

Quantum entanglement in manganese(II) hexakisimidazole nitrate: on electronic structure imaging - A polarized neutron diffraction and DFT study

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Abstract. Quantum entanglement has been visualized for the first time, in view of the spin density distribution and electronic structure for manganese in manganese(II)hexakisimidazole nitrate. Using polarized neutron diffraction and density functional theory modelling we have found for the complex, which crystallizes in the R3 spacegroup, $a = b = 12.4898(3) \text{ \AA}$, $c = 14.5526(4) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 120^\circ$, $Z = 3$, that spatially antisymmetric and spatially symmetric shaped regions of negative spin density, in the spin density map for manganese, are a result of quantum entanglement of the high spin d^5 configuration due to dative imidazole-manganese π - donation and σ -bonding interactions respectively. We have found leakage of the entangled states for manganese observed as regions of positive spin density with spherical ($3.758(2) \mu_B$) and non-spherical ($1.242(3) \mu_B$) contributions. Our results, which are supportive of Einstein's theory of general relativity, provide evidence for the existence of a black hole spin density distribution at the origin of an electronic structure and also address the paradoxical views of entanglement and quantum mechanics. We have also found the complex, which is an insulator, to be suitable for spintronic studies.

1. Introduction

In condensed matter, the state and structure of the electron is assessed through interactions with its environment. Quantum mechanics¹ suggests, for instance, for the entangled interactions between spin systems $S_A = |i\rangle_A$ and $S_B = |j\rangle_B$ in Hilbert space:

$$|\psi\rangle_{AB} = \sum_{i,j} c_{ij} |i\rangle_A \otimes |j\rangle_B \quad (1a)$$

that the final state of the system, $|\psi\rangle_{AB}$, disentangles when either $|i\rangle_A$ or $|j\rangle_B$ is measured providing:

$$c_{ij} = c_i^A c_j^B \quad (1b)$$

where c_{ij} is the coefficient matrix in the subspace ij .

Otherwise, the final state of the system $|\psi\rangle_{AB}$ remains entangled (correlated) providing:

$$c_{ij} \neq c_i^A c_j^B \quad (1c)$$



The quantum mechanical interaction of a spin- $\frac{1}{2}$ electron with an applied field $\mathbf{B}_z$ was first demonstrated in the Stern-Gerlach² experiment (figure 1, below).

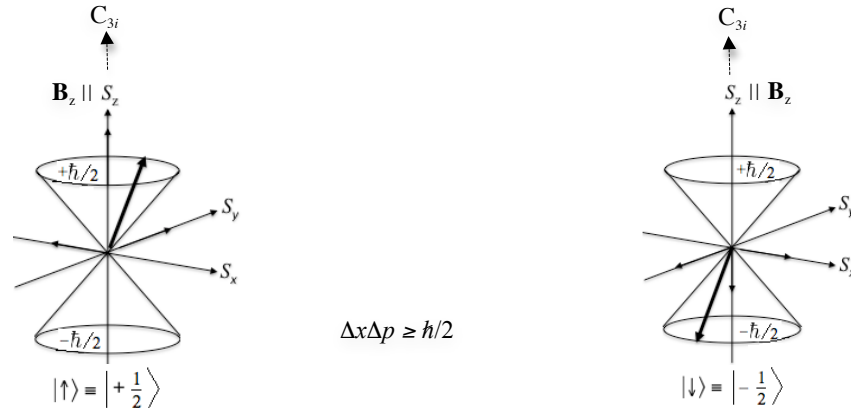


Figure 1: Precession cones associated with a spin- $\frac{1}{2}$ electron in applied field $\mathbf{B}_z$

In figure 1, the doubly degenerate spatially antisymmetric precession cones about $\mathbf{B}_z$, for the quantum entangled spin states $|\pm\frac{1}{2}\rangle$ of the spin- $\frac{1}{2}$ electron, confer an intrinsic C_{3i} point group. The C_{3i} point group breaks spherical (O_h) rotational symmetry about $\mathbf{B}_z$ by lifting the $t_{2g}(O_h)$ level and lowering the $e_g(O_h)$ level. The $t_{2g}(O_h)$ is transformed according to the spatially antisymmetric doubly degenerate E_g irreducible representation and the $e_g(O_h)$ transformed according to the spatially symmetric singly degenerate A_g irreducible representation, of the C_{3i} point group. The doubly degenerate spatially antisymmetric precession cones about $\mathbf{B}_z$, for the quantum entangled spin states $|\pm\frac{1}{2}\rangle$, suggest spin delocalization in the transformed $t_{2g}(O_h)$ associated with the E_g irreducible representation. By contrast, since there is no spatially symmetric precession about $\mathbf{B}_z$ a vacuum (spherical solution) is suggested for the transformed $e_g(O_h)$ associated with the singly degenerate A_g irreducible representation. We propose these qualitative symmetry assessments for the spin- $\frac{1}{2}$ electron in an applied field $\mathbf{B}_z$ reflect the intrinsic point group of the electron with respect to its magnetic moment.

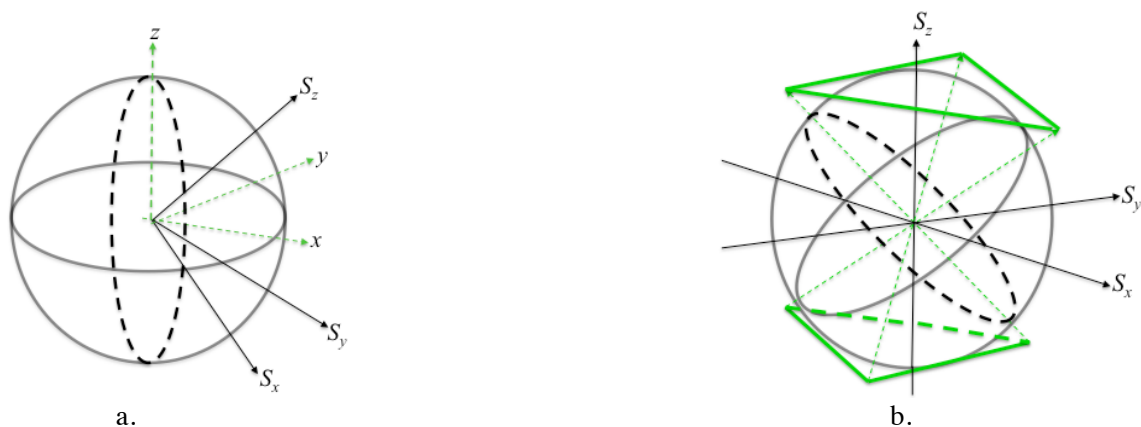


Figure 2: proposed schematic decomposing classical spherical symmetry for a spin- $\frac{1}{2}$ electron into irreducible states; a doubly degenerate spatially antisymmetric state (green-colored triangles), and a singly degenerate spatially symmetric state (black-lined sphere). Note: in b.) S_z is arbitrarily chosen as the spin angular momentum quantization vector.

Given figure 2b, we suggest that the spin angular momentum operator $\mathbf{S}$ for a spin- $\frac{1}{2}$ electron with an intrinsic electric field $\mathbf{E}$ be described as:

$$\mathbf{S} = \frac{\epsilon_0}{2i\omega} \sum_{i=x,y,z} \int (\mathbf{E}^{i*}(\mathbf{r} \times \nabla) \mathbf{E}^i) d^3\mathbf{r} \quad (2)$$

where ϵ_0 = the permittivity of vacuum in free space and i = cartesian components. Also, from figure 2b and equation (2), the electron's spin angular momentum arises from intrinsic spin precession (spin delocalization) in three-dimensional space.

We propose, according to figure 2b, classical spin entanglement for an electronic structure in Hilbert space, equations (3a - b) below. We describe a spatially antisymmetric classical entangled ferromagnetic spin exchange state, in the two-particle state problem:

$$|\Psi(t)\rangle = \frac{n}{\sqrt{2}} (|\downarrow\rangle_1 \otimes |\uparrow\rangle_2 - |\uparrow\rangle_1 \otimes |\downarrow\rangle_2) \quad (3a)$$

which is fermion-like, where $n = 3$ for three-fold orbital symmetry. We also describe a spatially symmetric classical entangled antiferromagnetic spin exchange state, which is boson-like:

$$|\Psi(t)\rangle = \frac{n}{\sqrt{2}} (|\downarrow\rangle_1 \otimes |\uparrow\rangle_2 + |\uparrow\rangle_1 \otimes |\downarrow\rangle_2) \quad (3b)$$

where, $n = 1$ for spherical orbital symmetry. The simultaneous occurrence of both fermion-like and boson-like spatial states in equations (3a and 3b), for our proposed description of an electronic structure in Hilbert space, is a likely consequence of an anyon-like³ intermediate during the two-particle spin states interchange. Further, since the electron has a rest mass (m_e) and rest energy it intrinsically follows $E_e = m_e c^2$ in view of Einstein's mass-energy⁴ equivalence. In this respect, the boson-like state in equation (3b) and the fermion-like state in equation (3a) define the mass-like and light-like nature, respectively, of our proposed electronic structure in Hilbert space. Our conclusions, in this respect, are akin to an observer's (mass-like) view of "past" and "future" (light-like) cones in Minkowski⁵ general relativistic space-time (figure 3, below).

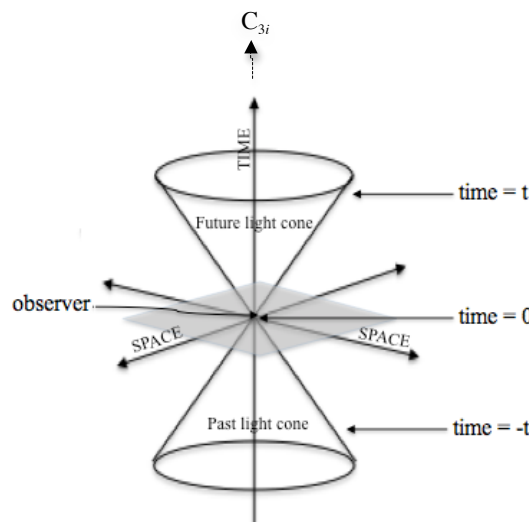


Figure 3: Minkowski⁵ general relativistic space-time for an observer's view of "past" and "future" light cones.

The paradox of quantum formalism implies that a measurement in Planck's time, for example through the application of an applied field, on a member of a two-particle classical entangled spin exchange state collapses the classical system before any space-like information between entangled members can be transmitted. In this work we will consider Einstein's possible solution⁶ to this paradox through our proposed view that hidden information, such as spatial symmetry (which confer spin distribution symmetry) and energy-momentum (which confer spin delocalization), pertaining to the classical entangled spin exchange state in Hilbert space, is carried by each classical entangled member and no information is transmitted between members during a quantum measurement. In this respect, we suggest the system remains entangled in the quantum world, albeit in a quantum entangled spin exchange state in Hilbert space (figure 4 below), during a quantum measurement on a member of the classical entangled world. Also, spatial and energy-momentum information leaked in the quantum entangled world will be representative of the hidden information of the classical entangled world. Furthermore, since we have proposed the coexistence of spatially antisymmetric and spatially symmetric classical entangled spin exchange states (equations (3a – b)) to be in view of the light-like and mass-like nature respectively of our proposed electronic structure in Hilbert space then their simultaneous assessment during measurement will be expected.

Figure 4 a. Proposed example of members of the classical entangled world (color-coded green and purple) in Hilbert space; and b. proposed example of a quantum entangled world in Hilbert space at the onset ($\Rightarrow$) of a measurement on a member of the classical world.

Finally, we assume ‘*action at a distance*’⁶ (that is, entanglement which is implicit of electron correlation in our discussion) to be relative. We note the premise of Einstein’s theory of general relativity⁷ that gravity is an intrinsic geometric property of space–time and that the curvature of space–time is related to the energy, momentum of matter present is in support of our proposed electronic structure in Hilbert space (equations (3a – b), figure 2b). For instance, since we have suggested no spin angular momentum is associated with the classical spatially symmetric (boson-like) entangled state (equations (2, 3b), figure 2) then Minkowski⁵ space–time (figure 3) for the associated spin density distribution, during a quantum measurement, is expected to be spherical and localized (at $t = 0$, the origin in figure 3). This spherical solution, referred to as the vacuum solution to Einstein’s field equations (EFE)⁸⁻⁹ since the energy–momentum tensor in EFE⁸⁻⁹ is zero, is defined by the Schwarzschild metric¹⁰⁻¹¹. Further, a black hole¹², an object with a radius smaller than the Schwarzschild radius¹⁰⁻¹¹ and having a predicted singularity¹³⁻¹⁴, is also expected to be found. (This suggests, within the context of the associated spin density distribution, a ‘black hole spin density distribution’ at the origin). By contrast if the energy–momentum tensor in EFE⁸⁻⁹ is not zero Minkowski⁵ space–time (figure 3) is spatially antisymmetric (at $t = +t$ and $t = -t$ in figure 3). In this respect, we expect during measurement that the spin density distribution associated with our proposed classical spatially antisymmetric (fermion-like) entangled state, which has intrinsic orbital angular momentum (equations (2, 3a), figure 2b), to be delocalized and spatially antisymmetric having C_{3i} symmetry.

2. Experimental overview

To explore experimentally and theoretically the aforementioned considerations, we investigate the spin density distribution and electronic structure for the interactions of manganese in the titled complex (figure 5 below) using polarised neutron diffraction (PND)¹⁵ and density functional theory modeling.

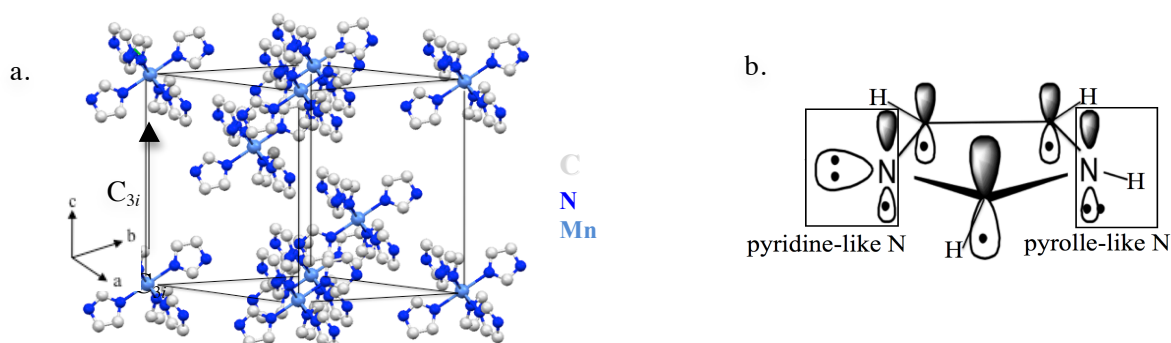


Figure 5: a. Trigonal unit cell for the titled complex. For clarity, hydrogen atoms and nitrate counter ions have been omitted; b. Schematic for imidazole, showing the pyridine-like nitrogen which coordinates to manganese in the titled complex.

2.1 Classical spin exchange entanglement, in Hilbert space, for the interactions of manganese and imidazole in the titled complex.

We propose¹⁶ that if the high spin d^5 -configuration for Mn(II) has the α -spin direction, or the β -spin direction, an occupied Φ_{3d} α -spin orbital, or an occupied Φ_{3d} β -spin orbital, is defined. The Lewis acidity of Mn(II) in this context, with respect to a coordinating imidazole moiety, is viewed as an unoccupied Φ_{3d} spin orbital on Mn(II) in the presence of an occupied spin orbital associated with a coordinating pyridine-like nitrogen of imidazole (Figure 5b), where imidazole acts as a Lewis base. In this respect, while considering the valence bond (also Heitler-London model), localized bonding, independent bond approaches,¹⁶⁻²¹ we suggest classical spin entanglement for an electronic structure in Hilbert space (equations (3a - b), figure 2b) associated with the interactions of manganese and imidazole in the titled complex. Within the context of spin states interaction, we suggest:

- *Dative imidazole-manganese σ -bonding interaction*, involving the spin states (arbitrarily assigned $\alpha(\uparrow)$ and $\beta(\downarrow)$) for the pair of electrons in the available sp^2 -hybridized orbital of the pyridine-like nitrogen of imidazole interacting with an unoccupied Φ_{3d} spin orbital associated with the e_g set of Mn(II). Additionally, we propose¹⁶ that dative imidazole-manganese σ -bonding interactions constitute antiferromagnetic spin exchange interaction, in the two particle problem, such that a classical spatially symmetric entangled exchange state in Hilbert space is defined as shown in equation (3b).
- *Dative imidazole-manganese π -donation interaction*, involving the unpaired electron in the p_z orbital of the pyridine-like nitrogen of the coordinating imidazole π -donating unto an unoccupied Φ_{3d} spin orbital associated with the t_{2g} set of Mn(II). This constitutes ferromagnetic spin exchange interaction, in the two particle state problem, such that a classical spatially antisymmetric entangled exchange state in Hilbert space is conferred equation (3a)).

2.2 Leakage of hidden information (spatial symmetry, energy-momentum) during a PND measurement of the titled complex:

- *For dative imidazole-manganese σ -bonding interaction* we suggest the leaked spatial information during measurement, associated with our proposed classical spatially symmetric entangled state in Hilbert space (equation (3b)), be described as the spherical symmetric ${}^6A_{1g}(t_{2g}^3 e_g^2)$ high spin crystal field state for manganese associated with the σ^* orbital on manganese. Also, since no orbital angular momentum is associated with dative imidazole-manganese σ -bonding interactions¹⁶, as the σ -bond quantization axis taken as the z-direction is projected towards the manganese nucleus, no spin delocalization (that is, zero energy-momentum) is associated with the ${}^6A_{1g}(t_{2g}^3 e_g^2)$ state. Further, in accordance with the theory of general relativity⁷, a zero value for the energy-momentum tensor in EFE⁸⁻⁹ imparts a vacuum solution to EFE⁸⁻⁹. This also confers an implicit black hole¹² having a radius smaller than the Schwarzschild radius⁹⁻¹⁰. We therefore expect an imaged black hole spin density distribution for our proposed ${}^6A_{1g}(t_{2g}^3 e_g^2)$ state for manganese during measurement. Analytically we define the measured magnetic moment $\mu_{\sigma^*}(\text{Mn})$, associated with the hole in the σ^* orbital on manganese, as:

$$\mu_{\sigma^*}(\text{Mn}) = (1 - k_{\text{Mn}\sigma} n_1) g \mu_B S \quad (4)$$

with $S = 5/2$, $n_1 = 1$ for the spherical ${}^6A_{1g}(t_{2g}^3 e_g^2)$ crystal field state, $k_{\text{Mn}\sigma}$ is the admixture coefficient on manganese (assessed from DFT modeling) due to dative imidazole-manganese σ -bonding interaction, $g = 2$ for the electron g -factor, μ_B is the Bohr magneton.

- *For dative imidazole-manganese π -donation interaction* we suggest the leaked spatial information during measurement, associated with our proposed classical spatially antisymmetric entangled state in Hilbert space (equation (3a)), be described as the three-fold spatially antisymmetric ${}^2T_{1g}(t_{2g}^5 e_g^0)$ low spin crystal field state for manganese associated with the π^* orbital on manganese. Also, since orbital angular momentum is intrinsic to dative imidazole-manganese π -donation interactions¹⁶, as the π -donation quantization axis taken as the z-direction is projected away from the manganese nucleus, spin delocalization (energy-momentum) is associated with the ${}^2T_{1g}(t_{2g}^5 e_g^0)$ state. We define the measured magnetic moment $\mu_{\pi^*}(\text{Mn})$, associated with the π^* orbital on manganese, as:

$$\mu_{\pi^*}(\text{Mn}) = (1 - (n_2 \eta_{\text{Mn}} + n_2 k_{\text{Mn}\pi})) g \mu_B S \quad (5)$$

with $S = 5/2$, $n_2 = 3$ for the three-fold ${}^2T_{1g}$ crystal field state, $k_{\text{Mn}\pi}$ is the admixture coefficient on manganese (assessed from DFT modeling) due to dative imidazole-manganese π -donation interactions, η_{Mn} is the spin delocalization for manganese.

Since π -donation by the coordinated imidazoles unto the t_{2g} set of manganese breaks the aromaticity of the imidazoles then spin delocalization $\eta_{\text{Imz}(\text{Mn})}$ for manganese (associated with the ${}^2T_{1g}$ state) is expected to be observed in the π^* orbital of each imidazole. We also expect spin delocalization $\eta_{\text{Imz}(\text{Mn})}$ for manganese to be observed in the σ^* orbital of each imidazole. In this respect, we re-define the measured moment for manganese due to dative imidazole-manganese π -donation interaction as:

$$\mu = \mu_{\pi^*}(\text{Mn}) + \mu_{\pi^*,\sigma^*}(\text{Mn}(\text{Imz})) \quad (6)$$

where, from (6), $\mu_{\pi^*,\sigma^*}(\text{Mn}(\text{Imz}))$ is the measured moment for manganese on each coordinate imidazole. We assume $k_{\text{Mn}\pi}$ (in equation (5) = $1/\mu_B(\mu_{\pi^*}(\text{Mn}) - \mu_{\pi^*,\sigma^*}(\text{Mn}(\text{Imz})))$).

Comparing equations (4 – 5), we note the value $n_1/n_2 = 1/3$ infers a black hole solution for a three-fold orbital state.

2.3 Given the spin density form factor f_s in q-space:

$$f_s(\mathbf{q}) = \int \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} \quad (7a)$$

where, ρ is the spin density and $f_s(\mathbf{q})$ is the fourier transform:

$$f_s(\mathbf{q}) = \int \psi_i^* \psi_j e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \quad (7b)$$

then, in terms of multipolar expansion²², the spin density form factor is re-expressed as:

$$f_s(q, \theta, \phi) = \sum_l \sum_m i^l M_l^m N_l^m \langle j_{n,l} \rangle Z_l^m(\theta, \phi) \quad (7c)$$

where, $l = 0, 2, 4$ and $-l \leq m \leq l$, $\langle j_{n,l} \rangle$ is the radial integral and, $Z_l^m(\theta, \phi)$ are multipole functions (tesseral harmonics):

$$\left. \begin{aligned} Z_l^m(\theta, \phi) &= Y_l^m \cos\theta \cos m\phi, m \geq 0 \\ &= Y_l^m \cos\theta \sin(-m\phi), m < 0 \end{aligned} \right\}$$

also, from (7c), N_l^m are normalization functions, M_l^m are multipole population parameters. In assessing our expected observation of spherical and non-spherical contributions to the spin density distribution on manganese in the complex the multipole functions Z_0^0 and $Z_2^0, Z_4^0, Z_4^{3+}, Z_4^{3-}$ will be considered.

3. PND results

Re-construction of the spin density map for manganese (Figure 6a, below), by inverse Fourier²³ of the observed spin density structure factors obtained from the PND experiment on a single crystal of the complex, shows regions of negative and positive spin density. The regions of negative spin density (see figure 6a) are due to spatially antisymmetric quantum entangled spin exchange (*) and spatially symmetric quantum entangled spin exchange (**) states, in Hilbert space, for manganese. We note the quantum entangled spin exchange states for manganese are associated with classical entangled spin exchange states of our proposed electronic structure for the complex in Hilbert space (equations (3a – b), figure 2, section 2.1). In figure 6a, the region of positive spin density at the origin, which was found to have a value $3.758(2)\mu_B$ using Multipolar Least Square Analysis (MPLSQ)²³, is due to leakage of the spherical symmetric ${}^6A_{1g}(t_{2g}^3 e_g^2)$ crystal field state for manganese associated with the spatially symmetric classical entangled state (sections 2.1 – 2.2). As shown in figure 6a, the spin density distribution at the origin constitutes a black hole spin density distribution for manganese. This is because no spin (electron) delocalization (that is, no energy-momentum) is associated with the ${}^6A_{1g}(t_{2g}^3 e_g^2)$ state for manganese. Our observation of a black hole spin density distribution at the origin (see also our discussion at the end of section 1) for manganese in figure 6a is supported by the theory of general relativity⁷, which predicts the occurrence of a black hole as an intrinsic consequence of the vacuum solution to EFE⁸⁻⁹. This conveys with relevance to dative imidazole-manganese σ -bonding interactions in the titled complex, a collapsing of the mass-like nature of spin density distribution for manganese at the origin, of our proposed electronic structure in Hilbert space (sections 2.1 – 2.2, equations (3a – b), figure 2b). The Schwarzschild radius¹⁰⁻¹¹ for $S = 5/2$ was calculated to be 0.6765×10^{-54} cm. We have measured a Schwarzschild radius of 0.65 cm based on figure 6a. The factor of 10^{-54} between the calculated and measured Schwarzschild radius is attributed to scaling.

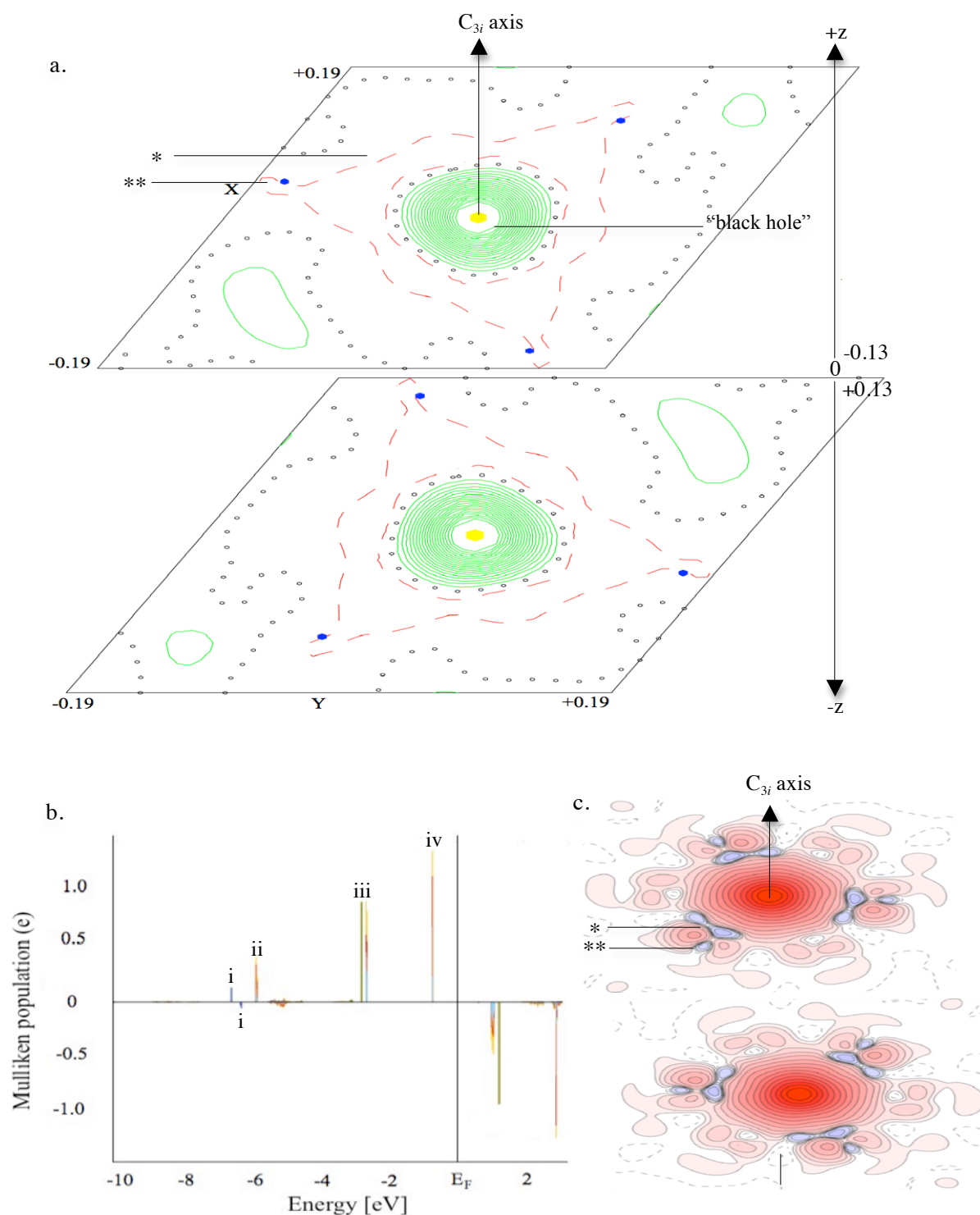


Figure 6: a. Re-construction of the spin density on Mn in the titled complex using the PND data; color code: Mn (yellow) and for clarity pyridine-type nitrogen (blue); X parallel to (100), Y parallel to (010), Z parallel to (001); (*) spatially antisymmetric shaped region of negative spin density; (**) spatially symmetric shaped region of negative spin density.
b. DFT modelled Mulliken spin populations on Mn;
c. DFT modelled spin density on Mn
(Plots of the spin density are 2-dimensional projections parallel to the z-bound projection of the complex)

In figure 6a the regions of positive spin density projected away (green-colored contours, figure 6a) from the origin, which were assessed to be $1.242(3) \mu_B$, are a result of spin delocalization (energy-momentum) for manganese. This is due to our proposed leakage of a (non-spherical) three-fold spatially antisymmetric ${}^2T_{1g} (t_{2g}^5 e_g^0)$ low spin crystal field state for manganese. Spin delocalization of the ${}^2T_{1g} (t_{2g}^5 e_g^0)$ state for manganese, which is associated with the π^* orbital on manganese, occurs also in the π^* and σ^* orbitals of the coordinated imidazole. In this respect our assessed value of $1.242\mu_B$ for the regions of positive spin density projected away from the origin in figure 6a takes in account equation 6 of section 2.2. Lastly, we conclude the value $1.242\mu_B/5\mu_B = 1/4$, which is indicative of the entropy associated with a black hole²⁴, is a result of orbital angular momentum conferring non-spherical spin density distribution for manganese. This inherently reduces the mass (in Bohr magneton units) of the black hole spin density distribution for manganese at the origin (in figure 6a) from $5\mu_B$ to $3.758\mu_B$.

4. DFT modeling overview, results

In modeling the spin density for manganese in the titled complex, the Dmol3 package²⁵⁻²⁶ was employed. We note the spin density $\rho_\sigma(\mathbf{r})$, given as a sum over all occupation points (k) for the function (Φ_k, σ):

$$\rho_\sigma(\mathbf{r}) = \sum_k^{occ} |\Phi_{k,\sigma}(\mathbf{r})|^2 \quad (8a)$$

$$\Phi_{k,\sigma}(\mathbf{r}) = \sum_{j,k,\sigma} c_{j,k,\sigma} \phi_j(\mathbf{r}) \quad (8b)$$

also, in spin basis σ , the density is represented:

$$\rho = \rho_\sigma + \rho_{-\sigma} \quad (8c)$$

and, due to variations in density, the total energy E_t minimized is given as:

$$E_t = \sum_k^{occ} \epsilon_k + \sum_\sigma \int \rho_\sigma \left(\epsilon_{xc} - \mu_{xc,\sigma} - \frac{V_e}{2} \right) d^3r + \sum_{\alpha,\beta} \frac{z_\alpha z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \quad (9)$$

where, V_e defines the electrostatic potential, α and β are spin up and spin down states respectively, and μ_{xc} the exchange correlation. A general eigenvalue matrix equation,²⁵⁻²⁶ where the matrix elements in the subspace ij are given as:

$$\sum_i h_{i,j} c_{j,k} = \epsilon_k \sum_i s_{i,j} c_{j,k} \quad (10a)$$

$$h_{i,j} = \int \phi_i(\mathbf{r}) \left\{ \frac{-\hbar^2}{2m} \Delta + V_s(\mathbf{r}) + \mu_{xc}(\mathbf{r}) \right\} \phi_j(\mathbf{r}) d^3r \quad (10b)$$

$$s_{i,j} = \int \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) d^3r \quad (10c)$$

Dmol3²⁵⁻²⁶ uses numeric orbitals $\phi_i(\mathbf{r})$ as the basis set calculated from multipolar functions. The multipole functions, which take into account the point group symmetry of the complex are defined through the expansion:

$$\rho_{\alpha,l,m}(s) = \frac{1}{\sqrt{4\pi} \sqrt{2l+1}} \times \int_{s=|\mathbf{r}-\mathbf{R}|} Y_{l,m}(\mathbf{r}-\mathbf{R}_\alpha) \rho_\sigma(\mathbf{r}) \rho(\mathbf{r}) d\Omega \quad (11)$$

The results of the DFT modeled spin density on manganese (figure 6c) intrinsically represents a leakage of spin density information consequential of the C_{3i} point group for the complex used to determine the numeric input basis set in equation (11). Comparing the Mulliken spin population plot (figure 6b) with the spin density plot (figure 6c), we note the spatially antisymmetric and spatially symmetric shaped regions of negative spin density in figure 6c are associated with states (i) and (ii) respectively in figure 6b. These are due to off-diagonal matrix elements for equation (10). The diagonal matrix elements for equation (10), attributed to triangular and circular contour regions of positive spin density along the C_{3i} axis in figure 6c, are associated with states (iii) and (iv) in figure 6b. States (iii) and (iv) in figure 6b, which are doubly and singly degenerate respectively, are contributions arising from the transformation of the $t_{2g}(O_h)$ and $e_g(O_h)$ sets for manganese according to the doubly degenerate E_g and singly degenerate A_g irreducible representations respectively of the C_{3i} point group. While states (i) and (ii) in figure 6b, which are doubly and singly degenerate respectively, are contributions arising from the transformations of s-type and p-type orbitals (for the coordinating pyridine-like nitrogen of imidazole) according to the doubly degenerate E_u and singly degenerate A_u irreducible representations respectively of the C_{3i} point group.

In comparing the DFT modeled spin density plot (figure 6c) and the PND spin density plot (figure 6a) the black hole spin density distribution for manganese at the origin in the PND spin density plot is absent in the DFT modeled spin density plot. This difference, we propose, is due to general relativistic⁷ considerations of energy–momentum, not taken into account in the DFT modeling which assumes special relativist²⁷. Furthermore, the DFT spin density model assumes complete decoupling of the entangled states shown in figure 7 below.

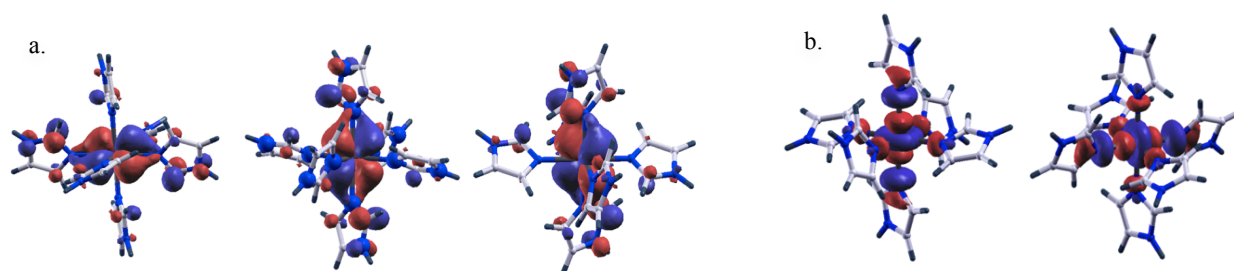


Figure 7: DFT modeled entangled states for the complex associated with π^* and σ^* orbitals on manganese due to dative imidazole-manganese π -donation interactions and dative imidazole-manganese σ -bonding interactions, respectively.

Given the results of the Mulliken spin population plot in figure 6b the admixture co-efficient for manganese $k_{Mn,\pi}$ (equation (5)) associated with dative imidazole-manganese π -donation interactions (figure 7a) was assessed to be 0.08. While the admixture coefficient for manganese $k_{Mn,\sigma}$ (equation (4)) associated with dative imidazole-manganese σ -bonding interactions (figure 7b) was assessed to be 0.25. Given the general relativistic⁷ consideration of energy–momentum, which is in view of spin delocalization η_{Mn} (equation (5)) for manganese associated with dative imidazole-manganese π -donation interactions, the value of the admixture co-efficient for manganese $k_{Mn,\pi}$ was re-assessed to be 0.29 ($\eta_{Mn} + k_{Mn,\pi}$, with $\eta_{Mn} = 0.21$).

5. Electronic structure, suitability of the complex for spintronic studies.

It is well known that quantum entanglement, an implicit consequence of bonding interactions between two spin systems, is associated with the electronic structure arising from antiferromagnetic (spin singlet) exchange and ferromagnetic (spin triplet) exchange in Hilbert space. The antiferromagnetic spin exchange is spatially symmetric and the ferromagnetic spin exchange is spatially antisymmetric. If the exchange interaction is strongly ferromagnetic the spin triplet exchange state is lower in energy than the spin singlet exchange state. Otherwise, if the exchange interaction is strongly antiferromagnetic the spin singlet exchange state is higher in energy than the spin triplet exchange state. Given the results for the titled complex, we suggest the spin triplet exchange state is associated with a non-spherical spin density distribution and the spin singlet exchange state associated with a spherical spin distribution. Using the nuclear structure for the titled complex, we modeled complex stability (figure 8, below) in view of trigonal (non-spherical) stability for the series $[M(\text{Imidazole})_6]^{2+}(\text{NO}_3^-)_2$, where M is a 3d-transition metal ion. According to figure 8, complex stability is greater for the d^5 configuration. The titled complex is therefore the best candidate in the series for observing quantum entangled, electronic structure in Hilbert space.

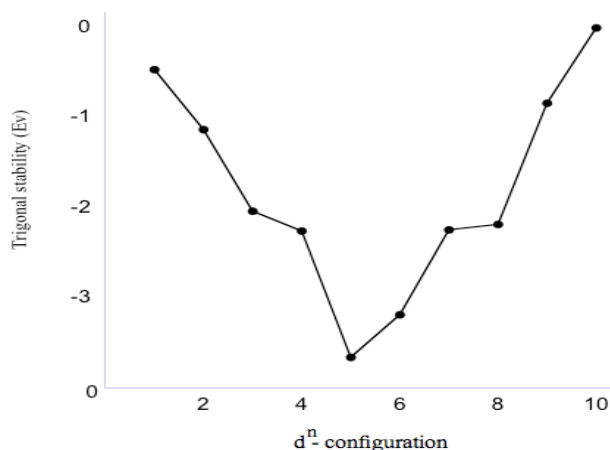


Figure 8: Trigonal stability (Ev) for the series of complexes $[M(\text{Imidazole})_6]^{2+}(\text{NO}_3^-)_2$, where M is a 3d-transition metal ion.

The suitability of the titled complex for spintronic studies, such as allowing the flow of spin-polarized currents over its surface, is firstly due to its expected conducting nature (state (iv) (figure 6b), which is spatially singly degenerate, being close to the Fermi level). And, secondly, due to the complex's expected insulating nature (state (iii) (figure 6b), which is spatially doubly degenerate, being further below the Fermi level in the bulk). The black hole spin density distribution for manganese at the origin in the PND spin density map (figure 6a), which we associate with the spherical symmetric ${}^6A_{1g}(t_{2g}^3 e_g^2)$ state for manganese, indicate the ability of the titled complex to be spin polarizing at its surface (see also state (iv), figure 6b) to spin polarized currents. While the spin density distribution for manganese projected away from the origin in the PND spin density map (figure 6a), which we attribute to spin delocalization associated with the three-fold spatially antisymmetric ${}^2T_{1g}(t_{2g}^5 e_g^0)$ state for manganese, indicate the ability of the titled complex to be spin depolarizing, insulating, in its bulk (see also state (iii), figure 6b) to spin polarized currents.

Conclusion

We have shown for the first time using polarized neutron diffraction, density functional theory a visualization of quantum entanglement in view of the spin density distribution, electronic structure associated with the interactions of manganese in the titled complex. Our results for the titled complex is in support of the Einstein's theory of general relativity and show that the solution to the paradox of quantum formalism assumes leakage of hidden information pertaining to the entangled state during measurement. Finally, our results show the suitability of the complex for spintronic studies.

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Appendix A

For crystal data, experimental information for the synthesis of titled complex see reference [16].

Appendix B

For nuclear structure determination of the titled complex in the non-PND experiment, see reference [16]. The PND experiment¹⁶ was performed with the same $2 \times 2.5 \times 5 \text{ mm}^3$, 40 mg deuterated single crystal used in the non-PND experiment, on the D3 diffractometer at the Institut Laue Langevin, France. A measuring temperature of 1.6 K was used. A field of 9.6 Tesla applied perpendicular to the horizontal plane of the crystal, which had the [010] direction vertical. A Heusler crystal was used to monochromate the incoming neutron beam at a wavelength of $0.825 \text{ \AA}$ with a polarisation of 0.975. A cryoflipper with 99% efficiency was used to change the direction of the polarization parallel and antiparallel relative to the direction of the applied field. As the complex crystallizes in the centrosymmetric space group $R\bar{3}$, the measured flipping ratio ($R(\mathbf{q})$) between the intensities $I^+(\mathbf{q})$ and $I^-(\mathbf{q})$ at the peak position of different Bragg reflections is defined by:

$$R(\mathbf{q}) = \frac{I^+(\mathbf{q})}{I^-(\mathbf{q})} = \frac{F_N(\mathbf{q})^2 + 2P^+ F_N(\mathbf{q}) F_M^+(\mathbf{q}) + F_M^+(\mathbf{q})^2}{F_N(\mathbf{q})^2 - 2P^- F_N(\mathbf{q}) F_M^+(\mathbf{q}) + F_M^+(\mathbf{q})^2} \quad (\text{B.1})$$

when the angle between the scattering vector and the magnetization direction is 90° , the flipping ratio $R(\mathbf{q})$ in (A.1) is re-defined as:

$$R(\mathbf{q}) = \frac{I^+(\mathbf{q})}{I^-(\mathbf{q})} = \frac{F_N(\mathbf{q})^2 + 2 F_N(\mathbf{q}) F_M(\mathbf{q}) + F_M(\mathbf{q})^2}{F_N(\mathbf{q})^2 - 2 F_N(\mathbf{q}) F_M(\mathbf{q}) + F_M(\mathbf{q})^2} \quad (\text{B.2})$$

Appendix C

Figure C1: Magnetization measurement on a powdered sample of the titled complex at 2 K , showing saturation at $5\mu_B$.

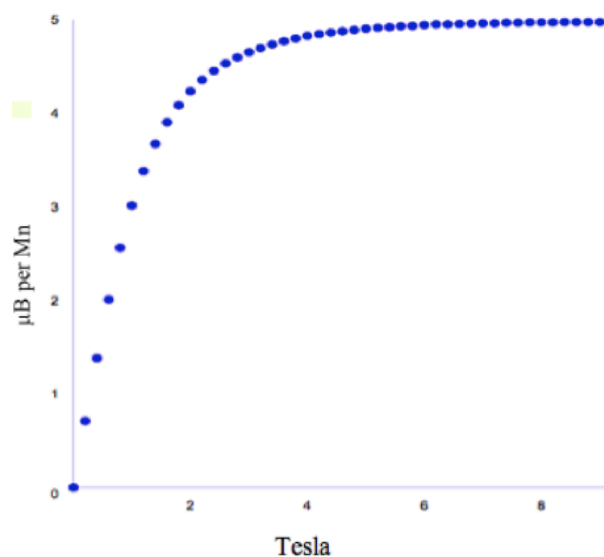


Figure C2: Temperature dependence of magnetic susceptibility performed on a powder sample of the titled complex at 500 Oe.

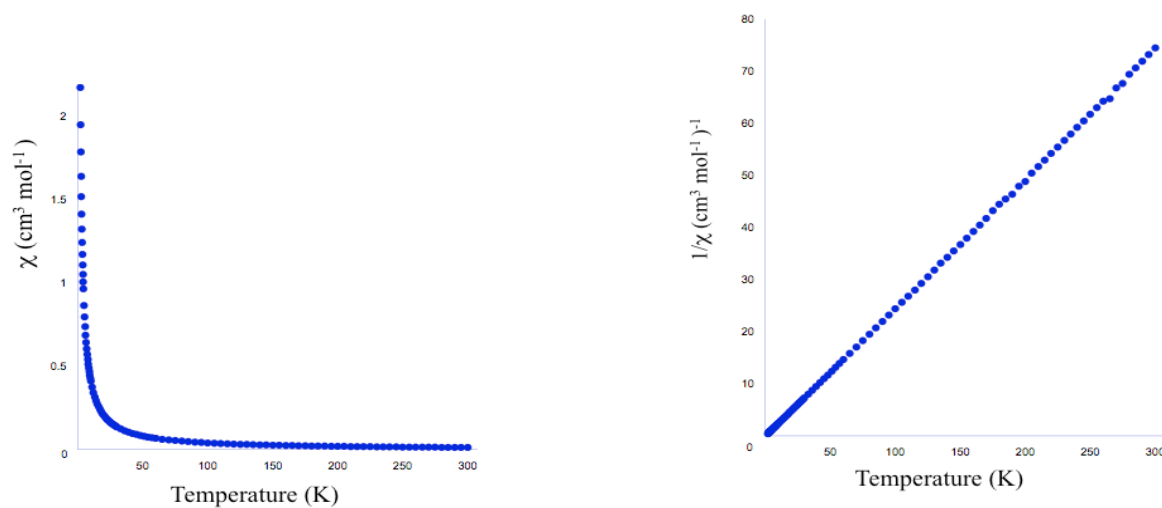
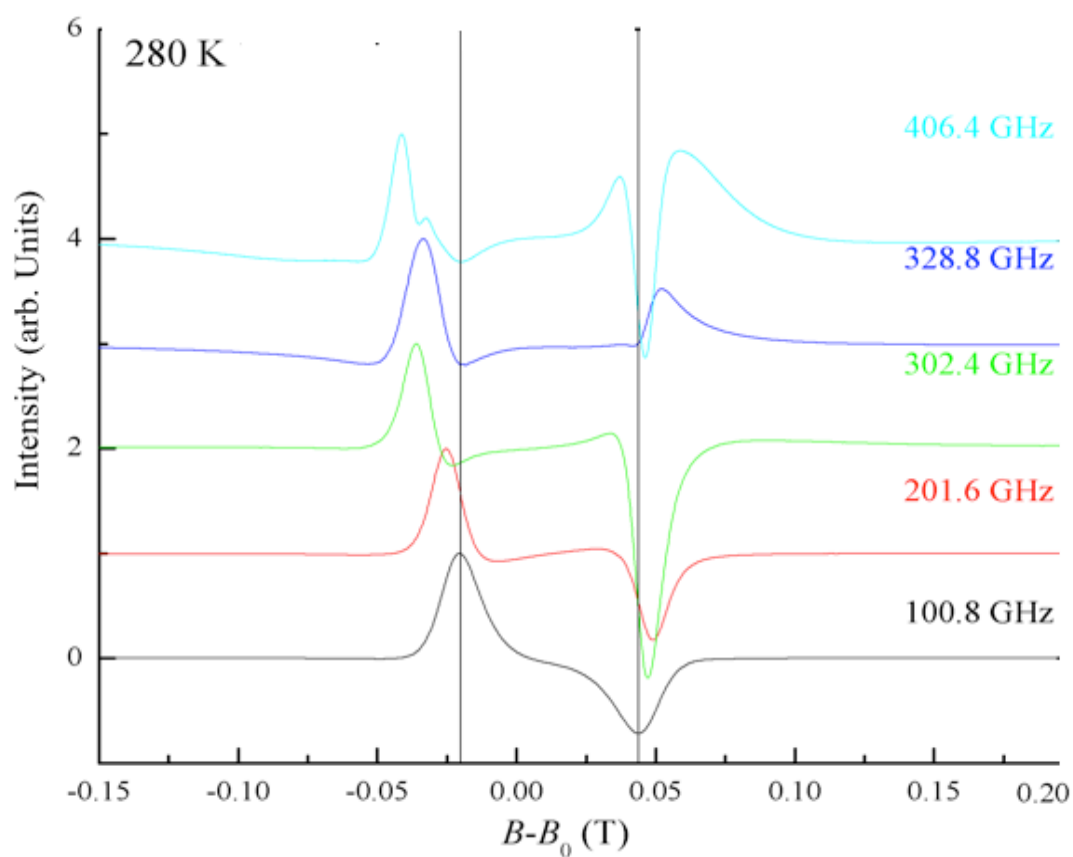


Figure C3: High field EPR spectra (obtained at 280 K) for a powdered sample of the complex at 100.8 GHz, 201.6 GHz, 302.4 GHz, 328.8 GHz, 406.4 GHz, showing no observed significant frequency dependence, an indication of entanglement for the electronic structure for manganese. The frequency independent splitting in the spectra cannot be described as an effect of electron g-factor anisotropy.



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