

THE PHOTOEXCITATION AND PHOTOLUMINESCENCE OF THE
CRYSTALLINE TETRAHEDRAL COMPLEX COMPOUND OF
MANGANESE(II) CHLORIDE WITH 3,5-LUTIDINE HYDROCHLORIDE

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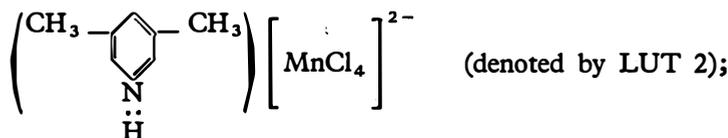
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Abstract: Two photoluminescent crystalline complex compounds of MnCl_2 with 3,5-lutidine hydrochloride were synthesized, wherein the Mn^{2+} ion is in tetrahedral (green luminescence) and octahedral symmetry (red luminescence). In the present work the experimental and theoretical results on the energy structure of the tetrahedral complex are reported. The excitation spectrum was recorded and all the ligand field excitation bands were identified for Mn^{2+} in tetrahedral symmetry. The Racah parameters B and C, the secular determinants for d^5 quartet levels, the ground terms ($10 Dq = 0$) and the field strength of this complex were calculated. Also the luminescence emission spectrum was recorded and the effect of temperature on its basic parameters was analyzed. A configurational coordinate diagram is given for the ground state ${}^6A_1(S)$ and for the lowest excited state ${}^4T_1(G)$.

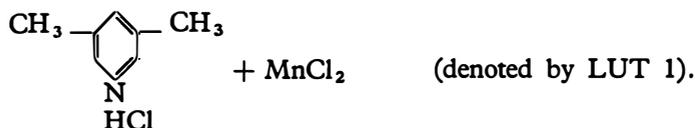
1. Introduction

Manganese(II) chloride forms with 3,5-lutidine hydrochloride two crystalline complexes:

— a complex in which the stoichiometric ration of the organic to inorganic component is 2 : 1 and the central Mn^{2+} ion is in tetrahedral symmetry



— a complex in which the stoichiometric ratio of the components is 1 : 1 and the central Mn^{2+} ion is in octahedral symmetry



Both complexes exist only in the crystal form (the absorption spectrum of ethanolic solution of the complexes shows the presence of only the Mn^{2+} , Cl^- and pyridinium ions) and belong to the class of complexes which in their external coordination sphere have organic ligands with a nitrogen ring. They exhibit an intense green (complex LUT 2) and red photoluminescence (complex LUT 1) and have so far not been reported in the literature.

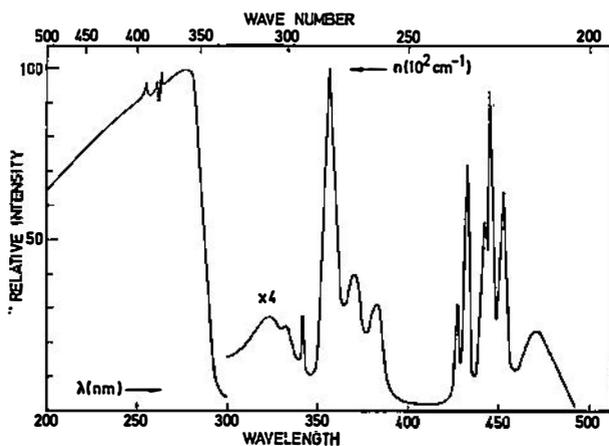


Fig. 1. Excitation spectrum of complex LUT 2 for $\lambda_{em} = 510$ nm at a temperature of 77 K.

The mechanism of excitation and luminescence of such a type of complex has been explained partly¹⁻⁵⁾ in terms of ligand field theory as follows : the Mn^{2+} ion is the luminescence center, its ground term is $S(^6A_1)$, excitation is carried out to the quartet terms 4G , 4D , 4P and 4F which, due to the orbital degeneracy caused by a ligand field of a strength of $10 Dq$, are split into ten energy levels $^4G(^4T_1, ^4T_2, ^4E, ^4A_1)$, $^4D(^4T_2, ^4E)$, $^4P(^4T_1)$ and $^4F(^4A_2, ^4T_1, ^4T_2)$; luminescence arises from the transition from the lowest excited level $^4T_1(G)$ to the ground level $^6A_1(S)$.

In the present work the results of experimental and theoretical investigations of the photoluminescence of complex LUT 2 are presented.

2. Experimental

The crystalline complex LUT 2 was synthesized by a direct reaction of equivalent quantities of MnCl_2 and previously synthesized 3.5-lutidine hydrochloride in an ethanolic solution, whereby a better yield was obtained. Green hygroscopic crystals were obtained by the standard procedure. The stoichiometric ratio of the components of the complex was established by a microanalysis.

The excitation spectrum was recorded at the temperature of liquid nitrogen, while the luminescence emission spectra were measured in a temperature range from -21 to $+84^\circ\text{C}$.

The spectra were investigated using an Aminco-Bowman spectrophotofluorimeter with corresponding accessories. The reproducibility of the spectra was confirmed by the use of a phosphoscope, which shows that the luminescence is due to a transition between states of different multiplicity (phosphorescence).

The spectra were corrected and other results were obtained by automatic data processing according to a programme made for this problem.

3. Results and discussion

Excitation spectrum. The structure and ratio of excitation spectral bands are independent of emission wavelength. The excitation spectrum (Fig. 1) was recorded at the emission maximum ($\lambda_{em} = 510$ nm).

All the bands characteristic of excitation transitions of d^5 configuration (the Mn^{2+} ion in tetrahedral symmetry) were identified (see Table 1). Bands corresponding to the ${}^4\text{E}(\text{G})$ and ${}^4\text{A}_1(\text{G})$ levels are separated due to the spin-orbit coupling. The band corresponding to the ${}^4\text{T}_2(\text{G})$ level exhibits three peaks which probably arise from interaction between ligands resulting in a further splitting of levels. At room temperature this pattern disappears.

A satisfactory interpretation of the excitation spectrum is obtained by means of Orgel's weak field matrices for d^5 quartet levels^{1,6}.

Since the ${}^4\text{E}$, ${}^4\text{A}_1(\text{G})$ and ${}^4\text{E}(\text{D})$ levels are independent of the field strength 10Dq , their matrix elements are linear combinations of the Racah parameters B and C. On identification of the spectral bands the secular determinants for the ${}^4\text{A}_1(\text{G})$ and ${}^4\text{E}(\text{D})$ terms were solved, the Racah parameters were evaluated and the position of the ${}^4\text{A}_2(\text{F})$ band was found (Table 1). Reduced secular determinants for ${}^4\text{T}_1$ and ${}^4\text{T}_2$ are:

$${}^4\text{T}_1({}^4\text{G}, {}^4\text{P}, {}^4\text{F}) \begin{vmatrix} 54.70708 - \epsilon & 0 & -0.44722 \delta \\ 0 & 39.70708 - \epsilon & -0.89444 \delta \\ -0.44722 \delta & -0.89444 \delta & 33.36220 - \epsilon \end{vmatrix} = 0$$

$${}^4\text{T}_2({}^4\text{G}, {}^4\text{D}, {}^4\text{F}) \begin{vmatrix} 54.70708 - \epsilon & -0.65466 \delta & -0.75591 \delta \\ -0.65466 \delta & 14.67244 - \epsilon & 0 \\ -0.75591 \delta & 0 & 40.36220 - \epsilon \end{vmatrix} = 0,$$

Table 1

Quartet terms	Calculated position (10Dq = 0) in cm^{-1}	Level in T_d symmetry	Experimental positions of excitation bands n_1 in cm^{-1} (nm)	Calculated positions of excitation bands n_2 (10Dq = 3650 cm^{-1}) in cm^{-1} (nm)	$n_2 - n_1$ (10^3 cm^{-1})
4G	23115	$^4T_1(G)$	21276 (470)	21261 (470.3)	-0.015
		$^4T_2(G)$	22099 (452.5) 22471 (445) 22598 (442.5)	22687 (440.8)	+0.216
		$^4A_1(G)$	23121 (432.5)		
		$^4E(G)$	23391 (427.5)		
4D	28005	$^4T_2(D)$	27027 (370)	27364 (365.4)	+0.337
		$^4E(D)$	27972 (357.5)		
4P	27499	$^4T_1(P)$	29240 (342)	29176 (342.7)	-0.064
4F	37910	$^4A_2(F)$	37879 (264)	37913 (263.8)	+0.016
		$^4T_1(F)$	38167 (262)	38112 (262.3)	-0.055
		$^4T_2(F)$	39216 (255)	38954 (256.7)	-0.262

Racah parameters: $B = 693 \text{ cm}^{-1}$, $C = 3238.2 \text{ cm}^{-1}$ ($C/B = 4.673$)

Table 2

T (K)	$a/m \cdot 10^{-4} \text{ cm}^{-1}$
252	0.381
258	0.346
268	0.370
276	0.368
293	0.332
306	0.354
318	0.322
331	0.340
344	0.361
357	0.343

where $\varepsilon = E/B$, and $\delta = 10 Dq/B$. Data for the energy level diagram were obtained by varying $10 Dq$ over the range $0-10000 \text{ cm}^{-1}$. The best fit value of field strength is

$$10 Dq = 3650 \text{ cm}^{-1}.$$

Table 1 gives the values of the ground terms ($10 Dq = 0$) and deviations of experimentally found band positions from calculated ones for $10 Dq = 3650 \text{ cm}^{-1}$.

The peak at 273 nm is due to 3,5-lutidine hydrochloride (it appears in the absorption spectrum of an aqueous or methanolic solution of 3,5-lutidine hydrochloride).

Non-identified bands are at 382.5, 332 and 322 nm.

Emission spectrum. The luminescence emission spectrum of complex LUT 2 has one narrow band the peak of which is at $\lambda_{\text{max}} = 510 \text{ nm}$ (19608 cm^{-1}) (see Fig 2). The position of the peak is temperature-independent (within a temperature range from -196 to $+84^\circ\text{C}$).

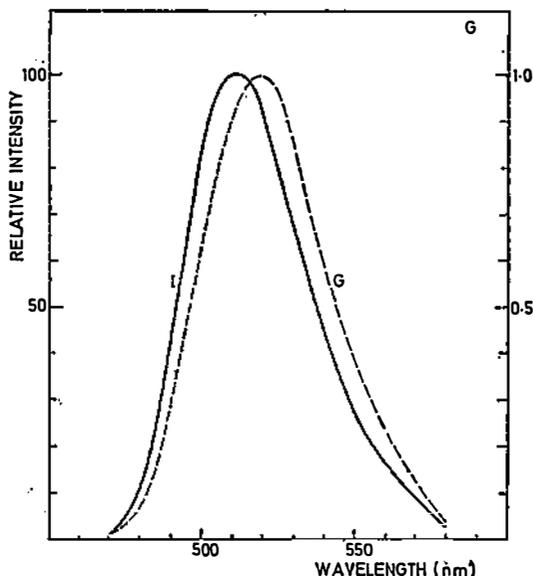


Fig. 2. Photoluminescence spectrum (I) and the distribution function of the matrix factor of dipole transition (G) of complex LUT 2 for $\lambda_{\text{exc}} = 357 \text{ nm}$ at $T = 293 \text{ K}$.

On heating the integral intensity, as well as maximum intensity, decrease according to the Mott-Sitz law. By fitting to the Mott-Seitz law the following equation is obtained for the variation of maximum intensity (relative energy per unit wavelength interval) with temperature

$$I = 108.3[1 + 501.6 \exp(-1202.9/T)]^{-1},$$

the maximum relative deviation of the fit being 3.2%. From this the activation energy for quenching is found to be $W_1 = 0.1037$ eV. The integral intensity fitting is obtained for $W_2 = 0.0964$ eV with a maximum deviation of the fit of 2.3%.

Emission band half-width, L , increases with rising temperature. By fitting to Payen's formula⁷ the following equation is obtained for L as a function of T

$$1/L^2 = 2.68 \operatorname{tgh}(201.1/T) + 0.942 \text{ (cm}^2\text{)},$$

with a maximum relative deviation of the fit of 6.1%. Since $h\nu_e/2k = 201.1$ K, the fundamental frequency of the excited state is $\nu_e = 0.8379 \cdot 10^{13} \text{ s}^{-1}$. By fitting to Ruamp's formula⁸) a value of $0.7649 \cdot 10^{13} \text{ s}^{-1}$ is obtained for ν_e , with a maximum deviation of the fit of 10%.

From the emission spectrum the distribution function of the matrix factor of dipole transition, $G(1/\lambda) = \lambda \cdot I$, is obtained (Fig. 2). From a plot of $\ln G$ as a function of $1/\lambda$ the rectilinear parameter m was determined as the slope of the bisectrix of horizontal chords, which expresses the asymmetry of the real Gaussian $G(1/\lambda)$ (see Fig. 3). Another characteristic parameter, a , of the $G(1/\lambda)$ curve was

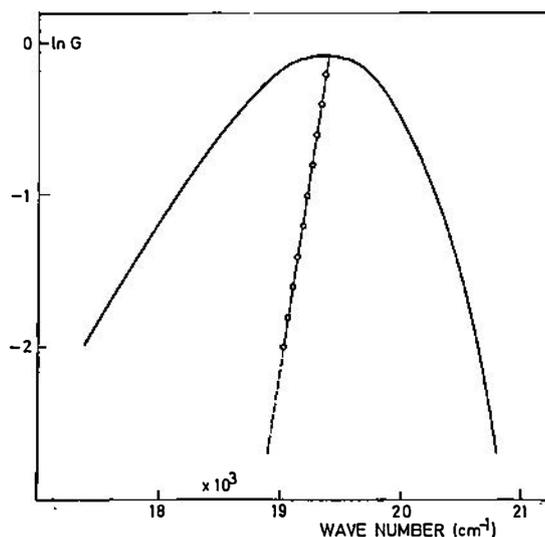


Fig. 3. The $\ln G$ -versus- $1/\lambda$ curve at a temperature of 293 K for complex LUT 2.

obtained from the slope of the $\ln G$ -versus- l^2 curve, where l is the difference between wave numbers which have the same corresponding $\ln G$ (Fig. 4). The ratio of these two parameters is approximately constant over the experimental temperature range (Table 2).

Configurational coordinate diagram. A thermal analysis of the emission spectrum of complex LUT 2 makes it possible to represent the energy level scheme of the emission center Mn^{2+} by the method of a single configurational coordi-

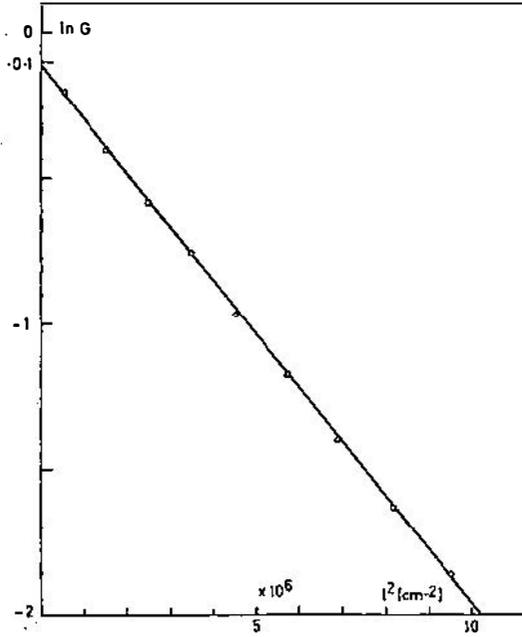


Fig. 4. The $\ln G$ -versus- L^2 curve at temperature of 293 K for complex LUT 2.

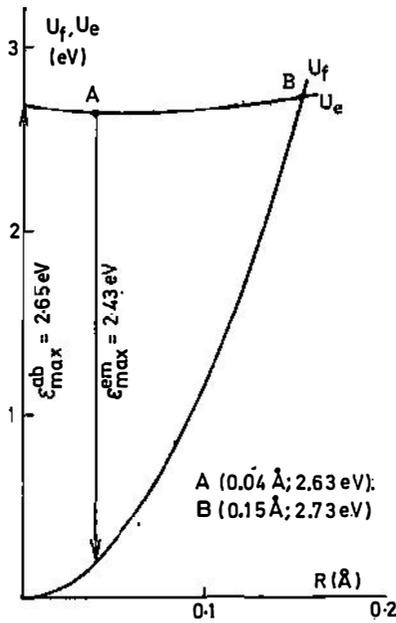


Fig. 5. Configurational coordinate diagram for complex LUT 2.

nate^{4,5}). Since the condition $a/m \approx \text{const}$ is fulfilled, the following characteristic quantities of configurational parabolas have been found by the known procedure:

- minimum of the potential energy U_e of the ${}^4T_1(G)$ level $U_0 = 2.63$ eV;
- configurational coordinate of the minimum of the U_e curve $R_0 = 0.04$ Å;
- configurational coordinate of thermal desactivation $R_1 = 0.15$ Å;
- fundamental frequency of the ground state $\nu = 0.3130 \cdot 10^{14}$ s⁻¹;
- wave number of the absorption peak $1/\lambda_a = 21380$ cm⁻¹.

The equations of the configurational parabolas (Fig.5) of the ground state (U) and of the ${}^4T_1(G)$ state (U_e) read

$$U = 110.1 R^2 \text{ (eV)} \quad \text{and} \quad U_e = 7.9 R^2 - 0.7 R + 2.7 \text{ (eV)}.$$

The experimentally obtained excitation peak for the ${}^4T_1(G)$ level is at 21276 cm⁻¹, which is in good agreement with the absorption peak of the configurational curves.

The Stokes separation between the excitation and emission peaks of complex LUT 2 is 1668 cm⁻¹ and, according to Furlani's criterion⁹), is an experimental confirmation that in this complex the Mn²⁺ ion is in tetrahedral symmetry.

References

- 1) L. E. Orgel, J. Chem. Phys. **23** (1955) 1822;
- 2) Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. **9** (1954) 753, 766;
- 3) D. Curie, C. Barthou and B. Canny, J. Chem. Phys. **61** (8) (1974) 3048;
- 4) H. Payen de la Garanderie, Thesis, Paris (1964); Ann. Phys., **9** (1964) 649;
- 5) K. Nikolić, F. Lignou and H. Payen de la Garanderie, J. of Lum. **8** (1973) 137;
- 6) K. Bingham and S. Parke, Phys. and Chem. of Glasses **6** (6) (1965) 224;
- 7) F. Lignou and H. Payen de la Garanderie, J. Physique **36** (1975) 1341;
- 8) J. Ruamps, J. Physique Rad. **21** (1960) 52 S;
- 9) C. Furlani, E. Cervone and P. Cancellieri, Lincei-Rend. Sc. fis. mat. e nat. **37** (1964) 446.

FOTOEKSCITACIJA I FOTOLUMINESCENCIJA KRISTALNOG TETRAEDARSKOG KOMPLEKSA MANGAN(II)HLORIDA SA HIDROHLORIDOM 3.5-LUTIDINA

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Sadržaj

Sintetizovana su dva fotoluminescentna kristalna kompleksa MnCl₂ sa hidrohloridom 3.5-lutidina: sa jonom Mn²⁺ u tetraedarskoj simetriji (zelena luminescencija) i oktaedarskoj (crvena luminescencija).

U radu su referisani eksperimentalni i teorijski rezultati o energetske strukturi prvog kompleksa. Izmeren je ekscitacioni spektar i identifikovane su sve trake

ligandnog polja za Mn^{2+} u tetraedarskoj simetriji. Izračunati su Racah-ovi parametri B i C, sekularne determinante za kvartetne nivoe d^5 , osnovni termovi ($10Dq = 0$) i jačina polja ovog kompleksa ($10Dq = 3650 \text{ cm}^{-1}$). Izmeren je emisijski luminescentni spektar i analiziran uticaj temperature na njegove osnovne parametre. Prikazan je također konfiguracioni dijagram za osnovno $A_1(S)$ i najniže pobuđeno stanje ${}^4T_1(G)$.