

Supporting Information

A black-box approach to the construction of metal-radical multispin systems and analysis of their magnetic properties

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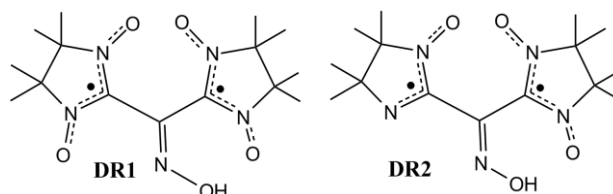
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1. **Calculations of the exchange interaction parameters (J) for binuclear complexes $[\text{Mn}_2(\text{tfa})_2(\text{hfac})(\text{DR}^1)_2]$, $[\text{Mn}_2(\text{tfa})_2(\text{hfac})_2(\text{DR}^2)_2]$ and $[\text{Ni}_2(\text{tfa})_2(\text{hfac})_2(\text{DR}^2)_2]$**

Chemical structures of the diradicals under study are shown in the following Scheme 1



Scheme 1.

The Heisenberg–Dirac–van-Vleck Hamiltonian (HDVV, 1), used to describe exchange interactions, contains of a number of parameters (J_{ij}) which have to be calculated.

$$\hat{H} = -2 \sum_{j < i} \sum_i J_{ij} (\hat{S}_i \hat{S}_j) \quad (1)$$

Figure S1 displays the structure of complex $[\text{Mn}_2(\text{tfa})_2(\text{hfac})_2(\text{DR}^1)_2]$ with six paramagnetic centers, e.g. two Mn(II) cations and four radical fragments (**A** and **B** types), and significant exchange interactions represented by arrows and corresponding J symbols. The exchange interactions between two centers are significant if these centers are covalently bonded (J_{dir} , J_{MnA} ; J_{MnB}), coordinated to the same cation (J_{AB}), or close to each other as for radical fragments of neighboring complexes (J_{int}).

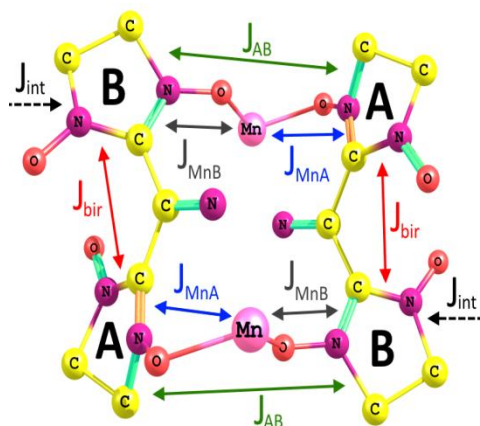


Figure S1. The structure of binuclear complex $[\text{Mn}_2(\text{tfa})_2(\text{hfac})_2(\text{DR}^1)_2]$ with schematic representation of paramagnetic centers and exchange interactions between them.

Calculations of the exchange interaction parameters were performed using both the density functional theory (DFT) and multi-configuration methods (CASSCF and NEVPT2). All calculations were done using the ORCA 3.0.3 and 4.0.0 program packages.¹ In the CASSCF calculations of the exchange interaction parameters between metal cation and radical fragment (J_{MnR}), the active spaces included five d-electrons on five 3d-orbitals of Mn(II) and different

numbers of electrons on the radical π -MOs. The results of CASSCF calculations are very sensitive to the size of the active space and choice of the MOs. We performed a series of CASSCF calculations with increasing the size of the active space. The initial orbitals were obtained from the preliminary DFT (UNO orbitals from UBP86/def2-SVP) or MP2 (RI-MP2/def2-SVP) calculations. The larger active space was based on the MOs obtained in the CASSCF calculation with smaller active space (notation **a** => **b** means that calculation **b** was based on the orbitals obtained in calculation **a**). In some calculations, the active and occupied orbitals were localized orbitals; this simplified the search of low-energy bonding π -orbitals.

1.1. Calculations of J_{MnA} and J_{MnB}

The strategy for calculations of the exchange interaction between Mn(II) and R^{1a} (A) or R^{1b} (B) was the following: the UNO BP86/def2-SVP MOs were taken for the smallest (6,6) active space, MOs obtained in the CASSCF(6,6) calculation were used for the following CASSCF(8,8) calculations. The MOs from the latter were localized and used for the CASSCF(10,10) calculations. Again, the localized MOs of the previous calculation were used for the next CASSCF(14,12) step and its localized MOs were used for the same CASSCF(14,12) calculation. Symbolically, this procedure can be represented as follows: UNO BP86/def2-SVP (TightSCF) => (6,6) => (8,8), l.o. => (10,10), l.o. => (14,12), l.o. => (14,12). Results of these calculations are shown in Table 3 of the main text.

1.2. Calculations of J_{dir}

Calculations of the J_{dir} values were performed for both the isolated diradical and for the whole binuclear complex with Mn(II) replaced by Zn(II) and with diamagnetic analogue of the second diradical. The strategy of the CASSCF calculations for isolated diradical was the following: RI-MP2/def2-SVP => (2,2); RI-MP2/def2-SVP =>(6,6) l.o. => (8,8), l.o. => (16,12). Two basis sets were employed in this case. The strategy of the CASSCF calculations for the model complex was the following: RI-MP2/def2-SVP => (2,2); RI-MP2 def2-SVP (def2-SVP/JK RIJK) =>(6,6) l.o. => (8,8), l.o. => (16,12). Only small basis set was possible to use in the calculations for so large system. Results of these calculations are displayed in Table 4 of the main text.

1.3. Calculations of the exchange interaction between radical centers coordinated to the same Mn(II) cation (J_{AB})

To estimate exchange interaction between radical fragments A and B coordinated to the same Mn(II) cation, the calculations at different levels using different models have been performed. These models were two isolated radical fragments (model 1), complex of Zn(II) with these radical fragments (model 2) and the whole complex with other paramagnetic centers substituted by

diamagnetic analogues (model 3). The BS-DFT calculations predict for these models weak AF interactions with J_{AB} being $-10.6, -19.9$ and -12.5 cm^{-1} for models 1 – 3, respectively.

For models 1 and 2, the strategy of CASSCF's calculation was the following RI-MP2/def2-SVP => (6,6). l.o. => (18,14). For model 3, the following strategy was used: RI-MP2/def2-SVP => (2,2) l.o. => (6,6) and RI-MP2/def2-SVP => (2,2), l.o. => (18,14). Results of calculations for models 1 – 3 are shown in Table S1.

Table S1. Results of CASSCF($m_{\text{orb}}, n_{\text{el}}$)/def2-SVP, CASSCF($m_{\text{orb}}, n_{\text{el}}$)/NEVPT2/def2-SVP, and BS-UB3LYP/def2-TZVP calculations of the $J_{R^{1a}R^{1b}}$ values (in cm^{-1}) for different models.

Method	$\{R^{1a} \dots R^{1b}\}$			$\{R^{1a}ZnR^{1b}\}$ (Fig. 4d)			$\{HR^{1b}R^{1a}Zn_2R^{1b}HR^{1a}\}$ (Fig. 4e)		
	(6,6)	(18,14)	BS-DFT	(6,6)	(18,14)	BS-DFT	(6,6)	(18,14)	BS-DFT
CASSCF	-1.8	-2.2	-10.6	-0.6	-1.0	-19.9	-0.8	-1.4	-12.5
NEVPT2	-3.9	-4.5		-2.2	-3.4		-3.0	-4.1	

1.4. Calculations of parameter J_{int} for the radical fragments of the neighboring binuclear complexes

Calculations for Mn(II) complexes. It was found using BS-DFT that every binuclear complex is linked to two neighbors by a noticeable exchange interaction (J_{int}). Parameter of this exchange interaction was calculated for a model 1 consisting of two radical fragments B. In addition, the same value was calculated for a pair derived from diradicals by replacing a remote radical fragment with a diamagnetic analog (model 2). For both models, the BS-DFT approach gives almost the same J_{int} values: -14.4 and -15.2 cm^{-1} , respectively. The strategy of the CASSCF calculations was the following: UNO BP86/def2-SVP => (2,2) => (6,6) l.o. => (18,12) => (18,14) for model 1 and RI-MP2/def2-SVP => (2,2) l.o. => (6,6) and RI-MP2/def2-SVP => (2,2) l.o. => (18,14) for model 2. Results of these calculations are shown in Table S2.

Table S2. Results of the CASSCF(M,N)/def2-SVP, CASSCF(M,N)/NEVPT2/def2-SVP, and BS-UB3LYP/def2-TZVP calculations of the J_{int} (cm^{-1}) parameter of the intermolecular exchange interaction in the crystals of $[\text{Mn}_2(\text{tfa})_2(\text{hfac})_2(\text{DR}^1)_2]$.

Method	Isolated pair $\{R^{1b} \dots R^{1b}\}$					$\{HR^{1a}R^{1b} \dots R^{1b}HR^{1a}\}$ (Fig. 5f)			
	(2,2)	(6,6)	(18,12)	(18,14)	BS-DFT	(2,2)	(6,6)	(18,14)	BS-DFT
CASSCF	-5.5	-2.5	-4.1	-4.1	-14.4	-0.8	-2.5	-4.0	-15.2
NEVPT2	-9.2	-10.4	-8.2	-8.2		-1.5	-6.2	-8.1	

Calculations for Ni(II) complex. In the calculations of the pair exchange interactions for the Ni(II) complex, only most accurate *ab initio* methods were utilized, although the accuracy of the BS-DFT approach was also tested. The maximum active space for the calculations consists of 17 electrons in 12 MOs (eight electrons in five d-orbitals of Ni and nine electrons in seven π -type MOs

of nitronyl nitroxide R^{2b} ; Figure 5 of main text). The active space for the $J_{NiR^{2a}}$ calculations includes 15 electrons in 11 MOs (eight electrons in five d-orbitals and seven electrons in seven orbitals of iminonitroxide R^{2a} , Figure 5 of main text).

Table S3. Results of CASSCF, NEVPT2, and FlipSpin-DFT calculations of $J_{NiR^{2a}}$ and $J_{NiR^{2b}}$ parameters of the exchange interaction between Ni(II) and radical moieties R^{2a} and R^{2b} , respectively.

Method	$J_{NiR^{2a}}, \text{cm}^{-1}$			$J_{NiR^{2b}}, \text{cm}^{-1}$		
	(15,11) def2-SVP	(15,11) def2-TZVP	FS-UB3LYP/ def2-TZVP	(17,12) def2-SVP	(17,12) def2-TZVP	FS-UB3LYP/ def2-TZVP
CASSCF	21.5	21.6	73.4	-96.20	-101.3	-439.6
NEVPT2	28.0	28.2		-214.2	-231.3	

Similar to the case of Mn(II) complexes, every binuclear Ni(II) complex is linked to two neighbors by a noticeable exchange interaction (J_{int}). We calculated exchange interaction between two radical fragments of the neighboring dinuclear complexes. Table S4 presents results of these calculations and demonstrates that exchange interactions between neighboring clusters are very weak and can be neglected in modelling.

Table S4. Results of CASSCF(18,14), CASSCF(18,14)/NEVPT2 and BS-DFT calculations of J_{int} (in cm^{-1}) for crystals of Ni(II) dinuclear complexes.

CASSCF def2-SVP	NEVPT2 def2-SVP	CASSCF def2-TZVP	NEVPT2 def2-TZVP	BS-UB3LYP def2-TZVP
0.1	-0.75	0.1	-0.6	-0.43

1.5. Estimation of the exchange interaction parameters using three-center model (A...Mn...B) and generalized broken-symmetry and CASSCF/NEVPT2 approaches

Calculations of exchange interactions in a system with several paramagnetic centers, for example, calculations of three parameters of exchange interactions in a system with three paramagnetic centers ($R1...Mn...R2$), are better calculate for the whole system. The system includes paramagnetic centers with spins 1/2, 1/2 and 5/2, which form four states with the spins 7/2, 5/2, 5/2, 3/2 and different energies. Calculations for this three-particle model were made using CASSCF(M,N)/NEVPT2/def2-SVP methods. The strategy of CASSCF calculations is RI-MP2/def2-SVP (def2-SVP/JK RIJK) => (7,7) l.o.=> (11,11) l.o. The results of calculations of the energy splitting are shown in Table S1. Finding of J_{ij} from these energies requires solving the system of non-linear equations. It was numerically solved using HDVV spin-Hamiltonian, and results are also shown in Table S5.

Table S5. The energy splittings between states with full spin equal to 7/2, 5/2, 5/2 or 3/2 and corresponding J_{ij} parameters calculated at the CASSCF and CASSCF/NEVPT2/def2-SVP level.

Method	ΔE and J in cm^{-1} :	(7,7)	(11,11)
CASSCF	$E_{ 3/2\rangle} - E_{ 5/2\rangle}$	-63.1	-100.7
	$E_{ 3/2\rangle} - E_{ 5/2\rangle}$	-93.4	-160.3
	$E_{ 3/2\rangle} - E_{ 7/2\rangle}$	-156.7	-261.7
	$J_{\text{MnA}}, J_{\text{MnB}}, J_{\text{AB}}$	-11.7, -14.4, -0.10	-18.3, -25.3, -0.35
NEVPT2	$E_{ 3/2\rangle} - E_{ 5/2\rangle}$	-119.2	-210.2
	$E_{ 3/2\rangle} - E_{ 5/2\rangle}$	-172.3	-320.9
	$E_{ 3/2\rangle} - E_{ 7/2\rangle}$	-291.2	-533.4
	$J_{\text{MnA}}, J_{\text{MnB}}, J_{\text{AB}}$	-22.5, -26.0, 0.15	-38.6, -50.3, -1.2

Comparison of the results of Table S5 with those of Tables 3 (see main text) shows that parameters calculated for three-spin system are close to those calculated for pairs. However, the former values are about twice smaller than the most reliable values of Tables 3. In our opinion, this is due to the use of smaller active space available for the larger three-spin system.

Only the most accurate calculations of the exchange interaction parameters were performed for $[\text{Mn}_2(\text{tfa})_2(\text{hfac})_2(\text{DR}^2)_2]$ and $[\text{Ni}_2(\text{tfa})_2(\text{hfac})_2(\text{DR}^2)_2]$ complexes. Results are shown in Tables 5 and 7 of the main text.

2. Calculation of ZFS tensors for Mn(II) and Ni(II) mononuclear complexes

2.1. Calculations for model mononuclear Mn(II) complex

There are two contributions to the D-tensor: due to spin-spin (SSC) and spin-orbital (SOC) couplings. The SSC component was calculated at the ROBP86/def2-TZVP level; the zero-field splitting (ZFS) parameters turned out to be $D = -0.047 \text{ cm}^{-1}$, $E/D = 0.32$. Both contributions were also calculated using CASCI/def2-TZVP approach taking into account all states originated from the d^5 -configuration, this led to $D = -0.045 \text{ cm}^{-1}$, $E/D = 0.25$. Thus, ZFS parameters are small, which is typical of high-spin Mn(II) complexes coordinated by nitrogen and oxygen atoms,² and can be neglected in the modeling of magnetic properties.

2.2. Calculations for model mononuclear Ni(II) complex

For Ni(II) hexacoordinated complexes having a triplet ground state, the D-parameters adopt values between -22 and $+12 \text{ cm}^{-1}$, all the g-factors exceed the spin-free value of 2.0023 and typically lie between 2.1 and 2.2. To calculate the g- and D-tensors for our model Ni(II) complex with diamagnetic ligands, the CASCI/def2-TZVP method was employed. Active space for CASCI(8,5) calculation included eight electrons on five 3d-orbitals of Ni(II) cation. Active space for CASCI(8,10) calculations included ten d-orbitals of so-called double-shell; inclusion in the

active space of double-shell orbitals is recommended for cations with more than half-filled d-shells. CASCI expansion space includes all states originated from d^8 configuration, i.e. 15 singlet and 10 triplet states. Results of calculations are shown in Table S6. It is seen, that the use of double-shell orbitals in the active space gave minor effect. The D value is predicted to be moderate ($\sim 4.2 \text{ cm}^{-1}$) and falls within the range of typical values for the hexacoordinated Ni(II) complexes. The CASCI calculations predicted overestimated g_{iso} value. In turn, the g_{iso} predicted by DFT is typical of such complexes.

Table S6. Results of calculation of the spin-Hamiltonian parameters of the model Ni(II) complex with diamagnetic ligands.

	CASCI(8,5)/ def2-TZVP	CASCI(8,10)/ def2-TZVP	UB3LYP/ def2-TZVP
D, cm^{-1}	4.26	4.14	-
E/D	0.20	0.27	-

3. Modelling of the temperature dependence of the magnetic susceptibility

$\chi(T)$

A new program taking into account more general spin-Hamiltonian (2) and paramagnetic centers with $S_k \geq 1/2$ has been written.

$$\hat{H} = \hat{H}_{ex} + \hat{H}_{ZFS} + \hat{H}_{Zee}, \text{ where} \quad (2)$$

$$\hat{H}_{ex} = -2 \sum_{k=1}^{ns-1} \sum_{l=k+1}^{ns} J_{kl} \hat{S}_k \hat{S}_l$$

$$\hat{H}_{ZFS} = \sum_{k=1}^{ns} D_k [S_{z,k}^2 - \frac{1}{2S_k(S_k + 1)} + E_k/D_k (S_{x,k}^2 - S_{y,k}^2)]$$

$$\hat{H}_{Zee} = \sum_{k=1}^{ns} g\beta \hat{S}_k \vec{B}$$

The following formula (3) was used for the calculation of the magnetic susceptibility temperature dependence

$$\chi T = \frac{N\mu_B^2}{3k} (\langle \sum_i g_i^2 \hat{S}_i^2 \rangle - \langle \sum_i g_i \hat{S}_{iz} \rangle^2), \quad (3)$$

where angular braces denote averaging over a canonical ensemble and index i enumerates paramagnetic centers. The fastest method of such averaging involves solving the problem of finding the energies of the eigenstates for the zero-field spin-Hamiltonian \hat{H} and calculation of the averages as

$$\langle A \rangle = \text{Tr} [\hat{A} \exp(-\hat{H}/T)]$$

For diagonalized \widehat{H} (\widehat{H}_d), this average form can be calculated in linear time, as

$$\text{Tr} \left[\widehat{A} \exp \left(-\widehat{H}/T \right) \right] = \text{Tr} \left[\widehat{A} \widehat{U} \exp \left(-\widehat{H}_d/T \right) \widehat{U}^T \right] = \text{Tr} \left[\widehat{U}^T \widehat{A} \widehat{U} \exp \left(-\widehat{H}_d/T \right) \right].$$

For diagonal \widehat{H} , this expression can be simplified as a dot product of main diagonals of $\exp \left(-\widehat{H}_d/T \right)$ and $\widehat{U}^T \widehat{A} \widehat{U}$.

Spin-Hamiltonian and total spin operators are constructed in Zeeman basis making heavy use of the following formula:

$$(\widehat{S}_1 \widehat{S}_2) = \widehat{S}_{1z} \widehat{S}_{2z} + \frac{1}{2} (\widehat{S}_{1+} \widehat{S}_{2-} + \widehat{S}_{1-} \widehat{S}_{2+})$$

and explicit formulas for matrix elements of spin-ladder operators. ZFS contribution is included in the form

$$\widehat{H}_{ZFS} = \sum_i D_i \left(\widehat{S}_{iz}^2 - \frac{\widehat{S}_i^2}{3} \right), \quad D_i = \frac{3}{2} D_{i,zz}$$

Here we assume that g-tensor for each center is isotropic and that the principal axis of all ZFS tensors are aligned by the same way. Anisotropic g-tensors are not supported at this moment.

Curie-Weiss temperature θ cannot be derived from this spin-Hamiltonian, so it is applied ad hoc in the final formula:

$$\chi T = \frac{T}{T-\theta} \frac{N\mu_B^2}{3k} \left(\langle \sum_i g_i^2 \widehat{S}_i^2 \rangle - \langle \sum_i g_i \widehat{S}_{iz} \rangle^2 \right).$$

After we obtain χT as a function of temperature, we can fit experimental data using weighted least-squares method. To compensate for uneven distribution of experimental points we have chosen weight for each experimental point as a temperature difference between its nearest neighbors. Results of the most accurate calculations were used as the guess parameters in the fitting process. The resulting code is written in Python 3 using NumPy (general calculations) and SciPy (sparse matrices, optimization routines) libraries.

References

1. (a) F. Neese, *Wires Comput. Mol. Sci.* **2012**, 2, 73; (b) F. Neese et al., ORCA – An ab initio, DFT and semi-empirical SCF-MO package, Mulheim a. d. Ruhr, version 3.0.3, **2015**; version 4.0.0, **2017**.
2. (a) C. Duboc, M.-N. Collomb, F. Neese, *Appl. Magn. Reson.* **2010**, 37, 229; (b) J. Rich, C. E. Castillo, I. Romero, M. Rodriguez, C. Dubic, M.-N. Collomb, *Eur. J. Inorg. Chem.* **2010**, 3650.