A Metal Nitride Carbodiimide with a Stuffed Skutterudite-type Structure: Synthesis, Crystal Structure and IR Spectra of $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$

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Coppery-red, transparent single crystals of $(Ba_6N_{5/6})_2[NbN_4][CN_2]_6$ ($Im\bar{3}$, no. 204, a = 1125.83(3) pm, Z = 2) are obtained by the reaction of Ba_2N and $ZnCN_2$ with the container walls of the arc-welded Nb ampoules at 1100 K. The title compound assumes a stuffed skutterudite-type structure in which edge-sharing $(Ba_6N_{5/6})$ octahedra form large voids which are occupied by either $[NbN_4]$ tetrahedra or by $[N{=}C{=}N]^{2-}$ units with symmetric C=N bond lengths of d = 121.8(6) pm but a bond angle deviating significantly from linearity ($\measuredangle$(N–C–N) = 175.3(9)°). The IR spectra corroborate this crystallographic result by the fact that *all* fundamental vibrations are visible in the IR spectrum [ν_1 = 1262 (symmetric stretching mode); ν_2 = 1957/2009 (antisymmetric stretching mode); ν_3 = 611/633/653 cm^{-1} (bending modes)], which is symmetry forbidden for $[N{=}C{=}N]^{2-}$ units having $D_{\infty h}$ symmetry but expected for the C_{2v} symmetry found in the title compound.

Key words: Barium, Carbodiimide, IR Spectroscopy, Niobium, Nitride, Skutterudite Structure, Structure Elucidation