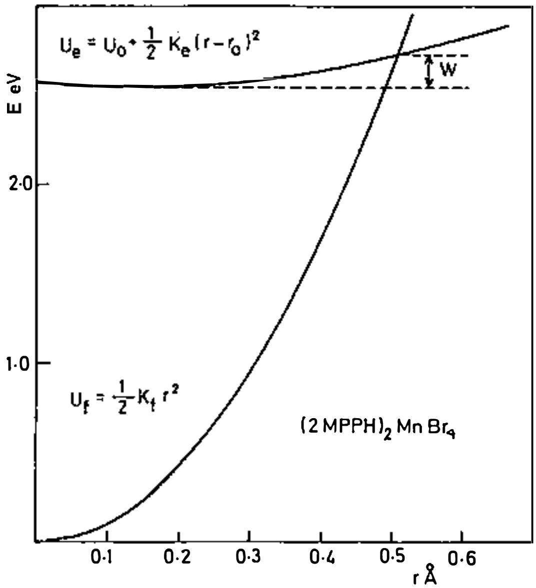


Fig. 7. Configurational coordinate curve of the ground and excited states of the investigated compound, constructed on the basis of calculated values.

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DIJAGRAM KONFIGURACIONIH KRIVIH TETRAEDARSKOG KOMPLEKSNOG JEDINJENJA MANGAN(II) BROMIDA SA 2-METILPIPERIDINOM

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Proučavane su fotoluminescentne osobine jedinjenja mangan(II) bromida sa 2-metilpiperidinom. Za interpretaciju emisionih luminescentnih spektara korišćena je teorija konfiguracionih krivih, pri čemu su dobijena dobra slaganja teorijskih i eksperimentalnih rezultata. Merenja emisionih spektara izvođena su na raznim temperaturama u intervalu od 77 do 333 K. Iz ovih spektara izračunate su karakteristične konstante na osnovu kojih su određene konfiguracione krive za ispitivano jedinjenje.