Calcium Carbodiimide Compounds Revisited – Syntheses, Single Crystal Structure Determination and Vibrational Spectra of Ca$_{11}$N$_6$[CN$_2$]$_2$, Ca$_4$N$_2$[CN$_2$] and Ca[CN$_2$]

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Single crystals of Ca$_{11}$N$_6$[CN$_2$]$_2$ (dark red needles, tetragonal, $P4_2/mnm$ (no. 136), $a = 1456.22(5)$, and $c = 361.86(2)$ pm, $Z = 2$), Ca$_4$N$_2$[CN$_2$] (transparent yellow needles, orthorhombic, $Pnma$ (no. 62), $a = 1146.51(11)$, $b = 358.33(4)$, and $c = 1385.77(13)$ pm, $Z = 4$) and Ca[CN$_2$] (transparent, colorless, triangular plates, rhombohedral, $R3m$ (no. 166), $a = 369.00(3)$, and $c = 1477.5(3)$ pm, $Z = 3$) were obtained by the reaction of Na$_2$[CN$_2$], CaCl$_2$ and Ca$_3$N$_2$ (if demanded by stoichiometry) in arc-welded Ta ampoules at temperatures between 1200–1400 K. Their crystal structures were re-determined by means of single crystal X-ray structure analyses. Additionally, the Raman spectra were recorded on these same single crystals, whereas the IR spectra were obtained with the KBr pellet technique. The title compounds exhibit characteristic features for carbodiimide units with $D_{\infty h}$ symmetry ($d$(C–N) = 121.7–123.8 pm and $\angle$(N–C–N) = 180°). The vibrational frequencies of these units are in the expected range (Ca$_{11}$N$_6$[CN$_2$]$_2$: $\nu_s = 1230$, $\nu_v = 2008$; $\delta = 673/645/624$ cm$^{-1}$; Ca$_4$N$_2$[CN$_2$]: $\nu_s = 1230$, $\nu_v = 1986$; $\delta = 672/647$ cm$^{-1}$; Ca[CN$_2$]: $\nu_s = 1274$, $\nu_v = 2031$, $\delta = 668$ cm$^{-1}$). The structural results are more precise than the previously reported data, and with the newly attained Raman spectrum of Ca$_{11}$N$_6$[CN$_2$]$_2$ we correct data reported earlier.

Key words: Calcium, Nitride, Carbodiimide, Cyanamide, Dinitridocarbonate, Crystal Structure, Raman Spectroscopy