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## COMMUNICATION

## A trinuclear metallasilsesquioxane of uranium(III).

Maxime Tricoire,<sup>†a</sup> Nadir Jori,<sup>†a</sup> Farzaneh Fadaei Tirani,<sup>b</sup> Rosario Scopelliti,<sup>b</sup> Ivica Živković,<sup>c</sup> Louise S. Natrajan<sup>d</sup> and Marinella Mazzanti<sup>\*a</sup>Received 00th January 20xx,  
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**The silsesquioxane ligand (iBu)<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub> (iBuPOSSH<sub>3</sub>) is revealed as an attractive system for the assembly of robust polynuclear complexes of uranium(III) and allowed the isolation of the first example of a trinuclear U(III) complex ([U<sub>3</sub>(iBuPOSS)<sub>3</sub>]) that exhibits magnetic communication and promotes dinitrogen reduction in presence of reducing agent.**

The design of polymetallic assemblies is attracting high interest in uranium chemistry because of their ability to promote small molecule activation,<sup>1-10</sup> and their interesting magnetic properties,<sup>11-15</sup> yet synthetic routes to such assemblies remain elusive. Moreover, the recent identification of the first example of actinide metal-metal bonding interactions in a trinuclear thorium complex<sup>16-17</sup> suggests that trinuclear assemblies may be used to promote metal-metal interactions in uranium compounds. Nevertheless, examples of trinuclear uranium complexes<sup>18-25</sup> remain rare with only two examples reported so far for the +III oxidation state.<sup>26-27</sup>

Siloxides were shown to act as versatile supporting ligands in low-valent uranium chemistry which have led to unprecedented reactivity including dinitrogen reduction and cleavage.<sup>28-30</sup> However, the use of the polydentate analogue silsesquioxane (POSS) in uranium chemistry remains limited to two reports describing the synthesis of mononuclear complexes [U(Cy<sub>7</sub>Si<sub>7</sub>O<sub>12</sub>)<sub>2</sub>]<sup>n-</sup> (Cy = cyclohexyl) with uranium in the oxidation

states +IV, +V and +VI.<sup>31-32</sup> In the most recent study by Hayton and coworkers,<sup>32</sup> the formation of a trimeric assembly of uranyl(VI) was also described suggesting, together with several reports of POSS based di- and tetrametallic clusters of lanthanides,<sup>33-34</sup> that POSS may provide a suitable ligand for the assembly of trinuclear U(III) complexes through silanolate bridges. Here we report the synthesis, structure and properties of the first example of a trinuclear complex of uranium(III) which is assembled by using the silsesquioxane ligand (iBu)<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub>, iBuPOSSH<sub>3</sub>.

The addition of one equiv. of iBuPOSSH<sub>3</sub> to equimolar [U(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>] in hexane at -40 °C led to a colour change from purple to dark brown (Scheme 1). The <sup>1</sup>H NMR spectrum of the reaction mixture measured at 25 °C in cyclohexane shows a complex pattern suggesting the presence of several solution species. Storage of the resultant reaction mixture at -40 °C allowed to obtain midnight blue XRD-suitable crystals of the complex [U<sub>3</sub>(iBuPOSS)<sub>3</sub>], **1** (Figure 1, a). Due to the high solubility of **1**, the careful removal of the HN(SiMe<sub>3</sub>)<sub>2</sub> formed during the reaction was challenging but crucial to isolate analytically pure complex **1**. After drying carefully the reaction mixture under dynamic vacuum for 16 h, complex **1** was isolated analytically pure in 19% yield, as a midnight blue powder, by recrystallization from cold (-40 °C) hexane (Scheme 1). Isolation of the trimeric complex in higher yields was prevented by its solubility and by the presence of species of higher nuclearity in the reaction mixture. Notably a few crystals of the tetranuclear complex [U<sub>4</sub>(iBuPOSS)<sub>4</sub>] (Figure 1, c) were isolated alongside the trinuclear complex when further concentrating the reaction mixture. The conditions required for the isolation of reasonable amounts of analytically pure [U<sub>4</sub>(iBuPOSS)<sub>4</sub>] could not so far be identified.

Complex **1** crystallizes in the *P*-1 space group and shows a triangular uranium core that is disordered over two positions in a 77:23 ratio. In the solid state, each uranium centre is coordinated by one iBuPOSS ligand.

<sup>a</sup> Group of Coordination Chemistry, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland  
E-mail: marinella.mazzanti@epfl.ch

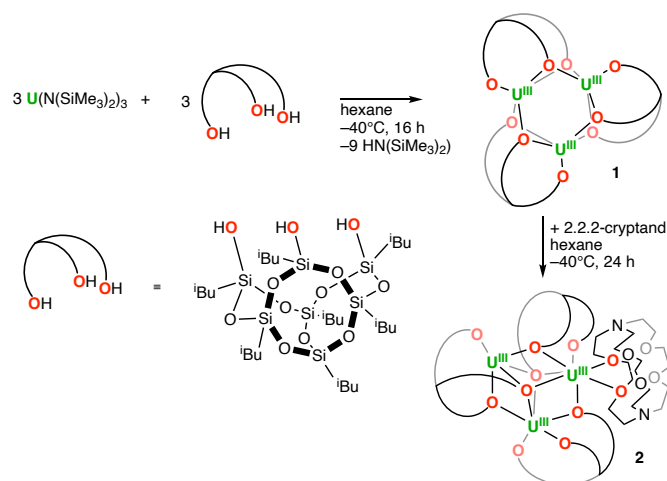
<sup>b</sup> X-ray Diffraction and Surface Analytics Platform, Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

<sup>c</sup> Laboratory for Quantum Magnetism, Institute of Physics, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

<sup>d</sup> Centre for Radiochemistry Research, Department of Chemistry, School of Natural Sciences and Photon Science Institute, The University of Manchester, Manchester M13 9PL, U.K.

<sup>†</sup> M. T. and N. J. contributed equally to the work

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Scheme 1. Synthesis of complex 1 and 2.

The three  $U(iBuPOSS)$  fragments are assembled in a trinuclear architecture with a  $U_3(\mu-O)_6$  core, with three oxygen atoms in a triangular arrangement located above the plane formed by the three uranium centres and three oxygen atoms below the plane. A similar  $An_3(\mu-X)_6$  topology has only been observed twice in actinide chemistry with  $X=Cl$ .<sup>35, 16</sup> Although a few additional examples of trinuclear oxo- or nitride centred complexes of uranium with a  $U_3(\mu-X)_6(\mu_3-Y)$  ( $Y = O, N$ ) core<sup>22 21, 25</sup> have been reported, none of them contains only  $U(III)$  centres. The structure of complex 1 (Figure 1, a) shows that in each  $U(iBuPOSS)$  moiety, the uranium ion is coordinated by three anionic siloxide oxygen atoms and two oxygens of the silyl ether backbone of the  $iBuPOSS$  ligand. Each uranium ion is also bound by two additional bridging anionic siloxide oxygens from an adjacent  $U(iBuPOSS)$  unit. The  $U-O_{siloxide}$  distances range from 2.125(16) Å to 2.568(17) Å (average value of 2.36(2) Å), which lie within the range of distances found in previously reported  $U(III)$  siloxide complexes<sup>36, 28, 37</sup> (2.182(3)–2.549(3) Å). The  $U_3(\mu-O)_6$  core in 1 displays alternating  $U-O$  bond lengths in which the shortest bonds are observed for an anionic oxygen from the coordinated  $iBuPOSS$  ( $U1-O1$ ,  $U2-O13$  and  $U3-O25$ ) and for two bridging anionic oxygens from an adjacent  $U(iBuPOSS)$  fragment ( $U1-O35$ ,  $U1-O36$ ,  $U2-O11$ ,  $U2-O12$ ,  $U3-O23$ ,  $U3-O24$ ), thus ensuring the trimeric architecture's rigidity (Figure 1). The  $U-U$  distances range from 3.6347(13) Å to 3.6493(12) Å, and are significantly shorter than the reported distance in the  $[U^{III}(OSi(O^iBu)_3)_2]_2$  dimer (3.9862(2) Å).<sup>36</sup> These values lie between the sum of the covalent radii of two uranium atoms (3.40 Å) and the sum of their Van der Waals radii (3.72 Å).<sup>38</sup> The observed arrangement of the  $U$  atoms in the  $U_3(\mu-O)_6$  core and the  $U-U$  short distance are similar to what observed in the trithorium  $Th_3(\mu-Cl)_6$  cluster displaying a  $\sigma$ -bonding  $Th-Th$  interaction with  $Th-Th$  distances in the 3.9896(4)–3.9947(5) Å range.<sup>16</sup>

The  $^1H$  NMR spectrum of isolated 1 recorded at  $25^\circ C$  in cyclohexane- $d_{12}$  shows the twenty-one peaks expected for the seven *iso*-butyl groups of the  $iBuPOSS$  ligands in a  $C_3$  symmetric coordination environment (Figure S1). Switching the solvent to  $thf-d_8$  led to a well resolved  $^1H$  NMR spectrum displaying 69 and

76 resonances at  $25$  and at  $-40^\circ C$  respectively (Figure S2 and S3), which indicates a loss of the  $C_3$  symmetry that is likely induced by  $thf$  coordination to the uranium centres. The fact that more than 63 peaks are observed suggests that not every *iso*-butyl is freely rotating at low temperature. Complex 1 did not show any sign of decomposition after 4 days at  $25^\circ C$  in cyclohexane- $d_{12}$  and is stable in  $thf-d_8$  at  $-40^\circ C$  up to a week but it slowly decomposes at  $25^\circ C$  in  $thf-d_8$  over a week. The values of the Stokes radii obtained by  $^1H$  DOSY NMR experiments (Table S1) in cyclohexane- $d_{12}$  (12.1 Å) and in  $thf-d_8$  (11.4 Å) correlates well with the 10.3 Å value estimated from the solid-state structure confirming that the trinuclear assembly of 1 is retained both in cyclohexane and in  $thf$  solution.

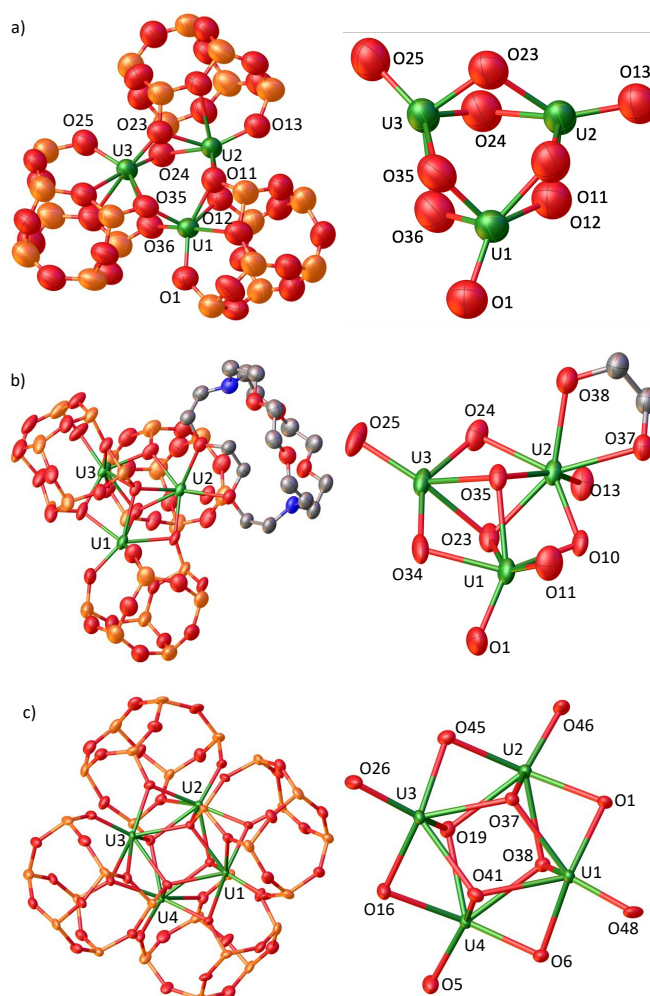


Figure 1. ORTEP of complexes 1 (a), 2 (b) and  $[U_4(iBuPOSS)_4]$  (c) with thermal ellipsoids drawn at 50% probability level, close-up view of their core structure are shown on the right. The *iso*-butyl groups and the minor part of the disorder have been omitted for clarity. Selected bonds distances (Å): 1:  $U(1)-U(2)$  3.6347(13),  $U(1)-U(3)$  3.6493(12),  $U(2)-U(3)$  3.6426(13). 2:  $U(1)-U(2)$  3.8163(5),  $U(1)-U(3)$  3.8124(5),  $U(2)-U(3)$  3.7139(6).

Attempts to reduce 1 by adding  $KC_8$  (up to 10 equiv.) and 2.2.2-cryptand (crypt) (1 equiv.) under Ar only led to the isolation of dark red crystals of a 2.2.2-cryptand adduct of 1,  $[U_3(iBuPOSS)_3(crypt-\kappa^2-O,O')]$  complex 2 (Figure 1, b). Complex 2 can be prepared in 48% yield by adding 1.0 equiv. of cryptand to 1.0 equiv. of complex 1 in hexane at  $-40^\circ C$  (Scheme 2).

Cryptand was previously found to encapsulate both low-valent lanthanides<sup>39-40</sup> and actinides<sup>41-43</sup>, but complex **2** is the first example of a bidentate cryptand coordinated to an actinide ion. Two examples of a similar bidentate binding mode were previously reported for rare-earth metals.<sup>44</sup> Complex **2** crystallizes in the *P-1* space group and shows an interesting reorganization of the *ibu*POSS ligands, leading to a modified core topology  $U_3(\mu-O)_3(\mu_3-O)_2$  that allows the coordination of the cryptand. The number of the bridging oxygens (five) is different with respect to complex **1** (six) with the five bridging oxygen atoms now forming a distorted trigonal bipyramidal coordination polyhedron. The cryptand binding results in a lengthening of the U–U distances (3.7139(6) Å to 3.8163(5) Å) compared to **1**.

The <sup>1</sup>H NMR spectrum of complex **2**, recorded at 25 °C in cyclohexane-*d*<sub>12</sub>, showed 63 peaks which is consistent with the loss of symmetry observed in the solid state upon cryptand coordination. Dissolving complex **2** in thf-*d*<sub>8</sub> showed unbound cryptand signals and the proton resonances corresponding to complex **1** in thf-*d*<sub>8</sub> indicating that cryptand is readily displaced in coordinating solvent (Figure S14).

To probe the impact of the structural differences observed in **1** and **2** on their magnetic properties, SQUID magnetic measurements were carried out in the 2–250 K range under an applied DC field of 1 T (Figure 2).

At 250 K, complex **1** displays an effective magnetic moment of 4.16 μ<sub>B</sub> (2.40 μ<sub>B</sub> per uranium centre) while a value of 5.12 μ<sub>B</sub> (2.95 μ<sub>B</sub> per uranium centre) was recorded for **2**. Both values are in reasonable agreement with the presence of uranium centres being in the +III oxidation state.<sup>45</sup> Upon cooling, the two complexes show different behaviours. Complex **2** displays a moderate and monotonic decrease of its magnetic moment to reach a value of 4.35 μ<sub>B</sub> (2.51 μ<sub>B</sub> per uranium centre) at 15 K before dropping to 3.58 μ<sub>B</sub> (2.07 μ<sub>B</sub> per uranium centre) at 2 K. The observed behaviour is similar to those measured for mononuclear complexes of U(III) suggesting that the three uranium centres in **2** are essentially magnetically independent.<sup>45, 46, 37</sup>

A different low temperature behaviour of the magnetic moment was observed for complex **1**. Upon lowering the temperature, the magnetic moment decreases almost monotonically until 6 K (1.15 μ<sub>B</sub> per complex, 0.67 μ<sub>B</sub> per uranium centre), and then with a steeper curve to reach a value of 0.54 μ<sub>B</sub> (0.31 μ<sub>B</sub> per uranium centre) at 2 K. The observed low value of the magnetic moment with a χT value approaching 0 at low temperature indicates the presence of a non-magnetic ground state (Figure S22). Such behaviour is rare in systems comprising an odd number of unpaired electrons and was previously only observed for a triangular pentavalent uranium [UO<sub>2</sub>L]<sub>3</sub> (L = 2-(4-tolyl)-1,3-bis(quinolyl)malondiiminate) system<sup>23-24</sup> and for several Dy<sub>3</sub> architectures.<sup>47-48</sup> The analysis the χ vs T plot for **1** revealed a sharp maximum of the susceptibility at 6 K which indicates the presence of an unambiguous antiferromagnetic coupling at low temperature (Figure 2). The observed magnetic exchange is probably due to superexchange through the bridging oxygen atoms although a contribution from direct exchange cannot be ruled out

considering the short U–U distances observed in the solid-state structure of complex **1**. Only a few examples of complexes showing unambiguous magnetic coupling between U(III) centres have previously been reported.<sup>49-50, 3, 9</sup> These results provide a rare example of structure-magnetic properties relation in uranium chemistry<sup>51</sup> showing that structural changes lead to dramatic differences in the magnetism of polynuclear U(III) complexes.

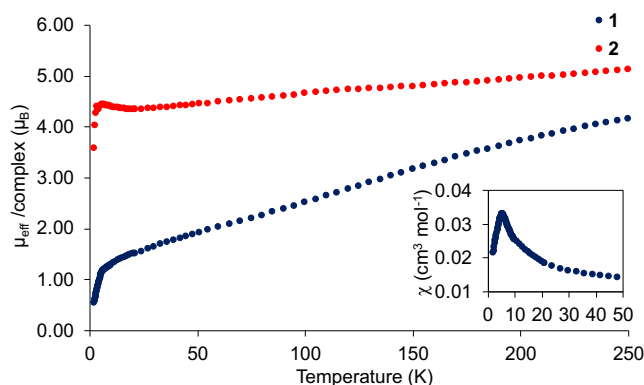


Figure 2. Solid-state  $\mu_{\text{eff}}/\text{complex}$  vs T data measured under an applied field of 1 T for complexes **1** and **2** and low temperature  $\chi$  vs T plot for **1** (inset).

Besides its interesting magnetic properties, the isolation of **1** also represented an excellent opportunity to study the reactivity of a trinuclear U(III) system. Exposing cyclohexane-*d*<sub>12</sub> or thf-*d*<sub>8</sub> solutions of complex **1** to N<sub>2</sub> (1 atm) at 25 °C and -40 °C respectively did not lead to any observable changes in the <sup>1</sup>H NMR spectrum. However, THF solutions of **1** were found to react with N<sub>2</sub> at -40 °C in presence of excess KC<sub>8</sub> (10 equiv.) leading to a slow color change from dark to pale brown over several days. The <sup>1</sup>H NMR spectrum of a thf-*d*<sub>8</sub> reaction mixture after 3 days at -40 °C showed only the complete disappearance of the resonances of **1**. Crystallization attempts did not allow us to identify the reaction product(s). However, treating the reaction mixture after 5 days with a 2M HCl solution in Et<sub>2</sub>O at -80 °C resulted in the formation of NH<sub>4</sub>Cl that was quantified to 2.0 equiv. per trimeric complex by <sup>1</sup>H NMR spectroscopy in DMSO-*d*<sub>6</sub>. To further confirm that N<sub>2</sub> activation had occurred the reaction was also performed with labelled <sup>15</sup>N<sub>2</sub> (Figure S19) yielding the distinctive signals of <sup>15</sup>NH<sub>4</sub>Cl after quenching. The observed reduction of N<sub>2</sub> by the complex **1** in the presence of KC<sub>8</sub> suggests that N<sub>2</sub> binding to the uranium centres must occur to some extent also in thf solution, but could not be detected by <sup>1</sup>H NMR spectroscopy. The observed stoichiometry of 2 NH<sub>3</sub> formed per complex suggested binding of one N<sub>2</sub> molecule by each U(III) trimer.

In conclusion the *ibu*POSS ligand revealed an attractive system for the assembly of robust polynuclear complexes of uranium(III) and allowed the isolation of the first example of a trinuclear U(III) complex showing magnetic exchange. Notably, the triangular U<sub>3</sub>(μ-O)<sub>6</sub> core of complex **1** results in unusually short U–U distances and an antiferromagnetic coupling between the U(III) centres leading to a non-magnetic ground state. Coordination of 2.2.2-cryptand to one U(III) centre leads

to a rearrangement to the core geometry and suppression of magnetic communication. Preliminary reactivity studies show that complex **1** promotes the reduction of one molecule of dinitrogen in the presence of an external reducing agent. These studies demonstrate the versatility of the silsesquioxane scaffold for assembling polymetallic complexes of low valent uranium that possess unusual properties.

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## Notes and references

- P. L. Arnold, C. J. Stevens, N. L. Bell, R. M. Lord, J. M. Goldberg, G. S. Nichol and J. B. Love, *Chem. Sci.*, 2017, **8**, 3609-3617.
- M. Falcone, L. Chatelain, R. Scopelliti, I. Zivkovic and M. Mazzanti, *Nature*, 2017, **547**, 332-335.
- M. Falcone, L. Barluzzi, J. Andrez, F. F. Tirani, I. Zivkovic, A. Fabrizio, C. Corminboeuf, K. Severin and M. Mazzanti, *Nat. Chem.*, 2019, **11**, 154-160.
- P. L. Arnold, T. Ochiai, F. Y. T. Lam, R. P. Kelly, M. L. Seymour and L. Maron, *Nat. Chem.*, 2020, **12**, 654-659.
- X. Q. Xin, I. Douair, Y. Zhao, S. Wang, L. Maron and C. Q. Zhu, *J. Am. Chem. Soc.*, 2020, **142**, 15004-15011.
- D. R. Hartline and K. Meyer, *Jacs Au*, 2021, **1**, 698-709.
- D. K. Modder, C. T. Palumbo, I. Douair, F. Fadaei-Tirani, L. Maron and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2021, **60**, 3737-3744.
- W. Fang, Q. Zhu and C. Q. Zhu, *Chem. Soc. Rev.*, 2022, **51**, 8434-8449.
- N. Jori, T. Rajeshkumar, R. Scopelliti, I. Zivkovic, A. Sienkiewicz, L. Maron and M. Mazzanti, *Chem. Sci.*, 2022, **13**, 9232-9242.
- X. Q. Xin, I. Douair, Y. Zhao, S. O. Wang, L. Maron and C. Q. Zhu, *Natl. Sci. Rev.*, 2023, **10**, nwac144.
- D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake and S. T. Liddle, *Nat. Chem.*, 2011, **3**, 454-460.
- V. Mougél, L. Chatelain, J. Pécaut, R. Caciuffo, E. Colineau, J. C. Griveau and M. Mazzanti, *Nat. Chem.*, 2012, **4**, 1011-1017.
- L. Chatelain, J. P. S. Walsh, J. Pécaut, F. Tuna and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2014, **53**, 13434-13438.
- L. Chatelain, F. Tuna, J. Pécaut and M. Mazzanti, *Chem. Commun.*, 2015, **51**, 11309-11312.
- D. K. Modder, M. S. Batov, T. Rajeshkumar, A. Sienkiewicz, I. Zivkovic, R. Scopelliti, L. Maron and M. Mazzanti, *Chem. Sci.*, 2022, **13**, 11294-11303.
- J. T. Boronski, J. A. Seed, D. Hunger, A. W. Woodward, J. van Slageren, A. J. Wooles, L. S. Natrajan, N. Kaltsoyannis and S. T. Liddle, *Nature*, 2021, **598**, 72-75.
- X. H. Lin and Y. R. Mo, *Angew. Chem. Int. Ed. Engl.*, 2022, **61**.
- D. L. Clark, J. C. Gordon, J. C. Huffman, J. G. Watkin and B. D. Zwick, *New J. Chem.*, 1995, **19**, 495-502.
- L. Karmazin, M. Mazzanti and J. Pécaut, *Inorg. Chem.*, 2003, **42**, 5900-5908.
- J. L. Kiplinger, J. A. Pool, E. J. Schelter, J. D. Thompson, B. L. Scott and D. E. Morris, *Angew. Chem. Int. Ed. Engl.*, 2006, **45**, 2036-2041.
- W. J. Evans, K. A. Miller, J. W. Ziller and J. Greaves, *Inorg. Chem.*, 2007, **46**, 8008-8018.
- C. P. Larch, F. G. N. Cloke and P. B. Hitchcock, *Chem. Commun.*, 2008, 82-84.
- L. Chatelain, V. Mougél, J. Pécaut and M. Mazzanti, *Chem. Sci.*, 2012, **3**, 1075-1079.
- S. Carretta, G. Amoretti, P. Santini, V. Mougél, M. Mazzanti, S. Gambarelli, E. Colineau and R. Caciuffo, *J. Phys. Chem. C*, 2013, **25**, 486001.
- J. T. Boronski, L. R. Doyle, A. J. Wooles, J. A. Seed and S. T. Liddle, *Organometallics*, 2020, **39**, 1824-1831.
- J. M. Manriquez, P. J. Fagan, T. J. Marks, S. H. Vollmer, C. S. Day and V. W. Day, *J. Am. Chem. Soc.*, 1979, **101**, 5075-5078.
- F. A. Cotton, W. Schwotzer and C. Q. Simpson, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 637-639.
- L. Barluzzi, M. Falcone and M. Mazzanti, *Chem. Commun.*, 2019, **55**, 13031-13047.
- M. Falcone, R. Scopelliti and M. Mazzanti, *J. Am. Chem. Soc.*, 2019, **141**, 9570-9577.
- N. Jori, L. Barluzzi, I. Douair, L. Maron, F. Fadaei-Tirani, I. Zivkovic and M. Mazzanti, *J. Am. Chem. Soc.*, 2021, **143**, 11225-11234.
- S. Giessmann, V. Lorenz, P. Liebing, L. Hilfert, A. Fischer and F. T. Edelmann, *Dalton Transactions*, 2017, **46**, 2415-2419.
- M. K. Assefa, G. Wu and T. W. Hayton, *J. Am. Chem. Soc.*, 2020, **142**, 8738-8747.
- V. Lorenz, A. Edelmann, S. Giessmann, C. G. Hrib, S. Blaurock and F. T. Edelmann, *Z. Anorg. Allg. Chem.*, 2010, **636**, 2172-2191.
- A. R. Willauer, A. M. Dabrowska, R. Scopelliti and M. Mazzanti, *Chem. Commun.*, 2020, **56**, 8936-8939.
- J. Old, A. A. Danopoulos and S. Winston, *New J. Chem.*, 2003, **27**, 672-674.
- V. Mougél, C. Camp, J. Pécaut, C. Coperet, L. Maron, C. E. Kefalidis and M. Mazzanti, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 12280-12284.
- M. Keener, R. A. K. Shivaraam, T. Rajeshkumar, M. Tricoire, R. Scopelliti, I. Zivkovic, A. S. Chauvin, L. Maron and M. Mazzanti, *J. Am. Chem. Soc.*, 2023, **145**, 16271-16283.
- P. Pyykkö, *J. Phys. Chem. A*, 2015, **119**, 2326-2337.
- D. N. Huh, J. W. Ziller and W. J. Evans, *Inorg. Chem.*, 2019, **58**, 9613-9617.
- D. N. Huh, S. R. Ciccone, S. Bekoe, S. Roy, J. W. Ziller, F. Furche and W. J. Evans, *Angew. Chem. Int. Ed. Engl.*, 2020, **59**, 16141-16146.
- D. N. Huh, C. J. Windorff, J. W. Ziller and W. J. Evans, *Chem. Commun.*, 2018, **54**, 10272-10275.
- D. N. Huh, J. M. Barlow, S. R. Ciccone, J. W. Ziller, J. Y. Yang and W. J. Evans, *Inorg. Chem.*, 2020, **59**, 17077-17083.
- C. A. P. Goodwin, S. R. Ciccone, S. Bekoe, S. Majumdar, B. L. Scott, J. W. Ziller, A. J. Gaunt, F. Furche and W. J. Evans, *Chem. Commun.*, 2022, **58**, 997-1000.
- A. B. Chung, D. N. Huh, J. W. Ziller and W. J. Evans, *Inorganic Chemistry Frontiers*, 2020, **7**, 4445-4451.
- D. R. Kindra and W. J. Evans, *Chem. Rev.*, 2014, **114**, 8865-8882.
- D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Science*, 2012, **337**, 717-720.
- J. K. Tang, I. Hewitt, N. T. Madhu, G. Chastanet, W. Wernsdorfer, C. E. Anson, C. Benelli, R. Sessoli and A. K. Powell, *Angew. Chem. Int. Ed. Engl.*, 2006, **45**, 1729-1733.
- L. Ungur, S. Y. Lin, J. K. Tang and L. F. Chibotaru, *Chem. Soc. Rev.*, 2014, **43**, 6894-6905.
- C. Camp, V. Mougél, J. Pécaut, L. Maron and M. Mazzanti, *Chem. Eur. J.*, 2013, **19**, 17528-17540.
- B. Vlasisyljevich, P. L. Diaconescu, W. L. Lukens, Jr., L. Gagliardi and C. C. Cummins, *Organometallics*, 2013, **32**, 1341-1352.
- G. Nocton, P. Horeglad, J. Pécaut and M. Mazzanti, *J. Am. Chem. Soc.*, 2008, **130**, 16633-16645.