

Isolation and Structural Determination of $\{(1,1,2,2\text{-Tetracyano-1,2-ethanediyl})\text{bis[imino(cyanomethylene)]}\text{bis(cyanamide)}\}$ ion(2-), $[\text{C}_{12}\text{N}_{12}]^{2-}$, a New Cyanocarbon

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The oxidative degradation of $[\text{N}(\text{PPh}_3)_2]_3[\text{Mn}^{\text{III}}(\text{CN})_6]$ leads to the isolation of the unprecedented $[\text{C}_{12}\text{N}_{12}]^{2-}$ dianion, which is characterized by single-crystal X-ray diffraction and spectroscopic techniques.

The study of cyanocarbons has led to several new classes of compounds based upon reduction of the nitrile triple bond.¹ In an attempt to prepare $[\text{Mn}^{\text{IV}}(\text{CN})_6]^{2-}$, oxidation of $[\text{N}(\text{PPh}_3)_2]_3[\text{Mn}^{\text{III}}(\text{CN})_6]$ led to the isolation of light-yellow crystals with anomalous infrared absorptions at 2199 and 2176 cm^{-1} , assigned to $\nu(\text{CN})$ and a very strong unassigned absorption at 1559 cm^{-1} . The absorptions below 2200 cm^{-1} were too low in frequency to be assigned to a nitrile, and were thought to be associated with a new cyanomanganate. Crystals

isolated from MeCN were suitable for X-ray diffraction and the structure of the unprecedented $\{(1,1,2,2\text{-tetracyano-1,2-ethanediyl})\text{bis[imino(cyanomethylene)]}\text{bis(cyanamide)}\}$ ion(2-), **1**, was determined.^{†,‡} The anion $[\text{C}_{12}\text{N}_{12}]^{2-}$ is centrosymmetric about the midpoint of the C(3)–C(3') bond, Fig. 1. Except for the C(3) cyano groups the dianion is planar with deviations from the plane ranging from 0.0012 to 0.0715 Å and averaging ± 0.023 Å. The chemically equivalent C≡N bond distances (1.138 Å) are comparable to the plethora of nitrile groups structurally determined. The 1.577(10) Å central $\text{sp}^3\text{-sp}^3$ C–C bond length is longer than the conventionally accepted value for the 1.54 Å and is significantly (0.09 Å) longer than the $\text{sp}^2\text{-sp}^2$ C–C single bond in $\text{C}_4(\text{CN})_6$ (1.487 Å).² The $\text{sp}^3\text{-sp}^3$ C(3)–CN bond distances average 1.508 Å while the $\text{sp}^2\text{-sp}^2$ C(2)–CN distance is 1.449 Å and the CN single bond [C(3)–N] is 1.403 Å. The delocalized CN bonds range from 1.314(7) to 1.342(7) Å for the C(2)–N bonds, and the short C(1)–N(2) bond (1.331 Å) reflects some double bond character. The significant differences in the C(2)–N bonds is a consequence of the asymmetry about C(2).

The IR absorptions at 2199 and 2176 cm^{-1} are consistent with $[\text{CN}]_6^{2-}$ [$\nu(\text{CN})$ at 2165 cm^{-1} ^{3a}] and $[\text{CN}]_8^{2-}$ [$\nu(\text{CN})$ at 2180 cm^{-1} ^{3b}] while the previously unassigned strong absorption at 1559 cm^{-1} is due to the C=N bonding. $[\text{N}(\text{PPh}_3)_2]_2[\text{C}_{12}\text{N}_{12}]$ has a λ_{max} at 34 725 cm^{-1} ($\epsilon = 24\,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) due to the conjugated chromophore. Absorptions at higher energy are attributed to the $[\text{N}(\text{PPh}_3)_2]^+$ cation.

The oxidative decomposition of $[\text{Mn}^{\text{III}}(\text{CN})_6]^{2-}$ undoubtedly leads to the formation of CN^- and CN^\bullet which reacts in a complex manner to form $[\text{C}_{12}\text{N}_{12}]^{2-}$ which crystallizes as the $[\text{N}(\text{PPh}_3)_2]^+$ salt. CN^\bullet dimerizes to form cyanogen and the reaction of cyanogen with CN^- leads to many products of which the best characterized is 1-*H*-imidazo[1,5-*b*]-*s*-2,5,7-tricarbonitrile, $[\text{C}_7\text{N}_7]^-$.⁴ Reduction of **2** or cyanogen leads to poly(cyanogen), C_nN_n .⁵ Hence, isolation of $[\text{C}_{12}\text{N}_{12}]^{2-}$ and **2** suggests that many unusual products as a consequence of C–C and CN, and in the case of **2**, N–N bond formation can be formed, *via* the reaction of cyanogen and CN^- .

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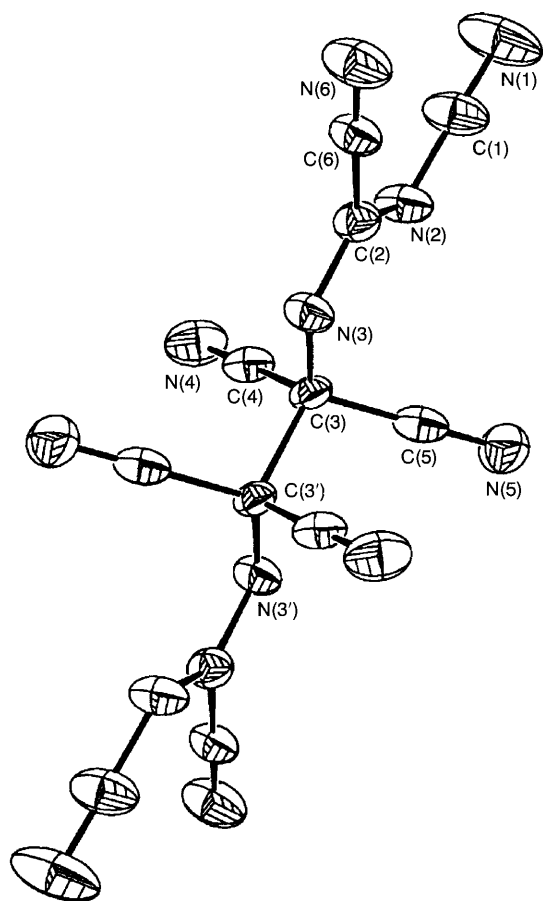
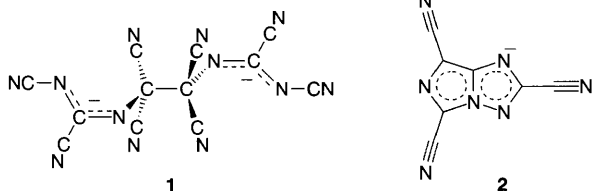


Fig. 1 Structure and labelling diagram of $[\text{C}_{12}\text{N}_{12}]^{2-}$



Footnotes

[†] Elemental analysis: Found: C, 72.15; H, 4.50; N, 13.95. Calc. for $\text{C}_{84}\text{H}_{60}\text{N}_{14}\text{P}_4$: C, 72.60; H, 4.35; N, 14.10%.

[‡] Crystal data for **1**: $\text{C}_{84}\text{H}_{60}\text{N}_{14}\text{P}_4$, $M = 1389.4$, monoclinic, space group $P2_1/n$, $a = 12.155$ (1), $b = 19.789$ (2), $c = 15.751$ (2) Å, $\beta = 104.52$ (1)°, $U = 3667.76$ Å³, $F(000) = 1444$, $Z = 2$, $D_c = 1.258 \text{ g cm}^{-3}$, $\lambda = 1.54184$ Å, crystal size 0.30 × 0.20 × 0.13 mm, $T = 18$ °C, $2\theta_{\text{max}} = 98^\circ$, R_w (on F) [R (on F)] = 0.0519 (0.0468), for 3839 unique reflections with $I > 3\sigma(I)$. Data was collected on a Syntex P1 diffractometer and the crystal structure solved using MOLEN software distributed by Enraf Nonius. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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