

# Synthesis, Crystal Structure and Optical Spectra of $\text{Yb}_2[\text{CN}_2]_3$

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Red-orange, transparent single crystals of  $\text{Yb}_2[\text{CN}_2]_3$  [trigonal,  $R\bar{3}c$  (no. 167),  $a = 630.02(3)$  and  $c = 2947.4(2)$  pm,  $Z = 6$ ] are obtained by the reaction of Yb, Sn,  $\text{Zn}[\text{CN}_2]$  and  $\text{NaN}_3$  in arc-welded Nb ampoules at 1100 K. The title compound exhibits characteristic C–N bond lengths and angles [ $d(\text{C–N}) = 122.7(3)$  pm and  $\angle(\text{N–C–N}) = 178.4(5)^\circ$ , respectively] within the  $[\text{N}=\text{C}=\text{N}]^{2-}$  unit as well as the expected fundamental frequencies in its optical spectra (Raman:  $\nu_s = 1338$ ;  $\delta = 643 / 683 / 695 \text{ cm}^{-1}$ ; IR:  $\nu_{as} = 2005 / 2037$ ;  $\delta = 640 / 679 \text{ cm}^{-1}$ ). Since  $\text{Yb}_2[\text{CN}_2]_3$  adopts a corundum-type structure,  $\text{Yb}^{3+}$  is octahedrally coordinated by six N atoms of different  $[\text{CN}_2]^{2-}$  anions [ $d(\text{Yb–N}) = 228.6(3)$  and  $233.4(3)$  pm,  $3 \times$  each] and every  $[\text{CN}_2]^{2-}$  group has four  $\text{Yb}^{3+}$  as next neighbours which form a distorted tetrahedron.

**Key words:** Trivalent Ytterbium, Carbodiimide, Cyanamide, Crystal Structure, Optical Spectroscopy

## Introduction

Nearly 60 years ago, Hartmann *et al.* reported the synthesis of  $\text{La}_2[\text{CN}_2]_3$ , but unfortunately without determining the crystal structure of the compound [1]. Recently, several rare earth carbodiimide compounds of the general formula  $\text{RE}_2[\text{CN}_2]_3$  were synthesized by the metathesis reaction of  $\text{Li}_2[\text{CN}_2]$  and  $\text{RECl}_3$  [2]. Two different structure types were identified: for  $\text{RE} = \text{Y, Pr, Nd, Sm, Gd, Tb, Dy, Ho}$  and  $\text{Er}$  the structure was found to crystallize in the monoclinic space group  $\text{C}2/m$ , for  $\text{RE} = \text{Tm, Yb}$  and  $\text{Lu}$  the trigonal space group  $R\bar{3}2$  was assigned. Both structure types are related and it depends on the cation size which one is adopted.

In this paper, we report an alternative synthesis for  $\text{Yb}_2[\text{CN}_2]_3$ , the X-ray single crystal structure analysis which yields a slightly different structure model than the one reported previously, and the Raman and IR spectra of the title compound.

## Experimental Section

### Synthesis

All manipulations were performed in a glove box under purified argon unless otherwise stated. 350 mg Yb (99.9 %, sublimed, dendritic pieces, Alfa Aesar), 200 mg Sn

(Johnson Matthey, 99.9 %), 20 mg  $\text{NaN}_3$  (99 %, powder, Aldrich, degassed at 400 K under dynamic vacuum for 2 h) and 210 mg  $\text{Zn}[\text{CN}_2]$  [obtained as described in [3] from  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Fluka,  $\geq 99\%$ ),  $\text{H}_2\text{CN}_2$  (Aldrich, 99 %) and  $\text{NaOH}$  (Merck, *p. a.*), dried and degassed at 400 K under dynamic vacuum for 2 h] were arc-welded into a clean Nb container. The metal container was sealed into an evacuated silica tube. The tube was placed upright in a box furnace and heated to 1100 K within 12 h. After 4 d reaction time the furnace was switched off and allowed to cool to r. t. The product contained a ball consisting of Na, Sn and Zn, some unreacted Yb fibers as well as YbN, and red-orange crystals of  $\text{Yb}_2[\text{CN}_2]_3$  (orange brown when ground) which were typically grown on or out of the metal fibers. Variations of the starting stoichiometry and of the reaction parameters did not yield single phase products.  $\text{Yb}_2[\text{CN}_2]_3$  is air and water stable.

### Qualitative elemental analysis

A microprobe analysis of the red-orange plate which was also used for the X-ray data measurements was made with an EDAX (ThermoNoran) equipped scanning electron microscope (Jeol JXA-8900R). It indicated only the presence of Yb. No other elements with  $Z \geq 10$  were detected.

### Crystallographic studies

Samples of the reaction mixture were removed from the glove box in polybutene oil for single crystal selection. A

Table 1. Details of the X-ray single crystal structure determination on Yb<sub>2</sub>[CN<sub>2</sub>]<sub>3</sub>.

Compound	Yb <sub>2</sub> [CN <sub>2</sub> ] <sub>3</sub>
Space group (No.), <i>Z</i>	<i>R</i> 3 <i>c</i> (167), 6
CSD number	416892
Lattice parameters: <i>a</i> , <i>c</i> , pm	630.02(3), 2947.4(3)
Calculated density, g cm <sup>-3</sup>	4.58
Crystal colour	transparent red-orange
Crystal shape	rectangular plate
Crystal size [mm <sup>3</sup> ]	0.12 × 0.10 × 0.03
Diffractometer	Bruker X8 Apex II equipped with a 4 K CCD
Radiation	MoK <sub>α</sub> (λ = 71.073 pm), graphite monochromator, 170(2) K
2θ <sub>max</sub> -Range	72.60°
<i>h</i> , <i>k</i> , <i>l</i> -Range	−10 → 9, −10 → 6, −48 → 39
Distance detector-crystal, mm	41
Number of frames	1429
Exposure time, s	20
Data correction	LP, SADABS [6]
μ, mm <sup>-1</sup>	27.5
Measured reflections	3492
Unique reflections	553
Unique reflections with <i>F</i> <sub>o</sub> ≥ 4σ( <i>F</i> <sub>o</sub> )	345
<i>R</i> <sub>int</sub>	0.0284
Refined parameters	19
Weight factors <i>x</i> / <i>y</i>	0.0185 / 0
<i>R</i> 1 <sup>a</sup> / <i>wR</i> 2 <sup>a</sup> / GooF <sup>a</sup> (all refl.)	0.0286 / 0.0360 / 0.980
Max. shift / esd, last refinement cycle	0.0001
Res. electron density: max, min	1.61 e Å <sup>-3</sup> , 285 pm to N; −1.39 e Å <sup>-3</sup> , 75 pm to Yb

<sup>a</sup> *R*1 = Σ||*F*<sub>o</sub>|| − ||*F*<sub>c</sub>|| / Σ||*F*<sub>o</sub>||; *wR*2 = [Σ*w*(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>)<sup>2</sup> / Σ(*wF*<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>; *w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (*xP*)<sup>2</sup> + *yP*] with *P* = [(*F*<sub>o</sub><sup>2</sup>) + 2*F*<sub>c</sub><sup>2</sup>]/3; GooF: *S* = [Σ*w*(*F*<sub>o</sub><sup>2</sup> − *F*<sub>c</sub><sup>2</sup>)<sup>2</sup> / (*n* − *p*)]<sup>1/2</sup>, with *n* being the number of reflections and *p* the number of parameters.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters of Yb<sub>2</sub>[CN<sub>2</sub>]<sub>3</sub>.

Atom	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (pm <sup>2</sup> )
Yb	12 <i>c</i>	0	0	0.16423(1)	51(1)
C	18 <i>e</i>	0.2977(7)	0	1/4	91(8)
N	36 <i>f</i>	0.5976(5)	0.0037(5)	0.0437(1)	105(5)

suitable specimen of Yb<sub>2</sub>[CN<sub>2</sub>]<sub>3</sub> was selected under a polarization microscope, mounted in a drop of polybutene oil sustained in a plastic loop, and placed onto the goniometer. A cold stream of nitrogen (*T* = 170(2) K) froze the polybutene oil, thus keeping the crystal stationary and protected from oxygen and moisture in the air. Preliminary examination and subsequent data collection were performed on a Bruker X8 Apex II diffractometer equipped with a 4 K CCD detector and graphite-monochromated MoK<sub>α</sub> radiation (λ = 71.073 pm). The orientation matrix and the respective rhombohedral cell constants (trigonal R-centered setting) were obtained by using APEX2 [4]. The program SAINT [5] was used to integrate the data. An empirical absorption correction was

Table 3. Anisotropic displacement parameters *U*<sub>ij</sub><sup>a</sup> (pm<sup>2</sup>) of Yb<sub>2</sub>[CN<sub>2</sub>]<sub>3</sub>.

Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>
Yb	61(1)	<i>U</i> <sub>11</sub>	30(1)	0	0	1/2 × <i>U</i> <sub>11</sub>
C	92(14)	156(23)	60(22)	−17(19)	−1(1)	78(11)
N	96(13)	167(14)	50(14)	−17(12)	−6(11)	52(12)

<sup>a</sup> The anisotropic displacement factor takes the form: *U*<sub>ij</sub> = exp[−2π<sup>2</sup>(*h*<sup>2</sup>*a*<sup>\*2</sup>*U*<sub>11</sub> + *k*<sup>2</sup>*b*<sup>\*2</sup>*U*<sub>22</sub> + *l*<sup>2</sup>*c*<sup>\*2</sup>*U*<sub>33</sub> + 2*hka*<sup>\*</sup>*c*<sup>\*</sup>*U*<sub>13</sub> + 2*hka*<sup>\*</sup>*b*<sup>\*</sup>*U*<sub>12</sub>)].

Table 4. Selected bond lengths and angles of Yb<sub>2</sub>[CN<sub>2</sub>]<sub>3</sub>.

Atoms	Multiplicity	<i>d</i> (pm)	Atoms	Multiplicity	<i>d</i> (pm)
Yb–N	3 ×	228.6(3)	N–C	1 ×	122.7(3)
	N	3 ×	Yb	1 ×	228.6(3)
C–N	2 ×	122.7(3)	Yb	1 ×	233.4(3)
∠(N–C–N)	1 ×	178.4(5)°			

applied using SADABS [6]. The initial input file for solving the crystal structure was prepared by XPREP [7]. This program suggested *R*3*c* (no. 161) and *R*3̄*c* (no. 167) only as possible space groups following the systemic absences (00*l* = 6*n*). The only satisfactory refinement was achieved in the centrosymmetric space group *R*3̄*c*. The initial Yb position was obtained by using Direct Methods in SHELXS-97 [8], the C and N positions were apparent from the positions of highest electron density on the difference Fourier map resulting from the first refinement cycle by full-matrix least-squares techniques with the use of SHELXL-97 [9]. Upon further refinement cycles, the refinement converged and resulted in a stable model for the crystal structure. Additional crystallographic details are described in Table 1. Atomic coordinates and equivalent isotropic displacement coefficients are shown in Table 2, Table 3 displays the anisotropic displacement parameters, and selected bond lengths and angles are listed in Table 4.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-416892.

#### Raman and IR spectroscopy

Single crystals in an evacuated and sealed pyrex tube were used for the Raman investigations [microscope laser Raman spectrometer: Jobin Yvon, 4 mW, excitation line at λ = 632.817 nm (HeNe laser), 20× magnification, 3 × 60 s accumulation time]. The symmetric stretching mode and the bending mode were found to be at ν<sub>s</sub> = 1338 and δ = 643 / 683 / 695 cm<sup>-1</sup>, respectively (Fig. 1). The IR spectrum (Bruker AFS 66 FT-IR, ground product with KBr pellet technique) showed the asymmetric stretching vibrations at ν<sub>as</sub> = 2005 / 2037 and the bending vibrations δ = 640 / 679 cm<sup>-1</sup> (Fig. 1).

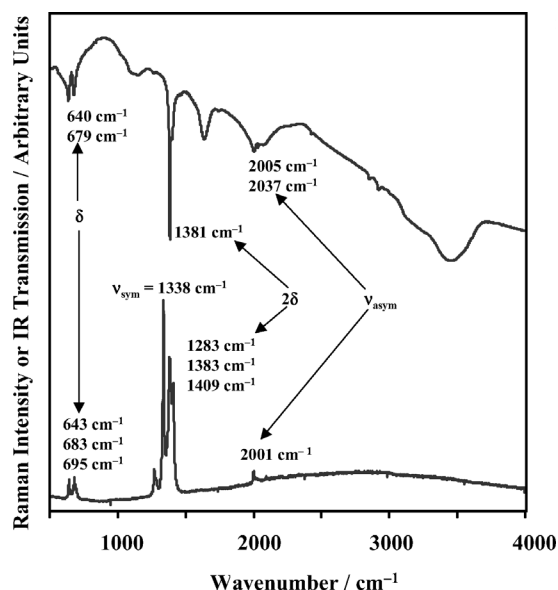


Fig. 1. Raman and IR spectrum of  $\text{Yb}_2[\text{CN}_2]_3$  (for details, see text).

## Results and Discussion

### Crystal structure

The crystal structure can be described emphasizing the cationic or the anionic partial structure. The  $[\text{CN}_2]^{2-}$  anions form a hexagonal close packing of these  $[\text{N}=\text{C}=\text{N}]^{2-}$  “sticks” which are tilted by approximately  $18.5^\circ$  from the crystallographic  $c$  axis.  $\text{Yb}^{3+}$  occupies 2/3 of the octahedral voids. This is essentially a corundum-type structure as is adopted by  $\text{Yb}_2\text{S}_3$  [ $R\bar{3}c$ ,  $a = 674.97(2)$  and  $c = 1820.11(9)$  pm,  $Z = 6$ ] [10]. The  $c$  axis reported for  $\text{Yb}_2\text{S}_3$  is nearly 1130 pm shorter than the one we found for  $\text{Yb}_2[\text{CN}_2]_3$  (Table 1) which is due to the differing sizes of the more or less spherical sulfide anions ( $\text{S}^{2-}$ ) as compared to the rod-like carbodiimide units ( $[\text{N}=\text{C}=\text{N}]^{2-}$ ) which are aligned nearly parallel to the  $c$  axis. The  $D_{\infty h}$  symmetry typical for a carbodiimide is found within the range of crystallographic resolution. The results of the crystal structure analysis are corroborated by the spectroscopic data, the symmetric stretching vibration being only found in the Raman spectrum as expected for molecules or ions with  $D_{\infty h}$  symmetry. As others have also observed,  $[\text{CN}_2]^{2-}$  can be considered a *pseudo*-chalcogenide anion.

The arrangement of the cations in  $\text{Yb}_2[\text{CN}_2]_3$  (Fig. 2) is related to the  $\text{Ca}[\text{CN}_2]$ -type [11] which is adopted by many ternary carbodiimides contain-

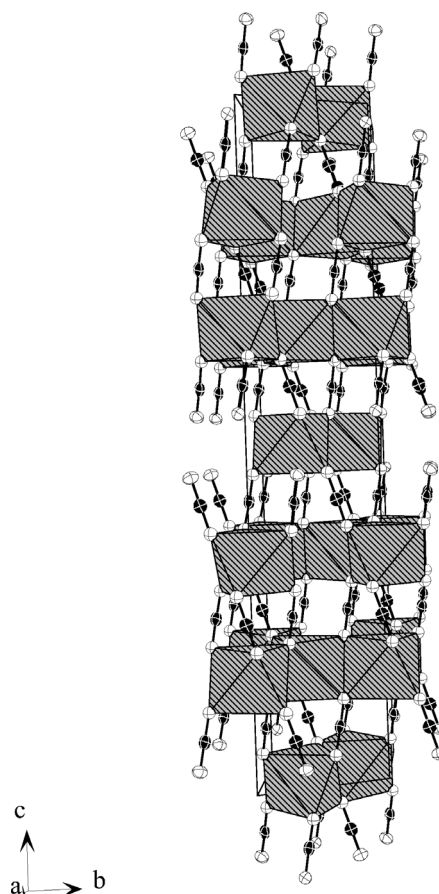


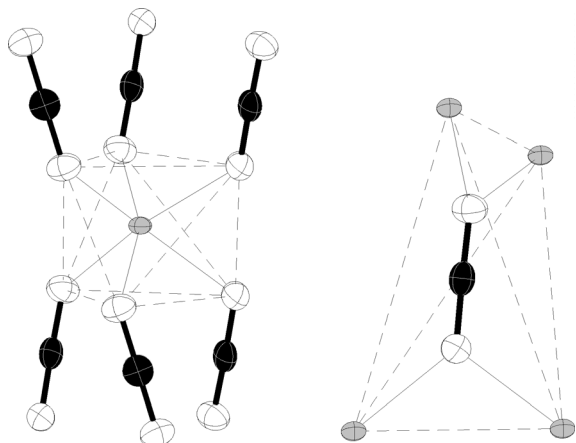
Fig. 2 Perspective view of the unit cell of  $\text{Yb}_2[\text{CN}_2]_3$  along the crystallographic  $a$  axis. The coordination polyhedra about  $\text{Yb}^{3+}$  are drawn as grey, hatched octahedra, C and N are displayed as crossed light grey, black and white circles, respectively. Displacement ellipsoids are drawn at the 95 % probability level.

ing divalent cations such as  $\text{Mg}^{2+}$  [12],  $\text{Sr}^{2+}$  [13],  $\text{Mn}^{2+}$  [14] or  $\text{Cd}^{2+}$  [15]. In these compounds, the  $\text{M}^{2+}$  cations form a cubic close packing with the stacking sequence  $\cdots \text{ABCABC} \cdots$ . In  $\text{Yb}_2[\text{CN}_2]_3$  the metal atoms still have the same stacking sequence, but due to the different charge of the cation each layer is lacking 1/3 of metal cations in a perfectly ordered way compared to the two-dimensionally close packed layers. The same kind of arrangement is known for the carbon layers in  $\beta$ - or 3R-graphite. The  $\text{Yb}^{3+}$  layers are held together by the triatomic  $[\text{CN}_2]^{2-}$  anions.

The crystal structures reported for  $\text{RE}_2[\text{CN}_2]_3$  ( $\text{RE} = \text{Tm}$ ,  $\text{Yb}$  and  $\text{Lu}$ ) [2] and the one we determined for  $\text{Yb}_2[\text{CN}_2]_3$  are very similar and closely symmetry related to each other. Some indications for this can be

Table 5.  $RE-N$  bond lengths in  $RE_2[\text{CN}_2]_3$  compounds.

Compound	Multiplicity	$d(RE-N)$ (pm)	Reference
$\text{Sm}_2[\text{CN}_2]_3$	$1\times / 1\times$	238.2(6) / 246.0(7)	[2]
	$2\times / 2\times$	247.9(4) / 249.8(4)	
	$1\times$	254.4(6)	
$\text{Lu}_2[\text{CN}_2]_3$	$3\times / 3\times$	228.2(7) / 232.5(6)	[2]
$\text{Yb}_2[\text{CN}_2]_3$	$3\times / 3\times$	228.6(3) / 233.4(3)	this work

Fig. 3. Coordination environment of the  $\text{Yb}^{3+}$  cation (left) and the  $[\text{N}=\text{C}=\text{N}]^{2-}$  anion (right).

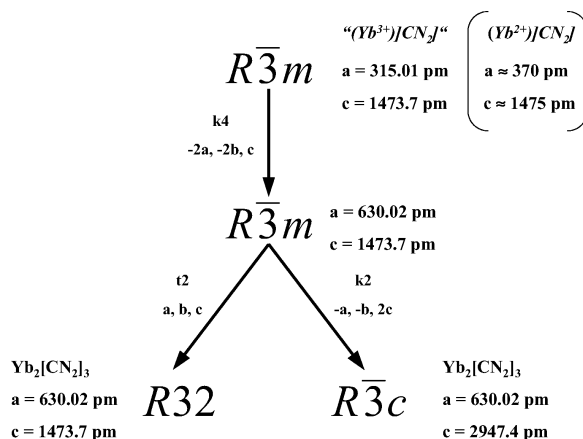
found looking at the  $RE-N$  distances and the sixfold octahedral coordination of the respective  $RE^{3+}$  which are virtually the same (Fig. 3 and Table 5). If the symmetry of the space groups and the lattice constants are inspected, it can be found that both structures are subgroups of  $R\bar{3}m$  with  $a = 630.02$  and  $c = 1473.7$  pm which is a  $k4$  (“*klassengleich*”) subgroup to the aforementioned  $\text{Ca}[\text{CN}_2]$  structure (Fig. 4). A re-integration of our intensity data assuming the smaller lattice parameters (Fig. 4) showed that this new data set can be refined yielding virtually the same structure as described above. Here the C and the N positions are not fully occupied and have both a site occupation factor of 50% which leads to the correct stoichiometry  $\text{Yb}_2[\text{CN}_2]_3$ . To get a “disorder free” description, the symmetry has to be lowered either by a  $t2$  (“*translationsgleich*”) transition (leaving out the mirror plane perpendicular to the twofold axis) as done in  $RE_2[\text{CN}_2]_3$  ( $RE = \text{Tm}, \text{Yb}$  and  $\text{Lu}$ ) [2] or by a  $k2$  transition as in our description (Fig. 4).

According to this reasoning, the lattice parameters for the virtual and unbalanced compound “ $(\text{Yb}^{3+})[\text{CN}_2]_3$ ” can be derived without problems assuming that it adopts the  $\text{Ca}[\text{CN}_2]$  structure type (Fig. 4). If the trivalent metal atom is replaced by its

Table 6. Lattice parameters of carbodiimide compounds adopting the corundum-type structure.

Compound	$a$ (pm)	$c$ (pm)	Reference
$\text{Tm}_2[\text{CN}_2]_3$	633.93	2953.2 <sup>a</sup>	[2]
$\text{Yb}_2[\text{CN}_2]_3$	629.4	2944.6 <sup>a</sup>	[2]
$\text{Lu}_2[\text{CN}_2]_3$	627.23	2941.6 <sup>a</sup>	[2]
$\text{In}_{2.24}[\text{CN}_2]_3$	606.09	2884.4	[16]
$\text{Yb}_2[\text{CN}_2]_3$	630.02	2947.4	This work

<sup>a</sup> Transformed from the original lattice parameters given in [2].

Fig. 4. Symmetry relationship of the different  $RE_2[\text{CN}_2]_3$  crystal structure descriptions on the example of  $\text{Yb}_2[\text{CN}_2]_3$ . For more details, see text.

divalent form to get “ $(\text{Yb}^{2+})[\text{CN}_2]_3$ ”, we expect the lattice parameters to be close to  $a \approx 370$  and  $c \approx 1475$  pm due to the larger ionic radius of  $\text{Yb}^{2+}$  and the  $[\text{CN}_2]^{2-}$  rods now being parallel to the  $c$  axis.

It is also interesting to note that symmetry and stoichiometry of the title compound are very similar to those found in  $\text{In}_{2.24}[\text{CN}_2]_3$  [16]. This compound contains both  $\text{In}^+$  and  $\text{In}^{3+}$  and if we apply the “anionic description”, the  $[\text{CN}_2]^{2-}$  units form again a corundum-type hexagonal close packing in which *all* octahedral voids are occupied by the indium cations (at least based on a description with fully occupied In positions). The similarity becomes even more obvious if one compares the lattice parameters of ternary carbodiimide compounds containing trivalent metal cations (Table 6).

## Conclusion

$\text{Yb}_2[\text{CN}_2]_3$  adopts a corundum-type structure and can be regarded as symmetry-related to the one of  $\text{Lu}_2[\text{CN}_2]_3$  reported recently [2], since both stem from the same superstructure which itself is related to the

$\text{Ca}[\text{CN}_2]$  structure type. The title compound shows the typical geometrical features of a carbodiimide containing  $[\text{CN}_2]^{2-}$  unit with  $D_{\infty h}$  symmetry. While the optical spectroscopy yielded asymmetric and bending modes in the expected range [17], the symmetric stretching mode is with  $\nu_s = 1338 \text{ cm}^{-1}$  the highest value reported so far. The formerly highest recorded symmetric stretching mode was observed for  $\text{Mg}[\text{CN}_2]$  with  $\nu_s = 1301 \text{ cm}^{-1}$  [12]. The data tabulated in [17] show that the higher frequency stretching modes are obtained when the cations are small and have a large formal charge. The relatively small trivalent  $\text{Yb}^{3+}$  therefore shows the symmetric stretching mode at higher wavenumbers than previously observed, but we would expect the mode in  $\text{Lu}_2[\text{CN}_2]_3$  to occur at

an even higher wavenumber and venture to predict  $\text{Sc}_2[\text{CN}_2]_3$  to mark the record among all rare earth metal(III) carbodiimides.

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