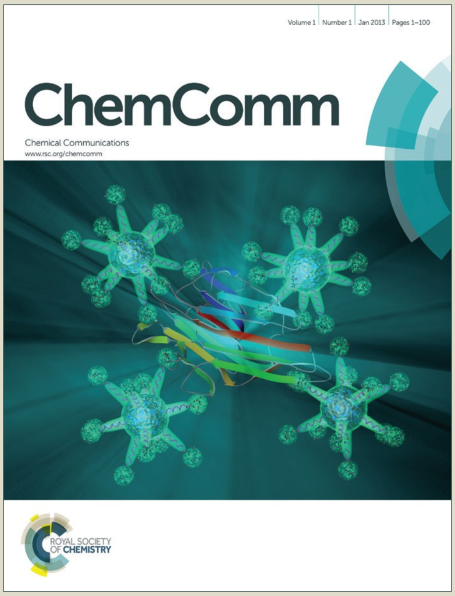
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Chemical Communications

COMMUNICATION

An S = 12 Semiquinoid Radical-Bridged Mn_6 Wheel Complex Assembled from an Asymmetric Redox-Active Bridging Ligand†

Ie-Rang Jeon and T. David Harris*

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

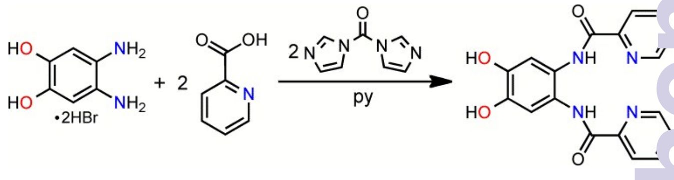
The asymmetric redox-active ligand 4,5-bis(pyridine-2-carboxamido)-1,2-catechol ($^{N,O}LH_4$) is prepared and metalated to afford the hexanuclear complex $[Mn_6(^{N,O}L)_6]^{6-}$. Structural analysis and magnetic measurements reveal this complex to feature Mn^{II} ions bridged by $^{N,O}L^{3-\bullet}$ radicals, which are antiferromagnetically coupled to give an S = 12 ground state.

Molecules that possess a high-spin ground state can potentially retain their net magnetization upon removal of an applied dc magnetic field, owing to the presence of a thermal spin relaxation barrier.[1] The molecules are known as single-molecule magnets, and they may find use in applications such as high-density spin-based information storage and processing.[2] The realization of such potential applications requires maximizing the spin relaxation barrier, which is correlated to both spin ground state (S) and axial zero-field splitting (D). In addition to these factors, the strength of magnetic coupling between spin centres in single-molecule magnets is critical to ensure thermal isolation of the spin ground state from excited states and to shut down deleterious fast relaxation pathways such as quantum tunnelling.[3]

One synthetic strategy toward the engenderment of strong coupling is to incorporate a paramagnetic radical ligand between high-spin metal centres.[4] Here, the ligand magnetic orbital will overlap with that of the metal, resulting in strong direct exchange coupling. Indeed, a number of molecular systems containing semiquinoid radicals have been shown to involve exclusive population of the spin ground state up to even 300 K, stemming from strong metal-ligand radical magnetic interactions.[5,6] Despite these advances with metal semiquinoid molecules, to our knowledge no such complex of nuclearity higher than two has been reported. Herein, we report the synthesis and characterization of a new asymmetric benzoquinoid bridging ligand, and its metalation to give a radical-bridged Mn_6 wheel complex. To our knowledge, this molecule represents the highest nuclearity and the highest spin ground state yet reported for a metal semiquinoid complex.

We targeted $^{N,O}LH_4$ based on previous reports of related ligands that have been shown to support metal complexes with radical redox-isomers, albeit resulting exclusively in low-spin complexes.[7,8] The synthesis of $^{N,O}LH_4$ was effected through a coupling reaction between 4,5-diaminocatechol and 2-picolinic acid in pyridine in the presence of 1,1'-carbonyldiimidazole, following a modified literature procedure (see Scheme 1).[7] Reaction of $^{N,O}LH_4$ with $Mn(CH_3COO)_3{\cdot}2H_2O$ in DMF, followed by treatment with a THF solution of Cp_2Co, yielded a dark violet precipitate. Subsequent diethyl ether vapour diffusion into a DMSO solution of the violet solid gave dark violet block-shaped crystals of $(Cp_2Co)_6[Mn_6(^{N,O}L)_6]{\cdot}8DMSO$ (**1**) in 38% yield.‡ Crystals of **1** are stable at ambient temperature under a dinitrogen atmosphere, but rapidly degrade upon exposure to air.

The structure of $[Mn_6(^{N,O}L)_6]^{6-}$ comprises a wheel-shaped assembly formed by six each alternating Mn ions and deprotonated $^{N,O}L^{n-}$ bridging ligands (see Figure 1). Each Mn centre resides in a distorted octahedral coordination environment, with two adjacent sites occupied by two oxygen donor atoms from the catechol unit of $^{N,O}L^{n-}$ and the other four sites bound to nitrogen donor atoms from two pyridines and two carboxamido groups of a second molecule of $^{N,O}L^{n-}$. The Mn centre is displaced by 0.814(2) Å out of the plane formed by four nitrogen atoms from the ligand. The average Mn-N and Mn-O distances are 2.235(14) and 2.170(9) Å, which can be unambiguously assigned to a high-spin Mn^{II} ion configuration. The presence of Mn^{II} ions, in conjunction with the overall 6



Scheme1. Synthesis of $^{N,O}LH_4$.

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston IL 60208-3113.
E-mail: dharris@northwestern.edu

†Electronic Supplementary Information (ESI) available: Experimental details, crystallographic data, crystal structure of **1**, additional magnetic data, and crystallographic information files (CIF). CCDC 1430715. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

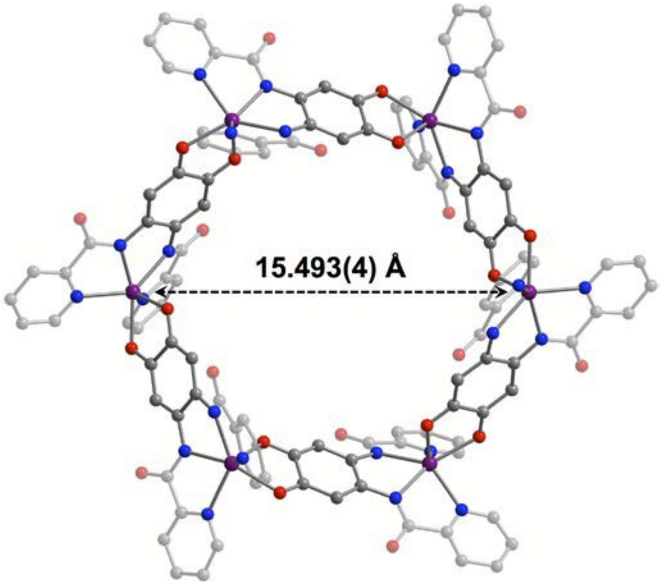


Figure 1. X-ray crystal structure of $[Mn_6(^{N,O}L)_6]^{6-}$, as viewed along the crystallographic *c* axis. Purple, red, blue, and gray spheres represent Mn, O, N, and C atoms, respectively; H atoms are omitted for clarity.

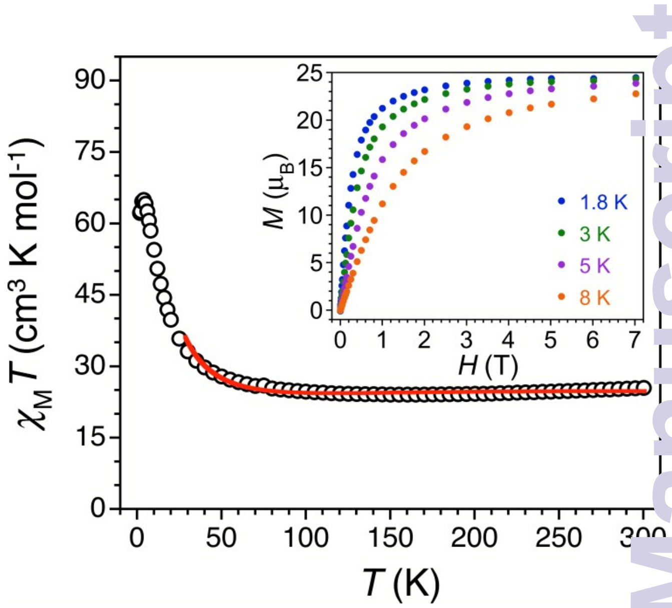


Figure 2. Variable-temperature dc magnetic susceptibility data for **1**, collected under an applied field of 1000 Oe. The red line corresponds to a fit of the data. Inset: Low-temperature magnetization data for **1** at selected temperatures.

complex charge, implies the presence of six $^{N,O}L^{3-\bullet}$ units. The Mn_6 complex features an intramolecular Mn···Mn distance of 15.493(4) Å along the diameter of the wheel. This distance is slightly longer than that of 14.734(8) Å previously reported for a structurally similar Mn_6 wheel complex containing nitronyl nitroxide bridging ligands.[9]

Within **1**, the charge of each $[Mn_6(^{N,O}L)_6]^{6-}$ anionic complex is compensated by six $[Cp_2Co]^+$ cations (see Figure S1 in the Electronic Supplementary Information). Three $[Cp_2Co]^+$ cations are situated above and three below the Mn_6 wheel, as viewed normal to the wheel diameter along the crystallographic *c* axis, with a closest Mn···Co distance of 6.243(4) Å. In addition, the individual Mn_6 complexes are closely packed in the solid state, as evidenced by shortest intermolecular Mn···Mn and C···C distances of 8.846(3) and 3.36(3) Å, respectively.

To probe and confirm the presence of a trianionic radical configuration for the bridging ligand, bond distances involving ligand-based atoms were carefully investigated. The mean C-C distance of the quinoid ring of 1.41(2) Å falls exactly intermediate of 1.405(4) and 1.425(3) Å previously reported for a related $^{N,N}L^{4-}$ ligand and its two-electron oxidized benzoquinone isomer, $^{N,N}L^{2-}$, respectively.[8] In addition, the mean $C\text{-}N_{amide}$ distance in **1** of 1.37(2) Å follows similar trend, being shorter and longer, respectively, than the C-N distances of 1.407(3) and 1.350(3) Å for $^{N,N}L^{4-}$ and $^{N,N}L^{2-}$. Finally, the C-O bond distance in **1** of 1.29(2) Å is close to that of 1.293(3) Å reported for molecular complexes containing trianionic tetraoxolene radicals.[10] Taken together, these structural observations confirm that the bridging ligand in **1** is best described as $^{N,O}L^{3-\bullet}$, giving an overall anionic complex formulation of $[Mn^{II}_6(^{N,O}L^{3-\bullet})]^{6-}$. To the best of our knowledge, **1** represents the first structurally-characterized complex containing a radical isomer of (pyridine-2-carboxamido)benzene derivatives, and the highest-nuclearity metal semiquinoid complex reported to date.

The presence of Mn^{II} and $^{N,O}L^{3-\bullet}$ in **1** likely results from a combination of ligand-to-metal electron-transfer and reduction by Cp_2Co. Here, a 1:1 electron-transfer from Mn^{III} to $^{N,O}L^{4-}$, followed by one-electron reduction of the ensuing product by Cp_2Co, would give rise to a $[Mn^{II}_6(^{N,O}L^{4-})]^{12-}$ complex rather than the observed $[Mn^{II}_6(^{N,O}L^{3-\bullet})]^{6-}$ species. If such a fully-reduced species is indeed formed transiently, it may then be oxidized by excess Mn^{III} or solvent. Alternatively, the reaction possibly proceeds via two-electron oxidation of the starting $^{N,O}L^{4-}$ ligand, assisted by excess Mn^{III}, and then reduction by Cp_2Co. Nevertheless, the exact mechanism associated with the formation of **1** is beyond the scope of this report. Note, however, that carrying out the reaction in the absence of Cp_2Co gives rise to a different product whose study is ongoing.

To probe the magnetic interactions in **1**, variable-temperature dc magnetic susceptibility data were collected on a solid sample under an applied field of 1000 Oe, and the resulting plot of $\chi_M T$ vs T is shown in Figure 2. At 300 K, $\chi_M T$ 25.5 cm^{3}K/mol, which is slightly lower than the value of 28 cm^{3}K/mol expected for magnetically isolated six $S = {}^5/_2$ Mn^{II} centres and six $S = {}^1/_2$ radical ligands with $g = 2$, suggesting the presence of antiferromagnetic interactions between the metal ions and the ligand radicals. Upon lowering the temperature, the $\chi_M T$ data undergo a gradual decrease, reaching a minimum of $\chi_M T = 24.0$ cm^{3}K/mol at 165 K. Upon further lowering the temperature, the $\chi_M T$ data undergo an abrupt increase to maximum of $\chi_M T = 64.9$ cm^{3}K/mol and then a steep downturn below 4 K. The observed maximum of $\chi_M T$ is slightly lower than the value of 78 cm^{3}K/mol expected for an $S = 12$ ground state, most likely due to the effects of intermolecular antiferromagnetic interactions and/or the population of low-lying excited states.

A precise quantitative determination of the magnetic interaction between Mn^{II} ions and radicals in **1**, considering a model based on a 12-member ring, was hindered due to the large number of spins. Nevertheless, a fit to the data using a chain model for alternating classical spins ($S = {}^{5}/_{2}$) and quantum spins ($S = {}^{1}/_{2}$) provided an estimated coupling constant of $J = -15.6(4)$ cm^{-1} with $g = 2.0(1)$.[11] Note that, in the case of alternating $S = {}^{5}/_{2}$ and $S = {}^{1}/_{2}$ spins, the theoretical estimation of magnetic susceptibility for a ring comprising three pairs of spins and that for an infinite chain are nearly identical above the temperature at which $\chi_{M}T$ reaches the minimum, while the increase of $\chi_{M}T$ at low temperature is steeper for a chain owing to longer-range magnetic correlation.[11] This divergence between the two models at low temperature likely explains the observed discrepancy between the fit and the experimental data for **1**.

In addition, according to this alternating chain analysis, the temperature at which $\chi_{M}T$ reaches a minimum value should provide an estimate of the strength of magnetic exchange between spins following the relationship $T = 7.194|J|$.[11,12] As such, this expression gives an estimated coupling constant of $|J| = 23$ cm^{-1} for **1**. In view of these two components of the chain model analysis, the magnetic coupling between Mn^{II} and $^{N,O}L^{3-\bullet}$ in **1** most likely falls within the range of 15-23 cm^{-1}. Finally, the observed coupling strength is smaller than what has been estimated for the Fe^{III} complexes containing $^{N}L^{-\bullet}$ and $^{N,N}L^{3-\bullet}$,[7,8] which likely stems from the high-spin Mn^{II} configuration and the significant displacement of the Mn^{II} centre from the N$_4$ ligand plane within the wheel structure in **1**.

To confirm the spin ground state of **1**, variable-field magnetization data were collected at 1.8, 3, 5, and 8 K (see Figure 3). The magnetization curve at 1.8 K follows an abrupt increase at low field and reaches a maximum of $M = 24.4$ μ_B at 4 T. This magnetization value confirms the presence of strong antiferromagnetic interaction between Mn^{II} ions and $^{N,O}L^{3-\bullet}$, leading to a spin configuration of $S = 12$ even under an applied dc field of 7 T. Additionally, such a rapid increase of magnetic moment at low field is reflective of the high-spin ground state of this compound. Indeed, magnetization data were compared with the simulated Brillouin function for an $S = 12$ ground state, revealing moderate agreement between experimental and simulated data (see Figure S2). The observed mismatch at lower field may stem from significant intermolecular antiferromagnetic interactions, as was discussed above. Note that **1** is a rare example of a compound that features a high-nuclearity radical-bridged molecule with a large spin ground state, exhibiting similarities to a wheel complex containing nitronyl nitroxide derivatives.[9] Moreover, to our knowledge, **1** represents the highest spin ground state yet reported for a metal semiquinoid complex. Finally, as depicted in the plot of M vs H/T, the magnetization curves at different temperatures are superimposed, suggesting the absence of any significant magnetic anisotropy in **1** (see Figure S2). In line with the observation, the variable-frequency ac susceptibility data collected on a solid sample of **1** indicate the absence of slow magnetic relaxation down to 1.8 K at frequencies up to 1500 Hz (see Figure S3).

The foregoing results demonstrate the utility of the new asymmetric redox-active ligand, 4,5-bis(pyridine-2-carboxamido)-1,2-catechol, in generating a semiquinoid radical-bridged hexanuclear Mn$_6$ wheel complex with an $S = 12$ ground state. To the best of our knowledge, this complex represents the first structurally-characterized example of a molecule incorporating radical isomers of (pyridine-2-carboxamido)benzene derivatives and the highest nuclearity and spin of any metal semiquinoid complex. Future efforts will focus on investigating the redox chemistry of **1** and synthesizing related wheel complexes with anisotropic metal ions.

This research was supported by the National Science Foundation Grant DMR-1351959, the Institute for Sustainability and Energy at Northwestern, and Northwestern University. Purchase of the SQUID magnetometer was supported in part by the International Institute of Nanotechnology.

Notes and references

‡ X-ray analysis for **1** ($C_{184}H_{168}Co_{6}Mn_{6}N_{24}O_{32}S_{8}$, fw = 4167.11) at $T = 100$ K: space group $R{-}3$, $a = b = 23.1209(12)$ Å, $c = 27.281(2)$ Å, $V = 12629.7(16)$ Å^3, Z = 3. $d = 1.644$ g cm^{-1}, $R_1 = 0.0981$, $wR_2 = 0.3117$.

1 D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, 2006; Winpenny, R. E. P. *Single Molecule Magnets and Related Phenomena.* Springer: Berlin, 2006, Vol. 122.

2 M. N. Leuenberger, D. Loss, *Nature*, 2001, **410**, 789; A. R. Rocha, V. M. García-suárez, S. W. Bailey, C. J. Lambert, J. Ferrer, S. Sanvito, *Nat. Mater.*, 2005, **4,** 335; L. Bogani, W. Wernsdorfer, *Nat. Mater.*, 2008, **7**, 179; P. C. E. Stamp, A. Gaita-Arino, *J. Mater. Chem.*, 2009, **19**, 1718. A. Ardavan, S. J. Blundell, *J. Mater. Chem.*, 2009, **19**, 1754.

3 O. Kahn, *Molecular Magnetism*, VCH: New York, 1993; S. Demir, I.-R. Jeon, J. R. Long, T. D. Harris, *Coord. Chem. Rev.*, 2015, **289**, 149.

4 A. Caneschi, D. Gatteschi, R. Sessoli, P. Rey, *Acc. Chem. Res.*, 1989, **22**, 392; K. E. Vostrikova, *Coord. Chem. Rev.*, 2008, **252**, 1409; R. G. Hicks, Stable Radicals, John Wiley and Sons, Ltd., United Kingdom, 2010; M. T. Lemaire, *Pure Appl. Chem.*, 2011, **83**, 141. H. Iwamura, H. *Polyhedron*, 2013, **66**, 3.

5 R. M. Buchanan, S. L. Kessel, H. H. Downs, C. G. Pierpont, D. N. Hendrickson, *J. Am. Chem. Soc.*, 1978, **100**, 7894; C. Benelli, A. Dei, D. Gatteschi, H. U. Güdel, D. I. Pardi, *Inorg. Chem.*, 1989, **28**, 3089; D. E. Wheeler, J. K. McCusker, *Inorg. Chem.*, 1998, **37**, 2296; H.-C. Chang, T. Ishii, M. Kondo, S. Kitagawa, *J. Chem. Soc., Dalton Trans.*, 1999, 2467; K. Chłopek, E. Nill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.*, 2005, **44**, 7087; K. Chłopek, E. Bothe, F. Neese, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.*, 2006, **45**, 6298; D. Guo, J. K. McCusker, *Inorg. Chem.*, 2007, **46**, 3257.

6 I.-R. Jeon, J. G. Park, D. J. Xiao, T. D. Harris, *J. Am. Chem. Soc.*, 2013, **135**, 16845; J. A. DeGayner, I.-R. Jeon, T. D. Harris, *Chem. Sci.*, 2015, DOI: 10.1039/C5SC02725J.

7 A.K. Patra, M. Ray, R. Mukherjee, *Inorg. Chem.* 2000, **39**, 65, S. K. Dutta, U. Beckmann, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.*, 2000, **39**, 3355.

8 U. Beckmann, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.*, 2003, **42**, 3355.

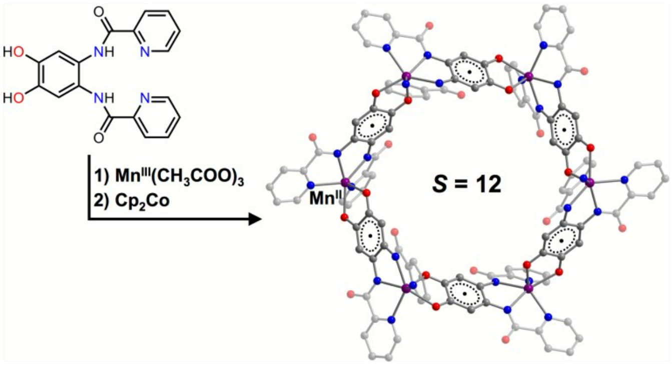
9 A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, R. Sessoli, C. Zanchini, J. Am. Chem. Soc., 1998, **110**, 2795.

10 K. S. Min, A. L. Rheingold, A. G. DiPasquale, J. S. Miller, *Inorg. Chem.*, 2006, **45**, 6135; K. S. Min, A. G. DiPasquale, J. A.

Golen, A. L. Rheingold, J. S. Miller, *J. Am. Chem. Soc.*, 2007, **129**, 2360.

11 J. Seiden, *J. Physique*, 1983, **44**, L947. The Hamiltonian used for the fit is given as $\hat{H} = -2J\Sigma\hat{S}_{L}g(\hat{S}_{Mn_i} + \hat{S}_{Mn_{i+1}})$.

12 A. Gleizes, M. Verdaguer, *J. Am. Chem. Soc.*, 1984, **106**, 3727. The relation is modified according to the Hamiltonian and the unit of *J* used in this paper.



The asymmetric redox-active ligand 4,5-bis(pyridine-2-carboxamido)-1,2-catechol ($^{N,O}LH_4$) is synthesized and metalated to afford the *S* = 12 semiquinoid radical-bridged wheel complex $[Mn^{II}_6(^{N,O}L^{3-\bullet})_6]^{6-}$.