Magnetic Exchange Interaction in Nitronyl Nitroxide Radical based Single Crystals of 3d Metal Complexes: A Combined Experimental and Theoretical Study

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Figure S1: The FT-IR spectra of the radicals (R₁ and R₂) and their metal complexes (I, 2, 3, and 4).

The IR spectra of the radicals R₁ and R₂ and their respective metal complexes are shown in Figure 5. The vibrational spectra of the nitroxides are not much exploited, thus the exact group frequency of the N–O• bond is not very well known. Moreover, the earlier reported group frequencies of the N–O• stretching vibration, ν(N–O•), have large variations which state that ν(N–O•) lies near 1350 cm⁻¹ (1380 –1310 cm⁻¹), between 1380 –1340 cm⁻¹, or 1370 – 1340 cm⁻¹ or 1380 –1339 cm⁻¹. In the present case, the radicals show strong signals at 1351 cm⁻¹ and 1365 cm⁻¹ for the R₁ and R₂ radicals, respectively. These are arise from the ν(N–O•) stretching of the nitronyl nitroxide moiety conforming the formation of nitronyl nitroxide radicals. Other more intense lines are observed at 1025, 1126, 1253, 1299 and 1604 cm⁻¹ for the radical R₁. Similarly, intense lines at 1041, 1079, 1132, 1172, 1326, 1398, 1450, and 1548 cm⁻¹ are observed for R₂. In the metal complexes, the ν(N–O•) stretching frequencies are found to shift for all compounds.
This is expected since the metal ion coordinate to nitroxide group directly in the complexes except 2 where nitroxide group form H-bond with water molecules. As a result, the N–O• bond weakens and the vibrational peak appears at lower wave number. However, the frequencies ~1600 cm⁻¹ and ~1548 cm⁻¹ of the radical $R^1$ and $R^2$ respectively shifts to higher values after formation of the metal complexes.

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Scheme S1: Derivation of the exchange coupling constants from the energy splittings between the different spin states of the metal-organic complexes

The most widely used operator for description of the magnetic interactions between spins is the Hamiltonian proposed by Heisenberg\(^1\) and developed for practical applications by Dirac\(^2\) and van Vleck,\(^3\) the so-called Heisenberg or HDVV Hamiltonian:

\[
\hat{H} = -2 \sum_i \sum_{j \neq i} J_{ij} \hat{S}_i \cdot \hat{S}_j \tag{S1}
\]

where \(\hat{S}_{ij}\) are the spin operators and \(J_{ij}\) is the effective exchange constant between the two spins. The scalar product \(2\hat{S}_i \cdot \hat{S}_j\) can be rewritten in the following way:\(^4\)

\[
2\hat{S}_i \cdot \hat{S}_j = \left(\hat{S}_i + \hat{S}_j\right)^2 - \hat{S}_i^2 - \hat{S}_j^2 = \hat{S}_{ij}^2 - \hat{S}_i^2 - \hat{S}_j^2 \tag{S2}
\]

and then the eigenvalues of the Hamiltonian become

\[
\langle \Psi | H | \Psi \rangle = -\sum_i \sum_{j \neq i} J_{ij} \left[\langle \Psi | S_{ij}^2 | \Psi \rangle - \langle \Psi | S_i^2 | \Psi \rangle - \langle \Psi | S_j^2 | \Psi \rangle\right] = -\sum_i \sum_{j \neq i} J_{ij} \left[S_{ij} (S_{ij} + 1) - S_i (S_i + 1) - S_j (S_j + 1)\right] \tag{S3}
\]

where \(S_{ij}, S_i,\) and \(S_j\) are the eigenvalues of the corresponding operators.

The way of applying the procedure to the studied hybrid-spin complexes can be illustrated on the example of model E (Figure 9 of the main manuscript) where Mn(II) is coordinated to two nitroxide radicals and to four other spinless ligands. This model system can be represented as a linear three-spin system with spins \(S=1/2\) on the organic radicals and spin \(S=5/2\) on Mn(II), which can adopt either a high-spin (\(↑↑↑\), O), a low-spin (\(↓↑↑\), Q) or a broken-symmetry (\(↓↑↑\), S) alignment. Then, the Hamiltonian (Eq. S1) may be written as:

\[
\hat{H} = -J \left(2\hat{S}_{R1} \cdot \hat{S}_{Mn} + 2\hat{S}_{Mn} \cdot \hat{S}_{R2}\right) - j \left(2\hat{S}_{R1} \cdot \hat{S}_{R2}\right) \tag{S4}
\]

where \(J\) is the exchange integral between Mn(II) and the radicals and \(j\) is the exchange coupling between the two organic radicals. Since the two nitrooxide radicals may be considered to be spin-coupled primarily to the metal center it is assumed that \(j=0\) and the Hamiltonian simplifies to:

\[
\hat{H} = -J \left(2\hat{S}_{R1} \cdot \hat{S}_{Mn} + 2\hat{S}_{Mn} \cdot \hat{S}_{R2}\right) \tag{S5}
\]

Note that \(J\) in Eq. S5 still contains contributions from the indirect radical-radical interaction whenever a spin-polarized quantum chemical method is employed for its estimation.

According to Eq. S3, the eigenvalues are then given by:
\[ \langle \Psi | H | \Psi \rangle = - J [S_{R1Mn}(S_{1Mn} + 1) + S_{nR2}(S_{nR2} + 1) - 2S_{Mn}(S_{Mn} + 1) - 2S_{R}(S_{R} + 1)] \langle \Psi | H | \Psi \rangle = - J [S_{R1Cu}(S_{R1Cu} + 1) - S_{Cu}(S_{Cu} + 1) - S_{R1}(S_{1} + 1) + S_{R2Cu}(S_{R2Cu} + 1) - S_{Cu}(S_{Cu} + 1) - S_{R2}(S_{R2} + 1)] = - J [S_{R1Cu}(S_{R1Cu} + 1) + S_{R2Cu}(S_{R2Cu} + 1) - 2S_{Cu}(S_{Cu} + 1) - 2S_{R}(S_{R} + 1)] \]

with \( S_{R} = S_{R1} = S_{R2} = 1/2 \) and \( S_{Mn} = 5/2 \). For the octet \( S_{R1Mn} = S_{MnR2} = S_{R} + S_{Mn} = 3 \) (the two spins in both pairs are parallel), for the quartet \( S_{R1Mn} = S_{MnR2} = S_{Mn} - S_{R} = 2 \) (the two spins in each pair are opposite), and for the sextet \( S_{R1Mn} = 3, S_{MnR2} = 2 \). Then the corresponding energies are:

\[ E_{O} = \langle \Psi_{O} | H | \Psi_{O} \rangle = - 5J \]  
\[ E_{S} = \langle \Psi_{S} | H | \Psi_{S} \rangle = J \]  
\[ E_{Q} = \langle \Psi_{Q} | H | \Psi_{Q} \rangle = 7J \]

Finally, by using Eqs. S7-S9 the exchange constant can be expressed as a function of the energy gap between the various multiplets:

\[ \Delta E_{QQ} = 7J - (-5J) = 12J \]  
\[ \Delta E_{SO} = J - (-5J) = 6J \]  
\[ \Delta E_{QS} = 7J - J = 6J \]

Analogously, the energy splittings in the other studied models are related to \( J \) as follows:

Model A: \( \Delta E_{DQ} = 4J \)  
Models B and C: \( \Delta E_{QS} = 6J \)  
Model D: \( \Delta E_{TQ} = 4J \)

The values obtained from Eqs. (S12) to (S15) are given in Table III of the manuscript.

In addition, if the second organic radical in model C bears spin the following total energies of the two most stable spin states are obtained: \( E_{\text{Quartet}} = -3744.065836 \) a.u. and \( E_{\text{Sextet}} = -3744.061728 \) a.u, resulting in \( J/k_{B} = -215 \) K.
Figure S2: Atomic spin densities of all multiplets of models A, B, C, D, and E

Figure S2: Atomic spin densities of all multiplets of models A, B, C, D, and E and of the unbound radicals (with geometry taken from the X-ray structure of the complexes); hydrogen atoms are omitted because they bear negligible spin density.

Figure S3: Atomic spin densities of all multiplets of models D and E and of the unbound radicals (with geometry taken from the X-ray structure of the complexes); hydrogen atoms are omitted because they bear negligible spin density.
Table S1: Occupation numbers ($N_{occ}$) of the SOMOs of the modelled hybrid systems.

| Model | Orbital | $N_{occ}$ | Model | Orbital | $N_{occ}$ |
|-------|---------|-----------|-------|---------|-----------|
| A     | SOMO1   | 1.285     |       | SOMO1   | 1.336     |
|       | SOMO2   | 1.169     |       | SOMO2   | 1.000     |
|       | SOMO3   | 1.000     |       | SOMO3   | 1.000     |
|       | SOMO4   | 0.831     |       | SOMO4   | 1.000     |
|       | SOMO5   | 0.715     |       | SOMO5   | 1.000     |
|       | SOMO6   | 0.664     |       | SOMO6   | 0.664     |
| B     | SOMO1   | 1.000     |       | SOMO1   | 1.337     |
|       | SOMO2   | 1.000     |       | SOMO2   | 1.221     |
|       | SOMO3   | 1.000     |       | SOMO3   | 1.000     |
|       | SOMO4   | 0.982     |       | SOMO4   | 1.000     |
|       | SOMO5   | 1.000     |       | SOMO5   | 1.000     |
|       | SOMO6   | 0.779     |       | SOMO6   | 0.779     |
| C     | SOMO1   | 1.285     |       | SOMO1   | 1.336     |
|       | SOMO2   | 1.000     |       | SOMO2   | 1.000     |
|       | SOMO3   | 1.000     |       | SOMO3   | 1.000     |
|       | SOMO4   | 0.831     |       | SOMO4   | 1.000     |
|       | SOMO5   | 0.715     |       | SOMO5   | 1.000     |
| D     | SOMO1   | 1.000     |       | SOMO1   | 1.337     |
|       | SOMO2   | 1.000     |       | SOMO2   | 1.221     |
|       | SOMO3   | 1.000     |       | SOMO3   | 1.000     |
|       | SOMO4   | 0.982     |       | SOMO4   | 1.000     |
|       | SOMO5   | 1.000     |       | SOMO5   | 1.000     |
|       | SOMO6   | 0.779     |       | SOMO6   | 0.779     |
| E     | SOMO1   | 1.285     |       | SOMO1   | 1.336     |
|       | SOMO2   | 1.000     |       | SOMO2   | 1.000     |
|       | SOMO3   | 1.000     |       | SOMO3   | 1.000     |
|       | SOMO4   | 0.831     |       | SOMO4   | 1.000     |
|       | SOMO5   | 0.715     |       | SOMO5   | 1.000     |
|       | SOMO6   | 0.664     |       | SOMO6   | 0.664     |

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