Introduction

The term rare earth elements is sometimes applied to the elements La-Lu plus yttrium. The reason for including Y is that this element has radii (atomic, metallic, ionic) that fall close to those of Er and Ho, and all of its chemistry is in the trivalent state \([\text{Y}^{3+}]\). Hence it resembles the late lanthanides closely in its chemistry and occurs with them in nature.

In the older literature in particular, it is not uncommon to find explicitly or implicitly the belief that an Y complex of a given set of ligands will be isostructural with the corresponding late lanthanide(III) compounds. The testing of this belief has been carried out for only a few species [2, 3]. We have decided to test the above viewpoint thoroughly at a more detailed level by preparing and characterizing Y(III) complexes of ligands containing O- and N-donors. Recently we prepared and structurally characterized [4] complexes \([\text{Y}(\text{NO}_3)_3(\text{bpy})_2]\) and \([\text{Y}(\text{NO}_3)_3(\text{phen})_2]\) (bpy=2,2'-bipyridine, phen = 1,10-phenanthroline) which were proved to be isostructural with their lanthanide(III) counterparts. This paper describes the investigation of the reaction between \([\text{Y}(\text{NO}_3)_3\cdot5\text{H}_2\text{O}]\) and the tridentate chelating N-ligand 2,2':6',2"-terpyridine (terpy) in MeCN. The 4f metal/NO$_3^-$/terpy chemistry has already been well developed [5 - 10]. Recently Semenova and White [9] reported the X-ray structure of the complex \([\text{Y}(\text{NO}_3)_3(\text{terpy})(\text{H}_2\text{O})_2] \cdot \text{terpy}\) isolated from MeCN/H$_2$O and containing a 9-coordinate \([\text{Y}]^{3+}\) atom. The complexes \([\text{Ln}(\text{NO}_3)_3(\text{terpy})\cdot(\text{H}_2\text{O})] \cdot \text{MeCN}\) have recently been described for Ln = Ho, Er [10].

Results and Discussion

Treatment of \([\text{Y}(\text{NO}_3)_3\cdot5\text{H}_2\text{O}]\) with 2 equivalents of terpy in MeCN yields a color change from colourless to pale green. The product obtained from this solution depends on the isolation conditions. Slowly crystallized small, well-formed prism-
Table 1. Selected bond distances (\(\text{Å}\)) and angles (°) relevant to the yttrium coordination sphere for complexes 1 and 2.

<table>
<thead>
<tr>
<th>Bond</th>
<th>1</th>
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<tr>
<td>Y-N(1)</td>
<td>2.534(3)</td>
<td>2.508(3)</td>
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<tr>
<td>Y-N(2)</td>
<td>2.477(3)</td>
<td>2.541(3)</td>
</tr>
<tr>
<td>Y-N(3)</td>
<td>2.481(3)</td>
<td>2.507(3)</td>
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<td>Y-O(1)</td>
<td>2.441(2)</td>
<td>2.458(3)</td>
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<tr>
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<td>2.475(3)</td>
</tr>
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<td>2.330(2)</td>
<td>2.414(3)</td>
</tr>
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<td>Y-O(8)</td>
<td>2.736(4)</td>
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<tr>
<td>Y-O(W)</td>
<td>2.311(3)</td>
<td>2.329(3)</td>
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<td>N(1)-Y-N(2)</td>
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<td>64.6(1)</td>
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<td>N(1)-Y-N(3)</td>
<td>129.9(1)</td>
<td>128.7(1)</td>
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<td>51.8(1)</td>
<td>51.6(1)</td>
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<td>O(4)-Y-O(5)</td>
<td>51.7(1)</td>
<td>51.3(1)</td>
</tr>
<tr>
<td>O(7)-Y-O(8)</td>
<td>47.6(1)</td>
<td></td>
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<tr>
<td>O(1)-Y-O(W)</td>
<td>71.1(1)</td>
<td>78.2(1)</td>
</tr>
<tr>
<td>O(W)-Y-N(3)</td>
<td>79.6(1)</td>
<td>142.0(1)</td>
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<tr>
<td>O(W)-Y-O(7)</td>
<td>79.8(1)</td>
<td>73.3(1)</td>
</tr>
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</table>

Fig. 1. ORTEP view of 1 with 50% thermal ellipsoids showing the atom labeling scheme.

A shaped yellow crystals were identified by crystallography as \([\text{Y(NO}_3\text{)}_3(\text{terpy})(\text{H}_2\text{O})])\) (2), which does not redissolve in MeCN. From concentrated reaction solutions, the yield is almost quantitative. In contrast, layering of diluted solutions with Et₂O and storage at 20 °C gave colorless prisms of \([\text{Y(NO}_3\text{)}_2(\text{terpy})(\text{H}_2\text{O})])\) (1), which readily redissolves in MeCN.

The following points are of synthetic interest:
(i) The reactions in MeCN are not dependent on the \(\text{Y}^{\text{III}}\) : terpy ratio; the 1:1 and 1:3 reaction mixtures yield complexes 1 and 2 depending on the isolation conditions. (ii) Increase of the reaction solution polarity by using MeCN/H₂O leads [9] to isolation of the ionic product \([\text{Y(NO}_3\text{)}_2(\text{terpy})(\text{H}_2\text{O})])\)(NO₃)₂H₂O.

Drawings of the molecular structures of complexes 1 and 2 are shown in Figs. 1 and 3, respectively; the coordination polyhedra are depicted in Figs. 2 (1) and 4 (2). Selected bond distances and angles are given in Table 1.

The structure of 1 contains discrete molecules in which yttrium(III) is nine-coordinate. Its coordination sphere is filled by one terdentate terpy molecule, two bidentate nitrates, one monodentate nitrate and one FbO molecule. The average Y-N bond length of 2.50(1) Å corresponds closely to that of 2.49(1) Å in nine-coordinate \([\text{Y(NO}_3\text{)}_2(\text{terpy})(\text{H}_2\text{O})])\)(NO₃)₂H₂O [9]. The most surprising aspect of the structure of 1 is the presence of a monodentate nitrate group which is rare for yttrium and the lanthanides [10]. The Y-O(7) distance to the monodentate nitrate group [2.330(2) Å] is more than 0.1 Å shorter than the average [2.445(2) Å] of the four Y-O distances from the chelating nitrate groups. The latter are very close to the average Y-O distances in other...
nine-coordinate yttrium(III) complexes containing bidentate chelating nitrate groups [9, 11]. The Y-O(W) distance of 2.311(3) Å may be compared with the corresponding distance of 2.321(8) Å in the nine-coordinate complex \([\text{Y(NO}_3]_2\text{qtpy})\cdot\text{H}_2\text{O}\) ([qtpy = 2,2':6',2":6",2m'-quaterpyridine]) [11]. The stereochemistry about the metal ion may be viewed as tricapped trigonal prismatic, the three capping atoms being O(1), O(4), and N(1), with the angle sum subtended by them at Y being 358.6°.

The three terpy rings in 1 are almost coplanar, the dihedral angles between the central ring and the peripheral rings being 12.9° \([\text{N}(2)\text{C}(6)\text{C}(7)\text{C}(8)\text{C}(9)\text{C}(10) / \text{N}(3)\text{C}(11)\text{C}(12)\text{C}(13)\text{C}(14)\text{C}(15)]\) and 4.2°; the Y\text{III} atom deviations from the ring planes containing atoms N(2), N(1), and N(3) are 0.073, 0.054, and 0.756 Å, respectively. Distortion from planarity is common to complexed terpy [5, 6, 12].

The crystal structure of 1 is stabilized by a hydrogen-bonding network among the H\text{2}O and the nitrate oxygen atoms O(8) \([x, y, z]\), O(8) \([0.5-x, 0.5+y, 1.5-z]\) creating an infinite chain along the b axis.

The structure of 1 shows great similarity to that of the cation \([\text{Y(NO}_3]_2\text{qtpy})\cdot\text{H}_2\text{O})^+\) where the monodentate nitrate of the former is replaced by one aquo ligand [9].

Complex 1 is isostructural with the recently reported complex \([\text{Tm(NO}_3]_3\text{qtpy})\cdot\text{H}_2\text{O})\) [10]. \([\text{Er(NO}_3]_3\text{qtpy})\cdot\text{EtOH})\], isolated from EtOH [7], comes also close to reproducing the structure of 1; it has two bidentate and one monodentate nitrate groups, and a terminal EtOH molecule instead of the terminal H\text{2}O molecule.

The asymmetric unit of 2 contains one \([\text{Y(NO}_3]_3\text{qtpy})\cdot\text{H}_2\text{O})\] molecule, one non-coordinated (lattice) terpy molecule and three MeCN molecules. The Y\text{III} atom is 10-coordinate with three nitrogen atoms from the \(\text{cis, cis}\) terdentate terpy, six oxygen atoms from the three chelating nitrate groups and one oxygen atom from a terminal H\text{2}O molecule. The N(6)O(7)O(8)O(9) nitrate exhibits a more asymmetric coordination mode than the other two nitrates \([\text{Y-O(7) 2.414(3) and Y-O(8) 2.736(4) Å}]\) and can be classified as anisobidentate using the criteria of Reedijk and coworkers [13]. The increased Y-N and Y-O distances in 2 are a consequence of the higher coordination number of the Y\text{III} atom compared to the structure of 1. Dihedral angles between the central ring skeletal plane of the coordinated terpy, and the two peripheral planes N(1)C(1)C(2)C(3)C(4)C(5) and N(3)C(11)C(12)-
C(13)C(14)C(15) are 4.3 and 10.6°, respectively. Of the proposed standard 10-coordinate polyhedra [14], the distorted sphenocorona (tetradecahedron) is the most appropriate for the description of the arrangement of the ten donor atoms in 2 (see Fig. 4).

Almost all free oligopyridines (including terpy [15]), whose structures have been determined by crystallography, contain adjacent pyridine rings in the trans conformation [6]. The interstitial (lattice) terpy molecule in 2 has the cis, cis conformation. This is due to the fact that its atoms N(11) and N(13) of the peripheral rings are strongly hydrogen-bonded to the O atom of the coordinated H2O forming [Y(NO3)3(terpy)(H2O)]·terpy pairs; the dimensions of the two hydrogen bonds are O(W)···N(11) [1 – x, 1 – y, 1 – z] 2.788 Å, O(W)···H(W(B)···N(11) [1 – x, 1 – y, 1 – z] 174.2°, and O(W)···N(13) [1 – x, 1 – y, 1 – z] 2.878 Å, O(W)···H(W(A)···N(23) [1 – x, 1 – y, 1 – z] 176.6°. This structural feature has been observed in the crystal structures of [SnPh3(NCS)(H2O)]·terpy [16] and [SnPb3Cl(H2O)]·terpy [17]. These hydrogen bonds and the steric effects between N(12) and O(W) disturb the planarity of the lattice terpy, the dihedral angles between the central and peripheral rings being 30.2 and 23.4°.

There appear to be intermolecular stacking interactions in the crystal lattice between inversion-related, parallel coordinated terpy arrays [the closest interatomic separation, C(2)···C(8) (x, 2 – y, – z), is 3.422 Å], and between coordinated and lattice terpy molecules [the closest separation, C(2)···C(27) (1 – x, 1 – y, – z), is 3.369 Å]; such interactions aid in stabilizing the crystal structure.

IR assignments are given in the Experimental Section. The terpy bands appear at similar frequencies in the spectra of 1 and 2. Two groups of very intense bands assigned to υ(C=–N) and υ(C=–C) appear at 1582 - 1560 and 1478 - 1422 cm–1 for free terpy. The two bands of the first group show a ~15 cm–1 shift to higher frequencies due to coordination/hydrogen bonding [18]. The second group shows some shift and splitting [18] but is strongly superimposed by the nitrate vibrations in this region. The broadness and the relatively low frequency of the υ(OH)coord.water band at 3365 - 3400 cm–1 are both indicative of strong hydrogen bonding.

The nitrate vibrations are taken from Nujol and hexachlorobutadiene mull spectra, since it is well known that pressing a KBr pellet affects the nitrate coordination [13]. The terpy frequencies are identical in both the KBr and mull spectra. The presence of both bidentate and monodentate nitrate groups in 1 (established by crystallography) also follows from the appearance of several crystallography bands. Since it has been established that a) the separation of the two highest-frequency bands is considerably smaller for the monodentate than the bidentate nitrates [19], and b) the highest-frequency NO stretching band belongs to the A1 species in the bidentate and to the B2 species in the monodentate nitrate, the pair at 1450 and 1306 cm–1 characterizes the monodentate nitrate. The mull spectrum of 2 is similar with that of 1.

The 1H NMR assignments for complexes 1 and 2 in CD3OD presented in the Experimental Part are based on the work of Fréchette and Bensimon [5] for the LaIII/NO3−/terpy systems. The spectrum of 1 in CD3OD is indicative of the presence of free terpy and a solution species containing coordinated terpy. The proton chemical shifts and their assignments presented with italics in the Experimental Section correspond to resonances of coordinated terpy. The remaining signals of uncoordinated terpy appear at exactly the same δ values as for free terpy in CD3OD. Because of a moderately slow exchange between the free and complexed terpy, the two series of 1H signals appear somewhat broad [5]. It is difficult to decide from 1H NMR experiments alone if the complex species in solution is [Y(NO3)3(terpy)(CD3OD)]. Surprisingly, the spectrum of 2 in CD3OD is identical with that of free terpy, indicating that the solution YIII species do not contain terpy. Fréchette and Bensimon [5] investigated the reaction between La(NO3)3·6H2O and terpy in CD3CN by means of 1H, 17O, and 139La spectroscopy. They showed that during the complexation/solvation process seven different LaIII species can be observed, two of which, namely [La(NO3)3S4] and [La(NO3)3S4·(H2O)] (S=solvent), do not contain terpy.

Concluding Comments

The nature of the products from the reactions between Y(NO3)3·5H2O and terpy presented in this work has been shown to depend on the crystallization method. This is not surprising for reaction solutions containing labile metal ions and ligands, since it seems likely that there are a num-
<table>
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<th>Formula[a]</th>
<th>Reaction solvent(s)</th>
<th>Metal coordination number(s)</th>
<th>Nitrate coordination mode(s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ln(NO₃)₃(terpy)(MeOH)₂] (Ln = Nd, Sm, Tb, Dy, Ho)</td>
<td>MeCN/2-bromodecanoic acid</td>
<td>11</td>
<td>bidentate</td>
<td>[6]</td>
</tr>
<tr>
<td>[Ln(NO₃)₃(terpy)(H₂O)] (Ln = Sm)</td>
<td>EtOH, MeCN</td>
<td>9</td>
<td>bidentate</td>
<td>[9]</td>
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<tr>
<td>[Ln(NO₃)₃(terpy)(H₂O)] (Ln = Ho, Er)</td>
<td>MeCN</td>
<td>9</td>
<td>bidentate</td>
<td>[10]</td>
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<tr>
<td>[Ln(NO₃)₃(terpy)(H₂O)]-terpy</td>
<td>MeCN</td>
<td>9</td>
<td>bidentate</td>
<td>[10]</td>
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<tr>
<td>[Ln(NO₃)₃(H₂O)]-terpy</td>
<td>MeCN</td>
<td>9</td>
<td>bidentate</td>
<td>[10]</td>
</tr>
<tr>
<td><a href="NO%E2%82%83">Ln(NO₃)₂(terpy)(H₂O)</a> (Ln = La, Gd, Tm)</td>
<td>MeCN/H₂O[b]</td>
<td>10</td>
<td>bidentate</td>
<td>[8, 9]</td>
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<tr>
<td><a href="NO%E2%82%83">Ln(NO₃)₂(terpy)(H₂O)</a> (Ln = Tb, Lu)</td>
<td>MeCN/H₂O</td>
<td>9</td>
<td>bidentate</td>
<td>[9]</td>
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<tr>
<td><a href="NO%E2%82%83">Y(NO₃)₂(terpy)(H₂O)</a></td>
<td>MeCN/H₂O</td>
<td>9</td>
<td>bidentate</td>
<td>[9]</td>
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[a] In addition, complexes (H₂terpy)₃[La(NO₃)₅]₂·3H₂O [6] and ([H₂terpy)(NO₃)](H₂terpy)[La(NO₃)₅] [10] have been structurally characterized, but these do not contain coordinated terpy; [b] lattice solvate molecules are not included in the formulae; [c] for the cation; [d] for the anion; [e] a single monodentate nitrate group belongs to the anion; [f] S= EtOH for the Er(III) complex [7] and S= H₂O for the Tm(III) complex [10]; [g] one of the nitrate ligands is monodentate; [h] for the La(III) complex [9]; [i] for the Gd(III) complex [8].

Table 2. Structurally characterized[6] Y(III), Ln(III)/NO₃⁻/terpy complexes (Ln = lanthanide); solvate molecules have been omitted from the formulae of the complexes.

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Ber of species present in solution. Compounds 1 and 2, along with the previously described [9] salt [Y(NO₃)₂(terpy)(H₂O)](NO₃)·2H₂O isolated from MeCN/H₂O, form a small family of well-characterized Y(III)/NO₃⁻/terpy complexes. It is interesting that no complex with more than one terpy ligand bonded to Y(III) could be isolated, even though metal/ligand ratios of 1:3 were employed. Such complexes are known only with weakly coordinating anions, e.g. ClO₄⁻, a typical example being [Y(terpy)₃](ClO₄)₃ [20].

The to-date structurally characterized Ln(III) or Y(III)/NO₃⁻/terpy complexes are summarized in Table 2 for convenient comparison (Ln = 4f metal). According to Drew and co-workers [10], the most important factors in determining which complex is precipitated from Ln(III)/NO₃⁻/terpy solutions are the Ln(III):terpy ratio, the size of the metal ion and the synthesis/crystallization solvent used. Focusing on the first factor, the addition of more than one molar equivalent of terpy favours the formation of the ion pair [Ln(NO₃)₂(terpy)]²⁺/[Ln(NO₃)₄(terpy)] for the larger lanthanides and complexes [Ln(NO₃)₃(terpy)(H₂O)]-terpy for the smaller lanthanides [10]. We could not confirm the second part of this conclusion for Y(III). The Y(III):terpy reaction ratios of 1:1, 1:2 and 1:3 all yield both 1 or 2 depending on the crystallization method.

As far as Y(III) is concerned, both 1 and 2 have their structural analogues in 4f metal/NO₃⁻/terpy chemistry. Complex 1 is isostructural with [Tm(NO₃)₃(terpy)(H₂O)]·2H₂O, while complex 2 is isostructural with [Ln(NO₃)₃(terpy)(H₂O)]-terpy (Ln = Ho, Er), but not with [Tm(NO₃)₂(terpy)(H₂O)]-terpy [10].

It is clear from the above study that the complexation properties of lanthanide(III) and yttrium(III) nitrates with weakly basic N-donors are very sensitive to the conditions under which the reaction and crystallization take place and that the coordination chemistry of Y(III) is flexible compared with that of the heavier, smaller lanthanides(III). With the above considerations in mind, this work is to be extended...
to Y^{III}/RCOO⁻/bpy, phen, terpy reaction systems. Our studies in this area of yttrium(III) chemistry, already well advanced, reveal significant differences with respect to the recently reported analogous 4f metal chemistry [21, 22].

**Experimental Part**

All manipulations were performed under aerobic conditions using starting materials (Merck) and solvents as received. Elemental analyses (C, H, N) were conducted by the University of Ioannina, Greece, Microanalytical Service. IR spectra (4000 - 500 cm⁻¹) were recorded on a Perkin-Elmer 16 PC FT spectrometer with samples prepared as KBr pellets and as Nujol or hexachlorobutadiene mulls between CsI discs. 400.1 MHz *H NMR spectra in CD₃OD were recorded on an Avance DPX spectrometer of Bruker at 25 °C. Chemical shifts, quoted on the scale and referenced versus external TMS or the proto impurity of the solvent employed, are assigned according to the atomic labeling scheme of complexes 1 and 2 (Figs. 1 and 3).

\[ [Y(NO_3)_3 \text{terpy}(H_2O)](1) \]

A stirred solution of Y(NO₃)₃·5H₂O (0.058 g, 0.16 mmol) in MeCN (11 ml) was added to a solution of terpy (0.075 g, 0.32 mmol) in the same solvent (9 ml). Layering of Et₂O (35 ml) over the pale green solution gave colorless prismatic crystals, which were collected by filtration, washed with MeCN/Et₂O (1:2 v/v), and dried in vacuo. The yield was ~65%. IR (KBr pellet): \( \nu = 3396 [\nu(OH)], 1648 [\delta(H_2O)], 1598, 1578, 1482, 1460, 1434 [\nu(C=\equiv N), \nu(C=\equiv C)], 1514 [\nu_1(\text{A}_1) \text{bidentate nitrate}], 1450 [\nu_5(\text{B}_2) \text{monodentate nitrate}], 1306 [\nu_1(\text{A}_1) \text{monodentate nitrate}], 1282 [\nu_5(\text{B}_2) \text{monodentate nitrate}], 1034, 1026 [\nu_2(\text{A}_1) \text{hurate}], 1014 [\text{pyridine ring breathing}], 834, 778, 744 [\nu(CH)], 814, 800 [\nu_6(\text{B}_1) \text{hurate}] \text{cm}^{-1}. - ^1H NMR (400.1 MHz, CD₃OD): \( \delta = 8.94 \text{[d, 2 H, H(1,15)]}, 8.68 \text{[d, 6 H, H(1,15)]}, 8.65 \text{[t, 6 H, H(4,12)]}, 8.46 \text{[t, 1 H, H(8)]}, 8.40 \text{[d, 6 H, H(7,9)]}, 8.34 \text{[m, 4 H, H(4,12) and H(7,9)]}, 8.23 \text{[td, 2 H, H(3,13)]}, 8.07 \text{[t, 3 H, H(8)]}, 8.02 \text{[td, 6 H, H(3,13)]}, 7.83 \text{[t, 2 H, H(2,14)]}, 7.49 \text{[t, 6 H, H(2,14)]}, 2.12 \text{[s, H_2O]}), - C_{15}H_{24}N_2O_10Y (5262.22): calcd C 34.23, H 2.49, N 15.97; found C 34.56, H 2.52, N 15.60.

\[ [Y(NO_3)_3 \text{terpy}(H_2O)] \text{-terpy-3MeCN (2)} \]

To a stirred solution of terpy (0.079 g, 0.34 mmol) in MeCN (4.5 ml) was slowly added a solution of Y(NO₃)₃·5H₂O (0.058 g, 0.16 mmol) in the same solvent (5.1 ml). Storage of the flask at ambient temperature for 2 d yielded small yellow prisms (some of them were of X-ray quality), which were collected by filtration, washed with MeCN and Et₂O, and dried in vacuo. Typical yields are in the 80-90% range (based on Y). The crystals were found to lose solvent readily, and they were kept in the mother liquor until a suitable crystal had been found for X-ray crystallography. The latter established the presence of solvent molecules; the dried analysis sample was analyzed as \([Y(NO_3)_3 \text{terpy}(H_2O)] \text{-terpy (MeCN-free)}\). IR (KBr pellet): \( \nu = 3365 [\nu(OH)], 1640 [\delta(H_2O)], 1596, 1578, 1570, 1434, 1425 [\nu(C=\equiv N), \nu(C=\equiv C)], 1485 [\text{ring stretching vibration}, \nu_1(\text{A}_1) \text{bidentate nitrate}], 1452 [\nu_5(\text{B}_2) \text{monodentate nitrate}], 1306 [\nu_1(\text{A}_1) \text{monodentate nitrate}], 1275 [\nu_5(\text{B}_2) \text{monodentate nitrate}], 1034 [\nu_2(\text{A}_1) \text{hurate}], 1014 [\text{pyridine ring breathing}, \nu_2(\text{A}_1) \text{hurate}], 834, 775, 768, 744 [\nu(CH)], 816, 799 [\nu_6(\text{B}_1) \text{hurate}] \text{cm}^{-1}. - ^1H NMR (400.1 MHz, CD₃OD): \( \delta = 8.67 \text{[d, 4 H, H(1,15)] and H(21,35)]}, 8.62 \text{[d, 4 H, H(4,12) and H(24,32)]}, 8.38 \text{[d, 4 H, H(7,9) and H(27,29)]}, 8.05 \text{[t, 2 H, H(8) and H(28)]}, 7.99 \text{[td, 4 H, H(3,13) and H(23,33)]}, 7.47 \text{[m, 4 H, H(2,14) and H(22,34)]}, 2.05 \text{[s, H_2O]}), - C_{20}H_{29}N_2O_10Y (882.65): calcd C 47.44, H 3.19, N 16.72; found C 47.09, H 3.11, N 16.72.

**Crystal structure determinations**

A colorless prismatic crystal of 1 (0.10 × 0.10 × 0.40 mm) and a pale yellow prismatic crystal of 2 (0.10×0.20×0.50 mm) were mounted in air and in a capillary filled with drops of mother liquid, respectively. Diffraction measurements were performed on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo Kα, radiation. Complete crystal data and parameters for data collection and refinement are reported in Table 3. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range 11 < 2θ < 23°. Intensity data were recorded using a θ - 2θ scan. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz, polarization, and ψ -scan absorption corrections were applied using Crystal Logic software. The structures were solved by direct methods using SHELXS-86 [23] and refined by full-matrix least-squares techniques on F² with SHELX-93 [24]. For both structures all hydrogen atoms were located by difference maps and refined isotropically, while all non-hydrogen atoms were refined anisotropically. Further crystallographic details on 1: 2θ(max) = 50°, scan speed 4.0°/min, scan range 2.3° + α₁/₀₂ separation, R1/wR2 (for all data) = 0.0502/0.0732. Further crystallographic details on 2: 2θ(max) = 48.5°, scan speed 3.0°/min, scan range 2.3° + α₁/₀₂ separation, R1/wR2 (for all data) = 0.0798/0.1064. Two X-ray crystallographic files for complexes 1 and 2, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC 148971 (1) and 148972 (2).
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Table 3. Crystal data, data collection, and structure refinement for 1 and 2.

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
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<tr>
<td>Formula</td>
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<tr>
<td>M&lt;sub&gt;r&lt;/sub&gt;</td>
<td>526.22</td>
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<tr>
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<tr>
<td>Space group</td>
<td>P₂₁/n</td>
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<tr>
<td>a (Å)</td>
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<tr>
<td>c (Å)</td>
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<tr>
<td>α (°)</td>
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<tr>
<td>β (°)</td>
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</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
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<tr>
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<td>T (°C)</td>
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<tr>
<td>hkl Range</td>
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<tr>
<td>Unique reflections</td>
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<tr>
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<td>Final wR2 [b]</td>
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</tr>
<tr>
<td>(Δρ)&lt;sub&gt;max&lt;/sub&gt;/ (Δρ)&lt;sub&gt;min&lt;/sub&gt; (e Å⁻³)</td>
<td>0.305/—0.235</td>
</tr>
</tbody>
</table>

[a] \( R1 = \frac{\sum |F_0| - |F_c|}{\sum |F_0|}; \)
[b] \( wR2 = \left[\frac{\sum w(F_0^2 - F_c^2)^2}{\sum w(F_0^2)^2}\right]^{1/2}. \)