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

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