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$LaSr_3F_5(CN_2)_2$: A Prototype Structure for Mixed-Valent $Eu_4F_5(CN_2)_2$

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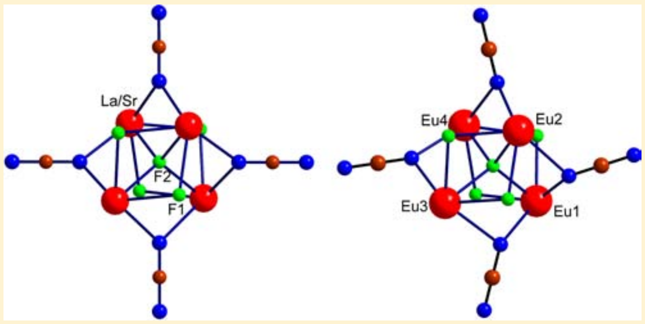
Supporting Information

ABSTRACT: The new compound $LaSr_3F_5(CN_2)_2$ was prepared and structurally characterized as a prototype structure for the remarkably distorted mixed-valent compound $Eu_4F_5(CN_2)_2$, which contains four distinct europium ions in the structure: one Eu^{3+} and three Eu^{2+}. Instead of repeating the given distorted structural pattern, $LaSr_3F_5(CN_2)_2$ forms a structure which can be considered as an ideal high-symmetry structure for $Eu_4F_5(CN_2)_2$, due to the occupation of La^{3+} and Sr^{2+} ions on one and the same crystallographic position. The crystal symmetry of this structure is an interesting issue to compare with what has been previously proposed.



INTRODUCTION

The mixed-valent compound $Eu_4F_5(CN_2)_2$ has been recently prepared and its crystal structure was refined by single-crystal diffraction in space group $P\bar{4}2_1c$ ($Z = 8$).[1] The presence of trivalent and divalent europium ions in 1:3 ratio was confirmed by ^{151}Eu−Mössbauer spectroscopy. The refined crystal structure of $Eu_4F_5(CN_2)_2$ contains four crystallographically distinct europium ions (Figure 1).

An analysis of the coordination environments of the europium ions has led to the assumption that one europium site (Eu1) in mixed-valent $Eu^{(3+)}Eu_3{}^{(2+)}F_5(CN_2)_2$ can be addressed as Eu^{3+}. A closer inspection of the crystal structure also revealed that a higher symmetry could be likely to appear if all europium ions would be slightly shifted and become crystallographically equivalent, and more eye-catching, if the $[N{=}C{=}N]^{2-}$ ions would be rotated relative to each other, also to become equivalent. A reversible thermal effect (near 600 °C) obtained in a DTA measurement of $Eu_4F_5(CN_2)_2$ was considered to represent a possible indication for a high symmetry structure to occur.

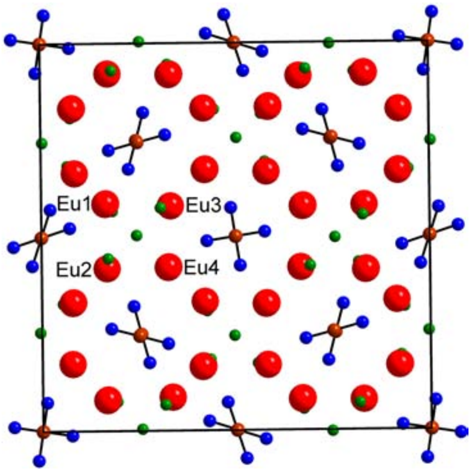


Figure 1. Crystal structure of $Eu_4F_5(CN_2)_2$ (space group $P\bar{4}2_1c$, $Z = 8$). The structure contains four crystallographically distinct $Eu^{2+/3+}$ cations (red), five distinct F^- ions (green), and three distinct carbodiimide ions (C brown and N blue).

In order to propose the space group of an idealized structure of $Eu_4F_5(CN_2)_2$, all atoms in the crystal structure were manually moved to what was considered as their *ideal* positions, and a reduced cell with $a' = a/2$, $b' = b/2$, and $c' = c$ was derived therefrom (Figure 2, center). The shifts of Eu and F ions are barely detectible when comparing the drawings of Figures 1 and 2 (center), but the rotations of $[N{=}C{=}N]^{2-}$ ions are obvious. A symmetry assignment of the structure displayed in Figure 2 (center) with the program system MISSYM[2] gave a 100% match for the space group $I\bar{4}2m$ ($Z =$

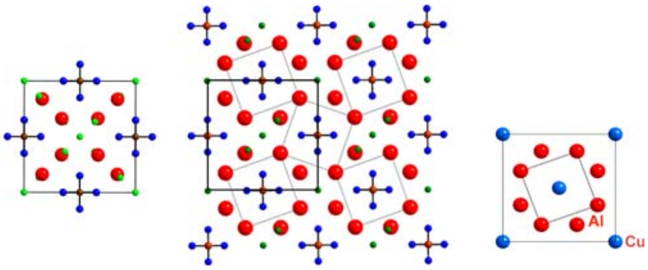


Figure 2. Projected crystal structure of $LaSr_3F_5(CN_2)_2$, space group $I\bar{4}2m$, $Z = 2$ (at left), idealized structure of $Eu_4F_5(CN_2)_2$, space group $I\bar{4}2m$, $Z = 2$ (center), and crystal structure of $CuAl_2$, space group $I4/mcm$, $Z = 2$ (right). The color code is as given in Figure 1.

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2) which was considered to represent the *idealized* space group for $Eu_4F_5(CN_2)_2$ in which all Eu ions (and carbodiimide ions) would be crystallographically equivalent.

A group−subgroup symmetry reduction was performed by space group theory from $I4/mcm$ (Z = 2) departing from the $CuAl_2$ structure (Figure 2), in which the positions of aluminum and copper atoms represent the distributions of europium and carbon atoms in the $Eu_4F_5(CN_2)_2$ structure, down to the (refined) space group $P\bar{4}2_1c$ of $Eu_4F_5(CN_2)_2$. Positions of nitrogen atoms of carbodiimide, and of fluoride ions, were introduced. However, what is considered as the ideal space group ($I\bar{4}2m$) was missed throughout the stepwise space group reduction, when departing from the designated high symmetry structure ($CuAl_2$).[1]

In the present work, we attempted to prepare a compound corresponding to the formula $La^{3+}M_3^{2+}F_5(CN_2)_2$ which was expected to reveal a distinction between cations, and thus could serve as an archetype for the distribution of europium ions in the parent $Eu^{(3+)}Eu_4{}^{(2+)}{}_3F_5(CN_2)_2$ structure.

EXPERIMENTAL SECTION

Synthesis. All manipulations of starting materials were performed in an argon filled glovebox. The new compound $LaSr_3F_5(CN_2)_2$ was prepared from carefully ground mixtures of LaF_3, SrF_2 (Riedel de Haen 99.99%), and Li_2CN_2 according to stoichiometric amounts given in reaction I. In another approach, $LaSr_3F_5(CN_2)_2$ was prepared by a reaction of LaF_3 with $SrCN_2$ according to reaction II. $SrCN_2$ was prepared by an ammonolysis reaction of $SrCO_3$ in a corundum vessel in a flow of dry NH_3 at 700 °C for 24 h.

The reaction mixtures (total mass: 250 mg) were loaded into clean copper tubes and sealed therein. The copper ampules were sealed into silica tubes under vacuum. Reactions of the mixtures were performed under similar conditions as previously reported for $Eu_4F_5(CN_2)_2$ by heating to 650 °C (2 °C/min) and annealing at this temperature for 2 days before cooling to room temperature (1 °C/min).

$$LaF_3 + 3SrF_2 + 2Li_2CN_2 \rightarrow LaSr_3F_5(CN_2)_2 + 4LiF \quad \text{(I)}$$

$$LaF_3 + SrF_2 + 2SrCN_2 \rightarrow LaSr_3F_5(CN_2)_2 \quad \text{(II)}$$

Products of both reactions were consistent with what is given in reactions I and II. Some unreacted SrF_2 was always present in the reaction product. Single-crystals of $LaSr_3F_5(CN_2)_2$ were obtained from reaction II after an additional heating step at 700 °C for one day.

X-ray Diffraction. Transparent single-crystals of $LaSr_3F_5(CN_2)_2$ were selected in air and fixed on the tip of a glass fiber for a single-crystal diffraction measurement (Stoe IPDS diffractometer, graphite monochromatized Mo Kα radiation) at room temperature (Table 1). Intensities were corrected for Lorentz factors, polarization, and absorption effects. $LaSr_3F_5(CN_2)_2$ was found to crystallize tetragonally with the space group $I\bar{4}2m$ (Z = 2). The crystal structure solution was performed with direct methods (SHELXS), and the refinement by full matrix least-squares refinements (SHELXL-97).[3] Atom positions are given in Table 2, and selected interatomic distances are provided in Table 3.

Table 1. Data from the Single-Crystal Structure Refinement of $LaSr_3F_5(CN_2)_2$

	chemical formula
	$LaSr_3F_5(CN_2)_2$
crystal system	tetragonal
a	8.086(2) Å
c	6.580(2) Å
Z	2
formula weight	576.83 g/mol
space group	$I\bar{4}2m$
T	293(2) K
λ	0.71073 Å
d_{calc}	4.45 g/cm^3
μ	23.4 1/mm
R_1, wR_2 (all data)	0.020, 0.056

Table 2. Atom Positions and Isotropic Equivalent Displacement Parameters (Å^2) in the Crystal Structure of $LaSr_3F_5(CN_2)_2$

	Wyckoff site	x	y	z	U_{eq}
La(1), Sr(1)[a]	8i	1627(1)	x	2556(1)	13(1)
C(1)	4c	0	1/2	0	23(2)
N(1)	8f	0	0.6493(8)	0	57(3)
F(1)	8i	3661(4)	x	1325(6)	23(1)
F(2)	2a	0	0	0	19(2)

[a] The mixed La(1) and Sr(1) site occupation was refined with a fixed 1:3 molar ratio, corresponding to $LaSr_3F_5(CN_2)_2$.

Table 3. Selected Interatomic Distances (Å) and Their Multiplicities (×) in the Crystal Structure of $LaSr_3F_5(CN_2)_2$

La(1), Sr(1)−F(1)	2.463(4)	1×
La(1), Sr(1)−F(1)	2.502(4)	1×
La(1), Sr(1)−F(1)	2.520(3)	2×
La(1), Sr(1)−F(2)	2.5076(7)	1×
La(1), Sr(1)−N(1)	2.621(4)	2×
N(1)−C(1)	1.207(6)	2×

The X-ray powder diffraction data of all samples were collected on a Stoe StadiP diffractometer using Ge-monochromatized Cu Kα1 radiation. The powder pattern of $LaSr_3F_5(CN_2)_2$ was indexed tetragonally (a = 8.0912(1) Å, c = 6.5901(1) Å), and a structure refinement was performed with the WinPlotr (FullProf)[4] program package, using the results from the single-crystal structure refinement. The structure refinement with WinPlotr (FullProf) took into account SrF_2 as side phase (Figure 3).

RESULTS AND DISCUSSION

In this work, we have prepared the new compound $LaSr_3F_5(CN_2)_2$ and refined its crystal structure (Table 1) which is reported here. The uniform character of the obtained samples was demonstrated by a Rietveld refinement (Figure 3). The crystal structure of $LaSr_3F_5(CN_2)_2$ is closely related to the reported crystal structure of $Eu_4F_5(CN_2)_2$. It turns out that the structure of $LaSr_3F_5(CN_2)_2$ perfectly represents what has been considered as an idealized structural arrangement for the previously reported compound $Eu_4F_5(CN_2)_2$. Crystals of mixed-valent $Eu_4F_5(CN_2)_2$ appear deep red, and crystals of $LaSr_3F_5(CN_2)_2$ appear colorless and transparent. The space group $P\bar{4}2_1c$ (Z = 8) of $Eu_4F_5(CN_2)_2$ is a *klassengleich* subgroup of the space group $I\bar{4}2m$ (Z = 2) of $LaSr_3F_5(CN_2)_2$.

Interestingly, strontium and lanthanum ions share the same 8i position in the structure of $LaSr_3F_5(CN_2)_2$ revealing a completely mixed occupation (Table 2). No indication was found for an ordering of these ions in the structure, as could be possibly established by a superstructure or by choosing another space group. The mixed La/Sr site occupation was refined with 1:3 molar ratio and fixed afterward with respect to the charge balanced composition $LaSr_3F_5(CN_2)_2$. In order to make sure that lithium ions do not play any role for the charge compensation in the refined crystal structure, a preparation was also done from LaF_3 and $SrCN_2$, according to reaction II.

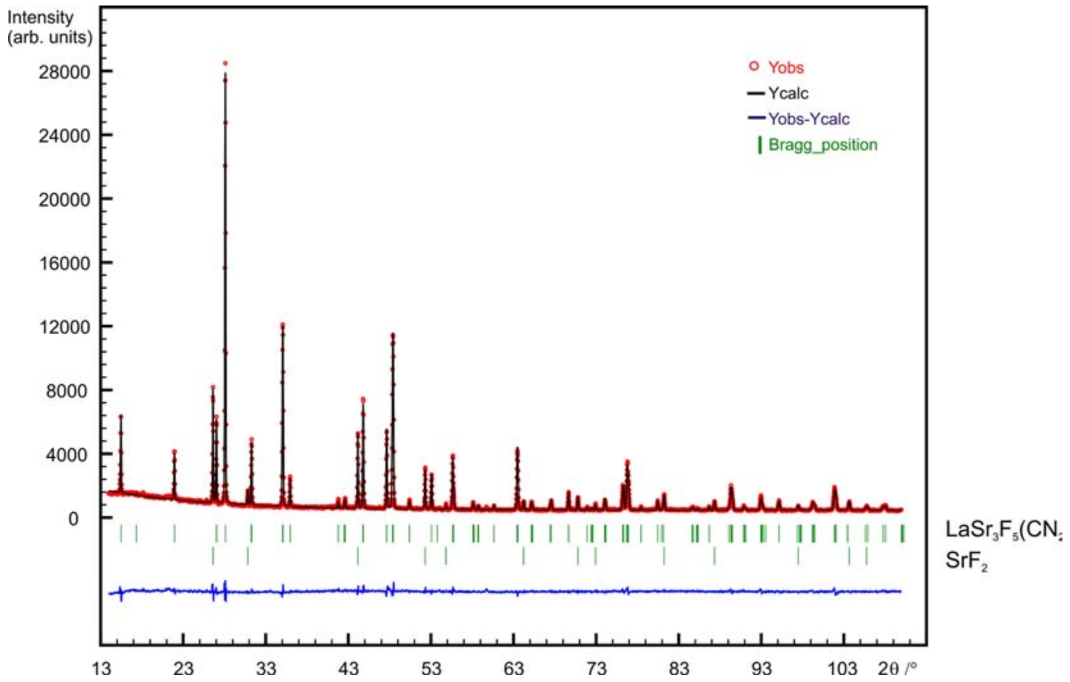

Figure 3. Rietveld structure refinement of $LaSr_3F_5(CN_2)_2$. Circles represent measured data; the calculated pattern is superimposed with the observed pattern (red). Ticks mark the Bragg reflections (green) of $LaSr_3F_5(CN_2)_2$ and the side phase SrF_2. The difference curve between the observed and calculated pattern is shown in the lower part of the graph (blue).

Hence, a mixed cation situation is present in the structure of $LaSr_3F_5(CN_2)_2$ versus an ordered cation distribution in $Eu_4F_5(CN_2)_2$. The difference of ionic radii (CN = 7) between La^{3+} (1.10 Å) and Sr^{2+} (1.21 Å) is a little less pronounced than the corresponding difference between Eu^{3+} (1.01 Å) and Eu^{2+} (1.20 Å) in mixed-valent $Eu_4F_5(CN_2)_2$.[5]

The previously refined crystal structure of $Eu^{(3+)}Eu_3^{(2+)}F_5(CN_2)_2$ (Figure 1) contains four crystallographically distinguishable Eu ions and is showing specific tilting of $[N{=}C{=}N]^{2-}$ ions as an obvious feature. The proposed idealized structure in which all europium ions would be considered symmetrically equivalent is displayed in the center of Figure 2, together with the projected structure of $LaSr_3F_5(CN_2)_2$ at left, and the high symmetry structure of $AlCu_2$ at right of Figure 2. The structure of $AlCu_2$ covers only the related positions of the "Eu_4C_2" and "$(LaSr_3)C_2$" sublattices of the parent structures. Hence, the choice of the orientation of $[N{=}C{=}N]^{2-}$ and the position of F^- ions was not restricted during the symmetry reduction process from the $AlCu_2$ structure to the (real) crystal structure of $Eu_4F_5(CN_2)_2$. What is considered as the ideal symmetry of $Eu_4F_5(CN_2)_2$ was missed by this procedure but determined manually, as explained in the introduction.

Surprisingly, the crystal structure of $LaSr_3F_5(CN_2)_2$ resembles the proposed high (ideal) symmetry, and this is due to the fact that La^{3+} and Sr^{2+} ions mix on the same crystallographic position, in a compound that was originally designed to prove distinct site occupations of divalent and trivalent cations in a structure like this. Hence, in $LaSr_3F_5(CN_2)_2$, all cation positions are equivalent. If this structure would occur for $Eu_4F_5(CN_2)_2$, the $Eu^{2+/3+}$ ions must be assumed to be disordered. But we may note that the Eu ions are well separated from each other, so that charge fluctuations may not be expected at ambient temperatures, at least not from the structural point of view.

The crystal structure of $LaSr_3F_5(CN_2)_2$ is displayed in a perspective projection in Figure 4. It can be discussed in several ways, as has been raised previously. Here we would like to highlight tetrahedral $(La/Sr)_4$ motifs having four edge-bridging and one central F^- ions making up $(La/Sr)_4F_5$ units ($d_{(La/Sr)-(La/Sr)}$ = 427.0(1) Å), forming a body centered arrangement in the structure. The motifs are interconnected by terminal (La/Sr)−F bridges with adjacent motifs at $\overline{d}_{(La/Sr)-F}$ = 2.503(4) Å, and by linear arrangements of centrosymmetric $[N{=}C{=}N]^{2-}$ ions with d_{C-N} = 120.7(6) Å. This distance within the carbodiimide ions represents a typical value being close to corresponding distances reported for $Eu_4F_5(CN_2)_2$ (1.233(9), 1.201(9), and 1.225(9) Å). Each of the (La/Sr) center is surrounded by five fluoride and two nitrogen atoms of carbodiimide groups with individual distances given in Table 3.

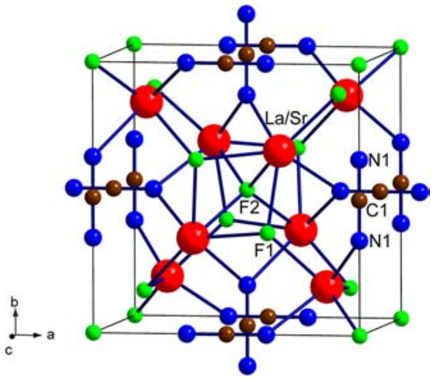

Figure 4. Perspective projection of the crystal structure of $LaSr_3F_5(CN_2)_2$.

When comparing the atomic positions refined for $LaSr_3F_5(CN_2)_2$ ($I\bar{4}2m$, $Z = 2$) and $Eu_4F_5(CN_2)_2$ ($P\bar{4}2_1c$, $Z = 8$), all atom positions, except those of the N atoms of carbodiimide groups, appear quite similar in both noncentrosymmetric space groups.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data for $LaSr_3F_5(CN_2)_2$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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