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Metal–organic frameworks with solvent-free lanthanide coordination environments: synthesis from aqueous ethanol solutions†

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A series of 12 new metal–organic frameworks based on lanthanide cations (Ln = Nd, Sm–Dy), octahedral cluster anions [Re₆S₈(CN)₆]^{4−} or [Re₆Se₈(CN)₆]^{4−} and adipamide (adp) were synthesized under mild conditions in aqueous ethanol solutions. Compounds of the general composition Cs[Ln(adp)₂(Re₆Q₈(CN)₆)]·3H₂O (Ln = Nd, Sm–Dy; Q = S or Se) crystallize in the hexagonal space group *P*6₄22. Despite the presence of solvate H₂O molecules in structure cavities, the crystal structures revealed that the coordination environment of lanthanide cations in these 3D polymers did not contain H₂O ligands. This rare feature is attributed to the combination of a bulk cluster anion and flexible adp molecules, which occupy the lanthanide coordination sphere to yield a stable lanthanide-based building block. This assumption was confirmed by synthesis of a second crystalline modification of the compound Cs[Nd(adp)₂(Re₆S₈(CN)₆)]·3H₂O (orthorhombic space group *C*ccm). Luminescence studies evidence the presence of the typical red luminescence of hexarhenium cluster complexes and the absence of observable luminescence of lanthanide cations for all the compounds except the Nd derivatives. Magnetic data indicate very weak antiferromagnetic exchange interactions between paramagnetic Ln³⁺ centers.

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Introduction

Synthesis of metal–organic frameworks (MOFs) based on functional building blocks is an important goal of chemistry and materials science, since MOFs often combine the properties determined by the topology of the framework with the properties of discrete building units.^{1–3} In some cases, the crystal structure of a MOF can be proposed based on the well-defined coordination chemistry of metal centers (mostly d-metals) in combination with the appropriate selection of rigid organic linkers.^{4,5} This allows for rational design of structures of multifunctional MOFs and their properties.^{6–10} The situation is different for MOFs based on 4f-element cations. The coordination environment of lanthanide ions is very flexible resulting in unpredictability of the crystal structures

of synthesized polymeric compounds.^{11,12} Additional complexity is created by the tendency of lanthanide ions to hydrolyse in aqueous solutions and the coordination of hard O-donor ligands, leading to the presence of a variable number of solvent molecules, such as H₂O or DMF, or hydroxo ligands in the coordination sphere.^{13–15} Because of this, predictable synthesis of MOFs with a certain geometry based on lanthanide cations is difficult. However, lanthanide-based MOFs are very attractive because 4f-metal centers impart unique properties to the polymeric materials, which can be used in catalysis,^{16,17} bio-visualization,^{18,19} and magnetic^{20–22} and sensing^{23–27} applications. The search for ways to control the coordination environment of lanthanide ions is therefore important in order to obtain building blocks for construction of MOFs in a controlled manner.

Over the past few years, the formation of coordination polymers and metal–organic frameworks based on 4f-metal cations and octahedral rhenium cyanide cluster complexes with the general formula [Re₆Q₈(CN)₆]^{3−/4−} (Q = S, Se or Te) has been studied.^{28–30} These cluster anions are based on six covalently bonded Re atoms, which form a stable octahedral Re₆ metallocuster.^{31,32} The metallocuster is supported by a set of the inner μ₃-Q ligands coordinating the trigonal faces of the octahedron and the apical CN ligands. Owing to the presence of ambidentate CN ligands, cluster anions are able

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to coordinate the cations of d- and f-metals, forming coordination polymers of various topologies.^{33,34} Clusters can act as structural analogues of mononuclear cyanide complexes of transition metals.³⁵ However, due to their larger volume and specific electronic structure, they often form polymeric compounds with unique structures, possessing interesting functional properties, such as red photoluminescence and reversible redox transitions.^{36–39} This leads to sustained interest in the use of transition metal octahedral cluster complexes as building blocks for the preparation of functional coordination polymers.

Recently, we have shown that cyanoclusters $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ and $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ can act as metallolinkers forming neutral frameworks with cations of 4f-elements in aqueous solutions in the presence of rigid polydentate organic ligands.^{40,41} We found that the cluster anions in the framework structures displayed luminescence and redox properties similar to those of discrete cluster complexes, which can be used for detection of strong oxidants in solution.⁴¹ In contrast, lanthanide cations in these compounds did not exhibit luminescence. Moreover, the luminescence of lanthanide cations was not reported previously for any of the obtained polymeric compounds based on octahedral rhenium clusters. The reason for that is supposed to be the presence of H_2O molecules in the coordination sphere of lanthanide cations that effectively quench luminescence due to the excitation of O–H vibrations.^{42–44}

Here we report on the synthesis and investigation of a series of new metal–organic frameworks based on $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ (Q = S or Se) cluster anions, Ln^{3+} cations and flexible linker adipamide ($\text{C}_6\text{H}_{12}\text{N}_2$, adp). An important feature of the compounds with the general formula $\text{Cs}[\text{Ln}(\text{adp})_2\text{Re}_6\text{Q}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ is the absence of H_2O molecules in the coordination sphere of Ln^{3+} cations, despite the fact that the compounds were obtained in aqueous solutions and contain solvate H_2O molecules in the crystal structures. The structure-forming role of cluster anions and the luminescence and magnetochemical properties of the new compounds are analyzed in this article.

Results and discussion

Synthesis and crystal structures

Compounds $\text{Cs}[\text{Ln}(\text{adp})_2\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ (1–6) and $\text{Cs}[\text{Ln}(\text{adp})_2\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ (7–12, Ln = Nd, Sm–Dy, respectively) were synthesized as crystalline solids by slow evaporation of water–ethanol solutions containing cluster anions $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ or $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$, cations Ln^{3+} and adipamide (adp). Optimization of the synthesis conditions allowed obtaining compounds in preparative quantities. The preparation of single crystals of compounds 1–12 for X-ray diffraction analysis was complicated by the small crystal size and the formation of polycrystalline aggregates. Nevertheless, high-quality single crystals were obtained for compound 11, which allowed us to study its structure and confirm the structures of the phases 1–10 and 12 by powder X-ray diffraction.

Compound 11 crystallizes in the non-centrosymmetric hexagonal space group $P6_422$. It exhibits a framework polymeric structure based on the covalent bonding of Tb^{3+} cations with CN^- ligands of cluster anions and adp molecules. The starting point and the most interesting feature of the crystal structure is the coordination environment of the Tb^{3+} ions. It includes four N atoms of cyano groups and four O atoms of adp (Fig. 1). The O and N atoms form a distorted square antiprism with ONON faces (Fig. 2a). The Tb–O and Tb–N distances are 2.33(2) and 2.49(2) Å, respectively. The coordination environment of Tb^{3+} cations does not contain H_2O molecules. This is a rare case, although not unique,^{45–47} for Ln^{3+} -based coordination polymers obtained in aqueous solutions. As shown in Fig. 2, adp molecules lie in the *ab* plane of crystal packing and form the cationic layers $\{\text{Tb}(\text{adp})_2\}_n^{3n+}$ by coordination with Tb^{3+} cations. The monodentate coordination of adp molecules is additional confirmation that amide groups did not hydrolyse during the reaction. The closest Tb···Tb distance in the cationic sub-lattice is 10.71 Å, while the closest Tb···Tb distance within the $\{\text{Tb}(\text{adp})_2\}_n^{3n+}$ layer is 10.83 Å. Most of the interlayer space is occupied by voluminous cluster anions $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ that bind Tb^{3+} cations of adjacent layers forming the negatively charged framework $[\text{Tb}(\text{adp})_2\text{Re}_6\text{Se}_8(\text{CN})_6]^-$ as shown in Fig. 2c and d. Adjacent layers $\{\text{Tb}(\text{adp})_2\}_n^{3n+}$ rotate relative to each other by 120° by the 6_4 axis lying along the *c* direction. Only four equatorial CN ligands of the cluster anion participate in the binding, while two CN ligands in the *trans*-position form weak interactions with Cs^+ cations and $-\text{NH}_2$ groups of adipamide. Visualization of the environment of Ln^{3+} ions, taking into account the van der Waals radii, shows that cluster anions occupy a large volume, forcing adipamide molecules to pack

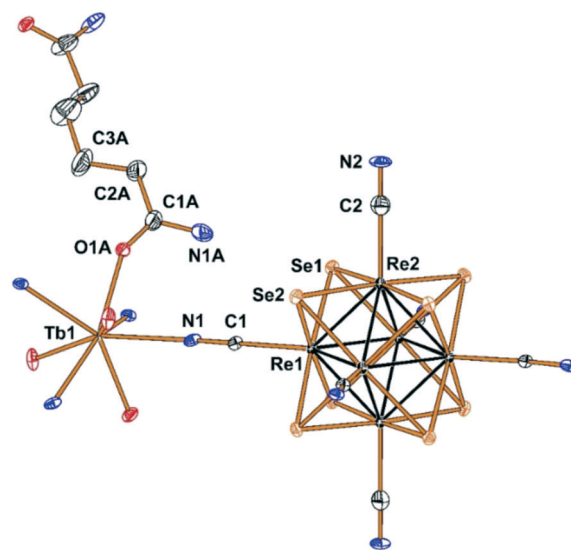


Fig. 1 Fragment of the structure of compound 11 with numbered atoms of the asymmetric unit. Atoms are represented by thermal ellipsoids drawn at 60% probability.

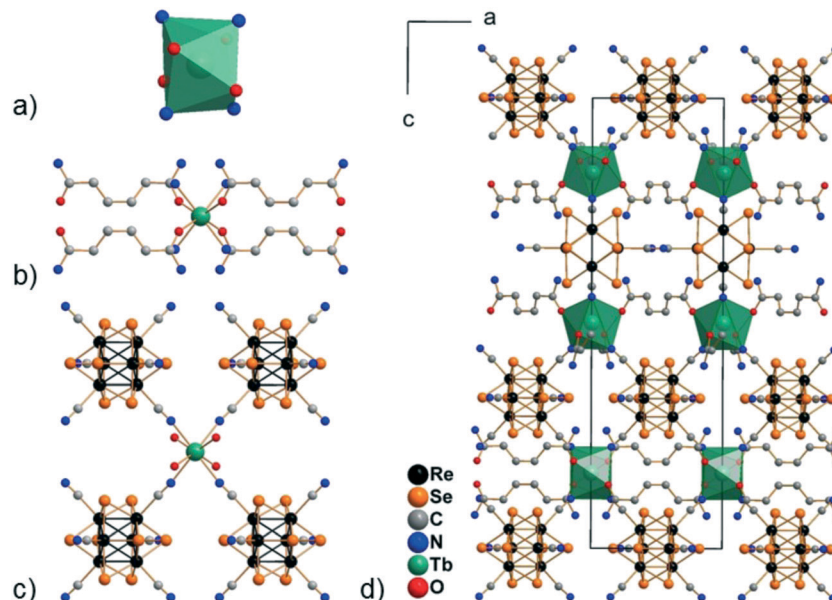


Fig. 2 Coordination polyhedron of the Tb³⁺ cation in the structure of compound **11** (a); coordination of adipamide molecules to the Tb³⁺ cation in the structure of compound **11** (hydrogen atoms are not shown for clarity, only N atoms of cluster anions are depicted) (b); coordination of [Re₆Se₈(CN)₆]⁴⁻ cluster anions to the Tb³⁺ cation in the structure of compound **11** (only O atoms of adipamide molecules are depicted) (c); cell packing of the framework [Tb(adp)₂Re₆Se₈(CN)₆]⁻ in the structure of compound **11** (view along the *b* axis; Cs⁺ cations, lattice H₂O molecules and H atoms are omitted for clarity) (d).

into layers and, apparently, preventing coordination of additional ligands to Ln³⁺ cations (Fig. S1†).

Analysis of the framework [Tb(adp)₂Re₆Se₈(CN)₆]⁻ using the Mercury CSD program showed that it contains cavities with a volume of about 15% of the cell volume, elongated along the *c* axis and penetrating layers {Tb(adp)₂Re₆Se₈(CN)₆]⁻ (Fig. S2†). Disordered Cs⁺ cations are located in these cavities and compensate the negative charge of the framework. There are two O atoms of symmetry equivalent lattice H₂O molecules in the coordination environment of Cs⁺ cations. The corresponding Cs⁺⋯O distance is 2.76(5) Å. In addition, lattice H₂O molecules form hydrogen bonds of about 3.0 Å with -NH₂ groups of adipamide. Bridging μ₃-Se ligands of cluster anions and N atoms of CN apical ligands as well as -NH₂ groups of adipamide complement the coordination environment of Cs⁺ cations. Given the Cs⁺ cations and their coordination environment, the framework Cs[Tb(adp)₂Re₆Se₈(CN)₆]⁻·3H₂O contains less than 2% of solvent-accessible voids.

The structure of the other compounds belonging to the Cs[Ln(adp)₂Re₆Q₈(CN)₆]⁻·3H₂O series could not be characterized by single crystal X-ray diffraction analysis due to the low quality of the crystals. However, X-ray powder diffraction confirmed that all 12 compounds are isostructural (Fig. S3, Table S3†), while elemental analysis showed the compliance of the composition with the proposed formula. Trying to obtain single crystals of these compounds, we investigated a wide range of reaction conditions, including slow crystallization of the compounds from solutions with different concentrations of the reagents. As a result, we obtained several single crystals of a new crystalline

modification of the compound Cs[Nd(adp)₂Re₆Se₈(CN)₆]⁻·3H₂O (**1a**). This compound crystallizes in the orthorhombic space group *Cccm*. The structure demonstrates similar connection of lanthanide cations, adipamide molecules and cluster anions to the previously described structure with *P*₆₄₂₂ symmetry (Fig. S4†). The coordination environment of Nd³⁺ cations consists of four adipamide oxygen atoms and four nitrogen atoms of CN ligands forming a square antiprism. The Nd–O and Nd–N bond lengths are 2.396(3) and 2.576(3) Å, respectively. The most important difference in the structure of the frameworks **11** and **1a** is the different rotation angles of the adjacent layers {Ln(adp)₂Re₆Se₈(CN)₆]⁻ and the cluster anions coordinated to them when viewed along the *c* axis. While the structure of **11** with *P*₆₄₂₂ symmetry demonstrates rotation of 120°, the structure of **1a** with *Cccm* symmetry has a rotation angle of 180° due to the presence of an inversion center (Fig. 3). It should be noted that the compound in structural type **1a** was obtained as several single crystals. The presence of *Cccm* type impurities was excluded for compounds **1–12** based on analysis of their X-ray powder diffraction patterns, which have well-distinguishable peaks at small angles (Fig. S5†). However, investigation of this structure showed that the tetragonal antiprismatic fragment {Ln(adp)₄[Re₆Q₈(CN)₆]₄} is a secondary building block, which can be involved in formation of different types of structures.

Cluster anions and adipamide as building blocks

Lanthanide cations are known as strong Lewis acids and strong oxophiles, which exist in aqueous or water/non-

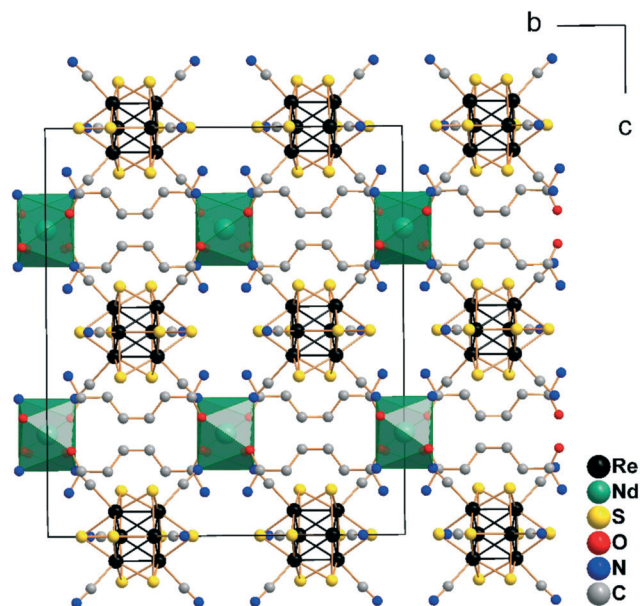


Fig. 3 Cell packing of the framework $[\text{Nd}(\text{adp})_2\text{Re}_6\text{S}_8(\text{CN})_6]^-$ in the structure of **1a** (view along the *a* axis; Cs^+ cations, lattice H_2O molecules and H atoms are omitted for clarity).

aqueous solvent mixtures as solvates with high Ln–O bonding energies.^{14,48} The synthesis of compounds that do not contain solvent molecules in the coordination sphere of rare-earth cations requires the presence of bulk multidentate ligands, which promote the kinetic inertness of lanthanide complexes,^{49–51} or synthesis in molten organic compounds.^{52–54} Since removal of solvent molecules from the coordination sphere often allows one to enhance the luminescence characteristics of 4f metal centers,⁴² synthesis of such compounds is a subject of interest. The synthesis of compounds **1–12** takes place in a water–ethanol (2:1 vol.) mixture, so a specific combination of linkers surrounding the metal centers can prevent the binding of water molecules to Ln^{3+} and ensure the formation of coordination polymers based on water-free lanthanide cations. This assumption was confirmed by obtaining of two crystalline modifications of the compounds $\text{Cs}[\text{Ln}(\text{adp})_2\{\text{Re}_6\text{S}_8(\text{CN})_6\}]\cdot 3\text{H}_2\text{O}$, namely **11** and **1a**, crystallizing in the space groups $P6_422$ and $Cccm$, respectively. The stoichiometry of the compounds, the coordination environment of the Ln cations and the geometry of the lanthanide coordination polyhedron remained the same despite the different packing of building blocks.

The chalcocyanide anions $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-/3-}$ (S, Se or Te) are widely used for the synthesis of coordination polymers due to their chemical stability, rigid geometry and functional properties, the most known one is luminescence in the red and NIR range.⁵⁵ Over the past few decades, a number of coordination polymers based on these cluster anions and transition metal cations including lanthanides have been characterized. It was shown that in most cases the cluster cores $\{\text{Re}_6\text{Q}_8\}^{2+}$ act as nodes in the structures. Thus, the

structure of inorganic cluster-based coordination polymers can be considered as a combination of two cationic nodes connected by bridging CN^- ligands. Prussian blue-type structures like $\text{Fe}_4[\text{Re}_6\text{Te}_8(\text{CN})_6]_3\cdot 27\text{H}_2\text{O}$ or $\text{Ga}_4[\text{Re}_6\text{Se}_8(\text{CN})_6]_3\cdot 38\text{H}_2\text{O}$ are classical examples of such compounds.³⁵ In the case of metal–organic coordination polymers, the octahedral cluster anion is able to act as a bulk spacer between cationic nodes connected by bridging organic ligands, as in the case of compounds $[\text{Cu}_2(\text{threo-tab})_3(\text{NH}_3)] [\text{Re}_6\text{Q}_8(\text{CN})_6]\cdot n\text{H}_2\text{O}$ ($\text{Q} = \text{S}$ or Te , *threo-tab* = 1,2,3,4-tetraaminobutane)³⁹ and $\text{K}[\text{Nd}(\mu\text{-C}_4\text{H}_{10}\text{O}_4)(\text{H}_2\text{O})_4\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ ($\text{C}_4\text{H}_{10}\text{O}_4$ = butan-1,2,3,4-tetraol).²⁸ Compounds **1–12** represent a new series of metal–organic coordination polymers based on hexarhenium cluster complexes. As in the above mentioned metal–organic frameworks based on octahedral clusters,^{40,41} the cluster anion can be described here as a bulk metal linker between layers of lanthanide cations connected by bridging organic ligands.

The bridging organic ligand that was used in the synthesis of compounds **1–12** is adipamide. The use of non-hydrolyzed adipamide derivatives as linkers is limited and, as a rule, there are bulk N,O-donor ligands.^{56,57} A product of its hydrolysis – adipate anion – is widely presented as a linker for coordination polymers with d- and f-metal cations.^{12,58–62} In contrast with adipate, adipamide demonstrates monodentate coordination and at the same time connects distant lanthanide centers, which allows one to place more voluminous ligands around the latter ones. It should be noted that our attempts to obtain coordination polymers based on hexarhenium clusters and lanthanide cations using adipic acid or adipates led to the obtaining of X-ray amorphous compounds. Thus, we can assume that the coordination sphere of lanthanide cations in compounds **1–12** does not contain water molecules due to the combination of bulk cluster anions and sterically flexible adipamide molecules, which form the stable and highly symmetrical node $\{\text{Ln}(\text{adp})_4[\text{Re}_6\text{Q}_8(\text{CN})_6]_4\}$.

Hydrolytic stability and thermal decomposition

Coordination polymers based on lanthanide cations often have low hydrolytic stability, which is caused by the high stability of lanthanide aqua complexes in solution. Compounds **1–12** follow this tendency. Being stable in the mother solution, they show slow dissolution in distilled water at room temperature. However, after dissolution the compounds can be recrystallized by addition of EtOH and slow evaporation. Recrystallization of the compounds based on different cluster anions leads to different results. Compound **11** based on the $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ anion can be repeatedly recrystallized while retaining the crystal structure of type **11**. At the same time, compound **1** based on the $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ anion was recrystallized with the formation of a mixture of crystalline phases in structural types **1a** and **11** (Fig. S6†). Thus, we can assume that the formation of

compounds in structural type **1a** is typical for compounds based on the cluster anion $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$, and the possibility of forming these phases is determined by the concentration of the Ln^{3+} cation or the total concentration of reagents in solution.

The thermal stability of the compounds in the solid state is characterized by a slow mass loss up to about 350 °C and a significant endothermic mass loss in the temperature interval of 350–550 °C (Fig. S7†). The slow mass loss at the initial stage is associated with the removal of solvate water molecules, which occurs in a very wide temperature range, possibly due to the intermediate formation of lanthanide oxo- and hydroxo-complexes. Further decomposition is associated with the pyrolysis of adipamide molecules and cyanide ligands of cluster anions. The products of the pyrolysis are stable up to ~700 °C, when decomposition of the cluster cores occurs. Finally, the type of lanthanide cation or cluster anion has a negligible effect on the positions of the maxima of the mass loss rate indicating that the thermal stability of the compounds is determined mainly by the structure of the framework.

Luminescence properties

Chalcocyanide complexes $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ (Q = S, Se or Te) are one of the first hexarhenium cluster complexes for which the luminescence properties were studied in solution⁶³ and then in the solid state.⁶⁴ Despite the fact that since 1998 many coordination polymers have been synthesized based on these anionic complexes and various transition metal cations,^{34,39,65–68} the luminescence properties of cyano-bridged polymers comprising the $\{\text{Re}_6\text{Q}_8\}^{2+}$ core have been described for the first time quite recently.³⁶ In particular, it was shown that the polymeric compounds $[\{\text{Ag}(\text{bpy})\}\{\text{Ag}_4(\text{bpy})_4(\mu\text{-CN})\}\{\text{Re}_6\text{Q}_8(\text{CN})_6\}]$ (Q = S or Se) emit luminescence in the visible and near-infrared regions upon ultraviolet light excitation. The broad and structureless spectrum of the polymer is similar to the spectra of soluble

salts of the starting complexes $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$. In addition, it was noted that the coordination of luminescent cyanide cluster units with such transition metal cations as Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} or even lanthanides led to elimination of their photoluminescence abilities.³⁶ Thus, the polymeric compounds with Ag^+ cations were declared as the first luminescent CN-bridged coordination polymers based on $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ complexes. In our recent publications metal-organic frameworks based on lanthanide complexes and cyanide hexarhenium clusters have been described.^{40,41} In the luminescence spectra of the MOFs a broad band of the corresponding cyanide cluster complex was observed while bands of lanthanides were not shown. In the current study the luminescence spectra of the solid samples of all 12 synthesized compounds $\text{Cs}[\text{Ln}(\text{adp})_2\{\text{Re}_6\text{Q}_8(\text{CN})_6\}]\cdot 3\text{H}_2\text{O}$ as well as the initial salt $\text{Cs}_3\text{K}[\text{Re}_6\text{Q}_8(\text{CN})_6]\cdot n\text{H}_2\text{O}$ were recorded using an IR-sensitive detector. The spectra of all the compounds except the complexes with neodymium (**1** and **7**) show the band characteristic of $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ without noticeable bands from the lanthanides that make up them (Fig. 4). The emission intensity of the compounds with gadolinium (**4** or **10**) and terbium (**5** or **11**) is comparable with that of the powdered sample of the corresponding precursor $\text{Cs}_3\text{K}[\text{Re}_6\text{Q}_8(\text{CN})_6]\cdot n\text{H}_2\text{O}$ (Fig. S8a†) while the luminescence intensity of the complexes with samarium (**2** or **8**), europium (**3** or **9**) and dysprosium (**6** or **12**) is significantly lower. The spectra of the neodymium compounds (**1** or **7**) do not display a band of the Re_6 cluster unit but show bands inherent to Nd^{3+} (Fig. S8b†). This can be attributed to the Förster resonance energy transfer (FRET) mechanism with the cluster complex acting as the donor and the Nd^{3+} cation as the acceptor⁶⁹ because of the overlap of the excitation spectrum of Nd^{3+} with the emission spectrum of $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$.

Magnetochemical properties

The SQUID magnetometry data of compounds **1–12** are shown in Fig. 5 as $\chi_m T$ vs. temperature T plots at 0.1 T and

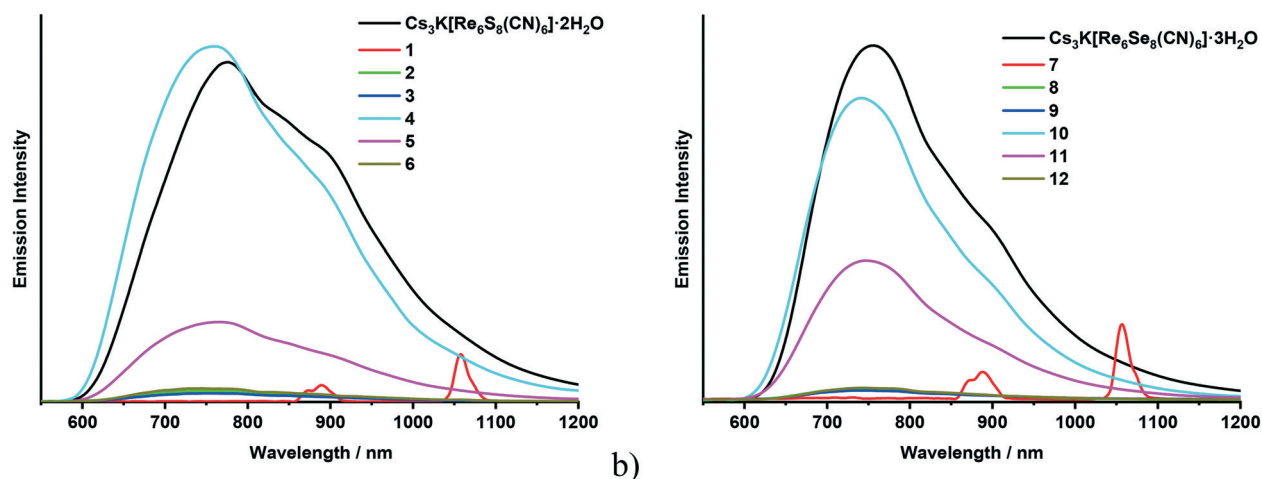


Fig. 4 Emission spectra of $\text{Cs}_3\text{K}[\text{Re}_6\text{S}_8(\text{CN})_6]\cdot 2\text{H}_2\text{O}$ and compounds **1–6** (a); emission spectra of $\text{Cs}_3\text{K}[\text{Re}_6\text{Se}_8(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ and compounds **7–12** (b).

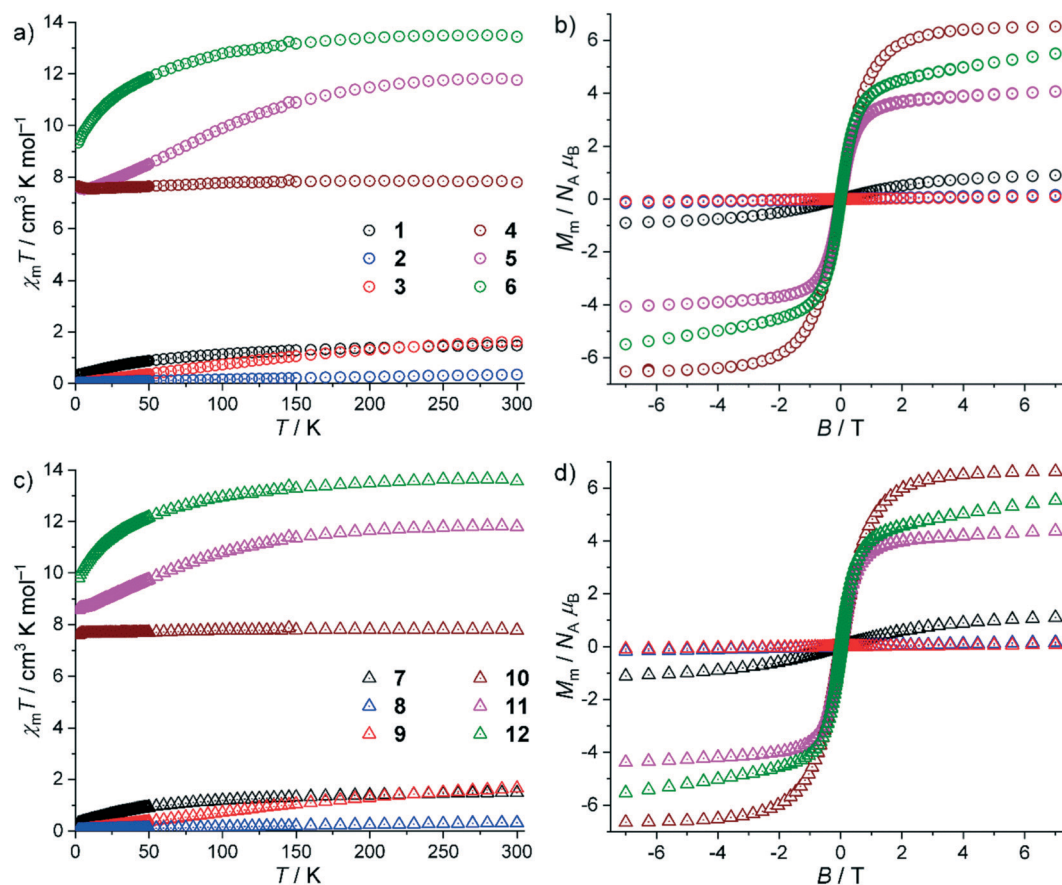


Fig. 5 Magnetic properties of 1–12: (a) $\chi_m T$ vs. T at 0.1 T and (b) M_m vs. B at 2.0 K of 1–6; (c) $\chi_m T$ vs. T at 0.1 T and (d) M_m vs. B at 2.0 K of 7–12.

molar magnetization M_m vs. magnetic field B plots at 2.0 K. For 1–6, the values of $\chi_m T$ at 300 K are within the expected ranges⁷⁰ of the respective lanthanide center (all values in $\text{cm}^3 \text{K mol}^{-1}$): 1: 1.47 (expected 1.4–1.5), 2: 0.35 (*ca.* 0.32), 3: 1.63 (*ca.* 1.5), 4: 7.84 (7.6–7.9), 5: 11.81 (11.7–12.0), and 6: 13.51 (13.0–14.1). These values are close to the values expected for the respective isolated Russell–Saunders ground terms of the free ions but for 2 and 3, for which the excited terms are energetically close to and distinctly mix into the corresponding ground term. Upon cooling the compounds, all values marginally decrease, and drop at temperatures below 150–50 K. In addition, there are increasing values of $\chi_m T$ observed for 4 and 5 at $T < 7$ K. At 2.0 K, $\chi_m T$ reaches the values of 0.34 (1), 0.03 (2), 0.01 (3), 7.64 (4), 7.65 (5) and $9.34 \text{ cm}^3 \text{K mol}^{-1}$ (6), respectively.

For 4, the values only slightly decrease due to the spin-like behavior of Gd^{3+} centers, while for the other compounds the decrease is more pronounced due to the thermal population of the distinctly split m_J energy levels. Besides these single-ion effects, there are very weak antiferromagnetic exchange interactions between the lanthanide centers, which add to or induce (4) the decrease of $\chi_m T$. The increases of $\chi_m T$ at low temperatures indicate also the presence of very weak ferromagnetic exchange interactions, at least for 4 and 5. At 2.0 K, the molar magnetizations M_m as a function of the

applied field B are linear in the range from about -0.5 to 0.5 T, and at higher fields notably decrease the slope of the curve without being saturated at the highest applied fields of ± 7.0 T. The values at 7.0 T are 0.9 (1), 0.2 (2), 0.1 (3), 6.5 (4), 4.1 (5) and $5.5 N_A \mu_B$ (6), which are either close to zero (2, 3), close to the saturation value (4, $M_{m,\text{sat}} = 7.0 N_A \mu_B$) or about half of the saturation value of about $g_J J N_A \mu_B$ (1, 3.3; 5, 9.0; 6, $10.0 N_A \mu_B$). For 2 and 3, this is partially due to the aforementioned distinct mixing of energy states, and in particular for 3 due to the $J = m_J = 0$ ground term of Eu^{3+} . The molar magnetization of 4 is close to the saturation value due to the almost isotropic Gd^{3+} center, while for 1, 5, and 6 (and partially 2) the observed features are essentially due to being the mean values of randomly oriented anisotropic centers (powder samples). Since all the curves additionally show a relevant slope at the highest applied fields, they are in agreement with the presence of very weak exchange interactions.

The magnetic properties of 7–12 are similar to those of the respective lanthanide compounds 1–6 with the following differences. At 300 K, the values of $\chi_m T$ are (all values in $\text{cm}^3 \text{K mol}^{-1}$): 7: 1.48, 8: 0.33, 9: 1.65, 10: 7.82, 11: 11.84, and 12: 13.65. These values are within the expected ranges and close to the values expected for the respective isolated Russell–Saunders ground terms of the free ions with the exception of 8 and 9, for the above-mentioned reasons. Upon decreasing

the temperature, all values marginally decrease, and drop at temperatures below 150–50 K. In addition, there are further small drop offs observed for **7**, **8**, **10** and **11** at $T < 4$ K. At 2.0 K, $\chi_m T$ reaches the values of 0.31 (**7**), 0.04 (**8**), 0.02 (**9**), 7.61 (**10**), 8.57 (**11**) and 9.82 cm³ K mol⁻¹ (**12**), respectively. As for **1–6**, the observed behaviors are mainly due to single-ion effects. The presence of very weak, possibly antiferromagnetic exchange interactions between the lanthanide centers cannot be excluded. The drop offs below 4 K are, however, most likely due to the Zeeman splitting of the energy states. The molar magnetizations M_m at 2.0 K are approximately linear functions of the applied field B from -0.5 to 0.5 T, and notably change their slope at higher fields without reaching saturation at ± 7.0 T. The values at 7.0 T are 1.1 (**7**), 0.2 (**8**), 0.1 (**9**), 6.6 (**10**), 4.4 (**11**) and 5.5 $N_A \mu_B$ (**12**), which are slightly above the values measured for the respective analogs **1–6**. This observation combined with the less pronounced decreases of $\chi_m T$ at $T < 150$ K most likely indicates overall slightly weaker antiferromagnetic exchange interactions in **7–12**. The overall similar magnetic properties of **1–6** in comparison to those of **7–12** with small differences can be rationalized by the structural information of the compounds. They crystallize in the same space group yet with slightly different distances of the lanthanide centers (influencing the strength of interactions), slightly different angles between the lanthanide centers *via* the bridging ligands (strength and type of interaction) and slightly different ligand–center distances/angles (single-ion effects).

Conclusion

In conclusion, we have discovered that self-assembly reactions between various Ln³⁺ cations, [Re₆Q₈(CN)₆]⁴⁻ cluster anions (Q = S or Se) and adipamide (adp) in aqueous ethanol solution lead to the formation of 3D framework compounds **1–12**. The structures of the frameworks consist of Ln³⁺ metal centers and {Re₆Q₈}²⁺ cluster units connected by CN⁻ groups and adp molecules. The interesting feature of the frameworks is the presence of lanthanide centers coordinated only by linkers without the presence of water molecules in the coordination sphere. We propose that, due to the combination of cluster complexes and flexible adp molecules, a stable lanthanide-based building block {Ln(adp)₄[Re₆Q₈(CN)₆]₄} was formed, which can be present in different types of structures. The combination of voluminous, highly symmetrical linkers with smaller and flexible ones could be used as a general approach for synthesis of Ln-based MOFs with solvate-free Ln centers.

Investigation of the luminescence of the new compounds in the solid state using an IR-sensitive detector showed that all the compounds with the exception of the Nd-based ones had no photoluminescence from the Ln center, while a broad band of the corresponding cyanide cluster complex was observed. This suggested that quenching of the luminescence of lanthanides in metal–organic frameworks can be caused not only by the presence of solvate molecules in the first

coordination sphere. However, the Nd-containing compounds **1** and **7** did not display a band of the Re₆ cluster unit but showed bands inherent to Nd³⁺. This can be attributed to the FRET mechanism due to the overlap of the excitation spectrum of Nd³⁺ with the emission spectrum of [Re₆Q₈(CN)₆]⁴⁻. Finally, the magnetic properties of the compounds are determined by the isolated lanthanide paramagnetic centers showing very weak antiferromagnetic exchange interactions.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 B. Li, H.-M. Wen, Y. Cui, W. Zhou, G. Qian and B. Chen, *Adv. Mater.*, 2016, **28**, 8819–8860.
- 2 T. R. Cook, Y.-R. Zheng and P. J. Stang, *Chem. Rev.*, 2013, **113**, 734–777.
- 3 H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673–674.
- 4 F. A. Almeida Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tomé, J. A. S. Cavaleiro and J. Rocha, *Chem. Soc. Rev.*, 2012, **41**, 1088–1110.
- 5 D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O’Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257–1283.
- 6 V. Guillermin, D. Kim, J. F. Eubank, R. Luebke, X. Liu, K. Adil, M. S. Lah and M. Eddaoudi, *Chem. Soc. Rev.*, 2014, **43**, 6141–6172.
- 7 O. K. Farha and J. T. Hupp, *Acc. Chem. Res.*, 2010, **43**, 1166–1175.
- 8 F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 1833–1835.
- 9 S. Kitagawa, R. Kitaura and S.-i. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375.
- 10 O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705–714.
- 11 K. Müller-Buschbaum, in *The Chemistry of Metal–Organic Frameworks*, ed. S. Kaskel, Wiley-VCH Verlag GmbH & Co. KGaA, 2016, ch. 9, pp. 231–270, DOI: 10.1002/9783527693078.ch9.
- 12 C. L. Cahill, D. T. de Lill and M. Frisch, *CrystEngComm*, 2007, **9**, 15–26.
- 13 Z. Zhang, Y. Zhang and Z. Zheng, in *Recent Development in Clusters of Rare Earths and Actinides: Chemistry and Materials*,

- ed. Z. Zheng, Springer Berlin Heidelberg, Berlin, Heidelberg, 2017, pp. 1–49, DOI: 10.1007/430_2016_12.
- 14 J.-C. G. Bünzli, *J. Coord. Chem.*, 2014, **67**, 3706–3733.
 - 15 E. N. Rizkalla and G. R. Choppin, in *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, 1991, vol. 15, pp. 393–442.
 - 16 C. Pagis, M. Ferbinteanu, G. Rothenberg and S. Tanase, *ACS Catal.*, 2016, **6**, 6063–6072.
 - 17 T. Zhang and W. Lin, *Chem. Soc. Rev.*, 2014, **43**, 5982–5993.
 - 18 G. A. Pereira, J. A. Peters, F. A. Almeida Paz, J. Rocha and C. F. G. C. Geraldes, *Inorg. Chem.*, 2010, **49**, 2969–2974.
 - 19 J. Wahsner, E. M. Gale, A. Rodríguez-Rodríguez and P. Caravan, *Chem. Rev.*, 2019, **119**, 957–1057.
 - 20 G. Huang, G. Fernandez-Garcia, I. Badiane, M. Camarra, S. Freslon, O. Guillou, C. Daiguebonne, F. Totti, O. Cador, T. Guizouarn, B. Le Guennic and K. Bernot, *Chem. – Eur. J.*, 2018, **24**, 6983–6991.
 - 21 B. V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J. L. Jordá, H. García, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem., Int. Ed.*, 2008, **47**, 1080–1083.
 - 22 T. K. Prasad, M. V. Rajasekharan and J.-P. Costes, *Angew. Chem., Int. Ed.*, 2007, **46**, 2851–2854.
 - 23 Y. Zheng, F.-Z. Sun, X. Han, J. Xu and X.-H. Bu, *Adv. Opt. Mater.*, 2020, **8**, 2000110.
 - 24 A. Abdallah, S. Freslon, X. Fan, A. Rojo, C. Daiguebonne, Y. Suffren, K. Bernot, G. Calvez, T. Roisnel and O. Guillou, *Inorg. Chem.*, 2019, **58**, 462–475.
 - 25 Y. Zhang, S. Yuan, G. Day, X. Wang, X. Yang and H.-C. Zhou, *Coord. Chem. Rev.*, 2018, **354**, 28–45.
 - 26 O. Guillou, C. Daiguebonne, G. Calvez and K. Bernot, *Acc. Chem. Res.*, 2016, **49**, 844–856.
 - 27 J. Rocha, L. D. Carlos, F. A. A. Paz and D. Ananias, *Chem. Soc. Rev.*, 2011, **40**, 926–940.
 - 28 M. S. Tarasenko, A. Y. Ledneva, D. Y. Naumov, N. G. Naumov and V. E. Fedorov, *J. Struct. Chem.*, 2011, **52**, 172–179.
 - 29 M. S. Tarasenko, N. G. Naumov, D. Y. Naumov, N. V. Kuratieva and V. E. Fedorov, *Russ. J. Coord. Chem.*, 2006, **32**, 494–503.
 - 30 S. B. Artemkina, N. G. Naumov, A. V. Virovets, S. A. Gromilov, D. Fenske and V. E. Fedorov, *Inorg. Chem. Commun.*, 2001, **4**, 423–426.
 - 31 V. E. Fedorov, Y. V. Mironov, N. G. Naumov, M. N. Sokolov and V. P. Fedin, *Russ. Chem. Rev.*, 2007, **76**, 529–552.
 - 32 G. Pilet and A. Perrin, *C. R. Chim.*, 2005, **8**, 1728–1742.
 - 33 Y. Kim, V. E. Fedorov and S.-J. Kim, *J. Mater. Chem.*, 2009, **19**, 7178–7190.
 - 34 V. E. Fedorov, N. G. Naumov, Y. V. Mironov, A. V. Virovets, S. B. Artemkina, K. A. Brylev, S. S. Yarovoi, O. A. Efremova and U. H. Peak, *J. Struct. Chem.*, 2002, **43**, 669–684.
 - 35 M. P. Shores, L. G. Beauvais and J. R. Long, *J. Am. Chem. Soc.*, 1999, **121**, 775–779.
 - 36 A. V. Ermolaev, A. I. Smolentsev, K. A. Brylev, N. Kitamura and Y. V. Mironov, *J. Mol. Struct.*, 2018, **1173**, 627–634.
 - 37 M. Amela-Cortes, S. Cordier, N. G. Naumov, C. Mériadec, F. Artzner and Y. Molard, *J. Mater. Chem. C*, 2014, **2**, 9813–9823.
 - 38 L. Xu, Y. Kim, S.-J. Kim, H. J. Kim and C. Kim, *Inorg. Chem. Commun.*, 2007, **10**, 586–589.
 - 39 Y. V. Mironov, N. G. Naumov, K. A. Brylev, O. A. Efremova, V. E. Fedorov and K. Hegetschweiler, *Angew. Chem., Int. Ed.*, 2004, **43**, 1297–1300.
 - 40 Y. M. Litvinova, Y. M. Gayfulin, J. van Leusen, D. G. Samsonenko, V. A. Lazarenko, Y. V. Zubavichus, P. Kögerler and Y. V. Mironov, *Inorg. Chem. Front.*, 2019, **6**, 1518–1526.
 - 41 Y. M. Litvinova, Y. M. Gayfulin, K. A. Kovalenko, D. G. Samsonenko, J. van Leusen, I. V. Korolkov, V. P. Fedin and Y. V. Mironov, *Inorg. Chem.*, 2018, **57**, 2072–2084.
 - 42 D. Mara, F. Artizzu, P. F. Smet, A. M. Kaczmarek, K. Van Hecke and R. Van Deun, *Chem. – Eur. J.*, 2019, **25**, 15944–15956.
 - 43 E. Kreidt, C. Kruck and M. Seitz, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. J.-C. G. Bünzli and V. K. Pecharsky, Elsevier, 2018, vol. 53, pp. 35–79.
 - 44 T. Förster, *Spec. Discuss. Faraday Soc.*, 1959, **27**, 7–17.
 - 45 N. Ponjan, F. Kielar, W. Dungkaew, K. Kongpatpanich, H. Zenno, S. Hayami, M. Sukwattanasinittf and K. Chainok, *CrystEngComm*, 2020, **22**, 4833–4841.
 - 46 Y. Pan, H.-Q. Su, E.-L. Zhou, H.-Z. Yin, K.-Z. Shaoc and Z.-M. Su, *Dalton Trans.*, 2019, **48**, 3723–3729.
 - 47 K. Zhang, X. Xie, H. Li, J. Gao, L. Nie, Y. Pan, J. Xie, D. Tian, W. Liu, Q. Fan, H. Su, L. Huang and W. Huang, *Adv. Mater.*, 2017, **29**, 1701804.
 - 48 T. Kimura, R. Nagaishi, Y. Kato and Z. Yoshida, *J. Alloys Compd.*, 2001, **323–324**, 164–168.
 - 49 F. Artizzu, P. Deplano, L. Marchiò, M. L. Mercuri, L. Pilia, A. Serpe, F. Quochi, R. Orrù, F. Cordella, F. Meinardi, R. Tubino, A. Mura and G. Bongiovanni, *Inorg. Chem.*, 2005, **44**, 840–842.
 - 50 A. Rodríguez-Rodríguez, D. Esteban-Gómez, R. Tripier, G. Tircsó, Z. Garda, I. Tóth, A. de Blas, T. Rodríguez-Blas and C. Platas-Iglesias, *J. Am. Chem. Soc.*, 2014, **136**, 17954–17957.
 - 51 B. El Aroussi, L. Guénée, P. Pal and J. Hamacek, *Inorg. Chem.*, 2011, **50**, 8588–8597.
 - 52 A. Zurawski, M. Mai, D. Baumann, C. Feldmann and K. Müller-Buschbaum, *Chem. Commun.*, 2011, **47**, 496–498.
 - 53 J. C. Rybak, L. V. Meyer, J. Wagenhöfer, G. Sextl and K. Müller-Buschbaum, *Inorg. Chem.*, 2012, **51**, 13204–13213.
 - 54 K. Müller-Buschbaum, *Z. Anorg. Allg. Chem.*, 2005, **631**, 811–828.
 - 55 S. Cordier, Y. Molard, K. A. Brylev, Y. V. Mironov, F. Grasset, B. Fabre and N. G. Naumov, *J. Cluster Sci.*, 2015, **26**, 53–81.
 - 56 H. Wang, S. Zhao, P. Qian, J. Dai, Z. Cao and K. Yu, *Polyhedron*, 1995, **14**, 407–412.
 - 57 X.-L. Wang, F.-F. Sui, H.-Y. Lin, J.-W. Zhang and G.-C. Liu, *Cryst. Growth Des.*, 2014, **14**, 3438–3452.
 - 58 X.-F. Tan, J. Zhou, H.-H. Zou, H.-P. Xiao, Q. Tang, T. Jiang and X. Zhang, *J. Cluster Sci.*, 2016, **27**, 2025–2033.
 - 59 A. L. Pochodylo, J. A. Wilson, J. W. Uebler, S. H. Qiblawi and R. L. LaDuca, *Inorg. Chim. Acta*, 2014, **423**, 298–306.
 - 60 C.-G. Wang, Y.-H. Xing, Z.-P. Li, J. Li, X.-Q. Zeng, M.-F. Ge and S.-Y. Niu, *Cryst. Growth Des.*, 2009, **9**, 1525–1530.
 - 61 Y.-Q. Zheng, D.-Y. Cheng, J.-L. Lin, Z.-F. Li and X.-W. Wang, *Eur. J. Inorg. Chem.*, 2008, **2008**, 4453–4461.

- 62 D. T. de Lill, A. de Bettencourt-Dias and C. L. Cahill, *Inorg. Chem.*, 2007, **46**, 3960–3965.
- 63 T. Yoshimura, S. Ishizaka, Y. Sasaki, H.-B. Kim, N. Kitamura, N. G. Naumov, M. N. Sokolov and V. E. Fedorov, *Chem. Lett.*, 1999, **28**, 1121–1122.
- 64 T. G. Gray, C. M. Rudzinski, E. E. Meyer, R. H. Holm and D. G. Nocera, *J. Am. Chem. Soc.*, 2003, **125**, 4755–4770.
- 65 L. G. Beauvais, M. P. Shores and J. R. Long, *Chem. Mater.*, 1998, **10**, 3783–3786.
- 66 K. A. Brylev, Y. V. Mironov, N. G. Naumov, V. E. Fedorov and J. A. Ibers, *Inorg. Chem.*, 2004, **43**, 4833–4838.
- 67 S. B. Artemkina, N. G. Naumov, A. V. Virovets and V. E. Fedorov, *Eur. J. Inorg. Chem.*, 2005, **2005**, 142–146.
- 68 N. G. Naumov, M. S. Tarasenko, A. V. Virovets, Y. Kim, S.-J. Kim and V. E. Fedorov, *Eur. J. Inorg. Chem.*, 2006, **2006**, 298–303.
- 69 B. Valeur and M. N. Berberan-Santos, *Molecular Fluorescence Principles and Applications*, Wiley-VCH, Weinheim, 2012.
- 70 H. Lueken, *Magnetochemie*, Teubner Verlag, Stuttgart, 1999.