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Synthesis and SMM behaviour of trinuclear *versus* dinuclear 3d–5f uranyl(v)–cobalt(ii) cation–cation complexes†

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Trinuclear *versus* dinuclear heterodimetallic $U^VO_2^+\cdots Co^{2+}$ complexes were selectively assembled *via* a cation–cation interaction by tuning the ligand. The trimeric complex **2**, with a linear [Co–O=U=O–Co] core, exhibits magnetic exchange and slow relaxation with a reversal barrier of 30.5 ± 0.9 K providing the first example of a U–Co exchange-coupled SMM.

Over the last ten years the chemistry of uranyl(v) has undergone an impressive development.[1] Despite the fact that uranyl(v) tends to disproportionate leading to U(vi) and U(iv) species, several stable complexes of uranyl(v) have been prepared and characterized using polydentate, macrocyclic and/or bulky ligands that prevent cation–cation interactions (CCIs).[2,3] CCIs are used to describe the interaction of the uranyl oxo group with the uranium centre from an UO_2^+ moiety or any other metal cation. The $UO_2^+\cdots UO_2^+$ interaction is thought to be a key intermediate in uranyl(v) disproportionation,[2d,4] but stable compounds containing $UO_2^+\cdots UO_2^+$ (ref. 2d, 4b and 5) and/or $UO_2^+\cdots M^{2/3+}$ interactions[3c,e,6] have been isolated in rigorously anaerobic aprotic solvents. CCIs are thought to play an important role both in the environmental migration of actinides and in nuclear fuel recycling technology.[1c,7] Moreover $UO_2^+\cdots M^{2+}$ interactions provide a very convenient route for the controlled assembly of oxo-bridged heteropolymetallic complexes of uranium and for the expansion of the poorly developed supramolecular chemistry of actinides. Heteropolymetallic 3d–5f complexes are of great interest for the design of molecules

presenting slow magnetic relaxation of a purely molecular origin (single molecule magnets or SMMs).[8] Notably the combination of the high single ion anisotropy of uranium with the high spin of the d-block transition metals provides a promising prospective for the preparation of SMMs with high barriers to the reversal of the magnetization and magnetic hysteresis at reasonable temperatures (essential requirements for the application of SMMs).[8] Recent studies demonstrated that the $UO_2^+\cdots UO_2^+$ and $UO_2^+\cdots M^{2/3+}$ interactions provide an efficient pathway for magnetic exchange affording rare[9] examples of unambiguous 5f–5f, 3d–5f and 4f–5f magnetic communication.[2e,3c,4b,5,6,10] Moreover, the first examples of actinide clusters showing both slow magnetic relaxation (SMM behaviour) and magnetic exchange were assembled through a CCI.[6a,b,11] In particular, we recently prepared several trinuclear complexes containing a linear [M–O=U=O–M] (M = Mn(ii), Fe(ii), Ni(ii)) core and all these complexes show SMM behaviour. The magnetic analysis of a series of complexes of different geometries containing different d-metals is key to the understanding of the structural parameters leading to slow relaxation in these complexes. However, the synthesis of such a series is not straightforward because the binding of metals to the uranyl groups may result in the disproportionation of the uranyl(v) moiety or in different cluster nuclearities.[2d,f]

Herein we report the first examples of heteropolymetallic uranium complexes containing $UO_2^+\cdots Co^{2+}$ interactions. We also show how the cluster nuclearity can be controlled to afford a trimeric compound that exhibits SMM behaviour.

The reaction of $[UO_2(\text{Mesaldien})K]_\infty$[2f] (Mesaldien)=*N*,*N*′-(2-aminomethyl)diethylenebis(salicylidene imine) with two equivalents of [Co(TPA)I]I (TPA = tris(2-pyridylmethyl)amine) in pyridine under an argon atmosphere affords a mixture of a dinuclear species {[Co(TPA)}{UO_2(Mesaldien)}]I **1** and [Co(TPA)I]I. Complex **1** was isolated analytically pure in 73% yield from the reaction of $[UO_2(\text{Mesaldien})K]_\infty$ with one equivalent of [Co(TPA)I]I in pyridine in 73% yield (Scheme 1). The dimeric complex is stable in the solid state and in pyridine or acetonitrile solution for months under an argon atmosphere (see the ESI†).

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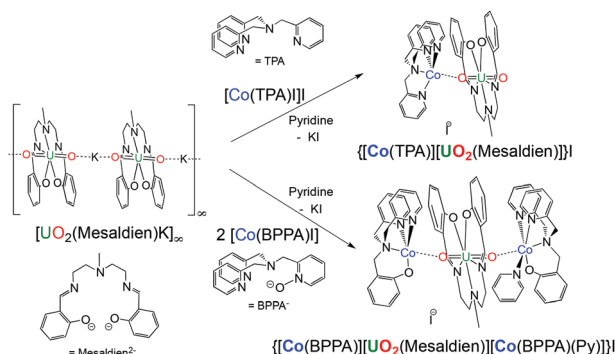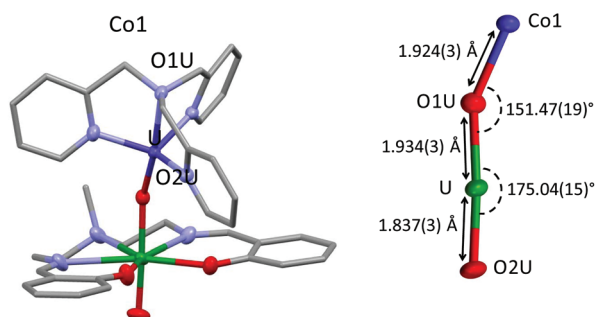
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Scheme 1 Synthesis of **1** and **2**.

Fig. 1 Solid-state molecular structure (top) of **1** and details of the core with associated distances and angles (bottom) (30% probability ellipsoids for heteroatoms, carbon atoms were represented in pipes, H, counter anion and co-crystallized solvent molecules were omitted for clarity) Colour code: uranium (green), cobalt (blue), oxygen (red), nitrogen (light blue) and carbon (grey).

The solid state structure of **1** (Fig. 1) consists of one $[Co(TPA)]^{2+}$ cation bound to one oxo group of the $[UO_2(Mesaldien)]^-$ anion through a cation–cation interaction (Fig. 1). The uranium atom is heptacoordinate with a slightly distorted pentagonal bipyramidal geometry.

The Co(II) cation is pentacoordinate, with a slightly distorted trigonal bipyramidal geometry defined by the four nitrogen atoms of the TPA ligand and one oxygen atom from the uranyl(v) group. In **1** the mean value of the U=O bond distances lies in the range of the values typically observed for uranyl(v) complexes, with the uranyl–metal interaction resulting in a slight lengthening of the U=O distance for the bound uranyl oxo group (1.931(3) Å) in **1** compared to the unbound one (1.840(3) Å). The Co–O_{yl} (where O_{yl} is the uranyl oxygen) bond distance in **1** (1.926(3) Å) is significantly shorter than that found in the only reported heterodimetallic uranyl(vi)–Co(II) complex (2.084(6) Å)[12] or in heterodimetallic UO_2^{2+}–Co(II) polymers (2.13–2.19 Å).[13] This is in agreement with the expected higher basicity of the uranyl(v) oxo group compared to the uranyl(vi) one.

Direct current (dc) magnetic susceptibility measurements were performed on a polycrystalline sample of **1** in the temperature range of 2–300 K, in an applied field of 0.5 T. The χT (χ = molar magnetic susceptibility) versus T plots for **1** is shown in Fig. 2. The χT value for the dinuclear cobalt **1** at room
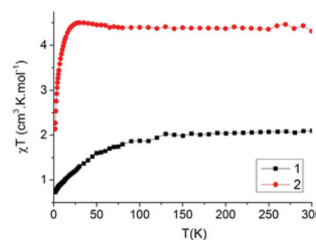

Fig. 2 Plots of χT versus T for polycrystalline samples of **1** and **2**, measured at the 0.5 T applied field.

temperature is approximately 2.3 cm³ K mol⁻¹; this value is in agreement with the spin-only value of a high-spin pentacoordinated Co(II) complex (1.875 cm³ K mol⁻¹ with $S = 3/2$ and $g = 2$) and one pentavalent uranium ion (0.32 cm³ K mol⁻¹, the value obtained from the trinuclear UO_2Cd_2 where the uranium has the same environment[6b]). The χT value remains constant on cooling to 120 K and then decreases constantly to reach 0.7 cm³ K mol⁻¹ at 2 K. This behaviour is likely due to antiferromagnetic coupling between Co(II) and U(v) ions, depopulation of Stark sublevels and/or zero-field splitting (zfs) effects. The magnetization dynamics for **1** were investigated by alternating current (ac) magnetic susceptibility measurements as a function of frequency ($\nu = 0.1$–1400 Hz) in zero dc field and under applied fields (1000 to 9000 G) (ESI†). In each case, the in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility do not show frequency dependency.

These results show that the reaction of the [Co(TPA)I]I complex with $[UO_2(Mesaldien)K]_\infty$ leads only to the formation of a dimeric complex. The dimeric complex **1** shows no evidence of $UO_2^+ \cdots M^{2+}$ magnetic coupling and does not exhibit slow relaxation of the magnetization. In contrast, previous reports from our group have shown that the trimeric complexes $[M(TPA)X][UO_2(Mesaldien)][M(TPA)X]^+$ $[M(TPA)X_2]$ (M = Mn(II), Fe(II), Ni(II); X = I⁻ or Cl⁻)[6b,d] all exhibited magnetic exchange between the uranyl ion and the d-block ion that resulted in SMM behaviour. These trimeric complexes were prepared using the same strategy used for the preparation of complex **1** by reacting $[UO_2(Mesaldien)K]_\infty$ with 2 equiv. of the complexes $[M(TPA)X_2]$ (M = Mn(II), Fe(II), Ni(II); X = I⁻ or Cl⁻).

However, we can note that in the reported trimeric complexes the halide remains bound to the d metal, while in the solid state structure of complex **1** the iodide does not bind the cobalt centre probably due to the fact that the octahedral geometry is not favourable for Co(II) in the coordination environment of **1**. Thus, the resulting $[Co(TPA)]^{2+}$ is a stronger Lewis acid than the $[M(TPA)I]^+$ (M = Mn, Fe, Ni, Cd) counterparts and therefore once bound to one of the uranyl(v) oxo groups it leads to a reduced basicity of the second oxo group preventing the occurrence of a second UO_2–Co cation–cation interaction and trimer formation. In order to promote the formation of a trimeric system we therefore decided to carry out the metathesis reaction in the presence of the cobalt(II) complex of a monoanionic tripodal ligand used as a less acidic fragment. A monoanionic tripodal tetradentate ligand, derived

of the TPA was used to complex the cobalt: BPPA$^-$ (BPPA$^-$ = bis(2-pyridylmethyl)(2-hydroxybenzyl)amine). The reaction of [UO$_2$(Mesaldien)K]$_\infty$^{2f} with two equivalents of the complex [Co(BPPA)I] affords the trinuclear assembly [{[Co(BPPA)][UO$_2$(Mesaldien)][Co(BPPA)(Py)]}]I, **2** in 92% yield. This demonstrates that the choice of the cobalt capping ligand is crucial for determining the nuclearity of the final structure. Notably the charge of the capping ligand can be used to tune the electrophilic character of the 3d cation. The use of mono-anionic BPPA$^-$ as the capping ligand yields a monocationic [Co(BPPA)]$^+$ unit which allows the selective self-assembly of the trimer **2** through two UO$_2$–Co cation–cation interactions.

X-ray quality single crystals of **2**·2.5Py were obtained by slow diffusion of hexane in a pyridine solution of the complex. This complex is stable for months under an argon atmosphere in the solid state and in pyridine or acetonitrile solution as indicated by NMR studies. The structure of **2** consists of one anionic uranyl(v) complex [UO$_2$(Mesaldien)]$^-$ linked to [Co(BPPA)(Py)]$^+$ and [Co(BBPA)]$^+$ moieties through the two oxo groups (Fig. 3). The uranium atom in **2** adopts a slightly distorted pentagonal bipyramidal geometry, similar to that found in **1**.

In **2**, the two transition metals are not in the same environment, the cobalt centre in [Co(BPPA)(Py)]$^+$ is six-coordinated with a slightly distorted octahedral arrangement by the four nitrogen atoms of the TPA ligand, one uranyl(v) oxo group and one pyridine nitrogen while the [Co(BBPA)]$^+$ cobalt complex does not contain a Co-bound pyridine and adopts a trigonal bipyramidal geometry. The U=O bond distances lie in the range of the values observed for uranyl(v) complexes, with the UO$_2$$^+$···Co^{2+} interactions resulting in a significant lengthening of the U=O bonds (1.913(6) Å) and (1.897(6) Å) compared to those found in the [UO$_2$(Mesaldien)K]$_\infty$ complex (1.862(2) and 1.79(2) Å).^{2f} Finally in **2**, the mean Co–O$_{yl}$ distance at 2.01(2) Å is longer than the Co–O$_{yl}$ distance in **1** (1.924(3) Å) suggesting a weaker interaction between the oxo groups of the uranyl(v) and the two cobalt complexes. In spite of this, the proton NMR studies of solutions of **2** show that the trinuclear complex is stable in pyridine and acetonitrile solutions for up to one month.
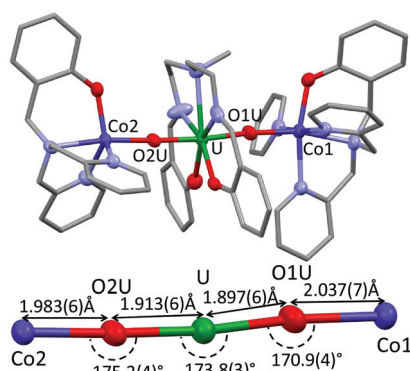
Direct current (dc) magnetic susceptibility measurements were performed on a polycrystalline sample of **2** in the temperature range of 2–300 K, in applied fields of 0.5 T. The χT versus T plots for **2** is shown in Fig. 2. The χT value for the trinuclear complex **2** at room temperature is approximately 4.1 cm^3 K mol^{-1}; this value is in agreement with the expected value for two S = 3/2 Co(II) ions (1.875 cm^3 K mol^{-1} per Co(II) ion, assuming g = 2) and one pentavalent uranium ion (0.32 cm^3 K mol^{-1}).

The χT product for **2** is nearly constant between 300 and 70 K, and increases slowly upon further cooling to reach a weak maximum of 4.5 cm^3 K mol^{-1} (at 1 T) at 30 K, before dropping rapidly at very low temperatures most likely due to zfs effects. The increase of χT with decreasing temperature indicates the occurrence of magnetic exchange coupling between uranium and cobalt ions in **2**; both antiferromagnetic and ferromagnetic exchanges are predicted to give an enhanced χT value at low temperatures.

In the case of **2**, alternating current (ac) experiments were carried out with an ac magnetic field of 1.55 Oe, oscillating at frequencies ranging from 1–1400 Hz at temperatures between 1.8–3 K both in zero and 1500 G dc fields. $\chi'(T, f)$ and $\chi''(T, f)$ maxima were not observed for **2** in zero dc field.

In contrast a well-defined frequency and temperature dependent maximum in the out-of-phase χ'' susceptibility was observed under the 1500 G dc field (Fig. 4 and ESI†). These observations are indicative of slow relaxation of the molecular magnetization, and hence of single molecule magnet (SMM) behaviour.

The relaxation time (τ) was determined from both $\chi''(T)$ and Argand $\chi''(f)$ diagrams (ESI†). The values of ΔE of 30.5 ± 0.9 K and of τ_0 of 2.9 × 10^{-9} s were calculated from the Arrhenius equation $\tau = \tau_0 \exp(\Delta E/k_B T)$, where ΔE is the thermal energy barrier for the relaxation of the magnetisation and τ_0 is the pre-exponential factor (ESI†). The different magnetic properties observed for the dimer and trimeric complexes may be correlated to the different geometries of the U=O–Co interaction that is almost linear in **2** (U=O–Co is 173 (2)°) but deviates significantly from linearity in **1** (U–O–Co = 151.5356(3)°). However, the value of ΔE measured under an applied field for **2** remains significantly lower than the highest values of ΔE measured so far in zero field for SMMs containing one Co(II)

Fig. 3 Solid-state molecular structure (top) of **2** and details of the core with associated distances and angles (bottom) (30% probability ellipsoids for heteroatoms, carbon atoms are represented in pipes, and H, counter anion and co-crystallized solvent molecules are omitted for clarity).
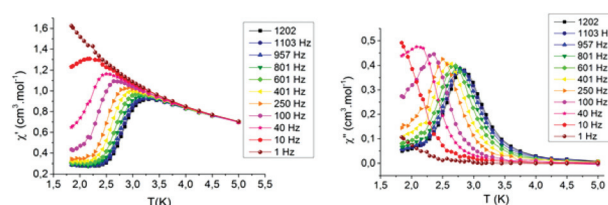

Fig. 4 Temperature dependence of the (left) real (χ') and (right) imaginary (χ'') ac susceptibility for **2** measured at 1500 G dc field and 1.55 G ac field.

ion amounting to 102 and 109 K were reported.[14] Moreover, high values of ΔE were measured at zero field for the UO_2Mn_2 (81 ± 0.5 K), UO_2Fe_2 (53.9 ± 0.9 K) and UO_2Ni_2 (27.4 ± 0.5 K) trimers that possess similar geometrical parameters compared to **2** and these values could be related to the spin of the d-block metal ion.[6b,d] The lack of SMM behaviour in the absence of an applied field in **2** could be due to quantum tunnelling of the magnetization arising from the presence of two anisotropic cations.[15]

In conclusion we have identified a versatile route to the controlled synthesis of dinuclear and trinuclear assemblies involving pentavalent uranyl and cobalt bound through cation–cation interactions. An appropriate choice of the ligand binding the 3d ion allows tuning of the number of CCIs between the uranyl(v) and cobalt cations affording dinuclear or trinuclear complexes. Complex **2** provides the first example of a stable complex of pentavalent uranyl involved in a cation–cation interaction with a Co^{2+} cation and the first example of a complex showing SMM behaviour originating from a U–Co exchange coupling. Future work will be devoted to extend this strategy to the synthesis of 3d–5f and 4f–5f complexes of different nuclearities and to establish a magneto-structural relationship.

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