$EuCN_2$ – The First, but Not Quite Unexpected Ternary Rare Earth Metal Cyanamide

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Abstract. Red-orange, transparent single crystals of $EuCN_2$ (*Pnma* (62), a = 1232.41(9), b = 395.26(3) and c = 539.43(4) pm, Z = 4) are obtained by the reaction of EuN, C and NaN_3 in arc-welded Ta ampoules at 1300 K. The first ternary rare earth metal cyanamide is isotypic to α-$SrCN_2$ and shows the characteristic frequencies for the CN_2^{2-} unit in the optical spectra (ν_s = 1244; ν_{as} = 1969 and 2087; δ = 655 / 666 cm^{-1}).

Keywords: Rare-earth metal; Europium; Cyanamide; Structure Elucidation; Optical spectroscopy

A side effect of the quest for C_3N_4 in the last decade is the increase of knowledge in the field of alkali and alkaline earth metal cyanamides [1, 2]. Quaternary rare earth metal cyanamides of the composition $Ln_2O_2(CN_2)$ [3] have been characterized, but strangly enough, ternary rare earth metal cyanamides have not yet been reported. We present here the first and may be the most obvious ternary rare earth metal cyanamide – $EuCN_2$.

Experimental

All manipulations of educts and products were performed in a glove box under purified argon. EuN (obtained by the reaction of Eu (99.9 %, ingot, Aldrich, cubic F with a = 502.2(2) pm) with nitrogen at 1300 K), carbon (Strem, powder, 99.999 %) and NaN_3 (99 %, powder, Aldrich, degassed at 400 K under dynamic vacuum for 2 h) were mixed in a 3:3:1 molar ratio (overall mass: 400 mg) and arc-welded into a clean tantalum container. The metal container was fused into an evacuated silica tube. The tube was placed in chamber furnace and heated to 1300 K within 16 hours. After 3 days reaction time the furnace was switched off and allowed to cool to room temperature. The product contained transparent, red-orange crystals of $EuCN_2$ and a dark brown (orange brown when ground) encrusted mass which consisted of $EuCN_2$, some remaining EuN (as identified by their respective X-ray powder pattern) and metallic Na. Variations of the starting stoichiometric ratio and of the reaction parameters did not yield single phase products. Raman investigations (microscope laser Raman spectrometer (Jobin Yvon, 10 mW, excitation line at λ = 632.817 nm (HeNe laser), 50× magnification, samples in glass capillaries, 2×25 s accumulation time) performed on the very specimen used for single crystal measurements showed ν_{sym} = 1244 and δ = 668 cm^{-1} (Figure 1). The IR spectrum (Bruker AFS 66 FT-IR spectrometer, ground product with the KBr pellet technique) was difficult to obtain due to strong absorption of EuN in the IR region, but ν_{as} = 1969 / 2087 and δ = 655 / 666 cm^{-1} were reproduceably observed. The crystal structure of $EuCN_2$ (Pnma (62), a = 1232.41(9), b = 395.26(3) and c = 539.43(4) pm, Z = 4) [4] was solved and refined using X-ray diffractometer data (Table 1, 2 and 3). Crystals of $EuCN_2$ are air and moisture sensitive.

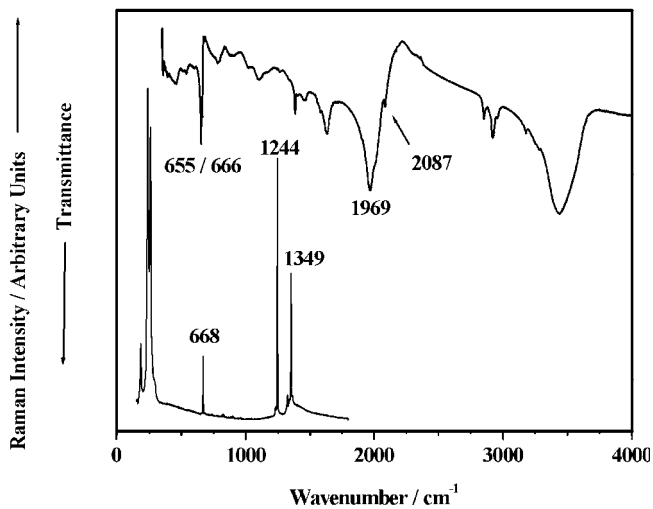

Figure 1 Raman and IR spectrum of $EuCN_2$.

Results and Discussion

Sr^{2+} and Eu^{2+} are known to exhibit very similar structural features in the solid state. Isotypic or structurally very closely related compounds such as Sr_4OCl_6 [5] and Eu_4OCl_6 [6], $Sr_3(BN_2)_2$ [7] and $Eu_3(BN_2)_2$ [8], or $Sr_2Si_5N_8$ [9] and $Eu_2Si_5N_8$ [10], are just a few examples that demonstrate this similarity. Not surprisingly then, $EuCN_2$ is isotypic to α-$SrCN_2$ [2]. Both compounds form layers parallel to the (ac) plane which contain both Eu^{2+} and CN_2^{2-} (Figure 2).The distorted metal centered octahedra are interconnected by corner sharing and by bridging $[N{=}C{=}N]^{2-}$ anions. The nitrogen positions are in turn coordinated by distorted, tetrahedra of three Eu and one carbon which atom are cornersharing via the carbon atom and eclipsed in respect to each other. The CN_2^{2-} ion (Figure 3) has $D_{\infty h}$ symmetry within three standard deviations

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Table 1 Summary of facts of the X-Ray Single Crystal Structure Determination on $EuCN_2$.

Compound	$EuCN_2$
Space Group (No.), Z	Pnma (62), 4
CSD-Nummer	412665
Lattice Constants/pm	1232.41(9), 395.26(3), 539.43(4)
Calc. Density/gcm^{-3}	4.853
Crystal Colour	transparent orange-red
Crystal Form	columnar
Crystal Size/mm^3	0.12×0.04×0.03
Diffractometer	Bruker CCD
Radiation, Monochromator,	Mo-K_α (λ = 71,073 pm),
Temperature/K	Graphite, 293(2)
Ranges/2θ_{max}; h, k, l	60.31°; −17→12, ±4, −4→7
Distance Detector-Crystal/mm	50
Increment $\Delta\varphi$/°	0.3
# Exposures	850
Exposure Time/s	20
Absorptions Corrections	Lorentz polarization
μ/mm^{-1}	23.52
Measured/Unique/Unique Reflections $F_o > 4\sigma(F_o)$	874 / 374 / 361
R_{int}	0.0872
Refined Parameter	26
R1/wR2/GooF (all Refl.)	0.0323/0.0829/1.121
Max. Shift/esd, last Refinement Cycle	< 0.0005
Res. elektron density: max, min	1.66, −1.94 e$^-$/Å^3, 75 pm to Eu

Table 2 Crystal Coordinates and isotropic thermal parameters of $EuCN_2$.

Atom	Wyckoff-site	x / a	y / b	z / c	U_{eq} [a]/ pm^2
Eu	4a	0.13145(3)	1/4	0.11764(7)	153(3)
C	4a	0.3780(8)	1/4	0.1182(15)	213(26)
N1	4a	0.3284(7)	1/4	0.0794(15)	212(17)
N2	4a	0.4231(6)	1/4	0.3186(14)	212(16)

[a] U_{eq} is defined as a third of the orthogonalised U_{ij} tensors.

Table 3 Selected Distances and Angles in $EuCN_2$.

Atoms		Distance / pm Angle / deg.
Eu − N2	1×	259.0(8)
N1	2×	261.2(5)
N2	2×	263.8(5)
N1	1×	265.0(8)
C − N1	1×	121.5(12)
N2	1×	122.9(12)
N1 − C	1×	121.5(12)
Eu	2×	261.2(5)
Eu	1×	265.0(8)
N1 − C	1×	122.9(12)
Eu	1×	259.0(8)
Eu	2×	263.8(5)
N1−C−N2	1×	177.4(9)

($\angle$(N=C=N) = 177.4(9)°, while the C-N bond lengths (121.5(12) pm and 122.9(12) pm are nearly equal despite the fact that the two nitrogen sites N1 and N2 are crystallographically independent.

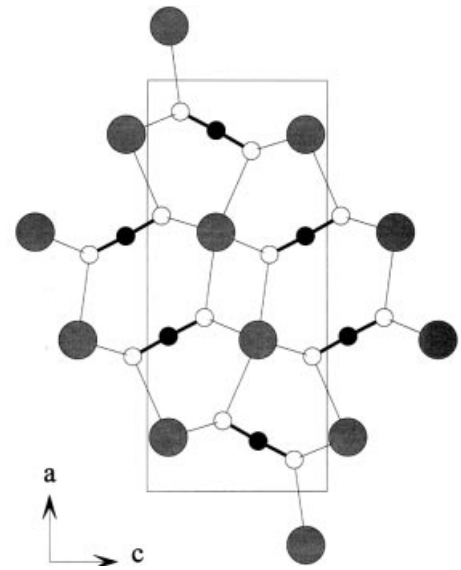

Figure 2 View on the unit cell of $EuCN_2$ parallel to the b axis. Eu, C and N are displayed as light grey, black and white circles, respectively.

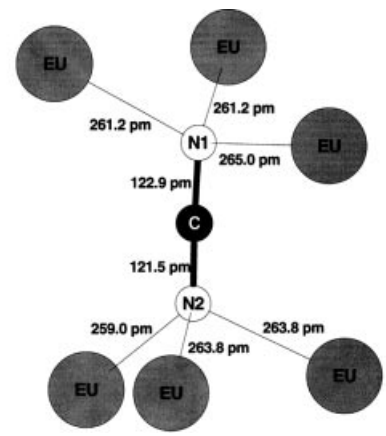

Figure 3 The coordination environment of the CN_2^{2-} ion and selected bond distances.

A rhombohedral form of strontium cyanamide, β-$SrCN_2$ ($R\bar{3}m$, a = 397.99(1) and c = 1494.08(7) pm) [11] is known which is isotypic to $CaCN_2$ [12]. It forms via ammonolysis of $SrCO_3$ [11] starting at 920 K. Since no analog precusor such as $EuCO_3$ is known yet, it will be a challenge to find out how far the similarities between Eu^{2+} and Sr^{2+} in the solid state reach.

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[4] Single crystals of $EuCN_2$ were selected under a microscope in a glove box and sealed into glass capillaries. The quality of the crystal was checked with some rotation pictures. The crystal structure solution and refinement were performed with the SHELXTL (G. M. Sheldrick, Göttingen **1997**) program package.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666, e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412665.

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