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Magnetic Relaxation in Dysprosium and Terbium 1D-zigzag Coordination Chains having only 4,4'-Bipyridine as Connector

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Keywords

Single Ion Magnets, Coordination Polymer, Dysprosium, Terbium, Magnetisation dynamics

Dedication

Dedicated to Maurizio Peruzzini on occasion of his 65th birthday

Abstract

The coordination chain {[Dy(dbm)₃bpy]·C₇H₈}_{*n*} (**1**) having only 4,4'-bipyridine as connector has been prepared in high yield and its structural and magnetic properties have been investigated. It is isostructural with the terbium analogue {[Tb(dbm)₃bpy]·C₇H₈}_{*n*} (**2**) and features units repeating in a 1D-zigzag fashion, where the metal is octa-coordinated in a distorted square antiprism geometry. Despite the 1D structure, the absence of paramagnetic connectors prevents the direct magnetic intrachain interaction among the lanthanide ions. In zero magnetic field, only a small fraction of the magnetization of **1** displayed slow dynamics with no dependence on temperature. Upon application of a 1 kOe magnetic field, a relaxation process appears, compatible with a mixed Raman/Direct mechanisms. Magnetic dilution in the diamagnetic Y(III)-based analogue revealed that actually two distinct relaxation processes are active for **1**, whose temperature dependence can be interpreted again with a mixed Raman/Direct relaxation model. Compound **2** displayed only in-field slow relaxation, compatible with the models employed for **1**.

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Introduction

Molecular systems with slow relaxing magnetization have attracted, since their discovery, huge scientific interest for their peculiar nature of nanosized, monodisperse, magnetic objects. As such, they have been used as tools for the elucidation of quantum effects on their magnetic properties, like the quantum tunnelling of the magnetization[1] or the Berry phase interference[2], both in their crystalline state, as well as nanostructured on top of nanoparticles[3] and metal[4] or superconducting surfaces[5]. After the discovery that a mononuclear Tb(III) bis-phtalocyaninato complex displayed magnetic hysteresis at the molecular level (SIM, Single Ion Magnet)[6], a wide experimental and theoretical research effort has been dedicated to the investigation of lanthanidebased magnetic molecules[7], foreseeing their potential as spintronics[8] or quantum computing[9] active units. Lanthanide ions like Tb(III) and Dy(III) are very attractive for the preparation of SIMs, due to their high number of unpaired electrons with largely unquenched orbital moment, leading to magnetic ground states with significant magnetic anisotropy[6,10,11]. The main factor influencing the low temperature magnetic behaviour of such systems is the symmetry of the first coordination sphere of the lanthanide ion[10], leaving space for coordination chemistry to modify the energy splitting within the ground state electronic multiplet of the ion and, ultimately, the barrier to the thermally activated magnetic relaxation. This approach has led to a dramatic increase of activation barriers to thermal relaxation in Dy(III) complexes with strongly axial crystal field, allowing the observation of magnetic hysteresis above the liquid nitrogen temperature[11e,12]. Nevertheless, additional factors compete in determining the low temperature electronic structure of these materials, such as the nature and the charge of the donor atoms attached to the magnetic ion[13], the structure of the second coordination sphere[14], and spin parity effects[15]. Moreover, the dynamics of the magnetization in these systems is also affected by the dipolar field exerted by the ions in the crystal lattice[16], as well as by the energy structure of the phonon bath of the medium[17].

In view of the significant interest in Ln(III)-based SIMs[7b,18], in the attempt to gain further insights in the correlation between the structure and magnetic properties of Dy(III) and Tb(III) compounds, we are reporting the study of the magnetic behaviour of a monodimensional coordination polymer (CP) having a neutral tris- β -diketonato dysprosium fragment as a node and the unfunctionalized 4,4'-bipyridine as a single linker. The use of β -diketonato ligands is a commonly employed strategy to increase the Lewis acidity of the lanthanide ions, and several complexes with the Ln(β -diketonato)₃L formula (where L is for instance 2,2' -bipyridine or 1,10-phenanthroline) have been studied[19]. A series of dibenzoylmethanato Dy(III) SIMs has been

synthesized where the nitrogen-containing auxiliary ligands can enhance the magnetic properties of the complexes by tuning the coordination symmetry and the ligand field around dysprosium[20]. Furthermore, pyrazine-bridged dinuclear compounds have shown a large anisotropic barrier to magnetization reversal[21]. From the point of view of 1D extended structures, only few CPs containing lanthanide tris-β-diketonato complexes as nodes have been reported in the literature, mainly with oxygen donor spacers. Among them, the family with the most interesting magnetic features is the one including nitronyl-nitroxide radical bridges, which allowed the experimental observation of magnetization dynamics theoretically foreseen by Glauber for mono-dimensional, strongly anisotropic magnetic structures[22]. Additional examples include CPs containing Ln(hfac)₃ as nodes and 1,4-diacetylbenzene or 1,4-dimethyltherephtalate[23] or bis-phosphane oxides[24] as connectors (hfac = hexa-fluoro-acetylacetonato). On the other hand, lanthanide CPs having only Ndonor ligands as spacers have been rarely reported, due to the high oxophilicity of lanthanoid ions. Indeed, for the preparation of lanthanoid extended networks with nitrogen donors spacers, syntheses have to be carried out under anhydrous conditions with the exclusion of any potential oxygen-donor ligand. Since the convenient and high yield synthetic procedure, previously reported[25] to yield isotipic {[Ln(dbm)₃bpy]·C₇H₈}_n (Hdbm = 1,3-diphenyl-1,3-propandione; Ln = Eu, Tb) appeared to be adaptable to other lanthanide centres as well as to mixed metal mono-dimensional LOFs, we report here the synthesis of $\{[Dy(dbm)_3bpy] \cdot C_7H_8\}_n$ (1) and of a mixed dysprosium/yttrium derivative (1.Y). Their magnetic properties, along with the ones of the Tb(III) analogue (2), have been studied and here compared.

Materials and Instrumentation.

Commercial dysprosium and yttrium oxide $[Dy_2O_3 (Fluka); Y_2O_3 (Strem Chemicals)]$ were used without further purification. Aqueous solution of the lanthanide chlorides were prepared by dissolving the appropriate metal oxide in diluted hydrochloric acid. The solution was then evaporated to dryness and the solid residue was dissolved in water[26]. $Y(O_2CNBu_2)_3$ was prepared according the literature[27]. { $[Tb(dbm)_3bpy] \cdot C_7H_8\}_n$ (2) has been prepared according to the literature procedure[25]. Dibutylamine (Aldrich) and 1,3-diphenyl-1,3-propandione [Hdbm (Fluka)] were used without further purification. FTIR spectra in the solid state were recorded with a Perkin-Elmer "Spectrum One" spectrometer, with ATR technique. The metal content of the products was determined according to this procedure: each sample was treated in a platinum crucible with diluted HNO₃ and the mixture gently warmed; the resulting solution was then evaporated to dryness. After calcination, the weight of the residue [Dy₂O₃ or Y₂O₃] was determined. EDS analysis was performed on a SEM-FEG Quanta 450, using an accelerating voltage of 15 kV. The images were obtained with a backscattered electron detector. Powders were deposited on a conductive tape before being introduced in the high vacuum chamber. EDS analysis was performed with a Quanta XFlash EDS detector in order to assess the Y/Dy atomic ratios.

Synthesis of Dy(O_2CNBu_2)₃. A solution of dibutylamine (12.0 mL, 71.2 mmol) in heptane (50 mL) was saturated with carbon dioxide and then added to 20.0 mL of an aqueous solution of hydrated DyCl₃ (20.0 mL, 5.6 mmol) at 0 °C. After shaking for a few seconds at 0 °C, the organic layer was separated and evaporated at reduced pressure (1.0×10^{-3} Torr, 40°C). The colorless residue was purified from the excess of amine by stripping. The residue was dissolved in few milliliters of anhydrous heptane and dried *in vacuo* (1.0×10^{-3} Torr). The procedure was repeated twice. A colorless solid (3.15 g) was obtained (83 % yield). El. Anal. Calcd. for $C_{27}H_{54}DyN_3O_6$: Dy 23.9 %. Found: Dy 23.5 %. The product is soluble in hydrocarbons and sensitive to moisture. ATR-IR (3200 - 650 cm⁻¹): 2956 (m); 2930 (m); 2872 (w); 1585 (m); 1487 (ms); 1424 (ms); 1376 (s) 1313 (ms); 1261 (s); 1102 (m); 1022 (w); 944 (w); 902 (mw); 861 (w); 803 (s); 733 (m); 662 (s).

Synthesis of [H₂NBu₂][RE(dbm)₄] [RE = Dy]. Hdbm (5.40 g, 24.0 mmol) was added to a solution of Dy(O₂CNBu₂)₃ (3.74 g, 5.5 mmol) in toluene (50 mL). The pale yellow suspension was stirred for 12 h and then filtered. The solid was washed with toluene (2 x 20 mL) and then dried under reduced pressure. 5.49 g of product were collected (84.0 % yield). El. Anal. Calcd. for [NH₂Bu₂][Dy(dbm)₄], C₆₈H₆₄DyNO₈: Dy 15.1. Found: Dy 14.7 %. ATR-IR (3200 - 650 cm⁻¹): 3060 (mw); 2958 (mw); 2929 (mw); 2871 (mw); 1596 (ms); 1552 (ms); 1511 (ms); 1472 (ms); 1423 (ms); 1309 (s); 1282 (s); 1218 (s); 1180 (w); 1105 (mw); 1067 (s); 1023 (s); 973 (w); 941 (m); 847 (mw); 811 (mw); 782 (s); 720 (ms); 689 (ms).

[RE= Y] The product was obtained (5.76 g, 86% yield) starting from $Y(O_2CNBu_2)_3$ (3.12 g, 5.2 mmol), and Hdbm (5.22 g, 23.3 mmol) in toluene (50 mL). El. Anal. Calcd. for [NH₂Bu₂][Y(dbm)₄], C₆₈H₆₄YNO₈: Y 8.0 %. Found Y 7.9 %. ATR-IR (3200 - 650 cm⁻¹): 3060 (mw); 2958 (mw); 2929 (mw); 2871 (mw); 1596 (ms); 1552 (ms); 1511 (ms); 1472 (ms); 1423 (ms); 1309 (s); 1282 (s); 1218 (s); 1180 (w); 1105 (mw); 1067 (s); 1023 (s); 973 (w); 941 (m); 847 (mw); 811 (mw); 782 (s); 720 (ms); 689 (ms).

Conversion of [NH₂Bu₂][RE(dbm)₄] in RE(dbm)₃ [RE= Dy]. [NH₂Bu₂][Dy(dbm)₄] (5.49 g; 4.6 mmol) was introduced in a weighed vial. The vial was put into a Schlenk tube and treated in vacuo at 150°C for 24 h. The weight loss proceeded smoothly and stopped at a value corresponding to the complete loss of one equivalent of HNBu₂ and Hdbm. 3.77 g of Dy(dbm)₃ were collected (97.8 %

yield). El. Anal. Calcd. for Dy(dbm)₃, $C_{45}H_{33}DyO_6$: Dy 19.5. Found: Dy 19.9 %. ATR-IR (3200 - 650 cm⁻¹): 3057 (m); 3026 (m); 1592 (ms); 1543 (ms); 1506 (ms); 1476 (ms); 1454 (ms); 1441 (ms); 1398 (ms); 1374 (ms); 1305 (ms); 1283 (ms); 1222 (s); 1180 (m); 1114 (w); 1066 (s); 1055 (s); 1021 (s); 1000 (m); 971 (w); 940 (m); 843 (mw); 812 (w); 783 (m); 749 (ms); 715 (ms); 683 (ms).

[RE= Y] The product Y(dbm)₃ was obtained (1.37 g, 93% yield) starting from [NH₂Bu₂][Y(dbm)₄] (2.15 g, 1.9 mmol). El. Anal. Calcd. for Y(dbm)₃, $C_{45}H_{33}YO_6$: Y 11.7. Found: Y 12.0 %. ATR-IR (3200 - 650 cm⁻¹): 3057 (m); 3026 (m); 1592 (ms); 1543 (ms); 1506 (ms); 1476 (ms); 1454 (ms); 1441 (ms); 1398 (ms); 1374 (ms); 1305 (ms); 1283 (ms); 1222 (s); 1180 (m); 1114 (w); 1066 (s); 1055 (s); 1021 (s); 1000 (m); 971 (w); 940 (m); 843 (mw); 812 (w); 783 (m); 749 (ms); 715 (ms); 683 (ms).

Synthesis of {[Dy(dbm)₃bpy]·C₇H₈}_{*n*} (1). [Dy(dbm)₃] (1.34 g; 1.6 mmol) was suspended in toluene (75 mL) and 4,4'-bipyridine (0.25 g; 1.6 mmol) was added. After 2 h stirring at about 85°C, the yellow solution was slowly cooled to room temperature. A suspension of a crystalline solid was obtained that was filtered and dried *in vacuo* (71% yield). El. Anal. Calcd. for {[Dy(dbm)₃bpy]·C₇H₈}_{*n*}, C₆₂H₄₉DyN₂O₆: C, 68.9; H, 4.6; Dy, 15.0; N, 2.6. Found: C 68.6; H 4.8; Dy 15.3; N 2.4%. ATR IR: (3200 - 650 cm⁻¹): 3056 (mw); 3028 (mw); 1593 (s); 1548 (s); 1513 (ms); 1478 (s); 1454 (ms); 1404 (ms); 1382 (ms); 1305 (s); 1219 (s); 1176 (m); 1155 (w);1067 (m);1023 (m); 1001 (m); 941 (m); 925 (w); 843 (w); 809 (s); 783 (m); 750 (m); 723 (ms); 689 (ms). The air stable product shows a modest solubility in toluene and can be easily recrystallized cooling down a toluene solution with formation of single crystals suitable for X-ray diffraction studies. Space group: $P2_1/n$; a = 10.41Å; b = 21.94Å; c = 23.16Å; $\beta = 97.50^{\circ}$.

Synthesis of { $[Y_{0.94}Dy_{0.06}(dbm)_3bpy] \cdot C_7H_8$ }_n (1·Y). [Dy(dbm)₃] (0.05 .g; 0.06 mmol) and [Y(dbm)₃] (0.82 g; 1.07 mmol) (molar ratio Y/Dy = 17.8) were suspended in toluene (100 mL) and 4,4'-bipyridine (0.18 g; 1.15 mmol) was added. After 1 h stirring at about 110°C, the yellow solution was slowly cooled to room temperature. The crystalline product was recovered after filtering the suspension and drying the solid *in vacuo* (63% yield). The actual Y/Dy ratio was determined to be 15.7 (corresponding to a Y_{0.94}Dy_{0.06} molar ratio) by means of Energy Dispersive X-ray Spectrometry (EDS, Figure S1 and Table S1) and magnetometry (Figure S2). El. Anal. Calcd. for { $[Y_{0.94}Dy_{0.06}(dbm)_3bpy] \cdot C_7H_8$ }_n, C₆₂H₄₉Y_{0.94}Dy_{0.06}N₂O₆: C, 73.6; H, 4.9; N, 2.8. Found: C 73.8; H 5.1; N 2.7%. ATR IR (3200- 650 cm⁻¹): 3056 (mw); 3028 (mw); 1593 (s); 1548 (s); 1513 (ms); 1478 (s); 1454 (ms); 1404 (ms); 1382 (ms); 1305 (s); 1219 (s); 1176 (m); 1155 (w);1067

(m);1023 (m); 1001 (m); 941 (m); 925 (w); 843 (w); 809 (s); 783 (m); 750 (m); 723 (ms); 689 (ms). The air stable product shows a modest solubility in toluene and can be easily recrystallized cooling down a toluene solution with formation of single crystals suitable for X-ray diffraction studies. Space group: $P2_1/n$; a = 10.42Å; b = 21.95Å; c = 23.16Å; $\beta = 97.68^{\circ}$.

Magnetometry

Samples used for direct current (dc) and alternating current (ac) magnetic investigations consisted of pellets made out of microcrystalline powders. Direct current magnetic investigations were performed using a Quantum Design MPMS instrument equipped with a 5 T magnet. The temperature dependence of the magnetization (M) was followed from 1.8 to 300 K by applying a 1 T field from 300 to 45 K and a 0.1 T field below 45 K to reduce magnetic saturation effects. Magnetic susceptibility per mole (χ_M) was then evaluated as $\chi_M = M_M/B$. Alternating current magnetic susceptibility analysis was performed with a Quantum Design PPMS setup working in the 10 – 10000 Hz range with zero and 0.1 T applied static field. Magnetic data were corrected for the sample holder contribution and for the sample diamagnetism using Pascal's constants[28]. The ac susceptibility data were analysed within the extended Debye model[29], in which a maximum in the out-of-phase component χ_{M} of the complex susceptibility is observed when the relaxation time τ equals $(2\pi v)^{-1}$. The adopted model includes two different relaxation processes to reproduce a nonzero χ_M " in the low frequency region of the plots; the corresponding relaxation times extracted from this low frequency component were however not described due to the huge uncertainty associated to them. The frequency dependence of χ_{M} at constant temperature was thus fitted using equation (1): $\chi_{M}^{\prime\prime}(\omega) = \chi_{M}^{\prime\prime}_{LF}(\omega) + \chi_{M}^{\prime\prime}_{FIT}(\omega)$ (1)

where each process corresponds to the function reported in equation (2):

$$\chi_{M}^{\prime\prime}(\omega) = (\chi_{T} - \chi_{S})[(\omega\tau)^{1-\alpha}\cos(\alpha\pi/2)]/[1 + 2(\omega\tau)^{1-\alpha}\sin(\alpha\pi/2) + (\omega\tau)^{2-2\alpha}]$$
(2)

where $\omega = 2\pi v$, χ_T and χ_S are the isothermal and adiabatic susceptibilities, *i.e.*, the susceptibilities observed in the two limiting cases $v \rightarrow 0$ and $v \rightarrow \infty$, respectively, and α is a parameter which accounts for a distribution of relaxation times.

Results and discussion

The syntheses of the metal CPs here described were performed according to a protocol previously developed for the europium derivative[25]. The sequence of reactions reported below starts with the extraction of the metal ions from an aqueous solution to a hydrocarbon medium, driven by NHBu₂ and CO₂ (equation 3)[30]. In this paper we report that also dysprosium ions can be extracted almost quantitatively from water as a dibutylcarbamato complex (equation 4). Extraction yields have been

established evaluating by complexometry the amount of the metal left in water. Reproducibly, the reaction work-up yielded a neutral product with the $[Dy(O_2CNBu_2)_3]$ composition. The high yields give a synthetic value to this procedure.

 $2 \text{ NHBu}_2 + \text{CO}_2 \qquad [\text{NH}_2\text{Bu}_2][\text{O}_2\text{CNBu}_2] \qquad (3)$ $DyX_3 + 3 [\text{NH}_2\text{Bu}_2][\text{O}_2\text{CNBu}_2] \rightarrow [Dy(\text{O}_2\text{CNBu}_2)_3] + 3 [\text{NH}_2\text{Bu}_2]X \qquad (4)$

IR spectrum is almost identical to that of the terbium[30a] and yttrium[27] analogues. Since the rare-earth metals Y and Dy can be extracted almost quantitatively from water, it is possible to extract them simultaneously in any desired molar ratio maintaining the same molar ratio in the extracted mixture.

The metal *N*,*N*-dibutylcarbamato complexes so obtained, $[M(O_2CNBu_2)_3]$ (M = Dy, Y) were reacted with dibenzoymethane (Hdbm) with formation of the ionic $[NH_2Bu_2][M(dbm)_4]$ (equation 5) that was easily transformed in $[M(dbm)_3]$ (M = Dy, Y) by release of Hdbm and NHBu₂ by thermal treatment at 150 °C in vacuo (equation 6).

$$[M(O_2CNBu_2)_3] + 4 Hdbm \rightarrow [NH_2Bu_2][M(dbm)_4] + 3 CO_2 + 2NHBu_2$$
(5)

 $[NH_2Bu_2][M(dbm)_4] \rightarrow [M(dbm)_3] + Hdbm + NHBu_2$ (6)

The reactions between the metal dibenzoylmethanato complexes $[M(dbm)_3]$ (M = Dy, Y) with 4,4'bipyridine, in a molar ratio 1:1, in toluene under anhydrous conditions at about 60 °C, afforded the monodimensional CPs { $[M(dbm)_3bpy] \cdot C_7H_8$ }_n (equation 7).

$$[M(dbm)_3] + bpy \rightarrow \{[M(dbm)_3 bpy] \cdot C_7 H_8\}_n$$
(7)

In the solid state the derivatives are stable in air and do not release toluene under vacuum at room temperature. The products were characterized by elemental analysis, IR and X-ray diffraction, resulting isostructural with other lanthanide complexes previously reported, $\{[Ln(dbm)_3bpy]\cdot C_7H_8\}_n$ (Ln = Eu, Tb)[25]. It can be useful to remind that the structures of these compounds contain zigzag chains as shown in Figure 1.



Figure 1. The structure of portion of the chains in 1, 1.Y and 2.

Toluene molecules are hosted between the bipyridine linkers of two parallel chains almost exactly in the middle. The phenyl plane of toluene is perpendicular to the nearest pyridine planes as shown in Figure 2 at a distance which may suggests edge-on π - π interactions.



Figure 2. View the solvent hosted within the chains in the crystal structure.

This finding agrees with the observation that toluene is not removed by treatment of the sample under vacuum at room temperature. Each metal is octa-coordinated in a distorted square antiprismatic geometry (Figure 3 and Table S2)[31].



Figure 3. The geometry of the metal coordination.

Six coordination sites are occupied by the oxygen atoms of the chelating β -diketonates and the other two by the nitrogen atoms of two bpy ligands. It is worth to mention that intrachain Ln^{...}Ln are 12.310 Å (measured for europium) while the shortest interchain distances (along the a axis) are 10.411 Å (other higher interchain distances being 12.17, 12.34, 12.38 and 13.31 Å).

Figure 4 reports the temperature dependence of the product of the molar magnetic susceptibility with temperature, $\chi_M T$, for **1** and **2**.



Figure 4. Temperature dependence of the $\chi_M T$ product of **1** (empty dots) and **2** (black lozenges). Inset: zoom of the low temperature part of the main panel, highlighting the change in slope of the curves below 6 K.

The value of the $\chi_M T$ product at 300 K for compounds 1 and 2 are, respectively, 14.2 and 11.7 emuK/mol, in line with what expected for free Dy(III) ion (whose ground electronic term, ${}^{6}H_{15/2}$, features a g value of 4/3, giving a theoretical $\chi_M T$ product of 14.17 emuK/mol) and Tb(III) ion (⁷F₆ ground state term, g value of 3/2, yielding a theoretical $\chi_M T$ product of 11.8 emuK/mol). Upon cooling, the $\chi_M T$ profile of both samples undergoes a monotonic decrease, reaching the values of 10.3 and 9.2 emuK/mol at 2 K, respectively, as expected upon thermal depopulation of the m_i sublevels of the ground state multiplet, split by the crystal field. Anyway, the presence of intermolecular antiferromagnetic interactions cannot in principle be ruled out, especially at low temperature. A focus at the region below 10 K of both plots (highlighted in the inset of Figure 4), in fact, shows a sharp change in slope of both curves, taking place at about 5.5 and 5.3 K for 1 and 2, respectively. This behaviour cannot be explained in terms of magnetic saturation effects, as can be understood looking the isothermal magnetization profiles, shown in Figure S3, and may suggest the onset of antiferromagnetic dipolar interactions at low temperature for both compounds. This finding is in line with the dynamic magnetic behaviour of 1, which is significantly affected by the dipolar field in the crystal (vide infra). The isothermal magnetisations of 1 attain the 5.56 $\mu_{\rm B}$ /mol value at 1.8 K and 50 kOe, without reaching saturation. Their non-overlapping nature (when plotted against field over temperature) suggests the presence of magnetic anisotropy. On the other hand, the terbium derivative 2 shows magnetic saturation at 4.30 $\mu_{\rm B}$ /mol and superimposable curves, pointing to a well isolated magnetic ground state.

In order to analyse the dynamics of the magnetisation of **1** and **2**, ac magnetic susceptibility has been used. With no static magnetic field applied, the majority of the susceptibility of **1** relaxed rapidly and displayed a very low value of out-of-phase magnetic susceptibility, χ_M " (Figure S4). Anyway, taking a closer look, this plot showed a frequency and temperature independent set of maxima, showing a relaxation process with a magnetisation sweeping frequency of 10.1 kHz, calculated as the inverse of the relaxation times extracted from the maxima of Figure S4b. Since this peak disappears upon dilution in a diamagnetic host, we attribute it to the presence of dipolar interactions in the crystal, opening additional pathways of the relaxation of the magnetization of the isolated ions. This behaviour has been previously observed in undiluted magnetic molecular materials, usually hampering the characterisation of the magnetisation dynamics of the molecules in their pure phase[16, 32]. In order to remove the effect of these dipolar interactions, the ac characterisation has been carried out with a static magnetic field of 1 kOe applied. In these conditions, a clear set of frequency dependent peaks appears in the out-of-phase magnetic susceptibility, reported in Figure 5.



Figure 5. *Left panel*: Frequency dependence of the in-phase (empty circles) and out-of-phase (full circles) magnetic susceptibility of **1**, measured in a 1 kOe static applied field. *Right Panel*: Arrhenius plot, reporting the logarithm of the relaxation time of the magnetisation versus the inverse of temperature, for **1** and **1**·**Y**, measured with or without a 1 kOe static applied magnetic field. The full lines represent the best fitting results obtained with the model described in the text.

Upon fitting of the $\chi_{M}''(\omega)$ curves with the extended Debye model, as discussed in the Materials and Instrumentation Section, it has been possible to extrapolate the temperature dependence of the relaxation time of the magnetisation, τ . The data are reported in the right panel of Figure 5 as an Arrhenius plot $(\ln \tau \ vs \ T^{-1})$. The zero field data show, as previously discussed, a temperature independent relaxation process, which can be ascribed to a quantum tunnelling of the magnetization induced by dipolar interactions. In the 1 kOe case a set of frequency and temperature dependent peaks appears in the $\chi_{M}''(\omega)$ curves, indicating SIM behaviour (Figure 5). The corresponding relaxation times show a non-linear behaviour of τ against *T*, and have been fitted with a model including two relaxation mechanisms, as described by equation 8:

$$\tau_0^{-1}(T) = CT^n + AT$$
(8)

In here, the first term describes a Raman mechanism, involving a crossing of the magnetic barrier through a virtual magnetic state, while the second term corresponds to a direct transition between the states belonging to different sides of the energy barrier, induced by a resonant phonon, (here *A*

is a weighting coefficient depending on several factors, among which the magnetic field and the speed of sound and the density of the material)[33]. The best fitting parameters are reported in Table 1.

	1	1·Y		
	1 kOe	zero field	1 kOe – High T process	1 kOe – Low T process
$A (\mathbf{s}^{-1} \mathbf{K}^{-1})$	$2.70(3) \cdot 10^3$	-	7(3)	619(44)
QTM (Hz)	-	114(16)	-	-
$C(\mathbf{s}^{-1}\mathbf{K}^{-n})$	2.5(2)	3(2).10-3	1(1).10-5	0.5(2)
п	9.16(9)	8.4(4)	8.3(4)	9.0(3)
\mathbf{R}^2	0.999	0.991	0.994	0.999

Table 1. Parameters extracted from the best-fitting procedure of the temperature dependence of the relaxation times of **1** and **1**·**Y**, according to the models described above.

In this approach, the value obtained for the Raman exponent n (8.8(1)) is in line with what expected for a Kramers ion like Dy(III)[34], and is not changing significantly upon dilution of **1** in a diamagnetic analogue (*vide infra*). As comparison, a fitting procedure based on a different hybrid model, merging a thermally induced overcome of an energy barrier (Δ , Orbach process) and a direct relaxation was employed as well, giving fits of comparable quality ($R^2_{Raman} = R^2_{Orbach} = 0.999$; the corresponding curve is reported in Figure S6). The value of the energy barrier obtained with this procedure is 16.7(4) cm⁻¹. A third procedure including Orbach and QTM, despite yielding fits of comparable quality, has not been included in the discussion since the fitted relaxation times have been measured with a static field applied, which we assume to completely suppress QTM. The best fitting parameters of the three models are summarized in Table S3.

A different strategy for the reduction of the dipolar interactions in the crystals consists in the dilution of the slow relaxing complexes in a diamagnetic, isostructural host. This route has been followed here with the preparation of the 1-D coordination polymer $\{[Y_{0.94}Dy_{0.06}(dbm)_3bpy]\cdot C_7H_8\}_n$ (1•Y from now on). The molar ratios of the two metal ion has been assessed by comparing the DC properties of 1•Y to the ones of the pure dysprosium derivative 1

(Figure S2). The homogeneity of the solid solution has been confirmed realizing an EDS analysis of the Y/Dy ratio in three different areas of the sample (Figure S1 and Table S1), and the isostructurality of 1.Y with respect to the Tb-based analogue [25] has been checked by means of powder XRD diffraction analysis (Figure S5). The relaxation of the magnetization of the diluted system is more complex than the one observed for the pure one. With no applied field, 1.Y shows frequency and temperature dependent peaks in the out-of-phase magnetic susceptibility (Figure S7), differently from 1. The corresponding relaxation times have been reported in Figure 5, and, despite what usually observed in the literature for Dy(III) complexes featuring slow relaxation of the magnetization, the relaxation times of 1.Y are significantly slower from the ones observed for the pure sample 1 in a 1.0 kOe static field. Figure S7c shows that peaks in the out of phase component of the magnetic susceptibility appear in the 4-10 K temperature range for 1.Y, while for 1 they were found in the 1.9 – 3.5 temperature region. A comparison of the Raman / QTM and Orbach / QTM fitting models, reported in Figure S8, confirms the former to yield a better reproduction of the experimental data, thus hinting to the magnetization to reorientate through a virtual state, in accordance with the behavior of the undiluted sample. In the present case, the reduction of the dipolar interactions via magnetic dilution is not sufficient to eliminate completely the quantum tunneling of the magnetization. This behavior can be interpreted considering the hyperfine interaction with the spin active ¹⁶¹Dy and ¹⁶³Dy isotopes, known to promote the QTM in Dy(III) mononuclear slow relaxing species[35]. In addition to that, upon dilution an additional relaxation process appears below our reachable lowest temperature (1.9 K, Figure S7c).

Appling a static field of 1 kOe on $1 \cdot Y$ slows the latter process down, making it detectable within our experimental possibilities (Figure S7d). The comparison between the Arrhenius plots arising from these low temperature χ_M " peak, taken for $1 \cdot Y$ in a 1 kOe field, and the ones measured for 1 with the same field suggest that the two processes may be actually the same (Figure S9). Another consequence of the static field is the rise of a slower relaxation process, located at higher temperature, in the 4 - 10 K range. Analysis and fitting of its Arrhenius plots again seems to point out to a Raman process mixed with a direct one (n = 8.3(4)), rather than an Orbach one (Figure S10). In line with previous reports about vanadyl-based molecular qbits candidates[36], and Dy(III) single ion magnets[37] relaxing via a Raman mechanism, the effect of the field is to reduce of about one order of magnitude the C parameter, leaving the n exponent almost unaffected. These findings suggest that the low temperature process is triggered by the application of the field, while the higher temperature one is hidden by the onset of dipolar interactions.

Globally, the analysis of the dynamics of 1 and $1 \cdot Y$ shows that two different relaxation models can be employed to reproduce them with comparable goodness. An unambiguous determination of the

relaxation mechanisms active here would require the use of spectroscopic techniques. However, several studies indicate that experimental barriers to the relaxation in $Dy(\beta$ -diketonate)₃N-N in distorted square-antiprism (pseudo D_{4d}) span the 30 – 90 cm⁻¹ range[38] while only one complex displays an activation barrier to the relaxation similar to what found for **1**[39]. This consideration, along with the slightly better curve reproduction with the Raman / direct model using a Raman exponent in line with the theoretical expectation for a Dy(III) ion, seem to suggest these to be the relaxation mechanisms working in this case.

The dynamic susceptibility of the {[Tb(dbm)₃bpy]·C₇H₈}_{*n*} complex (**2**) showed no out-of-phase signals in the absence of a static magnetic field applied (Figure S11), probably because of the non-Kramers nature of the Tb(III) ion or for the presence of dipolar interactions. In the presence of a 1 or 1.5 kOe field, however, a non-zero χ_M " signal appears, showing frequency and temperature dependent peaks (Figure S12). The corresponding Arrhenius plots have been fitted with the two mixed model used above, as reported in Figure S13. The *n* exponent of the Raman model, which is expected to be 5 for closely spaced multiplets, takes lower values (3.2(3) and 4.8(2) in 1.0 and 1.5 kOe fields, respectively). These values are in line with previous reports of Tb-based SIMs in the literature[37b] and support the Raman assignment of the relaxation mechanism in these kind of CPs.

Conclusions

The synthesis of the 1D-coordination polymer $\{[Dy(dbm)_3bpy]\cdot C_7H_8\}_n$, **1**, having only 4,4'bipyridine as a spacer, isostructural with the terbium analogue, **2**, has been carried out in high yield. The synthetic protocol can be used to prepare mixed compounds with two different rare-earth centres with a defined molar ratio. Although strictly anhydrous synthetic conditions are necessary, once recovered, the crystalline product is stable on air and does not lose toluene *in vacuo* at room temperature. The static magnetic behaviour of **1** and **2** discarded the presence of intrachain magnetic interactions. The dynamics of the magnetization of the dysprosium derivative are strongly affected by the dipolar interactions in the solid state: the pure system displays a Raman/direct mixed relaxation process in a field of 1 kOe, while upon magnetic dilution an additional, slower process takes place at higher temperatures. The temperature dependence of the relaxation times for both processes could be reproduced more satisfactorily with a mixed Raman/direct mechanism than with an Orbach/direct one. Isostructural dysprosium and terbium derivatives have been compared, showing that, despite the different Kramers nature of the ions, both systems share the same relaxation mechanism.

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References

[1] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, Nature 365 (1993) 141-143. https://doi.org/10.1038/365141a0.

[2] W. Wernsdorfer, R. Sessoli, Science 284 (1999) 133-135. https://doi.org/10.1126/science.284.5411.133.

[3] M. Perfetti, F. Pineider, L. Poggini, E. Otero, M. Mannini, L. Sorace, C. Sangregorio, A. Cornia, R. Sessoli, Small 10 (2014) 323-329. https://doi.org/10.1002/smll.201301617.

[4] (a) M. Mannini, F. Pineider, C. Danieli, F. Totti, L. Sorace, Ph. Sainctavit, M.-A. Arrio, E. Otero, L. Joly, J. C. Cezar, A. Cornia, R. Sessoli, Nature 468 (2010) 417-422. https://doi.org/10.1038/nature09478 (b) A. Cornia, M. Mannini, R. Sessoli, D. Gatteschi, Eur. J. Inorg. Chem. 5 (2019) 552-568. https://doi.org/10.1002/ejic.201801266

[5] G. Serrano, L. Poggini, M. Briganti, A. L. Sorrentino, G. Cucinotta, L. Malavolti, B. Cortigiani,
E. Otero, Ph. Sainctavit, S. Loth, F. Parenti, A.-L. Barra, A. Vindigni, A. Cornia, F. Totti, M. Mannini, R. Sessoli, Nature Mater. 5 (2020) 546-551. https://doi.org/10.1038/s41563-020-0608-9.

[6] N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, J. Am. Chem. Soc. 125 (2003) 8694-8695. https://doi.org/10.1021/ja029629n.

[7] (a) R. Sessoli, A. K. Powell, Coord. Chem. Rev. 253 (2009)2328-2341. https://doi.org/10.1016/j.ccr.2008.12.014 (b) D. N. Woodruff, R. E. P. Winpenny, R. A. Layfield, Chem. Rev. 113 (2013) 5110-5148. https://doi.org/10.1021/cr400018g (c) F. Pointillart, O. Cador, (2017)Guennic, L. Ouahab, Coord. Chem. Rev. 346 150-175. Β. Le https://doi.org/10.1016/j.ccr.2016.12.017

[8] M. Urdampilleta, S. Klyatskaya, J-P. Cleuziou, M. Ruben, W.Wernsdorfer, Nature Mater. 10 (2011) 502-506. https://doi.org/10.1038/nmat3050

[9] S. Thiele, F. Balestro, R. Ballou, S. Klyatskaya, M. Ruben, W. Wernsdorfer, Science 344 (2014) 1135-1138. https://doi.org/10.1126/science.1249802

[10] S. G. McAdams, A.-M. Ariciu, A. K. Kostopoulos, J. P. S. Walsh, F. Tuna, Coord. Chem. Rev. 346 (2017) 216–239. http://dx.doi.org/10.1016/j.ccr.2017.03.015

[11] (a) W. M. Wang, S. Y. Wang, H. X. Zhang, H. Y. Shen, J. Y. Zou,; H. L. Gao,; J. Z. Cui, B. Zhao, Inorg. Chem.Front. 3 (2016) 133–141. https://doi.org/10.1039/C5QI00192G (b) D. D. Yin, Q. Chen, Y. S. Meng, H. L. Sun, Y. Q. Zhang, S. Gao, Chem. Sci. 6 (2015) 3095–3101. https://doi.org/10.1039/C5SC00491H (c) K. Liu, X. J. Zhang, X. X. Meng, W. Shi, P. Cheng, A. K. Powell, Chem. Soc. Rev. 45 (2016) 2423–2439. https://doi.org/10.1039/C5CS00770D (d) K. Liu, H. H. Li, X. J. Zhang, W. Shi, P. Cheng, Inorg. Chem. 54 (2015) 10224–10231. https://doi.org/10.1021/acs.inorgchem.5b01356 (e) C. Goodwin, F. Ortu, D. Reta, N. Chilton, D. Mills, Nature 548 (2017) 439-442. https://doi.org/10.1038/nature23447

[12] F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki, R. A. Layfield, Angew. Chem. Int. Ed. 56 (2017) 11445-11449. https://doi.org/10.1002/ange.201705426

[13] D. Aravena, E. Ruiz, Inorg. Chem. 52 (2013) 13770–13778. https://doi.org/10.1021/ic402367c

[14] S. Sottini, G. Poneti, S. Ciattini, N. Levesanos, E. Ferentinos, J. Krzystek, L. Sorace, P. Kyritsis, Inorg. Chem. 55 (2016) 9537–9548. https://doi.org/10.1021/acs.inorgchem.6b00508

[15] M.-E. Boulon, G. Cucinotta, J. Luzon, C. Degl'Innocenti, M. Perfetti, K. Bernot, G. Calvez, A. Caneschi, R. Sessoli, Angew. Chem. Int. Ed. 52 (2013) 350–354. https://doi.org/10.1002/anie.201205938

[16] K. R. Meihaus, J. D. Rinehart, J. R. Long, Inorg. Chem. 50 (2011) 8484–8489. https://doi.org/10.1021/ic201078r

[17] A. Lunghi, F. Totti, R. Sessoli, S. Sanvito, Nature Commun. 8 (2017) 14620, 1-7. https://doi.org/10.1038/ncomms14620

[18] J. D. Rinehart, J. R. Long, Chem. Sci. 2 (2011), 2078–2085. https://doi.org/10.1039/C1SC00513H

[19] (a) N. F. Chilton, S. K. Langley, B. Moubaraki, A. Soncini, S. R. Batten, K. S. Murray, Chem. Sci. 4 (2013), 1719–1730. https://doi.org/10.1039/C3SC22300K (b) C. M. Liu, D. Q. Zhang, D. B. Zhu, Inorg. Chem. 52 (2013), 8933–8940. https://doi.org/10.1021/ic4011218 (c) W. B. Sun, B. L. Han, P. H. Lin, H. F. Li, P. Chen, Y. M. Tian, M. Murugesu, P. F Yan, Dalton Trans. 42 (2013) 13397–13403. https://doi.org/10.1039/C3DT51227D (d) K. Bernot, J. Luzon, L. Bogani, M. Etienne, E. C. Sangregorio, M. Shanmugam, A. Caneschi, R. Sessoli, D. Gatteschi, J. Am. Chem. Soc. 131 (2009) 5573–5579. https://doi.org/10.1021/ja8100038 (e) G. J. Chen, Y. N. Guo, J. L. Tian, J. K. Tang, W. Gu, X. Liu, S. P. Yan, P. Cheng, D. Z. Liao. Chem. Eur. J. 18 (2012) 2484–2487. https://doi.org/10.1002/chem.201103816

[20] Y. Dong, P. Yan, X. Zou, T. Liu, G. Li, J. Mater. Chem. C 3 (2015) 4407–4415. https://doi.org/10.1039/C5TC00321K

[21] Y. Ma, G. F. Xu, X. Yang, L. C. Li, J. K. Tang, S. P. Yan, P. Cheng, D. Z. Liao, Chem. Commun. 46 (2010) 8264–8266. https://doi.org/10.1039/C0CC01423K

[22] (a) K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi, R. Sessoli, J. Am. Chem. Soc. 128 (2006)
7947–7956. https://doi.org/10.1021/ja0611011 (b) C. V. Sarmiento, T. A. Araujo, S. G. Reis, M. S. de Souza, R. A. Allão Cassaro, M. A. Novak, M. G. F. Vaz, RSC Adv. 9 (2019) 30302-30308.
https://doi.org/10.1039/C9RA06506G

[23] S.V. Eliseeva, D.N. Pleshkov, K.A. Lyssenko, L.S. Lepney, J.G. Bunzli and N.P.J Kuzmina, Inorg.Chem. 49 (2010) 9300-9311. https://doi.org/10.1021/ic100974e

[24] (a) K. Miyata, Y. Konno, T. Nakanishi, A. Kobayashi, M. Kato, K. Fushimi, Y. Hasegawa, Angew. Chemie - Int. Ed. 52 (2013) 6413–6416. https://doi.org/10.1002/anie.201301448 (b) M. Hatanaka, Y. Hirai, Y. Kitagawa, T. Nakanishi, Y. Hasegawa, K. Morokuma, Chem. Sci. 8 2017 423–429. https://doi.org/10.1039/C6SC03006H

[25] L. Armelao, D. Belli Dell'Amico, L. Bellucci, G. Bottaro, L. Labella, F. Marchetti, S. Samaritani, Polyhedron 119 (2016) 371-376. https://doi.org/10.1016/j.poly.2016.09.009

[26] U. Baisch, D. Belli Dell'Amico, F. Calderazzo, R. Conti, L. Labella, F. Marchetti, E.A. Quadrelli, Inorg. Chim. Acta 357 (2004) 1538-1548. https://doi.org/10.1016/j.ica.2003.11.011

[27] D. Belli Dell'Amico, P. Biagini, G. Bongiovanni, S. Chiaberge, A. Di Giacomo, L. Labella, F. Marchetti, G. Marra, A. Mura, F. Quochi, S. Samaritani, V. Sarritzu; Inorg. Chim. Acta 470 (2018) 149-157. https://doi.org/10.1016/j.ica.2017.05.012

[28] G. A. Bain, J. F. J. Berry, J. Chem. Educ. 85 (2008) 532. https://doi.org/10.1021/ed085p532

Chem. 9 (1941)[29] (a) K. S. Cole, R. H. Cole, J. Phys. 341-351.; https://doi.org/10.1063/1.1750906 (b) C. Dekker, A. F. M. Arts, H. W. Dewijn, A. J. Vanduvneveldt and J. A. Mydosh, Phys. Rev. В 40 (1989)11243-11251. https://doi.org/10.1103/PhysRevB.40.11243

[30] (a) L. Armelao, D. Belli Dell'Amico, P. Biagini, G. Bottaro, S. Chiaberge, P. Falvo, L. Labella, F. Marchetti, Samaritani, Inorg. Chem. 53 (2014)4861-4871. S. https://doi.org/10.1021/ic402936z; (b) D. Belli Dell'Amico, M. De Sanctis, R. Ishak, S. Dolci, L. Labella. F.Marchetti, Polyhedron 99 (2015) 170-176. M. Lezzerini, https://doi.org/10.1016/j.poly.2015.06.037 (c) D. Belli Dell'Amico, P. Biagini, S. Chiaberge, L.

Falchi, L. Labella, M. Lezzerini, F. Marchetti, S. Samaritani, Polyhedron 102 (2015) 452-461. https://doi.org/10.1016/j.poly.2015.06.037 (d) D. Belli Dell'Amico, A. Di Giacomo, L. Falchi, L. Labella, M. Marelli, C. Evangelisti, M. Lezzerini, F. Marchetti, S. Samaritani, Polyhedron 123 (2017) 33-38. https://doi.org/10.1016/j.poly.2016.11.020 (e) L. Armelao, D. Belli Dell'Amico, L. Bellucci, G. Bottaro, L. Labella, F. Marchetti, S. Samaritani, Inorg. Chem. 55 (2016) 939-947. https://doi.org/10.1021/acs.inorgchem.5b02535 (f) J. De Bellis, D. Belli Dell'Amico, G. Ciancaleoni, L. Labella, F. Marchetti, S. Samaritani; Inorg. Chim. Acta, 495 (2019) 118937-118946. https://doi.org/10.1039/D0DT00449A

[31] M. Llunell, P. Alemany, S. Alvarez, Shape, http://www.ee.ub.edu/index.php?option=com_content&view=article&id=575:shapeavailable&catid=80:news&Itemid=466, 2013.

[32] L. Rigamonti, N. Bridonneau, G. Poneti, L. Tesi, L. Sorace, D. Pinkowicz, J. Jover, E. Ruiz, R. Sessoli, A. Cornia, Chem.-Eur. J. 24 (2018) 8857-8868. https://doi.org/10.1002/chem.201801026

[33] E. A. Suturina, D. Maganas, E. Bill, M. Atanasov, F. Neese, Inorg. Chem. 54 (2015) 9948-9961. https://doi.org/10.1021/acs.inorgchem.5b01706

[34] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Oxford University Press, Oxford, 1970. ISBN-13: 978-0199651528.

[35] a) F. Pointillart, K. Bernot, S. Golhen, B. Le Guennic, T. Guizouarn, L. Ouahab, O. Cador, Angew. Chem. 126 (2014) 1 – 5. http://dx.doi.org/10.1002/anie.201409887. b) J. Flores Gonzalez, F. Pointillart, O. Cador, Inorg. Chem. Front. 6 (2019), 1081-1086.

[36] a) L. Tesi, E. Lucaccini, I. Cimatti, M. Perfetti, M. Mannini, M. Atzori, E. Morra, M. Chiesa, Caneschi. A. L. Sorace, R. Sessoli, Chem. Sci. (2016).2074-2083. 7 https://doi.org/10.1039/C5SC04295J. b) M. Atzori, E. Morra, L. Tesi, A. Albino, M. Chiesa, L. Sorace, R. Sessoli. Am. Chem. Soc. 138 (2016),11234-11244. J. https://doi.org/10.1021/jacs.6b05574.

[37] a) O. Galangau, J. Flores Gonzalez, V. Montigaud, V. Dorcet, B. le Guennic, O. Cador, F. Pointillart, Magnetochemistry 6 (2020), 19-32; https://doi.org/10.3390/magnetochemistry6020019.
b) E. Rousset, M. Piccardo, M.-E. Boulon, R. W. Gable, A. Soncini, L. Sorace, C. Boskovic, Chem. Eur. J. 24 (2018), 14768 – 14785. https://doi.org/10.1002/chem.201702779.

[38] a) F. Mori, T. Nyui, T. Ishida, T. Nogami, K.-Y. Choi, H. Nojiri, J. Am. Chem. Soc. 128 (2006) 1440-1441. https://doi.org/10.1021/ja057183f b) L. Norel, K. Bernot, M. Feng, T. Roisnel, A. Caneschi, R. Sessoli, S. Rigaut, Chem. Commun. 48 (2012)3948-3950. https://doi.org/10.1039/C2CC30604B c) P. Hu, F.-P. Xiao, Y. Li, J.-F. Cao, Z.-S. Chen, L.-L. Zhu, W.-P. Huang. Inorg. Chem. Commun. 84 (2017)207 - 211. https://doi.org/10.1016/j.inoche.2017.07.015 d) Y. Kishi, L. Cornet, F. Pointillart, F. Riobé, B. Lefeuvre, O. Cador, B. Le Guennic, O. Maury, H. Fujiwara, L. Ouahab, Eur. J. Inorg. Chem. (2018) 458-468. https://doi.org/10.1002/ejic.201700893 e) O. Cador, B. Le Guennic, L. Ouahab, F. Pointillart, Eur. J. Inorg. Chem. 2 (2020), 148-164. https://doi.org/10.1002/ejic.201900981 [39] G. Cosquer, M. Kamila, Z.-Y. Li, B. K. Breedlove, M. Yamashita, Inorganics 6 (2018) 9. doi:10.3390/inorganics6010009.