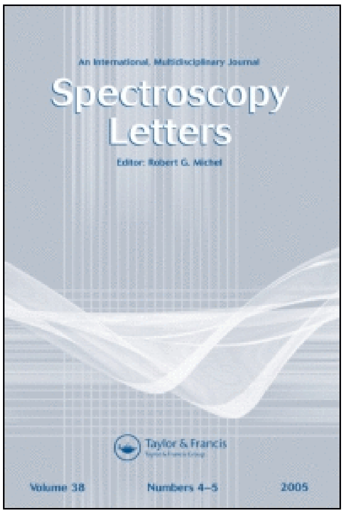

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Synthesis and Spectroscopic Study of a Terbium(III) 2,6-Pyridinedicarboxylate Complex

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Synthesis and Spectroscopic Study of a Terbium(III) 2,6-Pyridinedicarboxylate Complex

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ABSTRACT The terbium(III) 2,6-pyridinedicarboxylate complex $Na_3Tb(PDA)_3 \cdot 8H_2O$ with intense green luminescence was synthesized by liquid phase reaction and characterized by means of infrared (IR), ultraviolet (UV), ^1H nuclear magnetic resonance (^{1}HNMR), ^{13}C nuclear magnetic resonance (^{13}CNMR), and fluorescence spectra. In this complex, the coordination function of each PDA^{2-} group with terbium(III) center is tridentate chelate from two carboxyl oxygen and one heterocyclic nitrogen atoms while carboxylate group in a monodentate fashion. Terbium(III) is in nine-coordination configuration. Due to the high paramagnetic character and strong electron attraction ability of Tb^{3+} ion, the chemical shifts of ^{1}HNMR and ^{13}CNMR spectra on the complex heterocycle to lower field compared with free H_2PDA, while that of C_7 and C_8 of the complex move to higher fields probably due to shielding effects of the carboxyl group as well as conjugation system of two five-membered chelate cycles. Moreover, the ^{1}HNMR and ^{13}CNMR spectra of the complex have broader peak width than that of free H_2PDA. The excitation and emission spectra of the complex show that the energy of the $\pi(n)$-π^* excited state of $C_5H_3N(COO)_2^{2-}$ can be effectively transferred to Tb^{3+} ion, resulting in emission from the $^5D_4 \rightarrow {}^7F_j(j = 3\text{–}6)$ electronic transitions of Tb^{3+} ion. Because of the low symmetric center and strong coordination field that were affected, $^5D_4$ and $^7F_j(j = 6,5,4)$ energy levels of Tb^{3+} have split. In addition, the complex exhibits thermal stability below 460°C in air.

KEYWORDS 2,6-pyridinedicarboxylic acid, luminescence, spectra, terbium complex

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INTRODUCTION

The molecular design of efficient lanthanide complexes has become an important research goal involving many classes of ligands, that is, cryptands, calixarenes, β-diketones, macrocyclic ligands, carboxylic acid derivatives, heterobiaryl ligands, and the like.[1–3] In such complexes, due to strong absorption of ligand and efficient energy transfer from the ligand to the metal ion *antenna effect*, strong Ln(III) luminescence is observed.[4,5] Currently, a series of rare earth luminescent materials has attracted the attention of both physicists and chemists.[6–8]

Lanthanide aromatic carboxylates have not only good luminescence properties, but also suitable absorption characteristic in the near-UV region. These complexes also possess better photostability and thermal stability compared with lanthanide β-diketonates. 2,6-Pyridinedicarboxylic acid (H_2PDA) containing heterocyclic nitrogen atom and two carboxylate groups forms stable chelates when it reacts with simple metal ions and oxometal cations, and it displays widely varying coordination fashions, functioning as a bidentate,[9,10] tridentate,[11,12] meridian,[13] or bridging ligand[14,15] in complexes. The resulting coordination compounds solids usually possess 1D, 2D, or 3D structural characteristics. Interest in the PDA^{2-} salts is also due to their ability to assemble in helicates and other metal-based supramolecular structures and due to their potential for self-assembly of molecular devices and nanostructures.[16] In addition, a very important characteristic of dipicolinic acid and the other isomeric pyridine dicarboxylic acids is their diverse biological activity.[17–19] So the preparation and properties of metal ion dipicolinic acid complexes become more and more attractive for the researchers.[20–23] The relevant rare earth complex materials especially have been widely used in cathodoluminescent display screens, lasers, and lamps because their photoluminescence exhibits high quantum efficiencies and very sharp spectral bands.[24]

In recent years, the fabrication of luminescent complex materials based on lanthanide pyridine dicarboxylates has been reported in several works.[20,25–27] However, the synthesis and published data on spectroscopic research of the terbium salts of PDA^{2-} are comparatively scarce. In this article, the complex $Na_3Tb(PDA)_3 \cdot 8H_2O$ with very strong green luminescence and excellent thermal stability was successfully obtained. The details of the structure and properties of the complex analyzed by the IR, UV, ^{1}HNMR, ^{13}CNMR, excitation and emission spectra and TG-DTA were discussed.

MATERIALS AND METHODS

Reagents and Preparation of Materials

H_2PDA, Tb_4O_7, and NaOH are of analytical reagent grade. Terbium chloride was obtained by heat-dissolving Tb_4O_7 in dilute hydrochloric acid (volume ratio 1:1). Other chemicals were employed without further purification.

The terbium(III) 2,6-pyridinedicarboxylate complex was prepared by solution reaction method according to the route below. Terbium chloride and H_2PDA were fully mixed in molar ratio 1:3, $1\,\mathrm{mol \cdot L^{-1}}$ NaOH was added carefully until the pH was 5, and a clarifying solution was obtained. After stirring about 3 h at 80°C in water bath, a white precipitate was separated out. After digestion for 12 hr, the precipitate was filtered, and we washed it with warmer absolute ethanol and dried it in vacuum at room temperature for 24 hr. The component of the product was verified by FT-IR, elemental and thermal analysis. Anal. Calcd. (%) for $Na_3Tb(C_7H_3NO_4)_3 \cdot 8H_2O$: C, 29.03; H, 3.15; N, 4.62; Na, 7.35; Tb, 17.02. Found (%): C, 29.08; H, 2.91; N, 4.84; Na, 7.95; Tb, 17.32.

Analysis Methods

Elemental analyzer model GmbH Vario EL III, (Elementar Corp., Germany) was used for carbon, hydrogen, and nitrogen analyses, and optical emission spectrometer model OPTIMA 2000 DV (Perkin-Elmer Corp., United States) was used for the sodium and terbium analyses. Thermal analyzer (10°C/min, in air heating)models DTA 1700 and TGA (Perkin-Elmer Corp., United States) were used for TG-DTA-curves recording. FT-IR spectrometer ($4\,\mathrm{cm^{-1}}$ resolution, KBr pellets) model IR Prestige-21 (Shimadzu, Japan) was used for IR spectra. UV-vis spectrophotometer (deionizer water as reference) model Lambda 17 (Perkin-Elmer Corp., United States) was used for UV-vis measurement. Nuclear magnetic resonance spectroscope model INOVA 600 NB (Varian Corp., United States) was used for ^{1}HNMR and ^{13}CNMR studies of lanthanide dipicolinates. Fluorescence spectrophotometer model RF-5301 (Shimadzu, Japan) was used for solid fluorescent characteristic by mixing the complex with KBr (weight ratio 1:50).

RESULTS AND DISCUSSION

Figure 1 presents the thermal decomposition process of $Na_3Tb\ (PDA)_3 \cdot 8H_2O$. The sample was decomposed in three consecutive steps. The first weight loss occurred in the range of 20–116°C with 12.51%, and the second weight loss was 4.23% in the range of 116–460°C. The total weight loss of the two steps was 16.74% assigned to the loss of eight water molecules (calcd. 16.61%). The third weight loss took place in the range of 460–600°C with 35.81% and corresponded to the decomposition of PDA^{2-}. The DTA plot showed two distinct endothermic peaks at 99°C and 220°C and two exothermic peaks at 521°C and 576°C. Above 600°C, the TG curve got even, revealing that the complex had decomposed. The backbones of the compound have thermal stability below 460°C in air.

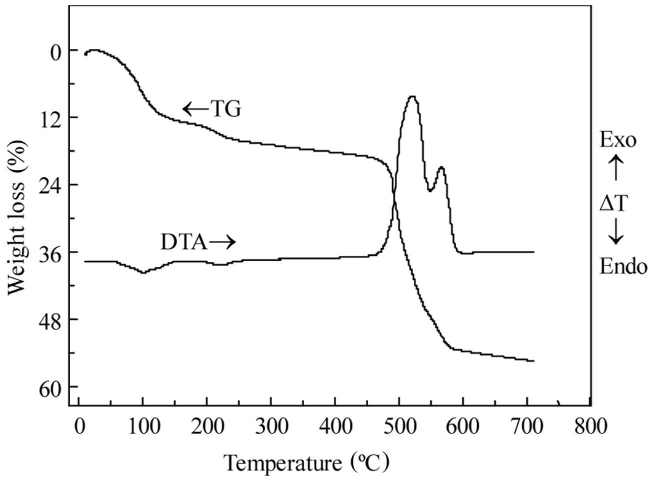

FIGURE 1 TG-DTA curve of $Na_3Tb\ (PDA)_3 \cdot 8H_2O$.

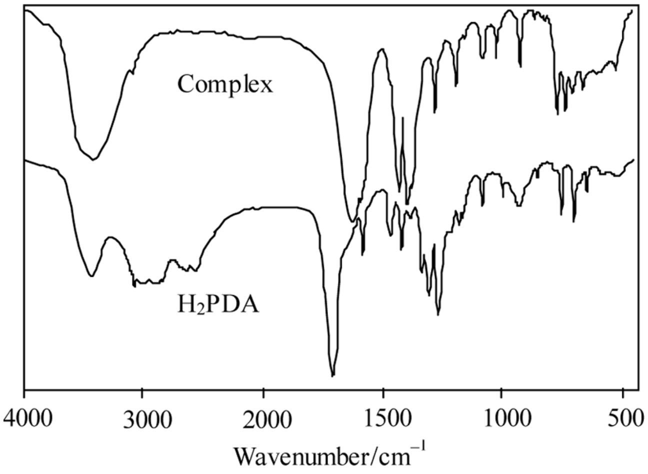

FIGURE 2 IR spectra of $Na_3Tb\ (PDA)_3 \cdot 8H_2O$ complex and H_2PDA.

Figure 2 shows the IR spectra of $Na_3Tb(PDA)_3 \cdot 8H_2O$ and H_2PDA. The main infrared absorption bands and the assignments are listed in Table 1. In the IR spectra of the free ligand H_2PDA, there is a very strong absorption band of the $v_{C=O}$ stretch of the free −COOH group at 1705 cm^{-1}. The presence of the −COOH group involved in the intramolecular hydrogen bonding is evident by a broad and irregularly shaped band in the 3431–2850 cm^{-1} region. In the IR spectra of the complex, the $v_{C=O}$, v_{OH}, and δ_{OH} bands of the carboxyl (−COOH) have not appeared, but the very strong antisymmetric and symmetric stretching vibrations of the carboxylate group (–CO–O$^-$) are observed at 1627 cm^{-1} and 1375 cm^{-1}, respectively. The Δv_{oco} ($v_{as} - v_s$) value of carboxylate group is 252 cm^{-1}. This considerable differences between v_{as} and v_s indicate strong coordination of the carboxylate oxygen to the terbium(III) acceptor.[15] Moreover, the coordination functions of carboxylate groups confirmed the monodentate mode[10,27–28], and the compound correspondingly belongs to the complex of the tridentate ligands. Lines with frequencies 1394 and 1416 cm^{-1} are assigned to stretching vibration of pyridine ring,[27] and the frequencies of the ring-breathing vibration 1021 and 997 cm^{-1} are observed in the spectra of $Na_3Tb(PDA)_3 \cdot 8H_2O$ and H_2PDA,[10] respectively. In addition, the CH, CC, and CN vibration absorption bands of heterocyclic ring shifted obviously. This result also reveals that the heterocyclic nitrogen coordinated to terbium. Because of a coordinated nitrogen atom situated between the carboxylate groups, so two five-membered chelate cycles are formed at coordination of oxygen atoms of carboxylate groups and nitrogen atom of pyridine ring by the lanthanide ion. Therefore, terbium(III) is in a nine-coordination environment.

Figures 3 and 4 show the ^{1}HNMR spectra of H_2PDA and $Na_3Tb(PDA)_3 \cdot 8H_2O$, respectively. The spectra of H_2PDA show two multiplets of H_3 and H_5 at 8.247 and 8.234 ppm, four peaks of H_4 at 8.165, 8.176, 8.179, and 8.191 ppm of pyridine ring, and one broad peak of H_7 and H_8 at 13.314 ppm assigned to carboxyl. However, the spectra of $Na_3Tb(PDA)_3 \cdot 8H_2O$ give only three single peaks of H_3 and H_5 at 42.065 ppm and H_4 at 37.555 ppm. They indicate that the Tb-O and Tb-N bonds are formed in

TABLE 1 **Absorption Bands and Assignments in the IR Spectra of Complex and H_2PDA**

$Na_3Tb(PDA)_3 \cdot 8H_2O$		H_2PDA	
Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment
3417, 3086	$v(H_2O)$, $v(CH)$	3431, 3068–2850	$v(OH)$, $v(CH)$
1627	$\nu_{as}(OCO)$	1705	ν (C=O)
1591	v (C=N)	1575	ν (C=N)
1435	ν $(C{=}C)_{ring}$	1462	$\nu(C{=}C)_{ring}$
1394	ν (py ring)	1416	ν (py ring)
1375	$\nu_s(OCO)$	1299, 1268	ν (C–O)
1279, 1080, 924,	δ (CH)	1215, 1082	δ (CH)
1193, 1155	ν (C–C)	1178, 1164	ν (C–C)
1021	ν (ring breathing)	997	ν (ring breathing)
		931	δ (OH)
770, 705	γ (CH)	855, 702	γ (CH)
736	δ (OCO)	753	δ (OCO)
662	β (C=N)	648	β (C=N)

the complex and in good agreement with IR result. The chemical shifts δc of H_3, H_4, and H_5 of the complex heterocycle are to lower field clearly.

In Figure 5, the ^{13}CNMR spectrum of the title complex (in D_2O) shows four peaks located at 178.529 (C_3, C_5), 297.646 (C_4), 313.500 (C_2, C_6), and 88.900 (C_7, C_8) ppm with methanol as internal reference. With TMS as internal reference, the ligand H_2PDA (in DMSO-D_6) gives four peaks of (C_3, C_5), C_4, (C_2, C_6), and (C_7, C_8) at 128.107, 139.843, 148.699, and 165.999 ppm, respectively. To compare the results of chemical shifts from the H_2PDA and the terbium(III) 2,6-pyridinedicarboxylate complex in different solvents, evidently the chemical shifts of all carbon atoms of the terbium(III) 2,6-pyridinedicarboxylate complex are changed greatly, so that δc of the carboxylic group (C_7, C_8) shifted from 165.999 to 88.900 ppm and the other carbon atoms increased. The influences on chemical shift and NMR spectra probably is due to strong electron attraction (induced effect) of Tb^{3+} ion by Tb-O and Tb-N bonds. PDA^{2-} group electron density shifted to the carboxylic group, resulting in the electron density increase and the local shielding effects of (C_7, C_8). So, the δc of carboxylic group carbon atoms shifted to higher field and made δc lower in great degrees. Similarly, due to induced effect by Tb-N bond, the electron density of all carbon atoms in the heterocyclic ring decreased, the δc shifted to lower field, and all values increased. This proves the formation of Tb-O and Tb-N bonds in the complex.

The above results suggest that, in the complex, six oxygen and three nitrogen atoms from three totally deprotonated PDA^{2-} groups coordinate to Tb atom, and the coordinate structure is in analogy to $Na_3[Nd(PDA)_3] \cdot 14H_2O$.[29] ^{1}HNMR spectra of the complex, H_3 and H_5, and H_4 are fused to one group peak, indicating the oxygen and nitrogen atoms of three 2,6-pyridinedicarboxylate anions use similar covalent bonds to coordinate to Tb atom, and each PDA^{2-} has equivalent and symmetric chelating form. Due to the high paramagnetic character[30] and strong electron attraction ability of Tb^{3+} ion, the che-

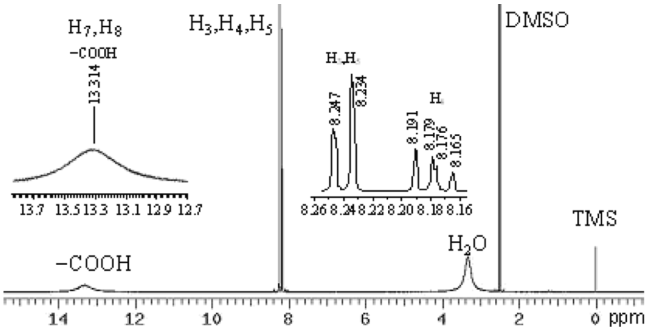

FIGURE 3 **^{1}HNMR spectrum of H_2PDA in DMSO-D_6.**

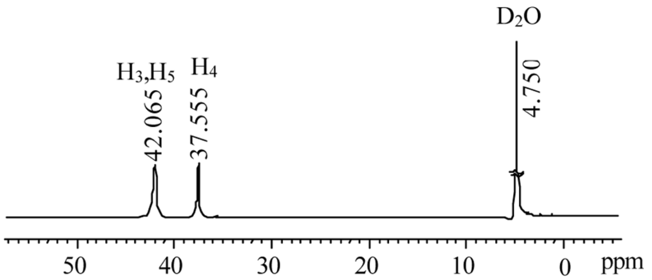

FIGURE 4 **^{1}HNMR spectrum of $Na_3Tb(PDA)_3 \cdot 8H_2O$ in D_2O.**

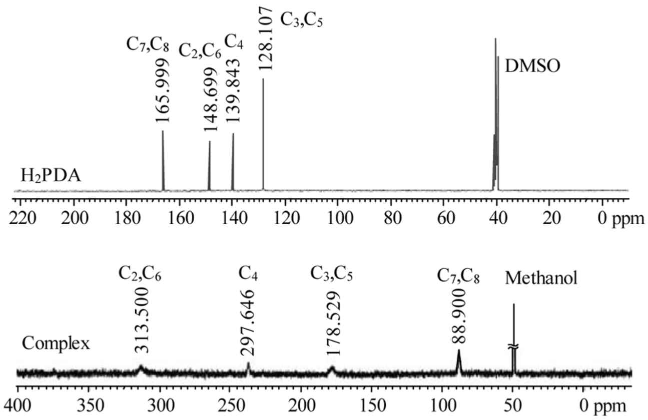

FIGURE 5 ^{13}CNMR Spectra of H_2PDA and $Na_3Tb(PDA)_3 \cdot 8H_2O$.

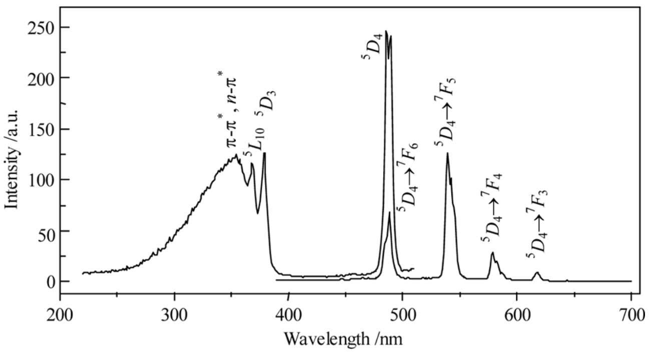

FIGURE 6 Excitation and Emission Spectra of $Na_3Tb(PDA)_3 \cdot 8H_2O$.

mical shifts of H_3, H_4, H_5, C_2, C_3, C_4, C_5, and C_6 of the complex are to lower field obviously. Moreover, the peaks in the ^{1}HNMR and ^{13}CNMR spectra of the complex are broadened, and the peak broadening values of ^{1}HNMR spectra are larger than those of ^{13}CNMR. The NMR signals of C_7 and C_8 of the complex have shifted remarkably to higher fields compared with free H_2PDA. This probably is because of shielding effects of the carboxylate groups and because the Tb^{3+} ion transfers some charge to C_7 and C_8 via conjugation system of two five-membered chelate cycles [31] after terbium(III) accepts the electron from heterocyclic nitrogen and carboxyl oxygen.

In the UV spectra of $Na_3Tb(PDA)_3 \cdot 8H_2O$ and H_2PDA, the strong $\pi-\pi^*$ and $n-\pi^*$ electronic transition absorption bands of ligands were observed at about 254 and 255 nm, respectively.

Figure 6 shows the excitation (left, $\lambda_{em} = 545$ nm) and emission (right, $\lambda_{ex} = 354$ nm) spectra of the solid complex (mixed KBr) at room temperature. In the excitation spectra, the sharp bands at 368, 379, and 486–489 nm are the characteristic transitions of Tb^{3+} ions, which correspond to $^5L_{10}$, $^5D_3$, and $^5D_4$ levels, respectively. The broad band at 354 nm is $\pi-\pi^*$ and $n-\pi^*$ transitions of the ligand. The emission spectra exhibit characteristic emission of Tb^{3+} ions at 488, 539, 579, and 617 nm, which are designated transitions of $^5D_4$ excitation state to $^7F_j(j = 6, 5, 4, 3)$ ground state of Tb^{3+} ion. The strongest peak at 539 nm ($^5D_4 \rightarrow {}^7F_5$) is characteristic green emission of terbium(III). In addition, from Figure 6, one can see clearly that the $^5D_4$, $^7F_6$, $^7F_5$, and $^7F_4$ have split into two or three energy levels. They suggest that the Tb^{3+} ion is in unsymmetric strong crystal field.[32]

Finally, we find that the solid complex $Na_3Tb(PDA)_3 \cdot 8H_2O$ provides a very sharp and intense green emission of Tb^{3+} ions when irradiated by ultraviolet light. This finding indicates that the interaction of the lanthanide ion with the ligand is stronger in the case of the three-dentate PDA^{2-} and that the excited state energy of organic ligand can transfer to rare earth ion efficiently. Because the complex possesses high thermal stability and good luminescence characteristics, it will be an excellent candidate for potentially light-emitting materials.

CONCLUSIONS

In this article, to compare the results of IR and NMR spectra from free H_2PDA and complex $Na_3Tb(PDA)_3 \cdot 8H_2O$, the coordination mode of carboxyl group and the influences of shifts' changing and ^{1}HNMR and ^{13}CNMR peaks' broadening have been discussed in detail. The investigation has demonstrated that the coordination function of carboxylate groups is monodentate in the complex and that the connection between each PDA^{2-} group and Tb^{3+} ion is tridentate chelate from two carboxyl oxygen and one heterocyclic nitrogen atoms. The cause of the shifts' changing and peaks' broadening can be explained by the strong coordination of carboxylate group to the terbium(III) acceptor and the induced effect, shielding effect, and high paramagnetic character of rare earth ions. Due to efficiency of energy transfer from ligand to terbium(III) ion, the complex can emit intense green luminescence. In the luminescence spectra, $^5D_4$ and $^7F_j(j = 6, 5, 4)$ energy levels of Tb^{3+} ion split because of the low symmetric center and strong coordination field. Besides, the complex possesses high thermal stability with intense fluorescence and may be used as a potential application in photoactive materials.

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REFERENCES

1. Fernandes, A.; Jaud, J.; Dexpert-Ghys, J.; Brouce-Cabarrecq, C. Study of new lanthanide complexes of 2,6-pyridinedicarboxylate: Synthesis, crystal structure of Ln(Hdipic)(dipic) with Ln = Eu, Gd, Tb, Dy, Ho, Er, Yb, luminescence properties of Eu(Hdipic)(dipic). *Polyhedron* **2001**, *20*, 2385–2391.
2. Lis, S.; Hnatejko, Z.; Barczynski, P.; Elbanowski, M. Luminescence studies of Eu(III) mixed ligand complexes. *J. Alloys Compd.* **2002**, *344*, 70–74.
3. Tang, Y.; Zhang, J.; Liu, W. S.; Tan, M. Y.; Yu, K. B. Preparation, properties and structure of uncommon(10,3)-a netted rare earth complexes with an amide type tripodal ligand. *Polyhedron* **2005**, *24*, 1160–1166.
4. Zheng, Y. X.; Lin, J.; Liang, Y. J.; Lin, Q.; Yu, Y. N.; Wang, S. B.; Guo, C.; Zhang, H. J. Green electroluminescent device with a terbium β-diketonate complex as emissive center. *Optical Materials* **2002**, *20*, 273–278.
5. Svetlana, E.; Oksana, K.; Oleg, M.; Kirill, A.; Leonid, L. Electroluminescent properties of the mixed-ligand complex of terbium salicylate with triphenylphosphine oxide. *Synth. Met.* **2004**, *141*, 225–230.
6. Pan, L.; Huang, X. Y.; Li, J.; Wu, Y. G.; Zheng, N. W. Novel single- and double-layer and three-dimensional structures of rare-earth metal coordination polymers: The effect of lanthanide contraction and acidity control in crystal structure formation. *Angew. Chem., Int. Ed.* **2000**, *39*, 527–530.
7. Capecchi, S.; Renault, O.; Moon, D.-G.; Halim, M.; Etchells, M.; Dobson, P. J.; Salata, O. V.; Christou, V. High-efficiency organic electroluminescent devices using an organoterbium emitter. *Adv. Mater.* **2000**, *12*, 1591–1594.
8. Edwards, A.; Claude, C.; Sokolik, I.; Chu, T. Y.; Okamoto, Y.; Dorsinville, R. Photoluminescence and electroluminescence of new lanthanide-(methyloxybenzoyl)benzoate complexes. *J. Appl. Phys.* **1997**, *82*, 1841–1846.
9. Herring, A. M.; Henling, L.; Labinger, J. A.; Bercaw, J. E. Structure of disodium trans-bis(2,6-pyridinedicarboxylate-O,N)platinate(II) hexahydrate. *Inorg. Chem.* **1991**, *30*, 851–853.
10. Puntus, L.; Zolin, V.; Kudryashova, V. Analysis of carboxylate coordination function of the isomeric lanthanide pyridinedicarboxylates by means of vibration spectroscopy. *J. Alloys Compd.* **2004**, *374*, 330–334.
11. Chatterjee, M.; Ghosha, S.; Wu, B.-M.; Mak, T. C. A structural and electrochemical study of some oxovanadium(IV) heterochelate complexes. *Polyhedron* **1998**, *17*, 1369–1374.
12. Qi, Y. J.; Wang, Y. H.; Fan, H. L.; Cao, M. H.; Mao, L.; Hu, C. W.; Wang, E. B.; Hu, N. H. Structure characterization and physical properties of a complex with supramolecular architectures $Co_2(2,6\text{-}DPC)_2Co(H_2O)_5.2H_2O$(DPC = 2,6-pyridinedicarboxylate). *J. Mol. Struct.* **2004**, *694*, 73–78.
13. Drew, M. G. B.; Fowles, G. W. A.; Matthews, R. W.; Walton, R. A. Silver(II) bis(pyridine-2,6-dicarboxylate) monohydrate. A novel six-coordinate structure. *J. Am. Chem. Soc.* **1969**, *91*, 7769.
14. Nardin, G.; Randaccio, L.; Bonomo, R. P.; Rizzarelli, E. Properties and structural characterization of copper(II) mixed complexes with 2,2-bipyridyl and iminodiacetate or pyridine-2,6-dicarboxylate. *J. Chem. Soc., Dalton Trans.* **1980**, 369–375.
15. Szorcsik, A.; Nagy, L.; Sletten, J.; Szalontai, G.; Kamu, E.; Fiore, T.; Pellerito, L.; Kalman, E. Preparation and structural studies on dibutyltin(IV) complexes with pyridine mono- and dicarboxylic acids. *J. Organomet. Chem.* **2004**, *689*, 1145–1154.
16. Lessmann, J. J.; Horrocks, W. D. W. Supramolecular coordination chemistry in aqueous solution: Lanthanide ion-induced triple helix formation. *Inorg. Chem.* **2000**, *39*, 3114–3124.
17. Sengupta, P.; Ghosh, S.; Mak, T. C. W. A new route for the synthesis of bis (pyridine dicarboxylato) bis (triphenylphosphine) complexes of ruthenium(II) and X-ray structural characterization of the biologically active trans-$[Ru(PPh_3)_2(L^1H)_2]$ (L^1H_2 = pyridine 2,3-dicarboxylic acid). *Polyhedron* **2001**, *20*, 975–980.
18. Laine, P.; Gourdon, A.; Launay, J. P. Chemistry of iron with dipicolinic acid. 1. mononuclear complexes of iron(II) or iron(III). *Inorg. Chem.* **1995**, *34*, 5129–5137.
19. Groves, J. T.; Kady, I. O. Sequence-specific cleavage of DNA by oligonucleotide-bound metal complexes. *Inorg. Chem.* **1993**, *32*, 3868–3872.
20. Puntus, L. N.; Zolin, V. F.; Babushkina, T. A.; Kutuza, I. B. Luminescence properties of isomeric and tautomeric lanthanide pyridinedicarboxylates. *J. Alloys Compd.* **2004**, *380*, 310–314.
21. Chevallier, P.; Soutif, J.-C.; Brosse, J.-C.; Grote, M. Synthesis of poly(amide-ester)s from 2,6-pyridine dicarboxylic acid and ethanolamine derivatives: Investigation of the polymer sorption behaviour towards heavy metal ions. *Reactive & Functional Polymers* **1999**, *42*, 129–146.
22. Brouca-Cabarrecq, C.; Fernandes, A.; Jaud, J.; Costes, J. P. Hydrothermal investigation of the lanthanide (Ln = La, Ce, Pr, Nd, Sm) 2,6-pyridinecarboxylate system. *Inorg. Chim. Acta* **2002**, *332*, 54–60.
23. Muller, G.; Muller, F. C.; Riehl, J. P. On the use of high-pressure to study the speciation, solvation, and excited state energetics of luminescent lanthanide complexes. *J. Alloys Compd.* **2004**, *380*, 79–83.
24. Blasse, G. Luminescence of rare earth ions at the end of the century. *J. Alloys Compd.* **1993**, *192*, 17–21.
25. An, B. L.; Ye, J. Q.; Gong, M. L.; Yin, X. H.; Yang, Y. S.; Zheng, X. G.; Deng, S. Z. Luminescence and thermal stability of sodium tris(pyridine dicarboxylate) terbate(III) complex incorporated in silica matrix by sol-gel method. *Mater. Res. Bull.* **2001**, *36*, 1335–1346.
26. Anne-Sophie, C.; Frederic, G.; Daniel, I.; Jean-Claude, G. B. Europium and terbium tris (dipicolinates) as secondary standards for quantum yield determination. *Spectros. Lett.* **2004**, *37*, 517–532.
27. Zolin, V.; Puntus, L.; Kudryashova, V.; Tsaryuk, V.; Legendziewicz, J. Charge transfer bands in the luminescence excitation spectra of isomeric pyridinedicarboxylic salts of europium. *J. Alloys Compd.* **2002**, *341*, 376–380.
28. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley InterScience: New York, 1990; 535.
29. Mondry, A.; Starynowicz, P. Optical spectroscopy and structure of neodymium complexes with 2,6-pyridine-dicarboxylic acid in solution and single crystal at room and low temperatures. *J. Alloys Compd.* **1995**, *225*, 367–371.
30. Biekofsky, R. R.; Muskett, F. W.; Schmidt, J. M.; Martin, S. R.; Browne, J. P.; Bayley, P. M.; Feeney, J. NMR approaches for monitoring domain orientations in calcium-binding proteins in solution using partial replacement of Ca^{2+} by Tb^{3+}. *FEBS Lett.* **1999**, *460*, 519–526.
31. Ansari, A. A.; Ahmed, Z.; Iftikhar, K. Nuclear magnetic resonance and optical absorption spectroscopic studies on paramagnetic praseodymium(III) complexes with β-diketone and heterocyclic amines. *Spectrochim. Acta, Part A* **2007**, *68*, 176–183.
32. Goldner, P.; Guillot-Noel, O. Understanding the luminescence of rare-earth-doped crystals through electron paramagnetic resonance spectroscopy. *J. Lumin.* **2007**, 122–123, 896–898.