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EPR STUDY OF Mn^{2+} ION DOPED IN POTASSIUM OXALATE MONOPERHYDRATE SINGLE CRYSTAL

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Abstract—An EPR study of Mn^{2+} ion-doped potassium oxalate monoperhydrate single crystal has been carried out at room temperature. Two magnetically equivalent but differently oriented interstitial sites have been found for the Mn^{2+} dopants. The spin-Hamiltonian parameters are found to be $g_x = g_y = 2.0010$, $g_z = 2.0015$; $b_2^0 = -440$, $b_2^2 = 150$, $b_4^0 = 0.1959$; $A_x = A_y = 97.5$, $A_z = 98.5 \times 10^{-4}$ cm^{-1} and polar angles $\theta = 25°$ and $\phi = 30°$. The results obtained are compared with those of the isotypic crystal Mn^{2+} ion-doped potassium oxalate monohydrate to assess the difference arising from the presence of H_2O_2 in the former and H_2O in the latter. Superposition model analysis of zero field splitting for Mn^{2+} ion-doped potassium oxalate monoperhydrate single crystal has been carried out.

In diamagnetic hosts, the Mn^{2+} ion has found wide use as an extremely powerful EPR probe in the study of the strength and symmetry of crystalline fields, lattice defects and structures of paramagnetic complexes.[1-10] In the present paper, we report the results of an EPR study and superposition model analysis of Mn^{2+} complexes in a potassium oxalate monoperhydrate ($K_2C_2O_4 \cdot H_2O_2$; henceforth POMPH) single crystal. It was more interesting because an EPR study of its counterpart, i.e. Mn^{2+} ion-doped potassium oxalate monohydrate ($K_2C_2O_4 \cdot H_2O$; henceforth POMH) has already been carried out[11] and a comparison between the two crystals would be very informative as regards the role played by an additional oxygen ion per formula unit in the former crystal over the latter. The comparison should be very meaningful because the crystals are isotypic and have the same number of molecules per unit cell.[12,13]

CRYSTAL STRUCTURE

The crystal structure of POMPH is monoclinic with space group $C_{2/c}$[13] and the unit cell dimensions $a = 8.858$, $b = 6.505$, $c = 10.872$ Å and $\beta = 108.38°$, with four formula units. The potassium ion has eight nearest oxygen neighbours in a distorted dodecahedral arrangement. The K—O distances range from 2.708 to 2.997 Å.

EXPERIMENTAL

POMH was sintered at 100°C for 12 h and furnace cooled to room temperature (RT). It was then dissolved in perhydrol (30% H_2O_2). Crystals of POMPH were grown by slow evaporation at RT. Manganese chloride was added to the solution as dopant. Good quality, light pink transparent crystals were obtained. The morphology of the crystal was the same as referred to by Pedersen and Kvick.[13] The composition of the crystal was checked by chemical analysis. A crystal was mounted on a quartz tube along three orthogonal axes *a*, *b* and c^* ($c^* = c \sin \beta$) in turn with an accuracy of ±1° and spectra were recorded at every 10° of rotation about these axes on an X-band ESR JES-RE2X spectrometer (JEOL, Japan), with 100 kHz field modulation. DPPH was used as field marker.

RESULTS AND DISCUSSION

The observed EPR spectrum is due to Mn^{2+} ions as characterized by the known fine and hyperfine

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structure (Fig. 1a) and may be attributed to two Mn^{2+} sites (henceforth called I and II). The EPR spectra of Mn^{2+} ions are described below.

When an external magnetic field (H) is applied along the c^*-axis in the ac^*-plane, the spectrum shows only 30 lines with five sextets, as shown in Fig. 1b. On performing an angular variation study in this plane, many variations in fine structure parameters due to site II and less variations due to site I were observed. In the *bc*-plane, greater variations in fine structure splitting due to site I and less variations due to site II were observed. In the *ab*-plane, when H is along 25° off the b-axis towards the a-axis, the spectrum shows maximal spread of site I (Fig. 2). In the maximal spread spectrum of site I, site II has small spread confined to near the central region and, therefore, the central region becomes quite congested. On performing an angular variation study in this plane, another maximal spread spectrum due to site II is observed 5° away from the a-axis towards the b-axis. In each plane, two more sites are also seen, but their intensities are very weak and cannot be followed through.

Observed spectra due to both sites have orthorhombic symmetry. Since EPR in general does not distinguish between orthorhombic and lower symmetries,[2,11,14] the crystal field symmetry at the Mn^{2+} site may be either orthorhombic or more probably lower. Figure 3 shows the angular variation of the allowed fine structure transition ($\Delta m = \pm 1$) of one of the magnetic complexes of the Mn^{2+} ion (site I) in the *ab*-plane.

The EPR spectra can be analysed by using the following general spin-Hamiltonian:[2,4,15]

$$\mathrm{H} = \beta g \cdot H \cdot S + \frac{1}{3}\sum_{n=0}^{2} b_2^n O_2^n + \frac{1}{60}\sum_{n=0}^{4} b_4^n O_4^n + I \cdot A \cdot S, \quad (1)$$

where the notations have the usual meanings. The spin-Hamiltonian parameters were calculated up to second order by using the expression given in ref. 5 and fitted by an iterative least-squares method (Table 1). For comparison, the values for POMH are also given in Table 1. It is clear that the Mn^{2+} site shows an orthorhombic distortion of the crystalline field ($b_2^2 \neq 0$).

On the basis of the crystal structure, we have

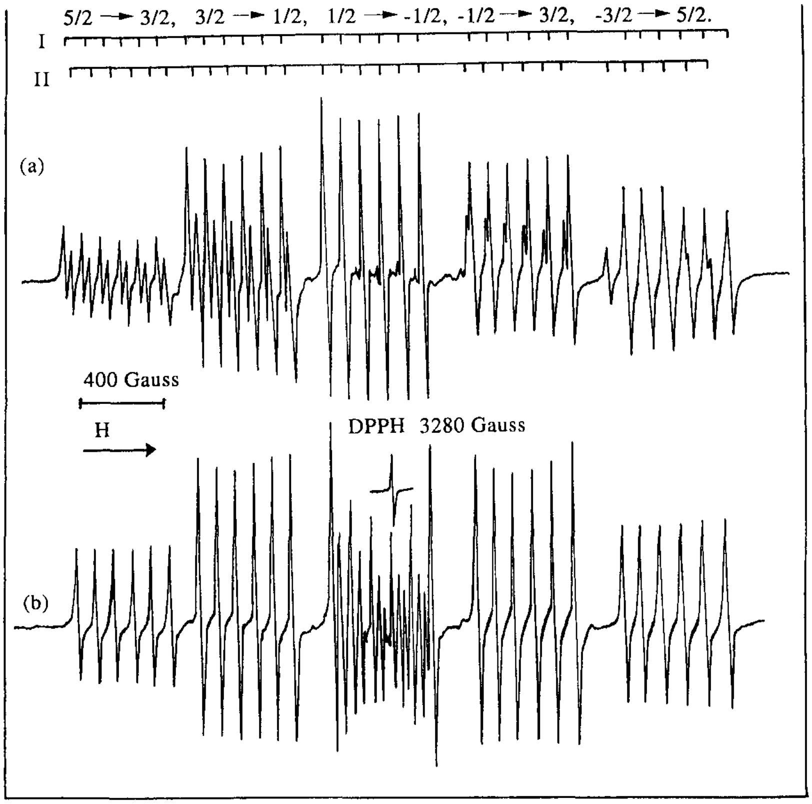

Fig. 1. The EPR spectra of Mn^{2+} ion doped in a POMPH single crystal at two orientations of magnetic field H in the ac^*-plane. (a) H is at 5° off the c^*-axis showing two sites (I and II) with five sextets. (b) H is along the c^*-axis, showing 30 lines with five sextets.

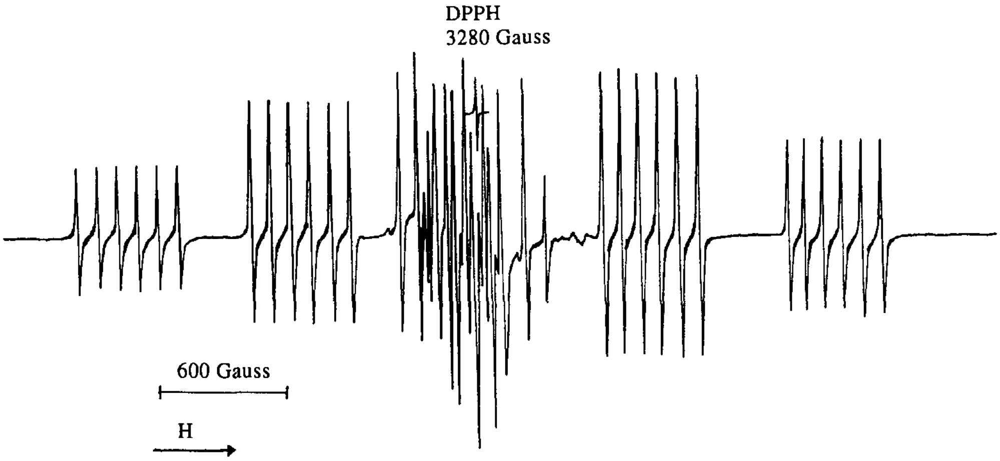

Fig. 2. Maximal spread spectrum of one of the complexes of the Mn^{2+} ion at site I inclined at 25° from the *b*-axis towards the *a*-axis in the *ab*-plane.

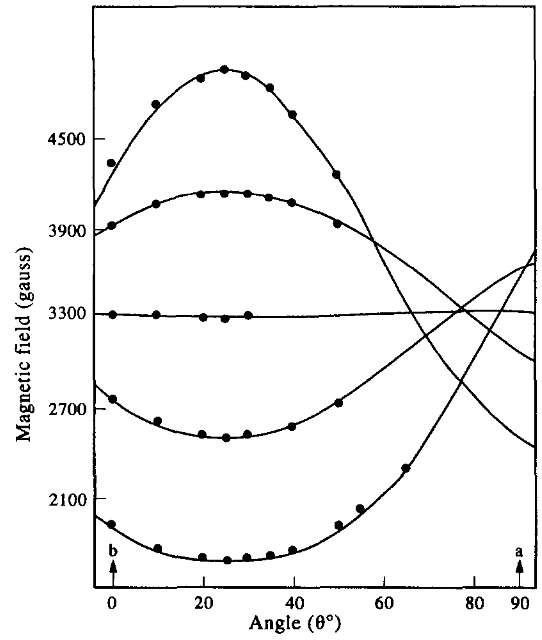

Fig. 3. Angular variation of EPR spectra of one of the magnetic complexes of Mn^{2+} ion at site I in the *ab*-plane. Dots are the experimental values and continuous lines are the theoretical curves.

attempted to locate the positions of sites I and II of the Mn^{2+} ion. If the Mn^{2+} ion is assumed to enter the lattice by substitution of a K^+ ion, the symmetry of the observed spectrum should match the symmetry of the crystal. In our experiment, the symmetry of the observed spectrum does not agree with the symmetry of the crystal, thus ruling out the possibility of substitutional replacement.

An alternative is that the Mn^{2+} ion occupies an interstitial site in the crystal lattice. In each unit cell, there are four rectangular planes of oxygens. All the planes are identical with sides of length 2.71 Å × 3.28 Å and they form two sets oriented differently. The favoured positions are the centres of nearest K^+–K^+ distances after displacing two K^+ ions for reasons of charge compensation. The centre of the two K^+ ions also lies at the centre of these planes. With this position of Mn^{2+} ion, its immediate oxygen ion environment was examined assuming that no other distortions take place in the lattice. On examining the crystal structure, the immediate environment of the Mn^{2+} ion is constituted by 12 oxygen ions, four ($O_1 = O'_1$ and $O_2 = O'_2$) coming from oxalate ligands and the other eight (all indexed as O_3) from H_2O_2 molecules. The environment of the Mn^{2+} ion in this position is shown in Fig. 4. As seen in Fig. 4, the nearest

Table 1. Comparative values of spin-Hamiltonian parameters of Mn^{2+} ion doped in POMPH and POMH single crystals (all parameters are given in units of $\times 10^{-4}$ cm^{-1} unless indicated otherwise)

System	$g_x = g_y$	g_z	b_2^0	b_2^2	b_4^0	$A_x = A_y$	A_z	θ(°)	φ(°)	Ref.
POMPH	2.0010	2.0015	−440	150	0.1959	97.5	98.5	25	30	Present work
POMH	2.0039	2.0065	−383	225	0.34	84	82.8	54	64	11

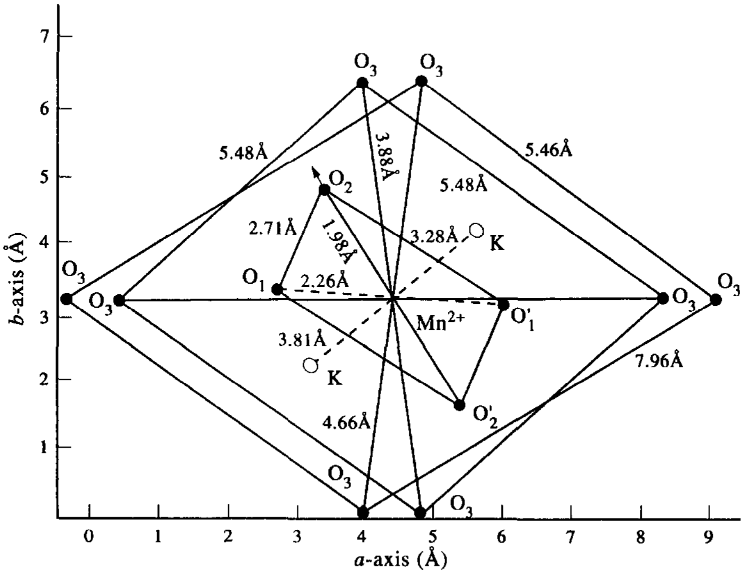

Fig. 4. Projection of the atomic positions of the coordination spheres of Mn^{2+} ion in POMPH : Mn^{2+} in the *ab*-plane.

oxygen ions (O_2,O_2') and (O_1,O_1') occur in pairs at distances of 1.98 and 2.26 Å oriented at 59° and 5° off the *a*-axis towards the *b*-axis, respectively. The maximal spread spectrum of site I is at 65° from the *a*-axis in the *ab*-plane, which is consistent with the assumption of magnetic complexes directed towards the nearest oxygen ions. The complex at site II is magnetically equivalent to that of site I, i.e. the spin-Hamiltonian parameters for both sites are the same but the principal axis of the complex at site II is directed along the Mn–O_2 vector of the other set of equivalent planes, as discussed earlier. A slight mismatch between the calculated direction[13] and the observed values may be due to the fact that when the Mn^{2+} ion is incorporated, a small rearrangement takes place in the lattice. Hence it can be concluded that the Mn^{2+} ions enter interstitial positions at the centres of the shortest K^+–K^+ distances in the lattice of the POMPH single crystal.

SUPERPOSITION MODEL

A small departure between the theoretical and experimental positions and orientations of the ligands surrounding the Mn^{2+} ion has been accounted for by superposition model (SPM) calculations. Newman and Urban[10] pointed out that the zero field splitting (ZFS) is due mainly to contributions from the nearest neighbours and proposed an empirical SPM relating the fine structure constant (b_2^0) to the actual arrangements of ligands around the impurity ion with the *S*-state as the ground state. The ZFS parameter at the central ion M is given by a sum of the contributions of the *i*th ligands (X_i) of the coordination spheres of the MX_i unit. The ZFS parameters b_n^m are written as[16]

$$b_n^m = \sum K_n^m(\theta_i, \phi_i) \cdot \bar{b}_n(R_i), \tag{2}$$

where the summation runs over all nearest neighbour ligands of the paramagnetic ion. K_n^m are the coordination factors (angular functions)[17] and $\bar{b}_n(R_i)$ are the radial intrinsic parameters. $\bar{b}_n(R_i)$ depend greatly on the ionicity of the ligands and are given by the following equation:[16]

$$\bar{b}_n(R_i) = \bar{b}_n(R_0)\left(\frac{R_0}{R_i}\right)^{t_n}. \tag{3}$$

R_0 is the reference distance,[18] t_n is a power law exponent and depends on the ligand type and metal ligand distance. All calculations have been done up to second order only with the conditions $m = 0$ and $n = 2$.

The ZFS parameter is calculated by assuming that the Mn^{2+} ion occupies the central position of the nearest K^+–K^+ distance after displacing two K^+ ions, and no other distortions take place in the lattice. In this situation, the environment of the Mn^{2+} ion is made up of 12 oxygen ions, four adjacent and the other eight at larger distances (Fig. 4). The nearer four coordinated oxygens are grouped into two sets at distances $R_1 = 1.98$ Å and $R_2 = 2.26$ Å at angles $\theta_1 = 59°$ and $\theta_2 = 5°$ from the *a*-axis in the *ab*-plane, respectively. The contributions from the eight, more distant oxygen ions are of very small magnitude and hence are neglected. The calculation gives $b_2^0 = -0.0362$ cm^{-1} and intrinsic parameters $\bar{b}_2(R_1) = -0.1217$ cm^{-1} and $\bar{b}_2(R_2) = -0.0487$ cm^{-1}. To assign the ZFS parameter, different values of lengths and angles for different oxygen ions are tried to get the best fit with the experimental value b_2^0 (-0.0440 cm^{-1}). The best fit is found by $R_1 = R_2 = 2.20$ Å and $\theta_1 = 65°$ and $\theta_2 = 5°$, respectively. It is found that an increase of about 11% in distance for oxygen (Mn–O_2) (from 1.98 to 2.20 Å) causes the angle θ_1 change to 65° from 59°, but for oxygen O_1 a decrease of about 2% in the distance (from 2.26 to 2.20 Å) does not change the angle. Considering these angles and lengths, the ZFS parameter b_2^0 is calculated and found to be equal to -0.0448 cm^{-1}, which matches very well with the experimental b_2^0 (-0.0440 cm^{-1}).

Before attempting a comparison between the surroundings of the Mn^{2+} sites in POMPH and POMH, a trivial mistake must be pointed out which the author has made in the selection of site for the Mn^{2+} ion in POMH.[11] As shown in Fig. 1 of ref. 11, reproduced below for clear understanding as Fig. 5 here, the position of the Mn^{2+} ion impurity is correctly shown at the centre of the 3.27 Å × 2.02 Å rectangle designated by $O_1O_2O'_1O'_2$, but the dimensions of this rectangle have been incorrectly given as 2.23 Å × 2.71 Å.[11] The dimensions of the rectangle $O_1O_2O'_1O'_2$ are actually 3.27 Å × 2.02 Å.[13] The rectangle with dimensions 2.23 Å × 2.71 Å can be formed by joining four oxygen ions of the same oxalate ligand and, as the single and double bonds of the oxalate ligand are in the *trans* positions, the centre of this rectangle coincides with the mid-point of the C—C separation, which cannot accommodate the Mn^{2+} ion. In the description of the rectangle at the centre of which the Mn^{2+} ion is situated, the author has been influenced by another work on POMH,[19] where the same mistake had been made earlier.[11] We have found the centre of the rectangle $O_1O_2O'_1O'_2$ to be occupied by Mn^{2+} ions (Fig. 6). Two oxygen ions (O_1O_2) are from one oxalate group and two ($O'_1O'_2$) are from another oxalate group. The second coordination sphere of the Mn^{2+} ion is defined by oxygen ions (O_3) contributed by the nearest H_2O molecules spaced at the vertices of another rectangle (5.56 Å × 6.48 Å). The centres of these rectangles are coincident and they are inclined to each other at an angle of 83°. This common centre is also the mid-point between the two nearest K^+–K^+ ions. These two K^+ ions are attached to two oxalate ligands contributing O_1,O_2 and O'_1,O'_2 oxygen ions, respectively, in the $O_1O_2O'_1O'_2$ rectangle.

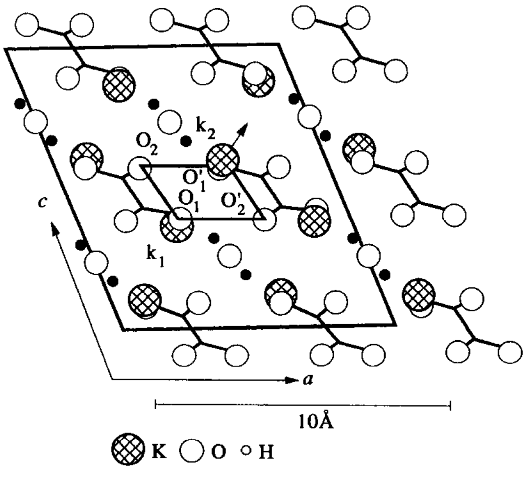

Fig. 5. Projection of the POMH single crystal structure on the *ac*-plane. The K_1–K_2 direction represents the principal axis of the Mn^{2+} ion complex.[11]

In POMPH, the Mn^{2+} ion occupies the centre of a rectangle (2.71 Å × 3.28 Å) defined by four oxygen ions, two from each of two different oxalate ligands. Because POMPH and POMH are isostructural, there is a one-to-one correspondence between this rectangle and the rectangle (2.23 Å × 2.71 Å) defined in POMH.[11] In POMH, the four oxygen ions (O_3) are from four surrounding H_2O molecules lying in the second coordination sphere, but in POMPH the next nearest neighbours are H_2O_2 molecules, each of which possess two oxygen ions, and thus second and third coordination spheres may be thought to exist. The near set of four oxygen ions of H_2O_2 define a square with dimensions 5.48 Å × 5.48 Å and the more distant set of four oxygen ions define a rectangle with dimensions 5.46 Å × 7.96 Å. The centre of both rectangles (2.71 Å × 3.28 Å and 5.46 Å × 7.96 Å) and the square (5.48 Å × 5.48 Å) are coincident. The square and rectangle defined by the oxygen ions of H_2O_2 cut the smallest rectangle at angles of 71° and 96°, respectively. As in POMH, here also the common centre is the mid-point between the nearest K^+–K^+ ions, and the K^+–K^+ vector (Fig. 4) has polar angles $\theta = 55°$ and $\phi = 50°$, with the K^+–K^+ separation = 3.81 Å (where θ is the angle between the Z-axis and the b-axis, and ϕ is the angle between the a-axis and the projection of Z on the ac-plane).

The main differences between POMH and POMPH are that, in the former, there are two magnetically equivalent Mn^{2+} complexes with different orientations and the principal direction of one of the magnetic complexes is parallel to the K^+–K^+ vector shown in Fig. 6 with $\theta = 56°$ and $\phi = 65°$ (where they are referred to the same axes as above) and the separation between the two K^+ ions equals

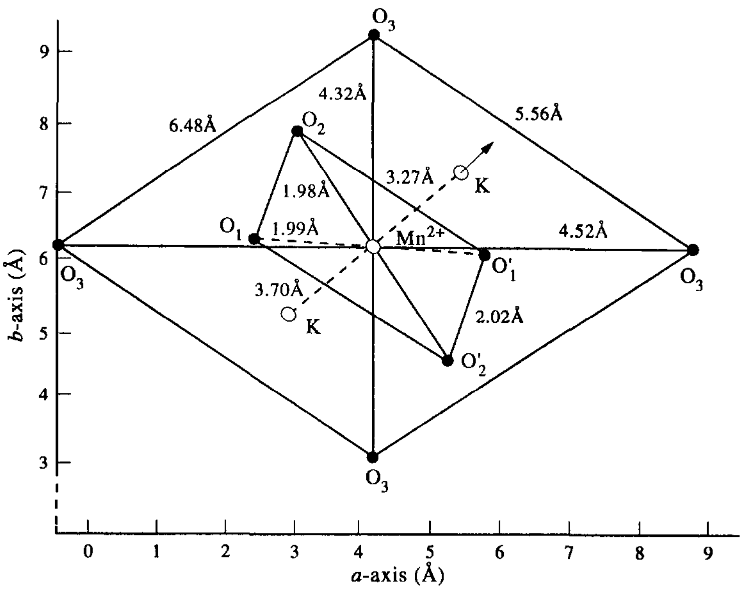

Fig. 6. Projection of the atomic positions of the coordination spheres of Mn^{2+} ion in POMH : Mn^{2+} in the *ab*-plane.

3.70 Å.[11] The principal axis of the other complex is directed along the K^+–K^+ vector of the other set of the equivalent plane in the unit cell as described earlier. In the present case, we have also found two magnetically equivalent Mn^{2+} complexes with the principal axis of one complex directed along Mn–O_2, as shown in Fig. 4, with polar angles $\theta = 25°$ and $\phi = 30°$. The principal axis of the other complex is directed along the Mn–O_2 vector of the other set of planes in the unit cell, which is equivalent to $O_1O_2O'_1O'_2$ described in Fig. 4.

The differences in the values of spin-Hamiltonian parameters shown in Table 1 must have been the result of substitution of H_2O_2 in place of H_2O. Besides differences in spin-Hamiltonian parameters in POMH and POMPH, there has been a remarkable change in the direction of the principal component of the magnetic complexes in the two cases, along the K^+–K^+ direction in POMH and along the Mn–O_2 direction in POMPH, as shown in Figs 4 and 6. This can be understood by considering the size of the smallest rectangle ($O_1O_2O'_1O'_2$) surrounding the Mn^{2+} ion and the disposition of the nearest K^+–K^+ vector in the two cases, which in turn might be related to the disposition of oxygen ions in the second and third coordination spheres as shown in Figs 4 and 6. In other words, it can be explained as due to the H_2O_2 being larger in size and having a greater dipole moment than that of H_2O and hence the dimensions of the smallest rectangle surrounding the Mn^{2+} ion in the two cases may be quite different and can account for the difference in the results. The charge distribution around the Mn^{2+} ion seems to be significantly affected on substituting H_2O_2 for H_2O.

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