The study of paramagnetic compounds based on 4d and 5d transition metals is an emerging research topic in the field of molecular magnetism. An essential driving force for the interest in this area is the fact that heavier metal ions introduce important attributes to the physical properties of paramagnetic compounds. Among the attractive characteristics of heavier elements vis-à-vis magnetism are the diffuse nature of their d orbitals, their strong magnetic anisotropy owing to enhanced spin–orbit coupling, and their diverse structural and redox properties. This critical review is intended to introduce readers to the topic and to report recent progress in this area. It is not fully comprehensive in scope although we strived to include all relevant topics and a large subset of references in the area. Herein we provide a survey of the history and current status of research that has been conducted on the topic of second and third row transition metal molecular magnetism. The article is organized according to the nature of the precursor building blocks with special topics being highlighted as illustrations of the special role of heavier transition metal ions in the field. This paper is addressed to readers who are interested in molecular magnetism and the application of coordination chemistry principles to materials synthesis (231 references).

1. Introduction

Molecular magnetism is a rapidly expanding field of research whose central theme is the design and study of magnetic molecules and materials with tunable properties for use in new types of electronic and magnetic devices.¹-⁶ The obvious importance of conventional solid state materials in current technologies notwithstanding, molecular magnetic materials...
offer key advantages including the fact that they are lightweight, soluble and exhibit multifunctionality.7−11 Furthermore, the discovery and development of single-molecule magnets (SMMs)12−15 and single-chain magnets (SCMs)16,17 has led to the realization of a fascinating intermediate regime between the realms of paramagnetism and long-range ordering and spawned study of a wide range of spin-dynamics. Single Molecule Magnets (SMMs), or molecular nanomagnets to use a broader term, refer to a class of compounds that exhibit superparamagnetic behavior below a blocking temperature \((T_B)\). Specifically, they exhibit magnetic hysteresis of purely molecular origin, thus behaving as "tiny magnets", and other unusual effects such as quantum tunneling of the magnetization. Analogous to SMMs, SCMs are composed of magnetically isolated chains for which a finite magnetization can be frozen in the absence of an applied magnetic field. The relaxation of the magnetization becomes very slow at low temperature such that these systems can then be considered to be real magnets.

The vast majority of molecular magnetic materials in the literature contain paramagnetic transition metal ions as the main spin carriers. First row transition metals have received most of the attention largely because they are easier to handle, both experimentally and theoretically, as compared to their 4d and 5d congeners. Although the wide availability of starting materials and the vast body of literature based on 3d metal ion chemistry render their continued study convenient and relevant, the use of the heavier transition metal ions as "synthons" for the design of magnetic materials offers significant benefits. The recognition of this fact is reflected by the increase in the number of research groups around the world who are participating in the quest for an improved understanding of 4d and 5d element magnetism.

In terms of specific differences between 3d metal ions and the heavier congeners: (i) the heavier metal ions are characterized by more radially extended valence orbitals with the trend being 5d > 4d > 3d; (ii) the 4d and 5d metal ions are characterized by large spin–orbit coupling (SOC) parameters \((\zeta)\); and (iii) these ions are found in a variety of oxidation states and redox events can be triggered photochemically or electronically. In terms of magnetochemistry, the diffuse nature of the 4d and 5d orbitals translates into stronger exchange interactions as a result of a greater spin density shared between the bridging ligand and increased orbital overlap.18 Strong SOC exhibited by these metal ions often leads to highly anisotropic \(g\) factors and unusually large zero-field splitting (ZFS) values; the latter describe various interactions of the energy levels of a spin \((S > \frac{1}{2})\) even in the absence of an applied magnetic field. The ZFS parameter is defined as \(D\) and can be positive or negative.19 Taken together with the anisotropic exchange coupling, the inherent characteristics of these metal ions introduce a high degree of magnetic anisotropy to molecule-based magnets.20−23 The anisotropic exchange coupling is described by the general spin Hamiltonian

\[
\mathbf{H} = -2J_x \mathbf{S}_x \cdot \mathbf{S}_y + J_y \mathbf{S}_y \cdot \mathbf{S}_z + J_z \mathbf{S}_z \cdot \mathbf{S}_x,
\]

where \(J_x = J_y = J_z\) corresponds to the Heisenberg model, \(J_x = J_y = 0, J_z \neq 0\) corresponds to the Ising model, and \(J_x, J_y, J_z \neq 0\). The facile changes in oxidation states and the ability to promote these changes via external stimuli, for example the use of light, to trigger charge transfer reactions, have attracted the attention of researchers in the area of multifunctional materials and produced numerous compounds with intriguing physical properties such as photomagnetism.24

Although it is certainly true that magnetochemistry of the heavier elements has gained momentum in the past decade, considerably more groundwork needs to be laid if we are to make progress in our quest for an improved understanding of their physical properties and the development of reliable models. The synthesis, characterization, and modeling of new magnetic materials with 4d and 5d metal ions provide valuable knowledge about the impact of both SOC and anisotropic exchange on the resulting properties of materials. Ultimately these results will provide the basis for a design strategy for future applications.

In spite of the heightened interest in 4d and 5d molecular magnetism, no general articles on this topic have appeared; the reader is directed, however, to several useful specific reviews of octacyanometallate compounds of the second and third row transition metal ions25−27 and one on magnetic materials based on dinuclear ruthenium paddlewheel complexes.28 Given that this critical review is the first broad treatment of the topic in the literature, the article is written in the spirit of highlighting the importance of 4d and 5d metal ions by providing an overview of the current developments in the field but with no intention to cover all reported results. To help researchers who are interested in, but not very familiar with this field, the starting materials being used by synthetic chemists are listed and discussed in Section 2. Specific topics reflecting the

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Kim R. Dunbar was born in Mount Pleasant, PA, and received a BS degree from Westminster College in 1980 and a PhD from Purdue University in 1984. After a post-doctoral stint at Texas A&M University, she joined the faculty of Michigan State University in 1987 and moved to Texas A&M University in 1999, where she is a Distinguished Professor and holds the Davidson Chair of Science. Her research spans topics in synthetic and structural inorganic chemistry, with a focus on the design of conducting and magnetic molecular materials, supramolecular anion interactions, and the anticancer properties of metal complexes. She is a Fellow of the American Association for the Advancement of Science, and a past Fellow of the Alfred P. Sloan Foundation and a Camille and Henry Dreyfus Teacher–Scholar. She received Distinguished Alumna Awards from Westminster College in 2000 and Purdue University in 2004, and a Distinguished Faculty Award from Michigan State University in 1998. In 2006 she received the Inaugural Distinguished Award for Graduate Mentoring from the Association of Former Students at Texas A&M University. She is an Associate Editor for the ACS journal Inorganic Chemistry and has served as Chair and Secretary of the ACS Division of Inorganic Chemistry.
advantages of the 4d and 5d metal ions are described in more detail in Section 3. Finally, in the conclusions section, an outlook for the future development of this field is provided.

2. Design of 4d and 5d molecular magnets

The coordination chemistry of the 4d and 5d transition metals is richer than that of the 3d series for several reasons. The heavier transition metal ions tend to be stable in higher oxidation states and have a greater predilection than 3d metal ions for exhibiting coordination numbers higher than six. In addition, the 4d and 5d transition metals are prone to forming stable metal–metal bonds, including multiple bonds, which is not common for the 3d metals. Given these characteristics, several possible approaches can be employed to synthesize molecular magnetic materials that contain these heavier metal ions. One straightforward strategy is to combine common starting materials with a suitable ligand that serves as a linker to other spin centers. This approach is not as useful as it is for 3d elements, however, as many of the 4d and 5d metal ions exist as very stable coordination compounds with ligands such as halides that are difficult to substitute. A second strategy involves the successful implementation of what is often referred to as the building block approach. By using appropriately designed starting materials equipped with ligands that are poised to bind to an additional metal center via a second donor atom, one can more easily introduce the 4d and 5d metal ions into assemblies. Given that the majority of 4d and 5d molecular magnetic materials are prepared by this modular method, this section is devoted to introducing the common building blocks used in the field (Fig. 1).

Compounds based on bridging cyanide ligands are the most numerous in the area of 4d and 5d molecular magnetism although there are other useful building blocks based on different ligands as well. The cyanide starting materials will be described according to the increasing number of cyano groups bound to the metal ion. Although we cannot cover all the examples and references due to the large quantity of publications, readers can easily access more information and additional references from the representative references provided.

2.1 Building blocks without cyanide ligands

Starting materials without cyanide ligands comprise two main groups, viz., metal–metal bonded compounds, such as diruthenium [Ru₂] complexes, and oxalates such as the monooxalate [Re IV Cl₄(ox)]²⁻, bis-oxalate [Re IV Cl₂(ox)₂]²⁻, and tris-oxalate [Ru III(ox)₃]³⁻ derivatives or very similar oxygen-donor ligands.

2.1.1 Metal–metal bonded compounds. Metal–metal bonded compounds constitute a large category of possible starting materials for the construction of molecular magnetic materials based on 4d and 5d transition metals. Compounds with the metal cores of the type [M₂]⁵⁺ (M = Mo, W, Re, Ru, Os, Pd) and [M₂]⁶⁺ (M = Os, Ir) configurations, to name a subset, are all possible paramagnetic starting materials. Many of them exhibit a so-called “paddlewheel” structure in which four bidentate bridging ligands are arranged symmetrically around the dimetal unit with weakly coordinated solvent molecules occupying two axial coordination sites. Magnetic materials composed of metal–metal bonded compounds are still relatively rare with the exception of compounds containing [Ru₂] cores which have been found to exhibit unusual properties.28,30

The [Ru₂] precursors are ideal starting materials for the elaboration of multifunctional magnetic materials for two reasons: (i) both redox states of [Ru₂ II,II] (S = 1, ½π₂δ²δ²π⁺) and [Ru₂ II,III] (S = 3/2, ½π₂δ²δ²π⁺) possess unpaired spins due to the near degeneracy of the δ and π* orbitals, and (ii) the complexes are known to undergo oxidation from [Ru₂ II,II] to [Ru₂ II,III] without significant structural rearrangement which bodes well for the construction of charge transfer compounds of intermediate states. One of the main interests in using the [Ru₂] complexes as starting materials is to bridge the paddlewheel units with organic ligands such as N,N'-bidentate ligands (e.g. pyz, 4,4'-bipy, dabco, phz, tmpyz etc.), redox active ligands (e.g. p-quinones: 1,4-bq, 1,4-nq; and organocyanide ligands: TCNE, TCNQ, DCNQI and their derivatives), organic radical ligands (e.g. nitroxide ligands), and cyanometallates such as [Mn III(CN)₆]³⁻, [Fe III(CN)₆]³⁻, [(Tp)Fe III(CN)₆]²⁻, [Cr III(CN)₆]³⁻, and [W IV(CN)₈]³⁻. More details about this fascinating class of compounds will be provided in Section 3.

2.1.2 Oxalatometallates: mono-oxalate [Re IV X₄(ox)]²⁻ (X⁻ = Cl, Br), bis-oxalate [Re IV X₂(ox)₂]²⁻ (X⁻ = Cl, Br), and tris-oxalate [Ru III(ox)₃]³⁻. The oxalate ligand is well known...
for its capability to transmit strong electronic interactions between the magnetic centers when acting as a bridge. The widely investigated oxalato layered materials [M^II][M^III](ox)_3] (A = cation; M = Mn, Fe, Co, Ni, Cu; M' = Cr, Fe) exhibit a variety of interesting physical properties and are useful platforms for introducing multifunctionality.\(^\text{7,37-39}\) Most of the examples come from the 3d metals, however, with corresponding research of the 4d and 5d metal ions being relatively rare. The interesting results to date will be presented and organized according to the number of oxalate ligands present: (i) mono-oxalate [Re^IV*X*2(ox)]\(^2\) (X = Cl, Br), (ii) bis-oxalate [Re^V*X*2(ox)]\(^2\) (X = Cl, Br), and (iii) tri-oxalate [Ru^II*(ox)]\(^3\)

The mono-oxalate anion [Re^IV*Cl*(ox)]\(^2\) was synthesized in 1999 as (Ph_4As)\(^2\)[Re^IV*Cl*(ox)]\(^2\) by Kremer and Faus et al. The central Re^IV ion is in a distorted octahedral geometry with a d\(^3\) configuration (S = 3/2) and a significantly large ZFS parameter (D \approx 60 cm\(^{-1}\)). Armed with this building unit, researchers successfully synthesized and characterized an entire series of magnetic compounds including dinuclear, M^III(dmphen)-[Re^IV*Cl*(ox)]\(^2\)CH_3CN (M = Mn, Fe, Co, Ni),\(^\text{42}\) trinuclear, (Bu_4N)_2[M^III(Him)][Re^IV*Cl*(ox)]\(^2\) (M = Mn, Co, Ni, Cu),\(^\text{43}\) tetranuclear, (Bu_4N)_4[M^III][Re^IV*Cl*(ox)]\(^2\) (M = Mn, Fe, Co, Ni, Cu),\(^\text{44}\) and 1-D (Cu^II(2,2'-bipy)[Re^IV*Cl*(ox)]\(^4\))\(^\text{40}\) and Cu^II(pym)[Re^IV*Cl*(ox)]\(^4\))\(^\text{45}\) compounds. Generally, antiferromagnetic coupling is observed for {M^II–Re^IV} pairs and ferromagnetic coupling is dominant for the {M^II–Re^IV} pairs when M is Fe^II, Co^II, and Ni^II. For Cu^II complexes, the magnetic exchange interactions depend on the geometry. Interestingly, the magnetic anisotropy of the Re^IV center leads to the observation of SMM behavior for all of the {M^II–Ru^III} compounds. Long range magnetic ordering was observed for several of them, with c values up to 13 K (Fig. 3b).

Apart from these interesting results, two series of compounds were reported.\(^\text{51}\) Later, Coronado et al. reported a fascinating new series of hybrid organometallic–inorganic layered magnets, (Z^III(Cp*)\(_2\))M^III[Ru^III*(ox)]\(_3\) (Z = Co and Fe; M = Mn, Fe, Co, Cu, Zn).\(^\text{52}\) All of these materials were characterized by X-ray powder diffraction, the results of which indicated that the compounds are composed of 2-D anionic hexagonal honeycomb layers with M^III ions bridged to Ru^III centers via oxalate bridges with counter cations located between the layers (Fig. 3a). Although Kahn proposed an antiferromagnetic interaction for the {Fe^II–Ru^III} and {Cu^II–Ru^III} pairs and ferromagnetic exchange for the {M^II–Ru^III} pair, Coronado and coworkers were able to rationalize ferromagnetic interactions for all of the {M^II–Ru^III} compounds. Long range magnetic ordering was observed for several of them, with T_c values up to 13 K (Fig. 3b).

Apart from these interesting results, two series of compounds were reported as [M^II(en)]\(_3\)Ru^III*(ox)]\(_3\)Cl\(_3\) and [M^II(2,2'-bipy)]\(_3\)-[Ru^III*(ox)]\(_3\)Cl\(_3\) (M = Ni, Cu) were reported with no structural...
A weak antiferromagnetic interaction was observed between the RuIII and CuII spin centers.53 In addition to the aforementioned starting materials there are some other potentially useful building blocks without cyanide ligands, such as \([\text{Ru}^{III}(\text{ox})_2(\text{acac})_2]^+\), \([\text{Ru}^{III}(\text{salen})(\text{CN})_2]^+\), \([\text{Os}^{III}(\text{salen})(\text{CN})_2]^+\), \([\text{Re}^{IV}\text{Cl}_4(\text{CN})_2]^2^-\). These four building units contain two trans-cyanide groups that can bridge two other metal centers. In these anions, the metal centers are in a distorted octahedral environment with an \(S = \frac{1}{2}\) spin state for RuIII and OsIII, and an \(S = 3/2\) spin state for ReIV. The first of these anions, \((\text{Ph}_4\text{P})[\text{Ru}^{III}(\text{acac})_2(\text{CN})_2]\), along with the heteronuclear 3-D ferromagnet, \((\text{Mn}^{II})[\text{Ru}^{III}(\text{acac})_2(\text{CN})_2]\) (Fig. 4), was synthesized and reported by Gao and Lau in 2001.63 Subsequently more compounds containing 3d metal ions (MnII, MnIII, CoII, NiII, CuII) as well as lanthanide information. A weak antiferromagnetic interaction was observed between the RuIII and CuII spin centers.53

In addition to the aforementioned starting materials there are some other potentially useful building blocks without cyanide ligands, such as \([\text{Ru}^{III}(\text{ox})_2(\text{acac})]^+\), \([\text{Ru}^{III}(\text{ox})(\text{acac})_2]^+\), \([\text{Ru}^{III}(\text{ox})_2(\text{H}_2\text{O})_2]^+\), \([\text{Ru}^{III}(\text{ox})_2\text{III,III,IVO}_3(\text{ox})_6]^2^-\), \([\text{Re}^{IV}\text{Cl}_3(\text{pyz})]^+\), \([\text{Ru}^{III}(\text{salen})(\text{PPh}_3)\text{Cl}]\), among others.54–57 These compounds will not be covered in further detail in this review.

### 2.2 Cyanometallate building blocks

Cyanometallate precursors offer a number of distinct advantages for the design of molecular magnets.58–62 They are generally stable in solution, the oxidation number and spin states of the metal can be controlled, the nature of magnetic coupling (ferromagnetic versus antiferromagnetic) is typically predictable, and the structures can be controlled by introducing specific capping ligands on one or more of the metal complex starting materials. Not surprisingly, cyanometallates are the most common building units being used in the field of 4d and 5d molecular magnetism. In this section we briefly review the common cyanometallate building blocks according to the number of cyanide ligands bound to the metal center. One major point that emerges after a perusal of the literature is that the chemistry of the 4d and 5d cyanometallate anions is more complex than that for the 3d ions. Many of the heavier element cyanide compounds are sensitive to oxygen, water, heat and/or light. Consequently, special precautions are required when working with these materials.

#### 2.2.1 Building blocks with two cyanide ligands: \(\text{trans-}[\text{Ru}^{III}(\text{acac})_2(\text{CN})_2]^+\), \(\text{trans-}[\text{Ru}^{III}(\text{salen})(\text{CN})_2]^+\), \(\text{trans-}[\text{Os}^{III}(\text{salen})(\text{CN})_2]^+\), \(\text{trans-}[\text{Re}^{IV}\text{Cl}_4(\text{CN})_2]^2^-\)

These anions contain two trans-cyanide groups that can bridge two other metal centers. In these anions, the metal centers are in a distorted octahedral environment with an \(S = \frac{1}{2}\) spin state for RuIII and OsIII, and an \(S = 3/2\) spin state for ReIV. The first of these anions, \((\text{Ph}_4\text{P})[\text{Ru}^{III}(\text{acac})_2(\text{CN})_2]\), along with the heteronuclear 3-D ferromagnet, \((\text{Mn}^{II})[\text{Ru}^{III}(\text{acac})_2(\text{CN})_2]\) (Fig. 4), was synthesized and reported by Gao and Lau in 2001.63 Subsequently more compounds containing 3d metal ions (MnII, MnIII, CoII, NiII, CuII) as well as lanthanide

![Fig. 3](image-url) (a) The 2-D hexagonal layer of the \((\text{Z}^{III}\text{Cp}\ast_2)\text{M}^{II}[\text{Ru}^{III}(\text{ox})_3]\) compounds with \((\text{Z}^{III}\text{Cp}\ast_2)^+\) cations located between the layers, and (b) plots of the \(\chi_M T\) vs. \(T\) and the ac susceptibility data (inset) for \((\text{CoCp}\ast_2)\text{Fe}^{II}[\text{Ru}^{III}(\text{ox})_3]\) which indicate magnetic ordering. Reprinted with permission from ref. 52. Copyright 2001 Elsevier.

![Fig. 4](image-url) (a) The 3-D diamondoid network of \(\text{M}^{II}[\text{Ru}^{III}(\text{acac})_2(\text{CN})_2]^2\) (M = Mn, Co) and (b) a depiction of the double interpenetration for the 3-D networks.
ions (Gd$^{III}$, Tb$^{III}$, Dy$^{III}$, Er$^{III}$) were synthesized using these ruthenium building blocks. Among the new compounds are trinuclear complexes ([Mn$^{III}$Ru$^{III}$-salen]) and ([Ni$^{II}$Ru$^{III}$-acac]), 64 1-D chains ([Ni$^{II}$Ru$^{III}$-2-acac]), 65-66 [M$^{III}$Ru$^{III}$-acac] (M = Mn$^{III}$, Fe$^{III}$), 66 [M$^{III}$Ru$^{III}$-acac] (M = Co, Ni), 66 and ([Mn$^{III}$Ru$^{III}$-salen]), 67 2-D layers ([Ln$^{III}$Ru$^{III}$-acac]), 68 Ln = Gd, Tb, Dy, Er, and ([Mn$^{II}$Ru$^{III}$-2-salen]), and 3-D interpenetrated networks ([Co$^{II}$[Ru$^{III}$acac)]$_2$CN)$_2$) (Fig. 4). 64,69 In addition, the Os$^{III}$ analogue, (Ph$_4$P)$_2$Os$^{III}$[salen]) is reported recently by the Long group. 70 Magnetic data revealed that the superexchange interactions between Ru$^{III}$/Os$^{III}$ and the 3d/4f metal centers are relatively weak. Ferromagnetic interactions were observed for most of the reported compounds, except for two Mn$^{II}$ derivatives (the trinuclear complex {Mn$^{II}$Ru$^{III}$-salen}) and the 2-D layered material {Mn$^{II}$Ru$^{III}$-salen}) and one {Ni$^{II}$Ru$^{III}$-2-acac} chain. 65 None of the low-dimensional compounds exhibit long range ordering, whereas the 3-D compounds of Mn$^{II}$ and Co$^{II}$ are ferromagnets at low temperatures.

Turning now to the unusual trans-[Re$^{IV}$Cl$_4$(CN)$_2$]$_2$– anion, the synthesis of (nBu$_4$N)$_2$[Re$^{IV}$Cl$_4$(CN)$_2$]DMF and a series of cyanide-bridged 1-D compounds Mn$^{II}$[DMF$_2$][Re$^{IV}$Cl$_4$(CN)$_2$] (M = Mn, Fe, Co, Ni) were reported by the Long group (Fig. 5). 71 The {Mn$^{III}$-N=C-C-Re$^{IV}$} pair exhibits antiferromagnetic coupling with all the other metal ion combinations leading to ferromagnetic interactions. Interestingly, due to the strong anisotropy of the Re$^{IV}$ ion, all of these materials behave as SCMs (Fig. 5). A fitting of the reduced magnetization data for the starting material ([nBu$_4$N]$2$[Re$^{IV}$Cl$_4$(CN)$_2$]DMF revealed a ZFS parameter of $D = -14.4$ cm$^{-1}$, the largest value reported to date for a cyanide complex. The g value was fit to a value of 1.66. These remarkable properties are a direct consequence of the considerable SOC exhibited by the Re$^{IV}$ center.

Very recently, the same group reported another 1-D compound ([nBu$_4$N]$2$[Cu$^{II}$-Tp][Re$^{IV}$Cl$_4$(CN)$_2$]) and (b) the field dependent magnetization data at different temperatures, showing the metamagnetic transition. The $n$Bu$_4$N$^+$ cations were omitted for the sake of clarity. Reprinted with permission from ref. 72. Copyright 2011 American Chemical Society.

![Fig. 5](image-url) (a) The 1-D chain of Mn$^{II}$[DMF$_2$][Re$^{IV}$Cl$_4$(CN)$_2$] (M = Mn, Fe, Co, Ni) and (b) and (c) the ac susceptibility data for the [Mn$^{II}$-Re$^{IV}$] compound showing the SCM behavior. The inset shows the Arrhenius plot of the relaxation time. The solid line corresponds to a linear fit to the data, giving $\Delta_\chi = 31$ cm$^{-1}$. Reprinted with permission from ref. 71. Copyright 2010 American Chemical Society.
2.2.2 Building blocks with three cyanide ligands: fac-Mo$^{III}$(Me$_3$tacn)(CN)$_3$, fac-[Re$^{II}$(triphos)(CN)$_3$]$_4^-$, and mer-[Ru$^{III}$(CN–sap)(CN)$_3$]$_2^{2-}$. The metal centers in both fac-Mo$^{III}$(Me$_3$tacn)(CN)$_3$ and fac-[Re$^{II}$(triphos)(CN)$_3$]$_4^-$ are in a slightly distorted octahedral environment with three fac-cyanide ligands, a situation that renders them ideal for the synthesis of cube molecules, although other types of architectures are also possible. Due to the strong SOC effects introduced by the Mo$^{III}$ ion in 2003 by Dunbar and coworkers. The Re$^{II}$ ion is in the meridional arrangement. These compounds include {Ni$^{II}$(triphos)(CN)$_3$}$_2^-$, {Ni$^{II}$(cyclam)(H$_2$O)}$_2^-$, and {Ni$^{II}$(cyclam)(Me$_3$tacn)Mo$^{III}$(CN)$_3$}$_2^-$-

In addition, the first cyanide-bridged SMM {Mn$^{II}$(Me$_3$tacn)Mo$^{III}$(CN)$_3$}$_3$(ClO$_4$)$_3$) was also reported (Fig. 7). Ferromagnetic interactions were observed for the {Ni$^{II}$–N=C–Mo$^{III}$} pairs and antiferromagnetic coupling was noted for the {Mn$^{II}$–N=C–Mo$^{III}$} pair. The {Ni$^{II}$(Me$_3$tacn)Mo$^{III}$(CN)$_3$}$_3$ and {Mn$^{II}$(Me$_3$tacn)Mo$^{III}$(CN)$_3$}$_3$ clusters, which will be discussed in a later section, are excellent illustrations of the fact that the incorporation of the 4d Mo$^{III}$ ion increases both the magnetic interaction and the magnetic anisotropy of the clusters.

The synthesis and magnetic properties of the 5d metal ion phosphine precursor (Et$_4$N)[Re$^{II}$(triphos)(CN)$_3$] were reported in 2003 by Dunbar and coworkers. The Re$^{II}$ ion is in the S = 1/2 ground state and experimental as well as theoretical studies revealed a very large temperature independent paramagnetism (TIP) resulting from strong SOC ($\lambda = 2000$–3000 cm$^{-1}$). Reaction of this building unit with 3d metal ions produced the series of compounds (M$^{III}$)$_4$(Re$^{II}$(triphos)(CN)$_3$)$_4$ (M = Mn, Co, Ni, Zn; X = Cl$^-$, Br$^-$, CH$_3$O$^-$) (Fig. 8).

These {M$^{III}$Re$^{II}$_4$} clusters exhibit a distorted cubic structure with alternating octahedral Re$^{III}$ and tetrahedral M$^{III}$ corners. A ferromagnetic interaction was found for the {Ni$^{II}$–N=C–Re$^{III}$} pair with all other analogues being dominated by antiferromagnetic interactions. Most importantly, the {M$^{III}$Re$^{II}$_4$} compound exhibits SMM behavior (Fig. 8b), one of the early examples for cyanide-based paramagnets. In addition to the magnetic properties, the redox activity of the Re$^{II}$ ion gives rise to an electron-transfer in the case of the reaction with Fe$^{III}$Cl$_2$. The resulting [Fe$^{II}$Re$^{I}$_4$] product with diamagnetic Re$^{II}$ ions exhibits remarkable electrochemistry with eight reversible or quasi-reversible redox events being observed in the cyclic voltammogram (Fig. 8c).

In terms of further chemistry, the {M$^{III}$Re$^{II}$_4$} compounds offer great potential as they are soluble, remain intact in solution and can be modified for use as SBUs (secondary building units). For example, a solvated derivative of the {M$^{III}$Re$^{II}$_4$} compound was used to prepare a network of SMMs. Specifically, the reaction of a solvated {M$^{III}$Re$^{II}$_4$} derivative with LiTCNQ resulted in a 1-D compound with {M$^{III}$Re$^{II}$_4$} cubes being bridged by σ-dimerized TCNQ (Fig. 9). The material is formulated as [M$^{III}$(TCNQ–TCNQ)(M$^{III}$(HTCNQ)(CH$_3$OH))]-[Re$^{III}$(triphos)(CN)$_3$]$_4$. Interestingly, the SMM behavior of the {M$^{III}$Re$^{II}$_4$} cube is retained in the 1-D chain.

Finally, the mer-[Ru$^{III}$(CN–sap)(CN)$_3$]$_2^{2-}$ (S = 1/2) precursor was recently reported by Gao and Lau et al., in which a Ru$^{III}$ center is located in a distorted octahedral geometry with three cyanide ligands in a meridional arrangement. Reaction of this building unit with Mn$^{III}$ or Co$^{III}$ ions afforded two isostuctural 1-D ladder compounds M$^{III}$(MeOH)$_3$-[Ru$^{III}$(CN–sap)(CN)$_3$]$_2$MeOH (M = Mn$^{III}$, Co$^{III}$) (Fig. 10).
isolated as the salt \((\text{Ph}_4\text{P})_3[\text{Mo}^3(\text{CN})_3(\text{NO})]\). The reported effective magnetic moment is 1.96 \(\mu_B\) which corresponds to a low spin \(d^5\) configuration with \(S = \frac{3}{2}\). A solid state EPR study on the anion diluted with \(K_2[\text{Co}^{III}(\text{CN})_6]\) provided values of \(g_{||} = 1.97\) and \(g_{\perp} = 2.02\). To the best of our knowledge, only one molecular magnet based on this unit, namely \(\text{K}_0.9\text{Mn}^{II}_0[\text{Mo}^1(\text{CN})_3(\text{NO})]\).5H_2O.1.9MeOH, is known, synthesized from the \textit{in situ} oxidation of \(\text{K}_4[\text{Mo}^0(\text{CN})_6(\text{NO})]\).2H_2O. This product exhibits a face-centered cubic structure reminiscent of Prussian blue phases and undergoes ferromagnetic ordering at 39 K.

### 2.2.5 Building blocks with six cyanide ligands: \([\text{M}^{III}(\text{CN})_6]^3–\) (\(M = \text{Mo, Ru, Os}\)) and \([\text{W}^{IV}/\text{V}(2,2\text{‘-bipy})(\text{CN})_6]^{2–}\). The larger ionic radius of the 4d and 5d metal ions as compared to the 3d ions leads to coordination numbers greater than six in many cases. In fact, the \([\text{M}^{III}(\text{CN})_6]^3–\) (\(M = \text{Mo, Ru, Os}\)) starting materials and molecular magnets based on them are quite rare. One issue that is important to note about these trivalent species is that they are known to be unstable both in the solid state and in solution. The \(\text{Mo}^{III}\) center is easily oxidized to \(\text{Mo}^{IV}\) by trace amounts of oxygen and the \([\text{M}^{III}(\text{CN})_6]^3–\) (\(M = \text{Ru, Os}\)) species are fairly unstable in water and reduce easily, especially in the case of Ru. These anions have received considerable attention from theorists due to their promising magnetic properties. The similarity of these anions to well investigated 3d congeners, especially \([\text{Fe}^{III}(\text{CN})_6]^3–\), is a topic of obvious interest for synthetic chemists as well. The reasons for the attention are simple: (i) the structures and properties of the final products can be predicted given the extensive knowledge of the 3d cyanometallate chemistry; (ii) the octahedral geometry of the metal center simplifies theoretical modeling compared to the cases with lower symmetries; and (iii) the octahedral geometry preserves the orbital degeneracy of the metal centers (for \(\text{Ru}^{III}\) and \(\text{Os}^{III}\)), which results in strong magnetic anisotropy.

The \([\text{Mo}^{III}(\text{CN})_6]^3–\) anion remained an elusive species until 2002 when Long and Beauvais reported the synthesis and structural characterization of \(\text{Li}_3[\text{Mo}^{III}(\text{CN})_6]\).6DMF. The molecule is nearly of \(O_h\) symmetry with the \(\text{Mo}^{III}\) center being in a \(t_{2g}\) electron configuration (\(S = 3/2\)). A theoretical study by Ruiz et al. in 2005 led to the prediction that the super-exchange between the \([\text{Mo}^{III}(\text{CN})_6]^3–\) anion and the early 3d metal centers (\(\text{V}^{III}, \text{Cr}^{III}\) through the cyanide ligand should be very strong and that Prussian blue phases based on these metal ion combinations may exhibit critical temperatures higher than the well-known \(\text{V}^{III}/\text{Cr}^{III}\) and \(\text{Cr}^{II}/\text{Cr}^{III}\) derivatives (552 K for \(\text{V}^{III}/\text{Mo}^{III}\) and 308 K for \(\text{Cr}^{III}/\text{Mo}^{III}\)). It was not until 2009, however, that a polynuclear complex based on this cyanometallate was reported. The molecule \([\text{V}^{III}(\text{PY5Me2})_2-\text{[Mo}^{III}(\text{CN})_6]^{2–}\text{(PF}_6\text{)}_3\text{]}\) with a star-like \(\text{V}^{III}\text{Mo}^{III}\) core (Fig. 11) exhibits unusually strong antiferromagnetic coupling between the \(\text{V}^{III}\) and \(\text{Mo}^{III}\) ions with a \(J = -61\) cm\(^{-1}\) albeit not as strong as what was predicted. In 2010, Dunbar et al. reported two pentanuclear \([\text{M}^{III}_2\text{Mo}^{III}_2]\) complexes containing the \([\text{Mo}^{III}(\text{CN})_6]^3–\) anion, \([\text{M}^{II}(\text{tmphen})_2]\text{[Mo}^{III}(\text{CN})_6]\text{(solvent)}\) (\(M = \text{Co, Ni}\)) (Fig. 12) by unexpected displacement of a cyanide ligand from the \([\text{Mo}^{III}(\text{CN})_6]^3–\). The molecules exhibit a trigonal bipyramidal (TBP) structure with two axial...
2H₂O was reported to be prepared in water and its crystal structure and magnetic properties investigated. The low spin d⁵ (Fe, Ni, M₀) M=Fe, Ni, M⁰=Mo, W V center strongly influences the magnetic coupling. It was found that ferromagnetic interaction is operative for the (Co II–N₁–Mo III) pair and that antiferromagnetic coupling occurs for the compounds with the [Mn II–N₁–Co II] pair. As for the [Mn II–N₁–M₀–Co II] pairs, both ferro- and antiferromagnetic couplings are observed. The collective results to date indicate that the [W V(2,2'-bipy)(CN)₆]³⁻ anion is very promising for entry in molecular magnets, especially for the synthesis of low-dimensional materials.

2.2.6 Building units with seven cyanide ligands: [Mo III(CN)₆]³⁻ and [Re IV(CN)₇]³⁻. The [Mo III(CN)₆]³⁻ and [Re IV(CN)₇]³⁻ anions exhibit a pentagonal bipyramidal geometry with five equatorial and two axial cyanide ligands. The low symmetry engendered by this geometry as compared to the octahedron.

No molecular materials based on [Ru III(CN)₆]³⁻ have been reported to date.

The chemistry of the [Os III(CN)₆]³⁻ anion has a similar history to that of the [Ru III(CN)₆]³⁻ anion. Despite the successful synthesis of (Bu₄N)[Os III(CN)₆] in 1968,¹⁰⁰ the anion was only recently structurally characterized and its magnetic properties investigated as the (Ph₅P)₃[Os III(CN)₆]·6H₂O salt.¹⁰¹ The Os III ion exhibits a very large SOC constant (λ = ±2900 cm⁻¹ for the ground state) with a t₂₉ electronic configuration (S = ½).¹⁰² The theoretical studies reported by Mironov indicate that the [Os III(CN)₆]³⁻ anion is of particular interest for the elaboration of high blocking temperature SMMs.¹⁰³ As of late 2010, there are only a few examples of materials based on this building block, including two trigonal bipyramidal clusters [Mo III(tmphen)₂][Os III(CN)₆]₂:(solvent) (M = Fe, Ni),¹⁰³,¹⁰⁴ two Prussian blue phases M=Fe, Ni,¹⁰³,¹⁰⁵ and one trinuclear complex (Et₄N)₂Mn III(5-Brasalen)₃(MeOH)·[Os III(CN)₆]·6H₂O.¹⁰⁶ The [Ni₃O₃II₃] molecule will be discussed later in more detail. The [Fe III(OH)₃] complex exhibits a reversible temperature and charge transfer induced spin transition centered at room temperature whose origin is a transformation from the Fe LS to the Fe HS state.¹⁰⁴ The Prussian blue phase Ni₃[Os III(CN)₆]₃ behaves as a ferromagnet with a Tc = 6.2 K.¹⁰³ The Co III[Os III(CN)₆]₂:6H₂O material exhibits interesting magnetic properties including photomagnetism, the details of which are included in a later section.¹⁰⁵ The trinuclear (Mn IIIII₃O₃) compound is the first SMM based on the [Os III(CN)₆]³⁻ unit.¹⁰⁶

The anion [W V(2,2'-bipy)(CN)₆]⁻, which contains six cyanide ligands but is eight coordinate due to the additional 2,2'-bipy ligand, was first reported and characterized as the (Ph₅As)[W V(2,2'-bipy)(CN)₆]·4H₂O polymeric material.¹¹¹ The geometry around the W V center strongly influences the magnetic coupling. It was found that ferromagnetic interaction is operative for the (Co I–N≡C–Wo V) pair and that antiferromagnetic coupling occurs for the compounds with the [Mn II–N≡C–Wo V] pair. As for the [Mn II–N≡C–Co II–Wo V] pairs, both ferro- and antiferromagnetic couplings are observed. The collective results to date indicate that the [W V(2,2'-bipy)(CN)₆]⁻ anion is very promising for entry in molecular magnets, especially for the synthesis of low-dimensional materials.

[Mo III(CN)₆]³⁻ units connected to three equatorial Co III or Ni III units. Ferromagnetic interactions were observed for both the [Co III–N≡C–Mo III] and [Ni III–N≡C–Mo III] pairs.

Unlike the [Mo III(CN)₆]³⁻ anion which was only recently prepared, the existence of the [Ru III(CN)₆]³⁻ anion was documented nearly sixty years ago.⁹⁵,⁹⁶ The salts (Et₂N)₂[Ru III(CN)₆] and (But₄N)₂[Ru III(CN)₆]₂·2H₂O were reported to be prepared in water and its crystal structure and magnetic properties investigated.⁹⁹ The low spin d⁵ (S = ½) Ru III ion is in a slightly distorted octahedral geometry due to an expected Jahn–Teller distortion and g = 1.95. Density functional theory (DFT) calculations led to the prediction of significantly higher spin densities on the cyanide ligands for the [Ru III(CN)₆]³⁻ anion as compared to [Fe III(CN)₆]³⁻, indicating the potential of the [Ru III(CN)₆]³⁻ anion for engendering stronger magnetic interactions with metal-based spin centers through the bridging cyanide ligand.
of the [MnII(H2O)2]3– anions results in a high degree of anisotropy, rendering them important targets for incorporation into large molecules and extended phases. Experimental studies on the materials based on these anions remain relatively scarce, however, due to the synthetic challenges involved in their preparation and handling.

During the period from 1932, when the preparation of K4[MoIII(CN)7]2H2O was first reported,115 to 1998, when Kahn et al. published the first molecular magnet based on [MoIII(CN)7]4–,116,117 studies were mainly focused on the physical properties of the anion. The MoIII center is in a low-spin d3 electronic configuration (S = 1/2 in an approximate D3h geometry) with a highly anisotropic g factor (g⊥ = 3.89 and g∥ = 1.77 for NaK3[MoIII(CN)7]2H2O).118 The [MoIII(CN)7]4– anion favors low symmetry structures which may induce anisotropy in the dipolar interactions. Furthermore, the magnetic interaction between the 3d metal ions and the MoIII center is predicted to have a significant anisotropic component due to the SOC of the MoIII ion. Theoretical investigations suggest that [Mo(CN)7]4– may be useful for the design of high Tb SMMs as a result of its strong anisotropic exchange.20

Despite such promising predictions, magnetic materials based on [Mo(CN)7]4– remain elusive, with the exception of the work of Kahn et al. and subsequent studies by several other groups who prepared a number of 2-D and 3-D magnets with [MoIII(CN)7]4– and MnII ions: 2-D compounds include K4[MoIII(H2O)2][MoIII(CN)7]2-6H2O,119,120 and [MnIII(dpdp)]2-[MoIII(CN)7][MoIV(CN)6]116,117,122,123 19.5H2O;121 and 3-D networks include MnII(H2O)6[MoIII(CN)7]nH2O (n = 4, α phase),116,117,122,123 n = 4.75, β phase),117,124 (Me4N)2[MnIII(H2O)2][MoIII(CN)7]12-2H2O,125 (NH4)2MnII(H2O)6[MoIII(CN)7]2-4H2O,126 MnIII(α-pass)–[MoIII(CN)7]nH2O (n = 0, 2,127 MnIII[MoIII(Hdman)]2-[MoIII(CN)7]2-2H2O (n = 0, 2,128 and MnIII2[MoIII(CN)7](pm)2-2H2O).129 These studies have revealed that the magnetic interaction between the {MnII–N–C–MoIII} pairs is antiferromagnetic and that the extended frameworks typically show long range ordering with Tc values ranging from 40 to 106 K. The compounds K4[MoIII(H2O)2][MoIII(CN)7]2-6H2O and MnII2(H2O)3-[MoIII(CN)7]nH2O (n = 4, α phase; n = 4.75, β phase) were completely characterized, including studies of the anisotropic magnetic measurements of single crystals, DFT calculations, and neutron diffraction experiments. More details on the 3-D α phase MnII2(H2O)3[MoIII(CN)7]4H2O will be provided in the next section.

Another interesting compound is the material MnII[MnII(Hdman)]2[MoIII(CN)7]2-2H2O. The compound exhibits a cyanide-bridged 3D Mn–Mo network in which each MoIII center is linked to six MnII ions and each MnII is connected to four MoIII units (Fig. 14a). By using the chiral ligand Hdman, the material can be obtained as a racemic mixture or as a chiral R- or S-enantiomer. A magnetic sponge effect, wherein the magnetic ordering temperature can be switched by the absorption/desorption of guest molecules, was observed. The magnetic ordering temperature is reversibly switched from 85 K upon dehydration and rehydration (Fig. 14b).

Apart from the MnII containing derivatives, the only other studies are those that reported an amorphous compound with FeII and two microcrystalline materials with VII and NiII.129–131 No structural information for the FeII compound was provided but it has been proposed to have the formula FeII2[MoIII(CN)7]·8H2O and reported to be a magnet.

Fig. 13 The 1-D chain of the compound [MnIII(npsalcn)]–-[WV(2,2′-bipy)(CN)6]·H2O.

Fig. 14 (a) The 3-D structure of the compound MnII[MnII(Hdman)]2[MoIII(CN)7]2-2H2O and (b) the M–T curves of the dehydrated and rehydrated materials indicating the reversible changes in the critical temperatures. Reprinted with permission from ref. 128. Copyright 2007 American Chemical Society.
below 75 K.\textsuperscript{130} The Ni\textsuperscript{II} compound exhibits ferromagnetic ordering with a $T_c = 28$ K and the V\textsuperscript{II} compound exhibits the highest $T_c$ value (110 K) for any [Mo\textsuperscript{III}(CN)]\textsuperscript{4–} based magnet.\textsuperscript{129,131}

Very recently, Dunbar and Wang \textit{et al.} reported the first discrete polynuclear complex based on the [Mo(CN)]\textsuperscript{7–} anion, \textit{viz.}, an anionic nanosized docosanuclear \{Mn\textsuperscript{II}Mo\textsuperscript{III}\}_{10} complex, [Mn\textsuperscript{II}dpop(H2O)]\textsubscript{10}–[Mn\textsuperscript{II}dpop](H2O)[Mo\textsuperscript{III}(CN)\textsubscript{6}]\textsubscript{6}–H2O (Fig. 15).\textsuperscript{132} The large [Mn\textsuperscript{II}Mo\textsuperscript{III}\textsubscript{10}] complex consists of a buckled Mn\textsubscript{6}Mo\textsubscript{6} loop spanned by two Mn\textsuperscript{II}Mo\textsuperscript{III} crosslinks and four terminal Mn\textsuperscript{II} units situated along the perimeter of the molecule. If one includes the terminal Mn\textsuperscript{II} units, the complex is approximately 3.0 × 3.5 nm, which is the largest cyanide-bridged molecule known to date and with the most paramagnetic centers (22) among the cyanide-bridged polynuclear complexes. The antiferromagnetic interaction between the \{Mn\textsuperscript{II}–N}R\textsuperscript{C–Mo\textsuperscript{III}} pairs leads to a ground state spin value of $S = 31$ which is the highest known value for cyanide bridged compounds and is among one of the highest for any molecules including the oxide family.

Although the diamagnetic species [Re\textsuperscript{III}(CN)]\textsuperscript{4–} was prepared and structurally verified long ago,\textsuperscript{133} the paramagnetic [Re\textsuperscript{IV}(CN)]\textsuperscript{3–} anion was not known until 2003 when it was reported as the (Bu\textsubscript{4}N)n[Re\textsuperscript{IV}(CN)]\textsubscript{3} salt.\textsuperscript{134} As in the case of [Mo\textsuperscript{III}(CN)]\textsuperscript{4–} analog, the spectral and magnetic analyses of the [Re\textsuperscript{IV}(CN)]\textsuperscript{3–} anion are in accord with a low-spin d\textsuperscript{3} ground state ($S = \frac{3}{2}$); the average $g$ value is reported to be 2.33. The EPR spectrum at 20 K revealed strong anisotropy with $g_{||} = 3.66$ and $g_{\perp} = 1.59$. Although (Bu\textsubscript{4}N)n[Re\textsuperscript{IV}(CN)]\textsubscript{3} is fairly stable in air both in the solid state and in nonprotic solvents, a spontaneous one-electron reduction can occur as in the case of the 3-D framework Mn\textsuperscript{II}$_2$(H2O)$_2$[Re\textsuperscript{IV}(CN)]\textsubscript{3}·3H2O, which contains the diamagnetic [Re\textsuperscript{III}(CN)]\textsuperscript{4–} unit. Synthesis at low temperature ($\sim -40$ °C) prevented the reduction of the Re\textsuperscript{IV} ion and led to the successful isolation of the pentanuclear \{Mn\textsuperscript{II}Re\textsuperscript{IV}\} complex [Mn\textsuperscript{II}(PY5Me2)$_2$][Re\textsuperscript{IV}(CN)\textsubscript{3}](PF$_6$)$_5$·6H2O which exhibits SMM behavior (Fig. 16).\textsuperscript{135}

The molecular structure of the \{Mn\textsuperscript{II}Re\textsuperscript{IV}\} complex is that of a star-like motif with a central [Re\textsuperscript{IV}(CN)]\textsuperscript{3–} unit connected via cyanide bridges (two axial and two equatorial) to four Mn\textsuperscript{II} centers. Very recently the same authors reported the detailed studies of these star-like molecules with the more electron-rich metal ions (Co\textsuperscript{II}, Ni\textsuperscript{II}, Cu\textsuperscript{II}), a strategy that is aimed at stabilizing the Re\textsuperscript{IV} ion with respect to undesired reduction.\textsuperscript{136} Indeed, the stable [Ni\textsuperscript{II}Re\textsuperscript{IV}]\textsubscript{5} cluster was successfully obtained at room temperature. In the case of the Co\textsuperscript{II} reaction, an intramolecular Co\textsuperscript{II} to Re\textsuperscript{IV} charge transfer accompanies the formation of the cluster to give rise to a \{Co\textsuperscript{II}Co\textsuperscript{II}Re\textsuperscript{III}\} species. The situation for Cu\textsuperscript{II} is similar to what was observed for the Mn\textsuperscript{II} ion in that a one-electron reduction was observed to give the \{Cu\textsuperscript{II}Re\textsuperscript{IV}\} pentanuclear complex at room temperature, but the \{Cu\textsuperscript{II}Re\textsuperscript{IV}\} compound is obtained at low temperatures. Ferromagnetic coupling, strong uniaxial magnetic anisotropy, and slow magnetic relaxation were observed for the \{Ni\textsuperscript{II}Re\textsuperscript{IV}\} and \{Cu\textsuperscript{II}Re\textsuperscript{IV}\} compounds.

2.2.7 Building blocks with eight cyanide ligands: [M\textsuperscript{IV}(CN)\textsubscript{8}]$^{2–/3–}$ (M = Mo, W), [Nb\textsuperscript{IV}(CN)\textsubscript{8}]$^{5–/4–}$, [Re\textsuperscript{IV}(CN)\textsubscript{8}]$^{3–}$ . The octacyanometallate anions [M(CN)\textsubscript{8}]$^{n–}$ can be divided into two groups, the paramagnetic ([M\textsuperscript{IV}(CN)\textsubscript{8}]$^{3–}$ (M = Mo, W) and [Nb\textsuperscript{IV}(CN)\textsubscript{8}]$^{5–}$) and diamagnetic ([M\textsuperscript{IV}(CN)\textsubscript{8}]$^{4–}$ (M = Mo, W), [Nb\textsuperscript{IV}(CN)\textsubscript{8}]$^{5–}$ and [Re\textsuperscript{IV}(CN)\textsubscript{8}]$^{3–}$) analogues, respectively. The paramagnetic anions are in the $S = \frac{3}{2}$ ground state and have been used extensively for the preparation of molecular magnets. The diamagnetic species are of special importance, however, as they exhibit interesting photomagnetic phenomena, especially for the Mo and W analogs; the Nb and Re octacyanometallates are much less studied. Detailed results of the magnetic materials based on the octacyanometallates, with a focus on Mo\textsuperscript{IV}/W\textsuperscript{IV}, will not be provided here since excellent reviews have been published and the reader is directed to these papers for details.\textsuperscript{25–27}

The [M\textsuperscript{IV}(CN)\textsubscript{8}]$^{4–/3–}$ (M = Mo, W) starting materials have been isolated as a variety of salts of general formula $A_n$[M\textsuperscript{IV}(CN)\textsubscript{8}] (A = K\textsuperscript{+}, Cs\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, Me\textsubscript{2}N\textsuperscript{+}, Et\textsubscript{3}N\textsuperscript{+},

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig15.png}
\caption{(a) The [Mn\textsuperscript{II}Mo\textsuperscript{III}$_2$] anion in the compound ([Mn\textsuperscript{II}dpop]$_{10}$–[Mn\textsuperscript{II}dpop](H2O)$_2$)[Mo\textsuperscript{III}(CN)\textsubscript{6}]$_6$ and (b) the field dependent magnetization and the hysteresis loop at 1.8 K. The line represents a fit to the Brillouin function. Reprinted with permission from ref. 132. Copyright 2010 Wiley-VCH Verlag GmbH & Co. KGaA.}
\end{figure}
precursors. In addition, unusual 4d-4d' materials were obtained from reactions of the [W^V(CN)_8]^{3-} anion with the [Ru_2] starting materials. 36

A leading example of the use of a family of cyanide building blocks to prepare high spin molecules is the series of compounds that adopt a pentadecanuclear six-capped body centered cubic structure of general formula \([M^{V-M}_{900}, C_{123}H_{2014}, 143] \quad \text{Co}^{II}\left[\text{Co}^{II}(\text{CH}_3\text{OH})_3\right]_{8-}[\text{W}^V(CN)_8]_{6-}\text{DMF}_{148}\] The SMM behavior of the latter compound was confirmed by the fact that it exhibits frequency dependent ac signals and that hysteresis loops appear at low temperatures (Fig. 17). The superexchange is antiferromagnetic for the \([\text{Co}^{III}-\text{N} \equiv \text{C} \equiv \text{M}^0\]) pair and ferromagnetic for the \([\text{Ni}^{II}-\text{N} \equiv \text{C} \equiv \text{W}^V\]) pair, the result of which is the ground state of 21/2 and 12 for the [Mo^{V}W^{V}_{6}] and [Ni^{II}W^{V}_{6}] compounds, respectively. Furthermore, these \([\text{Mo}^{V}W^{V}_{6}]) complexes can be modified by replacing one or three of the \([\text{Mo}^{V}W^{V}_{6}]) centers for diamagnetic Rev centers. The lowering of the symmetry of the molecule by the substitution, however, does not lead to an overall increase in the magnetic anisotropy. 149 Also, these \([\text{Mo}^{V}W^{V}_{6}]) complexes can be used as building blocks for the larger extended magnetic networks, as demonstrated by a 2-D square grid layer with [Mo^{V}W^{V}_{6}] connected by 4,4'-bipy ligands. 146

Rich magnetic behavior including SMM, SCM, long range magnetic ordering, and multifunctional properties have been observed for materials based on the [M(CN)_8]^{3-} precursors. It is important to note that it is not trivial to predict the type or magnitude of the magnetic coupling between the \([\text{Mo}^{V}W^{V}_{6}]) centers and the 3d metal ions without careful and accurate analyses of structural details. The exchange interactions are strongly dependent on the geometry of \([\text{Mo}^{V}W^{V}_{6}]) centers. Owing to the stereochemical non-rigidity of the [M(CN)_8]^{3-} anions, these octacyanometallate species easily interconvert between three different geometries, viz., the square antiprism (SAP, \(D_{4h}\)), dodecahedron (DD, \(D_{2d}\)), and bicapped trigonal prism (TPR, \(C_{2v}\)) (Fig. 1). These symmetries translate to very different d orbital arrangements that directly affect the overlap of magnetic orbitals. Moreover, the different orientations and bridging modes for the cyanide ligands significantly influence the magnetic coupling as a result of the spin density on the C and N atoms which depends on their exact positions in the

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**Fig. 16** (a) The structure of the \([\text{Mn}^{II}Rev^V]) complex, \([\text{Mn}(\text{PySMe}_2)]_{4-}[\text{Re}^{III}(\text{CN})_7])^{5-}\) and (b) the out-of-phase signal of the ac susceptibility data in the zero dc field which indicates SMM behavior. Reprinted with permission from ref. 135. Copyright 2008 American Chemical Society.

"Bu_3N^+\), H Bu_3N^+ etc.). The cations play an important role in the chemistry since they influence the solubility of the anions in aqueous and organic solvents. Before the use of \([\text{M}^{IV-V}(\text{CN})_8]^{2+/3-} \quad (M = \text{Mo}, \text{W})\) anions as building blocks for extended structures in the 1990’s, the studies focused primarily on the structural, spectroscopic, redox, and photochemical properties of these anions. The research has garnered much more attention in the past decade and blossomed into an active area of molecular magnetism. 25-27

Two main strategies are used to control the dimensionality of networks based on the octacyanometallates. Reactions with cations equipped with capping groups including solvent and chelating ligands lead to lower dimensional structures and the use of ancillary bridging ligands (in addition to the “built-in” cyanide bridges) leads to increased dimensionality architectures. A wide variety of topologies and magnetic properties have been documented when these building units are combined with 3d (\([\text{Mn}^{III}, \text{Fe}^{III}, \text{Co}^{II}, \text{Ni}^{II} \text{and Cu}^{II}\]) and 4f metal cationic structures.
coordination sphere. For example, in the DD configuration, the CN groups located on vertices B possess noticeably larger spin density values than those located on vertices A. Theoretical approaches, including DFT and molecular field theory, were used to estimate the sign and the magnitude of the magnetic coupling parameters. The spin density on the cyanide groups, and thus the magnetic coupling through these bridges, has been found to vary from DD_{site} > SAP > DD_{site} (Fig. 18). This trend was further confirmed by experimental results in various series of compounds.

In contrast to the widely investigated anions $[\text{M}^\text{V}(\text{CN})_8]^{3-}$ ($\text{M} = \text{Mo}, \text{W}$), the Group 5 $[\text{Nb}^\text{IV}(\text{CN})_8]^{4-}$ analog is relatively underexplored. The reported synthesis of $\text{K}_4[\text{Nb}^\text{IV}(\text{CN})_8]_2$ involves the electrolytic reduction of $\text{Nb}^{\text{V}}\text{Cl}_5$ to $\text{K}_5[\text{Nb}^{\text{III}}(\text{CN})_8]$ using a mercury-pool cathode and further reduction (Fig. 17). $\text{K}_4[\text{Nb}^\text{IV}(\text{CN})_8]_2$ (3pyCH$_2$OH)$_2[\text{Nb}^\text{IV}(\text{CN})_8]_2.15\text{H}_2\text{O}$ and various 3-D networks ($\text{Mn}^\text{II}(\text{pyz})_2[\text{Nb}^\text{IV}(\text{CN})_8]_2\text{pyz}\cdot3\text{H}_2\text{O}$, $\text{Mn}^\text{II}(\text{pzdo})_2(\text{H}_2\text{O})_4[\text{Nb}^\text{IV}(\text{CN})_8]_2.5\text{H}_2\text{O}$, $\text{Mn}^\text{II}(\text{bpym})(\text{H}_2\text{O})_3[\text{Nb}^\text{IV}(\text{CN})_8]_3$, $\text{Mn}^\text{II}(\text{Him})_2(\text{H}_2\text{O})_4[\text{Nb}^\text{IV}(\text{CN})_8]_4$-$4\text{H}_2\text{O}$, $\text{Mn}^\text{II}(\text{pyz})(\text{H}_2\text{O})_4[\text{Nb}^\text{IV}(\text{CN})_8]_4\text{H}_2\text{O}$, and $\text{Mn}^\text{II}(\text{pyrazole})_2[\text{Nb}^\text{IV}(\text{CN})_8]_4\text{H}_2\text{O}$) are all known from chemistry involving the $[\text{Nb}^\text{IV}(\text{CN})_8]^{4-}$ anion. One 3-D compound with $\text{Mn}^\text{II} - \text{L} - \text{[Nb}^\text{IV}(\text{CN})_8]$ repeat units where $\text{L}$ represents a secondary bridging ligand such as pyz, pzdo, bpym, imidazole, pyrazole, etc. The magnetic coupling in the $[\text{Mn}^\text{II}\text{N}_3\text{C} - \text{C} - \text{N}^\text{V}]$ pair is antiferromagnetic, leading ultimately to ferrimagnetic ordering for the 3-D networks with the $T_c$ values ranging from 27 to 62 K. Interestingly, magnetization-induced secondary harmonic generation (MSHG), which is a nonlinear magneto-optical effect in which the second harmonic generation can be modified by the magnetization, was observed for the 3-D ferrimagnet, $\text{Mn}^\text{II}(\text{pz})_2[\text{Nb}^\text{IV}(\text{CN})_8]_2.4\text{H}_2\text{O}$ (Fig. 19). The electric polarization is along the $b$-axis and the magnetic easy axis is located along the $c$-axis (Fig. 19b). The SH intensity rapidly increases near the ordering temperature (48 K) due to spontaneous magnetization (Fig. 19c).
subset of the fascinating results in the literature, we aim to demonstrate the importance of this area of molecular magnetism and inspire newcomers to the field.

3.1 Diffuse orbitals with increased overlap

One of the lessons learned from studying 3d cyanide magnetism is that strong magnetic coupling is crucial for the enhancement of ordering temperatures of a magnet and for achieving an isolated ground state for magnetic molecules with improved SMM behavior. Stronger magnetic coupling is expected as a result of the radial extension of the valence orbitals for 4d and 5d metal ions. Despite the plethora of reports of 4d and 5d magnetic materials that have accumulated in the literature over the past decade, theoretical and experimental evidence for increased magnetic coupling with the replacement of a 3d metal for a 4d or 5d metal in a compound with otherwise identical composition and structure is limited. This situation is presumably related to the complexity of computational studies and the more challenging chemistry associated with the heavier elements in a given group. Nevertheless, there are key examples that support the contention of enhanced magnetic coupling with the substitution of heavier metal centers as described in this section.

The first series of compounds that we will describe are composed of the building blocks \([\text{M}^\text{III}(\text{Me}_3\text{tacn})(\text{CN})_3]^-\) (\(\text{M} = \text{Cr}, \text{Mo}\)) which were used to form trinuclear \([\text{Ni}^\text{II}M^\text{III}]_3^\text{3}\) and heptanuclear \([\text{M}^\text{III}M^\text{III}]_7^\text{0}\) (\(\text{M} = \text{Cr}, \text{Mo}\)) complexes.\(^{76,77}\) For the linear trinuclear species, substitution of Mo for Cr clearly leads to stronger magnetic exchange coupling by as much as 60\% (\(J_{\text{Ni-Cr}} = 10.9\ \text{cm}^{-1}\) vs. \(J_{\text{Ni-Mo}} = 17.6\ \text{cm}^{-1}\)). For the “star-like” heptanuclear complexes, the increase of the magnetic exchange interaction is also evident (\(J_{\text{Mo-Cr}} = -3.0\ \text{cm}^{-1}\) vs. \(J_{\text{Mo-Mo}} = -6.7\ \text{cm}^{-1}\)). The enhancement of the super-exchange for the Mo cyanide bridged molecules has been confirmed by DFT calculations.\(^{165}\)

In the case of the hexacyanometallates \([\text{M}^\text{III}(\text{CN})_6]^\text{3}^-\) (\(\text{M} = \text{Cr}, \text{Mo}; \text{or Fe}, \text{Ru}, \text{Os}\)), an increase in magnetic coupling for the heavier congeners is supported by both theoretical and experimental data. Four years before the first report of the \([\text{Mo}^\text{III}(\text{CN})_6]^\text{3}^-\) containing heteronuclear complex, a theoretical study led to the prediction that the Mo ion would lead to stronger antiferromagnetic coupling as compared to the Cr analogues,\(^{18}\) a contention that was later confirmed experimentally with the synthesis of the \([\text{Cr}^\text{III}(\text{CN})_6]^\text{3}^-\) pentanuclear molecule \([\text{Cr}^\text{III}(\text{CN})_6]^\text{3}^-\) (\(\text{M} = \text{Mo}, \text{W}\)) building units have appeared in the literature but functional examples of photochemically driven magnetic properties for such materials remain rare. Key examples of such photomagnetic compounds are presented in the next section.

3. Special topics

In the previous sections of the article, we delineated the commonly used 4d and 5d precursors and briefly described their fundamental magnetic properties. This section focuses on special topics discussed in more detail in order to underscore the intrinsic characteristics of materials with second and third row transition metal centers. Specifically, three key features of the chemistry and physics of these materials are emphasized, viz., the diffuse nature of the 4d and 5d orbitals, their inherent anisotropy, and their rich redox properties. By highlighting a
strongly anisotropic with \( J_{\text{Ni-Ox}}^{\text{Ni}} = 23.8 \) cm\(^{-1}\) and \( J_{\text{Ni-Ox}}^{\text{Ni}} = 1.2 \) cm\(^{-1}\).\(^{103,167}\) Increased magnetic coupling for the 5d \([\text{Os}^{	ext{III}}(\text{CN})_3]^3^−\) anion is also observed for the very recently reported trinuclear compounds \([\text{Mn}^{	ext{II}}\text{M}^{	ext{III}}] (\text{M} = \text{Fe}, \text{Os}) (J_{\text{Mn-Ox}}^{\text{Mn}} = −15.3 \) cm\(^{-1}\) and \( J_{\text{Mn-Ox}}^{\text{Mn}} = 0 \) cm\(^{-1}\) versus \( J_{\text{Mn-Fe}}^{\text{Mn}} = −2.9 \) cm\(^{-1}\) and \( J_{\text{Mn-Fe}}^{\text{Mn}} = −1.6 \) cm\(^{-1}\).\(^{106}\)

Finally, we turn to compounds based on \([\text{M}^\text{IV}(\text{CN})_6]^3^−\) (\( \text{M} = \text{Mo, W} \)). We mention here two sets of compounds that deserve a comment in this context: the trinuclear complexes \([\text{Ni}^{	ext{II}}\text{M}^{	ext{V}}] (\text{M} = \text{Mo, W}) \).\(^{168}\) Regardless of the nature of the magnetic coupling (ferromagnetic for the \([\text{Ni}^{	ext{II}}\text{N} \equiv \text{C} \equiv \text{M}^{	ext{V}}] \) pair and antiferromagnetic for the \([\text{Mn}^{	ext{III}}\text{N} \equiv \text{C} \equiv \text{M}^{	ext{V}}] \) pair), the strength of the magnetic coupling increases when the 4d ion \( \text{Mo}^\text{V} \) is replaced with the 5d ion \( \text{W}^\text{V} \). For the \([\text{Ni}^{	ext{II}}\text{N} \equiv \text{C} \equiv \text{M}^{	ext{V}}] \) cases, DFT calculations were employed in an attempt to understand the nature of the magnetic coupling and a marked increase in the magnetic coupling was found when the \( \text{Mo}^\text{V} \) ion is substituted with \( \text{W}^\text{V} (J_{\text{Ni-Mo}} = 13.5 \) cm\(^{-1}\) and \( J_{\text{Ni-W}} = 18.7 \) cm\(^{-1}\)).\(^{151}\)

### 3.2 Magnetic anisotropy of 4d and 5d based materials

One of the most important attributes of the 4d and 5d metal ions is their high degree of magnetic anisotropy, which can arise from both the local and global origin. The local anisotropy encompasses both the \( g \) factor anisotropy and the ZFS, whereas the global factors include anisotropic exchange interactions, the antisymmetric interaction (Dzyaloshinsky–Moriya interaction, whose Hamiltonian takes the form \( H = −D_{ij} \langle S_i \times S_j \rangle \)) with \( D_{ij} \) being the DM vector, which leads to a noncollinear spin structure with the energy being minimized when two adjacent spins are perpendicular to each other).\(^{169−171}\) The anisotropic dipolar interaction and the shape anisotropy (for a non-spherical material, the demagnetizing field depends on the direction of magnetization and will not be equal for all directions, thereby creating the anisotropy).\(^{172}\)

The \( g \) factors for the 4d and 5d metal centers are often highly anisotropic and the \( D \) values for some of the starting materials are significantly higher than those found for 3d metal ions. Moreover, anisotropic interactions for the 4d and 5d metal centers, resulting from the synergistic effect of the local SOC and the interaction between the excited states and ground states of the ion and adjacent ions, become more important since SOC increases significantly as the metal ions go from 3d to the 4d and 5d shells. The spin–orbit coupling is proportional to \( Z_{\text{eff}} \) (\( Z_{\text{eff}} \) is the effective atomic number) and the \( \lambda \) of the 4d and 5d ions is approximately 1000 cm\(^{-1}\) or higher. Therefore, the more generalized Hamiltonian \( H = −2D \langle S_i, S_j \rangle + J_{\text{S}^1 \text{S}^2 +} \) \( J_{\text{S}^1 \text{S}^2} \) is used to interpret the experimental results.

The following section is devoted to the discussion of three magnetic problems closely related to the magnetic anisotropy: (i) the anisotropic long-range ordered magnets, (ii) SMMs and SCMs that exhibit magnetic bistability and slow magnetic relaxation, and (iii) for comparison sake, lanthanide containing systems with the highest anisotropy. A brief summary of the current state of the research in the area and representative examples of each topic are provided.

#### 3.2.1 Anisotropy and long-range magnetic ordering

Although most of the 4d and 5d magnets exhibit magnetic anisotropy, carefully documented evidence must be obtained for an improved understanding of the effects. To better investigate and understand the anisotropy, magnetic measurements performed on oriented single crystals are necessary, as these data relate directly to intrinsic properties of the materials including the anisotropy type (easy-axis or easy-plane), field induced spin-flip, or spin-reorientation phase changes along one specific axis, and even detailed magnetic phase diagrams.

Unfortunately, well-shaped single crystals that are sufficiently large for such measurements are difficult to obtain. The following compounds are several rare examples of 4d and 5d magnetic materials for which magnetic data on single crystals have been reported: the \([\text{Mn}^\text{III}(\text{salen})\text{H}_2\text{O}]\text{[W}^\text{V}(\text{CN})_6]\text{H}_2\text{O} \) tetranuclear complex,\(^{173}\) 2-D-(tetrenH\(_5\))\(_0.8\text{Cu}^\text{II}\)\(_a\)\(_2\text{H}_2\text{O} (n = 4, \phi \text{ phase); } n = 4.75, \beta \text{ phase}),\(^{116,122,124}\) 2-D-KMn\(_{\text{III}}\text{H}_2\text{O} (\text{Mo}^\text{III}(\text{CN})_7)\text{2H}_2\text{O}, \text{119}\) and the 3-D architectures Mn\(_{\text{III}}\text{pyz}(\text{H}_2\text{O})\text{[Nb}^\text{V}(\text{CN})_8]\)\(_4\)\(_2\text{H}_2\text{O}\),\(^{159,160}\) and Mn\(_{\text{III}}\text{pyz}(\text{H}_2\text{O})\text{[W}^\text{V}(\text{CN})_8]\)\(_2\text{H}_2\text{O} \).\(^{175}\)

The 3-D material Mn\(_{\text{III}}\text{H}_2\text{O} (\text{Mo}^\text{III}(\text{CN})_7)\) (4H\(_2\)O) \( (\phi \text{ phase}) \) is an excellent illustration of the power of single-crystal magnetic measurements (Fig. 20).\(^{116,122}\) This compound exhibits a 3-D structure in which bent ladders composed of edge-sharing “lozenge” motifs (MoCNMnNC)\(_2\) that propagate along the \( a \) direction and are linked further along the \( b \) and \( c \) directions (Fig. 20a and 20b). Magnetic data were measured along the three crystallographic directions \( a, b, \) and \( c \), which were confirmed as being the magnetic axes by the angular magnetization (Fig. 20c). On the basis of the detailed magnetic data the authors were able to establish a magnetic phase diagram that consists of four domains (Fig. 20d).

#### 3.2.2 SMMs and SCMs containing 4d and 5d ions

Single molecule magnets are of great interest to the molecular magnetism community due to their inherently unusual quantum magnetic properties and potential applications in spintronics and quantum computing.\(^{12−15}\) A SMM is characterized by the presence of an energy barrier \( U \) to the reversal of its magnetization below a particular blocking temperature \( T_B \) which, in the canonical case, is governed by the molecular ground state spin value \( S \) and the easy-axis anisotropy parameter, a negative axial zero-field splitting parameter, \( D \), \( (U = |D|S^2 \text{ for integer spin systems}) \).\(^{12}\) At initial glance one is tempted to conclude that the magnitudes of the \( |D| \) and \( S \) values are independent and that it should be possible to control either \( |D| \) or \( S \) values to increase the \( U \). It has been pointed out, however, that the two parameters are intimately connected such that \( |D| \) decreases as \( S \) increases.\(^{176,177}\) This scenario appears to be supported by the fact that SMMs with higher \( T_B \) have not been found for molecules with higher \( S \) values and that even relatively small ground state spin values with higher \( |D| \) values are capable of behaving as SMMs. Clearly 4d and 5d metal containing molecules with
higher anisotropy are logical targets for the pursuit of high \( T_B \) SMMs.

Currently, there are only a few compounds that contain 4d and 5d metal ions reported to exhibit SMM behavior; the abbreviated formulae for these molecules are \{CoII WIV ReV\}, \{NiII MoVI\}, \{NiII WVI\}, \{CuII TBIV MoV\}, \{NiII WIV\}, \{NiII WIV\}, \{NiII MoVI\}, \{NiII TBIV\}, \{NiII TBIV\}, \{CuII TBIV MoV\}, \{MII CrIII\} (M = Mn, Ni, Cu) exhibit SMM behavior which are anisotropic. These predictions proved to be accurate magnetic interactions with 3d metal centers in a trigonal bipyramidal arrangement with the \{NiII ReIV\} (M = Mn, Ni, Cu) exhibit SMM behavior which are anisotropic.

Apart from the two aforementioned heptacyanometallates, the orbitally degenerate \{OsIII(CN)6\}3– anion is also predicted to exhibit a strongly anisotropic magnetic exchange interaction with 3d metal centers in a trigonal bipyramidal arrangement (with the \{OsIII(CN)6\}3– units residing in the axial positions). Such compounds were promoted as prototypes for the discovery of new generations of high \( T_B \) SMMs.21 The calculations indicate that the \{CrIII OsIII\}2 and \{MnIII OsIII\}2 pentanuclear species are the most promising candidates for SMMs. It was also pointed out that the \{NiII OsIII\}2 compound would not be an SMM since its ground state would be a singlet. It was further predicted that the magnetic interaction for \{NiII N≡C–OII\} pair would be ferromagnetic and strongly anisotropic. These predictions proved to be accurate by the recent isolation and structural characterization of the \{NiII OsIII\}2 TBP molecule in our laboratories.103,167 Magnetic measurements and theoretical analyses of the \{NiII OsIII\}2 TBP revealed ferromagnetic coupling and an anisotropic interaction (\( J_{+} = 23.8 \text{ cm}^{-1} \) and \( J_{=} = 1.2 \text{ cm}^{-1} \)), and, as predicted, the compound does not behave as an SMM.103,167 As a matter of fact, the first SMM compound based on the \{OsIII(CN)6\}3– unit, viz., ((EtN)[NiII(5-Brsalen)(MeOH)]2–[OsIII(CN)6]), was reported very recently.166 Interestingly, this compound exhibits higher blocking temperatures than those observed for the isoostructual compound with the [FeIII(CN)6]3– unit. It is logical to assume that the enhanced properties stem from the stronger anisotropic magnetic interaction for the \{MnIII N≡C–OsIII\}2 pair as compared to the \{MnIII N≡C–OsIII\}2 pairs. 

Given the complicated nature of magnetic anisotropy and the difficulty in modeling such systems, additional theory and experiments are needed to establish guiding principles. It should be pointed out, however, that theoretical studies have already provided the chemistry community with insights into the design of possible high \( T_B \) SMMs with 4d and 5d metal ions. Specifically, theory has identified the anisotropic exchange interaction as a key player in determining the barrier height of the SMMs. In one example, Mironov et al. reported that the MoIII–C≡N–MnII superexchange pathway is extremely anisotropic for the \{MoIII(CN)7\}4– ion; the interaction can be described by an Ising-like spin Hamiltonian \( H = -2J_{\text{Mo–O}}S_{\text{Mo}}S_{\text{O}} \) for the apical pairs and by the \( H = -2J_{\text{Mo–O}}S_{\text{Mo}}S_{\text{O}} + J_{\text{ex}}S_{\text{Mo}}S_{\text{O}} + S_{\text{Mo}}S_{\text{O}} \) for the equatorial pairs. The highly anisotropic spin–spin couplings combined with large exchange parameters represent a very important source of the global magnetic anisotropy for polynuclear magnetic complexes. As a result, the \( U \) values of the magnetic clusters may become quite large—even several hundred wavenumbers. The same argument holds true for the 5d cyanometallate analog \{ReIV(CN)7\}3–, for which the exchange coupling and anisotropy would further increase since the SOC of the Re ion is considerably greater than that of Mo (\( k_{\text{Re}} = 2000–2500 \text{ cm}^{-1} \) vs. \( k_{\text{Mo}} = 600–1000 \text{ cm}^{-1} \)). Experimentally, the \{ReIV(CN)7\}3– based pentanuclear complexes \{MII ReIV\} (M = Mn, Ni, Cu) exhibit SMM behavior which is the characteristic behavior of an SMM, it must be noted that the barriers, \( U \), are quite small (12 to 48 \text{ cm}^{-1} \). Nevertheless, the increased anisotropy of the clusters due to the inclusion of 4d or 5d metal ions clearly promotes SMM behavior, as evidenced by the compound \{MnII CrIII\} which is isoostructural to the \{MnII MoVI\} analogue and has the same ground state spin \( S = 13/2 \), but does not exhibit any sign of SMM behavior owing to the smaller anisotropy of the CrIII as compared to the MoIII ion.29

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Fig. 20 (a) Ladder architecture composed of edge-sharing motifs running along the a direction for the \( \gamma \) phase \( \text{MnII}_3(\text{H}_2\text{O})_6\text{MoVI(CN)}_{12} \times 4\text{H}_2\text{O} \), (b) the 3-D network depiction of the compound emphasizing the connections of the ladders through C4–N4 groups, (c) the \( M–T \) curves along the \( a, b \) and \( c^* \) axes, and (d) the \( H–T \) magnetic phase diagram of the compound which consists of four domains. Reprinted with permission from ref. 122. Copyright 1998 American Chemical Society.
compared to the SMMs, with only several compounds having been reported thus far; these are compounds based on the fundamental metal units: \([\text{M}^{11}\text{Re}^{11}V]\) (\(\text{M} = \text{Mn, Fe, Co, Ni}\)),\(^{71}\) \([\text{Fe}^{11}\text{Nb}^{11}V]\), \([\text{Mn}^{11}\text{Mo}^{11}V]\), \([\text{Mn}^{11}\text{W}^{11}V]\), \([\text{Mn}^{11}\text{W}^{11}V]\), \([\text{Mn}^{11}\text{W}^{11}V]\),\(^{113}\) \([\text{Cu}^{11}\text{Dy}^{11}\text{Mo}^{11}V]\).\(^{182}\) In the case of \([\text{Mn}^{11}\text{Re}^{11}V]\), the source of the anisotropy is clearly the 5d \(\text{Re}^{11}V\) center since the \(\text{Mn}^{11}\) ion is isotropic.\(^{71}\) The origin of the properties is questionable for the other compounds, however, because they also contain another anisotropic metal center such as \(\text{Dy}^{11}V\), \(\text{Mn}^{11}V\), and \(\text{Fe}^{11}V\). It is obvious that more studies of 1-D compounds based on \([\text{Re}^{11}V(\text{CN})_{6}]^{2}\)-, \([\text{Mo}^{11}V(\text{CN})_{6}]^{2}\)- and \([\text{Os}^{11}V(\text{CN})_{6}]^{2}\)- are required to shed more light on the role of the 4d and 5d ions in SCM behavior.

### 3.2.3 Compounds with 4d or 5d metal ions combined with rare earth metals

The rare earth ions are well known for their magnetic properties which arise from the intrinsic nature of the shielded 4f orbitals as well as their strong unquenched orbital angular momenta and SOC (\(\bar{J}\) values from 600 to 3000 cm\(^{-1}\)). These characteristics make the lanthanide ions very interesting subjects but also very difficult to model and understand.\(^{183,184}\) The combination of the anisotropy from both the 4f and 4d or 5d metal ions is thus very attractive for the elaboration of anisotropic magnetic materials. Compounds containing both 4f and 4d or 5d materials can be organized into two main categories, namely the 4d/5d-4f bimetallic and the 3d-4d/5d-4f trimetallic systems. Most of these compounds are based on the building unit \([\text{M}^{11}\text{V}(\text{CN})_{6}]^{2}\) (\(\text{M} = \text{Mo, W}\)) with the exception of a few examples with \([\text{Ru}^{11}(\text{acac})_{2}(\text{CN})_{6}]^{2}\) and \([\text{Ru}^{11}I_{2}(\text{CO})_{4}]^{2}\).\(^{188-185}\)

In the case of 4d-4f and 5d-4f bimetallic materials, the compounds are of general composition \(\text{Ln}^{11}\text{(L)}-\text{[M}^{11}\text{V(CN)}_{6}\text{]}^{2}\), where \(\text{L}\) is an ancillary ligand such as DMF, DMA, \(\text{H}_{2}\text{O}\), \(\text{NO}_{3}\), \(\text{pzam, terpy} etc.\)\(^{186-195}\) For the 3d-4d/5d-4f trimetallic species, including the series \(\text{[M}^{11}\text{II}-\text{Lu}^{11}\text{II}-\text{M}^{11}\text{V}^{11}\text{]}^{2}\) (\(\text{M}^{11} = \text{Ni, Cu}; \text{Ln} = \text{La, Gd, Tb, Dy, Ho, Er}; \text{M}^{11} = \text{Mo, W}\)) (Fig. 21), the compounds were prepared in a stepwise fashion by first forming the stable 3d-4f molecular assemblies before introducing the additional 4d or 5d metal building blocks.\(^{178,182,196-198}\) The ligands spanning the 3d and 4f centers contain mixed \(\text{[N}_{2}\text{O}_{3}]\) coordination spheres for the 3d ions and \(\text{[O}_{2}\text{O}_{2}]\) ligand sets well-suited for the coordination requirements of 4f ions (Fig. 21a). Not surprisingly, the magnetic interactions are generally quite weak and the critical temperature for long range ordering, if observed at all, is very low.

Although the weak exchange of lanthanide ions with other spin centers through bridges is a disadvantage of 4f element magnetism, it is pointed out that the magnetic anisotropy can be finely tuned by the 4f ions as demonstrated by the following examples. The series \(\text{Ln}^{11}\text{(pzam)3(}H_{2}\text{O)}[\text{Mo}^{11}(\text{CN})_{6}]\cdot H_{2}\text{O}(\text{Ln} = \text{Nd, Gd, Tb, Dy, Ho, Er})\) \(\text{[M}^{11}(\text{CN})_{6}]^{2}\) and \(\text{[Mo}^{11}(\text{CN})_{6}]^{2}\) sub-units (Fig. 22a).\(^{190,193,198}\) Ferromagnetic interactions were observed for \(\text{[Nd}^{11}\text{II} \equiv \text{C} \equiv \text{Mo}^{11}\) \(\text{]} \) and \(\text{[Tb}^{11}\text{II} \equiv \text{C} \equiv \text{Mo}^{11}\) \(\text{]} \) pairs and an antiferromagnetic interaction occurs in the \(\text{[Gd}^{11}\text{II} \equiv \text{C} \equiv \text{Mo}^{11}\) \(\text{]} \) pair. Long range ordering was observed only in the cases of the \(\text{[Gd}^{11}\text{Mo}^{11}\) \(\text{]} \) \((T_{c} = 0.7 \text{ K})\) and \(\text{[Tb}^{11}\text{Mo}^{11}\) \(\text{]} \) \((T_{c} = 1.0 \text{ K})\) compounds. Importantly for this discussion, the three different lanthanide ions introduce different levels of anisotropy. For the isotropic \(\text{Gd}^{11}\) containing compound, a ferrimagnetic Heisenberg chain model works well to model the magnetic data. For the \(\text{Nd}^{11}\text{Mo}^{11}\) material, the exchange coupling between the \(\text{Nd}^{11}\) (effective spin \(S = \frac{7}{2}\)) and the \(\text{Mo}^{11}\) spin \((S = \frac{3}{2})\) is found to approximate an XY (planar) anisotropy. Finally, for the \(\text{Tb}^{11}\text{Mo}^{11}\) compound, the \(\text{Tb}^{11}\) magnetic moment is treated as an effective spin of \(S = \frac{7}{2}\) with a uniaxial Ising-type \(g\) tensor \((g_{\|} = 10\) and \(g_{\perp} = 0)\). The field dependent magnetization and the heat capacity data are well described by an Ising \(S = \frac{7}{2}\) chain model (Fig. 22b).

### 3.3 Applications based on the rich redox properties of 4d and 5d metal ions

As a further illustration of the rich chemistry of 4d and 5d metal ions we now turn to two special applications of the redox properties of the 4d and 5d metal ions that are attracting a great deal of attention: (i) the study of multifunctional magnetic materials involving \(\text{[Ru}^{2}\) building units and (ii) the investigation of 4d and 5d photomagnetic compounds.

#### 3.3.1 Applications of \(\text{[Ru}^{2}\) building units to molecular magnetism

In recent years, the trend of using metal-metal bonded dinuclear complexes as building blocks to form extended networks has opened up a new realm of possibilities for multifunctional materials research. The fact that they can be equipped with a multitude of ligand types and their ability to form stable, open-shell species render metal–metal bonded...
compounds suitable precursors. This strategy has been used to prepare metal organic frameworks with interesting optical, magnetic, and conducting properties. The properties are a reflection of two characteristics of second and third row metal–metal bonded transition metal complexes; specifically, they possess diffuse molecular orbitals that are capable of engaging in back-donation with π orbitals of the organocyanide ligand to effect strong magnetic coupling and their redox chemistry can be tuned readily by subtle changes in the bridging ligands due to their close HOMO/LUMO levels. Among the systems that have been investigated, key examples are charge transfer molecules (Fig. 23), but it exhibits long range magnetic ordering below 95 K. Even more interesting are the reactions of [Ru₂(OC₂Ph-x-F)₄](THF)₂ (x = m, o, and p) with BDTA-TCNQ which result in three networks polymers: 3-D [Ru₂(OC₂Ph-x-F)₄](BDTA-TCNQ)·1.6(CH₂Cl₂, 2-D [Ru₂(OC₂Ph-x-F)₄](BDTA-TCNQ)·4CH₂Cl₂ and 2-D [Ru₂(OC₂Ph-x-F)₄](BDTA-TCNQ)·2CH₂Cl₂·2(4-chlorotoluene). The magnetic properties of this type of material can be easily tuned by adjusting the redox chemistry of both the [Ru₂] donors and the organic acceptors. An excellent illustration of this point is the combination of [Ru₂(O₂CPh-x-F)₄](THF)₂ (x = m, o, and p) with the TCNQ derivatives (TCNQF₄, TCNQX₂ (X = F, Cl, Br), and BDTA-TCNQ). Although the TCNQX₂ (X = F, Cl, Br) derivatives do not result in full electron-transfer and the resulting materials are paramagnets, the more powerful oxidant TCNQF₄ leads to an oxidation of [Ru₂] to [Ru₂] with concomitant formation of TCNQF₄ radicals to give the product [Ru₂(O₂CCF₃)₄]₂(TCNQF₄)·3(p-xylene) with the average redox unit being [Ru₂]₄₅⁺–(TCNQ)–Ru₂₄₅⁺. This compound exhibits a 2-D hexagonal structure analogous to [Ru₂]·(OC₂CF₃)₄](TCNQ)·3(toluene) (Fig. 23), but it exhibits long range magnetic ordering below 95 K.

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Another interesting series of compounds that deserve mention are those based on the use of [Ru₂] complexes as spin carriers in extended solids with bridging cyanometallates [M(III)(CN)]₃⁻ (M = Cr, Mn, Fe, Co). Early reports of materials containing the [M₂] and [M(III)(CN)]₃⁻ units include the 2-D K₃[Ru₂(OC₂CH₃)₄]₃[Co(III)(CN)]₉. The magnetic properties of this type of material can be easily tuned by adjusting the redox chemistry of both the [Ru₂] donors and the organic acceptors. An excellent illustration of this point is the combination of [Ru₂(O₂CPh-x-F)₄](THF)₂ (x = m, o, and p) with the TCNQ derivatives (TCNQF₄, TCNQX₂ (X = F, Cl, Br), and BDTA-TCNQ). Although the TCNQX₂ (X = F, Cl, Br) derivatives do not result in full electron-transfer and the resulting materials are paramagnets, the more powerful oxidant TCNQF₄ leads to an oxidation of [Ru₂] to [Ru₂] with concomitant formation of TCNQF₄ radicals to give the product [Ru₂(O₂CCF₃)₄](TCNQF₄)·3(p-xylene) with the average redox unit being [Ru₂]₄₅⁺–(TCNQ)–Ru₂₄₅⁺. This compound exhibits a 2-D hexagonal structure analogous to [Ru₂]·(OC₂CF₃)₄](TCNQ)·3(toluene) (Fig. 23), but it exhibits long range magnetic ordering below 95 K.

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the 1-D $K[Ru^{II,III}(chp)_4][Co^{III}(CN)_6]$ compounds.\textsuperscript{210} Not surprisingly, the presence of the diamagnetic $[Co^{III}(CN)_6]^{3-}$ unit turns off magnetic coupling and there is no long range ordering for these materials. The related materials $[Ru^{II,III}(O_2CC(CH_3)_{3})_4]_3[H_2O][M^{III}(CN)_6]_xH_2O$ ($M = Fe, Co$) were also synthesized and characterized.\textsuperscript{31} These phases exhibit a 2-D (4,4) network with $[M^{III}(CN)_6]^{3-}$ nodes with the layers being stitched together by hydrogen bonds to form an overall 3-D architecture. Miller \textit{et al.} also reported a similar series of compounds that includes the cyanometallate $[Cr^{III}(CN)_6]^{3-}$. The starting materials $[Ru^{II,III}(O_2CCH_3)_4]^+$ and $[Ru^{II,III}(O_2CH)_4]^+$ were also used to prepare the homologous series $[Ru^{II,III}(O_2CC(CH_3)_{3})_4][M^{III}(CN)_6]$ (solvent) ($M = Cr, Fe, Mn, Co$) and $[Ru^{II,III}(O_2CH)_4][M^{III}(CN)_6]$ ($M = Co, Fe$).\textsuperscript{33,203,207,208} These compounds were analyzed by powder synchrotron X-ray diffraction and found to exhibit 3-D body centered interpenetrated cubic structures (Fig. 25a). Antiferromagnetic coupling through the bridging cyanide ligand between the $[Ru^{II}]^{+}$ units and the Fe$^{II,III}$ centers leads to long range magnetic ordering for the compounds $[Ru^{II,III}(O_2CC(CH_3)_{3})_4][M^{III}(CN)_6]$ ($M = Cr, T_c = 33 K$; $M = Fe, T_c = 2.1 K$), $[Ru^{II,III}(O_2CC(CH_3)_{3})_4][M^{III}(CN)_6]_2H_2O$ ($M = Cr, T_c = 37.5 K$; $M = Fe, T_c = 4.8 K$), and $[Ru^{II,III}(O_2CH)_4][Cr^{III}(CN)_6]$ ($T_c = 13.4 K$). The magnetic properties of the material $[Ru^{II,III}(O_2CCH_3)_{3}][Cr^{III}(CN)_6]$ were studied at ambient and applied pressures.\textsuperscript{33,207} It was found that the compound exhibits an antiferromagnetic ground state arising from antiferromagnetically coupled ferromagnetic sub-lattices and that it is a metamagnet below 33 K. Under external pressure, however, the ordering temperature increases linearly with applied pressure by 83% up to 59 K at 12.8 kbar (Fig. 25b).

The growing database of results with metal–metal bonded compounds indicates that they constitute some of the most important starting materials for multifunctional materials based on 4d metal ions and more exciting results and extensions to 5d metal ions are highly likely in the near future.

### 3.3.2 Photomagnetic compounds of 4d and 5d metal ions

Another consequence of the varied redox properties of 4d and 5d metal complexes is the property of photomagnetism which

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**Fig. 24** (a) The framework structure and temperature dependent susceptibility data for $[Ru_2(O_2CPh-m-F)_4](BDTA-TCNQ)$. The carboxylate ligands and solvents were omitted for the sake of clarity. (b) the zero-field cooled, field cooled and remnant magnetization (ZFCM, FCM and RM) curves in a 3 Oe field illustrating the ordering at 107 K. Reprinted with permission from ref. 199. Copyright 2008 Wiley–VCH Verlag GmbH & Co. KGaA.

**Fig. 25** (a) The interpenetrated cubic lattice (red and blue) of the material $[Ru^{II,III}(O_2CCH_3)_{3}][Cr^{III}(CN)_6]$ and (b) ZFCM and FCM curves at different external pressure from ambient pressure up to 12.8 kbar. The higher pressures lead to a shift of the magnetization curves to higher temperatures. Reprinted with permission from ref. 33 and 205. Copyright 2005 and 2007 Wiley–VCH Verlag GmbH & Co. KGaA.
promotes spin state changes through the intermediacy of excited states. The details of the physics of this process are out of the scope of this review and we have endeavored to present only a brief introduction to the basic concepts and state-of-the-art of the field. A very recent review by Bleuzen et al. is recommended for those who wish to gain a broader vision of the topic.\textsuperscript{24} According to this review, “photomagnetism can be defined as the process that changes the magnetism of a system after absorption of a photon.”

Generally speaking, several different mechanisms are responsible for triggering a photomagnetic event: irreversible photochemical-reaction-induced spin state changes, light-induced spin crossover, and light-induced electron transfer. The properties of most of the photomagnetic compounds with the $[\text{M(CN)}_6]^{4-}$ building blocks are based on a light-induced electron transfer mechanism. The most investigated photomagnetic materials that contain the $[\text{Mo}^{IV}(\text{CN})_8]^{\pm}$ anion are those based on the $\{\text{Cu}^{II}-\text{N} \equiv \text{C} - \text{Mo}^{IV}\}$ pair. One electron is transferred from the Mo$^{IV}$ to the Cu$^{II}$ center when the material is exposed to light, producing the metastable $\{\text{Cu}^{I}-\text{N} \equiv \text{C} - \text{Mo}^{IV}\}$ redox state. Although the net spin number for the isolated spin centers remains the same after the photoinduced process, the newly generated Mo$^{V}$ centers couple magnetically to the remaining paramagnetic Cu$^{II}$ centers, the result of which is long range ordering for the extended frameworks and high-spin ground states for isolated clusters. Among the compounds that have been reported are those which are molecular, e.g. the $[\text{Cu}_2\text{Mo}^{IV}_2]$ trinuclear complexes $[\text{Cu}^{II}(2,2’-\text{bipy})_2][\text{Mo}^{IV}(\text{CN})_6]$(solvent),\textsuperscript{211,212} the $[\text{Cu}^{II}\text{Mo}^{IV}]^2$ pentanuclear complex $[\text{Cu}^{II}(\text{psal})_2][\text{Mo}^{IV}(\text{H}_2\text{O})_2][\text{Mo}^{IV}(\text{CN})_6]\cdot\text{H}_2\text{O}$,\textsuperscript{213} the $[\text{Cu}^{II}6\text{Mo}^{IV}]^8$ heptanuclear complex $[\text{Cu}^{II}\text{tren}]_6[\text{Mo}^{IV}(\text{CN})_6]\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$,\textsuperscript{214,215} and the $[\text{Cu}^{II}_6\text{Mo}^{IV}_2]$ decanuclear complex $[\text{Cu}^{II}\text{psal}]_6\cdot[\text{Cu}^{II}(\text{psal})(\text{H}_2\text{O})_2][\text{Mo}^{IV}(\text{CN})_6]\cdot\text{H}_2\text{O}$.\textsuperscript{213} Additional compounds are the 1-D chains $[\text{Ni}^{III}(\text{cyclam})][\text{Cu}^{II}(\text{Me}_{2}\text{en})_2][\text{Mo}^{IV}(\text{CN})_6]\cdot\text{ClO}_4\cdot4\text{H}_2\text{O}$ and $[\text{Mn}_{2}\text{dpp}(\text{H}_2\text{O})][\text{Mo}^{IV}(\text{CN})_6]\cdot5\text{H}_2\text{O}$,\textsuperscript{217} the 3-D frameworks $\text{Cs}_2\text{Cu}^{II}_2[\text{Mo}^{IV}(\text{CN})_6]\cdot6\text{H}_2\text{O}$,\textsuperscript{218,219} and $\text{Cu}^{II}_2[\text{Mo}^{IV}(\text{CN})_6]\cdot8\text{H}_2\text{O}$,\textsuperscript{211,219} as well as nanoparticles and nanofilms of $\text{Cu}^{II}_4\text{Ni}^{III}[\text{Mo}^{IV}(\text{CN})_6][\text{pyr}]-\text{(H}_2\text{O})_9$.\textsuperscript{222,223} Comprehensive studies have been conducted and include investigations of the structures, spectroscopy and magnetism of both the original compounds and the photo-induced excited state products. The thermodynamics and kinetics of the photo-induced electron transfer, the lifetime of the metastable state, and the possible application of the compounds and nanoparticles as device switches have also been probed.

The $[\text{Cu}^{II}\text{Mo}^{IV}]$ heptanuclear complex $[\text{Cu}^{II}\text{tren}]_6[\text{Mo}^{IV}(\text{CN})_6]\cdot\text{ClO}_4\cdot\text{H}_2\text{O}$ is highlighted as an example of the interesting behavior of $\{\text{Cu}^{II}-\text{N} \equiv \text{C} - \text{Mo}^{IV}\}$ based photomagnetic materials. This $[\text{Cu}^{II}\text{Mo}^{IV}]$ heptanuclear compound contains one $[\text{Mo}^{IV}(\text{CN})_6]^{\pm}$ anion which is connected to six $[\text{Cu}^{II}\text{tren}]^2^+\$ units through CN$^-$ bridges (Fig. 26a). Since the Mo$^{IV}$ ion is diamagnetic, six Cu$^{II}$ $S = \frac{1}{2}$ spins behave as isolated paramagnets. After 10 h of irradiation at 406 nm, however, the $3M^2T$ curve changes drastically and the data are consistent with strong ferromagnetic interactions between the spin carriers due to the photoinduced electron transfer from Mo$^{IV}$ to Cu$^{II}$, leading to the formation of a paramagnetic-centered species: the excited state redox unit is Mo$^{V}$Cu$^{II}$Cu$^{III}_3$ with $S = 3$ (Fig. 26b). Interestingly, the phenomenon is both thermally and optically reversible, namely both an annealing treatment at 300 K or irradiation at 840 nm can reverse the electron transfer.

Apart from the Cu$^{III}$-Mo$^{IV}$ bimetallic compounds, the most interesting photomagnetic system containing the $[\text{M}^{IV}(\text{CN})_6]^{\pm}$ centers are compounds containing the $\{\text{Co}^{III}-\text{N} \equiv \text{C} - \text{W}^{IV}\}$ bridge; these materials include the 3-D network $[\text{Co}^{II}(\text{pm})_2][\text{Co}^{III}(\text{H}_2\text{O})_2][\text{W}^{IV}(\text{CN})_8]\cdot\text{H}_2\text{O}$ and the 2-D layered material CsCo$^{III}(3\text{-CNpd})_2[\text{W}^{IV}(\text{CN})_8]\cdot\text{H}_2\text{O}$ (Fig. 27a).\textsuperscript{224–229} Interestingly, although the final photoactive species in these compounds are based on the $\{\text{Co}^{III}-\text{N} \equiv \text{C} - \text{W}^{IV}\}$ redox pair, these compounds were synthesized from the Co$^{III}$ and [W$^{IV}(\text{CN})_8]^{3-}$ starting materials. The $\{\text{Co}^{III}-\text{N} \equiv \text{C} - \text{W}^{IV}\}$ redox state observed

![Fig. 26](image-url)
at room temperature is paramagnetic ($\text{Co}^{II}$, $3d^7$, HS, $S = \frac{3}{2}$ and $W^V$, $5d^1$, $S = \frac{1}{2}$). When the temperature is lowered, however, a thermally-induced charge transfer from $\text{Co}^{II}$ to $W^V$ converts the paramagnetic ($\text{Co}^{II}$–$W^V$) state to the low-temperature diamagnetic state ($\text{Co}^{III}$, $3d^6$, LS, $S = 0$ and $W^{IV}$, $5d^2$, $S = 0$) (Fig. 27b). The light-induced electron transfer from $W^{IV}$ back to $\text{Co}^{III}$ occurs with irradiation by red light at low temperature which generates the metastable ($\text{Co}^{II}$–N≡C–$W^V$) pairs which couple ferromagnetically and order at 30 K (for the 2-D network, Fig. 27c) and 40 K (for the 3-D network).

As is well-known for the photomagnetic cyanide-bridged Co–Fe Prussian blue analogs, the crystal field of the $\text{Co}^{II}$ center in the tungsten containing materials is critical for tuning the electron transfer process.\cite{230,231} This conclusion is supported by the fact that, for the 3-D compound [Co$^{II}$H$^2$(H$_2$O)$_2$][W$^V$(CN)$_8$]$_2$(pm)$_2$H$_2$O in which the crystal field around the $\text{Co}^{II}$ ion was altered by the substitution of one pm ligand with one water molecule, neither thermal- nor light-induced electron transfer occurs.\cite{228} Furthermore, the transition from the high- to the low-temperature phase can be triggered by application of an electric field for the compound $\text{3-D-[Co}^{II}$(pm)$_2$][Co$^{II}$(H$_2$O)$_2$][W$^V$(CN)$_8$]$_2$H$_2$O, a finding that opens up a promising approach to realizing electrically switchable devices.\cite{229}

The other photomagnetic systems based on the [M$^{IV}$(CN)$_8$]$_4$–anions are compounds with {M$^{IV}$–C≡N–M$^{II}$} and {W$^{IV}$–C≡N–M$^{II}$} pairs for which a light-induced magnetic change occurs as a result of either a reversible charge transfer between Mo$^{IV}$ and Mn$^{II}$ ions at low temperatures or an irreversible photo-oxidation of Mo$^{IV}$ to Mo$^{VI}$ at room temperature in the presence of oxygen.

As mentioned earlier, the CoFe Prussian blue analogs have been the source of much inspiration and the study has contributed greatly to the understanding of photomagnetic phenomena.\cite{230,231} We recently synthesized the first 5d metal congener of a photomagnetic Prussian blue analog based on the [Os$^{III}$(CN)$_6$]$_3^-$ anion and the $\text{Co}^{II}$ cation.\cite{105} The material, Co$^{II}$(Os$^{III}$(CN)$_6$)$_2$6H$_2$O, exhibits a charge transfer induced spin transition at 245 K as well as photomagnetism upon irradiation at low temperatures (Fig. 28). The ordering temperature increases from 2 to 16.5 K after the irradiation. The new findings allow, for the first time, a comparison of the nature of photomagnetic 5d transition metal analogs to the well-studied 3d analog of the Prussian blue family. Given that the structural parameters are essentially the same, differences in magnetic phenomena are ascribed to the nature of the exchange interactions and charge-transfer properties of the 5d Os versus the 3d Fe ions.

Finally, to date, there are no reports in the literature regarding photomagnetic materials based on [Nb$^{III}$(CN)$_8$]$_{5^-}$ or [Re$^{V}$(CN)$_8$]$_{3^-}$ anions but the argument can be made that they should be quite viable candidates for photomagnetic studies based on the fact that redox reactions involving

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**Fig. 27** (a) The 2-D framework of CsCo$^{II}$(3-CNpd)$_2$[W$^V$(CN)$_8$]H$_2$O, (b) temperature dependence of the $\chi_M T$ value in a field of 5000 Oe measured during cooling (○) and warming (●), and (c) FCM curves in a field of 10 Oe before irradiating with light (□), after irradiating (○), and after thermal treatment (5 K → 120 K → 5 K) (●). Reprinted with permission from ref. 227. Copyright 2003 American Chemical Society.

**Fig. 28** Temperature dependence of $\chi_M T$ for Co$^{II}$(Os$^{III}$(CN)$_6$)$_2$:6H$_2$O from 2 to 300 K for (a) slow cooling and rapid quenching states. Inset: ZFC/FC data for the quenching state with an ordering temperature of 17.5 K and (b) the non-irradiated (blue) and irradiated (red) samples. Inset: ZFC/FC plot of the photomagnetic state for which $T_c = 16.5$ K. Reprinted with permission from ref. 105. Copyright 2010 American Chemical Society.
3-CNpd 3-cyanopyridine
CN-sap 2-(2-hydroxyphenyl)-2-(2-hydroxyphenyl-
amino)acetonitrile dianion
Cp* pentamethyl-cyclo-pentadienyl
cyclam 1,4,8,11-tetraazacyclotetradecane
dabc 1,4-diazabicyclo[2.2.2]octane
DMA N,N'-dimethylacetamide
DCNQI 2,5-dimethyldicyanoquinodimide
DMF N,N'-dimethylformamide
dmpphen 2,9-dimethyl-1,10-phenanthroline
dpa− 2,2'-dipyridyldiamine anion
dpop 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-
[12.3.1]octadeca-1(18),2,12,14,16-pentaene
dthp 2,12-dimethyl-3,7,11,17-tetraaza-
bicyle[11.3.1]heptadeca-1(17),2,11,13,
15-pentaene
Et4N+ tetraethylammonium cation
Hdman N,N'-dimethylalaninol
Him imidazole
Hpmsal N-[2-(pyridyl)-methyl]-salicylimine
Hpesal N-[2-(pyridyl)-ethyl]-salicylimine
mal2− malonate dianion
H2valpn N,N'-bis(3-
methoxysalicylidene)propylenediamine
H2valen N,N'-bis(3-
methoxysalicylidene)ethylenediamine
L Me2 N,N',2,2'-dimethylpropylened(3-methoxy-
salicylideneiminate) dianion
Me3en N,N'-dimethylthelyleneiminediacetate
Me2tacn N,N',N''-trimethyl-1,4,7-triazacyclononane
m-F-PhCO2 N m-fluorobenzoate
npsalen N,N'-bis(1'-hydroxy-2'-acetophenylidene)-
1,2-diaminoethane dianion
1,4-nq 1,4-naphthoquinone
ox2− oxalate dianion
phen 1,10-phenanthroline
phz phenazine
pm pyrimidine
PPPh3 triphenylphosphine
Ph3P+ tetraphenylphosphonium cation
PPN+ bis(triphenylphosphiniminium cation
PY5Me2 2.6-bis(1,1-bis(2-pyridyl)ethyl)pyridine
3pyCH2OH 3-methanolpyridine
pyim 2-(2-pyridyl)imidazole
pyr monomer of poly(vinyl pyrrolidone)
pyz pyrazine
pzam pyrazine-2-carboxamide
salchen2− N,N'-bis(salicylidene)-o-cyclohexylen-
diamine dianion
salen2− N,N'-bis(salicylidene)ethylenediamine
dianion
salphen3− N,N'-bis(salicylidene)-1,2-diaminobenzene
dianion
TCNE tetracyanoethylen
TCNQ 7,7,8,8-tetracyanoquinodimethane
TCNQF4 2,3,5,6-tetrafluoro-7,7,8,8-
tetracyanoquinodimethane
TCNQX2 2,5-halogen substituted-7,7,8,
8-tetracyanoquinodimethane

4. Conclusions

This review offers the reader an opportunity to become familiarized with the growing database of interesting magnetic materials reported for molecular magnets based on 4d and 5d metal ions. It is obvious, however, that there is a veritable gold mine of opportunities for fruitful activity in this field. Our aim in highlighting numerous recent examples of heavier transition element magnetism is to underscore the importance of the magnetic anisotropy introduced by 4d and 5d metal ions. A great deal of additional work will be required before the potential of this area of molecular magnetism is fully realized, however, including the development of more advanced theoretical tools and the synthesis of many new compounds. Indeed, one of the greatest challenges in this area is to model the complex magnetic interactions between the 4d or 5d and other metal spin carriers. Initial calculations have focused on theoretical predictions of how the incorporation of 4d and 5d metal centers is expected to alter the properties of known classes of compounds and materials for which only 3d metals are known. The models are finally being tested experimentally as pointed out in this article, and we are gradually gaining a deeper understanding of the properties. The ultimate goal is to increase the operating temperatures of bistable materials and magnets. The only way to realize these aspirations is to continuously refine our approaches by combining the knowledge gained from theory and experiment and then returning to the bench.

As a final comment, it is important to note that the incorporation of 4d and 5d metal centers has led to increased blocking temperatures for SMMs, novel photomagnetic materials, new examples of spin crossover and charge transfer induced spin transitions, as well as exciting advances in the study of charge transfer complexes. Given the fact that this area of molecular magnetism is a nascent field, it is likely to blossom a great deal in the coming decades with advances in the synthesis and theoretical understanding of these complex materials.

Abbreviations

aac− acetylacetonate anion
Ph3As+ tetraphenylarsenium cation
BDTA-TCNQ bis(1,2,3-thiadiazole)tetracyanoquinodimethane
2,2'-bipy 2,2'-bipyridine
4,4'-bipy 4,4'-bipyridine
bpym 2,2'-bipyrimidine
1,4-bq 1,4-benzonuqnone
5-Brsalen N,N'-ethylenebis(5-bromosalicylideneiminate) dianion
"Bu4N+ tetra-n-dutylammonium cation
chp 6-chloro-2-hydroxy pyridinato

\[ \text{Nb}^{III} \leftrightarrow \text{Nb}^{IV} \text{ and Re}^{IV} \leftrightarrow \text{Re}^{V} \] pairs are known to readily occur under mild conditions. By choosing the appropriate ligands to adjust the possible ligand field around the other metal center, metal-to-metal charge transfer may be anticipated for clusters or networks that incorporate these building blocks.
Acknowledgements

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Notes and references

1 O. Kahn, Molecular Magnetism, VCH, New York, 1993.