

Prediction of Exchange Coupling Constant for Mn₁₂ Molecular Magnet Using Dft+U

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Abstract. Single-molecule magnets are perspective materials for molecular spintronic applications. Predictions of magnetic coupling in these systems have posed a long standing problem, as calculations of this kind require a balanced description of static and dynamic electron correlation. The large size of these systems limits the choice of theoretical methods used. Two methods feasible to predict the exchange coupling parameters are broken symmetry Density Functional Theory (BSDFT) and DFT with empirical Hubbard U parameter (DFT+U). In this contribution we apply DFT+U to study Mn-based molecular magnets using Vanderbilt Ultrasoft Pseudopotential plane wave DFT method, implemented in Quantum ESPRESSO code. Unlike most previous studies, we adjust U parameters for both metal and ligand atoms using two dineuclear molecular magnets [Mn₂O₂(phen)₄]²⁺ and [Mn₂O₂(OAc)(Me₄dtne)]³⁺ as the benchmarks. Next, we apply this methodology to Mn₁₂ molecular wheel. Our study finds antiparallel spin alignment in weakly interacting fragments of Mn₁₂, in agreement with experimental observations.

Keywords: DFT+U, Heisenberg exchange constant, Molecular magnet, Magnetic Wheel, molecular spintronics, quantum computing.

1 Introduction

Single molecule magnets (SMMs) have been of considerable interest to scientists ever since their initial discovery in 1993.[1, 2] SMMs are transition metal complexes that have a large spin ground state and considerable negative anisotropy leading to a barrier for the reversal of magnetization. These molecules show slow magnetization relaxation and can be magnetized below their blocking temperature.[3] The first SMM to be discovered was [Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄]₂CH₃COOH, 4H₂O, a dodecanuclear manganese cluster with a S=10 ground state, that is commonly known as Mn₁₂-acetate.[1, 2] This complex shows magnetization hysteresis and also shows quantum tunneling of the magnetization as evidenced by steps at regular intervals in the hysteresis loop.[3]

Since the discovery of Mn_{12} -acetate, a large number of new SMMs have been reported with a wide variety of topologies and nuclearities, incorporating a variety of different metal atoms. A majority of molecules reported to show SMM behavior have been synthesized using manganese, iron or nickel. Manganese clusters that show SMM behavior are the most abundant. Many derivatives of Mn_{12} acetate have been reported to show SMM behavior. Examples of these include $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{H}_2\text{O})_4]$ [4] and the mixed-carboxylate complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCHCl}_2)_8(\text{O}_2\text{CCH}_2\text{Bu}^t)_8(\text{H}_2\text{O})_3]$, which were reported [5] to have an $S=10$ ground state. The complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4-2-\text{CH}_3)_{16}(\text{H}_2\text{O})_4] \cdot \text{CH}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ reported by Rumberger et al., [6] is another SMM with Jahn-Teller isomerism. The complex $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]\text{Br}_8$ is one of the most extensively studied iron SMMs; it has a $S=10$ ground state and incorporates the ligand triazocyclononane (tacn).

SMMs containing other transition metals such as cobalt or vanadium are relatively rare. An example of a cobalt SMM is the $[\text{Co}_4(\text{hmp})_4(\text{MeOH})_4\text{Cl}_4]$ complex, which has four Co (II) ions, was reported by Yang et al. and shows magnetization hysteresis at low temperatures. [7] The 2-hydroxymethylpyridine (hmp) ligand is a chelating ligand in this complex. Some of the different topologies seen in SMMs include Mn_4 dicubane [8] complexes and the $S=9/2$ Mn_4 cubane [9] complexes. Other interesting topologies include molecular wheels and rod-shaped SMMs such as the Mn_6 clusters. One-dimensional chains of weakly interacting SMMs are also known, such as the complex $[\text{Mn}_4(\text{hmp})_6\text{Cl}_2]_n(\text{ClO}_4)_n$, reported by Yoo et al. [10] Perhaps the most interesting of these topologies is that of the wheel-shaped SMMs. Scientists have been fascinated with molecular wheels for a number of reasons. Odd-numbered molecular wheels, such as $[(\text{C}_6\text{H}_{11})_2\text{NH}_2] \cdot [\text{Cr}_8\text{NiF}_9(\text{O}_2\text{CC}(\text{CH}_3)_3)_{18}]$ are of interest to scientists studying spin frustration.¹⁴ One of the smallest of these molecular wheels is the recently reported tetranuclear manganese complex, with the formula $[\text{Mn}_4(\text{anca})_4(\text{Htea})_2(\text{dbm})_2] \cdot 2.5 \text{Et}_2\text{O}$. [11] Larger wheels include the Mn_{24} wheel, reported in 2006, which consists of eighteen Mn(III) ions and six Mn(IV) ions linked together to form a wheel-shaped topology. [12] It is believed that molecular wheels could be used in design of quantum computer. [13]

The family of wheel-shaped complexes that shows SMM behavior is steadily growing. Among these complexes are the Mn_{22} wheel [14] and the Mn_{84} wheel, which is the largest wheel-shaped SMM known to date. The largest reported spin ground state for a wheel-shaped SMM is the $S=14$ ground state reported for the complex $[\text{Mn}_{16}\text{O}_2(\text{OCH}_3)_{12}(\text{tmp})_8(\text{CH}_3\text{COO})_{10}] \cdot 3\text{Et}_2\text{O}$. [15] Among the family of wheel-shaped SMMs is a smaller family of single-stranded wheels including the Mn_{16} wheel²³, which has the largest single-stranded loop known to date and was reported in 2005. A series of $[\text{Mn}_{12}]$ wheels reported by Rumberger et al. [6] in 2005 are also examples of single-stranded wheels.

In this contribution we predict Heisenberg exchange constant for Mn-based magnetic wheel using DFT+ U method. We successfully validated the method for two Mn(IV) bimetallic system and then applied the same protocol to predict the value of the Heisenberg constant, which could not be predicted in the previous study using Hybrid Density functional theory. [16]

2 Computational Details

All the reported calculations were done using the PWSCF package,[17] which utilizes PBE exchange-correlation functional, Vanderbilt ultrasoft pseudopotentials [18] and a plane-wave basis set. The energy cutoffs for the wave functions and charge densities were set at 35 and 360 Ry to ensure total energy convergence. The Marzari-Vanderbilt [19] cold smearing with smearing factor 0.0008 was used for spin polarized calculation. All molecular structures were optimized in ferromagnetic state starting from atomic coordinates, obtained with X-Ray diffraction experiments. First we validated our method for two Mn(IV) complexes (I and II) and then applied to the Mn₁₂ complex, referred as complex III. The DFT+*U* method described by Cao et. al.[20] was used for the calculations. We applied Hubbard *U* parameter on Mn atom, as well on the ligand oxygen and nitrogen atoms, coordinating the Mn atom. Since the Quantum-ESPRESSO code doesn't allow using *U* parameter on nitrogen, we modified the source code accordingly. Self-consistent Hubbard-*U* method has been incorporated to determine the *U* value for Mn which turns out to be 2.6 eV for this system. For oxygen and nitrogen we used the *U* values of 1.50 eV. Local Thomas-Fermi mixing mode was used to improve SCF convergence.

3 Results and Discussions

To obtain Heisenberg exchange constant of molecular magnet, we used DFT+U method and we used *U* parameter on both the coordinating centers and on the transition metals. The Heisenberg Hamiltonian in general can be written as

$$H = -\sum J_{ij} \cdot S_i \cdot S_j$$

here *J* represents the coupling constant between the two magnetic centers *S_i* and *S_j*. The positive *J* values indicate the ferromagnetic ground state and the negative indicate antiferromagnetic ground state.

3.1 Calculation of *J* for Bimetallic Mn(IV) Complexes and Validation of *U* Values

We started with the X-ray crystal structures of two molecules having bi-manganese (IV) center represented in Fig.1 (complex I) and Fig.2 (complex II). The difference between the two molecules is the acetate bridge in the complex II. According to the previous study,[21] the Hybrid DFT is unable to predict the *J* values for complex II and some other molecules with acetate bridge[21, 22], while it was successful for the complex I. Though BSDFT method is the most used method to predict theoretical *J* values, but for complexes having specific ligand or for very small value of Heisenberg exchange constant, [23-26] this method is not successful so much. That calculation reported the *J* value ~ -37 cm⁻¹ whereas the experiment reports -100 cm⁻¹. The reason for failure in predicting *J* suggested as the BS-DFT approach [27] fails to predict the Heisenberg exchange constant related to the delocalization of unpaired electron orbitals over both manganese centers. To deal with this problem we followed

the procedure used by Cao et. al.[20] in order to predict J . By adjusting two different U values (one for Mn atom, and another for N and O atoms), we obtained a reasonable agreement with experimental J values for both complexes I and II. The results are reported in the Table 1. The J values for complex I and complex II using BS-DFT method are obtained from reference [21], for complex III [16] the cited J is the Heisenberg exchange constant between Mn1 –Mn6' center.

Table 1. Calculation of Heisenberg exchange constant for Mn complexes

Molecular magnet	Experimental $J \text{ cm}^{-1}$	Calculated		U(Mn), eV	U(O), eV	U(N), eV
		with BSDFT $J \text{ cm}^{-1}$	Calculated with DFT+ U $J \text{ cm}^{-1}$ (this work)			
Complex I	-147 ^a	-131 ^c	-177.2	2.5	1.6	1.6
Complex II	-100 ^b	-37 ^c	-85.9	2.5	1.6	1.6
Complex III		0.0 ^d	-26.17	2.5	1.6	1.6
Mn1 –Mn6'						

^a Experimental data is taken from [28]

^b Experimental Data is taken from [29]

^c BSDFT calculation from ref [21]

^d BSDFT calculation from ref [16]

Our calculated data agree with the experimental value to within 15%, for both molecule with and without Acetate Bridge, compare to 65% deviation given by broken symmetry Density Functional theory.

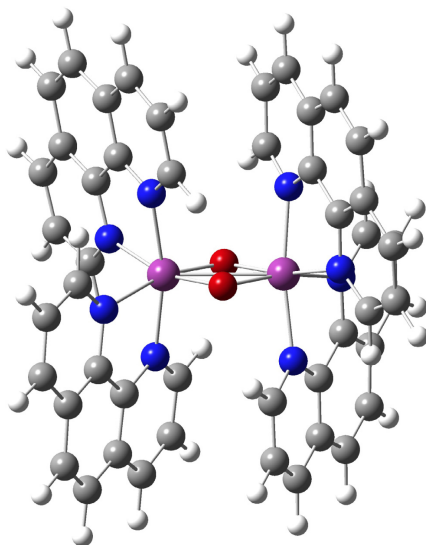


Fig. 1. $[\text{Mn}_2\text{O}_2(\text{phen})_4]^{4+}$ Complex I (violet balls refer to Mn(IV) atoms, grey ones are carbon atoms, white ones are hydrogen, red ones are oxygen, blue ones are nitrogen atoms)

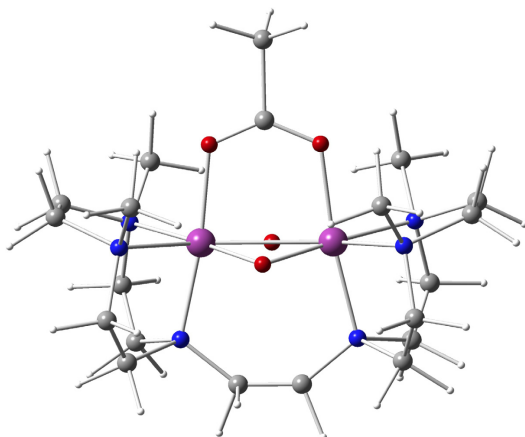


Fig. 2. [Mn₂O₂(OAc)(Me₄dtne)]³⁺ Complex II

3.2 Calculations of J for Mn₁₂ System

After validating the value for both molecular magnet having Mn(IV) center we applied our protocol for Mn₁₂ wheel [Mn₁₂(O₂CMe)₁₄(mda)₈] (where mda is N-methyl diethanolamine). The Mn₁₂ wheel has two different valence centers with different coordinations (the Mn(III) is hexa- and Mn(II) is penta-coordinated). Fig. 3 shows the spin arrangement predicted by previous DFT study [2].

The reason for using the parameter U for both the p and d orbital was explained by Cao et al.[20] They suggested that Coulomb interactions between oxygen $2p$ electrons are comparable to those between d electrons, [30, and 31] and should hence be taken into consideration as well. However, since oxygen usually bears a fully occupied p -shell, this correlation effect is often negligible. Therefore, in most cases, DFT+ U^d can already yield a satisfactory description of the ground state without oxygen $2p$ -electron corrections. Nevertheless, DFT+ $U^{d,p}$ has to be taken into consideration explicitly here for both the $3d$ and oxygen $2p$ electrons in order to obtain the correct ground state for this molecule. Previous B3LYP study on this molecule [2] was unable to predict the correct antiferromagnetic ordering for Mn1'-Mn6 and Mn1-Mn6' center shown in Fig. 4, where zero J value was obtained. This study, however, did not consider the entire molecule due to its large size. The molecule was divided into smaller fragments that contained only two or three Mn centers. In our calculation we used all twelve manganese centers and optimized the geometry with PBE exchange-correlation functional. Thus obtained relaxed geometry was then used to calculate the J parameter between 6-center fragments, described in Fig. 4. The energy difference between two states shows this center has antiferromagnetic coupling, which is in agreement with the experiment [2] which suggested a $S=7$ ground state of the [Mn₁₂O₂CMe)(HO₂CMe)₃(OMe)²⁻(mda)].

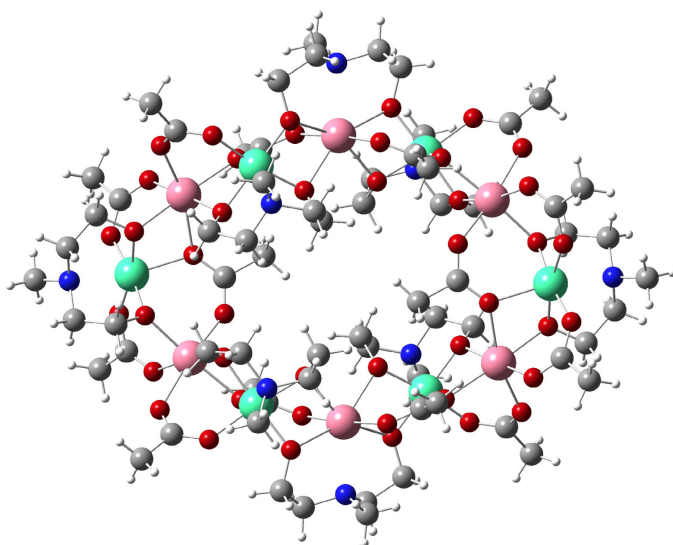


Fig. 3. $[\text{MnIIMnII}(\text{O}_2\text{CMe})(\text{HO}_2\text{CMe})_3(\text{OMe})^2(\text{mda})]$ Complex III (pink Mn refers Mn(III) and green ball refers Mn(II))

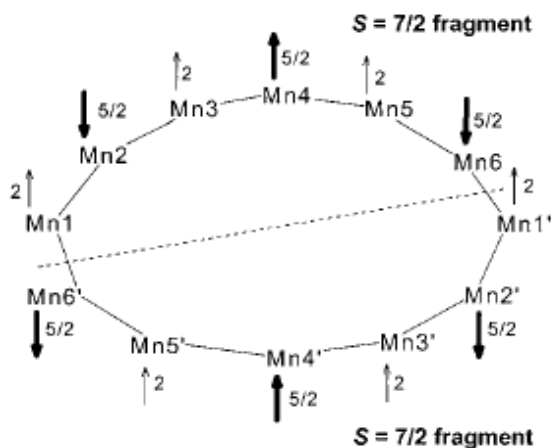


Fig. 4. Depiction of the spin alignments in the $S=7$ ground state [16] of complex III predicted by the DFT calculations, with the Mn1–Mn6' and Mn1'–Mn6 interactions antiferromagnetic. The dashed line separates the two $S=7/2$ fragments that are coupled by the interactions between Mn1–Mn6' and Mn1'–Mn6; if these interactions are antiferromagnetic (negative J values), the resultant spin of the complete molecule is $S=7$. [16].

4 Conclusions

We have performed DFT and DFT+ U calculations for two Mn_2 (IV) and one Mn_{12} molecular magnets. Because of the strong magnetic orbital delocalization in these

systems, the broken symmetry pure DFT and hybrid DFT approach fails to predict correct exchange coupling parameter values. The inclusion of a Hubbard-*U* like term for both the Mn 3d and O, N 2p electrons greatly enhances the localization of the magnetic orbitals for both high and low spin states, and is essential in order to obtain the correct ground-state and exchange-coupling parameter values. These properties were successfully reproduced by the Quantum ESPRESSO plane-wave pseudopotential DFT calculations.

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References

1. Sessoli, R., Tsai, H.L., Schake, A.R., Wang, S., Vincent, J.B., Folting, K., Gatteschi, D., Christou, G., Hendrickson, D.N.: High-spin molecules: [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄]. *Journal of the American Chemical Society* 115, 1804–1816 (1993)
2. Sessoli, R., Gatteschi, D., Caneschi, A., Novak, M.A.: Magnetic bistability in a metal-ion cluster. *Nature (London, United Kingdom)* 365, 141–143 (1993)
3. Friedman, J.R., Sarachik, M.P., Tejada, J., Maciejewski, J., Ziolo, R.: Steps in the hysteresis loops of a high-spin molecule. *Journal of Applied Physics* 79, 6031–6033 (1996)
4. Soler, M., Artus, P., Folting, K., Huffman, J.C., Hendrickson, D.N., Christou, G.: Single-Molecule Magnets: Preparation and Properties of Mixed-Carboxylate Complexes [Mn₁₂O₁₂(O₂CR)₈(O₂CR')₈(H₂O)₄]. *Inorganic Chemistry* 40, 4902–4912 (2001)
5. Soler, M., Wernsdorfer, W., Sun, Z., Ruiz, D., Huffman, J.C., Hendrickson, D.N., Christou, G.: New example of Jahn-Teller isomerism in [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄] complexes. *Polyhedron* 22, 1783–1788 (2003)
6. Rumberger, E.M., Shah, S.J., Beedle, C.C., Zakharov, L.N., Rheingold, A.L., Hendrickson, D.N.: Wheel-Shaped [Mn₁₂] Single-Molecule Magnets. *Inorganic Chemistry* 44, 2742–2752 (2005)
7. Yang, E.-C., Hendrickson, D.N., Wernsdorfer, W., Nakano, M., Zakharov, L.N., Sommer, R.D., Rheingold, A.L., Ledezma-Gairaud, M., Christou, G.: Cobalt single-molecule magnet. *Journal of Applied Physics* 91, 7382–7384 (2002)
8. Yoo, J., Yamaguchi, A., Nakano, M., Krzystek, J., Streib, W.E., Brunel, L.C., Ishimoto, H., Christou, G., Hendrickson, D.N.: Mixed-valence tetranuclear manganese single-molecule magnets. *Inorganic chemistry* 40, 4604–4616 (2001)
9. Aubin, S.M.J., Wemple, M.W., Adams, D.M., Tsai, H.-L., Christou, G., Hendrickson, D.N.: Distorted MnIVMnIII₃ Cubane Complexes as Single-Molecule Magnets. *Journal of the American Chemical Society* 118, 7746–7754 (1996)
10. Yoo, J., Wernsdorfer, W., Yang, E.-C., Nakano, M., Rheingold, A.L., Hendrickson, D.N.: One-Dimensional Chain of Tetranuclear Manganese Single-Molecule Magnets. *Inorganic Chemistry* 44, 3377–3379 (2005)

11. Beedle, C.C., Heroux, K.J., Nakano, M., DiPasquale, A.G., Rheingold, A.L., Hendrickson, D.N.: Antiferromagnetic tetranuclear manganese complex: Wheel or cubane? *Polyhedron* 26, 2200–2206 (2007)
12. Scott, R.T.W., Milios, C.J., Vinslava, A., Lifford, D., Parsons, S., Wernsdorfer, W., Christou, G., Brechin, E.K.: Making ‘wheels’ and ‘cubes’ from triangles. *Dalton Transactions*, 3161–3163 (2006)
13. Affronte, M., Casson, I., Evangelisti, M., Candini, A., Carretta, S., Muryn, C.A., Teat, S.J., Timco, G.A., Wernsdorfer, W., Winpenny, R.E.P.: Linking rings through diamines and clusters: Exploring synthetic methods for making magnetic quantum gates. *Angewandte Chemie, International Edition* 44, 6496–6500 (2005)
14. Murugesu, M., Wernsdorfer, W., Abboud, K.A., Christou, G.: New structural motifs in manganese single-molecule magnetism from the use of triethanolamine ligands. *Angewandte Chemie, International Edition* 44, 892–896 (2005)
15. Manoli, M., Prescimone, A., Mishra, A., Parsons, S., Christou, G., Brechin, E.K.: A high-spin molecular wheel from self-assembled ‘Mn rods’. *Dalton Transactions*, 532–534 (2007)
16. Foguet-Albiol, D., O’Brien, T.A., Wernsdorfer, W., Moulton, B., Zaworotko, M.J., Abboud, K.A., Christou, G.: DFT computational rationalization of an unusual spin ground state in an Mn₁₂ single-molecule magnet with a low-symmetry loop structure. *Angewandte Chemie, International Edition* 44, 897–901 (2005)
17. Baroni, S.e.a.: Quantum-ESPRESSO (2006), <http://www.pwscf.org>
18. Vanderbilt, D.: Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Physical Review B* 41, 7892–7895 (1990)
19. Marzari, N., Vanderbilt, D., Payne, M.C.: Ensemble density-functional theory for ab initio molecular dynamics of metals and finite-temperature insulators. *Physical review letters* 79, 1337–1340 (1997)
20. Cao, C., Hill, S., Cheng, H.-P.: Strongly Correlated Electrons in the [Ni(hmp)(ROH)X]₄ Single Molecule Magnet: A DFT+U Study. *Physical Review Letters* 100, 167206/167201–167206/167204 (2008)
21. Rudberg, E., Salek, P., Rinkevicius, Z., Agren, H.: Heisenberg exchange in dinuclear manganese complexes: A density functional theory study. *Journal of Chemical Theory and Computation* 2, 981–989 (2006)
22. Zhao, X.G., Richardson, W.H., Chen, J.L., Li, J., Noodleman, L., Tsai, H.L., Hendrickson, D.N.: Density functional calculations of electronic structure, charge distribution, and spin coupling in manganese-oxo dimer complexes. *Inorganic chemistry* 36, 1198–1217 (1997)
23. Taylor, P.R.: Weakly coupled transition-metal centres: High-level calculations on a model Fe(IV)-Fe(IV) system. *Journal of Inorganic Biochemistry* 100, 780–785 (2006)
24. Ghosh, A., Taylor, P.R.: High-level ab initio calculations on the energetics of low-lying spin states of biologically relevant transition metal complexes: first progress report. *Curr. Opin. Chem. Biol.* 7, 113–124 (2003)
25. Ciofini, I., Daul, C.A.: DFT calculations of molecular magnetic properties of coordination compounds. *Coordination Chemistry Reviews* 238, 187–209 (2003)
26. Ali, M.E., Datta, S.N.: Theoretical investigation of magnetic properties of a dinuclear copper complex [Cu-2(mu-OAc)(4)(MeNHph)(2)]. *Journal of Molecular Structure-Theochem.* 775, 19–27 (2006)
27. Rudberg, E., Salek, P., Rinkevicius, Z., Agren, H.: Heisenberg Exchange in Dinuclear Manganese Complexes: A Density Functional Theory Study. *J. Chem. Theory Comput.* 2, 981–989 (2006)

28. Stebler, M., Ludi, A., Burgi, H.B.: [(Phen)₂Mn-4(m-O)₂Mn-3(Phen)₂](PF₆)₃.CH₃CN and [(Phen)₂Mn₄(m-O)₂Mn₄(Phen)₂](ClO₄)₄CH₃CN (Phen = 1,10-Phenanthroline) - crystal structure analyses at 1000K, interpretation of disorder, and optical, magnetic and electrochemical results. *Inorganic chemistry* 25, 4743–4750 (1986)
29. Schafer, K.O., Bittl, R., Zwegart, W., Lenzian, F., Haselhorst, G., Weyhermuller, T., Wieghardt, K., Lubitz, W.: Electronic structure of antiferromagnetically coupled dinuclear manganese ((MnMnIV)-Mn-III) complexes studied by magnetic resonance techniques. *Journal of the American Chemical Society* 120, 13104–13120 (1998)
30. McMahan, A.K., Martin, R.M., Satpathy, S.: Calculated effective Hamiltonian for lanthanum copper oxide (La₂CuO₄) and solution in the impurity Anderson approximation. *Physical Review B: Condensed Matter* 38, 6650–6666 (1988)
31. Yoo, J., Brechin, E.K., Yamaguchi, A., Nakano, M., Huffman, J.C., Maniero, A.L., Brunel, L.C., Awaga, K., Ishimoto, H., Christou, G., Hendrickson, D.N.: Single-molecule magnets: a new class of tetranuclear manganese magnets. *Inorganic chemistry* 39, 3615–3623 (1988)