Cyanide-bridged tetradecanuclear $\mathrm{Ru^{II}{}_3M^{II}{}_{11}}$ clusters ($\mathrm{M^{II}} = \mathrm{Zn^{II}}$ and $\mathrm{Cu^{II}}$) based on the high connectivity building block $[\mathrm{Ru_3(HAT)(CN)_{12}}]^{6-}$: structural and photophysical properties†‡

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Received (in Cambridge) 30th April 2008, Accepted 11th June 2008
First published as an Advance Article on the web 25th July 2008
DOI: 10.1039/b807364c

Reaction of the anionic cyanometallate chromophore $[\{\mathrm{Ru(CN)_4}\}_3(\mu_3\text{-HAT})]^{6-}$ with $[\mathrm{M^{II}(tren)}]^{2+}$ complexes (M = $\mathrm{Zn^{II}}$, $\mathrm{Cu^{II}}$) provides discrete tetradecanuclear clusters of formula $[\{\mathrm{M^{II}(tren)(\mu\text{-}CN)}\}_{11}\{\mathrm{Ru_3(HAT)(CN)}\}]^{16+}$; the weak luminescence of the $\mathrm{Ru_3}$ chromophore is substantially enhanced in the presence of $\mathrm{Zn^{II}}$ ions, whereas it is completely quenched when $\mathrm{Cu^{II}}$ centers are present.

Currently, the self-assembly of cyano-linked metal complexes attracts a lot of interest not only because of their potential applications in fields as diverse as molecular magnetism,[1] photochemistry,[2] hydrogen storage[3] or host–guest chemistry,[4] but also because of their fascinating structural diversity and topologies.[5] The main strategy used to prepare heteropolynuclear cyanometallates is to use a stable cyanometallate anion as a ligand toward either fully solvated metal ions or metal complexes whose coordination spheres are partially blocked with polydentate end-cap ligands. Generally, highly insoluble three-dimensional cyano-bridged polymers are obtained when the cation is fully solvated[6] whereas lower dimensionality heterometallic compounds result if the outer metal ions have only a few coordination sites available, with others blocked.[7]

Recently, we described the synthesis, structure and spectroscopic properties of $[\{\mathrm{Ru(CN)_4}\}_3(\mu_3\text{-HAT})]^{6-}$ (**Ru3-HAT**) in which three $\{\mathrm{Ru(CN)_4}\}^{2-}$ units are connected to the tritopic ligand hexaazatriphenylene (HAT).[8] The extended aromatic bridging ligand and the presence of three chromophoric centres resulted in a remarkably intense, low energy, and highly solvatochromic absorption of light. The potential connectivity of up to 12 at a single 'node', provided by the externally directed cyanide binding sites, was unprecedented in cyanide-based coordination networks, for which the highest potential connectivity until then was from octacyanometallates of Nb, Mo and W.[9] We used **Ru3-HAT** as the basis of coordination networks with lanthanide cations and demonstrated that this complex can act as a light-harvesting 'antenna' generating sensitized near-infrared luminescence from f-block ions.[10] Up to eight of the twelve cyanide groups were involved in bridging interactions to Ln(III) ions.

As a part of our studies on the reactivity of the **Ru3-HAT** complex with metal ions and metal complexes, we herein show that it is possible to increase the connectivity of **Ru3-HAT** and, at the same time, to ensure the formation of single molecules, by following the strategy of assembling **Ru3-HAT** with *capped* complexes that possess only one accessible free coordination position for the nitrogen atoms of the cyanide groups. Thus, reaction of **Ru3-HAT** with $[\mathrm{M^{II}(tren)}]^{2+}$ complexes [M = Zn, Cu; tren = tris(2-aminoethyl)amine], prepared *in situ* by reaction of equimolar amounts of tren and $\mathrm{M^{II}}$ perchlorate salts, generates discrete heterometallic clusters $[\{\mathrm{M^{II}(tren)CN}\}_{11}\mathrm{Ru_3(HAT)(CN)}](\mathrm{ClO_4})_{16}\cdot n\mathrm{H_2O}$ [M = Zn (**1**), Cu (**2**)], in which the **Ru3-HAT** unit is linked through cyanide bridging groups to eleven $[\mathrm{M^{II}(tren)}]^{2+}$ units.§ X-Ray crystallographic studies revealed that **1** and **2** are isostructural compounds crystallizing in monoclinic space group $P2_1/c$ (see ESI†).

The structure of **1** consists of tetradecanuclear $[\{\mathrm{Zn^{II}(tren)(\mu\text{-}CN)}\}_{11}\{\mathrm{Ru_3(HAT)(CN)}\}]^{16+}$ cations, perchlorate anions and additional lattice solvent molecules. Within the tetradecanuclear cations (Fig. 1), Ru(1A) and Ru(1B) are linked to four $[\mathrm{Zn(tren)}]^{2+}$ fragments by one bridging cyanide each, whereas Ru(1C) is linked to only three of these fragments, with the remaining cyanide being terminal. The HAT ligand is almost planar; the largest deviation from the mean plane is 0.171 Å at C(8). Ru(1A), Ru(1B) and Ru(1C) are respectively +0.188, +0.081 and −0.230 Å out of this plane. Because the HAT ligand is slightly bent, the cyanide groups belonging to different Ru atoms and lying below the HAT plane are separated from each other by greater distances than those lying above this plane. This leads to an increase of steric

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† Electronic supplementary information (ESI) available: X-Ray structure determination details for **1** and **2**, Table S1: Crystal data and structure refinement for **1**. Table S2: Selected crystallographic bond lengths and angles for **1**, Fig. S2: $\chi_M T$ *vs.* temperature plot for **2**. Fig. S3: magnetisation *vs.* magnetic field plot for **2**. CCDC 686538. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b807364c

‡ The authors would like to dedicate this paper to the memory of Sam Hawxwell, smart chemist and friend, who recently passed away.

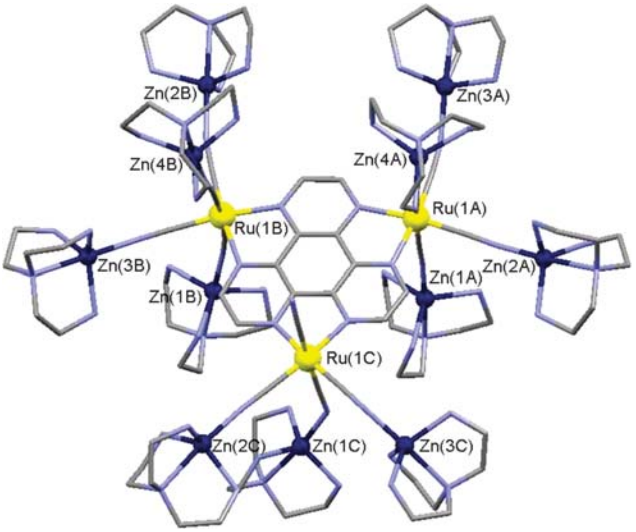

Fig. 1 Crystal structure of the 14-nuclear cation of the $[\{Zn^{II}(tren)(\mu\text{-}CN)\}_{11}\{Ru_3(HAT)(CN)\}](ClO_4)_{16}$ cluster **1** (C = grey, N = light blue, Zn = dark blue, Ru = yellow). For clarity only the metal ions are labelled. Selected ranges for interatomic distances (Å) and angles (°): Ru···Zn 4.878–5.288; Ru–C 1.965(4)–2.058(4); Ru–N(HAT) 2.106(3)–2.142(3); Zn–N(cyano) 2.012(4)–2.072(4); Zn–N_{ax}(tren) 2.241(4)–2.340(4); Zn–N_{eq}(tren) 2.039(4)–2.094(4); N(HAT)–Ru–N(HAT)′ 79.40(12)–79.47(12); Ru–C≡N 173.7(4)–178.7(4); C≡N–Zn 138.0(3)–175.1(4); N(cyano)–Zn–N_{ax}(tren) 170.58(15)–177.30(15); N(cyano)–Zn–N_{eq}(tren) 91.10(15)–106.81(18); N_{ax}(tren)–Zn–N_{eq}(tren) 79.03(16)–82.82(14).

crowding in the "upper part" of the molecule, thus preventing the coordination of twelve $[M^{II}(tren)]^{2+}$ units around the **Ru3-HAT** complex. Each Ru atom is coordinated by two HAT nitrogen atoms and four cyanide carbon atoms in a conventional distorted octahedral geometry. The main factor accounting for this distortion is the small bite angle N(HAT)–Ru–N(HAT)′ of the chelating HAT [79.40(12)° Ru(1A), 79.47(12)° Ru(1B), 79.46(12)° Ru(1C)], which is typical of chelating diimine ligands. Ru–N and Ru–C distances are close to those observed in previously reported structures containing the $[Ru_3(HAT)(CN)_{12}]^{6-}$ unit.[10] Although Ru–C≡N groups are close to linearity [174.8(4)–177.4(4)° Ru(1A), 173.7(4)–178.7(4)° Ru(1B), 175.4(4)–178.5(4)° Ru(1C)] the Zn–N≡C angles are more bent [160.0(4)–172.3(5)° Ru(1A), 160.4(3)–175.1(4)° Ru(1B), 138.0(3)–175.0(4)° Ru(1C)]. The geometry of each Zn^{II} centre in **1** can be described as distorted trigonal bipyramidal, with the nitrogen atoms of the primary amines on each tren ligand occupying equatorial positions around the Zn centre and the nitrogen atoms of the tertiary amine and the cyanide located at the axial positions. Significant variations in both Zn–N distances and N–Zn–N angles are found in the equatorial plane. The N(eq)–Zn–N(ax) angles are reduced from 90°, thus the N(eq)–Zn–N(cyano) angles are greater than 90° with the Zn centres sitting outside the plane formed by the primary amine nitrogens towards the bridging cyano groups.

For complex **2** the diffraction data was too weak to permit a complete refinement and accurate description of the structure, but it was however enough to prove that **2** is isostructural to **1**. The magnetic properties of **2** are consistent with the presence of eleven uncoupled Cu^{II} ions (Fig. S1, ESI†). At $T > 20$ K, the $\chi_M T$ product is almost constant with a 4.75 cm^3 K mol^{-1} value, which is close to the theoretical value of 4.64 cm^3 K mol^{-1} calculated for eleven independent spins with $S = 1/2$ and $g = 2.12$. Below 20 K, the $\chi_M T$ slightly decreases, pointing out the existence of a weak antiferromagnetic exchange interaction between next nearest Cu^{II} centers through the diamagnetic NC–Ru–CN bridges. The magnetization of **2** reveals the expected behaviour for uncoupled Cu^{II} ions fitting well with a Brillouin function for eleven independent spins $S = 1/2$ (Fig. S2, ESI†).

Solid-state reflectance electronic spectra of **Ru3-HAT** (sodium salt), **1** and **2** are shown in Fig. 2. For **Ru3-HAT**, the spectrum shows an intense and broad ^{1}MLCT band centered at 550 nm. As we reported recently, the broadness of this band is due to the existence of a manifold of several closely spaced ^{1}MLCT absorptions associated with the presence of a manifold of closely-spaced, low-lying π* orbitals on the HAT ligand.[10] In (**1**), coordination of $[Zn^{II}(tren)]^{2+}$ units to the **Ru3-HAT** centre through the cyanide bridges leads to a substantial blue-shift of the ^{1}MLCT absorption maximum to 480 nm. A similar effect is observed in **2** in which the **Ru3-HAT** based ^{1}MLCT absorption band shifts to 508 nm when $[Cu^{II}(tren)]^{2+}$ units coordinate to the cyanides of the **Ru3-HAT** core. Additionally, intense d–d absorption bands are observed in the red/near-IR region of the spectrum for this Cu(II) adduct.[11]

The blue shift of the **Ru3-HAT** based ^{1}MLCT band observed in **1** and **2** is understandable in terms of the electron-withdrawing effect of the $[M^{II}(tren)]^{2+}$ units which stabilises the d(π)-orbitals of the **Ru3-HAT** chromophore; the π-electron density is drawn away from the Ru-center and the energy of the HOMO orbital is lowered, thereby increasing the energy of the MLCT transitions. This 'metallochromic' effect is similar to those observed in related systems in which protons, alkali,

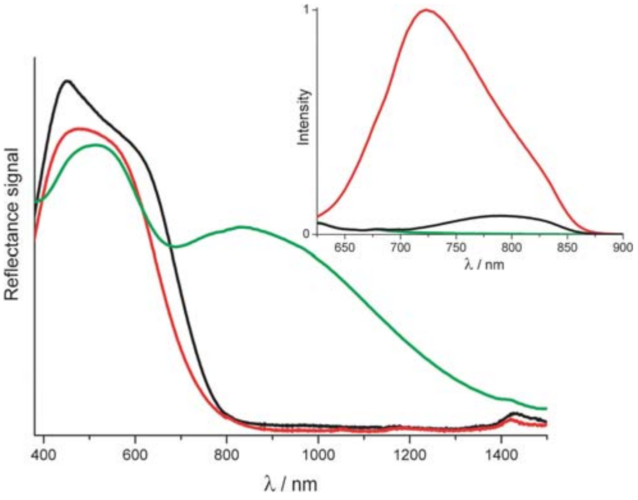

Fig. 2 Solid-state reflectance electronic spectra of **Ru3HAT** (sodium salt, black line), (**1**) (red line) and (**2**) (green line) [^{1}MLCT transition bands between 400–700 nm in all three cases; d–d absorption manifold between 700–1400 nm characteristic for Cu^{II} ions in complex **2**]. The inset shows the luminescence spectra as powders using the same colour scheme.

alkali earth and transition metal ions act as Lewis acids to mononuclear $[Ru(bipy)(CN)_4]^{2-}$ units.[12]

The solid-state luminescence spectrum of **Ru3-HAT** shows a very weak ^{3}MLCT luminescence maximum at 790 nm. The time-resolved luminescence decay from this sample appeared to be too short to be measured by conventional single-photon counting methods at room temperature. However, from transient IR spectroscopic measurements, the ^{3}MLCT lifetime of **Ru3-HAT** in aqueous solutions (that is, hydrated but not interacting with any additional metal ions) is about 18 ns. In **1**, coordination of the $[Zn(tren)]^{2+}$ units to the cyanides leads to the appearance of a much stronger and blue-shifted ^{3}MLCT luminescence ($\approx$720 nm emission maximum) compared to the parent **Ru3-HAT** salt. The time-resolved luminescence decay from **1** fitted well to a double exponential decay with lifetime components of 250 ns (major component, 97%) and 27 ns (minor component, 3%).¶ Conversely, the ^{3}MLCT emission of **2** is completely quenched as a consequence of the coordination of $[Cu^{II}(tren)]^{2+}$ centers, with low-lying d–d states which can quench higher-lying excited states, to the Ru3-HAT chromophore.[13]

In conclusion, we have obtained, using a *bottom up* approach, nano-sized discrete clusters in which the $[Ru_3(HAT)(CN)_{12}]^{6-}$ unit is linked through cyanide bridging groups to eleven $[M^{II}(tren)]^{2+}$ units. These compounds demonstrate the highest connectivity so far reported for cyanide-bridged polynuclear complexes. Substantial changes in the luminescence properties of the $[Ru_3(HAT)(CN)_{12}]^{6-}$ chromophore occurs on going from **1** to **2**, depending of the nature of the metal cation to which is linked. Thus, the luminescence is substantially enhanced in the presence of Zn^{II} ions whereas it is completely quenched when Cu^{II} centers are present. This could lead to possible applications of $[Ru_3(HAT)(CN)_{12}]^{6-}$ derivates as luminescent sensors. Work focusing on the preparation and photophysical and photomagnetic characterisation of other cyanide-bridged Ru^{II}–$M^{II/III}$ ($M = Cu^{II}$, Zn^{II}, Fe^{III} and Mn^{III}) systems is currently in progress in our lab.

We thank the Spanish Ministry of Education and Science, The Junta de Andalucía, and the EPRSC for funding.

Notes and references

§ *Syntheses*. **1**: A solution of tris(2-amino)ethylamine (0.11 g, 0.75 mmol) in water–acetonitrile (1 : 1, 5 mL) was added to a solution of $Zn^{II}(ClO_4)_2\cdot 6H_2O$ (0.26 g, 0.7 mmol) in water (5 mL). The mixture was stirred for 10 min. before the addition of $Na_6[Ru_3(HAT)(CN)_{12}]\cdot 12H_2O$ (0.05 g, 0.05 mmol) dissolved in a minimum of water–acetonitrile (1 : 1) mixture. Slow evaporation of the resulting solution over a period of 60 h at 4 °C resulted in a crop of deep-red crystals that were filtered off, washed with a minimal amount of cold water and dried *in vacuo*. Yield: 63%. IR (KBr): ν_{max}/cm^{-1}: 3343(vs), 2920(m), 2126(m), 2089(s), 1087(vs), 626(s). Anal. Found: C, 22.27; H, 4.87; N, 17.51. Calc. for $(\mathbf{1})\cdot 20H_2O\cdot 4CH_3CN$: C, 22.23; H, 4.87; N, 17.46%. ESMS: m/z 2284.99 $\{[Zn^{II}(tren)(\mu\text{-}CN)\}_{11}\{Ru_3(HAT)(CN)\}](ClO_4)_{14}\}^{2+}$, 1490.01 $\{[\{Zn^{II}(tren)(\mu\text{-}CN)\}_{11}\{Ru_3(HAT)(CN)\}](ClO_4)_{13}\}^{3+}$.
2: This was prepared as for **1** but using $Cu^{II}(ClO_4)_2\cdot 6H_2O$. Yield: 45%. IR (KBr): ν_{max}/cm^{-1}: 3438(vs), 2930(m), 2149(m), 2119(s), 1091(vs), 627(s). Anal. Found: C, 21.73; H, 4.73; N, 17.37. Calc. for $\mathbf{2}\cdot 17H_2O\cdot CH_3CN$: C, 21.69; H, 4.77; N, 17.32%. ESMS: m/z 2275.01 $\{[Cu^{II}(tren)(\mu\text{-}CN)\}_{11}\{Ru_3(HAT)(CN)\}](ClO_4)_{14}\}^{2+}$, 1483.69 $\{[\{Cu^{II}(tren)CN\}_{11}\{Ru_3(HAT)(CN)\}](ClO_4)_{13}\}^{3+}$.

¶ Luminescence lifetimes were measured on solid samples using an Edinburgh Instruments Mini-τ instrument with a pulsed 405 nm diode laser as the excitation source.

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