3D Knitting Patterns. Two Independent, Interpenetrating Rutile-related Infinite Frameworks in the Structure of $Zn[C(CN)_3]_2$

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The structure of $Zn[C(CN)_3]_2$ consists of two independent infinite rutile-related frameworks whose complex entanglement resembles 3D knitting.

The results described here form part of exploratory studies based on the notion that an extensive and potentially useful class of new solid materials may be afforded by connecting together rod-like or plate-like molecular building blocks in various ways.[1] Each of a number of simple structures (*e.g.* diamond, PtS, α-polonium) can be regarded as the prototype for a whole family of new frameworks in which bonds of the prototype are replaced by a range of molecular rods. Because of its simplicity, the linear –C≡N– unit is particularly attractive as a rod-like connector in exploratory studies. Linking tetrahedral centres together by linear –C≡N– units affords diamond-related frameworks {*e.g.* in $[NMe_4][Cu^IZn^{II}(CN)_4]$[1]} whilst similar linking together of equal numbers of square-planar and tetrahedral centres gives a PtS-related framework {*e.g.* in $[NMe_4][Cu^IPt^{II}(CN)_4]$[2]}. In some cases these polymeric structures evolve as single infinite frameworks leaving relatively large cavities and/or channels {*e.g.* in $[C(p\text{-}C_6H_4CN)_4]Cu^I(BF_4)\cdot xPhNO_2$ and $[NMe_4][CuZn(CN)_4]$[1]}; in others, the cavities are neatly filled by one or more identical but independent frameworks [*e.g.* in $Zn(CN)_2$[1]]. These rare examples of concatenated or interpenetrating structures resembling 3D knitting are of fundamental importance as special geometrical types and may show unusual properties arising from this structural feature.

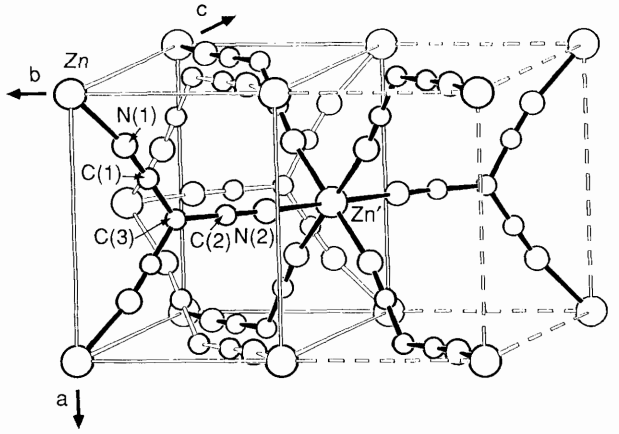

Fig. 1 Unit cell of $Zn[C(CN)_3]_2$ and atom numbering scheme. The left half of the figure represents the actual unit cell. One framework is omitted from the right half so that the relationship to rutile of the framework extending into both halves is easily recognised. Selected interatomic distances (Å) and angles (°): Zn–N(1) 2.120(2), Zn–N(2) 2.211(2), C(1)–N(1) 1.150(2), C(1)–C(3) 1.399(2), C(2)–C(3) 1.411(4), C(2)–N(2) 1.151(3), N(1)–Zn–N(1′) 84.4(1), N(1)–Zn–N(1″) 95.6(1), N(1)–Zn–N(2′) 89.1(1), N(1)–Zn–N(2″) 90.9(1), C(1)–N(1)–Zn 170.0(1), N(1)–C(1)–C(3) 178.5(2), C(1)–C(3)–C(1′) 117.4(2), C(1)–C(3)–C(2) 121.2(1), N(2)–C(2)–C(3) 178.9(3), C(2)–N(2)–Zn′ 166.8(2).

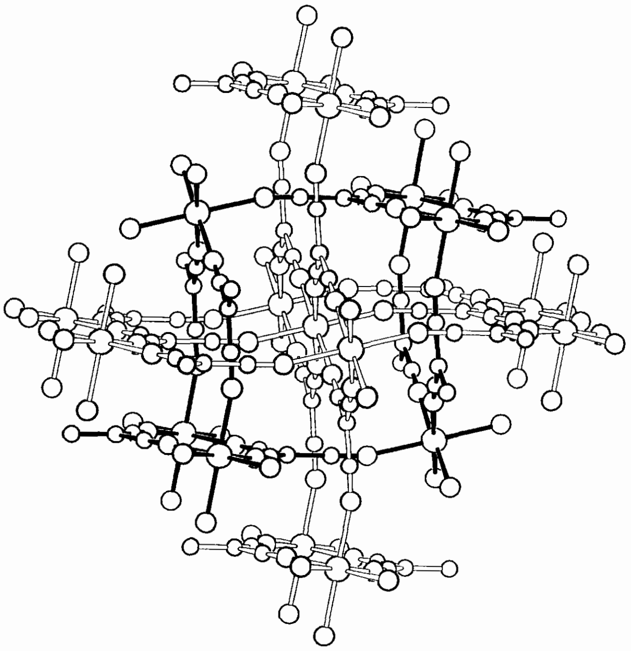

Fig. 2 View of $Zn[C(CN)_3]_2$ revealing the nature of the interpenetration of the two independent frameworks

The rutile structure is of basic importance in inorganic and structural chemistry being described in countless texts on the subject; it represents one particular way of three-dimensionally linking together 3-connected, trigonal centres (O^{2-}) and half as many 6-connected, octahedral centres (Ti^{4+}). α-PbO_2 provides an example of an alternative way of linking such centres to form an infinite 3D array. We report here an example of a rutile-related infinite molecular framework in which trigonal carbon centres are linked *via* –C≡N– units to half as many octahedral Zn^{2+} centres; the structure, in addition, exhibits two-fold interpenetration.

$Zn[C(CN)_3]_2$ was prepared as described previously.[3] Crystals suitable for X-ray diffraction studies† were grown slowly from an aqueous solution of $Zn(NO_3)_2$ and $K[C(CN)_3]$ at room temperature. The unit cell and atom numbering scheme are shown in Fig. 1 which also provides bond lengths and angles. The left half of Fig. 1 corresponds to the actual unit cell and indicates the presence of two completely independent frameworks. In order to illustrate how the unit cell would have appeared if only a single framework had been present, one of the two frameworks is continued into the right half of the figure thereby producing the readily recognised rutile cell. The second framework can be generated from the first by the translation b. The presence of the second framework halves one of the edges perpendicular to the tetragonal axis of what would have been the rutile-like unit cell if only a single framework had been present but the other two dimensions remain unchanged. The resulting cell is therefore orthorhombic with b very nearly equal to $0.5c$. This effect of the introduction of a second framework is to be contrasted with that in $Zn(CN)_2$,[1] where the symmetry is such that the face-centred cubic unit cell that would have been applicable if only one diamond-related framework had been present, is halved along all three edges to generate a new primitive cubic cell with only one eighth the volume of the first.

Fig. 2 reveals the nature of the interpenetration in $Zn[C(CN)_3]_2$. If the structure is regarded as composed of zinc centres and trigonal carbon C(3) centres linked by rods then the smallest rings present are 4-membered $[Zn_2C(3)_2]$ and 6-membered $[Zn_3C(3)_3]$; five atoms [3Zn + 2C(3)] of each 6-membered ring are common to two 6-membered rings which differ only in their sixth centre [a C(3)] as can be seen in Fig. 2. The –C≡N– units involved in the 4-membered rings are all of the C(1)N(1) type. If the C(3)C(1)N(1)Zn rods retained their preferred linearity and if the C(1)–C(3)–C(1) angle were close to the expected 120°, the N(1)–Zn–N(1) angle would be an unacceptably low 60°; or, if the angle at Zn were 90° the angle at C(3) would be unacceptably low. A significant bend from linearity at N(1) [Zn–N(1)–C(1) 170°] which occurs largely within the plane of the 4-membered ring allows the angles at both Zn (84.4°) and C(3) (117.4°) to approach their preferred values.

Every 6-membered ring of one framework has a rod of the other framework projecting through it but projection of rods through 4-membered rings does not occur. The regions of the two frameworks (which are of course equivalent) where a rod of one passes through a ring of the other are in the vicinity of C(2); indeed, the C(2) atoms of both frameworks fall almost exactly on a line parallel to a. However the C(2) ····· C(2) interframework contacts [3.733(1) Å] are by no means the smallest present, the closest being C(1) ····· C(1), 3.135(4) and 3.138(4) Å; C(2) ····· N(1), 3.193(3) Å; C(1) ····· N(1), 3.286(3) Å; C(1) ····· C(2), 3.333(2) Å. Clearly, the interpenetration forces certain regions of the two independent frameworks into unusually close proximity. The frameworks buckle to relieve to some extent these repulsive interactions as Fig. 2 reveals. Most of this buckling occurs at N(2) [Zn–N(2)–C(2) 166.8°]. Whilst the bending at N(1) which relieves angle strain

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† *Crystal data*: $Zn[C(CN)_3]_2$, M = 245.5, orthorhombic, space group *Pmna* (No. 53), a = 7.466(2), b = 5.3171(5), c = 10.482(2) Å, U = 416.1(2) Å^3, Z = 2, D_c = 1.96, D_m = 1.99(1) g cm^{-3}, μ(Mo-Kα) = 29.6 cm^{-1}, $F(000)$ = 240. Intensity data were measured at 295(1) K with Mo-K radiation (graphite monochromator) using an Enraf–Nonius CAD-4F diffractometer and employing the ω/2θ scan method; absorption corrections were applied. A full-matrix least-squares refinement (SHELX-76) was employed with anisotropic thermal parameters applied to all atoms; at convergence R = 0.030 and R_w = 0.033 for the 738 observed reflections [$I \geq 3\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

in the 4-membered rings occurs largely within the plane of the $C(CN)_3$, that at N(2) occurs in a plane perpendicular to the $C(CN)_3$ so that the Zn attached to N(2) is displaced 0.7 Å from that plane. The result of this buckling is that the C(2)N(2) rod component is not forced into such close contact with the V-shaped $Zn[N(1)C(1)C(3)]_2$ system of the other framework as would have been the case had the entire $C(CNZn)_3$ remained planar.‡ The efficient 3D packing in $Zn[C(CN)_3]_2$ arising from the concatenation is reflected in the small average volume per atom of 13.9 Å^3 which may be contrasted with that for example in $Zn(CN)_2$ of 20.5 Å^3.

A number of X-ray crystallographic studies of basically ionic solids containing essentially discrete $C(CN)_3^-$ ions which are planar or deviate only slightly from planarity have been reported.[4] $Ag[C(CN)_3]$ has a unique structure in which two puckered 'hexagonal mesh chicken wire' sheets interpenetrate; composite, double interwoven sheets of this type are then stacked one on top of the other without further interpenetration.[5] A report of a structural study of $Cu[C(CN)_3]_2$[6] contains inconsistencies which are completely explicable in terms of a two-fold interpenetrating rutile-related structure analogous to that of $Zn[C(CN)_3]_2$; no mention was made in that report of the presence of a second, independent, interpenetrating framework nor was the relationship to rutile noted.

A number of new infinite 3D structural types should be accessible using $C(CN)_3^-$ units to link together cationic species with various stereochemical preferences. The present study points to the feasibility of producing other rutile-related frameworks using larger and more elaborate trigonal building blocks than $C(CN)_3^-$.

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‡ A calculation of atomic coordinates in a hypothetical structure in which N(2) was held linear indicates inter-nuclear inter-framework separations as low as 2.8 Å.

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