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Tricyanomethanides of the scandium group obtained from aqueous solution: syntheses, crystal structures and Raman spectra of $Sc[C(CN)_3]_3(H_2O)_3$, $Y[C(CN)_3]_3(H_2O)_2$ and $La[C(CN)_3]_3(H_2O)_4$

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Abstract: Metathesis reactions with $Ag[C(CN)_3]$ and rare-earth metal trichlorides $RECl_3$ (*RE* = Sc, Y or La) in water yielded colorless single crystals of $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**, $Y[C(CN)_3]_3(H_2O)_2$ **(II)** and $La[C(CN)_3]_3(H_2O)_4$ **(III)**. **(I)** crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with the lattice parameters a = 964.73(7), b = 1024.26(7), c = 1096.48(8) pm, α = 70.767(3), β = 64.936(3), γ = 62.481(3)°, Z = 2; **(II)** adopts the orthorhombic space group $P2_12_12_1$ (no. 19, a = 1011.06(7), b = 1172.54(8), c = 1419.21(9) pm, Z = 4), while **(III)** exhibits the monoclinic space group $C2/c$ (no. 12, a = 2843.17(19), b = 789.74(5), c = 1812.31(12) pm, β = 106.938(3)°, Z = 8). In **(I)**, a quasi-molecular dimer forms with *C.N.*(Sc^{3+}) = 7, **(II)** shows a rather complex framework with *C.N.*(Y^{3+}) = 8, while **(III)** is built up by chains with *C.N.*(La^{3+}) = 9. The experimentally determined volumes of these compounds are compared with the calculated *Biltz* volumes. The Raman spectra were also recorded to corroborate the presence of the planar star-shaped tricyanomethanide anion $[C(CN)_3]^-$.

Keywords: scandium; yttrium; lanthanum; tricyanomethanide hydrates; *Biltz* volumes; Raman spectrum

1 Introduction

Data regarding tricyanomethanides of the rare-earth metals are quite rare or hard to find. Quite easily accessible is the report regarding the synthesis and crystal structure of $KLa[(C(CN)_3]_4(H_2O)$,[1] but in a doctoral thesis,[2] a plethora of different compounds were synthesized. Either structurally or spectroscopically characterized are compounds such as $Ln[C(CN)_3]_3(H_2O)_5$ (*Ln* = La–Pr), $Ln[C(CN)_3]_3(H_2O)_4$ (*Ln* = Nd, Sm–Gd), $Ln[C(CN)_3]_3(H_2O)_2$ (*Ln* = Tb–Lu), $KLn[C(CN)_3]_4(H_2O)$ (*Ln* = La–Nd, Sm–Gd) and $KLn[C(CN)_3]_4$ (*Ln* = Tb–Lu). Even in the otherwise comprehensive book "*Chemie der Pseudohalogenide*" (*Chemistry of the Pseudohalides*),[3] this class of compounds is not even mentioned. This is probably due to the fact that no unusual properties in terms of crystal structure, magnetic and optical properties, electrochemistry or conductivity are expected from these strictly ionic compounds. Additionally, in solution the trivalent metal cations form complexes with many anionic species, which precipitate owing to their low solubility, hampering the crystallinity of the resulting products. Nevertheless, the scarcity of information motivated us to have a closer look at this class of compounds using the well-established metathesis strategy employing $Ag[C(CN)_3]$ and a suitable metal halide.[4] We report here the syntheses, crystal structures and Raman spectra of $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**, $Y[C(CN)_3]_3(H_2O)_2$ **(II)** and $La[C(CN)_3]_3(H_2O)_4$ **(III)**. Additionally, volume increment calculations were employed to verify the plausibility of the title compounds and of the earlier reported lanthanoid tricyanomethanide hydrates.

2 Methods and experimental

2.1 Source of material

$Ag[C(CN)_3]$ was synthesized by blending an aqueous solution containing 1.13 g (10 mmol) of $Na[C(CN)_3]$ (>98 %, TCI,

Dedicated to Professor Mathias S. Wickleder on the Occasion of his 60th Birthday.

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Eschborn, Germany) with an aqueous solution of 2.04 g (12 mmol) $Ag[NO_3]$ (≥99 %, Sigma-Aldrich, St. Louis, MO, USA). The resulting off-white precipitate was washed with deionized water and dried using an aspirator. 340 mg (3 mmol) of $Ag[C(CN)_3]$ was added to 5 mL of demineralized water containing the respective rare-earth metal chloride (150 mg (0.99 mmol) of $ScCl_3$, 195 mg (1 mmol) of YCl_3, or 245 mg (1 mmol) $LaCl_3$). All anhydrous chlorides were obtained from ChemPur (Karlsruhe, Germany) with a purity of >98 %. After stirring the mixture for 6 h, the resulting solution was filtered to remove the precipitated AgCl and the excess of $Ag[C(CN)_3]$. The water was allowed to evaporate under ambient temperature and atmospheric conditions. After a few days, colorless and transparent, irregular crystals of the three title compounds were identified as the sole products in quantitative yield considering the employed amount of rare-earth metal trichloride.

2.2 Crystallographic studies

Single-crystal selection was carried out with the help of a polarization microscope, and suitable crystals were sealed into thin-walled glass capillaries (Hilgenberg, Malsfeld, Germany). Intensity data sets for **(I)** and **(III)** were collected with a STOE Stadivari diffractometer equipped with a Dectris Pilatus detector, a graded multilayer mirror monochromator and Mo-K_α radiation (λ = 71.07 pm) at room temperature. The collected intensity data was handled with the program package X-Area.[5] A multi-scan absorption correction was applied using STOE Lana.[6] A set of intensity data for **(II)** was collected with a Nonius Kappa-CCD diffractometer with graphite-monochromatized Mo-K_α radiation (λ = 71.07 pm) also at room temperature. The processing of the X-ray diffraction data was performed with the software package that came with the diffractometer.[7] The intensity data was corrected for Lorentz and polarization effects as well as for absorption with the program Habitus.[8] For all three title compounds the position of the respective rare-earth metal cation was obtained by using Direct Methods with the program Shelxs-97.[9] The positions of light atoms (including hydrogen) became apparent from the highest electron density on the difference Fourier map resulting from the first refinement cycles by full-matrix least-squares calculations on F^2 (Shelxl-97[10]). The crystallographic data are listed in Table 1, atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2 and selected interatomic distances and angles of the title compounds can be found in Table 3.

Crystallographic data (including structure factors) for the three structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Further details of the crystal structure investigation may be obtained free of charge from the joint CCDC/ICSD Karlsruhe online deposition service: https://www.ccdc.cam.ac.uk/structures by quoting the deposition number CCDC 2386319 for $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**, CCDC 2422431 for $Y[C(CN)_3]_3(H_2O)_2$ **(II)** and CCDC 2422430 for $La[C(CN)_3]_3(H_2O)_4$ **(III)**.

2.3 Calculation of the incremental volume sum according to *Biltz*

The incremental volume sum was calculated according to *Biltz* by adding up the respective volume increments of the respective trivalent cations ($V(Sc^{3+})$ = 3.3 Å^3, $V(Y^{3+})$ = 10.0 Å^3 and $V(La^{3+})$ = 13.3 Å^3), the crystal water (27 Å^3) (all volumes according to *Biltz*[11]) and the volume increment of the $[C(CN)_3]^-$ anion (113(4) Å^3, taken from ref. 12). The thus obtained and the experimentally determined volumes of rare-earth metal tricyanomethanide hydrates are displayed in Table 4.

2.4 Raman spectroscopy

Raman spectroscopy was always performed with the single crystal used for the X-ray measurements on a XploRA spectrometer (Horiba, Kyoto, Japan) with 25 mW, excitation line at λ = 532 nm.

3 Results and discussion

3.1 The tricyanomethanide $[C(CN)_3]^-$ anion

The rigid $[C(CN)_3]^-$ anion (often dubbed as tcm$^-$) as basic building block in all three title compounds exhibits only small deviations from ideal D_{3h} point symmetry (Table 3, Figures 1–3). The C–C bond lengths ranging from 138.5(2) to 141.0(3) pm are consistent with 141 pm obtained from DFT data for the free $[C(CN)_3]^-$ anion; the C≡N bond lengths are found in the interval from 113.5(2) to 116.0(3) pm being somewhat shorter than the distance of 117 pm calculated with DFT methods for the free $[C(CN)_3]^-$ anion.[13] These bond lengths range between the distances expected for a C–C single (154 pm) and a C=C double bond (133 pm)[12] or a C=N double (122 pm) and a C≡N triple bond (111 pm),[14] respectively, indicating a highly delocalized electronic system with so-called Y aromaticity.[15]

Table 1: Summary of single-crystal X-ray diffraction structure determination data for **(I)**, **(II)** and **(III)**.

Compound	$Sc[C(CN)_3]_3(H_2O)_3$ (I)	$Y[C(CN)_3]_3(H_2O)_2$ (II)	$La[C(CN)_3]_3(H_2O)_4$ (III)
M_r, g·mol^{-1}	369.22	395.15	481.18
Crystal color	transparent colorless	transparent colorless	transparent colorless
Crystal shape	rectangular plate	irregular block	irregular block
Crystal size, mm^3	0.18 × 0.11 × 0.08	0.22 × 0.18 × 0.14	0.17 × 0.12 × 0.05
Crystal system	triclinic	orthorhombic	monoclinic
Space group (no.) / Z	$P\bar{1}$ (2) / 2	$P2_12_12_1$ (19) / 4	$C2/c$ (15) / 8
Lattice parameters			
a, pm / α, deg	964.740(7) / 70.767(3)	1011.06(7) / 90	2843.17(19) / 90
b, pm / β, deg	1024.26(7) / 64.936(3)	1172.54(8) / 90	789.74(5) / 106.938(3)
c, pm / γ, deg	1096.48(8) / 62.481(3)	1419.21(9) / 90	1812.31(12) / 90
V, Å^3	858.27(11)	1682.5(2)	3892.8(4)
D_{cal}, g·cm^{-3}	1.43	1.56	1.64
$F(000)$, e^-	372	776	1856
μ, mm^{-1}	0.46	3.49	2.2
Diffractometer	STOE Stadivari	Nonius Kappa-CCD	STOE Stadivari
Radiation / λ, pm	Mo-K_α / 71.07	Mo-K_α / 71.07	Mo-K_α / 71.07
Ranges $2\theta_{max}$, deg / h, k, l	66.00 / ±14, ±15, ±6	54.98 / ±13, ±15, ±18	63.62 / ±41, ±11, ±26
Transmission, min. / max.	0.175 / 1.000	0.330 / 0.648	0.643 / 0.801
Data correction	*LP*, STOE Lana[6]	*LP*, Habitus[8]	*LP*, STOE Lana[6]
Measured / unique reflections	37695 / 6097	23423 / 3,815	33481 / 6434
Unique refl. with $F_o > 4\,\sigma(F_o)$	4059	3174	5728
R_{int} / R_σ	0.034 / 0.038	0.090 / 0.051	0.043 / 0.024
Flack parameter	–	−0.029(7)	–
Refined parameters	250	234	267
R_1[a] / wR_2[b] / GoF[c] (all reflections)	0.069 / 0.095 / 0.972	0.052 / 0.061 / 1.048	0.038 / 0.075 / 1.042
Factors x / y (weighting scheme)[b]	0.052 / 0.000	0.0101 / 0.72	0.048 / 3.51
Max. shift, esd, last ref. cycle	<0.001	<0.001	<0.001
$\Delta\rho_{fin}$ (max, min), e^- Å^{-3}	0.25 (73 pm to N32), −0.28 (8 pm to Sc)	0.32 (94 pm to Y), −0.37 (74 pm to Y)	0.96 (72 pm to La), −0.87 (118 pm to La)
CSD number	2386319	2422431	2422430

[a] $R_1 = \Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma(wF_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(xP)^2+yP]$, where $P = [(F_o^2)+2F_c^2]/3$ and x and y are constants adjusted by the program; [c] GoF(S) = $[\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$, with n being the number of reflections and p being the number of refined parameters.

3.2 Crystal structure of $Sc[C(CN)_3]_3(H_2O)_3$ (I)

Compound (**I**) crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with the lattice parameters a = 964.73(7), b = 1024.26(7), c = 1096.48(8) pm, α = 70.767(3), β = 64.936(3), γ = 62.481(3)° for two formula units per unit cell (Table 1). Its crystal structure contains a crystallographically unique Sc^{3+} cation coordinated by three water molecules and four star-shaped tricyanomethanide anions $[C(CN)_3]^-$ forming a distorted pentagonal bipyramid $[ScO_3N_4]$ with their grafting oxygen and nitrogen atoms. Two seven-fold coordinated Sc^{3+} cations are assembled to a dinuclear unit (Figure 4), which represents the entire molecular and crystal structure of $Sc[C(CN)_3]_3(H_2O)_3$. In this centrosymmetric dimer, two $(tcmA)^-$ and $(tcmB)^-$ anions work as terminal ligands with N1A and N1B, while two $(tcmC)^-$ anions link the two Sc^{3+} centers with N1C and N2C (Figure 1) to keep them at a distance of 796.9(1) pm. The molecular dimers $^0_\infty\{(Sc[C(CN_3]_2(H_2O)_3)_2\}$ are arranged with alternating barycenters as shown in Figure 5, held together by a vast hydrogen bond system and some Y-aromatic π-stacking. The former consists of hydrogen bonds between water molecules and nitrogen atoms of $[C(CN)_3]^-$ anions, which are not involved in the Sc^{3+} coordination (H1A···N3C: 204 pm, H1B···N3A: 206 pm, H2A···N2A: 243 pm, H2B···N2B: 182 pm, H3A···N2A: 212 pm, H3B···N3B: 196 pm). Interestingly, even shorter Sc^{3+}···Sc^{3+} distances occur between two dimers (619.4(1) pm, 746.2(1) pm and 779.8(1) pm *plus* 838.5(1) pm) than within these dimers (796.9(1) pm, *vide supra*).

3.3 Crystal structure of $Y[C(CN)_3]_3(H_2O)_2$ (II)

Compound (**II**) crystallizes in the orthorhombic space group $P2_12_12_1$ (no. 19) with the lattice parameters a = 1011.06(7), b = 1172.54(8), c = 1419.21(9) pm and four formula units per unit cell (Table 1). The crystallographically unique Y^{3+} cation, is coordinated by two H_2O molecules and six $[C(CN)_3]^-$

Table 2: Fractional atomic coordinates and equivalent isotropic displacement parameters for $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**, $Y[C(CN)_3]_3(H_2O)_2$ **(II)** and $La[C(CN)_3]_3(H_2O)_4$ **(III)**. All atoms occupy the general *Wyckoff* positions 2*i* for **(I)**, 4*a* for **(II)** and 8*f* for **(III)**.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}/pm²
Sc	0.22753(3)	0.80785(2)	0.27098(2)	307(1)
C0A	0.05660(16)	0.40592(14)	0.82470(14)	382(3)
C1A	0.03588(16)	0.64923(14)	0.19847(14)	386(3)
C2A	0.15008(17)	0.31729(15)	0.91250(14)	410(3)
C3A	0.94147(18)	0.45205(17)	0.24298(15)	477(3)
N1A	0.11206(15)	0.69636(12)	0.21669(14)	465(3)
N2A	0.22542(18)	0.24363(16)	0.98437(16)	640(4)
N3A	0.93915(19)	0.33764(17)	0.30041(17)	754(5)
C0B	0.75057(15)	0.15828(14)	0.16042(14)	373(3)
C1B	0.90568(15)	0.06707(13)	0.17211(13)	354(3)
C2B	0.69759(16)	0.31382(15)	0.13253(16)	458(3)
C3B	0.64159(16)	0.09319(16)	0.17846(15)	436(3)
N1B	0.03344(13)	0.98647(12)	0.18148(13)	446(3)
N2B	0.64916(18)	0.44119(15)	0.10852(19)	754(5)
N3B	0.55038(17)	0.04386(17)	0.19265(17)	665(4)
C0C	0.40643(15)	0.29519(12)	0.49273(13)	331(3)
C1C	0.47690(15)	0.74681(12)	0.44441(13)	343(3)
C2C	0.35288(15)	0.44233(13)	0.42456(13)	338(3)
C3C	0.33419(15)	0.19711(13)	0.50646(14)	367(3)
N1C	0.38221(15)	0.77644(12)	0.39333(13)	480(3)
N2C	0.31094(14)	0.56303(12)	0.36990(13)	433(3)
N3C	0.27342(16)	0.11962(15)	0.51657(15)	561(4)
O1	0.03625(14)	0.85093(12)	0.45648(11)	426(2)
H1A	0.052(2)	0.1233(19)	0.5352(19)	530(50)
H1B	0.957(2)	0.179(2)	0.4735(19)	564(50)
O2	0.44352(13)	0.72975(12)	0.10457(12)	469(2)
H2A	0.495(2)	0.773(2)	0.069(2)	1135(90)
H2B	0.492(2)	0.364(2)	0.8976(19)	675(50)
O3	0.28605(14)	0.00181(11)	0.20347(13)	490(3)
H3A	0.255(2)	0.067(2)	0.1514(19)	674(60)
H3B	0.362(2)	0.002(2)	0.213(2)	825(70)
Y	0.26290(2)	0.21944(2)	0.74654(2)	273(1)
C0A	0.3864(3)	0.4414(3)	0.4270(2)	360(8)
C1A	0.0000(3)	0.0848(3)	0.6238(2)	363(8)
C2A	0.2640(4)	0.4008(4)	0.3953(2)	505(10)
C3A	0.1036(3)	0.4949(4)	0.0105(3)	414(9)
N1A	0.0929(3)	0.1083(3)	0.6659(2)	450(8)
N2A	0.1664(4)	0.3663(4)	0.3686(3)	897(14)
N3A	0.0945(3)	0.4435(3)	0.0782(2)	623(10)
C0B	0.3413(3)	0.2074(3)	0.0846(2)	371(8)
C1B	0.4611(3)	0.2185(3)	0.1329(2)	360(8)
C2B	0.2285(3)	0.1652(3)	0.1300(2)	416(8)
C3B	0.3326(3)	0.2388(3)	0.9892(2)	369(9)
N1B	0.0598(3)	0.2724(3)	0.8280(2)	463(8)
N2B	0.1357(3)	0.1305(3)	0.1658(2)	640(10)
N3B	0.3209(3)	0.2614(3)	0.9117(2)	443(8)
C0C	0.4257(3)	0.0925(3)	0.4335(2)	335(8)
C1C	0.3823(3)	0.1384(3)	0.5188(2)	332(8)
C2C	0.0478(3)	0.3777(3)	0.6060(2)	322(8)
C3C	0.3454(4)	0.0156(3)	0.3840(2)	399(9)
N1C	0.3442(3)	0.1763(3)	0.5880(2)	400(8)
N2C	0.1449(3)	0.3547(3)	0.6422(2)	430(8)
N3C	0.2139(3)	0.0488(3)	0.8399(2)	527(9)
O1	0.4664(2)	0.1397(2)	0.7623(2)	416(6)
H1A	0.004(5)	0.367(5)	0.189(4)	1125(220)
H1B	0.017(4)	0.360(4)	0.283(3)	470(127)
O2	0.3945(3)	0.3777(2)	0.7358(2)	464(7)
H2A	0.386(4)	0.427(3)	0.702(3)	534(147)
H2B	0.469(4)	0.380(3)	0.768(3)	569(124)
La	0.134890(3)	0.142214(12)	0.443774(6)	124.4(4)
C0A	0.42695(7)	0.2093(3)	0.32912(12)	195(4)
C1A	0.41021(7)	0.2840(3)	0.38703(12)	201(4)
C2A	0.39303(8)	0.1589(2)	0.25952(13)	199(4)
C3A	0.47704(8)	0.1668(3)	0.34451(14)	241(4)
N1A	0.39674(8)	0.3448(2)	0.43473(12)	264(4)
N2A	0.36531(8)	0.1192(3)	0.20211(13)	293(4)
N3A	0.48210(9)	0.1331(3)	0.14282(14)	412(6)
C0B	0.05354(7)	0.2074(3)	0.15135(11)	187(4)
C1B	0.07832(8)	0.1783(3)	0.22907(13)	218(4)
C2B	0.00401(8)	0.1620(3)	0.12160(13)	216(4)
C3B	0.07823(7)	0.2888(3)	0.10352(12)	221(4)
N1B	0.09829(8)	0.1554(3)	0.29305(13)	330(5)
N2B	0.03690(8)	0.1260(3)	0.40247(13)	328(5)
N3B	0.09771(9)	0.3556(3)	0.06477(14)	36!(5)
C0C	0.24575(7)	0.2588(2)	0.15246(11)	172(3)
C1C	0.27434(7)	0.3761(2)	0.12606(12)	160(3)
C2C	0.24914(8)	0.2518(3)	0.23136(12)	211(4)
C3C	0.21526(8)	0.1458(2)	0.09932(13)	187(4)
N1C	0.29707(7)	0.4736(2)	0.10288(11)	213(3)
N2C	0.25242(8)	0.2473(3)	0.29580(11)	324(4)
N3C	0.19079(7)	0.0559(3)	0.05411(11)	265(4)
O1	0.39320(7)	0.3441(2)	0.09175(11)	321(4)
H1A	0.4237(18)	0.312(6)	0.102(3)	707(128)
H1B	0.3785(16)	0.274(6)	0.115(2)	666(119)
O2	0.10236(6)	0.4401(2)	0.43977(11)	237(3)
H2A	0.0799(12)	0.476(5)	0.412(2)	338(86)
H2B	0.1057(16)	0.487(6)	0.482(3)	784(138)
O3	0.30426(7)	0.1796(2)	0.45512(11)	298(4)
H3A	0.2910(19)	0.119(6)	0.477(3)	752(150)
H3B	0.2948(17)	0.190(6)	0.407(3)	716(131)
O4	0.18689(6)	0.3484(2)	0.38949(11)	216(3)
H4A	0.2015(13)	0.313(4)	0.363(2)	406(91)
H4B	0.1731(12)	0.432(4)	0.368(2)	394(88)

anions. The attached oxygen and nitrogen atoms are assembled like a distorted trigonal dodecahedron $[YO_2N_6]$ (Figure 6). Only one of the three independent $[C(CN)_3]^-$ anions $(tcmA)^-$ acts as a terminal ligand with N1A, while the remaining two, namely $(tcmB)^-$ and $(tcmC)^-$, link the Y^{3+} centers to create a three-dimensional framework. Thereby, $(tcmB)^-$ is grafted with N1B and N3B, but $(tcmC)^-$ even with N1C, N2C and N3C (Figure 2) in order to provide connections into all three spatial directions ($d(Y^{3+}\cdots Y^{3+})$ = 757.4(1) pm (2×), 791.5(1) pm (2×), 866.3(1) pm (2×), 876.9(1) pm (2×) and 882.2(1)

Table 3: Comparison of selected bond lengths (in pm) and angles (in deg) for $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**, $Y[C(CN)_3]_3(H_2O)_2$ **(II)** and $La[C(CN)_3]_3(H_2O)_4$ **(III)**.

	$Sc[C(CN)_3]_3(H_2O)_3$ (I)	$Y[C(CN)_3]_3(H_2O)_2$ (II)	$La[C(CN)_3]_3(H_2O)_4$ (III)
d(*RE*–O)	209.7(1)	227.1(2)	250.9(2)
	212.3(1)	228.9(3)	252.1(2)
	212.7(1)		254.6(2)
			257.9(2)
d(*RE*–N)	224.0(1)	243.7(3)	261.2(2)
	225.5(1)	244.1(3)	262.7(2)
	225.8(1)	244.8(3)	266.9(2)
	228.0(1)	245.0(3)	266.9(2)
		246.6(3)	268.1(2)
		247.6(3)	
d(C–C)	138.5(2)–140.8(2)	139.1(5)–140.5(4)	139.8(3)–141.0(3)
d(C–N)	113.5(2)–115.2(2)	113.2(5)–115.0(4)	114.3(3)–116.0(3)
∡(C–C–C)	118.5(1)–121.1(1)	118.1(3)–121.9(3)	119.1(2)–121.1(2)
d(O–H)	73(2)–84(2)	79(4)–88(4)	77(4)–88(4)

pm (2×)). Owing to a smaller number of water molecules, the hydrogen bonding system between water molecules and nitrogen atoms of $[C(CN)_3]^-$ anions, which are not involved in the Y^{3+} coordination (H1A···N2A: 203 pm, H1B···N3A: 194 pm, H2A···N2A: 233 pm, H2B···N2B: 193 pm), remains rather simple.

3.4 Crystal structure of $La[C(CN)_3]_3(H_2O)_4$ (III)

Compound (**III**) crystallizes in the monoclinic space group *C*2/*c* (no. 15) with the lattice parameters a = 2843.17(19), b = 789.74(5), c = 1812.31(12) pm and β = 106.938(3)° for eight formula units per unit cell (Table 1). Once again, the crystal structure exhibits just a singular RE^{3+} cation, which carries four water molecules and five $[C(CN)_3]^-$ anions. The resulting $[LaO_4N_5]$ polyhedron resembles a tricapped trigonal prism with O1, O4 and N1A as caps (Figure 7), where the N1A cap represents the nitrogen atom of a terminally attached $[C(CN)_3]^-$ anion, namely $(tcmA)^-$. The remaining two $[C(CN)_3]^-$ anions serve as bidentately grafting ligands, bridging two La^{3+} cations each, $(tcmB)^-$ with N1B and N2B as well as $(tcmC)^-$ with N1C and N3C (Figure 3). In this way the connectivity leads to an infinite chain propagating along the [101] direction as shown in Figure 7 with La^{3+}···La^{3+} distances of 789.9(1) pm (2×). It is worth mentioning that shorter contacts between two La^{3+} cations are found again, such as 649.2(1) pm (1×), but also longer ones, with the shortest of them being 876.9(1) pm (1×). The considerable amount of water molecules provides an extended hydrogen bond system between them and nitrogen atoms of the $[C(CN)_3]^-$ anions, which are not involved in the La^{3+} coordination (H1A···N3A: 214 pm, H1B···N2A: 211 pm, H2A···N3A: 215 pm, H2B···N3B: 201 pm, H3B···N2C: 207 pm, H4A···N2C: 221 pm, H4B···N2A: 205 pm), but also attractive contacts among each other (H3A···O4: 233 pm).

3.5 *Biltz* volume sums versus experimentally determined volumes

In general, the sum of the volume increments is smaller than the volumes determined experimentally by crystallographic means (Table 4). The deviations range between 1.3 and 5.4 %.

Table 4: Comparison of experimentally determined volumes per formula unit (f.u.) with the corresponding *Biltz* volume sums of $RE[C(CN)_3]_3(H_2O)_n$ examples.

Compound	*V*(f.u.) in Å^3	*V*(*Biltz*) in Å^3	SG (no.)	*a* / *b* / *c* (in pm) *α* / *β* / *γ* (in deg)	Reference
$La(tcm)_3(H_2O)_4$	486.6	460.3	*C*2/*c* (15)	2843.07 / 789.84 / 1812.18 90 / 106.936 / 90	This work
$Y(tcm)_3(H_2O)_2$	420.6	403.0	$P2_12_12_1$ (19)	1011.06 / 1172.54 / 1419.21 90 / 90 / 90	This work
$Sc(tcm)_3(H_2O)_3$	429.1	423.3	$P\bar{1}$ (2)	964.74 / 1024.26 / 1096.48 70.767 / 64.936 / 62.481	This work
$La(tcm)_3(H_2O)_5$	453.5	487.3	*P*2/*c* (13)	871.8 / 888.5 / 1270.9 90 / 112.89 / 90	[2]
$Eu(tcm)_3(H_2O)_4$	464.2	458.1	$P2_1/c$ (14)	1402.0 / 768.8 / 1804.1 90 / 107.27 / 90	[2]
$Yb(tcm)_3(H_2O)_2$	416.1	401.6	$P2_12_12_1$ (19)	1006.4 / 1171.3 / 1412.0 90 / 90 / 90	[2]

Table 5: Raman-spectroscopic data of the title compounds $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**, $Y[C(CN)_3]_3(H_2O)_2$ **(II)** and $La[C(CN)_3]_3(H_2O)_4$ **(III)** compared to infrared-spectroscopic data of $Yb[C(CN)_3]_3(H_2O)_2$, $Eu[C(CN)_3]_3(H_2O)_4$ and $La[C(CN)_3]_3(H_2O)_5$.[2] All wavenumbers are given in cm^{-1}; intensity coding: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad.

	$Sc[C(CN)_3]_3(H_2O)_3$ **(I)**	$Y[C(CN)_3]_3(H_2O)_2$ **(II)**	$La[C(CN)_3]_3(H_2O)_4$ **(III)**
δ(C–C_3, i.p.)	422 vw, 476 w	415 vw / 474 w / 491 w	427 vw / 537 vw
δ(C–C≡N, i.p.)	579 vw / 618 w, 697 m	615 w / 687 w / 704 w	603 m / 665 m / 679 m
ν(C–C)	–	1256 w / 1271 w / 1277 w	1253 w / 1379 w / 1441w
ν(C≡N)	2182 vs / 2213 s / 2247 s / 2254 vs / 2264 vs	2181 vs / 2198 vs / 2227 s / 2249 sh / 2265 s	2179 vs / 2195 sh / 2228 sh / 2242 s
$\nu(H_2O)$	2900–3600 br	2900–3700 br	2700–3700 br
	$Yb[C(CN)_3]_3(H_2O)_2$	$Eu[C(CN)_3]_3(H_2O)_4$	$La[C(CN)_3]_3(H_2O)_5$
δ(C–C_3, i.p.)	489 vw	488 sh	–
δ(C–C≡N, i.p.)	569 m / 624 w	566 vs / 618 sh	570 m / 618 w
ν(C–C)	1254–1275 m	1243 vw / 1265 vw	1239 vw / 1264 w
δ(O–H)	1627 s / 1661 s	1651 s	1616 m
ν(C≡N)	2147–2264 vs	2174 vs / 2192 vs / 2202 vs / 2249 sh	2169 vs / 2200 vs / 2242 sh
$\nu(H_2O)$	3000–3600 br	3000–3700 br	3000–3600 br

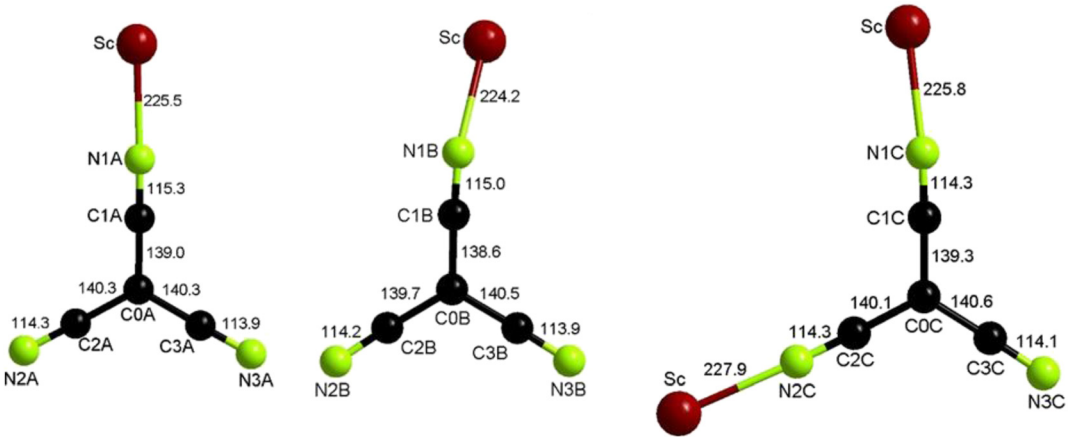

Figure 1: Structure and coordination of the $[C(CN)_3]^-$ anions in $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**.

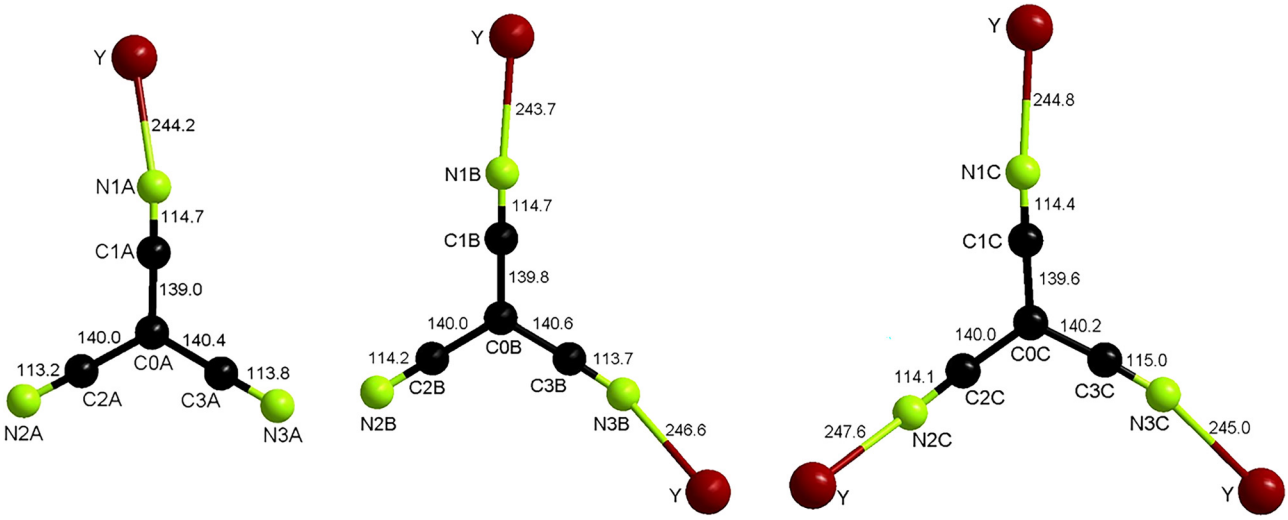

Figure 2: Structure and coordination of the $[C(CN)_3]^-$ anions in $Y[C(CN)_3]_3(H_2O)_2$ **(II)**.

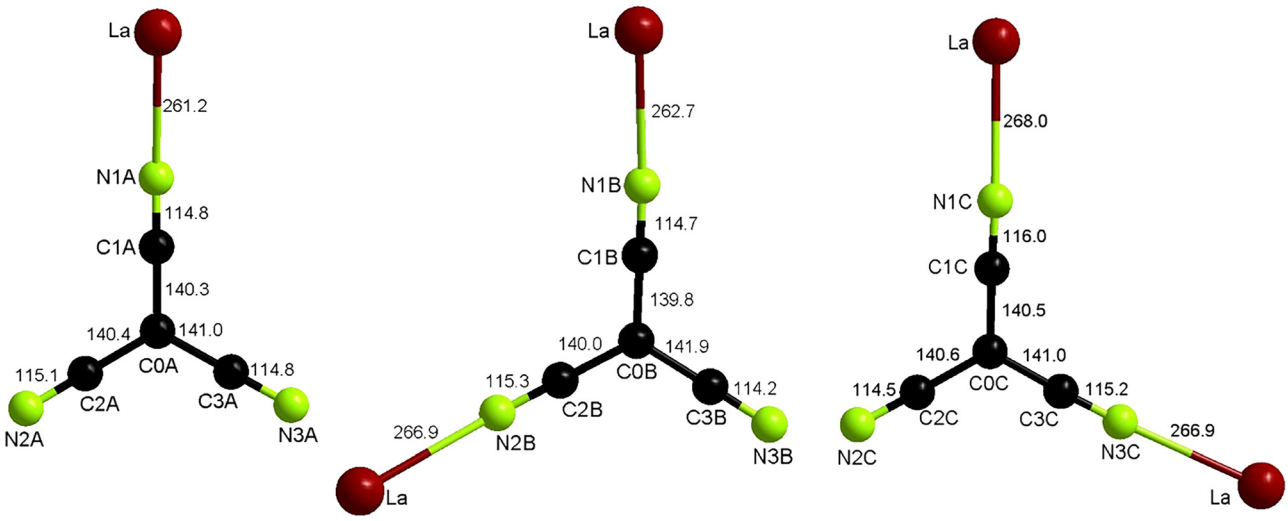

Figure 3: Structure and coordination of the $[C(CN)_3]^-$ anions in $La[C(CN)_3]_3(H_2O)_4$ **(III).**

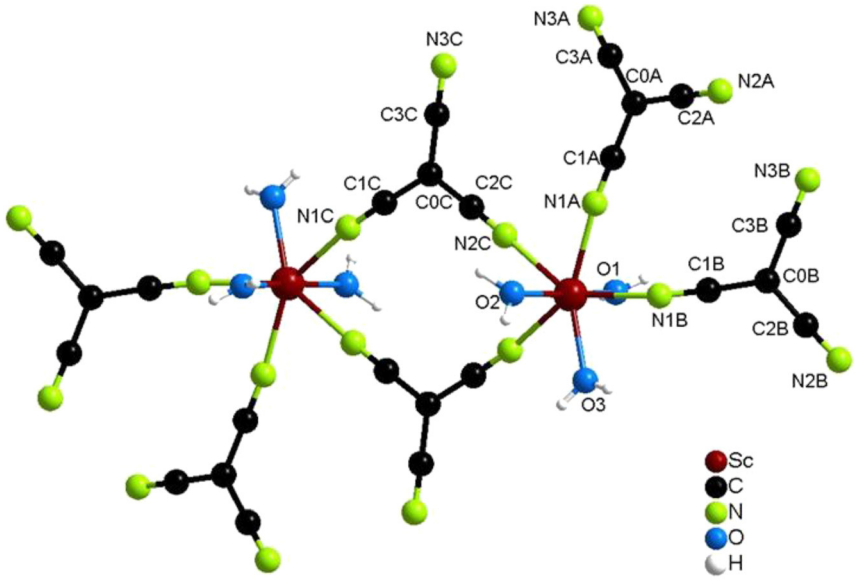

Figure 4: Quasi-molecular dimers in the crystal structure of $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**.

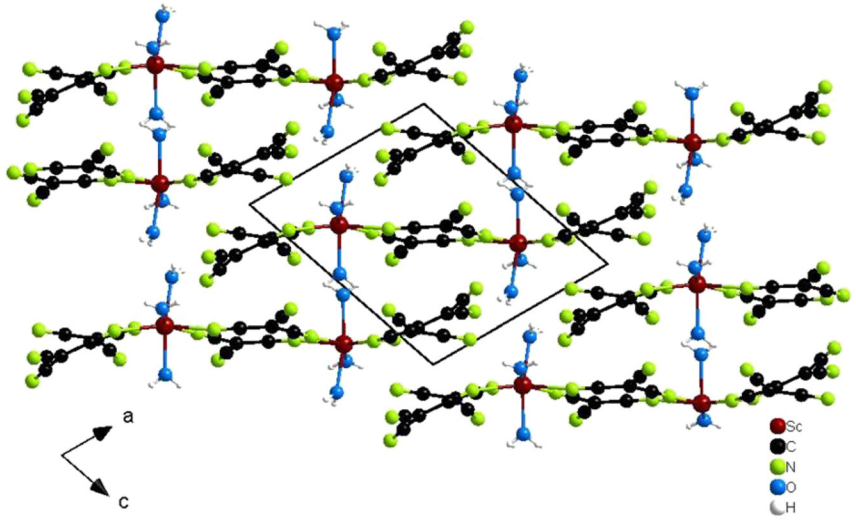

Figure 5: View at the crystal structure of $Sc[C(CN)_3]_3(H_2O)_3$ **(I)** as seen along [010].

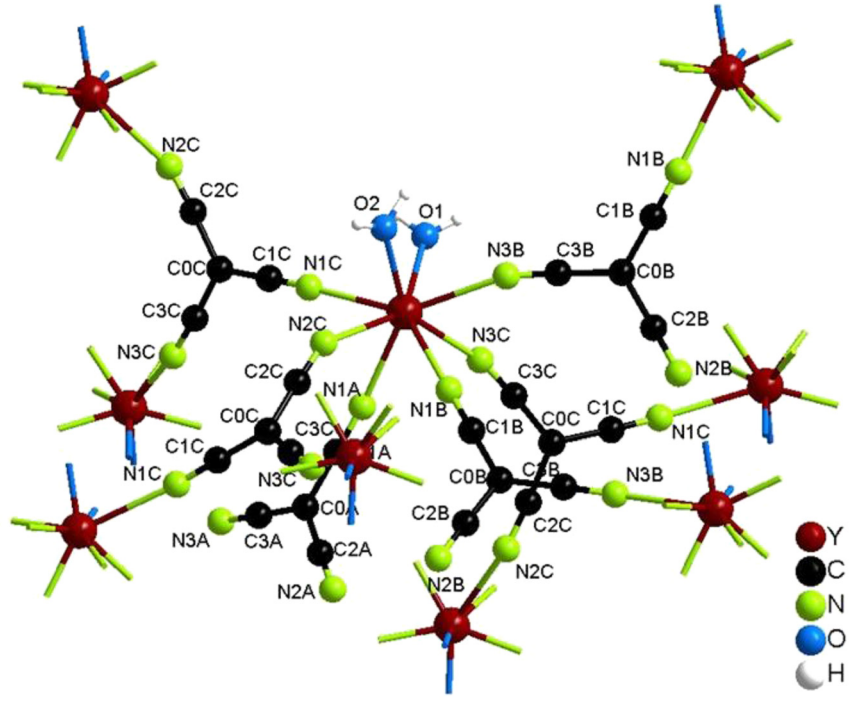

Figure 6: Coordination pattern of Y^{3+} in the crystal structure of $Y[C(CN)_3]_3(H_2O)_2$ **(II)**.

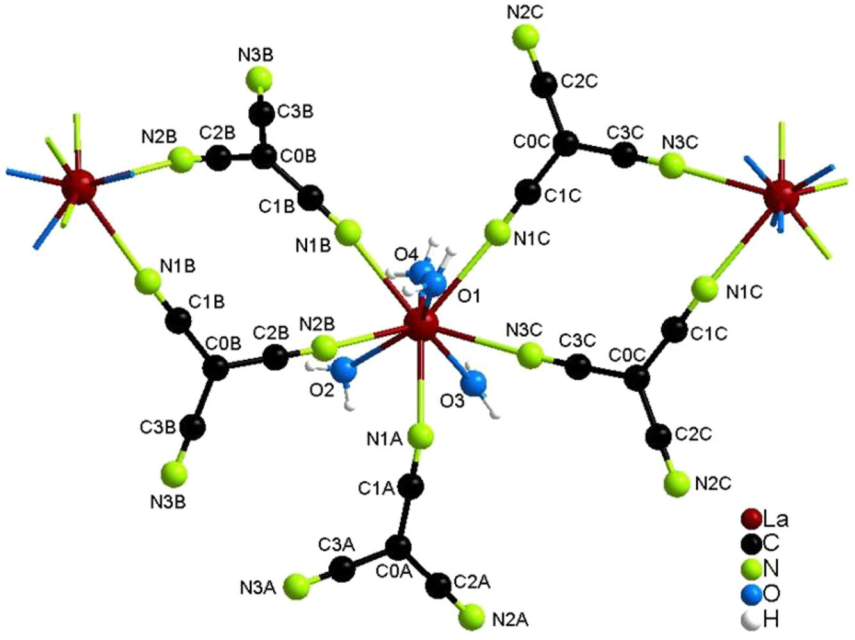

Figure 7: Coordination pattern of La^{3+} in the crystal structure of $La[C(CN)_3]_3(H_2O)_4$ **(III)**.

Since the employed method is rather simple, with no claims to be of highest accuracy, the results can nevertheless be regarded as an indication for the correctness of the respective composition. Only the volume calculated for $La[C(CN)_3]_3(H_2O)_5$[2] is with more than 7.4 % larger than the experimentally determined volume. Since the crystallographic data reported in the doctoral thesis[2] are not unambiguous, if taken just for themselves, the comparison with the data newly acquired by us raises some questions about the reliability of the reported data.

3.6 Raman spectra

The frequencies obtained from the Raman spectra of the three title compounds (Figure 8 and Table 5) are very similar

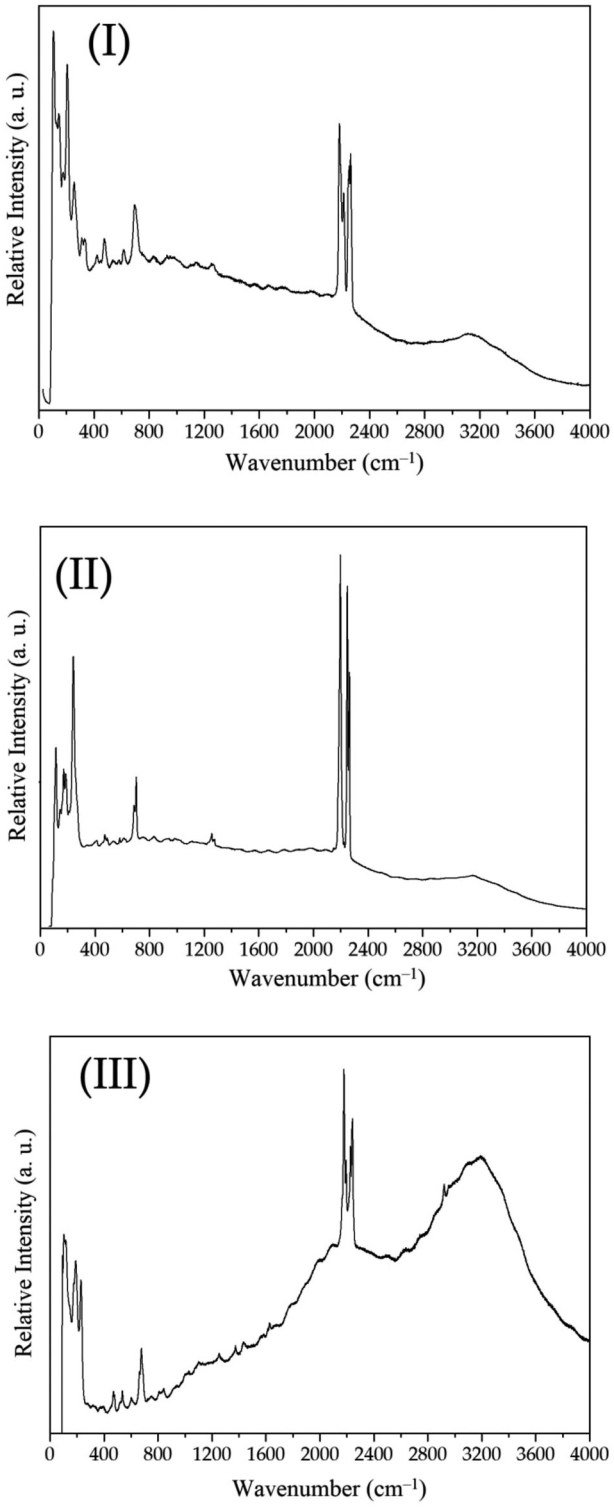

Figure 8: Raman spectra of $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**, $Y[C(CN)_3]_3(H_2O)_2$ **(II)** and $La[C(CN)_3]_3(H_2O)_4$ **(III)**. On the vertical axis, Raman intensities are displayed in arbitrary units. Wavenumbers are given in cm^{-1}.

to those obtained from IR spectra of other $Ln[C(CN)_3]_3(H_2O)_n$[2] examples, corroborating the presence of tricyanomethanide anions. Especially the C≡N stretching modes found around 2200 cm^{-1} are clearly visible and typical for the tricyanomethanide anion next to the less prominent lines around 700 cm^{-1}, representing the C–C≡N in-plane mode of $[C(CN)_3]^-$. The broad humps around 3200 cm^{-1} are characteristic for the presence of crystal water.

4 Conclusions

With $Sc[C(CN)_3]_3(H_2O)_3$ **(I)**, $Y[C(CN)_3]_3(H_2O)_2$ **(II)** and $La[C(CN)_3]_3(H_2O)_4$ **(III)**, three different rare-earth metal tricyanomethanide hydrates $RE[C(CN)_3]_3(H_2O)_n$ were obtained from aqueous solutions and have been characterized by single-crystal X-ray diffraction and Raman spectroscopy. They are not solely distinguished by individual stages of hydration (**(I)** with $n = 3$, **(II)** with $n = 2$, **(III)** with $n = 4$), but also exhibit individual coordination numbers (**(I)** with *C.N.*$(Sc^{3+}) = 7$, 3 × O and 4 × N; **(II)** with *C.N.*$(Y^{3+}) = 8$, 2 × O and 6 × N; **(III)** with *C.N.*$(La^{3+}) = 9$, 4 × O and 5 × N) according to their position in the periodic table of the elements. Based on these facts and with the versatility in the coordination modes of the $[C(CN)_3]^-$ anions, which can serve as both terminal and differently bridging ligands, zero-, one- and three-dimensional crystal structures emerge for **(I)**, **(III)** and **(II)**, respectively. The spectroscopic results reported here are in accordance with a previous report[2], covering *lanthanoid* chemistry of tricyanomethanide hydrates $Ln[C(CN)_3]_3(H_2O)_n$ (*Ln* = La–Lu *ex* Pm), but show some inconsistencies regarding the compositions and the crystal structures. Further research is necessary and should show, which structures and hydratation numbers *n* prevail, since differences in the water content (e.g., for $La[C(CN)_3]_3(H_2O)_4$ reported here as compared to that for $La[C(CN)_3]_3(H_2O)_5$[2]), accompanied by inconsistencies regarding their volumes need to become scrutinized.

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Data availability: Crystallographic data can be obtained as indicated in the manuscript.

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