

Synthesis and Characterization of Tb[N(CN)₂]₃·2H₂O and Eu[N(CN)₂]₃·2H₂O: Two New Luminescent Rare-Earth Dicyanamides

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Received March 23, 2006. Revised Manuscript Received September 7, 2006

Two new rare-earth dicyanamides, namely, Tb[N(CN)₂]₃·2H₂O and Eu[N(CN)₂]₃·2H₂O, have been prepared by ion exchange in aqueous solution, followed by evaporation of the solvent at room temperature. The structures of both compounds have been solved and refined from single-crystal and powder X-ray diffraction data, respectively. The two compounds are isostructural and are built up from irregular quadratic antiprismatic LnN₆O₂ polyhedra connected to each other by three crystallographically independent dicyanamide ([N(CN)₂]₃⁻) ions (Tb[N(CN)₂]₃·2H₂O, *P*2₁/*n*, *Z* = 4, *a* = 7.4632(15) Å, *b* = 11.523(2) Å, *c* = 13.944(3) Å, β = 94.06(3)°, *V* = 1196.2(4) Å³; Eu[N(CN)₂]₃·2H₂O, *P*2₁/*n*, *Z* = 4, *a* = 7.4780(3) Å, *b* = 11.5429(5) Å, *c* = 13.9756(7) Å, β = 93.998(4)°, *V* = 1203.41(10) Å³). Annealing of the hydrated phases of Ln[N(CN)₂]₃·2H₂O (Ln = Eu, Tb) at 150 °C under an argon atmosphere leads to the formation of nonhydrated Ln[N(CN)₂]₃ (Ln = Eu, Tb). Both the hydrated (Eu[N(CN)₂]₃·2H₂O) and nonhydrated (Eu[N(CN)₂]₃) europium(III) dicyanamides show red luminescence due to the dominant intensity of ⁵D₀–⁷F_{*J*} (*J* = 1, 2, 4) emission lines by excitation at 365 nm. The broad excitation band of europium(III) dicyanamide (FWHM = 8000 cm⁻¹) ranging between 260 and 420 nm with λ_{max} ≈ 30000 cm⁻¹ is ascribed to a Eu–N charge-transfer transition, which is significantly shifted to lower energy compared to that of oxo compounds due to the nephelauxetic effect. Similarly, both the hydrated (Tb[N(CN)₂]₃·2H₂O) and nonhydrated (Tb[N(CN)₂]₃) terbium(III) dicyanamides show green emission at λ_{exc} = 365 nm, arising mainly from the dominant ⁵D₀–⁷F₄ transition. However, unlike europium(III) dicyanamide, the broad excitation band of terbium(III) dicyanamide ranging between 250 and 400 nm with a maximum at 33000 cm⁻¹ can be assigned to the 4f⁸–4f⁷5d¹ transition of Tb³⁺.

Introduction

There is a growing interest in the development of new saturated-color-emitting materials that combine good mechanical, thermal, and chemical stability in air with high room-temperature emission quantum yields.^{1–3} Inorganic materials involving integration of organic and inorganic components into the same compound, leading to formation of hybrid skeletons, can have a wide variety of unique applications.^{4–7} In some cases, this increase in structural complexity gives rise to significant scientific and technological opportunities by combining attractive features of both

components within a single material.⁸ The association of molecular units with transition or rare-earth metals allows for the tuning of their electronic and magnetic properties due to the versatility of its coordination. Recently, a significant increase in the research of molecular materials in which metal ion centers are bridged through organic molecules has been observed, due to potential application in optoelectronics, magnetism, and catalysis.^{9–11} There is an attempt to replace the traditional inorganic solid-state compounds in luminescent lighting and display devices by molecular materials, because of advantages such as mass production by solution processing or gas-phase deposition, potential flexibility by means of polymer-based packaging of such thin-film devices, and finally low cost.

As a fundamental class of compounds of special importance for molecular chemistry, cyanamides and dicyanamides have gained increasing attention within the past decade.^{12,13}

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In fact, a number of alkali-metal,^{14–17} alkaline-earth-metal,^{18–20} transition-metal,^{21–25} and also main-group²⁶ cyanamides and dicyanamides were obtained following different synthetic routes. In this context, the dicyanamide anion ($[\text{N} \equiv \text{C} - \text{N} - \text{C} \equiv \text{N}]^-$) is considered to play an important role because of its variation in coordinating ability with metal ions by terminal and/or bridging nitrogen atoms, resulting in monodentate, bidentate, or even tridentate coordination. On the other hand, introduction of lanthanides within the hybrid skeleton may create an unusual architecture because of high and variable coordination of rare-earth ions and may also give unique properties stemming from their $f-f$ electronic transitions owing to high chromaticity and long-lived excited states.²⁷ However, in the field of inorganic dicyanamides, most of the solids reported until now have been dicyanamide complexes containing lanthanide ions.²⁸ Only a very few rare-earth compounds have been described which contain $\text{Ln} \cdots \text{N} - \text{CN}$ bonds.^{29–32} In an attempt to optimize lanthanide-centered emission in both the hydrated and nonhydrated lanthanide dicyanamides and to explore the mechanism of excitation and emission processes, we have prepared two new luminescent rare-earth dicyanamides, hydrated europium(III) dicyanamide ($\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$) and hydrated terbium(III) dicyanamide ($\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$) showing red and green emissions, respectively. The structures of both the hydrated compounds are isotopic and were solved from single-crystal and powder diffraction data, respectively. Also, the excitation and emission properties of isostructural nonhydrated europium(III) dicyanamide ($\text{Eu}[\text{N}(\text{CN})_2]_3$) and nonhydrated terbium(III) dicyanamide ($\text{Tb}[\text{N}(\text{CN})_2]_3$) are explored.

Experimental Section

Syntheses and Chemical Analysis. $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}, \text{Tb}$) were prepared by ion exchange in aqueous solution at room temperature. A column containing 5 mL of a strongly acidic ion-

exchange resin (Merck, Ionenaustauscher I, Art. 4765) with an ion exchange capacity of 1.7×10^{-3} mol/mL was completely filled with a solution of 0.02 M $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar). The complete loading of Ln^{3+} was indicated by the change of acidic to neutral pH, i.e., the pH of the $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ solution. After the column was fully loaded, the exchange resin was washed thoroughly with deionized water, and the removal of excess chloride was substantiated by the AgNO_3 method. Subsequently, a solution of sodium dicyanamide ($\text{Na}[\text{C}_2\text{N}_3]$; Fluka, >96%) was poured onto the column, and the eluate was evaporated at room temperature. The concentration of sodium dicyanamide solution was varied from 0.01 to 0.5 M to obtain suitable single crystals for structure determination. Under these conditions, tiny colorless crystals of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ were obtained, allowing the structure determination of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ from single-crystal diffraction data. On the other hand, $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ does not produce good single crystals under these conditions. Furthermore, other attempts for obtaining single crystals of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ by using other solvent systems as a crystallization medium or solute/vapor diffusion processes also failed. Hence, the structural parameters of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ were refined from powder diffraction data using the cell parameters and atomic coordinates of isostructural $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ as the starting values. The nonhydrated $\text{Eu}[\text{N}(\text{CN})_2]_3$ and $\text{Tb}[\text{N}(\text{CN})_2]_3$ were obtained by annealing the corresponding hydrated phases in an ampule under argon to a temperature of 150 °C. Both the hydrated and nonhydrated phases are photostable and also stable in air. The initial characterization was carried out using powder X-ray diffraction, thermogravimetric analysis, and infrared spectroscopy.

Thermal analysis was performed on a simultaneous thermogravimetry/differential thermal analyzer (Setaram thermoanalyzer TGA 92-2400) in the temperature range 25–800 °C (heating rate 10 °C/min) in an argon atmosphere. Infrared spectra were recorded at room temperature using a Bruker IFS 66v/S FTIR spectrometer in the range 2000–400 cm^{-1} by dispersing the sample in anhydrous KBr pellets. Diffuse reflectance spectra of the powder samples were recorded between 200 and 700 nm with a Varian Cary 500 spectrophotometer. Excitation and emission spectra were obtained at room temperature using a spectrofluorometer FL900 (Edinburgh Instruments) with a Xe lamp as a light source fitted with a Hamamatsu photomultiplier. The excitation and emission spectra presented are corrected for the FL900 spectrometer sensitivity and excitation lamp characteristics.

The quantum efficiency (QE) is defined as the ratio of the number of emitted quanta to the number of absorbed quanta. The QE values of unknown phosphors were determined in comparison with those of standard phosphors, the efficiencies of which were reported previously. The quantum efficiencies ($\text{QE}_{\text{sample}}$) of the unknown phosphors were calculated using the equation^{33,34}

$$\text{QE}_{\text{sample}} = \left(\frac{1 - R_{\text{std}}}{1 - R_{\text{sample}}} \right) \left(\frac{\int I_{\text{sample}}}{\int I_{\text{std}}} \right) \text{QE}_{\text{std}} \quad (1)$$

where QE_{std} is the quantum efficiency of the standard phosphor, R_{std} and R_{sample} are the amounts of exciting radiation reflected by the standard and by the sample, respectively, and $\int I_{\text{std}}$ and $\int I_{\text{sample}}$ are the integrated emission intensities for the standard and sample phosphor, respectively. The values of R_{std} , R_{sample} , $\int I_{\text{std}}$, and $\int I_{\text{sample}}$ are obtained under identical conditions such as sample weight,

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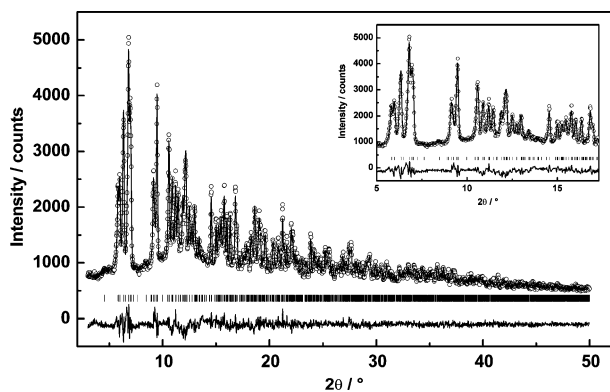


Figure 1. Final Rietveld refinement plot for $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$. Observed (open circles), calculated (line), and difference profiles of the X-ray powder diffraction are plotted on the same scale. Bragg peaks are indicated by vertical lines for $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$. An enlargement of the low-angle range is represented in the inset.

instrument settings (excitation and emission slit widths), temperature (room temperature), and excitation wavelength. The standard phosphors which were used are Philips U744 ($\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, QE = 84% for 254 nm excitation) and Lumogen red from BASF (perylene dye, QE = 42.3% for 365 nm excitation) for Eu^{3+} samples and Philips U763 ($\text{LaPO}_4:\text{Ce}^{3+}, \text{Tb}^{3+}$, QE = 90% for 254 nm excitation) $\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$ from Philips (QE = 81.3% for 365 nm excitation) for Tb^{3+} samples.

For the calculation of CIE (Commission Internationale d'Éclairage) color coordinates (x , y), the emission spectra were weighted by the 10° standard observer CIE color matching functions. After summarizing, the obtained tristimulus values were normalized to obtain CIE 1933 color coordinates.

Structure Determination. The ion exchange synthesis of $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ led to isolated single crystals of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and microcrystalline powdered samples of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$. Single-crystal structure determination of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ was performed at room temperature on an ENRAF-NONIUS Kappa CCD diffractometer equipped with a rotating anode producing graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The reflections were corrected for Lorentz and polarization effects. A semiempirical absorption correction using ψ scans was applied. The space group could be unambiguously determined as $P2_1/n$ (No. 14). The crystal structure was solved by direct methods using the software package SHELXS-97³⁵ and refined using the full-matrix least-squares method implemented in SHELXL-97³⁶ with anisotropic displacement parameters for all non-hydrogen atoms. The positions of the hydrogen atoms of the crystal water molecule could also be determined from difference Fourier maps and refined isotropically. Details of the structure determination are given in Table 1. Atomic coordinates and bond distances and angles are provided in the Supporting Information.

For X-ray diffraction investigation of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, powders of the samples were enclosed in glass capillaries with a diameter of 0.3 mm. The measurements were carried out in Debye-Scherrer geometry on a STOE Stadi P powder diffractometer with Ge(111)-monochromatized Mo K α radiation ($\lambda = 0.7093 \text{ \AA}$). The X-ray diffractometry study indicates that the diffraction pattern of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ could be indexed with lattice constants similar to those of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and the same space group as $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$; these compounds were found to be isotypic (Figure 1). Hence, the Rietveld refinements were performed with

Table 1. Crystallographic Data and Structure Refinement of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$

formula	$\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$
mol wt	393.1
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
T/K	293
diffractometer	Kappa CCD
radiation ($\lambda/\text{\AA}$)	Mo K α (0.71073)
$a/\text{\AA}$	7.4632(15)
$b/\text{\AA}$	11.523(2)
$c/\text{\AA}$	13.944(3)
β/deg	94.06(3)
$V/\text{\AA}^3$	1196.2(4)
Z	4
$\rho_{\text{calcd}}/\text{g}\cdot\text{cm}^{-3}$	2.183
$F(000)$	736
μ/mm^{-1}	5.923
cryst size/ mm^3	$0.11 \times 0.09 \times 0.06$
diffraction range	$3.1 \leq \theta \leq 27.48$
index range	$-9 \leq h \leq +9, -14 \leq k \leq +14, -18 \leq l \leq +17$
total no. of reflns	19462
no. of independent reflns	2723
no. of independent reflns	1992 ($R_{\text{int}} = 0.0370$)
no. of refined params	177
corrections	absorption, Lorentz, polarization
abs correction	multiscan
min/max trans ratio	0.530/0.691
min/max residual electron density/ $\text{e}\cdot\text{\AA}^{-3}$	$-0.302/0.585$
GOF	1.025
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0193, wR2 = 0.0376$
R indices (all data)	$R1 = 0.0334, wR2 = 0.0419$ with $w = [\sigma^2(F_o^2) + (0.0000P)^2 + 0.4464P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$

Table 2. Crystallographic Data Structure Refinement of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$

formula	$\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$
mol wt	386.15
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
radiation ($\lambda/\text{\AA}$)	Mo K α (0.7093)
$a/\text{\AA}$	7.4780(4)
$b/\text{\AA}$	11.5429(5)
$c/\text{\AA}$	13.9756(7)
$\beta/\text{\AA}$	93.998(4)
$V/\text{\AA}^3$	1203.41(10)
Z	4
$\rho_{\text{calcd}}/\text{g}\cdot\text{cm}^{-3}$	2.131
profile range	$3 \leq 2\theta \leq 50$
no. of data points	4699
no. of positional params	66
no. of profile params	19
R values	$R_c^2 = 0.08029$ $wR_p(\text{fit}) = 0.0467$ $R_p(\text{fit}) = 0.0368$ $wR_p(\text{back}) = 0.0513$ $R_p(\text{back}) = 0.0392$

the program GSAS³⁷ using the atomic coordinates of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ as the starting values. To describe the profile of the X-ray reflections, a pseudo-Voigt function with special symmetry was used.³⁸ Details of the structure determination are summarized in Table 2. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, e-mail crysdata@FIZ-karlsruhe.de, on quoting the depository numbers CSD-416308

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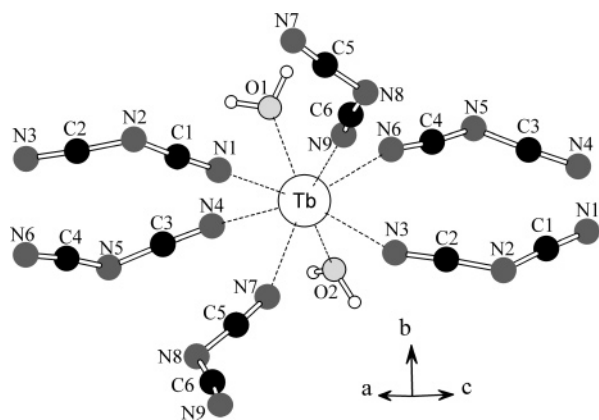


Figure 2. Coordination modes of Tb^{3+} in $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$.

($\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$) and CSD-416309 ($\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$) and the name of the author(s) and citing the paper.

Results and Discussion

Both $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ are isostructural and crystallize in the monoclinic space group $P2_1/n$. Furthermore, $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ are also isostructural with previously reported $\text{Gd}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$.³² The lanthanide ions (Tb, Eu) are eight-coordinated as is displayed with a complete coordination sphere in Figure 2. The polyhedron around $\text{Ln}(\text{III})$ can be described as an irregular quadratric antiprism. Each lanthanide ion is surrounded by six nitrogen atoms coming exclusively from three crystallographically independent dicyanamide ions ($[\text{N}(\text{CN})_2]^-$). There are two water molecules completing the coordination sphere of the lanthanide ion. The interatomic distances are close to those usually reported for rare-earth(III) solids; $\text{Tb}/\text{Eu}-\text{N}$ distances vary from 2.45 to 2.48 Å, and $\text{Tb}/\text{Eu}-\text{O}$ distances are between 2.38 and 2.40 Å. The dicyanamides coordinate to Ln^{3+} only by the terminal N atoms (N1, N3, N4, N6, N7, and N9), resulting in a bidentate terminal coordination. The angles ($\text{N}-\text{C}\equiv\text{N}$, $173-175^\circ$; $\text{C}-\text{N}-\text{C}$, $118-122^\circ$) and bond distances (terminal $\text{C}\equiv\text{N}$, 1.14–1.15 Å; bridging $\text{N}-\text{C}$, 1.29–1.30 Å) of the dicyanamide ions are similar to those of other dicyanamides.³⁹ The site symmetry of the dicyanamide ion $[\text{N}\equiv\text{C}-\text{N}-\text{C}\equiv\text{N}]^-$ is reduced to C_1 because of slightly different bond lengths $\text{C}\equiv\text{N}$ and angles $\text{N}-\text{C}\equiv\text{N}$.

Figure 3 shows the polyhedral representation of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$. It exhibits a three-dimensional network built up from eight-coordinated lanthanide ions forming LnO_2N_6 polyhedra. These units are connected to each other through the dicyanamide moieties. This arrangement of six dicyanamide groups around the lanthanide ion leads to a structure of two-dimensional sheets. The metal ions in two adjacent sheets are approximately 8 Å apart. These layers interact with each other through $\pi-\pi$ stacking as well as through hydrogen bonding. There are four $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds, two of them running to terminal N atoms (N7 and N9 with $\text{O}-\text{N}$ distances of 3.1636 and 3.196 Å, respectively) and two to the bridging N atoms (N2 and N8

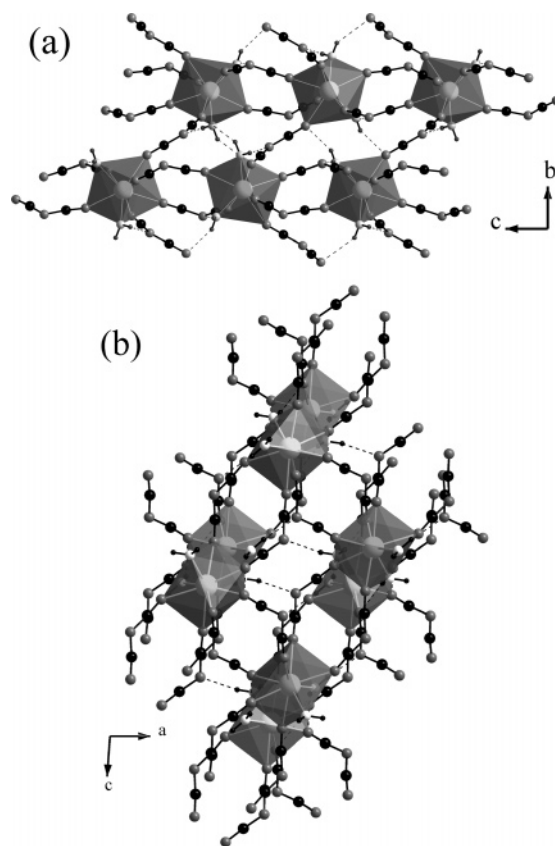


Figure 3. Polyhedral representation of the structure of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ along the (a) a axis and (b) b axis. Terbium, carbon, nitrogen, oxygen, and hydrogen are represented as large white spheres, large black spheres, gray spheres, small white spheres, and small black spheres, respectively.

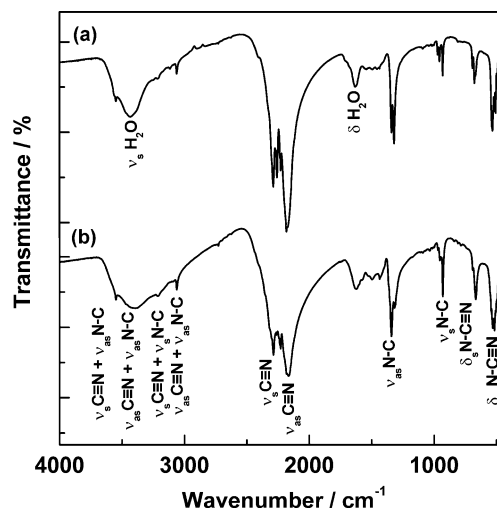


Figure 4. Infrared spectra of (a) $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and (b) $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$.

with $\text{O}-\text{N}$ distances of 2.8219 and 2.9121 Å, respectively) of dicyanamide ions.

The infrared spectra of $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}, \text{Eu}$) clearly show the presence of the vibrational bands characteristic for $\text{C}\equiv\text{N}$ and $\text{N}-\text{C}$ as shown in Figure 4, confirming the presence of the dicyanamide group within the solids.⁴⁰ Additionally, the broad band between 3600 and 3000 cm^{-1} and sharp signal at 1610 cm^{-1} originate from the stretching

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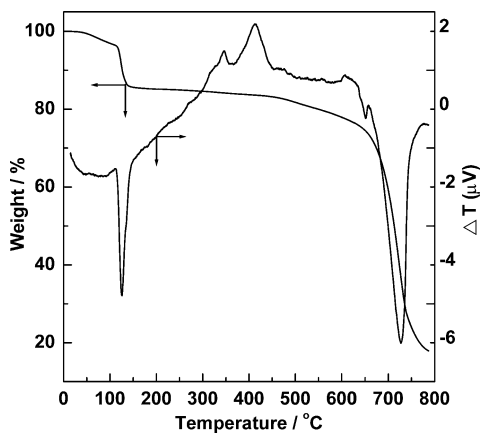


Figure 5. TG/DTA curve of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ recorded under an argon atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

and bending vibrations of water molecules, confirming the presence of H_2O group in $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}, \text{Eu}$).

The thermal stability of $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{Tb}, \text{Eu}$) has been studied using thermogravimetric/differential thermal analysis (TG/DTA). Since $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ contains water molecules, structural changes at higher temperatures were expected for this compound. The TG/DTA measurements, performed between 20 and 800°C , have shown identical results for both compounds with two weight losses (Figure 5). The initial weight loss of 15% in the range of $100\text{--}150^\circ\text{C}$ corresponds to the loss of adsorbed water and lattice water, and the second weight loss of 60% in the range of $450\text{--}750^\circ\text{C}$ corresponds to the loss of organic moieties. These are also indicated by the two endothermic effects of the DTA curve at 120 and 725°C , respectively. The dehydration of $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ occurs at 150°C , leading to the formation of anhydrous $\text{Ln}[\text{N}(\text{CN})_2]_3$, the structure of which shows the removal of water molecules and the rearrangement of dicyanamide groups.³⁹ The crystallinity of the compound is kept after the first structural change. The crystallinity remains up to 350°C , indicating the thermal stability of the compounds. Above 400°C , the decomposition of dicyanamide is indicated by the exothermic effect of the DTA curve, leading to the formation of an X-ray amorphous powder which at higher temperature converts to the corresponding oxides.

The nonhydrated $\text{Ln}[\text{N}(\text{CN})_2]_3$ ($\text{Ln} = \text{Eu}, \text{Tb}$) are isostructural with other lanthanide dicyanamides, the structure of which has been previously reported by Jürgens et al.³⁹ The nonhydrated phases crystallize with orthorhombic symmetry having space group $Cmcm$. In the crystal structure there are two crystallographically independent dicyanamide ions ($[\text{N}(\text{CN})_2]^-$) which are coordinated with Ln^{3+} . The Ln^{3+} ions are coordinated by three bridging N atoms and six terminal N atoms of the dicyanamide ions, forming a tricapped trigonal prism of LnN_9 polyhedra.

It has been demonstrated for inorganic molecular compounds that the luminescence of the trivalent rare earths might arise because of absorption in the ligand group followed by intramolecular transfer of energy from the lowest excited triplet state that is populated via intersystem crossing from the excited singlet state involving the ligand-to-metal charge-transfer (LMCT) state in lanthanide compounds.

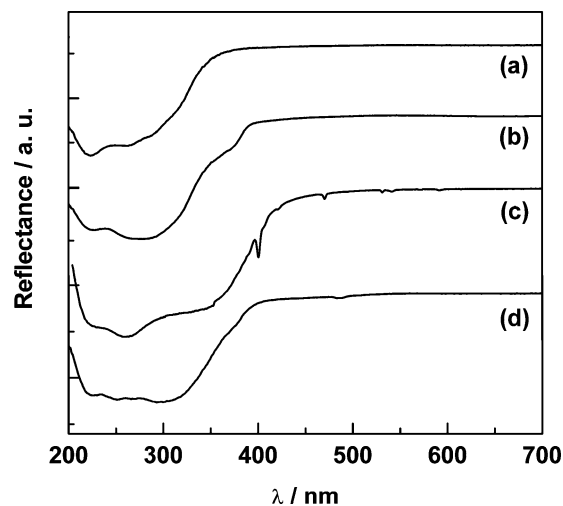


Figure 6. Diffuse reflectance spectra at room temperature of $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$: (a) $\text{La}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, (b) $\text{Gd}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, (c) $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, and (d) $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$.

There are two methods of energy transfer; one is intramolecular energy transfer between 4f states of the lanthanide ion and the LMCT state, and the other one is the intramolecular energy transfer between ligand states (singlet and triplet) and the LMCT state. The theory developed by Faustino et al.⁴¹ and experimentally confirmed by Carlos et al.⁴² estimates that the energy transfer through the ligand–LMCT state transfer process is the dominant case by several orders of magnitude over that through the former lanthanide ion–LMCT state transfer process. To find whether the LMCT states take part in the excitation–emission process of $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, the diffuse reflectance spectra are recorded for $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Gd}, \text{Tb}$) at room temperature (Figure 6). Furthermore, the arithmetic difference between the diffuse reflectance spectra of isostructural Eu^{3+} and Gd^{3+} compounds allows for the explicit identification of low-lying LMCT states for Eu^{3+} , since for Gd^{3+} the energy difference between the first excited state and the fundamental levels is too high to allow the detection of a charge-transfer state in the UV–vis range. The effects of LMCT states on the Eu^{3+} emission quantum yield have recently been described in a notable theoretical approach that modeled the intramolecular LMCT state–4f levels and LMCT state–ligand energy-transfer processes. Numerical estimates for the luminescence quenching via LMCT– Eu^{3+} energy transfer show that when the LMCT state lies approximately between 10000 and 20000 cm^{-1} , quenching is extremely high (emission quantum yields close to zero), corresponding to the exhaustion of the $^5\text{D}_0$ and $^5\text{D}_1$ level populations. The diffuse reflectance spectrum of lanthanum dicyanamide consists of a broad band in the UV region with maxima at 220 and 280 nm (Figure 6a). Apart from a shoulder around 370 nm , the absorption spectrum of $\text{Gd}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ shows features similar to those of the lanthanum dicyanamide spectrum (Figure 6b). The shoulder in the spectrum of $\text{Gd}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ might be appearing

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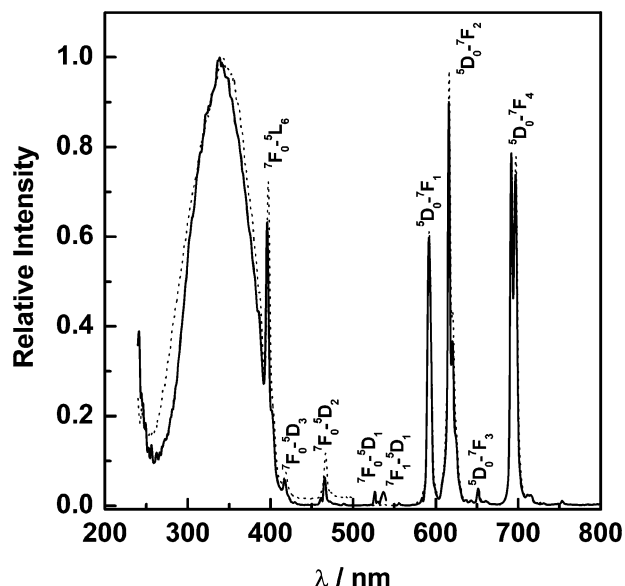


Figure 7. Excitation ($\lambda_{\text{em}} = 616$ nm) and emission ($\lambda_{\text{exc}} = 365$ nm) spectra of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ (solid line) and $\text{Eu}[\text{N}(\text{CN})_2]_3$ (dotted line).

due to some impurities since it is not observed in lanthanum dicyanamide and also isostructural $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ (Figure 6d). Furthermore, the absorption band at 220 nm remains unchanged for all the lanthanide dicyanamides and is also observed in the case of $\text{Na}[\text{N}(\text{CN})_2]$, indicating that this absorption might correspond to transition in the dicyanamide ligands. The diffuse reflectance spectrum of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ consists of a very broad absorption band extending from 200 to 400 nm and a sharp line at 395 nm which can be attributed to ${}^7\text{F}_0 - {}^5\text{L}_6$ intra- $4f^6$ transition. The absorption bands around the 220–300 nm region are very similar to those observed in the spectra of other lanthanide dicyanamides $\text{Ln}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Gd}, \text{Tb}$). Furthermore, absorption at a wavelength around 340 nm has no correspondence in the spectra of La^{3+} , Gd^{3+} , or Tb^{3+} and is therefore ascribed to a Eu–N charge-transfer transition. However, the diffuse reflectance spectrum of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ does not show the presence of a low-lying LMCT band overlapping with the ${}^5\text{D}_0$ and ${}^5\text{D}_1$ levels of Eu^{3+} , which in turn ruled out the quenching of Eu^{3+} luminescence by a nonradiative process through low-energy LMCT states.⁴³

Figure 7 shows the room-temperature excitation (PLE) and emission (PL) spectra of hydrated $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and nonhydrated $\text{Eu}[\text{N}(\text{CN})_2]_3$. The emission spectrum of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, recorded at $\lambda_{\text{exc}} = 365$ nm, is composed of the typical Eu^{3+} intra- $4f^6$ emission lines which can be assigned to transitions between the first excited state (${}^5\text{D}_0$) and the ground multiplets (${}^7\text{F}_{0-4}$). However, the presence of all the multiplets in the emission lines due to $2J + 1$ Stark components of J -degeneracy splitting cannot be well resolved due to room-temperature measurements except for the 2-fold degeneracy of the ${}^5\text{D}_0 - {}^7\text{F}_2$ line as well as the 2-fold degeneracy of the ${}^5\text{D}_0 - {}^7\text{F}_4$ line. Furthermore, the ${}^5\text{D}_0 - {}^7\text{F}_1$ line is known to originate from magnetic dipole transition, while the ${}^5\text{D}_0 - {}^7\text{F}_2$ and ${}^5\text{D}_0 - {}^7\text{F}_4$ lines originate from electric dipole transitions.⁴⁴ According to the Judd–Ofelt theory,^{45,46}

the magnetic dipole transition is permitted while the electric dipole transition is forbidden. The latter are allowed only for the condition that the Eu^{3+} ions occupy a site without an inversion center and are sensitive to local symmetry. In the case of europium dicyanamide, the electric dipole transition is much stronger than the magnetic dipole transition, suggesting that Eu^{3+} occupies a low-symmetry site without an inversion center. Moreover, Malta et al.^{47–49} theoretically calculated the intensity parameters of ${}^5\text{D}_0 - {}^7\text{F}_2$ and ${}^5\text{D}_0 - {}^7\text{F}_4$ transitions in the Eu^{3+} complex taking into account the forced electric dipole and dynamic coupling mechanism and using magnetic dipole allowed ${}^5\text{D}_0 - {}^7\text{F}_1$ as a reference (as it does not depend on the local ligand field) and interpreted the high experimental intensity of the ${}^5\text{D}_0 - {}^7\text{F}_2$ line as a consequence of the hypersensitive behavior, pointing to a highly polarizable chemical environment around the Eu^{3+} ion.

The excitation spectrum (PLE), monitored at $\lambda_{\text{em}} = 612$ nm, the most intense emission line of Eu^{3+} , exhibits a large broad band between 260 and 420 nm, with a maximum at around 335 nm, superimposed with sharp peaks centered at wavelengths extending from 390 to 550 nm. The sharp peaks can be attributed to inner 4f shell ${}^7\text{F}_0 - {}^5\text{L}_6$ (395 nm), ${}^7\text{F}_0 - {}^5\text{D}_3$ (417 nm), ${}^7\text{F}_0 - {}^5\text{D}_2$ (465 nm), ${}^7\text{F}_0 - {}^5\text{D}_1$ (525 nm), and ${}^7\text{F}_1 - {}^5\text{D}_1$ (538 nm) transitions of Eu^{3+} .⁵⁰ The broad excitation spectra of the trivalent rare-earth ions can be ascribed to either (i) charge-transfer transitions ($4f^n \rightarrow 4f^{n+1}\text{L}^{-1}$, where L = ligand) or (ii) $4f^n \rightarrow 4f^{n-1}5d$ transitions. Charge-transfer transitions are found for rare-earth ions which like to be reduced, whereas $4f-5d$ transitions are observed for the rare earth ions which like to be oxidized. Hence, the broad band in the case of europium dicyanamides can only be ascribed to originate from Eu–N charge-transfer (CT) transitions, i.e., the electron transfer from nitrogen to the Eu^{3+} ion because it is easy to reduce Eu^{3+} to Eu^{2+} in the excited state. The full width at half-maximum (8000 cm^{-1}) of the Eu–N charge-transfer band is quite comparable with that of the Eu–O charge-transfer band in oxide lattices; however, the position of the Eu–N charge-transfer band is significantly shifted to lower energies compared to that of the oxo compounds. The charge-transfer band of Eu–F in $\text{YF}_3:\text{Eu}^{3+}$ appears around 150 nm (66000 cm^{-1}), whereas in the case of $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$, the charge-transfer band of Eu–O is shifted to longer wavelength and appears around 250 nm (40000 cm^{-1}). Therefore, one can expect a red shift of the Eu–N charge-transfer transition band around 335 nm (30000 cm^{-1}) due to the nephelauxetic effect; i.e., with increasing covalency ($\text{F} < \text{O} < \text{N}$) the interaction between the electrons is reduced since they spread out over wider orbitals, and hence,

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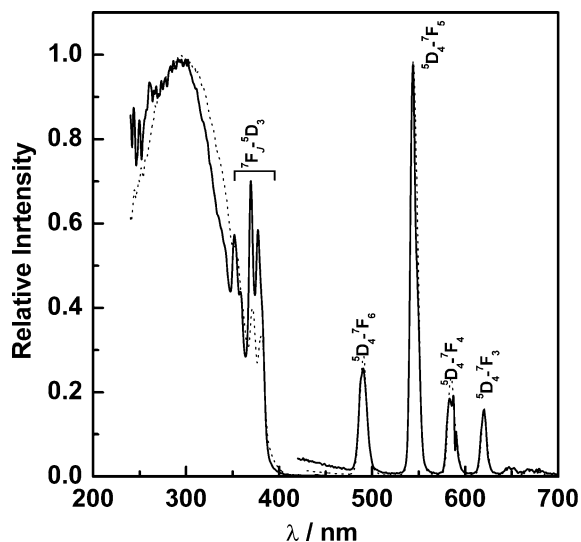


Figure 8. Excitation ($\lambda_{em} = 545$ nm) and emission ($\lambda_{exc} = 365$ nm) spectra of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ (solid line) and $\text{Tb}[\text{N}(\text{CN})_2]_3$ (dotted line).

the energy required to remove an electron from a ligand atom decreases in the order $\text{F} > \text{O} > \text{N}$, which in turn shifts the electronic transitions toward lower energies ($\text{Eu}-\text{N} < \text{Eu}-\text{O} < \text{Eu}-\text{F}$).⁵¹ Moreover, the excitation spectrum of the nonhydrated $\text{Eu}[\text{N}(\text{CN})_2]_3$ shows features similar to those of the spectrum of the hydrated compound except for a slight shift (~ 10 nm) of the excitation maximum toward longer wavelength (348 nm), indicating that excitation mechanisms are essentially the same for both the hydrated and nonhydrated phases. The slight shift toward the longer wavelength can be attributed to the different crystal structures of hydrated and nonhydrated europium(III) dicyanamides. Further, the red shift of the charge-transfer band of hydrated versus nonhydrated europium(III) dicyanamides is also to be expected due to the more covalent environment around Eu^{3+} in nonhydrated $\text{Eu}[\text{N}(\text{CN})_2]_3$ with EuN_9 polyhedra. On the other hand, the emissions of hydrated and nonhydrated $\text{Eu}[\text{N}(\text{CN})_2]_3$ arise from intra- $4f^6$ $^5\text{D}_0-^7\text{F}_J$ ($J = 0-4$) transitions of Eu^{3+} , which are not very sensitive to the local environment as the $4f$ orbital is well shielded by the $5s$ and $5p$ orbitals. Only the $^5\text{D}_0-^7\text{F}_2$ transition depends on the local environment of Eu^{3+} and therefore is called a hypersensitive transition. Closer inspection of the emission spectra of hydrated and nonhydrated europium dicyanamide (Figure 7) reveals an increase in intensity of the $^5\text{D}_0-^7\text{F}_2$ line in the case of nonhydrated $\text{Eu}[\text{N}(\text{CN})_2]_3$ compared to the hydrated compound.

Figure 8 shows the excitation (PLE) and emission (PL) spectra of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and $\text{Tb}[\text{N}(\text{CN})_2]_3$. The excitation spectrum of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, monitored at Tb^{3+} green emission at 545 nm ($^5\text{D}_4-^7\text{F}_5$), mainly consists of a wide band from 250 to 400 nm with a maximum at 300 nm superimposed with sharp lines around 370 nm. The sharp lines originate from intra- $4f$ transitions of Tb^{3+} . However, unlike europium dicyanamide, the broad band at 33000 cm^{-1} ($\text{fwhm} \approx 9000\text{ cm}^{-1}$) in the excitation spectra of the Tb compounds cannot be ascribed to a Tb-N charge-transfer

transition, which is expected to be located at much higher energy because of the formation of unstable divalent lanthanides such as Tb^{2+} in the excited states. Hence, the broad band can only be ascribed to an f-d transition of Tb^{3+} . The structure of the f-d excitation spectra could be explained by crystal-field and spin-orbit interactions for the $5d$ electron and the Coulomb interaction between the $4f$ and $5d$ electrons giving rise to splitting between the low-spin (LS) and high-spin (HS) states. The excitation of one "inner" f state to an "outer" d state can be regarded as the first step of the removal of the electron and thus produces stable tetravalent rare-earth ions such as Tb^{4+} , which is expected to have a lower energy than the corresponding charge-transfer state, which in turn forms unstable divalent Tb^{2+} . The ground configuration of the Tb^{3+} ion is $4f^8$. The excited configuration is $4f^75d^1$, in which the $4f$ shell is half-filled. Because the lowest excited $4f$ level within the $4f^7$ configuration is located at very high energy (32000 cm^{-1} for Gd^{3+}), the f-d excitation spectrum of Tb^{3+} is expected to be quite similar to that of Ce^{3+} ($4f^0-5d^1$ configuration in the excited state) showing a band corresponding to the different $5d$ states. The $4f^8-4f^75d$ transition of Tb^{3+} is generally observed in a relatively higher energy region in the case of fluoride or oxide compounds.^{52,53} In the present case, a lower energy shift of f-d transitions can be expected due to the nephelauxetic effect. In fact, in the case of Ce^{3+} a low-energy excitation band is observed even in oxide lattices.⁵⁴ Therefore, the broad excitation band of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ as well as $\text{Tb}[\text{N}(\text{CN})_2]_3$ can be explained as the $4f^8-4f^75d$ transition of Tb^{3+} . Excitation into the $4f^8-4f^75d$ transition of Tb^{3+} at 300 nm yields the characteristic $^5\text{D}_4-^7\text{F}_J$ ($J = 3-6$) emission of Tb^{3+} , with $^5\text{D}_4-^7\text{F}_5$ green emission as the most intense one ($\lambda_{max} = 545$ nm). Similar to $\text{Eu}[\text{N}(\text{CN})_2]_3$, nonhydrated $\text{Tb}[\text{N}(\text{CN})_2]_3$ also shows a red shift (~ 10 nm) in the excitation maximum compared to hydrated $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, which can be explained as different local symmetries of Tb^{3+} between hydrated and nonhydrated compounds due to different crystal structures and coordination, which in turn affects the energy of the d orbital, resulting in excitation maxima at longer wavelengths.

The CIE color coordinates (x , y) of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ (0.633, 0.359), $\text{Eu}[\text{N}(\text{CN})_2]_3$ (0.638, 0.356), $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ (0.319, 0.509), and $\text{Tb}[\text{N}(\text{CN})_2]_3$ (0.334, 0.568) are quite comparable to those of commercial red- and green-emitting phosphors, respectively.

The quantum efficiencies were measured for both hydrated and nonhydrated phases under monitoring wavelengths of 256 and 365 nm to compare these two phosphors with standard lamp phosphors. The quantum efficiencies described here are overall quantum efficiencies of the luminescent materials. For $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, the standard phosphor $\text{Y}_2\text{O}_3:\text{Eu}$ powder (from Philips) with a QE of 84% for 254 nm excitation and 84.5% absorption was used as a reference. For this excitation wavelength, the $\text{Eu}(\text{III})$ emission of $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ is completely quenched. Similar is the case

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for nonhydrated $\text{Eu}[\text{N}(\text{CN})_2]_3$. For an excitation wavelength of 365 nm, $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ shows a QE of 6% compared to standard Lumogen red, a perylene dye (from BASF) which has a QE of 42.3%. In the case of nonhydrated $\text{Eu}[\text{N}(\text{CN})_2]_3$ the QE increased to 10.5%. In the case of $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, the commercial phosphor $\text{LaPO}_4:\text{Ce}, \text{Tb}$ powder (from Philips) with a quantum efficiency of 90% for 254 nm excitation and 96.7% absorption was used as a reference. The sample $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ showed 95.2% absorption of the excitation light and a quantum efficiency of 15.7%. For an excitation wavelength of 365 nm, $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ shows a QE of 18% compared to standard $\text{SrSi}_2\text{N}_2\text{O}_2:\text{Eu}$ (from Philips), which has a QE of 81.3%. In the case of nonhydrated $\text{Tb}[\text{N}(\text{CN})_2]_3$ the QE increased to 25.4%. The QE study clearly shows that the hydrated phases exhibit comparatively lower efficiencies than the corresponding nonhydrated phases. It is well-known that the nonradiative effect of the OH oscillators of the H_2O molecule affects the luminescence features of the trivalent lanthanides.⁵⁵ Therefore, comparatively low quantum efficiencies of hydrated dicyanamides can be explained with nonradiative losses due to multiphonon emission involving the water molecules. In addition, strong concentration quenching might be expected due to energy transfer between two adjacent Tb^{3+} or Eu^{3+} ions in $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ or $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, respectively. However, the Eu–Eu or Tb–Tb distance within a layer is about 8 Å, which ruled out the energy migration through exchange interaction (critical distance (R_c) ≤ 5 Å), resulting in strong concentration quenching.⁵¹ Only weak multipolar interaction can occur between two Tb^{3+} or Eu^{3+} ions in $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ or $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$, respectively. On the other hand, at higher concentrations of the activators there is also a possibility of cross-relaxation in which the higher energy level emissions of Tb^{3+} or Eu^{3+} can be quenched. The low-energy excitation maxima of terbium or europium dicyanamide open up the possibility to develop white LEDs in combination with blue GaN-based LEDs and lanthanide carbon nitrides, which is a developing field of research in the present day.³ However, a better efficiency can be obtained by further shifting the excitation maxima toward longer wavelength to achieve better energy overlap between the emission spectrum of a blue GaN-based

LED and the excitation spectra of rare-earth-based phosphors. This can be obtained by tailoring the ligands of lanthanide carbon nitride compounds, which is presently in progress. Furthermore, an attempt has been made to prepare isostructural $\text{Gd}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ doped with Eu^{3+} or Tb^{3+} . However, doping is not effective in this case as the hydrated phases are prepared by ion exchange in aqueous solution and the nonhydrated phases are obtained by heat treatment of the hydrated phases at 150 °C, which is very low compared to the temperature of the diffusion-controlled high-temperature solid-state reactions. Therefore, the resulting product yields heterogeneous mixtures of two phases of gadolinium dicyanamides and europium or terbium dicyanamides, respectively, even at a very low concentration of dopants, and the resulting emission intensities of the compounds are extremely low due to the presence of a nonemissive $\text{Gd}[\text{N}(\text{CN})_2]_3$ phase.

Conclusions

The synthesis, structure, and characterization of new rare-earth dicyanamides have been accomplished. The presence of a rare earth and molecular units such as $[\text{N}(\text{CN})_2]_3^-$ resulted in low-energy excitation bands yielding efficient red and green emission from Eu^{3+} and Tb^{3+} , respectively. Other similar compounds are currently under investigation to explore the emission by tailoring the ligand to shift the excitation wavelength suitable for applications in lighting and display devices.

Acknowledgment. We thank Dr. P. Mayer for single-crystal data collection and J. Kechele and A. Sattler for conducting the TG/DTA measurement (all Department of Chemistry and Biochemistry of LMU Munich), and H. Ohland (Philips Research) for luminescence measurements. Financial support by the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm “Lanthanoidspezifische Funktionalitäten in Molekül und Material”, Project SCHN 377/10-2) and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic information files (CIFs) for $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and $\text{Eu}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and tables of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for $\text{Tb}[\text{N}(\text{CN})_2]_3 \cdot 2\text{H}_2\text{O}$ and diffuse reflectance spectrum of sodium dicyanamide (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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