overinterpret the data. Despite the above mentioned concerns, we believe the supramolecular aspects of the crystal structures to be valid.

[22] Crystal data for **1**: crystal dimensions $0.50 \times 0.25 \times 0.10$ mm^3, monoclinic space group $C2/c$ (No. 15), $a = 35.645(11)$, $b = 4.851(3)$, $c = 24.804(9)$ Å, $\beta = 98.55(3)^\circ$, $V = 4241(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.185$ g cm^{-3}, $\mu = 0.067$ mm^{-1}, F(000) = 1584; 6107 reflections with $1.16 < \theta < 21.98^\circ$. Structure solution and refinement for 2591 independent reflections ($R_{int} = 0.192$) with $I > 2\sigma(I)$ and 272 parameters, $R = 0.0541$, $R_w = 0.0600$, max./min. residual electron density 0.139/ – 0.140 e Å^{-3}.

[23] Crystal data for **1**–F$_{15}$: crystal dimensions $0.80 \times 0.08 \times 0.08$ mm^3, monoclinic space group $P2_1/c$ (No. 14), $a = 18.308(7)$, $b = 4.887(4)$, $c = 27.145(14)$ Å, $\beta = 96.38(4)^\circ$, $V = 2414(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.784$ g cm^{-3}, $\mu = 0.186$ mm^{-1}, F(000) = 1272; 6965 reflections with $1.12 < \theta < 21.97^\circ$. Structure solution and refinement for 2943 independent reflections ($R_{int} = 0.088$) with $I > 2\sigma(I)$ and 406 parameters, $R = 0.0869$, $R_w = 0.0742$, max./min. residual electron density 0.250/ – 0.229 e Å^{-3}.

[24] Crystal data for **1**:**1**–F$_{15}$ (1:1 complex): crystal dimensions $0.30 \times 0.05 \times 0.05$ mm^3, triclinic space group $P\bar{1}$ (No. 2), $a = 7.4913(5)$, $b = 14.0798(9)$, $c = 22.2722(14)$ Å, $\alpha = 94.779(1)^\circ$, $\beta = 92.692(1)^\circ$, $\gamma = 91.580(1)^\circ$, $V = 2337.3(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.459$ g cm^{-3}, $\mu = 0.126$ mm^{-1}, F(000) = 1032; 23084 reflections with $0.92 < \theta < 28.66^\circ$. Structure solution and refinement for 10394 independent reflections ($R_{int} = 0.162$) with $I > 2\sigma(I)$ and 676 parameters, R = 0.0628, $R_w = 0.0582$, max./min. residual electron density 0.144/ – 0.172 e Å^{-3}.

[25] It has been noted that organofluorine almost never accepts hydrogen bonds; see: J. D. Dunitz, R. Taylor, *Eur. J. Chem.* **1997**, *3*, 89.

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Inorganic – Organic Hybrid Materials Constructed from $[(VO_2)(HPO_4)]_\infty$ Helical Chains and $[M(4,4'\text{-bpy})_2]^{2+}$ (M = Co, Ni) Fragments[**]

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The design and synthesis of inorganic–organic hybrid materials have generated significant interest for their potential application in the fields of catalysis, biology, and optical and electromagnetic functional materials.[1] Huge structures have been reported for these materials over the past few years, in which various architectures with one- (1D), two- (2D), and three-dimensional (3D) connections between inorganic and organic species are displayed. Polyoxoanions associated with organic templates[2] or with metal coordination compounds[3, 4] have become a well-established class of inorganic–organic materials, among these the major interest has been shown in the few helical or chiral structures reported. For instance, a double helical chain has been described in $[(CH_3)_2NH_2]K_4[V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7] \cdot 4H_2O$,[5] spirals of InO$_6$ octahedra in RbIn(OH)PO$_4$,[6] and a spiral-shaped chain in $[\{Cu(en)(OH_2)\}Mo_5P_2O_{23}]^{4-}$.[7] The rational synthesis of inorganic–organic compounds containing a helical array is a challenging goal.[8] Our aim was to synthesize such helical structures for the inorganic–organic compounds generated from a combination of vanadium phosphates[9] and metal coordination compounds. The diversity of polyhedra and valence states of vanadium together with the coupling characteristics of the components in the synthetic system provide the basis for constructing unusual structures.

Unlike the above examples, herein we report the synthesis and X-ray crystal structure analyses of the inorganic–organic hybrid materials **1** and **2**, which have not only an infinite helical chain $[(VO_2)(HPO_4)]_\infty$, but also both left-handed and right-handed helical chains in one compound.

$[M(4,4'\text{-bpy})_2(VO_2)_2(HPO_4)_4]$
(**1**: M = Co; **2**: M = Ni; bpy = bipyridine)

Compounds **1** and **2** were synthesized by the hydrothermal reaction of NaVO$_3$, NaH$_2$PO$_4$, Co(NO$_3$)$_2$ (for **1**) or Ni(NO$_3$)$_2$ (for **2**), 4,4'-bpy, and H$_2$O in a molar ratio 1:1:1:1:556 at 160 °C for five days. The crystalline product in each case was characterized by elemental analysis, IR spectroscopy, thermogravimetric analysis/differential thermal analysis (TGA–DTA), and single-crystal X-ray diffraction analysis.[10]

Single-crystal X-ray diffraction analysis revealed that **1** and **2**, which are analogues, have a novel 3D structure constructed from two subunits, namely $[(VO_2)(HPO_4)]_\infty$ helical chains and $[M(4,4'\text{-bpy})_2]^{2+}$ fragments. These helical chains are composed of alternately corner-sharing HPO$_4$ tetrahedra and VO$_4$N trigonal bipyramids (Figure 1). The central axis of each helical chain is a twofold screw axis. Two oxygen atoms from adjacent VO$_4$N and HPO$_4$ units in the helical chain chelate an M atom of $[M(4,4'\text{-bpy})_2]$, generating a 3-ring {MVPO$_3$}. These 3-rings link the left-handed helical and right-handed helical $[(VO_2)(HPO_4)]_\infty$ chains to produce a layer motif {MV$_2$P$_2$O$_{20}$} in the (101) plane (Figure 1 a). Adjacent M/V/P/O layers are connected by 4,4'-bpy ligands, which generates a 3D structure (Figure 2).

Each vanadium atom resides in a distorted trigonal-bipyramidal environment, coordinated to four oxygen atoms and to a nitrogen atom from 4,4'-bpy. Three of the four oxygen atoms lie in an equatorial plane; one of these oxygen atoms is terminal, and two are bridging, one with P and one with M. The remaining oxygen atom, which bridges P and the N atom from 4,4'-bpy, is oriented axially, perpendicular to the equatorial plane. PO$_4$ tetrahedra link two V atoms, an M atom, and a proton. The M atoms reside in octahedral environments, coordinated to four oxygen atoms from VO$_4$N and HPO$_4$ in the equatorial plane and to two nitrogen atoms from 4,4'-bpy ligands occupying the axial positions.

When 4,4'-bpy functions as a rodlike ligand it usually coordinates with only central metals. In the case reported herein, it acts as a bifunctional organic ligand, directly linked to M (Co or Ni) and to V atoms in the P-V-O chains. To our knowledge, this coordination mode has not been observed in

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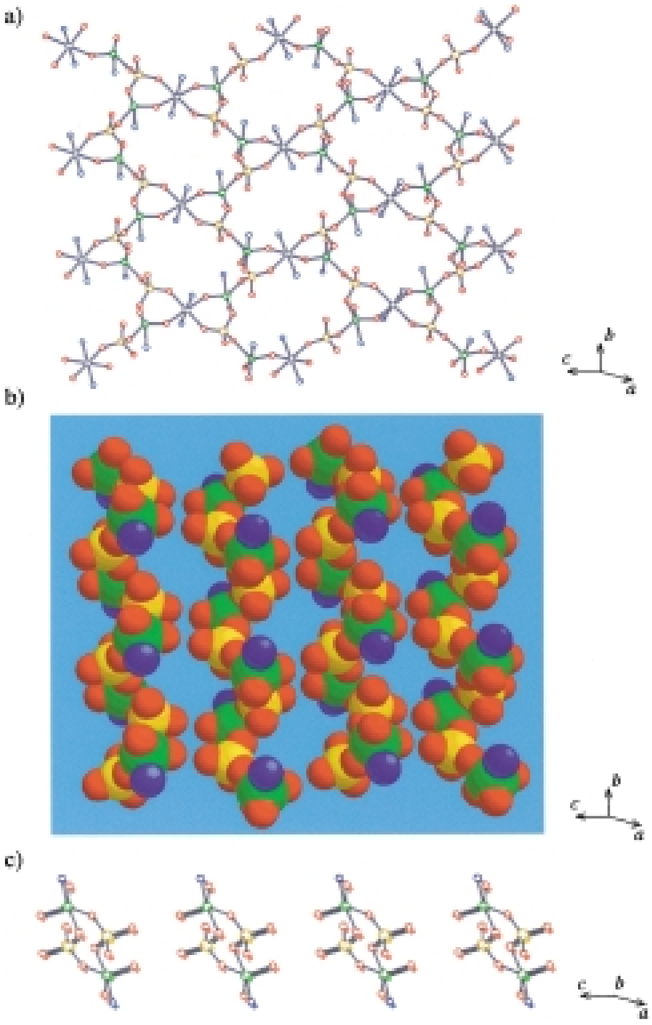

Figure 1. a) View of the structure of the M/V/P/O layer. b) View of the space-filling plot of the left-helical and right-helical V-P-O chains. c) View of the V-P-O helix along the *b* axis. Color code: M (Co or Ni): gray; V: green; P: yellow; O: red; N: blue.

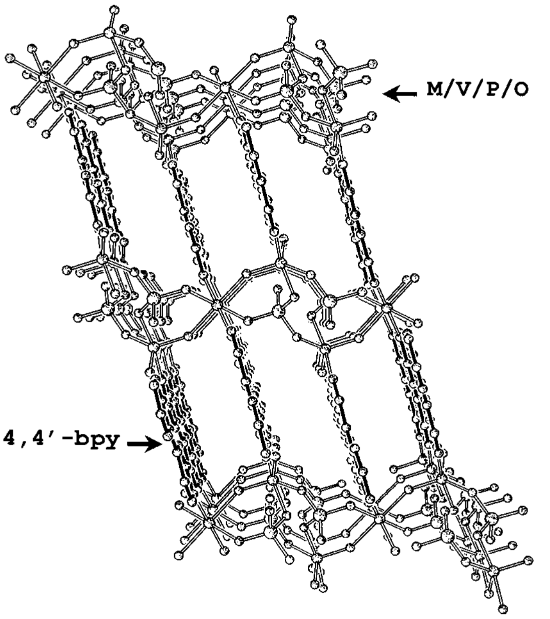

Figure 2. View of the structure of **1** and **2** along the (101) plane, showing the channels.

other compounds. The formation of the helix in the structure may be partly due to the introduction of an extra-force from the [M(4,4'-bpy)$_2$] fragment. The interaction of the [M(4,4'-bpy)$_2$] fragment with each vanadium atom on the helical chains may be very important for stabilizing the helix. Moreover, in the (101) plane the M-O-V and M-O-P units form an angle of about 48.5° with the M-N $\approx$ N-V connection line; this is necessary for building up the helix.

The structures of the two novel inorganic–organic hybrid compounds reported herein not only contain helical chains, but also possess left-handed and right-handed helical chains in one compound. These compounds could be important in terms of the rational synthesis and properties of helical inorganic–organic compounds.

Experimental Section

The syntheses were performed in 20-mL Teflon-lined stainless steel vessels filled to 50% at room temperature.

1: A mixture of $NaVO_3 \cdot H_2O$ (0.158 g), $NaH_2PO_4 \cdot H_2O$ (0.156 g), $Co(NO_3)_2 \cdot H_2O$ (0.291 g), 4,4'-bpy $\cdot H_2O$ (0.192 g), and H_2O in a molar ratio 1:1:1:1:556 was heated at 160°C for five days. This gave dark red columnar crystals of **1**. Elemental analysis (%) calcd for $C_{20}H_{18}N_4CoV_2P_2O_{12}$: C 32.95, H 2.49, N 7.68, Co 8.08, P 8.50, V 13.97; found: C 32.79, H 2.60, N 7.51, Co 8.11, P 8.62, V 13.82; IR (KBr pellet): $\tilde{\nu} = 1610$ (s), 1537 (m), 1489 (m), 1410 (s), 1304 (m), 1215 (m), 1142 (s), 1078 (m), 1026 (s), 1010 (s), 966 (s), 941 (s), 909 (s), 817 (s), 724 (m), 640 (s), 588 (m), 568 (m), 528 (s), 491 (m), 476 (m), 433 (m) cm^{-1}. Thermogravimetric analysis showed a weight loss of about 44% in the range from 380–520°C in air corresponding to the removal of 4,4'-bipyridine and the removal of H_2O from HPO_4.

2: A mixture of $NaVO_3 \cdot H_2O$ (0.158 g), $NaH_2PO_4 \cdot H_2O$ (0.156 g), $Ni(NO_3)_2 \cdot H_2O$ (0.291 g), 4,4'-bipy $\cdot H_2O$ (0.192 g), and H_2O in a molar ratio 1:1:1:1:556 was heated at 160°C for five days. This gave dark red blocks of **2**. Elemental analysis (%) calcd for $C_{20}H_{18}N_4NiV_2P_2O_{12}$: C 32.96, H 2.49, N, 7.69, Ni 8.05, P 8.50, V 13.98; found: C 32.83, H 2.58, N 7.75, Ni 8.00, P 8.61, V 13.84; IR data and results of thermogravimetric analysis were similar to those of **1**.

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[10] Crystal structure analysis: The data were collected at 293(2) K on a Bruker SMART-CCD diffractometer (graphite-monochromated $\mathrm{Mo_{K\alpha}}$-radiation: $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXTL Version 5.10) and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Crystal data for $C_{20}H_{18}N_4CoP_2V_2O_{12}$ (**1**): Crystal dimensions $0.170 \times 0.070 \times 0.070$ mm, monoclinic, space group *C*2/c (no. 15), $a = 25.1399(15)$, $b = 8.1532(5)$, $c = 15.6510(10)$ Å, $\beta = 127.0030(10)°$, $V = 2561.9(3)$ Å^3. $Z = 4$, $\rho_{\mathrm{calcd}} = 1.890\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 1.552\ \mathrm{mm^{-1}}$. Of the 6086 reflections measured ($2.60 \leq \theta \leq 23.24°$), 1832 symmetry-independent reflections were used to solve the structure. Based on all these data and 223 refined parameters, $R1 = 0.0349$ (all data), $wR2 = 0.0824$, and goodness-of-fit on F^2 is 1.039. Crystal data for $C_{20}H_{18}N_4NiP_2V_2O_{12}$ (**2**): Crystal dimensions $0.160 \times 0.080 \times 0.050$ mm, monoclinic, space group *C*2/c (no. 15), $a = 25.025(3)$, $b = 8.1660(12)$, $c = 15.610(2)$ Å, $\beta = 127.477(3)°$, $V = 2531.5(6)$ Å^3. $Z = 4$, $\rho_{\mathrm{calcd}} = 1.913\ \mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo_{K\alpha}}) = 1.659\ \mathrm{mm^{-1}}$. Of the 6008 reflections measured ($2.05 \leq \theta \leq 23.27°$), 1822 symmetry-independent reflections were used to solve the structure. Based on all these data and 223 refined parameters, $R1 = 0.0385$ (all data), $wR2 = 0.0876$, and goodness-of-fit on F^2 is 1.089. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137922 (**1**) and CCDC-137923 (**2**). 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).

Salen as a Chiral Activator: *anti* versus *syn* Switchable Diastereoselection in the Enantioselective Addition of Crotyl Bromide to Aromatic Aldehydes**

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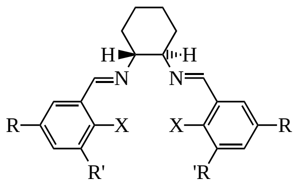
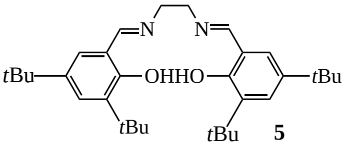
Achille Umani-Ronchi*

Diastereoselective addition of organometallic reagents is widely used in preparative organic synthesis.[1] The stereochemical outcome of the reaction derives from the ability of the metal to behave as a Lewis acid and therefore to control the addition "via" a cyclic or acyclic transition state. Stereogenic allyl chromium reagents normally add to carbonyl compounds to furnish the corresponding homoallylic alcohols with a high level of *anti* diastereoselection "via" a cyclic Zimmermann–Traxler-type transition state.[2] Moreover, when the above-mentioned nucleophilic addition is performed with a catalytic redox cycle ([Cr] 7 mol%, Mn, Me_3SiCl), the same level of diastereoselection is observed.[3] Herein we report that by changing the amount of the salen ligand (**1**)[4] employed (salen = (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) it is possible to switch the simple diastereoselection from *anti* to *syn* in the catalytic addition of chiral organochromium reagents to aromatic aldehydes. Recently, we described the first enantioselective version of the Nozaki–Hiyama reaction performed in the presence of a catalytic amount of a [Cr(salen)] complex.[5]



1: X = OH, R = *t*Bu, R' = *t*Bu;
2: X = OMe, R = *t*Bu, R' = *t*Bu;
3: X = OH, R = *t*Bu, R' = H;
4: X = OH, R = *t*Bu, R' = Br;



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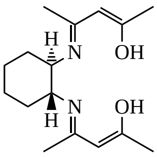

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