ELECTRON PARAMAGNETIC RESONANCE OF Mn^{2+} IN $(C_5H_5NH)_2Mn_xZn_{1-x}Cl_4$ AND $((CH_3)_4N)_2Mn_xZn_{1-x}Cl_4$

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Green luminescent tetrahedral complexes $(C_5H_5NH)_2MnCl_4$ and $((CH_3)_4N)_2MnCl_4$ have been extensively studied. But their E. P. R. spectra show only very wide bands without any fine and hyperfine structure. By incorporating low concentrations of Mn^{2+} ($x = 1\%$) in isomorphous $(C_5H_5NH)_2Mn_xZn_{1-x}Cl_4$ or $((CH_3)_4N)_2Mn_xZn_{1-x}Cl_4$, we could derive from angular variations the whole set of parameters of the spin Hamiltonian. The tetrahedra are highly distorded, resulting (in all cases) in a C_1-symmetry.

1. Introduction

Organo-metallic complexes, where the manganese ion is present, are well known for their strong luminescence[1-4]. In these compounds, the magnetic properties and phase transformations have been also extensively studied[5]. These complexes are, either tetrahedral, either octahedral. Here we study tetrahedral complexes, however, it has been found that strong distortions occur from the

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regular tetrahedron, and the crystal field symmetry is not higher as T_d. It is the purpose of this paper to determine accurately the site symmetry, the crystal field parameters and the ground state splitting of the Mn^{++} ion.

It is well known that the E. P. R. techniques are most convenient for achieving this aim when Mn^{2+} ion is involved[6,7]. However, this could be done correctly only if some concentration conditions are fulfilled, which allow to observe fine and hyperfine structure. Thus we use organometallic zinc complexes containing dilute manganese, as in our case, Zn compounds and Mn compounds cristallize in the same space group[8,9].

In the first part of this paper, we describe the cristallographic data and in the second part, we determine the spin Hamiltonian parameters. The zero-field splitting of the ground state is also given.

2. Preparation and crystallographic data

By mixing in stoechiometric proportions solutions in anhydrous ethanol of pyridinium chloride or tetramethylammonium chloride, with hydrated zinc or manganese chloride, one obtains by slow evaporation from the mother solution, single crystals as platelets whose dimensions are of the order of $5 \times 5 \times 2 \; mm^3$. The chemical formulae are $(C_5H_5NH)_2Mn_xZn_{1-x}Cl_4$ and $((CH_3)_4N)_2Mn_x Zn_{1-x}Cl_4$ as it was shown by analysis. In both compounds they are green-yellow for $x = 1$ and $x = 0,3$, colorless for $x \leq 0.1$. The crystals corresponding to $x = 0$ and $x = 1$ are isomorphic.

$(C_5H_5NH)_5MnCl_5$ crystallize in the P_1 space group[9]. The unit cell parameters are:

$$a = 1.2711 \; nm; \quad b = 0.8158 \; nm; \quad c = 0,7681 \; nm$$

$$\alpha = 100.38°; \quad \beta = 93.43°; \quad \gamma = 88.78°.$$

The position of the neighbouring ions is described in Fig. 1-a.

$((CH_3)_4Mn_xZn_{1-x}Cl_4$ belongs to the space group D_{2h}^{16} [8] with a unit cell defined by:

$$a = 1.2276 \; nm, \quad b = 0.8998 \; nm, \quad c = 1.5541 \; nm \; for \; x = 0$$

and

$$a = 1.233 \; nm, \quad b = 0.906 \; nm, \quad c = 1.564 \; nm \; for \; x = 1.$$

The position of the neighbouring ions (for $x = 0$) is described in Fig. 1-b. In all cases, the local symmetry for the metallic ions is C_1.

3. E. P. R. experiments

The E. P. R. spectra were recorded on a Varian E 115 spectrometer, operating in the Ka band (35 GHz) at room temperature, and in the X band at 9 GHz at liquid helium temperature. The magnetic field values were measured with a Systron Donner N. M. R. Gaussmeter. In each case, the crystal was carefully fixed in the cavity, and by using well defined growing planes, particular orientations are deter-
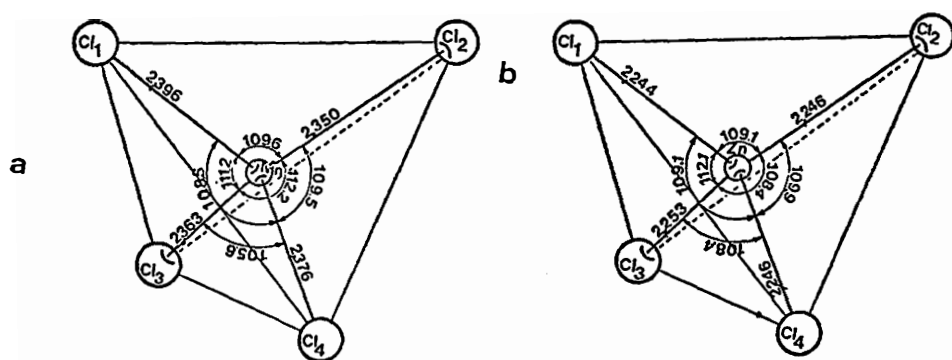
Fig. 1: C_1 site symmetry of M^{2+} ion in a) $(C_5H_5NH)_2MnCl_4$ and b) $((CH_3)_4N)_2ZnCl_4$.

mined. Then the magnet could be rotated to any required angle in the horizontal plane so that the complete angular variation of the spectra is recorded. Corresponding to the allowed transitions $\Delta M_S = 1$, $\Delta M_I = 0$, where M_S refers to electronic spin and M_I to nuclear spin, 30 lines could be observed as it is shown in Fig.2.
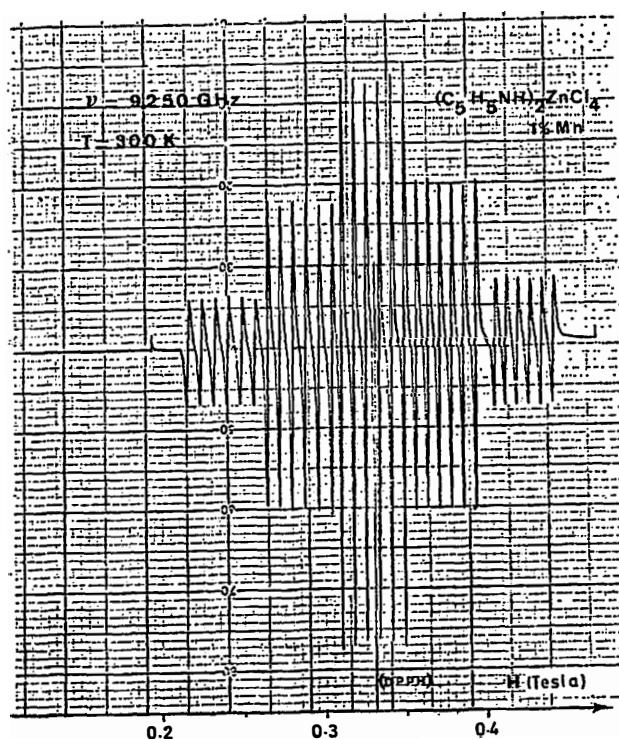

Fig. 2: E. P. R. spectrum of Mn^{2+} at room temperature in $(C_5H_5NH)_2Mn_xZn_{1-x}Cl_4$ for $x = 0.01$. The magnetic field is perpendicular to the b axis.

Each spectrum is composed by 5 groups of 6 lines, the angular variations Fig. 3 and Fig. 4 are associated to the center of gravity of the groups, corresponding to the $M_S \rightarrow M_S - 1$ transitions. Due to the linewidth, no ligand hyperfine structure
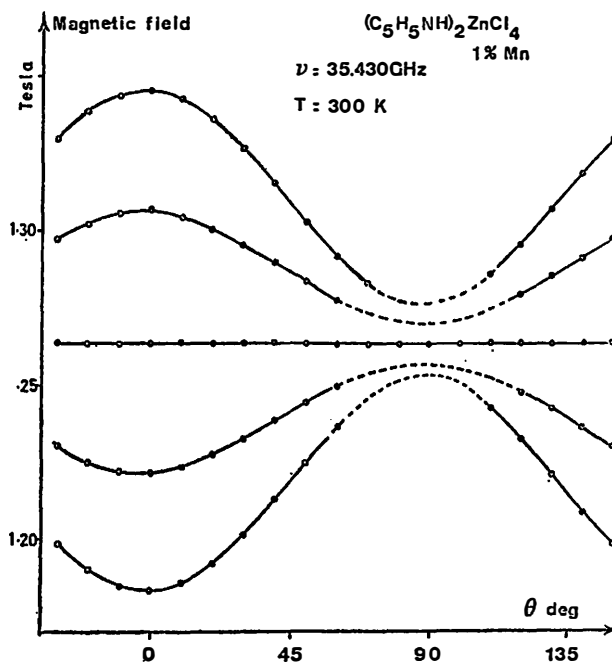

Fig. 3: Angular variation of the $M_S \rightarrow M_S-1$ transitions in $(C_5H_5NH)_2Mn_xZn_{1-x}Cl_4$. $\Theta = 0$ corresponds to $H \| a$.

could be available so that the superhyperfine interaction term could be dropped out the spin Hamiltonian. So we only consider the Zeeman term, the internal crystal field contribution and the hyperfine term due to the $I = \dfrac{5}{2}$ nuclear spin of the Mn^{2+} ion. As the g-tensor and the A-tensor are almost isotropic in the Mn^{2+} case, the spin Hamiltonian we use is:

$$\mathscr{H} = \beta \, H \, g \, S + B_q^k \, O_q^k + A \, I \, S$$

where β is the Bohr magneton and the tensor operators O_q^k are those defined by Smith and Thornley[10]. The B_q^k parameters are computed by a least square fit method[11] minimizing the discrepancy between the theoretical and experimental angular variations of the spectra. In the case of a C_1 symmetry, k values are 2 and 4 values run over $-k$ to $+k$, thus 14 parameters can be obtained. We determine the real and imaginary part of each parameters, using formula[12]

$$B_{-q}^k = (-1)^q \, (B_{-q}^k)^*.$$
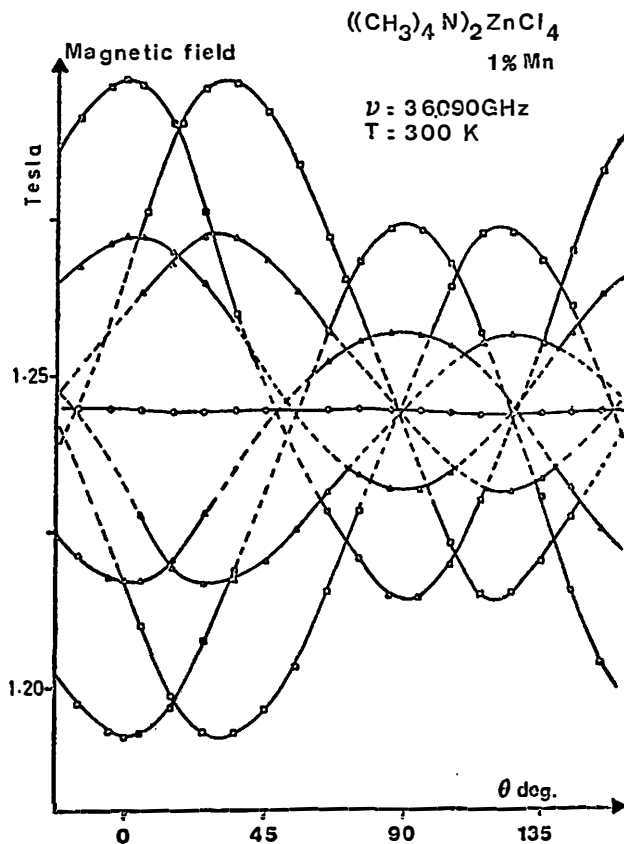
Fig. 4: Angular variation of the $M_S \to M_S{-}1$ transitions in $((CH_3)_4N_2)Mn_xZn_{1-x}Cl_4$ with two non magnetically equivalent sites.

Line indexation: At room temperature, the intensity of the $M_S \to M_S{-}1$ transition is proportional to the quantity $(S(S{+}1){-}M(M{-}1))$ in first approximation. For Mn^{2+} ion with $S = 5/2$, we expect the relative intensities as $5 : 8 : 9 : 8 : 5$, the sign of M_S value being not determined. At low temperature, the population of the highest Zeeman sublevels are smaller than of the lowest, and the intensity of the transition is different according to positive or negative value of M_S. Thus in an E. P. R. experiment at liquid helium temperature, we can determine the sign of M_S in the $M_S \to M_S{-}1$ transition as it is shown on Fig. 5.

4. Results

1° $(C_5H_5NH)_2ZnCl_4$, 1% Mn

This needle shaped crystal grows along the crystallographic z axis which is choosen perpendicular to the magnetic field plane in our experiments. The Mn^{2+}
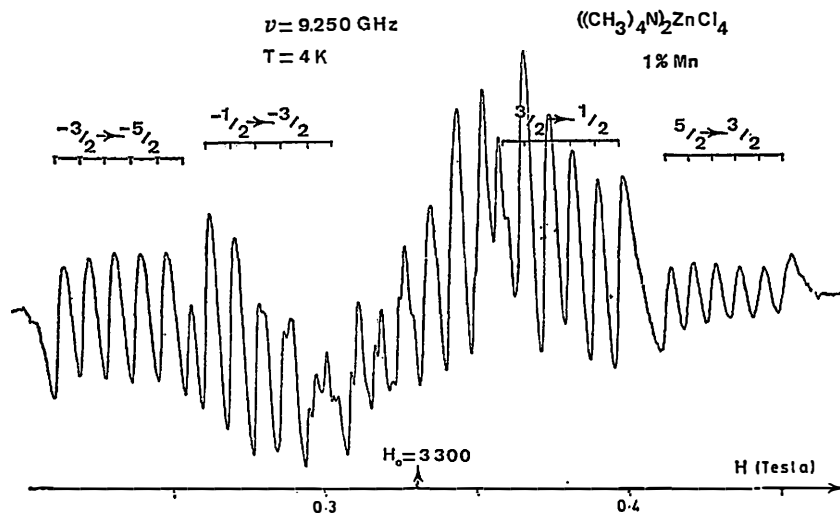
Fig. 5: Lines indexation at liquid helium temperature on the $((CH_3)_4N)_2Mn_xZn_{1-x}Cl_4$ E. P. R spectrum.

Table 1

Crystal		$(C_5H_5NH)_2Mn_xZn_{1-x}Cl_4$		$((CH_3)_4N)_2Mn_xZn_{1-x}Cl_4$	
B_0^2		—146.60 $10^{-4}\,cm^{-1}$		—81.00 $10^{-4}\,cm^{-1}$	
B_{-1}^2	R	— 9.82	,,	—22.95	,,
	I	— 6.17	,,	— 2.28	,,
B_{-2}^2	R	—44.53	,,	— 3,95	,,
	I	— 0.46	,,	+52.34	,,
B_0^4		— 0.35	,,	+ 0.17	,,
B_{-1}^4	R	+ 3.69	,,	— 4.19	,,
	I	+ 1.28	,,	— 0.17	,,
B_{-2}^4	R	— 0.09	,,	0.	,,
	I	— 0.05	,,	+ 6.19	,,
B_{-3}^4	R	— 3,49	,,	+ 1.35	,,
	I	— 2.08	,,	+ 0.06	,,
B_{-4}^4	R	— 0.15	,,	+ 0.22	,,
	I	— 0.04	,,	— 0.57	,,
δE $H = 0$		0.075 cm^{-1}		0.096 cm^{-1}	

Values of the computed b_q. Re and Im stand for real and imaginary part of the parameters. All B's are in units of $10^{-4}\,cm^{-1}$.

ions can be situated in two magnetically equivalent sites, which are related by inversion. The parameters for a C_1 symmetry are given in Table 1, and:

$$g_x = g_z = 2.0036$$

$$g_y = 2.0049$$

$$A_x = A_y = A_z = 7.87 \text{ mT}.$$

The standard deviation between experimental and theoretical values calculated over 90 points is in this case less than 0.13 mT. The zero field splitting computed for the ground state is then $\delta = 0.096 \text{ cm}^{-1}$.

2° $((CH_3)_4N)_2ZnCl_4$, 1% Mn

In these crystal, the manganese ion is located in a C_1 symmetry environment, and there are two possible sites related by a mirror plane in the unit cell. Except for some particular directions, we can observe 60 lines, that is to say 10 groups according to the $M_S \to M_S - 1$ transitions. The crystal was fixed in the resonant cavity with the crystallographic a axis parallel to the magnetic plane. When H is parallel to this a axis, the two sites are equivalent and the lines coalesce in pairs, the recorded spectrum shows 30 lines. During the angular variation (Fig. 4), the central part is not well resolved except for the $\frac{1}{2} \to -\frac{1}{2}$ lines, thus some incertitude appears in the line positions leading to a standard deviation of 1 mT when computing B' s values. However the values obtained for B_0^2 and B_0^2 give good agreement with D and E tensors previously calculated[13]. The B's are given in Table 1 and within the scope of experimental errors we can conclude:

$$g_x = g_y = g_z = 2.003$$

$$A_x = A_y = A_z = 7.85 \text{ mT}.$$

The zero field splitting of the ground state is $\delta = 0.075 \text{ cm}^{-1}$.

5. Conclusion

Due to the fact that in our compounds, manganese and zinc ions can be situated in the same lattice site, it has been possible to substitute Mn^{2+} to zinc and therefore to obtain crystals containing the Mn^{2+} ion at low concentrations. Therefore a good resolution in both optical and vibronic spectra and E. P. R. has been achieved.

Extensive data on Jahn-Teller coupling in the materials have been published elsewhere[14] and the results were accounted for by the assumption that Mn^{2+} ions were situated in distorted tetrahedral clusters, with a predominant coupling between ^4E electronic states and type E strains.

In the present paper, we describe the angular variatios of the E. P. R. spectra. The fitting of these spectra supports our previous assumption of a local C_1 symmetry for the Mn^{2+} ions (which was made on the basis of crystallographic data). In addition, we determine completely the set of parameters of the spin Hamiltonian.

The techniques which have been used in this work can be extended to analogous materials, even possessing low symmetries, the magnetic ion being used as a structural probe. However, for an accurate determination of the crystal field parameters, a previous crystallographic study is usefull.

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ELEKTRONSKA PARAMAGNETNA REZONANCA Mn^{2+} U $(C_5H_5NH)_2Mn_xZn_{1-x}Cl_4$ I $((CH_3)_4N)_2Mn_xZn_{1-x}Cl_4$

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Proučavana su tetraedarska kompleksna jedinjenja sa zelenom luminiscencijom i to $(C_5H_5NH)_2MnCl_4$ i $((CH_3)_4N)_2MnCl_4$ čiji E. P. R. spektri imaju samo vrlo široke trake bez neke fine i superfine strukture. Iz podataka o izomorfnim jedinjenjima $(C_5H_5NH)_2Mn_xZn_{1-x}Cl_4$ ili $((CH_3)_4N)_2Mn_xZn_{1-x}Cl_4$ sa malim koncentracijama Mn^{2+} ($x = 1\%$) moguće je po ugaonim varijacijama odrediti potpuni skup parametara spinskog hamiltonijana. Kristali imaju strukturu C_1 simetrije kod koje postoje jako deformisani Mn^{2+} koordinacioni tetraedri.