

Crystals **2012**, *2*, 1084–1091; doi:10.3390/cryst2031084

OPEN ACCESS

crystals

ISSN 2073-4352

www.mdpi.com/journal/crystals

Short Note

[KDy(Hptc)₃(H₃ptc)]_n·2n(Hbipy)·5n(H₂O), a Layered Coordination Polymer Containing DyO₆N₃ Tri-Capped Trigonal Prisms (H₃ptc = Pyridine 2,4,6-Tricarboxylic Acid, C₈H₅NO₆; Bipy = 2,2'-Bipyridine, C₁₀H₈N₂)

Shoaib Anwar ¹, Irfana Mariam ², Islam Ullah Khan ^{1,*}, Ejaz ¹, William T. A. Harrison ^{3,*} and Sohail Anwar ¹

¹ Materials Chemistry Laboratory, Department of Chemistry, Government College University, Lahore-54000, Pakistan; E-Mails: shoaib.anwer731@gmail.com; (Sh.A.); ejaz_lhr_pk@yahoo.com (E.); sohail.anwar21@gmail.com (So.A.)

² Department of Chemistry, Queen Mary College for Girls, Lahore, Pakistan; E-Mail: majied.irfana@yahoo.com

³ Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, UK

* Authors to whom correspondence should be addressed; E-Mails: iuklodhi@yahoo.com (I.U.K.); w.harrison@abdn.ac.uk (W.T.A.H.); Tel.: +92-042-99213338 (I.U.K.); +44-1224-272897 (W.T.A.H.); Fax: +44-1224-272921 (W.T.A.H.).

Received: 10 May 2012; in revised form: 7 June 2012 / Accepted: 25 June 2012

Published: 3 August 2012

Abstract: The synthesis, structure and properties of the bimetallic layered coordination polymer, [KDy(C₈H₃NO₆)₃(C₈H₅NO₆)]_n·2n(C₁₀H₈N₂)·5n(H₂O) = [KDy(Hptc)₃(H₃ptc)]_n·2n(Hbipy)·5n(H₂O), are described. The Dy³⁺ ion is coordinated by three O,N,O-tridentate doubly-deprotonated pyridine tri-carboxylate (Hptc) ligands to generate a fairly regular DyO₆N₃ tri-capped trigonal prism, with the N atoms acting as the caps. The potassium ion is coordinated by an O,N,O-tridentate H₃ptc molecule as well as monodentate and bidentate Hptc ligands to result in an irregular KNO₉ coordination geometry. The ligands bridge the metal-atom nodes into a bimetallic, layered, coordination polymer, which extends as corrugated layers in the (010) plane, with the mono-protonated bipyridine cations and water molecules occupying the inter-layer regions: Unlike related structures, there are no dysprosium–water bonds. Many O–H···O and N–H···O hydrogen bonds consolidate the structure. Characterization and bioactivity data are described. Crystal data: C₅₂H₄₂DyKN₈O₂₉, M_r = 1444.54, triclinic, P $\bar{1}$ (No. 2), Z = 2, a = 9.188(2) Å,

$b = 15.7332(17) \text{ \AA}$, $c = 19.1664(19) \text{ \AA}$, $\alpha = 92.797(6)^\circ$, $\beta = 92.319(7)^\circ$,
 $\gamma = 91.273(9)^\circ$, $V = 2764.3(7) \text{ \AA}^3$, $R(F) = 0.029$, $wR(F^2) = 0.084$.

Keywords: coordination polymer; layered supramolecular network; dysprosium

1. Introduction

Coordination polymers, in which bridging ligands connect metal atoms into an extended network [1], have been intensively studied for the past 100 years. This area of chemistry is so vast that a journal solely devoted to reviewing the field—*Coordination Chemistry Reviews*—publishes some 3000 pages per year.

In this paper we describe the synthesis and structure of the new bimetallic coordination polymer $[\text{KDy}(\text{C}_8\text{H}_3\text{NO}_6)_3(\text{C}_8\text{H}_5\text{NO}_6)]_n \cdot 2n(\text{C}_{10}\text{H}_9\text{N}_2) \cdot 5n(\text{H}_2\text{O})$: (1) Related structures containing Dy^{3+} ions in combination with pyridine 2,4,6-tricarboxylate (ptc) ligands include α - $[\text{Dy}(\text{C}_8\text{H}_2\text{NO}_6)(\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$ [2], $[\text{Dy}(\text{C}_8\text{H}_2\text{NO}_6)(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ [3], β - $[\text{Dy}(\text{C}_8\text{H}_2\text{NO}_6)(\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$ [4] and $[\text{Dy}_2(\text{C}_8\text{H}_2\text{NO}_6)_2^-(\text{H}_2\text{O})_5]_n \cdot n\text{H}_2\text{O}$ [5]. In all these compounds, the tri-anionic ptc ligand forms an O,N,O-tridentate link to one metal ion and also bridges to other Dy^{3+} ions to form a coordination network. One or more water molecules are also directly coordinated to the dysprosium ion.

The crystal structures of $[\text{K}(\text{VO}_2)(\text{C}_8\text{H}_3\text{NO}_6)]_n \cdot n\text{H}_2\text{O}$ [6], $[\text{KCaEr}(\text{C}_8\text{H}_2\text{NO}_6)_2(\text{H}_2\text{O})]_n$ [7] and $[\text{KBa}(\text{C}_8\text{H}_2\text{NO}_6)(\text{H}_2\text{O})_2]_n$ [7] have been reported but there are no mixed-metal K/Dy/ptc coordination polymers yet known.

2. Results and Discussion

2.1. Crystal Structure of $[\text{KDy}(\text{C}_8\text{H}_3\text{NO}_6)_3(\text{C}_8\text{H}_5\text{NO}_6)]_n \cdot 2n(\text{C}_{10}\text{H}_9\text{N}_2) \cdot 5n(\text{H}_2\text{O})$ (1)

Compound 1 is a bimetallic, layered coordination polymer: The complex asymmetric unit contains one K^+ cation, one Dy^{3+} cation, three doubly-deprotonated $(\text{C}_8\text{H}_3\text{NO}_6)^{2-}$ (Hptc^{2-}) dianions, one neutral $\text{C}_8\text{H}_5\text{NO}_6$ (H_3ptc) molecule, two singly protonated bipyridinium $(\text{C}_{10}\text{H}_9\text{N}_2)^+$ cations and five water molecules (Figure 1).

The dysprosium ion in 1 is coordinated by the three O,N,O-tridentate $\text{C}_8\text{H}_3\text{NO}_6$ dianions (in which two carboxylate protons have been lost from the $\text{C}_8\text{H}_5\text{NO}_6$ neutral molecule) to generate a near-regular tri-capped trigonal prismatic DyO_6N_3 coordination geometry with the N atoms serving as the caps protruding through the prismatic side-faces (Figure 2). Each ligand forms one Dy–O bond to the “top” triangular face and one to the bottom. The dihedral angle between the O1/O7/O13 and O5/O11/O17 triangular faces is $4.30(4)^\circ$ and the metal ion is displaced by $-1.6580(13) \text{ \AA}$ from the first triplet of O atoms and by $1.6133(13) \text{ \AA}$ from the second. The Dy–N bond lengths (Table 1) (mean = 2.501 \AA) are longer than all but one of the Dy–O bonds (mean = 2.413 \AA). The Dy^{3+} bond-valence sum (BVS), calculated using the Brown–Altermatt [8] formalism, is 3.18, compared to an expected value of 3.00.

Figure 1. The asymmetric unit of 1 (50% displacement ellipsoids for the non-hydrogen atoms). The water molecules are omitted for clarity.

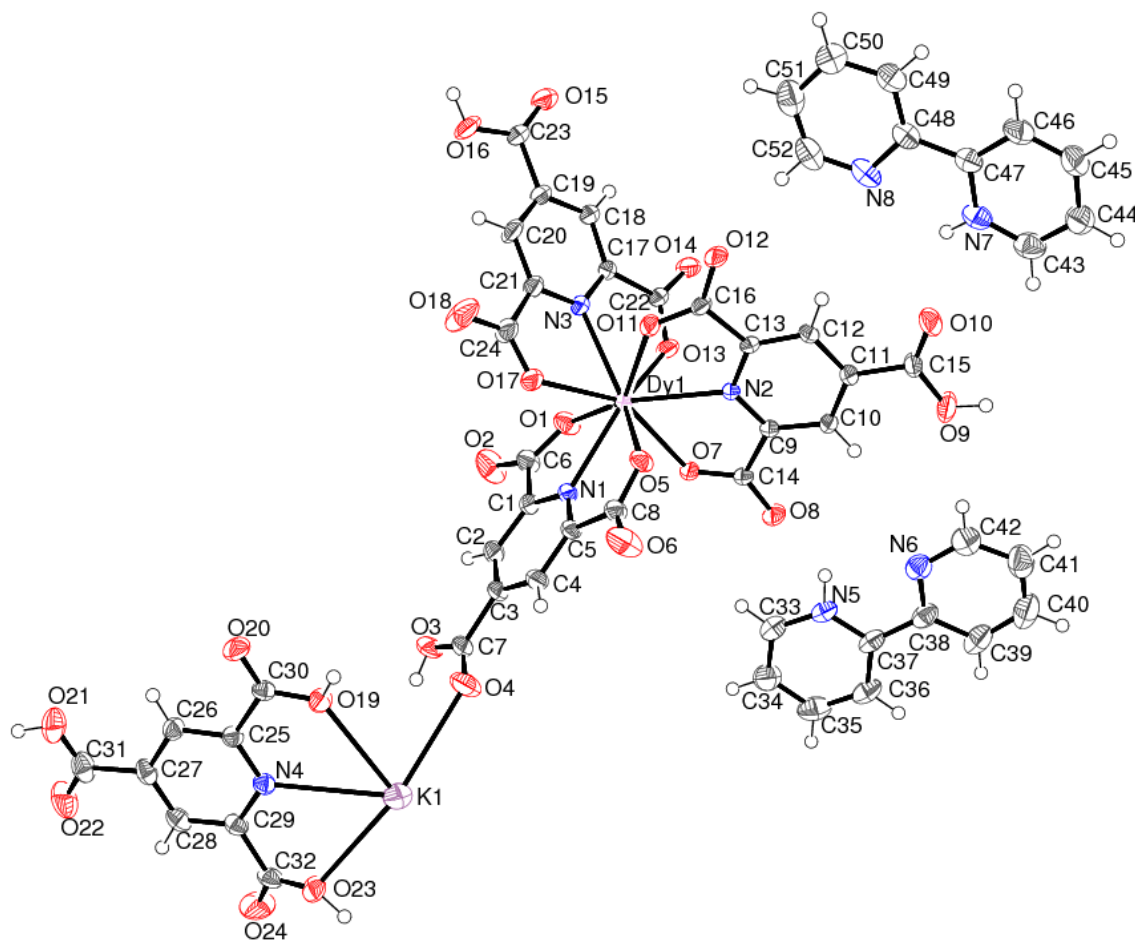


Figure 2. Detail of the structure of 1 showing the tri-capped trigonal prismatic coordination of the Dy^{3+} ion (50% displacement ellipsoids, arbitrary spheres for the C atoms). Note the overall, approximate, local C_3 symmetry of these atoms.

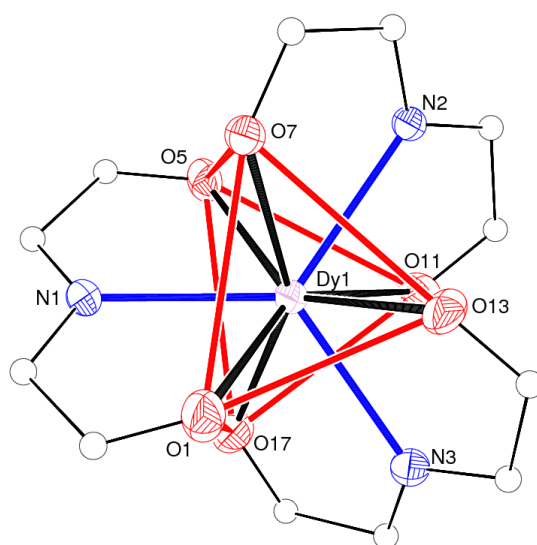


Table 1. Selected bond-distances (Å) in 1.

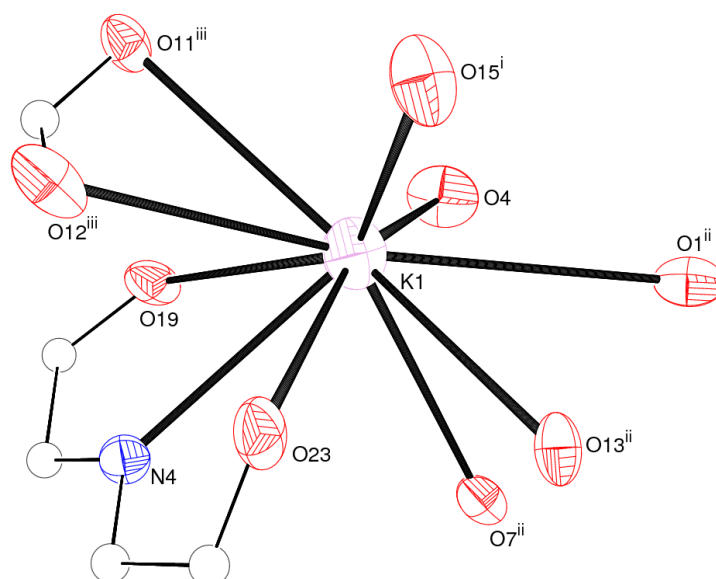
K1–O19	2.885(2)	K1–O23	2.946(2)
K1–O4	2.949(2)	K1–O15 ⁱ	2.958(2)
K1–O13 ⁱⁱ	3.025(2)	K1–O11 ⁱⁱⁱ	3.073(2)
K1–N4	3.074(2)	K1–O7 ⁱⁱ	3.201(2)
K1–O12 ⁱⁱⁱ	3.388(3)	K1–O1 ⁱⁱ	3.432(3)
Dy1–O1	2.366(2)	Dy1–O17	2.392(2)
Dy1–O13	2.397(2)	Dy1–O11	2.397(2)
Dy1–O5	2.440(2)	Dy1–N1	2.481(2)
Dy1–O7	2.4838(19)	Dy1–N3	2.500(2)
Dy1–N2	2.523(2)		

Symmetry codes: (i) $x, y, z-1$; (ii) $1-x, 1-y, 1-z$; (iii) $-x, 1-y, 1-z$.

The geometrical parameters for the three Dy-bonded ligands (containing atoms N1, N2 and N3) are unexceptional, and all the carboxylate groups are close to coplanar with their attached rings. In each case, the protonated (carboxylic acid $-\text{CO}_2\text{H}$) grouping is the one not bonded to the rare-earth ion at the para position with respect to the pyridine N atom.

The potassium ion in 1 is coordinated by the O,N,O-tridentate $\text{C}_8\text{H}_5\text{NO}_6$ neutral molecule (containing N4), as well as monodentate and bidentate dianions also bonded to the dysprosium ion to generate a KNO_9 coordination polyhedron (mean $\text{K}-\text{O} = 3.095 \text{ \AA}$) that can only be described as irregular (Figure 3). It is also decidedly asymmetric with the potassium ion displaced by 0.481 \AA from the geometric centroid of its attached atoms. The next-nearest O atom is over 4.0 \AA from the K^+ ion and the BVS for potassium is 0.87 (expected value = 1.00). The existence of a protonated carboxylic acid forming a coordinate bond to a potassium ion from its OH moiety is uncommon, but some examples such as $[\text{K}(\text{C}_5\text{H}_4\text{N}_2\text{O}_4)(\text{C}_5\text{H}_3\text{N}_2\text{O}_4)]_n$ [9] and $[\text{K}(\text{C}_8\text{H}_8\text{O}_2\text{S})(\text{C}_8\text{H}_7\text{O}_4\text{S})]_n$ [10] have been structurally characterised previously.

Figure 3. Detail of 1 (50% displacement ellipsoids, arbitrary spheres for the C atoms) showing the potassium-ion coordination. Symmetry codes as in Table 1.



A notable feature of this phase is the sharing of some of the ligand O atoms (*i.e.*, as μ^2 bridges) by the dysprosium and potassium ions: In particular, the three oxygen atoms of the O1/O7/O13 triangular face of the Dy-trigonal prism also bond to the K^+ ion. This leads to polymeric chains of alternating DyO_6N_3 and KNO_9 units, which propagate in the [100] direction (Figure 4).

Figure 4. Fragment of a [100] chain of DyO_6N_3 and KNO_9 polyhedra in 1 (50% displacement ellipsoids). Note how Dy1 and $K1^{ii}$ are linked via a triangular face but Dy1 and $K1^i$ are linked by a single O atom. Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$.

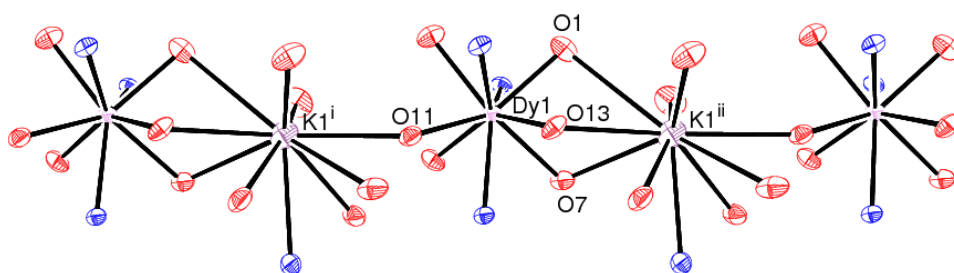
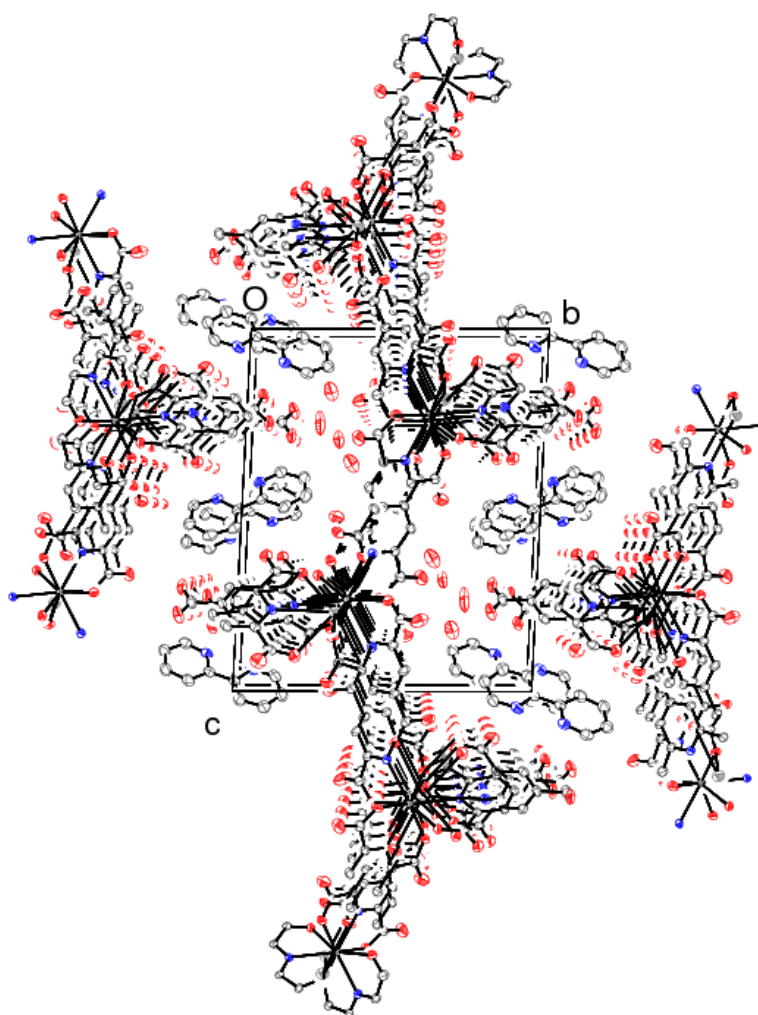


Figure 5. The packing for 1 viewed approximately down [100] showing the wavy (010) polymeric sheets with the organic cations and water molecules occupying the inter-sheet regions.



When ligand bridging via the aromatic rings is also considered, a layered anionic network of stoichiometry $[\text{KDy}(\text{C}_8\text{H}_3\text{NO}_6)_3(\text{C}_8\text{H}_5\text{NO}_6)]^{2n-}$ results, which propagates in the (010) plane (Figure 5). The layer is corrugated and the $(\text{C}_{10}\text{H}_9\text{N}_2)^+$ bipyridinium cations and water molecules occupy the inter-layer regions. The dihedral angles between the aromatic rings of the bipyridinium cations are $5.23(17)^\circ$ and $3.39(18)^\circ$ for the N5- and N7-containing ions, respectively. To complete the structure of 1, numerous O–H \cdots O and N–H \cdots O hydrogen bonds occur (Table 2). The acceptor atoms are either carboxylate O atoms or water O atoms.

Table 2. Hydrogen-bond geometries for 1.

O3–H3o \cdots O7 ⁱⁱ	0.81	1.79	2.537(3)	153
O9–H9o \cdots O4w ^{iv}	0.92	1.60	2.511(4)	169
O16–H16o \cdots O12 ^v	0.85	1.63	2.458(3)	163
O19–H19o \cdots O5 ⁱⁱⁱ	0.96	1.57	2.502(3)	162
O21–H21o \cdots O1w ^{vi}	0.93	1.65	2.515(3)	152
O23–H23o \cdots O14 ⁱⁱ	0.96	1.57	2.514(3)	168
N5–H5n \cdots O8	0.95	1.96	2.772(3)	142
N7–H7n \cdots O10	0.87	2.23	2.882(3)	132
O1w–H1w \cdots O2 ^{vii}	0.92	1.80	2.702(4)	167
O1w–H2w \cdots O18	0.92	1.77	2.672(4)	165
O2w–H3w \cdots O1w	0.92	2.37	3.044(5)	130
O2w–H4w \cdots O17	0.92	2.05	2.865(4)	146
O3w–H5w \cdots O5w	0.92	1.92	2.816(5)	163
O3w–H6w \cdots O22 ^{viii}	0.92	1.97	2.878(4)	171
O4w–H7w \cdots O3w	0.92	1.87	2.709(6)	151
O4w–H8w \cdots O2w	0.85	2.06	2.909(6)	180
O5w–H9w \cdots O1	0.92	1.95	2.844(4)	164
O5w–H10w \cdots O15 ^{ix}	0.92	2.01	2.891(4)	161

The four columns specify the D–H, H \cdots A and D \cdots A separations (Å) and the D–H \cdots A angle ($^\circ$), respectively. Symmetry codes: (ii) 1–x, 1–y, 1–z; (iii) –x, 1–y, 1–z; (iv) x, y–1, z; (v) –x, 1–y, 2–z; (vi) –x, 2–y, 1–z; (vii) x–1, y, z; (viii) 1–x, 2–y, 1–z; (ix) 1–x, 1–y, 2–z.

2.2. Bacteriological Tests

Seven bacterial strains including two Gram positive *Staphylococcus aureus* and *Micrococcus luteus* and five Gram negative, *Escherichia coli*, *Salmonella setubal*, *Salmonella typhimurium*, *Enterobacter aerogenes* and *Bordetella bronchiseptica* were used. Roxithromycin (R) and Cefixixme (C) drugs were used as positive controls, which had shown maximum growth inhibition at $1 \text{ mg}\cdot\text{mL}^{-1}$ concentrations and DMSO was used as a negative control. Compound 1 shows significant antibacterial activity against all these bacterial strains (Table 3) except *Salmonella typhimurium*.

Table 3. Bacteriological data.

Minimum Inhibitory Concentration (MIC)					
<i>M. luteus</i>	<i>S. aureus</i>	<i>Ent. bac</i>	<i>B. step</i>	<i>E. coli</i>	<i>S. typhi</i>
30 ppm	150 ppm	200 ppm	70 ppm	110 ppm	Nil

3. Experimental Section

The nominal pyridine 2,4,6-tricarboxylic acid (H₃ptc) starting material was prepared by oxidizing 2,4,6-trimethyl pyridine with KMnO₄ solution, as described by Syper *et al.* [11]. This evidently generated a potassium salt: A 0.5-mmol solution was prepared by heating 0.11 g of the solid product in 10.0 mL water in a 50-mL round bottom flask. Then, 0.0063 g of 2,2-bipyridine in 5 mL methanol was added, and the mixture was refluxed for 25 min. Then, a 0.125 mmol solution of DyCl₃·6H₂O was prepared by dissolving 0.040 g of the metal chloride in 10 mL distilled water and this solution was added to the flask. The Dy:H₃ptc:bipy molar ratio was 1:4:4. The mixture was refluxed for four hours and transferred to a vial for crystallization. After ten days, pale pinkish needle like crystals of the title compound were obtained. IR (cm⁻¹): 3410 [ν(O–H)], 1631[ν_{asym}(O–C–O)], 1373 [ν(C_{ar}–C)], 1265 [ν_{sym}(O–C–O)], 539 [ν(M–O, M–N)]. TGA showed an initial weight loss of about 5% between 70 °C and 120 °C, presumably attributable to the loss of the water molecules of crystallization (calc. = 6%). From 205 °C to 300 °C (the limit of the experiment), a continuous weight loss of 55% occurred.

The single-crystal data for 1 (pale pink block 0.30 × 0.25 × 0.25 mm) were collected using a Bruker Kappa APEX II CCD diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at room temperature. Data reduction with SAINT then proceeded and the structure was solved by direct methods with SHELXS. The resulting atomic model was developed and refined against |F|² with SHELXL [12] and the “observed data” threshold for calculating the R(F) residuals was set as I > 2σ(I). The model was analyzed and validated with PLATON [13].

The C-bound H atoms were placed in idealised locations (C–H = 0.96–0.97 Å) and refined as riding atoms. The ligand N-bond and O-bound and water H atoms were located in difference maps and refined as riding atoms in their as-found relative locations. The constraint U_{iso}(H) = 1.2U_{eq}(carrier) was applied in all cases. The difference maps in the regions around the water molecules O2w and O4w were not very well defined, and the possibility of disorder of the H atoms attached to these O atoms cannot be ruled out. Full refinement details and software references are given in the deposited cif.

Crystal data for 1: C₅₂H₄₂DyKN₈O₂₉, M_r = 1444.54, triclinic, P $\bar{1}$ (No. 2), Z = 2, a = 9.188(2) Å, b = 15.7332(17) Å, c = 19.1664(19) Å, α = 92.797(6)°, β = 92.319(7)°, γ = 91.273(9)°, V = 2764.3(7) Å³, F(000) = 1454, T = 296(2) K, ρ_{calc} = 1.736 g·cm⁻³, μ = 1.532 mm⁻¹, 37880 reflections measured (−7 ≤ h ≤ 12, −20 ≤ k ≤ 20, −25 ≤ l ≤ 25; 4.88° ≤ 2θ ≤ 56.74°), R_{int} = 0.025, 13445 merged reflections, 12100 with I > 2σ(I), 825 variable parameters, R(F) = 0.029, wR(F²) = 0.084, w = 1/[σ²(F_o²) + (0.0387P)² + 3.7247P], where P = (F_o² + 2F_c²)/3, min./max. Δρ = −0.74, +1.12 e Å⁻³. Cambridge Structural Database deposition number: CCDC-879106.

4. Conclusions

The synthesis and crystal structure of [KDy(Hptc)₃(H₃ptc)]_n·2n(Hbipy)·5n(H₂O) has been described. The coordination of the dysprosium ion by three tridentate Hptc ligands in this compound is distinctly different to those of the compounds noted in the introduction, in which only one ptc ligand bonds in this way, as well as monodentate bridging ligands and water molecules.

References

1. Batten, S.R.; Champness, N.R.; Chen, X.-M.; Garcia-Martinez, J.; Kitagawa, S.; Öhrström, L.; O’Keeffe, M.; Suh, M.P.; Reedijk, J. Coordination polymers, metal–organic frameworks and the need for terminology guidelines. *CrystEngComm* **2012**, *14*, 3001–3004.
2. Wang, H.-S.; Zhao, B.; Zhai, B.; Shi, W.; Cheng, P.; Liao, D.-Z.; Yan, S.-P. Syntheses, structures and photoluminescence of one-dimensional lanthanide coordination polymers with 2,4,6-pyridine-tricarboxylic acid. *Cryst. Growth Des.* **2007**, *7*, 1851–1857.
3. Li, C.-J.; Peng, M.-X.; Leng, J.-D.; Yang, M.-M.; Lin, J.; Tong, M.-L. Synthesis, structure, photoluminescence and magnetic properties of new 3-D lanthanide-pyridine-2,4,6-tricarboxate frameworks. *CrysEngComm* **2008**, *10*, 1645–1652.
4. Das, M.C.; Ghosh, S.K.; Sanudo, E.C.; Bharadwaj, P.K. Coordination polymers with pyridine-2,4,6-tricarboxylic acid and alkaline-earth/lanthanide/transition metals: Synthesis and X-ray structures. *Dalton Trans.* **2009**, 1644–1658.
5. Lin, J.-L.; Xu, W.; Zhao, L.; Zheng, Y.-Q. Synthesis, crystal structure and properties of a new lanthanide pyridine-2,4,6-tricarboxylato coordination polymer. *Z. Naturforsch. B* **2011**, *66*, 570–576.
6. Holder, A.A.; VanDerveer, D. Potassium (4-carboxypyridine-2,6-dicarboxylato)-dioxido-vanadate(V) monohydrate. *Acta Cryst.* **2007**, *E63*, m2051-m2052.
7. Zhang, W.-Z.; Lv, T.-Y.; Wei, D.-Z.; Xu, R.; Xiong, G.; Wang, Y.-Q.; Gao, E.-J.; Sun, Y.-G. Synthesis, crystal structures and luminescence properties of two novel 3D heterometallic coordination polymers. *Inorg. Chem. Commun.* **2011**, *14*, 1245–1249.
8. Brown, I.D.; Altermatt, D. Bond-Valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Cryst.* **1985**, *B41*, 244–247.
9. Nichol, G.S.; Clegg, W. Classical hydrogen bonding and weaker C–H···O interactions in complexes of uracil-5-carboxylic acid with the alkali metals Na-Cs. *Polyhedron* **2006**, *25*, 1043–1056.
10. Mak, T.C.W.; Wai-Hing, Y.; Smith, G.; O’Reilly, E.J.; Kennard, C.H.L. Metal (phenylthio)acetic acid interactions 3. The crystal structures of anhydrous barium (phenylthio)-acetate and the potassium (phenylthio)acetate (phenylthio)acetic acid adduct. *Inorg. Chim. Acta* **1984**, *88*, 35–39.
11. Syper, L.; Kloc, K.; Młochowski, K. Synthesis of ubiquinone and menaquinone analogues by oxidative demethylation of alkenylhydroquinone ethers with argentic oxide or ceric ammonium nitrate in the presence of 2,4,6-pyridine tricarboxylic acid. *Tetrahedron* **1980**, *36*, 123–129.
12. Sheldrick, G.M. A short history of SHELX. *Acta Cryst.* **2008**, *A64*, 112–122.
13. Spek, A.L. Structure validation in chemical crystallography. *Acta Cryst.* **2009**, *D65*, 148–155.

© 2012 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).