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$Ni(tpt)(NO_3)_2$—A Three-Dimensional Network with the Exceptional (12,3) Topology: A Self-Entangled Single Net[**]

Brendan F. Abrahams, Stuart R. Batten,
Martin J. Grannas, Hasan Hamit, Bernard F. Hoskins,
and Richard Robson[*]

In Memory of Dr. George Winter

Extended framework solids are currently of considerable interest and importance because of the scope they offer for the generation by design of new materials with a range of potentially useful properties.[1] A valuable conceptual approach to building and describing extended frameworks, in particular those involving interpenetration,[2] is based on the idea of a net, a valuable catalogue of which has been provided by Wells.[3]

Connecting ligands providing two or more bidentate metal-binding sites that are now starting to be explored,[4] are particularly appealing as building blocks for coordination polymers because they promise robust networks with good electronic communication between metal centers. When an octahedral metal center takes on three ligands of this type the metal center itself adopts the role of 3-connecting node giving access to a range of still little known 3-connecting nets. We suspect that many examples of 3-connected nets will appear in the near future. The symbol (n,3) can be used to characterize the topologies of nets in which all nodes are 3-connecting and where the shortest circuits involving all three different pairs of connections radiating from each node are n-gons. An interesting question that arises when one considers the set of (n,3) nets is "what is the largest possible value for n?"—or, in other words "what is the three-dimensional (3D) 3-connected net whose shortest circuits are as large as possible?". The (12,3) net is the one with the largest value of n considered by Wells.[1, 5] What we describe here is, to the best of our knowledge, the first real chemical example of a (12,3) net.

A representation of a (12,3) net with planar nodes is shown in Figure 1. The net, which is intrinsically chiral, can be visualized in terms of "double" sixfold helices, all of the same handedness and all parallel, connected together by links that are perpendicular to the helical axis. The extension of the (12,3) net in the direction of the helical axis is dictated by the angle at each node internal to the helix which can, in principle, take any value from 120° (regular trigonal nodes) to 180° (T-shaped nodes)—the larger this angle, the greater the pitch of the helices and the more extended in the direction of the helical axis does the structure become.

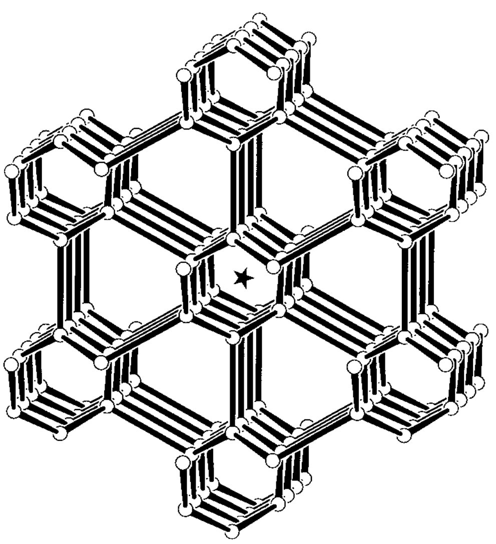
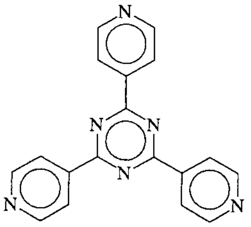


Figure 1. Representation of the (12,3) net in which all nodes are planar and equivalent. One sixfold double helix is highlighted with a star for ease of identification.

Whilst neither strictly trigonal nodes alone nor strictly T-shaped nodes alone can be used to generate the (12,3) net, it can be constructed in a completely strain-free manner from alternating T and trigonal nodes. This is precisely what we observe, as described below, in the structure of the crystalline coordination polymer[6] obtained from nickel nitrate and the trigonal 3-connecting ligand tri-4-pyridyl-1,3,5-triazine (tpt; **1**). This geometrically simple ligand has already afforded a> wide variety of unusual and symmetrical 3D coordination networks.[7] The crystal consists of a well-defined coordination polymer framework with the (12,3) topology containing equal numbers of tpt and Ni^{2+} centers. Disordered solvent occupies the chiral channels running parallel with the helical axes. The essence of the connectivity of the network is



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[*] Dr. R. Robson, Dr. B. F. Abrahams, Dr. S. R. Batten,
Dr. M. J. Grannas, H. Hamit, Dr. B. F. Hoskins
School of Chemistry, University of Melbourne
Parkville, Victoria 3052 (Australia)
Fax: (+61) 3-9347-5180
E-mail: r.robson@chemistry.unimelb.edu.au

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represented in Figure 2. The particular crystal studied in detail had the absolute configuration shown in Figure 2 but a second crystal chosen at random was found to have the opposite handedness. All nickel centers (the T-nodes[8] in Figure 2) are equivalent as are all tpt units (the trigonal nodes in Figure 2 which are located at the midpoints of the tpt triazine rings). Each nickel center together with one of its coordinated pyridyl groups lies on a twofold axis, the other two pyridyl groups are *cis* to the first and related to each other by the twofold axis. The octahedral coordination of the nickel center is completed by oxygen atoms from monodentate and bidentate nitrate anions which are disordered around the twofold axis.

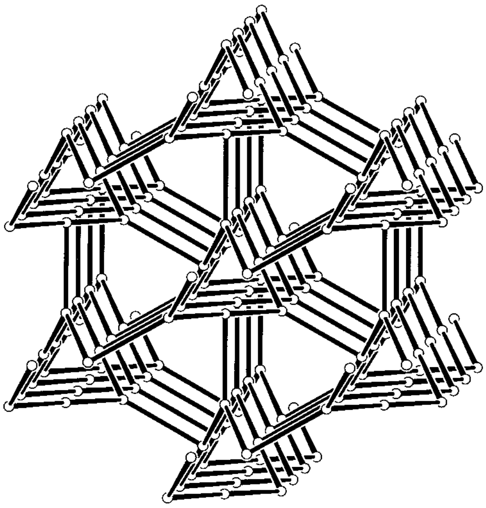

Figure 2. Representation of the (12,3) net consisting of alternating trigonal and T-shaped nodes as seen in the structure of solvated Ni(tpt)$(NO_3)_2$. The trigonal nodes are located at the centers of the tpt triazine rings and the T-shaped nodes are located at the Ni centers. Node-to-node separation 7.64 Å.

The presence of the two types of 3-connecting centers (trigonal and T) means that the double sixfold helices have now become double threefold helices with a triangular cross-section, as can be clearly seen in Figure 2. In the (12,3) net consisting of T-shaped nodes with 90° angles and regular trigonal nodes with 120° angles the orientation of the trigonal units to the hexagonal axes is "fixed" by the geometry and the proportions of the unit cell are predetermined ($a/c = 2/\sqrt{6} = 0.8165$). There is a very close correspondence between these proportions dictated by simple geometry and those observed in the real crystal ($a/c = 0.8159$).

A representation of the beautifully interwoven network, showing all the non-hydrogen atoms of the tpt units and the nickel centers in three adjacent double helices, is presented in Figure 3.

Within the series of uniform (n,3) nets the (12,3) net is exceptional in showing self-entanglement such that some of its *shortest* circuits have *other shortest circuits* passing through them. Figure 4 provides an example of two 12-gons passing one through the other. It is true that if one were prepared to search for continuous circuits that are large enough, one could identify, in any extended network, pairs of such circuits that pass one through the other, but generally they would be very much larger than the shortest circuits that constitute one of the fundamental characterizing features of the net topology. It does appear to us, therefore, that nets in which two s*hortest* circuits pass one through the other constitute a special topological class which could properly be described as *self-penetrating* and/or *self-entangled.* It is interesting that as n increases in the series of (n,3) nets a point is reached where the system, in a manner of speaking, "folds back on itself", as occurs in (12,3) with the formation of double helices within what still remains a single net; the catenane-related self-penetration stems from this, as can be seen in Figure 4. If examples with $n > 12$ were to be capable of existence it seems likely this catenane-like self-entanglement would prove to be one of their inherent features.

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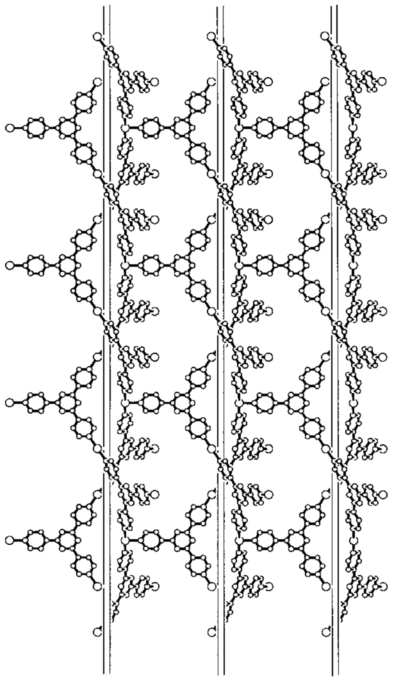

Figure 3. Three interconnected double helices showing the C, N, and Ni atoms. For ease of visualization the double helices are wrapped around imaginary "poles".

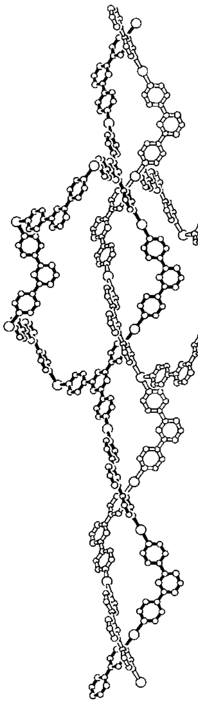

Figure 4. A double helix and one of the catenane-like pairs of 12-gons associated with it. One chain of the double helix and the 12-gon associated with it are here differentiated from the other chain/12-gon combination but all are part of a single 3D net.

Keywords: coordination polymers · crystal engineering · nickel · supramolecular chemistry

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[5] We do not know whether $n = 12$ is a mathematically imposed upper limit or whether topologically uniform (n,3) nets with $n > 12$ "exist" and are awaiting discovery or whether such nets have already been considered by others unbeknown to us.

[6] Crystals of $Ni(tpt)(NO_3)_2 \cdot$solvate were obtained by layering a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (45 mg) in ethanol (10 mL) on top of a solution of tpt (25 mg) in 1,1,2,2-tetrachloroethane (10 mL); ethanol (5 mL) served as a "buffer layer" between the two solutions. Crystals grew over a period of days as the solutions slowly interdiffused. Crystal stucture data: $0.45 \times 0.25 \times 0.25$ mm^3, trigonal, $P3_121$, $a = 15.216(2)$ $c = 18.650(6)$ Å, $V = 3740(1)$ Å^3, $Z = 3$, $\rho_{calcd} = 1.554$ g cm^{-3}, $2\theta_{max} = 55°$, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, ω:2θ scan mode, $T = 130$ K, 7302 measured reflections, 5719 independent reflections ($R_{int} = 0.0216$). Corrections were applied for Lorentz and polarization effects. Absorption coorrections applied (indexed crystal faces, SHELX-76[9]), $\mu = 1.29$ mm^{-1}, min./max. transmission factors 0.5784, 0.7343. Structure solved by using Patterson methods (SHELXS-86[10]). Full-matrix least squares refinement based on F^2, 321 parameters (SHELXL-97[11]), pyridyl hydrogen atoms placed at geometrically estimated positions, $R1 = 0.0839$, $wR2 = 0.2352$, max. residual electron density 1.049 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-108609. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Pentacarba-*arachno*-tridecaalane $(AlMe)_8(CCH_2Ph)_5H$ with an Al_8C_5 Skeleton—The First Polyhedral Carbaalane[**]

Werner Uhl[*] and Frank Breher

Carbaboranes contain clusters formed by boron and carbon atoms. Owing to their unique structures and bonding they have been intensively investigated in the last few decades and have been included in inorganic chemistry textbooks for a long time.[1] Up to now the corresponding carbaalanes with a skeleton containing only aluminum and carbon atoms were unknown; however, some compounds in which single aluminum atoms are inserted into borane or carbaborane clusters have been reported.[2] A suitable method for the synthesis of carbaboranes is based on the hydroboration of alkynyldialkylboranes with an excess of dialkylboron hydrides, but often the yields are very low.[3] Recently, our group has begun systematic investigations into the related hydroalumination reaction, in particular with regard to the synthesis of polyaluminum compounds. The latter have been attracting growing interest as chelating Lewis acids in phase-transfer processes or for the recognition of anions.[4] The hydroalumination of aluminum alkynides was described once before, however, the products were never isolated or characterized, and subsequent work up by hydrolysis generally yielded a mixture of hydrocarbons.[5] Similar treatment was reported for the products of the hydroalumination of organic alkynes.[6] The organoaluminum intermediates are, however, of great interest with regard to our investigations, and one of our aims is to isolate them in a pure form for a complete characterization. We report here on the remarkable reaction of dimethylaluminum hydride with dimethylaluminum phenylethynide (**1**).

When **1** was treated with dimethylaluminum hydride in *n*-pentane in a stoichiometric ratio, the color of the reaction mixture changed to red, but the ethynide was recovered in an almost quantitative yield. Compound **1** was only consumed completely when it was dissolved in an excess of the dimethylaluminum hydride and heated without a solvent to 80 °C over a period of two days. Monitoring the reaction by NMR spectroscopy indicated the formation of a large amount of trimethylaluminum, which was distilled off in vacuo at room temperature. Recrystallization of the reddish, solid residue from cyclopentane gave colorless crystals of the product **2** in 60 % yield [Eq. (a)].

$$11\ Me_2AlH + 5\ \underset{\mathbf{1}}{Me_2Al{-}C{\equiv}C{-}Ph} \longrightarrow \underset{\mathbf{2}}{(AlMe)_8(CCH_2Ph)_5H} + 8\ AlMe_3 \qquad \text{(a)}$$

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[*] Prof. Dr. W. Uhl, Dipl.-Chem. F. Breher
Fachbereich Chemie der Universität
Postfach 2503, D-26111 Oldenburg (Germany)
Fax: (+49) 441-798-3329

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