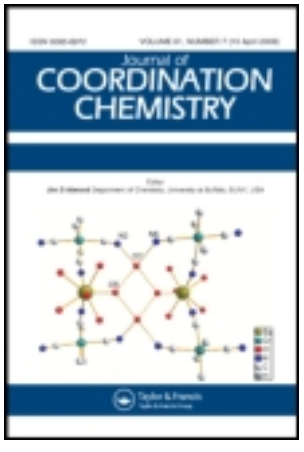

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Two yttrium(III) coordination compounds containing a3-ptz or atza [a3-ptz=5-[N-acetato(3-pyridyl)]tetrazole; atza=5-aminotetrazole-1-acetato]

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Two yttrium(III) coordination compounds containing a3-ptz or atza [a3-ptz = 5-[N-acetato(3-pyridyl)]tetrazole; atza = 5-aminotetrazole-1-acetato]

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Two yttrium(III) coordination compounds, $[Y(a3\text{-}ptz)_2(H_2O)_5]Cl \cdot 4H_2O$ (**1**) and $[Y(atza)_2(H_2O)_2(CH_3OH)]Cl$ (**2**) [a3-ptz = 5-[N-acetato(3-pyridyl)]tetrazole; atza = 5-aminotetrazole-1-acetato], have been synthesized. Single-crystal X-ray diffraction analysis reveals that **1** has a distorted monocapped square-antiprism coordination geometry around Y^{III}. Complex **2** is a distorted pentagonal bipyramid with coordination from four atza ligands, two waters, and one methanol; the coordination of atza in **2** leads to its 1-D polymeric chain structure. **1** and **2** are self-assembled to form 3-D supramolecular structures through hydrogen bonds. The luminescence properties of **1** and Ka3-ptz were investigated at room temperature in the solid state.

Keywords: Yttrium(III); Crystal structures; 5-[N-acetato(3-pyridyl)]tetrazole; 5-Aminotetrazole-1-acetato

1. Introduction

The design and preparation of hybrid materials, whose properties arise from defined interactions throughout the lattice, *e.g.* hydrogen-bonding, π stacking networks, porosity, and formation of cavities, require extensive knowledge of the solid-state structural behavior of targeted metal/ligand systems [1]. Ligands are often designed to engineer formation of specific lattice structures; however, for complex multifunctional molecules, the crystal packing can be unpredictable. Due to multiple coordination modes, the chemistry of tetrazoles and derivatives with transition metals and main group metals has been investigated [2]. As a result of the four lone pairs directed out from the nitrogens, its aromatic nature, and its weak basicity, the tetrazolate ring is potentially able to form molecular solids characterized by strong interactions between the molecular units. Moreover, the biologically safe nature of tetrazoles [3], which have been widely used as substitutes for carboxylic acid functionality in pharmaceutical

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preparations, makes these ligands very promising for the design of materials with biomedical applications [4].

Complexes of trivalent lanthanides are used in diagnostic, biological, and pharmaceutical chemistry [5, 6]. Properties such as luminescence [7] and magnetism [8], as well as the fact that they are heavy elements, make them suitable as optical, X-ray, and MRI contrast agents [7, 9], or as luminescent markers in immunoassays [7, 10]. The preparation of lanthanide tetrazolate complexes, bearing both a metal and ligand of low toxicity, allows preparation of hybrid compounds with applications in medicinal chemistry. However, because of their extreme oxophilic nature, the chemistry of the rare earth elements with tetrazolate and its derivatives remains largely unexplored, with limited synthetic and structural studies appearing [11], and the investigation of the rare earth element complexes containing tetrazole-based carboxylic acid ligands has been less studied [12]. Carboxylates and tetrazolyl nitrogens have good coordination, indicating carboxylate-tetrazole ligands as excellent and versatile building blocks for construction of coordination compounds. We have been interested in the synthesis and characterization of coordination compounds containing carboxylate-tetrazole ligands, 5-[N-acetato(4-pyridyl)]tetrazole(a4-ptz), 5-(2-pyridyl)]tetrazole-2-acetato(pytza), 5-aminotetrazole-1-acetato(atza), tetrazole-5-acetato(tza), and 5-[(4-nitryl)phenyl]tetrazole-1-acetato(nptza) [13]. In this manuscript, we treat yttrium(III) chlorides with the carboxylate-tetrazoles 5-[N-acetato(3-pyridyl)]tetrazole(a3-ptz); 5-aminotetrazole-1-acetato(atza), giving $[Y(a3\text{-}ptz)_2(H_2O)_5]Cl \cdot 4H_2O$ (**1**) and $[Y(atza)_2(H_2O)_2(CH_3OH)]Cl$ (**2**). Herein, we report their synthesis, crystal structures, and luminescent properties.

2. Experimental

2.1. *Physical measurements*

In this study, 5-(3-Pyridyl)tetrazole (designated as H3-ptz) was prepared by [2 + 3] cycloaddition according to the procedures previously described [14], by treating 3-cyanopyridine with NaN_3 in toluene in the presence of triethylammonium chloride. The reaction of H3-ptz with chloroacetic acid in methanolic potassium hydroxide solution gave mostly N(pyridyl)-substituted products (Ka3-ptz) [15]. Katza was prepared according to a reported procedure [16]. All other chemicals were obtained from commercial sources and used without purification. C, H, and N were determined using a Carlo–Erba EA1110 elemental analyzer. Infrared (IR) spectra were recorded with a Nicolet Magna–IR 550 spectrometer with KBr pellets from 4000 to 400 cm^{-1}. Photoluminescence spectra were performed on a Perkin Elmer LS55 spectrofluorometer.

2.2. *Preparation of $[Y(a3\text{-}ptz)_2(H_2O)_5]Cl \cdot 4H_2O$ and $[Y(atza)_2(H_2O)_2(CH_3OH)]Cl$*

2.2.1. Synthesis of $[Y(a3\text{-}ptz)_2(H_2O)_5]Cl \cdot 4H_2O$ (1). Ka3-ptz (0.4 mmol) was dissolved in a 4 : 1 methanol/water solution (10 mL). Then, $YCl_3 \cdot 6H_2O$ (0.2 mmol) was added.

The mixture was stirred at 80°C for 1 h and then cooled to room temperature and filtered. Diethyl ether (40 mL) was allowed to diffuse into the filtrate at ambient temperature for 2 weeks, forming green block crystals of **1**. The yield was 36% based on Y^{3+} consumed. Anal. Calcd for $C_{16}H_{30}N_{10}O_{13}ClY$: C, 27.66; H, 4.35; and N, 20.16. Found: C, 27.80; H, 4.46; and N, 20.02%. IR (KBr, cm^{-1}): 3412(s), 1662(s), 1640(s), 1615(s), 1529(m), 1441(m), 1408(m), 1385(m), 1345(m), 735(m), and 619(m).

2.2.2. Synthesis of $[Y(atza)_2(H_2O)_2(CH_3OH)]Cl$ (2). Complex **2** was prepared in a similar manner to **1**, except that Katza was used instead of Ka3-ptz in 51% yield based on Y^{3+} consumed. Anal. Calcd for $C_7H_{16}N_{10}ClO_7Y$: C, 17.64; H, 3.38; and N, 29.39. Found: C, 17.82; H, 3.41; and N, 29.54%. IR (KBr, cm^{-1}): 3146(s), 1613(s), 1490(m), 1451(s), 1401(m), 1323(m), 1143(m), 1012(m), 825(m), 762(m), and 628(m).

2.3. *X-ray diffraction analysis*

Suitable single crystals of **1** and **2** were mounted on a Rigaku SCXmini-CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 291 K. All absorption corrections were performed using the CrystalClear programs. The crystal structures of **1** and **2** were solved by direct methods and refined on F^2 by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms [17]. Hydrogens were generated geometrically and refined using a riding model. Crystallographic data and other pertinent information for **1** and **2** are summarized in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystallographic data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{16}H_{30}N_{10}O_{13}Ycl$	$C_7H_{16}N_{10}O_7Ycl$
Formula weight	694.86	476.66
Temperature (K)	291(2)	291(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*P*2(1)/*c*
Unit cell dimensions (Å, °)		
a	29.013(6)	5.1092(10)
b	12.614(3)	17.386(4)
c	7.8893(16)	19.964(4)
β	100.27(3)	95.18(3)
Volume (Å^3), *Z*	2841.0(11), 4	1766.2(6), 4
Calculated density $_{(}$g cm^{-3})	1.625	1.793
Absorption coefficient (mm^{-1})	2.224	3.509
F(0 0 0)	1424	960
Independent reflection	3259 [*R*(int) = 0.1401]	3074 [*R*(int) = 0.1191]
Number of observations [$I > 2.00\sigma(I)$]	1994	2383
Number of variables	179	239
Goodness-of-fit[a]	1.047	0.995
R^b, wR^c	0.0796, 0.1551	0.1028, 0.2238
Δ/ρ_{max} (e Å^{-3})	0.520	2.734
Δ/ρ_{min} (e Å^{-3})	−0.675	−1.487

[a]GOF = $\{\Sigma[(F_o^2 - F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined; [b]$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; and [c]$Rw = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Complex **1**			
Y(1)–O(1)	2.409(4)	Y(1)–O(2)	2.490(2)
Y(1)–O(3)	2.379(2)	Y(1)–O(4)	2.403(2)
Y(1)–O(5)	2.364(2)		
O(5A)–Y(1)–O(5)	78.74(10)	O(5)–Y(1)–O(3)	140.63(10)
O(5)–Y(1)–O(4)	75.22(7)	O(5A)–Y(1)–O(4)	139.36(7)
O(3)–Y(1)–O(4)	70.99(6)	O(5A)–Y(1)–O(4A)	75.22(7)
O(4A)–Y(1)–O(4)	141.97(10)	O(1)–Y(1)–O(5)	80.85(12)
O(5A)–Y(1)–O(1)	126.59(11)	O(3)–Y(1)–O(1)	73.58(11)
O(4)–Y(1)–O(1)	79.17(12)	O(4A)–Y(1)–O(1)	90.21(12)
O(1A)–Y(1)–O(1)	147.2(2)	O(5A)–Y(1)–O(2)	73.54(9)
O(5A)–Y(1)–O(2A)	72.96(6)	O(3A)–Y(1)–O(2)	111.89(5)
O(4A)–Y(1)–O(2)	70.06(7)	O(4A)–Y(1)–O(2A)	125.74(9)
O(1A)–Y(1)–O(2)	143.89(11)	O(1A)–Y(1)–O(2A)	53.34(11)
O(5)–Y(1)–O(2)	72.96(6)	O(2A)–Y(1)–O(2)	136.22(10)
Complex **2**			
Y(1)–O(1)	2.204(6)	Y(1)–O(2A)	2.356(5)
Y(1)–O(3)	2.368(6)	Y(1A)–O(4)	2.182(6)
Y(1)–O(5)	2.318(6)	Y(1)–O(6)	2.309(6)
Y(1)–O(7)	2.332(5)		
O(4A)–Y(1)–O(1)	171.4(2)	O(4A)–Y(1)–O(6)	99.1(2)
O(1)–Y(1)–O(6)	88.7(2)	O(4A)–Y(1)–O(5)	88.5(3)
O(1)–Y(1)–O(5)	83.1(3)	O(6)–Y(1)–O(5)	142.0(2)
O(4A)–Y(1)–O(7)	89.06(18)	O(1)–Y(1)–O(7)	96.96(18)
O(6)–Y(1)–O(7)	71.33(18)	O(5)–Y(1)–O(7)	146.4(2)
O(4A)–Y(1)–O(2A)	91.6(2)	O(1A)–Y(1)–O(2)	87.3(2)
O(6A)–Y(1)–O(2)	71.3(2)	O(5A)–Y(1)–O(2)	71.3(2)
O(7A)–Y(1)–O(2)	142.25(17)	O(4A)–Y(1)–O(3)	85.2(2)
O(1)–Y(1)–O(3)	90.7(2)	O(6)–Y(1)–O(3)	144.0(2)
O(5)–Y(1)–O(3)	73.4(2)	O(7)–Y(1)–O(3)	72.99(18)
O(2A)–Y(1)–O(3)	144.7(2)		

Symmetry codes: (**1**) A: $1-x$, y, $0.5-z$; and (**2**) A: $1+x$, y, z.

3. Results and discussion

3.1. *Structural description*

Single-crystal X-ray diffraction analysis reveals that **1** is mononuclear (figure 1). The complex crystallizes in the monoclinic space group $C2/c$, with only half of the molecule belonging to the asymmetric unit. The nine-coordinate environment around Y^{III} is completed by nine oxygens from two chelating carboxylates of two a3-ptz ligands and five waters, forming a distorted monocapped square-antiprism. The remaining chloride and four free waters are located outside the first coordination sphere. The Y–O bond lengths [2.364(2) ~ 2.490(2) Å] (table 2) for **1** are in good agreement with literature values for Y-carboxylate complexes [18]. The four N-donors of the tetrazolate are not coordinated to Y^{III}, but are acceptors of O–H···N hydrogen bonds. $[Y(a3\text{-}ptz)_2(H_2O)_5]^+$ is bridged through hydrogen bonds [O(3)···O(1) 2.698(4) Å/162°, $1-x$, $-y$, $-z$; O(4)···N(4) 2.771 Å/166°, $1-x$, $-y$, $-z$; O(4)···O(7) 2.883 Å/167(4)°, x, $-1+y$, $-1+z$; O(5)···N(4) 3.234 Å/131°, $1-x$, $-y$, $-z$; O(5)···N(5) 2.770 Å/159°, $1-x$, $-y$, $-z$; O(5)···Cl 3.114 Å/159°, $1-x$, $-y$, $-z$; O(7)···O(4) 2.883 Å/165°, x, $1+y$, $1+z$; O(7)···O(4) 2.980 Å/171°, x, $1-y$, $1/2+z$; C(7)···Cl 3.607 Å/159°, $1-x$, $1-y$, $-z$] to form a 2-D network structure extended along the *ab* plane (figure 2).

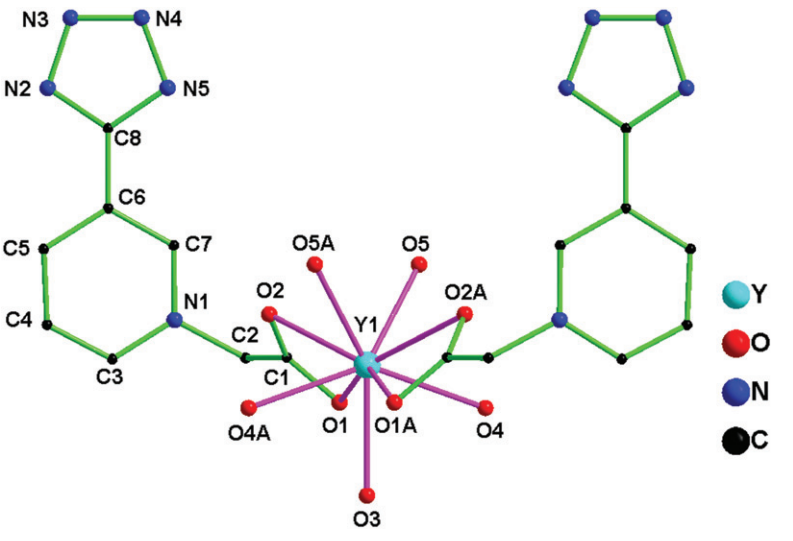

Figure 1. The coordination environment of Y^{III} of **1**. Hydrogens are omitted for clarity.

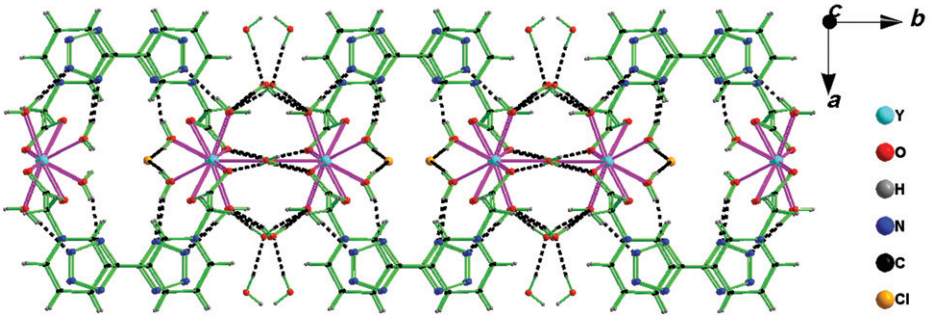

Figure 2. The network structure of **1** formed *via* H-bonding.

Complex **2** crystallizes in monoclinic space group $P2_1/c$ and the asymmetric unit contains one $[Y(atza)_2(H_2O)_2(CH_3OH)]Cl$. Each Y^{III} is seven-coordinate from four oxygens from four atza ligands, two from two waters and one from a methanol, forming a distorted pentagonal bipyramid (figure 3). Each atza ligand is bidentate bridging in **2** and the coordination mode can be compared to $[Tb(atza)_2(H_2O)_4]Cl$ [12]. Two neighboring Y^{III} ions are doubly bridged by two carboxylates from two atza ligands in a $\mu_{1,3}$-COO *syn–syn* bridging mode, forming a 1-D chain extending along the *a*-axis with $Y\cdots Y$ distance of 5.109 Å and the $Y\cdots Y\cdots Y$ bite angle of 180° (figure 4). The adjacent 1-D chains are further connected by seven kinds of hydrogen-bonding interactions [$N(5)\cdots N(9)$ 3.062(2) Å/162°, $-1+x$, $1/2-y$, $1/2+z$; $O(5)\cdots Cl(1)$ 3.008(8) Å/140°, $-x$, $-1/2+y$, $1/2-z$; $O(5)\cdots Cl(1)$ 3.035(8) Å/150°, $-1-x$, $-1/2+y$, $1/2-z$; $O(6)\cdots Cl(1)$ 3.051(6) Å/155°; $O(7)\cdots N(8)$ 2.691(8) Å/169(3)°, $-1-x$, $1-y$, $-z$; $N(10)\cdots N(4)$ 3.105(11) Å/160°, $1+x$, $1/2-y$, $-1/2+z$; $N(10))\cdots Cl(1)$ 3.516(9) Å/172°, $-1-x$, $-1/2+y$, $1/2-z$] forming a 3-D network (figure 5).

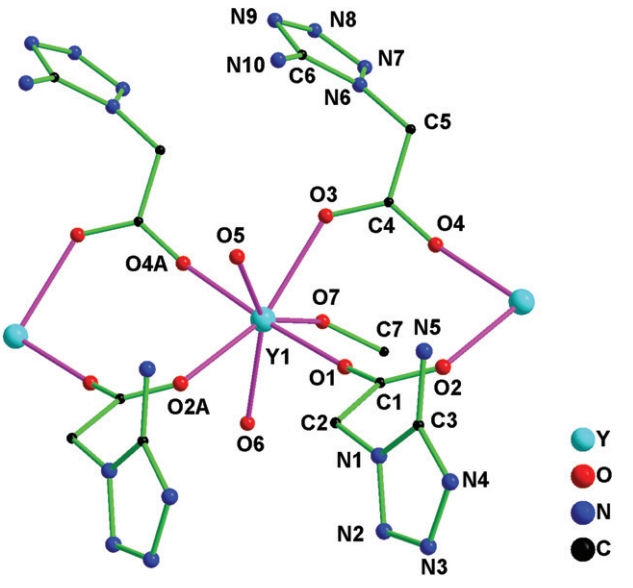

Figure 3. The coordination environment of Y^{III} of **2**. Hydrogens are omitted for clarity.

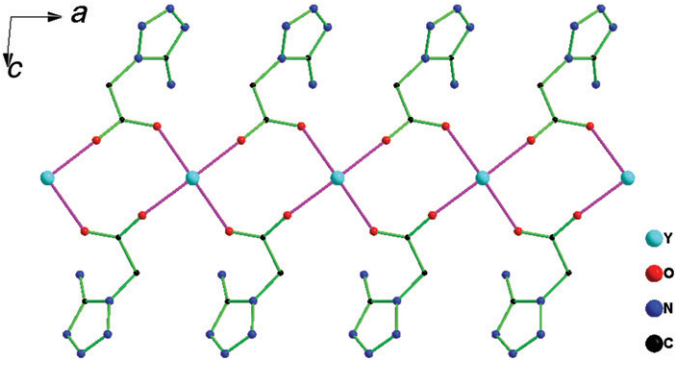

Figure 4. The 1-D chain structure of **2** extending along the *a* axis. Hydrogens and waters are omitted for clarity.

3.2. *Fluorescence properties*

The luminescent properties of free Ka3-ptz and **1** were investigated at room temperature in the solid state (figure 6). Free Ka3-ptz shows one emission peak at 360 nm when excited at 315 nm. Upon excitation at 270 nm, **1** exhibits an emission at 407 nm that can be assigned to intraligand fluorescent emission. Compared with the emission spectrum of Ka3-ptz, a red shift of 47 nm in **1** arises from the coordination effect of Y^{III} with the ligand. Free Katza and **2** have no fluorescent emission, even though $[Eu(atza)_2(H_2O)_3]Cl$ and $[Tb(atza)_2(H_2O)_4]Cl$ [12] exhibit characteristic lanthanide-centered luminescence.

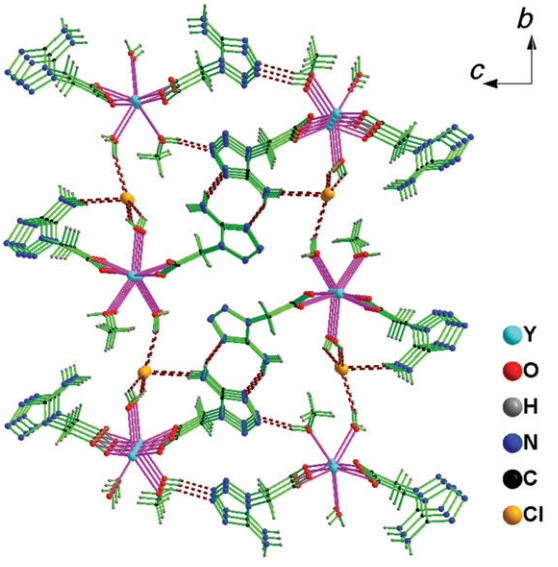

Figure 5. The 3-D network structure of **2** formed *via* H-bonding.

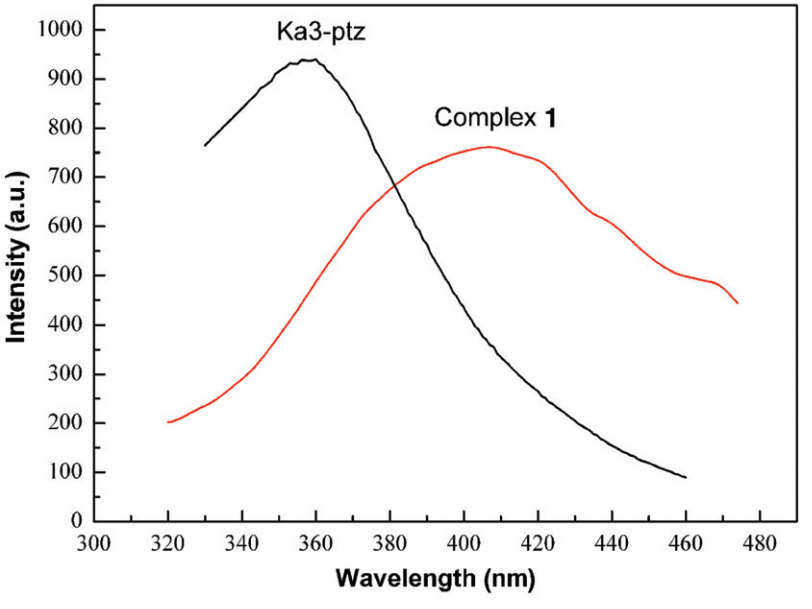

Figure 6. The emission spectra of **1** and free ligand Ka3-ptz at room temperature in the solid state ($\lambda_{ex} = 270$ nm for **1**; $\lambda_{ex} = 315$ nm for Ka3-ptz).

4. Conclusions

We are the first to investigate yttrium(III) coordination compounds containing a3-ptz and atza; $[Y(a3\text{-}ptz)_2(H_2O)_5]Cl \cdot 4H_2O$ (**1**) and $[Y(atza)_2(H_2O)_2(CH_3OH)]Cl$ (**2**) have been synthesized and structurally characterized. The a3-ptz is chelating bidentate in **1**.

Previously a4-ptz exhibits monodentate coordination in $[UO_2(a4\text{-}ptz)_2 \cdot (H_2O)_3]$ and bidentate bridging *via* carboxylate-O and tetrazolate-N in $[Zn(a4\text{-}ptz)_2 \cdot (H_2O)_2] \cdot 2H_2O$ [13b]. Compound (**2**) forms a 1-D polymeric chain through the atza linker which exhibits different coordination modes in lanthanide-based coordination compounds [12]. These two compounds are further linked *via* hydrogen–bonding interactions forming a supramolecular framework. The luminescence of **1** and free Ka3-ptz were investigated at room temperature in the solid state.

Supplementary material

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-739903 (**1**) and CCDC-739902 (**2**). Copies of the data can be obtained free of charge on application to CHGC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk).

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