**Final Report (2002-2014) for DOE grant (DE-FG02-02ER45999)**

**Kim R. Dunbar, Department of Chemsitry, Texas A&M University**

**Summary of Training**

Over the course of this period of funding, the PI published 62 papers and graduated 15 Ph.D. students supported by the grant. In addition 17 undergraduate students, 10 postdocs and 16 Visiting Scholars were also involved in this research. Over 150 talks at national and international conferences on the topic were given by the PI and her research group.

**Summary of Broader impacts**

In addition to the training of undergraduate students, graduate students, Visiting Professors and Visiting Scholars, the PI and her group participated in numerous acitivities encompassing outreach and community service. The development and education of students is of utmost importance to the field of chemistry. Fostering a diverse and positive learning environment is vital for the development and future of science. The versatility of skills required to work on this project represented a golden opportunity for students to learn the synthesis and characterization of organic and inorganic compounds as well as essential methods of characterization techniques. The students worked closely with the PI and the collaborators to learn first-hand how to perform all of the measurements and to interpret magnetic and conductivity data. The PI sent her students to work with both domestic and international collaborators one-on-one, so that students could obtain a better understanding of the techniques and methods of characterization that could not be carried out at her home institution.

The PI has been committed to upholding the value of education and providing opportunities for her students to enhance their experience not only through collaborations, but through attending in-house seminars, meetings with visiting professors and participating in conferences, especially those that focus on their field of study. The PI has sent many students to special conferences/meetings/workshops throughout the past twelve years of DOE support. The PI has also supported the advancement of the education of her students by sending them to facilities such as the Advanced Light Source at Lawrence Berkeley National Laboratory and the Advanced Photon Source at Argonne National Laboratory in order to gain hands-on experience, efforts that have been very important for their education. These opportunities are invaluable for their future success in careers in both academics or industry. The PI has encouraged the students to apply for and has helped them to prepare Fellowship applications to the NSF, Ford Foundation, DOE and the *Louis Stokes Alliances for Minority Participation* (LSAMP), many of which have been awarded.

The PI is also committed to recruiting students from underrepresented backgrounds. The PI wrote a local section ACS grant several years to start a chapter of NOBCChE (National Organization of Black Chemists and Chemical Engineers) at Texas A&M which will help in the recruitment and retention of African American undergraduate and graduate chemistry students. The PI and her students are also strongly committed to reaching out to younger

generations in order to enhance their passion for science and enriching their education by volunteering in the community. These efforts consist of development of educational materials, giving demonstrations at several events and local schools, offering free tutoring and acting as coaches and Specific instances are Coaches Clinic Lab, SACNAS free tutoring service since 2011- http://sacnas.tamu.edu/node/15, Community Outreach Bryan School District- Chemistry and Nanotechnology Workshops, Organized chemistry demonstrations for the National Chemistry Week for the CHEM 116 showroom (since 2004), Science fair judge at Harmony Science Academy, Science Bowl judge, Science Olympiads Chem Lab C, Expanding your horizons in Science and Mathematics.

**Geometrical and Electronic Control of Anisotropy in Mononuclear Complexes.**

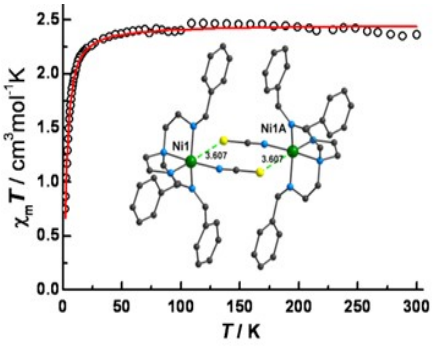


**Figure 1.** Molecular structure and DC magnetic data for [Ni(trenbn,H)(NCS)][ClO4]MeOH.

We found that the treatment of tren$^{Bn,H}$, $Ni(H_2O)_6[ClO_4]_2$ and NaNCS in acetonitrile affords the compound $[Ni(tren^{bn,H})(NCS)][ClO_4]$·MeOH (Figure 1). The Ni ion is located in a distorted tetragonal pyramid instead of the expected trigonal bipyramidal geometry due to close intermolecular Ni···S contacts (3.607 Å). As a result, a small $D_{Ni}$ value (-0.23 $cm^{-1}$) was found. Bulkier substituents are required for rendering the equatorial plane more crowded in order to maintain the TBP geometry.

**Incorporation of Titanium Ions into Magnetic Materials**

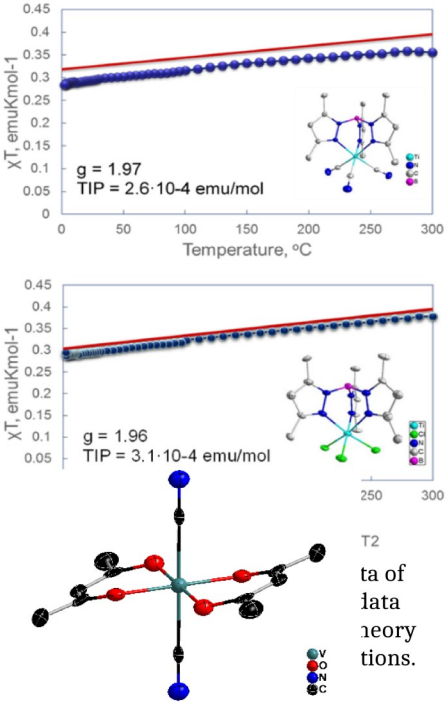


**Figure 4**. [(acac)2V(CN)2]-anion.

**Table 1.** Calculated ligand field energies in $cm^{-1}$.

| State | $(Et_4N)[Tp^*TiCl_3]$ | $(Et_4N)[Tp^*Ti(CN)_3]$ |
|---|---|---|
| | | 22910 22920 |
| | | 1642 |

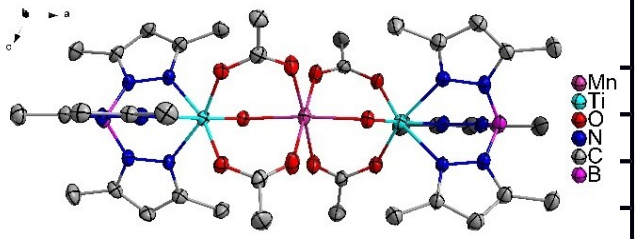


Figure 3. The {(Tp*Ti(CN)2)2(μ-OAc)4(μ-O)2Mn}-anion.

In the last year of this DOE grant we continued working on the $Ti^{III}$ building block, $(Et_4N)[Tp^*Ti(CN)_3]$ and initiated a collaboration with Dr. Alessandro Soncini from the University of Melbourne who performed *ab initio* CASSCF calculations on $(Et_4N)[Tp^*Ti(CN)_3]$ and $(Et_4N)[Tp^*TiCl_3]$. Using the atom

coordinates, the ligand field spectra and magnetic properties were predicted from these calculations. As shown in Figure 2, the theory results are in excellent agreement with experimental data. Table 1 shows the calculated ligand field energies of the starting materials. From this we can see that the ground state of this compound is non-degenerate, which is not ideal for having first-order spin-orbit coupling (emanating from a degenerate ground state in a trigonally distorted systems). Replacing the methyl substituents on the Tp* ligand for a bulkier group such as phenyl would likely promote a trigonal elongation and stabilize the degenerate $^2$E state. The $[Et_4N](Tp^*Ti(CN)_3)$ forms trinuclear molecules of general formula $\{(Tp^*Ti(CN)_2)_2(\mu\text{-}OAc)_4(\mu\text{-}O)_2M\}^{0/1-}$ (M = $Cr^{III}$, $Co^{II}$, $Mn^{II}$) Figure 3 in the presence of trace $H_2O$. The chromium analog contains an $[Et_4N]^+$ cation in its structure, which means that at least one of the titanium centers remains trivalent. This represents a rare example of a $Ti^{III}$ containing molecule; magnetic measurements are currently underway. The Mn compounds contain only $Ti^{IV}$. The $Tp^*Ti^{IV}$ therefore acts as a diamagnetic cap and would be an ideal system for testing isolated pseudo-octahedral environments for mononuclear SMMs. According to recent theory, $d^1$, $d^2$, $d^6$, and $d^7$ transition metal ions have the possibility for exhibiting large anisotropy in octahedral environments. Because of this, particular focus is on the $Fe^{II}$ and $Co^{II}$ analogs.

**Trans-dicyanide building blocks for chains.** In an effort to expand the library of SCM cyanide building blocks, $[V(acac)_2Cl(THF)]$ was used to prepare $PPN[(acac)_2V(CN)_2]\cdot PPNCl$ (Figure 4) and [V(Salphen)Cl(DMF)] was reacted with $CN^-$ to give $PPN[V(Salphen)(CN)_2]$. The analogous salen-based building blocks $PPN[V(MeOSalen)(CN)_2]$ and $PPN[V(Salen)(CN)_2]$ were also isolated.

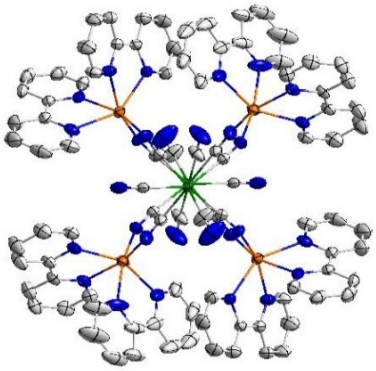

**Figure 5**. Molecular structure of the {[MnII(bpy)2]4[MoIII(CN)7]2} octahedral molecule.

**Cyanometallate Chemistry of Highly Anisotropic Metal Ions**

We found an interesting alternative to TBP product formation by using 2,2'-bipyridine (bpy) instead of tmphen. The reaction of $[Mo^{III}(CN)_7]$ with $[Mn^{II}(bpy)_2]^{2+}$ in a $H_2O$/MeOH mixture produces the octahedral molecule $\{[Mn^{II}(bpy)_2]_4[Mo^{III}(CN)_7]_2\}$ as confirmed by single crystal X-ray data (Figure 5). The self-assembly with bpy appears to be solvent independent and selective for octahedral molecules. Interestingly the magnetic data revealed strong ferromagnetic interactions between the $Mo^{III}$ and $Mn^{II}$ centers with a Weiss constant of +43 K. The compound exhibits the onset of frequency dependence in the out-of-phase AC susceptibility data consistent with SMM behavior.

**Compounds with Dianionic Organocyanide Ligands**

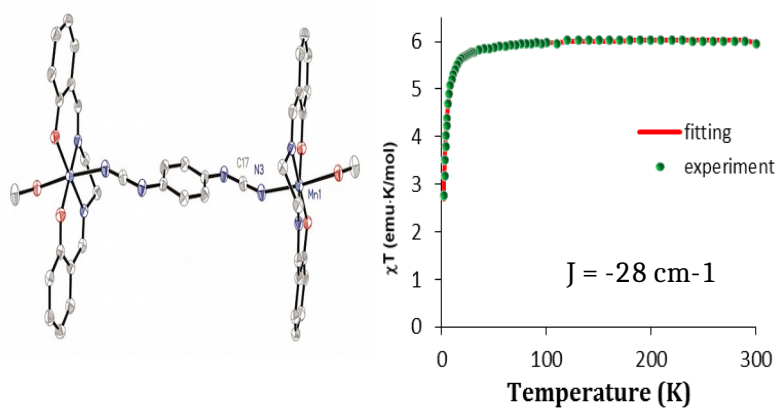


Figure 6. Structure and plot of χT versus T for 1.

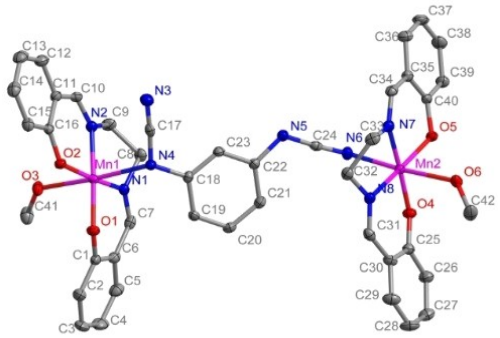


Figure 7. Molecular structure of 2.

A series of proposed model dinuclear compounds bridged by para- and ortho-dicyanamidobenzene dianions were synthesized and their magnetic properties studied: {Mn(salen)$(CH_3OH)\}_2$(μ-DCNQI) (**1**), {Mn(salen)$(CH_3OH)\}_2$(μ-anti-N(cyano),N(amido)-DCYD) (**2**), {Cr(salen)$(CH_3OH)\}_2$(μ-DCTL) (**3**), and {Mn(salen)$(CH_3OH)\}_2$(μ-DM-DCNQI) (**4**) ($DCNQI^{2-}$ = 1,4-dicyanamidobenzene dianion, DM-$DCNQI^{2-}$ = 2,5-dimethyl-1,4-dicyanamidobenzene dianion, $DCYD^{2-}$ = 1,3-dicyanamidobenzene dianion and $DCTL^{2-}$ = 2,6- dicyanamidotoluene). The premise of this work was to test computational results that predicted strong ferromagnetic and antiferromagnetic exchange coupling interactions between trivalent 3d transition metals, on the order of ±75-150 $cm^{-1}$ for these diamagnetic linkers. Unlike what was predicted by theory, it was found that the coupling between the trivalent $Mn^{III}$ centers was much weaker than predicted (Figure 6). We attribute this situation to the strong Jahn-Teller distortion of the $Mn^{III}$ $d^4$ unit which leads to long Mn-N bond distances (2.242 Å). In the case of $DCYD^{2-}$, an unexpected structure was obtained with one of the $Mn^{III}$ ions coordinated to an amido-N instead of the terminal cyano-N (Figure 7). Therefore, a methyl group was employed to block the free rotation to obtain $DCTL^{2-}$, and even with the Jahn-Teller inactive octahedral $Cr^{III}$ ion in place of $Mn^{III}$, only very weak antiferromagnetic interactions are observed.

**DOE Publications Supported by DE-FG02-02ER45999**

1. 1,3-Dithiolan-2-one. Eric Reinheimer, John Bacsa and Kim R. Dunbar Acta Cryst. Section E, 2004, E60, 1206-1207.

   *We gratefully* acknowledge *the service provided by Dr Joseph Reibenspies and the X-ray facility at Texas A&M University. We thank the National Science Foundation for PI and NIRT grants (CHE-9906583 and DMR-0103455) and for equipment grants for the CCD X-ray equipment (CHE9807975). We thank the Department of Energy for a PI grant (DE-FG03-02ER45999). Support from the Welch Foundation (A-1449) and from a Telecommunications and Informatics Task Force (TITF) Grant from Texas A&M University is also gratefully acknowledged.*

2. Bis(pyridine-2-ylmethanolato-$\kappa^2$ *N,O*) bis(trifluoroacetato )nickel(II). John Bacsa, Hanhua Zhao and Kim R. Dunbar *Acta Cryst*. **2004**, *E60*, m1040-m1042.

   *We gratefully acknowledge the service provided by Dr Joseph Reibenspies and the X-ray facility at Texas A&M University. We thank the National Science Foundation for PI and NIRT grants (CHE-9906583 and DMR-0103455) and for equipment grants for the CCD X-ray equipment (CHE9807975). We thank the Department of Energy for a (DE-FG03-02ER45999). Support from the Welch Foundation (A-1449) and from a Telecommunications and Informatics Task Force (TITF) Grant from Texas A&M University gratefully acknowledged.*

3. Syntheses, Structure, and Magnetic Properties of New Types of Cu(II), Co(II), and Mn(II) Organophosphonate Materials: Three-Dimensional Frameworks and a One-Dimensional Chain Motif. Deyuan Kong, Yang Li, Xiang Ouyang, Andrey V. Prosvirin, Hanhua Zhao, Joseph H. Ross, Jr., Kim R. Dunbar and Abraham Clearfield *Chem. Mater.* **2004**, *16*, 3020-3031.

   *The authors acknowledge the Robert A. Welch Foundation No. A1526 and the Department of Energy, Basic Sciences Division (DE-FG03-00ER 15806), for the financial support. K.R.D. gratefully acknowledges the National Science Foundation support from Nanoscale Science and Engineering (NIRT) Grant (DMR-0103455), the Telecommunication and Informatics Task Force (TITF 2001-3) at Texas A&M University, DOE (DE-FG03-02ER45999), and the National Science Foundation for an Equipment grant to purchase a SQUID magnetometer (NSF-9974899).*

4. Molecular Cube of $Re^{II}$ and $Mn^{II}$ That Exhibits Single-Molecule Magnetism. Eric J. Schelter, Andrey V. Prosvirin and Kim R. Dunbar *J. Am. Chem. Soc.* **2004**, *126*, 15004-15005.

*K.R.D. gratefully acknowledges the Department of Energy (DE-FG03-02ER45999) for funding of this research. The SMART APEX CCD diffractometer and the SQUID magnetometer were purchased by funds provided by the National Science Foundation (Grants NSF-9807975 and NSF-9974899). Highfrequency AC susceptibility experiments were performed at the National High Magnetic Field Laboratory in Tallahassee, FL. We thank Dr. Alexei Souslov for his assistance with these measurements. Use of the TAMU/LBMS-Applications Laboratory and help from Ms. Vanessa Santiago are also acknowledged.*

5. Films of $Mn_{12}$-acetate deposited by low-energy laser ablation. J. Means, V. Meenakshi, R. V. A. Srivastava, W. Teizer, Al. A. Kolomenskii, H. A. Schuessler, H. Zhao and K. R. Dunbar *J. Magnetism & Magnetic Mater.* **2004**, *284*, 215-219.

*We thank C. Berlinguette, V. Pokrovsky,N. Sinitsyn and W. Lackowski for helpful discussions. J. Means is supported by a Doctoral Research Fellowship from Sandia National Laboratories. The authors gratefully acknowledge the following support: (1) Robert A. Welch Foundation, (2) Texas Advanced Research Program (010366-0038-2001), (3) The US Department of Energy (DOE–DE-FG03-02ER45999), (4) National Science Foundation for support from Nanoscale Science and Engineering (NIRT) Grant (DMR-0103455) and for an equipment grant to purchase a SQUID magnetometer (NSF-9974899).*

6. $Mn_{12}$-acetate film pattern generated by photolithography methods. K. Kim, D. M. Seo, J. Means, V. Meenakshi, W. Teizer, H. Zhao and K. R. Dunbar *Appl. Physics Lett.* **2004**, *85*, 3872-3874.

*This research was supported by the Texas Advanced Research Program (010366-0038-2001), by the Welch Foundation (A.1585) the National Science Foundation (DMR0103455, NSF-9974899), the Telecommunication and Informatics Task Force (TITF 2001-3) at Texas A&M University, DOE-DE-FG03-02ER45999. Use of the TAMU/CIMS Materials Characterization Facility is acknowledged.*

7. The step-wise assembly of an undecanuclear heterotrimetallic cyanide cluster. Curtis P. Berlinguette and Kim R. Dunbar *Chem. Comm.* **2005**, 2451-2453.

*K.R.D. acknowledges the Department of Energy (DE-FG03-02ER45999) and the National Science Foundation (CHE9906583) for support and is grateful for equipment grants to purchase the CCD X-ray equipment (CHE-9807975) and the SQUID magnetometer (NSF-9974899).*

8. Structural and magnetic properties of iron(II) complexes with 1,4,5,8,9,12-hexaazatriphenylene (HAT). Mikhail Shatruk, Abdellatif Chouai, Andrey V. Prosvirin and Kim R. Dunbar *Dalton Trans*. **2005**, 1897-1902.

   *This research was supported by NSF (PI grant CHE-9906583) and DOE (grant DE-FG03-02ER45999). Funding of the CCD diffractometer (CHE-9807975) and the SQUID instrumentation (NSF-9974899) by NSF is gratefully acknowledged*.

9. Control of the Barrier in Cyanide Based Single Molecule Magnets $Mn(III)_2Mn(II)_3$: Theoretical Analysis. Boris S. Tsukerblat, Andrew V. Palii, Sergei M. Ostrovsky, Sergei V. Kunitsky, Sophia I. Klokishner and Kim R. Dunbar *J. Chem. Theory Comput*. **2005**, *1*, 668-673.

   *B.S.T. thanks the Council for Higher Education of Israel for the financial support. Financial support of U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF, award MOC2-2611-CH-04) and Moldovan Research and Development Association (MRDA, award No. MTFP04-07 under funding from CRDF) is appreciated. K.R.D. gratefully acknowledges the Department of Energy (DOE-FG03-02ER45999)*.

10. Synthesis, crystal structures and magnetic properties of two new coordination polymers based on the tricyanoethenolate ligand: $\{Fe(C_5N_3O)_2(CH_3CN)_2\}_\infty$ and $\{Co(C_5N_3O)_2(C_4H_4O)_2\}_\infty$. Hanhua Zhao, John Bacsa, Andrey Prosvirin, Nazario Lopez and Kim R. Dunbar *Polyhedron* **2005**, *24*, 1907-1912.

    *Kim R. Dunbar gratefully acknowledges the National Science Foundation for support from Nanoscale Science and Engineering Grant (NIRT: DMR0103455), the Telecommunication and Informatics Task Force (TITF 2001-3) at Texas A&M University, DOE-DE-FG03-02ER45999 and the National Science Foundation for an Equipment grant to purchase SQUID magnetometer (NSF-9974899)*.

11. Enhanced magnetic anisotropy of $Mn_{12}$-acetate. D.M. Seo, V. Meenakshi, W. Teizer, H. Zhao, K.R. Dunbar *J. Mag. Mag. Mat*. **2006**, *301*, 31-36.

    *This research was supported by the Texas Advanced Research Program (010366-0038-2001), the Robert A. Welch Foundation (A-1585), the National Science Foundation (DMR-0103455 and NSF-9974899), DOE (DOE-DE-FG03-02ER45999), and the Telecommunications and Informatics Task Force (TITF 2001-3) at Texas A&M University. Use of the TAMU/CIMS Materials Characterization Facility is acknowledged. We thank D. Naugle for helpful discussions*.

12. Influence of anions on the dimensionality of extended networks based on Cu1 cations and 1,4,5,8,9,12-hexaazatriphenylene (HAT) ligands. Mikhail Shatruk, Abdellatif Chouai and Kim R. Dunbar Dalton Trans. 2006, 2184-2191.

    *This research was supported by the National Science Foundation (PI grant CHE-9906583) and the Department of Energy (grant DE-FG03-02ER45999). Funding of the CCD diffractometer (CHE-9807975) by NSF is gratefully acknowledged. We also thank Dr Joseph Reibenspies (Texas A & M University) for helpful discussion of some crystallographic problems.*

13. Highly Anisotropic Orbitally Dependent Superexchange in Cyano-Bridged Clusters Containing Mn(III) and Mn(II) Ions. Andrew Palii, Sergey M. Ostrovsky, Sophia I. Klokishner, Boris S. Tsukerblat and Kim R. Dunbar *Chem. Phys. Chem.* **2006**, *7*, 871-879.

    *Financial support from the U.S. Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF, award MOC2-2611-CH-04) and the Moldovan Research and Development Association (MRDA, award No. MTFP04-07 under funding from CRDF) is appreciated. BST thanks the Council for Higher Education of Israel and VATAT for financial support. KRD gratefully acknowledges the Department of Energy (DOE-FG03-02ER45999).*

14. Syntheses and reactivity studies of solvated dirhenium acetonitrile complexes. Jitendra K. Bera, Eric Schelter, Sanjib K. Patra, John Bacsa and Kim Dunbar, *Dalton Trans.* **2006**, 4011-4019.

    *K. R. D. gratefully acknowledges the Welch Foundation, the Department of Energy (DE-FG03-02ER45999), and the National Science Foundation for a PI Grant (CHE-9906583) and for equipment grants to purchase the CCD X-ray equipment (CHE9807975). J. K. B. thanks IIT-Kanpur for grants to purchase the electrochemical workstation.*

15. Syntheses, Structural Studies, and Magnetic Properties of Divalent Cu and Co Selenites with Organic Constituents. Mei-Ling Feng, Andrey V. Prosvirin, Jiang-Gao Mao and Kim R. Dunbar, *Chem. Eur. J.* **2006**, *12*, 8312-8323.

    *J.G.M. gratefully acknowledges financial support from the National Natural Science Foundation of China (20371047). K.R.D. gratefully acknowledges the Department of Energy (DE-FG03-02ER45999), the National Science Foundation (NIRT-NSF DMR-0103455), the Welch Foundation A1449, and Texas A&M University (TITF) for funding of this research. The SQUID magnetometer was purchased by funds provided by the National Science Foundation (NSF-9974899).*

16. Long-Range Ordered Magnet of a Charge-Transfer $Ru_2^{4+}$/TCNQ Two-Dimensional Network Compound. Hitoshi Miyasaka, Toru Izawa, Nao Takahashi, Masahiro Yamashita, and Kim R. Dunbar, *J. Am. Chem. Soc.*, **2006**, *128*, 11358-11359.

    *This work was financially supported by CREST, JST, and a Grant-in-Aid for Scientific Research on Priority Areas (Grant No. 17036054 "Chemistry of Coordination Space") from the Ministry of Education, Science, Sports, and Culture, Japan. K.R.D. gratefully acknowledges support from the Department of Energy (Grant DE-FG02-02ER45999).*

17. Origin of the Single Chain Magnet Behavior of the Co($H_2$L) ($H_2$O) Compound with a 1D Structure. Andrei V. Palii, Sergei M. Ostrovsky, Sophia I. Klokishner, Oleg S. Reu, Zhong-Ming Sun, Andrei V. Prosvirin, Han-Hua Zhao, Jiang-Gao Mao, and K.R. Dunbar, *J. Phys. Chem. A.*, **2006**, *110*, 14003-14012.

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18. Lanthanide-3d cyanometalate chains Ln(III)-M(III) (Ln = Pr, Nd, Sm, Eu, Gd, Tb; M = Fe) with the tridentate ligand 2,4,6-tri (2-pyridyl)-1,3,5-triazine (tptz): evidence of ferromagnetic interactions for the Sm(III)-M(III) compounds (M = Fe, Cr). Hanhua Zhao, Nazario Lopez, Andrey Prosvirin, Helen T. Chifotides and Kim R. Dunbar, *Dalton Trans.*, **2007**, 878-888.

    *Kim R. Dunbar gratefully acknowledges the National Science Foundation for support from the Nanoscale Science and Engineering Grant (NIRT: DMR-0103455), the Robert A. Welch Foundation (A-1449), the Telecommunication and Informatics Task Force (TITF 2001–3) at Texas A & M University, DOE-DE-FG03-02ER45999 and the National Science Foundation for an equipment grant to purchase the SQUID magnetometer (NSF9974899). Dr John Bacsa is gratefully acknowledged for solving the structure of 5.*

19. Systematic Investigation of Trigonal-Bipyramidal Cyanide-Bridged Clusters of the First Row Transition Metals. Mikhail Shatruk, Kristen Chambers, Andrey V. Prosvirin, Kim R. Dunbar, *Inorg. Chem.*, **2007**, *46*, 5155-5165.

    *This research was supported by the NSF (PI grant CHE-0610019) and partially by the DOE grant DE-FG03-02ER45999). Funding of the CCD diffractometer (CHE-9807975) by the NSF is gratefully acknowledged.*

20. Enhanced alignment of $Mn_{12}$-acetate micro-crystals. D. Seo, W. Teizer, H. Zhao, and K.R. Dunbar, *J. Mag. Mag. Mat.*, **2007**, *312*, 205-209.

    *This research was supported by the Robert A. Welch Foundation (A-1585) and the National Science Foundation (DMR-0103455). KRD gratefully acknowledges DOE for funding (DE-FG02-02ER45999). Use of the TAMU/ CIMS Materials Characterization Facility is acknowledged. We thank V. Pokrovsky for helpful discussions.*

21. A Family of Mixed Metal Cyanide Cubes with Alternating Octahedral and Tetrahedral Corners Exhibiting a Variety of Magnetic Behaviors Including Single Molecule Magnetism. Eric J. Schelter, Ferdi Karadas, Carolina Avendano, Andrey V. Prosvirin, and Kim R. Dunbar, *J. Am. Chem. Soc.*, **2007**, *129*, 8139-8149.

    *K.R.D gratefully acknowledges the Department of Energy (DE-FG03-02ER45999), National Science Foundation (NIRT-NSF DMR-0103455), the Welch Foundation A1449, and Texas A&M University for funding of this research. The SMART CCD diffractometer and the SQUID magnetometer were purchased by funds provided by the National Science Foundation (Grants NSF-9807975 and NSF-9974899). Use of the TAMU/LBMS Applications Laboratory, Ms. Vanessa Santiago, and Dr. Shane E. Tichy are acknowledged. John Bacsa is acknowledged for a preliminary contribution.*

22. Magnetic anisotropy in the octanuclear $(Re_4Mn_4)$-$Mn^{II}$ cluster exhibiting Single-Molecule Magnet behavior: Quantum-spin and classical-spin approaches. A. V. Palii, S. M. Ostrovsky, S. I. Klokishner, B.S. Tsukerblat, E. J. Schelter, A. Prosvirin and K. R. Dunbar, *Inorg. Chim. Acta*, **2007**, *360*, 3915-3924.

    *The research described in this publication was made possible in part by Award MOC2-2611-CH-04 of the US Civilian Research & Development Foundation for the Independent States of the Former Soviet Union (CRDF) and MTFP-04-07 Follow-On Award of the Moldovan Research and Development Association (MRDA under funding from CRDF). Financial support of the Supreme Counsil for Sciences and Technological Development of Moldova is also appreciated. AVP thanks the Generalidad Valenciana for a visiting grant. BST thanks the Council for Higher Education of Israel and VATAT for financial support. KRD gratefully acknowledges the Department of Energy (DOE-FG03-02ER45999).*

23. Nanopatterning of Mn-12-acetate single-molecule magnet films. K. Kim, A. Ford, V. Meenakshi, W. Teizer, H. Zhao and K. R. Dunbar, J. Appl. Phys., 2007, 102, 094306:1-5.

*This research was supported by the Robert A. Welch Foundation A.1585. One of the authors K.R.D. gratefully acknowledges the National Science Foundation DMR0103455, NSF-9974899, the Telecommunication and Informatics Task Force TITF 2001-3 at Texas A&M University, and DOE DE-FG03-02ER45999. Use of the TAMU/CIMS Materials Characterization Facility is also acknowledged.*

24. A Family of Cyanide-Bridged Molecular Squares: Structural and Magnetic Properties of $[\{M^{II}Cl_2\}_2\{Co^{II}(triphos)(CN)_2\}_2]\cdot xCH_2Cl_2$, M = Mn, Fe, Co, Ni, Zn. Ferdi Karadas, Eric J. Schelter, Andrey V. Prosvirin, John Bacsa, Dmitry Smirnov, Andrew Ozarowski, J. Krzystek, Joshua Telser, and Kim R. Dunbar, **2008**, *Inorg. Chem.*, *47*, 2074-208247.

*Acknowledgment. This research was supported by NSF (PI grant CHE-0610019), in part, DOE (DE-FG03-02ER45999) and the Robert A. Welch Foundation (KRD). Funding of the CCD diffractometer (CHE-9807975) at Texas A&M University and the SQUID magnetometer (NSF 9974899) by NSF is also gratefully acknowledged. EPR studies were supported by the National High Magnetic Field Laboratory, which is funded by NSF through Cooperative Agreement DMR 0084173, the State of Florida, and the DOE. The 25-T resistive magnet was funded by the W. M. Keck Foundation.*

25. Hexacyanoosmate(III) chemistry: Preparation and magnetic properties of a pentanuclear cluster and a Prussian blue analogue with Ni(II). Matthew Hilfiger, Michael Shatruk, Andrey Prosvirin, and Kim R. Dunbar, *Chem. Commun.*, **2008**, 5752 – 5754.

*We would like to acknowledge Carolina Avendan˜o and Dr Nattamai Bhuvanesh for providing assistance and for useful discussions. This research was supported, in part, by the National Science Foundation (PI grant CHE-0610019) and the Department of Energy (grant DE-FG03-02ER45999). Funding of the CCD diffractometer by the NSF (CHE-9807975) is gratefully acknowledged.*

26. Pentanuclear Trigonal-Bipyramidal Cyanide Complexes: A Powerful Platform for the Systematic Assessment of the Magnetic Properties of Cyanide-Bridged Compounds. Kristen E. Funck, Matthew G. Hilfiger, Curtis P. Berlinguette, Michael Shatruk, and Kim R. Dunbar, *Forum issue on Molecular Magnetism*, *Inorg. Chem.*, **2009**, *48*, 3438-3452.

*Acknowledgment. We thank a number of collaborators who have assisted us in various stages of this ongoing project. Prof. Catalina Achim and Dr. Alina Dragulescu-Andrasi at Carnegie Mellon University are gratefully acknowledged for their assistance and expert advice on the spin-ransition behavior in the Fe-containing TBP complexes. We are also indebted to Prof. Boris Tsukerblat at Ben-Gurion University of the Negev, Israel, as well as Prof. Sophia Klokishner, Dr. Serghei strovsky, and Dr. Andrei Palii at the Institute of Applied Physics, Academy of Sciences of Moldova for their theoretical contributions to the understanding of SMM for the*

*Mn3Mn2 complex and for their valuable contributions to many areas of exchange-coupling modeling. We thank Jose´- Ramo´ n Gala´n-Mascaro´ s (Universita`t de Valencia) for helpful discussions, Dr. Andrey Prosvirin for assistance with some of the magnetic measurements, and Dr. Joseph Reibenspies for help with the setup of low-temperature crystallographic experiments. The research was supported, in part, by the National Science Foundation (NSF; Grant CHE-0610019) and the Department of Energy (DOE; Grant DE-FG03-02ER45999). Funding of the CCD diffractometer (GrantCHE-9807975) by the NSF is gratefully acknowledged.*

27. Magnetic molecules based on M(V) (M= Mo,W) and Ni(II) ions: a new class of trigonal bipyramidal cluster and confirmation of SMM behavior for the pentadecanuclear molecule {NiII[NiII(tmphen)(MeOH)]6[Ni(H2O)]2[μ-CN]30[WV(CN)3]6). Matthew G. Hilfiger, Hanhua Zhao, Andrey Prosvirin, Wolfgang Wernsdorfer, Kim R. Dunbar, Dalton Trans., 2009, 5155-5163.

    *This research was supported by the National Science Foundation (PI grant CHE-0610019) and by the Department of Energy (grant DE-FG03-02ER45999). Funding of the CCD diffractometer (CHE-9807975) and the SQUID magnetometer (CHE-9974899) by the NSF is also gratefully acknowledged. We would like thank Dr Lisa P´ erez, Dr Michael Shatruk, and Carolina Avenda˜ no for useful discussions. We would also like to acknowledge the Laboratory for Molecular Simulation at Texas A & M University for providing software and support on the Medusa supercomputer, NSF (Grant No. CHE-0541587).*

28. Heterospin Single-Molecule Magnets Based on Terbium Ions and $TCNQF_4$ Radicals: Interplay Between Single-Molecule Magnet and Phonon Bottleneck Phenomena Investigated by Dilution Studies. Nazario Lopez, Andrey V. Prosvirin, Hanhua Zhao, Wolfgang Wernsdorfer and Kim R. Dunbar, *Chem. Eur. J.*, **2009**, *15*, 11390-11400.

    *K.R.D. gratefully acknowledges DOE (DE-FG02-02ER45999), NSF (CHE-0610019), and the Welch Foundation (A-1449) for support of this research, as well as the NSF for grants to purchase a SQUID magnetometer (NSF-9974899) and a CCD diffractometer (NSF-9807975). W.W. thanks ANR-PNANO MolNanoSpin no. ANR-08-NANO-002, ERC Advanced Grant MolNanoSpin no. 226558, and STEP olSpin QIP for support. The authors are grateful to Dr. J. R. Gal 拼 n-Mascar 拼 s, Dr. B. Gastel, and Dr. M. Shatruk for helpful discussions.*

29. Charge-transfer two-dimensional layers constructed from a 2:1 assembly of paddlewheel diruthenium(II, II) complexes and bis[1,2,5]dithiazolotetracyanoquinodimethane: Bulk magnetic behavior as a function of inter-layer interactions. Natsuko Motokawa, Tomomi Oyama, Satoshi Matsunaga, Hitoshi Miyasaka, Masahiro Yamashita and Kim R. Dunbar, *Crystal Engineering - Special Issue on Molecular Magnetism*, **2009**, *11*, 2121-2130.

*This work was financially supported by The Asahi Glass Foundation and in part by the CREST project, Japan Science and Technology Agency (JST). N.M. thanks the JSPS Research Fellowships for Young Scientists for financial support. K.R.D. thanks the National Science Foundation and the Department of Energy (DE-FG02-02ER45999) for support of this project at Texas A&M University.*

30. Cyanide Lability and Linkage Isomerism of Hexacyanochromate(III) Induced by the Co(II) ion. Carolina Avendano, Ferdi Karadas, Matthew Hilfiger, Michael Shatruk, and Kim R. Dunbar, *Inorg. Chem.*, **2010**, *49*, 583–594.

*Acknowledgment. The authors would like to thank Dr. Joseph H. Reibenspies for his help with single-crystal X-ray crystallography. This research was supported by the NSF (PI grant CHE-0610019) and partially by the DOE (grant DE-FG03-02ER45999). K.R.D. gratefully acknowledged financial support from the Welch Foundation (A-1449). Funding of the CCD diffractometer (CHE-9807975) and the SQUID magnetometer (NSF 9974899) by the NSF is also gratefully acknowledged.*

31. An Unprecedented Charge Transfer Coupled Spin Transition in a Cluster with Fe(II) and Os(III) Centers. Matthew G. Hilfiger, Meimei Chen, Tatiana V. Brinzari, Tanya M. Nocera, Doros T. Petasis, Janice L. Musfeldt, Catalina Achim, Kim R. Dunbar, *Angew. Chem. Int. Ed.*, **2010**, *49*, 1410-1413.

*The authors acknowledge Carolina Avendao for useful discussions. This research was supported by the National Science Foundation (CHE-0610019 to K.R.D., DMR-0600089 to J.L.M.), the Department of Energy (DE-FG03-02ER45999 to K.R.D.) and the ACS-PRF Fund (AC3-44200 to C.A.). Crystallographic parameters can be found in the Supporting Information (Table S4) and cif files under CSD numbers 753301 and 753302.*

32. Unprecedented Binary Semiconductors Based on TCNQ: Single Crystal X-ray Studies and Physical Properties of Cu(TCNQ$X_2$) X = Cl, Br. Nazario Lopez, Hanhua Zhao, Akira Ota, Andrey V. Prosvirin, Eric Reinheimer and Kim R. Dunbar, *Adv. Mater.*, **2010**, *22*, 986–989.

*K.R.D. gratefully acknowledges the DOE (DE-FG02-02ER45999), NSF (CHE-0610019), and Welch Foundation (A-1449) for support of this research, as well as NSF for grants to purchase a SQUID magnetometer (NSF-9974899) and a CCD diffractometer (NSF-9807975). The authors are grateful to Dr. Helen Chifotides and Dr. Xinyi Wang for helpful discussions. The authors acknowledge the Materials Characterization Facility at Texas A&M University for assistance with the confocal microscope and XPS measurements, and the Microscopy and Imaging Center for SEM measurements. Supporting Information is available online through Wiley InterScience or from the authors.*

33. A Homologous Heterospin Series of Mononuclear Lanthanide/$TCNQF_4$ Organic Radical Complexes. Nazario Lopez, Hanhua Zhao, Andrey V. Prosvirin, Wolfgang Wernsdorfer and Kim R. Dunbar, *Dalton Trans*., **2010**, *39*, 4341-4352.

*K. R. D. gratefully acknowledges DOE (DE-FG02-02ER45999) for partial financial support of a student (N. Lopez) and full support of a postdoctoral researcher (A. Prosvirin) to perform the synthesis, X-ray crystallography and magnetic studies. The Welch Foundation (A-1449) is also acknowledged for partial support of N. Lopez during these studies. The National Science Foundation provided the funds to purchase a SQUID magnetometer (NSF-9974899) and a CCD diffractometer (NSF-9807975). W.W. thanks ANR-PNANO MolNanoSpin No. ANR-08-NANO-002, ERC Advanced Grant MolNanoSpin No. 226558, and STEP MolSpinQIP for support. The authors acknowledge the Electron Microprobe Laboratory at Texas A&M University and Dr R. Guillemette for assistance with the quantitative compositional analyses for YGd and YDy. The authors are grateful to Dr N. Bhuvanesh and Dr B. Gastel for helpful discussions.*

34. Control of Charge-Transfer in a Series of $Ru_2^{II,II}$/TCNQ Two-Dimensional Networks by Tuning Electron-Affinity of TCNQ Units: A Route to Synergistic Magnetic/Conducting Materials. Hitoshi Miyasaka, Natsuko Motokawa, Satoshi Matsunaga, Masahiro Yamashita, Kunihisa Sugimoto, Tatsuya Mori,[‡] Naoki Toyota, and Kim R. Dunbar, *J. Am. Chem. Soc*., **2010**, *132*, 1532-1544.

*We acknowledge Mr. T. Izawa and Ms. N. Takahashi at Tokyo Metropolitan University and Mr. N. Shibata at Tohoku University for syntheses of compounds, Prof. T. Akutagawa at Hokkaido University for his pointed advice for the syntheses of TCNQRx, and Dr. S. Takaishi at Tohoku University for measurements of electrical conductivity and helpful discussions. H.M. is grateful for financial support from a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (Grant 21350032) and The Asahi Glass Foundation. N.M. thanks the JSPS Research Fellowships for Young Scientists for financial support. K.R.D. thanks Texas A&M University and is grateful for support from the Department of Energy (DE-FG02-02ER45999), the National Science Foundation, and the Welch Foundation (A-1449).*

35. Cyanide-Bridged $Co^{II}_2M^{II}$ and $Co^{II}_2M^{II}_2$ Complexes Based on the $Co^{II}(triphos)(CN)_2$ Building-Block: Syntheses, Structures, Magnetic Properties and Density Functional Theoretical Studies. Ferdi Karadas, Michael Shatruk, Lisa M. Perez, and Kim R. Dunbar, Chem. Eur. J., **2010**, 16, 7164-7173.

*This research was supported in part by the National Science Foundation (PI grant CHE-0610019), the Department of Energy (grant DE-FG03- 02ER45999) and the*

*Welch Foundation (A-1449). Funding of the CCD diffractometer (CHE-9807975) by the NSF is gratefully acknowledged.*

36. A Docosanuclear Mo8Mn14 Cluster Based on $[Mo(CN)_7]^{4-}$. Xin-Yi Wang, Andrey V. Prosvirin, and Kim R Dunbar, Angew. Chem. Int. Ed., 2010, 49, 5081-5084 (featured on the cover).

    *This work was supported by the Department of Energy (DE-FG02-02ER45999) from a grant to KRD.*

37. Temperature and Light Induced Bistability in a $Co_3[Os(CN)_6]_2$ Prussian Blue Analog. Carolina Avendano, Matthew G. Hilfiger, Andrey Prosvirin, Codi Sanders, Darryl Stepien, Kim R. Dunbar, *J. Am. Chem Soc*., **2010**, *132*, 13123–13125.

    *Acknowledgment. The authors acknowledge Dr. Nattamai Bhuvanesh for help with the powder XRD experiments. This research was supported by the Department of Energy (DE-FG02-02ER45999 to K.R.D.). Funding of the SQUID (NSF 9974899) and the X-ray powder diffractometer (CHE 0079822) by the NSF is gratefully acknowledged.*

38. Tetranuclear, Oxygen Centered Copper(II) Clusters Linked Together with Guanidine-Guanidinate Ligands Gina M. Chiarella. Doris Y. Melgarejo, Andrey V. Prosvirin, Kim R. Dunbar, John P. Fackler Jr, *J. Clust. Sci.* **2010**, *21*, 551–565.

    *Support from the Robert A. Welch Foundation, A-0960, Houston, Texas and a Dreyfus Senior Mentor award to JPF are gratefully acknowledged. KRD acknowledges the Department of Energy, DOE- for support.*

39. Light-Induced Charge Transfer and LIESST Effect in Pentanuclear Cyanide-Bridged Clusters. Kristen E. Funck, Andrey Prosvirin, Corine Mathonière, Rodolphe Clérac, Etienne Harté, Marguerite Kalisz, and Kim R. Dunbar, *Inorg. Chem.*, **2011**, *50*, 2782-2789.

    *We thank Prof. Curtis Berlinguette (University of Calgary) and Prof. Michael Shatruk (Florida State University) for their pioneering work on these compounds in the K.R.D. laboratories. We are grateful to Prof. Catalina Achim and Dr. Alina Dragulescu-Andrasi (Carnegie Mellon University) for their earlier collaborative work on the spin-crossover behavior of the compounds discussed herein. K.R.D. acknowledges the Department of Energy (Grant DE-FG03-02ER45999) for the support of this research which has provided all of the funds to prepare and characterize the compounds as well as to make X-ray and magnetic measurements at Texas A&M University. The Welch Foundation (A-1449) (a private foundation in the State of Texas) is acknowledged for summer support for K.E.F. during the course of her Ph.D. studies. We thank NSF for an equipment grant to purchase the SQUID magnetometer (NSF-9974899). C.M./R.C acknowledge the University of Bordeaux,*

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40. Molecular Magnetic Materials Based on 4d and 5d Transition Metals. Xin-Yi Wang, Carolina Avendano and Kim R Dunbar, *Chem. Sov. Rev*. (invited critical review), **2011,** *40*, 3213-3238**.**

    *KRD thanks the Department of Energy (DOE-DE-FG02-02ER45999) for generous support of research on the role of magnetic anisotropy in governing the properties of cyanide molecular magnets.*

41. Beyond the spin model: Exchange coupling in molecular magnets with unquenched orbital angular momenta. Andrei Palii, Boris Tsukerblat, Sophia Klokishner, Kim R. Dunbar, Juan Modesto Clemente-Juan, Eugenio Coronado, *Chem. Sov. Rev*., (invited critical review, featured on the cover), **2011**, *40*, 3130-3156.

    *B.T. and K.R.D. gratefully acknowledge financial support from the USA-Israel Binational Science Foundation, BSF (Grant No. 2006498). B.T. thanks the Israel Science Foundation, ISF, for the financial support (grant no. 168/09). K.R.D. is grateful for support of this research by the Department of Energy. A.V.P. and S.I.K. gratefully acknowledge financial support from STCU (project N 5062). J.M.C.J. and E.C. thank Spanish MICINN (CSD2007-00010 CONSOLIDERINGENIO in Molecular Nanoscience, MAT2007-61584, CTQ-2008-06720 and CTQ-2005-09385), Generalitat Valenciana (PROMETEO program), and the EU (MolSpinQIP project and ERC Advanced Grant SPINMOL) for financial support. We also thank the people that during many years have been collaborating with us in molecular magnetism. Their names appear in this review paper.*

42. Vibronic model for Cooperative Spin-Crossover in Pentanuclear $\{[M^{III}(CN)_6]_2[M'^{II}(tmphen)_2]_3\}$ (M/M' = Co/Fe, Fe/Fe) Compounds. Sergei. Ostrovsky, Andrei Palii, Sophia Klokishner, Michael Shatruk, Kristen E. Funck, Kim R. Dunbar, Boris, Tsukerblat, *J. Phys. Chem.C.*, **2011**, *115*, 21666-21677.

    *B.T. and K.R.D. gratefully acknowledge financial support of the Binational U.S. Israel Science Foundation (BSF Grant 2006498). B.T. is grateful to the Israel Science Foundation for financial support (ISF Grant 168/09). K.R.D. acknowledges support from the Department of Energy (DE-FG02-02ER45999) for the synthetic portion of this work. The Welch Foundation (A-1449) is acknowledged for summer support for K.F. S.O., A.P., and S.K. thank STCU (Project N5062) for financial support. Financial support of the Supreme Council for Science and Technological Development of Moldova is also appreciated. We thank Professor Catalina Achim for providing unpublished experimental data on Mossbauer spectra as well as helpful comments.*

43. A Mn(III) Chain Derived from $Mn_{12}$-Acetate that Exhibits Both Glauber Dynamics and Antiferromangetic Ordering Regimes. Andrey Prosvirin, Hanhua Zhao and Kim R. Dunbar**,** *Inorg. Chim. Acta*., (*Jon Zubieta special issue)*, **2012**, *389*, 118-121.

    *K.R.D. gratefully acknowledges DOE (DE-FG02-02ER45999) for the magnetism*

*portion of this work and the Welch Foundation (A-1449) for support of the synthetic part. We thank NSF for Grants to purchase a SQUID magnetometer (NSF-9974899) and a CCD diffractometer (NSF-9807975). The authors are grateful to Dr. C.J. Gómez-García and Dr. J.R. Galán-Mascarós for helpful discussions.*

44. Crystal-to-Crystal Transformation of Magnets Based on $[Mo(CN)_7]^{4-}$ with Dramatic Changes in Coordination Mode and Ordering Temperature. Qing-Lun Wang, Heather Southerland, Jian-Rong Li, Andrey V. Prosvirin, Hanhua Zhao, and Kim R. Dunbar, *Angew. Chem. Int. Ed.*, **2012**, *51*, 932-934.

    *This work was supported by the U.S. Department of Energy (DEFG02-02ER45999) and the National Natural Science Foundation of China (no. 21071085).*

45. A Porous Sm(III) Coordination Nanotube with Hydrophobic and Hydrophilic Channels, Nazario Lopez, Hanhua Zhao, Dan Zhao, Hong-Cai Zhou, Joseph P. Riebenspies and Kim R. Dunbar, *Dalton Trans.*, **2013**, *42*, 54-57.

    *K.R.D. gratefully acknowledges DOE (DE-FG02-02ER45999) for support of this work and the Welch Foundation (A-1449) for partial summer support of Nazario Lopez. The NSF generously provided funds to purchase a CCD diffractometer (NSF-9807975). We thank Prof. M. Dincă for helpful discussions.*

46. Spin-Crossover Materials: Properties and Applications in "*Charge Tansfer-Induced Spin Transitions in Cyanometallate Materials*", Chapter 6. "Malcolm Halcrow, Editor. Wiley-Blackwell. Kim R. Dunbar, Michael Shatruk, Catalina Achim, **2013**, 171-202. (**book chapter**)

    *KRD thanks the Department of Energy for generous support of her project in cyanide magnetism including results highlighted in this chapter. The authors thank their co-workers who contributed to their collaborative research on the topics presented herein.*

47. Reversible Switching from Antiferro- to Ferromagnetic Behavior by Solvent-Mediated, Thermally-Induced Phase Transitions in a Trimorphic MOF-based Magnetic Sponge System Mario Wriedt, Andrey A. Yakovenko, Gregory J. Halder, Andrey Prosvirin, Kim R. Dunbar and Hong-Cai Zhou, *J. Am. Chem. Soc.*, **2013**, *135*, 4040-4050.

    *Funding was provided by U.S. Department of Energy (DESC0001015 and DE-FC36-07GO17033) and the Welch Foundation (A-1725). Dr. Mario Wriedt thanks the Postdoc Program of the German Academic Exchange Service (DAAD) for his financial support. Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under contract no. DE-AC02-06CH11357. We thank Prof. Karen Wooley for access to her experimental facilities and Mr. Kevin Pollack for his support in the TG-DSC-MS measurements. Special thanks to Prof. Christian Näther from the University of Kiel for useful discussions. The magnetic measurements were conducted in the Department of Chemistry SQUID Facility with a magnetometer obtained by a grant from the National Science Foundation (CHE-9974899). Prof. Dunbar thanks the DOE*

*(DE-FG02-02ER45999) for support of Dr. Andrey Prosvirin. A detailed description is provided in the SI.*

48. An unprecedented double layered $Fe_{36}$ phosphonate cage. Christine M. Beavers, Tina Tezgerevska, Andrey V. Prosvirin, John D. Cashion, Brendan F. Abrahams, Carmel Abrahams, Kim R. Dunbar, and Anne F. Richards, *Inorg. Chem.*, **2013**, 52,1670-1672.

    *A.F.R. acknowledges the ARC for the award of a Future Fellowship (Grant FT100100003). K.R.D. gratefully acknowledges the DOE (Grant DE-FG02-02ER45999) and the NSF for a grant to purchase a SQUID magnetometer (Grant NSF-9974899). The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, DOE, under Contract DE-AC02-05CH11231.*

49. A tetranuclear oxofluorovanadium(IV) cluster encapsulating a $Na(H_2O)_n^+$ subunit. Tiffany M. Smith, Nika Mahne, Andrey Prosvirin, Kim R. Dunbar, and Jon Zubieta, *Inorg. Chem. Commun.*, **2013**, *33*, 1-5.

    *KRD thanks the National Science Foundation for funds to purchase the SQUID magnetometer and the Department of Energy (DE-FG02-02ER4599) for providing the funds to support AP who made magnetic measurements and interpreted the data.*

50. One-Dimensional Square- and Ladder-Type Architectures Incorporating Octacyanometallates of Molybdenum(V) and Tungsten(V**),** Hanhua Zhao, Andrew J. Brown, Andrey V. Prosvirin, Kim R. Dunbar, *George Christou Special Issue*, *Polyhedron*, **2013**, *12*, 321–327.

    *We gratefully acknowledge DOE (DE-FG02-02ER45999) for supporting Dr. Hanhua Zhao and Dr. Andrey Prosvirin to carry out the syntheses and magnetism studies. We thank the Welch Foundation (A-1449) for support of Andrew J. Brown for summer support to perform crystallographic studies. We thank NSF for grants to purchase a SQUID magnetometer (NSF-9974899) and a CCD diffractometer (NSF-9807975).*

51. A Single-Molecule Magnet Based on $[Mo^{III}(CN)_7]^{4-}$ with the Highest Energy Barrier for a Cyanide Compound Xin-Yi Wang, Kun Qian, Xing-Cai Huang, Chun Zhou, Xiao-Zeng You, and Kim R. Dunbar, *J. Am. Chem. Soc.*, **2013**, *135*, 13302-13305.

    *X.-Y.W. thanks the Major State Basic Research Development Program (2013CB922102), NSFC (91022031, 21021062, 21101093) and the NSF of Jiangsu province (BK2011548) for financial assistance. The synthetic work by X.-Y.W. while he was a Postdoctoral Research Associate in the Dunbar laboratories was supported by the U.S. Department of Energy (DE-FG02-02ER45999).*

52. A Neutral Fe(III) Compound Exhibiting A Two-Step Spin Transition and Dielectric Anomalies. Zhao-Yang Li, Jing-Wei Dai, Kevin J. Gagnon, Hong-Ling Cai, Takashi Yamamoto, Yasuaki Einaga, Han-Hua Zhao, Shinji Kanegawa, Osamu Sato, Kim R. Dunbar, and Ren-Gen Xiong, *Dalton Trans.*, **2013**, *42*, 14685-14688.

    *The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract no.*

*DE-AC02- 05CH11231. KRD thanks the Department of Energy for support of this collaborative work (DE-FG02-02ER45999).*

53. Squaring the cube: A Family of Octametallic Lanthanide Complexes Including a $Dy_8$ Single-Molecule Magnet Ming Fang, Hanhua Zhao, Andrey V. Prosvirin, Dawid Pinkowicz, Kim R. Dunbar, Bin Zhao, Wei Shi, Peng Cheng, Wolfgang Wernsdorfer and Euan K. Brechin, *Dalton Trans*., **2013**, *42*, 14693-14701. (Cover art article).

    *KRD thanks the Department of Energy (DOE-DE-FG02-02ER445999) for generous support of this research. DP gratefully acknowledges the financial support of the European Commission within the Marie Curie International Outgoing Fellowship (grant agreement no. PIOF-GA-2011-298569).*

54. Trigonal bipyramidal 5d-4f Single Molecule Magnets. Mohamed R. Saber and Kim R. Dunbar, *Chem. Commun*., **2014**, *50*, 2177-2179.

    *The authors gratefully acknowledge the Department of Energy (DE-FG02-02ER45999) for financial support of this work.*

55. Variations in Topology and Magnetic Properties of Hepta- and Octacyanometallates of Molybdenum with Manganese (II). Qing-Lun Wang, Yuan-Zhu Zhang, Heather Southerland, Andrey V. Prosvirin, Hanhua Zhao and Kim R. Dunbar, *Dalton. Trans*., **2014**, *43*, 6802-6810.

    *This project was supported by the Department of Energy (DE-FG02-02ER45999). The salary of Q.-L. Wang, a Visiting Scholar, was provided by the National Natural Science Foundation of China (no. 21071085, 21371104) and the Tianjin Natural Science Foundation (no. 11JCYBJC03500). Funds for the SQUID magnetometer were obtained from the National Science Foundation*.

56. Hydrothermal Synthesis, Structure and Magnetic Properties of a Three-Dimensional Cobalt(II) – Aminophenyltetrazolate Coordination Polymer, Tiffany M. Smith, Yuan-Zhu Zhang, Kim R. Dunbar, and Jon Zubieta, Dalton. Trans., 2014, 43, 7263-7268.

    *This work was funded by a grant from the National Science Foundation (CHE-0907787). K.R.D. thanks the National Science Foundation for funds to purchase the SQUID magnetometer. Magnetic measurements in the Dunbar laboratories were funded by the Department of Energy (DE-FG02-02ER45999).*

57. Record antiferromagnetic coupling for a 3d/4d cyanide bridged compound, Dawid Pinkowicz, Heather Southerland, Xin-Yi, Wang and Kim R. Dunbar, J. Am. Chem. Soc., 2014, 136, 9922–9924.

*K.R.D. thanks the Department of Energy (DE-FG02-02ER45999) for financial support. D.P. gratefully acknowledges the financial support of the European Commission within the Marie Curie International Outgoing Fellowship, Project MultiCyChem (Grant Agreement PIOF-GA-2011-298569), and the START Fellowship of the Foundation for Polish Science (2013 edition).*

58. Single-Chain Magnetic Behavior in a Hetero-Tri-Spin Complex Mediated by Supramolecular Interactions with TCNQF-• Radicals, Zhao-Xi Wang, Xuan Zhang, Yuan-Zhu Zhang, Ming-Xing Li, Hanhua Zhao, Marius Andruh and Kim R. Dunbar, Angew. Chem. Int. Ed., 2014, 53, 11567-70.

    *Z.-X.W. thanks the China Scholarship Council (No. 201206895004) and National Natural Science Foundation of China (No. 21171115) for financial support to visit Texas A&M. K.R.D. and Y.-Z.Z. thank the Department of Energy, Basic Energy Sciences Division (DE-FG02-02ER45999) for generous support.*

59. Synthesis, Characterization, and Reactivity of Iron(III) Complexes Supported by a Trianionic ONO3- Pincer Ligand, Matias E. Pascualini, Natali V. Di Russo, Pedro A. Quintero, Annaliese A. Thuijs, Dawid Pinkowicz, Khalil A. Abboud, Kim R. Dunbar, George Christou, Mark W. Meisel, and Adam S. Veige, Inorg. Chem. 2014, 53, 13078–13088.

    *This work was supported, in part, by the National Science Foundation (NSF) via CHE-1265993 (ASV), DMR-1213030 (GC), DMR-1202033 (MWM), DMR-1157490 (NHMFL), and CHE-0821346 (KAA). Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-FG02-02ER45999 (KRD). ASV also acknowledges UF support and the resources provided by the UF High-Performance Computing Center. NVD is an HHMI International Student Research fellow. We thank Prof. A. Angerhofer and U. Twahir for assistance in the EPR measurements, Prof. A. Roitberg for assistance with DFT calculations, and Dr. E. Čižmár for training on the use of EasySpin codes.*

60. Synthesis, Characterization, and Reactivity of Iron(III) Complexes Supported by a Trianionic ONO3- Pincer Ligand, Matias E. Pascualini, Natali V. Di Russo, Pedro A. Quintero, Annaliese A. Thuijs, Dawid Pinkowicz, Khalil A. Abboud, Kim R. Dunbar, George Christou, Mark W. Meisel, and Adam S. Veige, Inorg. Chem. 2014, 53, 13078–13088.

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61. Cyanide Single Molecule Magnets Exhibiting Reversible, Solvent Dependent "On" and "Off" Exchange Bias Behavior. Dawid Pinkowicz, Heather I. Southerland, Carolina Avendaño, Andrey Prosvirin, Wolfgang Wernsdorfer, Kasper S. Pedersen, Jan Dreiser, Rodolphe Clérac and Kim R. Dunbar, *J. Am. Chem. Soc.*, **2015**, *137*, 14406-14422.

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62. Trigonal Antiprismatic Mononuclear Co(II) Single Molecule Magnets with Large Uniaxial Anisotropies, Yuan-Zhu Zhang, Andrew J Brown, Silvia Gómez-Coca, Mohamed R. Saber, Xuan Zhang, Kim R. Dunbar, **2016**, accepted-Advanced Article-*Chemical Science*.

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**Graduate Student Dissertation Research Supported By DOE Grant DE-FG02-02ER45999**

**Curtis Paul Berlinguette** – 2004 – Nanomagnetic molecular materials based on the hexacyanometallate building block: The preparation and characterization of high-spin cluster and chain compounds.

*Professor, University of British Columbia, Canada*

**Eric John Schelter** – 2004 – Cyanide clusters of $Re^{II}$ with 3d metal ions and their magnetic properties: incorporating anisotropic ions into metal-cyanide clusters with high spin magnetic ground states.

*Associate Professor, University of Pennsylvania*

**Eric Reinheimer** – 2007 – Inorganic-Organic, Organic Charge Transfer and Radical Based Compounds with Chalcofulvalene Donors and Organic Acceptors.

*Manager of Small Molecule Crystallography, Rigaku Americas Corporation*

**Ferdi Karadas** – 2009 – Preparation and Characterization of Cyanide-Bridged Molecular Clusters and Extended Networks Using the Building-Block Approach.

*Assistant Professor, Bilkent University, Turkey*

**Matthew Hilfiger** – 2010 – Incorporation of 4d and 5d Transition Metal Cyanometallates into Magnetic Clusters and Materials

*Petroleum Engineer, Aramco Services Houston, Texas*

**Nazario Lopez** – 2010 – Tuning the Properties of Molecular Magnets and Conductors Based on Lanthanide and Transition Metal Ions Bridged by TCNQ Derivatives or Cyanometallate Ligands by Varying the Dimensionality of the Structure and Metal Ion Identity

*Assistant Professor, Universite Autonoma del Estado de Morelos, Cuernavaca, Mexico*

**Carolina Avendano** – 2010 – Cyanide Bridged Molecular Magnetic Materials with Transition Metals Ions that Exhibit Strong Spin-Orbit Coupling: Investigation of Bistable Magnetic Phenomena

*Director of Operations the Rice Office of STEM Engagement, Office of Research, Rice University*

**Kristen Chambers Funck** – 2010 – Magnetic Properties and Reactivity Studies of Families of Trigonal Bipyramidal Cyanide Bridged Clusters

*Assistant Professor of Chemistry, James Madison University*

**Zhongyue Zhang** (PhD) – 2013 – New Conducting and Electrically Switching Molecular Materials Based on Main Group and Transition Metals Bridged by TCNQ Derivatives

*Assistant Professor, Laboratory of Advanced Materials, Nagoya University, Japan*

**Heather Southerlan**d (PhD) – 2013 – Investigation of Molecular Magnetic Compounds Incorporating 4d and 5d Transition Metal Cyanometallates.

*Saplin Learning Center, Austin, Texas*

**Mohamed R. M. Saber** (PhD) – 2013 – Enhancing Magnetic Properties of Molecular Magnetic Materials: The Role of Single Ion Anisotropy.

*Assistant Professor, Fayoum University, Fayoum, Egypt*

**Andrew Brown** (PhD) – 2015 – A Modular Approach to Bistable Molecular Magnets of Molecules and Extended Architectures.

*Intel Corporation, Phoenix, Arizona*

**Xuan Zhang** (PhD) – 2016 – Hybrid Magnetic and Semiconducting Materials Based on Organocyanide Electron Acceptors and Metal Complexes.

*Postdoctoral Fellow, Department of Chemistry, Northwestern University, Illinois*

**Toby J. Woods** (PhD) – 2016 – Electronic Control of the Magnetic Properties of First-Row Transition Metal Complexes.

*X-ray Specialist, Department of Chemistry, University of Illinois, Urbana-Champaign*

**Codi Anne Sanders** (PhD) – 2016 – Investigation of Magnetic Behavior and the Tuning of Spin-Transitions and Redox Properties in Pentanuclear Cyanide Architectures.

*Intel Corporation, Portland, Oregon*

*Postdoctoral Research Supported By DOE Grant DE-FG02-02ER45999*

**Dr. John Bacsa, Ph.D. Univ. of the Witwatersrand South Africa, 1998**

*X-ray Specialist, Emory University*

**Dr. Michael Shatruk, Ph.D. Moscow State U., Russia 2001,**

*Associate Professor, Florida State University, Tallahassee, FL*

**Dr. Eric Reinheimer, Ph.D., Texas A&M, 2007**

*Manager of Small Molecule Crystallography, Rigaku Americas Corporation*

**Dr. Xinyi Wang , Ph. D., Peking University, 2006**

*Assistant Professor, Nanjing University, Nanjing, China*

**Dr. Akira Ota, Ph. D., Kyoto University, 2006**

*Entrepreneur, Kyoto, Japan*

**Dr. Andrey Prosvirin, Ph. D., Russian Academy of Sciences, 1998**

*Research Associate, Department of Physics, Texas A&M University*

**Dr. Dawid Pinkowicz, Marie Curie Fellow, Ph.D., Jagiellion U., Poland, 2010**

*Assistant Professor, Jagiellion U., Krackow, Poland*

**Dr. Yuan-Zhu Zhang, Ph. D., Peking University, 2006,**

*Assistant. Professor, South U. of Science and Technology of China*

**Dr. Silvia Gomez-Coca, Ph. D., U. of Barcelona, 2015**

*Postdoctoral Researcher, University College London, UK*

**Dr. Hanhua Zhao, Ph.D.,** Nanjing University

**Undergraduate Students who Contributed to Research on DOE Grant DE-FG02-02ER45999**

1. Aurélie Buckelew, B.S. 2001 — M.S. Texas A&M University
2. Derek Vaughn, B.S. 2001 — Chemist, Benchmark Research, Houston, TX
3. †Dr. Carolina Avendano, REU, 2003 — Ph.D., Texas A&M University
4. Kristen Chambers, REU Student, 2003 — Ph.D.,Texas A&M University
5. Darryl Stepien, B.S. Chemistry, 2009 — Research Chemist, Baker Hughes
6. Codi Sanders, B.S. Chemistry, 2009 — Ph.D., Texas A&M University
7. Michael Woodie, B.S. Chemistry, 2010
8. Ashley Dittmer, B.S. Chemistry, 2010 — Lieutenant, United States Air Force
9. Charles Culbertson, REU, Summer 2013 — B.S., Indiana U. Pennsylvania
10. † Briana Zamora, B.S. Texas A&M, 2013 — Development Chemist, Ascend Performance Materials
11. † Bianca Ramirez, B.S. Texas A&M, 2013 — Ph.D. student, U. of Minnesota
12. Connor Daly , REU 2015 — B.S., Shippensburg State U. PA
13. Zhilin Go, B.S., Visiting Undergraduate Scholar — B.S., Nankai University, China
14. James Hollas — B.S., candidate, Texas A&M University
15. †Anastasia Lopez — B.S., Texas A&M University
16. Jason McCandless — B.S., Texas A&M University
17. †Tia'Asia James, REU Summer 2016 — B.S. candidate, Arkansas State University

† Minorities

**Visiting Scholar Research Supported By DOE Grant DE-FG02-02ER45999**

1. Prof. Boris Tsukerblat, Visiting Scholar, Ben Gurion Univ. of the Negev, Beer Sheva, Israel (2002, 2004)
2. Prof. Hitoshi Miyasaka, Visiting Scholar, Tokyo Metropolitan University, Tokyo, Japan (2/03)
3. Prof. Kazuko Matsumoto, Visiting Scholar, Waseda University, Tokyo, Japan (3/03)
4. Prof. Gui Li Ning, Visiting Scholar, Dalian University of Technology, Dalian, China (11/03-05/04)
5. Dr. Sergei Ostrovosky, Visiting Scholar, Inst. of Applied Physics, Chisinau, Moldova (9/04-12/04; 06/08)
6. Dr. José Ramón Galán-Mascarós, University of Valencia, Valencia, Spain, (2/05-7/05)
7. Prof. Sophia Klokishner, Inst. of Applied Physics, Academy Sciences, Kishinev, Moldova (7/06; 06/08)
8. Dr. Andrei Palii, Inst. of Applied Physics of the Academy of Sciences, Kishinev, Moldova (7/06; 06/08))
9. Dr. Akira Ota, Tokyo Institute of Technology, Ookayama, Japan (4/07-9/10)
10. Dr. Ahmed Youssef, Faculty of Science – Ain Shams U., Egypt (7/08-4/09).
11. Maria Fernanda Ballesteros Rivas, Visiting Ph.D. Student Intern, Mexico (9/09-9/10).
12. Ming Fang, Visiting Ph.D. Student Intern, Nankai, China (9/10-8/11).
13. Dr. Qing-lun Wang, Visiting Chinese Scholar, Nankai University (4/11-2/12).
14. Prof. Anne Richards, Visiting Professor, LaTrobe University, Australia (1/13-4/13).
15. Zhaoyang Li, Visiting Ph.D. Student Scholar, Kyushu University, Japan (10/12-3/13)

16. Prof. Zhao-Xi Wang, Visiting Professor, Department of Chemistry, Shanghai University (10/13-9/14)