

EXCITATION AND EMISSION LUMINESCENCE SPECTRA AND
STRUCTURE OF 2,6-DIMETHYLPYPERIDINIUM MANGANESE(II)
TETRACHLORIDE IN SOLID STATE

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Excitation and emission luminescence spectra of compound formed from manganese(II) chloride and 2,6-dimethylpiperidine hydrochloride are determined. The *Crystal Field Theory* (CFT) is applied to the excitation spectra, and the Racah parameters B and C and the value of the crystal field strength parameter Dq are determined. The emission spectrum parameters are determined according to the *Configurational Curves Theory* (CCT). It is shown that the centre of luminescence is the complex anion $(\text{MnCl}_4)^{2-}$, that its structure is tetrahedral and that the emission process is phosphorescence. The covalency parameter is determined which shows that the metal-ligand bonds of this complex anion are not purely ionic.

1. Introduction

In a number of previous papers¹⁻¹²⁾ we studied optical spectra of manganese(II) complexes which belong to complexes of type $(\text{RH})_2\text{MnX}_4$ or $\text{RH}(\text{MnX}_3)$, where R is a weak organic base, and X is a halid (C, Br or J). We also studied^{13, 14)} luminescence spectra of crystalphosphorouses doped by Mn^{2+} . In this paper we determine the excitation and emission spectra of the compound formed from manganese(II) chloride (MnCl_2) and hydrochloride of 2,6-dimethylpiperidine (2DMPPHCl).

* Zavod za fizičku hemiju.

2. Experimental

The complex studied here was prepared by adding hydrochloric acid (HCl) to a methanol solution of equivalent amounts of 2DMPP and MnCl_2 . The obtained solution evaporated at room temperature until it crystallized. The obtained microcrystals were dried in vacuum over phosphorus pentoxid (P_2O_5).

By elemental analysis it was established that the ratio of 2DMPP to manganese(II) is 2 : 1.

These excitation and the emission luminescence spectra of the sample were determined at room temperature and the temperature of liquid nitrogen by AMINCO-BOWMAN spectrophotofluorimeter.

These spectra were corrected¹⁵⁾, while the Racah parameters B and C and the crystal field parameter Dq were automatically determined by original programme, on the basis of experimentally determined positions of band maximums in excitation spectra.

3. Results and discussion

The excitation (Fig. 1) and the emission (Fig. 2) spectra of the considered compound show appearance characteristic for manganese(II) in cubic crystal field of symmetry type T_d .

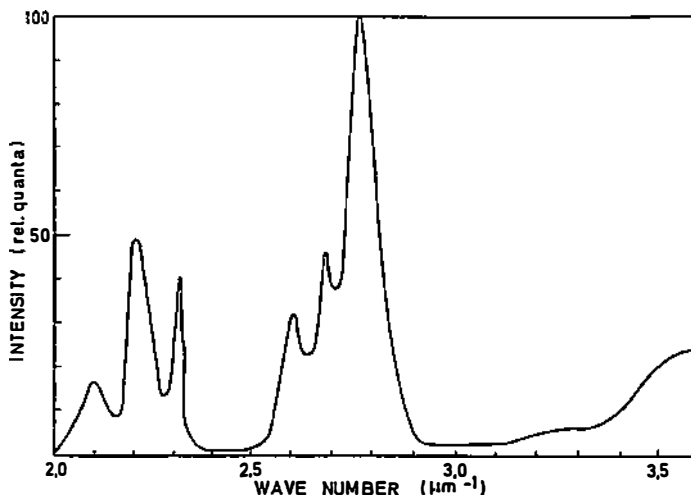


Fig. 1. Excitation spectrum of $(2\text{DMPPH})_2\text{MnCl}_4$ at 77 K.

3.1. Excitation spectrum

Excitation spectrum bands of tetrahedral complex anion $(\text{MnCl}_4)^{2-}$ take place as a result of transitions from the ground state of manganese(II) in cubic crystal field ${}^6\text{A}_1({}^6\text{S})$ to one of its excited states ${}^4\text{T}_1({}^4\text{G})$, ${}^4\text{T}_2({}^4\text{G})$, ${}^4\text{A}_1$, ${}^4\text{E}({}^4\text{G})$, ${}^4\text{T}_2({}^4\text{D})$, ${}^4\text{E}({}^4\text{D})$, ${}^4\text{T}_1({}^4\text{P})$,...

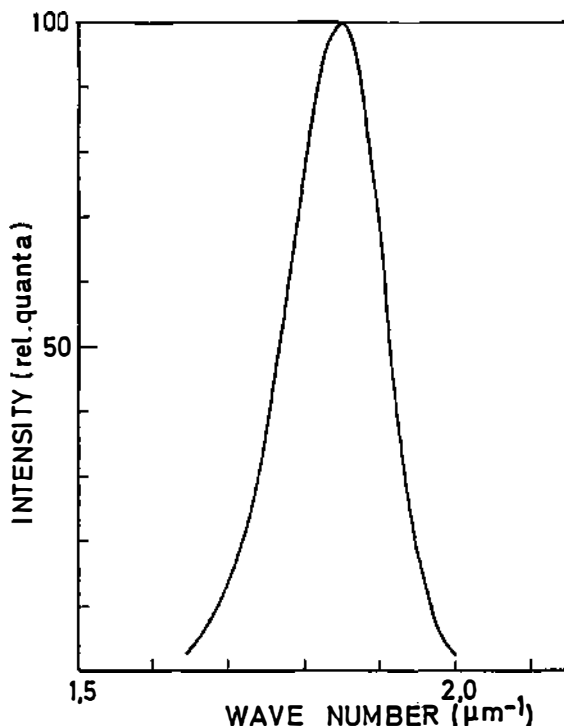


Fig. 2. Emission spectrum of $(2\text{DMPPH})_2\text{MnCl}_4$ at 77 K.

If the positions of excitation spectrum band maximums are taken as energies of these transitions, then those energies can be determined by weak field Orgel matrices¹⁶⁾ for given values of parameters B , C and Dq . Finally, it is possible to choose such values of these parameters which show best agreement between experimental and calculated values. The parameters B and C can be determined as spectroscopic constants, on the basis of the positions of band maximums 4A_1 , 4E (4G) and 4E (4D)^{17,18)}. The programme for automatic analysis of excitation (and other optical) spectra of manganese(II) in cubic crystal field is founded on this method, and it determines the value of Dq which gives the best agreement between the calculated and experimentally determined band maximum positions.

The results of automatic analysis of excitation spectrum of the sample at room temperature (293 K) and at the liquid nitrogen temperature (77 K) are given in Table 1. They show good agreement for all bands except for 4T_1 (4P), as noticed by other authors^{17,19-22)}.

The value of the crystal field strength parameter Dq ($\approx 400 \text{ cm}^{-1}$) and higher degree of covalency ($\beta \approx 0.700$) show that the considered compound contain complex anion of tetrahedral configuration.

The disagreement between experimentally determined and calculated values of the band position 4T_1 (4P) is explained¹⁹⁾ by the higher reduction of the Racah parameter B of manganese(II) in cubic crystal field of T_d symmetry type in comparison with the free ion B_0 .

TABLE 1.

Crystal field levels	77 K		293 K	
	Exp.	Calc.	Exp.	Calc.
${}^4T_1({}^4G)$	21 030	21 026	21 000	20 998
${}^4T_2({}^4G)$	22 040	22 497	22 400	22 509
${}^4A_{1g}, {}^4E({}^4G)$	23 150	23 150	23 150	23 150
${}^4T_2({}^4D)$	25 950	26 117	26 250	26 261
${}^4E({}^4D)$	26 900	26 900	27 050	27 050
${}^4T_1({}^4P)$	27 680	30 485	27 950	30 368
Unassigned	32 500	—	35 500	—
Parameters: B		536		557
C		3 559		3 516
Dq		425		425
β		0.682		0.709

All values (except β) in cm^{-1} .

Experimental and calculated values of band maxima in the excitation spectrum $(2\text{DMPPH})_2\text{MnCl}_4$ at 77 and 293 K, the Racah parameters, the crystal field strength parameter and degree of covalency.

3.2. Emission spectra

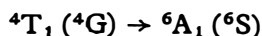
The considered complex has the emission luminescence spectrum in the green region. This is characteristic for complexes which contain a tetrahedral complex anion^{2,3}). Table 2 gives emission spectra parameters of the sample according to CCT⁸). Among them there is the Stokes loss (Φ) whose value also indicates the presence of a tetrahedral complex anion^{2,4}).

TABLE 2.

Parameters	Units	77 K	293 K
ν_m	μm^{-1}	1.851	1.885
ν_o	μm^{-1}	1.844	1.871
L	μm^{-1}	0.156	0.273
α	μm^2	-28.5	-9.31
m	μm	91.9	31.5
a/m	μm	-0.310	-0.296
Φ	μm^{-1}	0.152	0.210

Parameters obtained from emission spectrum $(2\text{DMPPH})_2\text{MnCl}_4$ at 77 and 293 K.

Excitation and emission spectrum of the considered compound takes place as a result of electronic transition of manganese(II) in cubic crystal field of symmetry type T_d , which means that the considered complex contain the complex anion $(\text{MnCl}_4)^{2-}$ as the centre of luminescence. The emission transition



is forbidden with respect to the spin-selection rule and corresponds to *phosphorescence*. The validity of this hypothesis can be confirmed by measuring the *Lifetime* of the excited state or *Decay time*.

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EKSCITACIONI I EMISIONI SPEKTRI LUMINISCENCIJE I
STRUKTURA 2,6-DIMETILPIPERIDINIJUM MANGAN(II)
TETRAHLORIDA U ČVRSTOM STANJU

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Određeni su ekscitacioni i emisioni spektri luminiscencije jedinjenja dobivenog od mangan(II)hlorida i 2,6-dimetilpiperidinhidrohlorida. Na ekscitacione spektre primenjena je *Teorija kristalnog polja* (CFT) i određeni su RACAH-ovi parametri *B* i *C* i vrednost parametra jačine kristalnog polja *Dq*. Određeni su parametri emisionog spektra prema *Teoriji konfiguracionih krivih* (TCC). Pokazano je da je centar luminiscencije kompleksni anjon $(MnCl_4)^{2-}$, da je njegova struktura tetradarska i da je emisioni proces — fosforescencija. Određen je parametar kovalentnosti koji pokazuje da veze metal-ligand u ovom kompleksnom anjonu nisu čisto jonske.

* Zavod za fizičku hemiju.