lengths are expected to be 56 and 27 nm for PAC-**1** and PAC-**2**, respectively, which correspond approximately to the actual average PAC lengths adsorbed in the presence of alkanes. Therefore, we suggest that the length distribution of PACs in solution is preserved upon co-adsorption of PAC and alkanes. Apparently, PACs and alkanes co-assemble at the interface without interfacial reorganization.

In summary, almost perfectly straight and epitaxially oriented chains of metallosupramolecular coordination-polyelectrolyte–amphiphile complexes formed from rigid ditopic metal ion receptors are self-assembled on the basal plane of graphite by using long chain alkanes as an orienting template layer. Through a sequence of molecular recognition steps comprising metal ion coordination, electrostatic interactions, and amphiphilic self-assembly the adsorption of nanoscopic assemblies can be performed at an interface in a predictable manner. Controlling the correlation of position and orientation is of paramount importance for encoding new properties and functions.[15] On-going research in our laboratories indicates that this approach is of general utility. The modularity of this approach provides an entry to encode the value-adding physicochemical properties of metallosupramolecular devices into nanoscopic architectures that can be addressed and manipulated individually by scanning probe techniques.

Experimental Section

Ligands **1**, **2**, and **3** were prepared according to literature procedures.[16] The assembly of MEPE and PAC was carried out according to previously published procedures.[8] Alkanes ($C_{32}H_{66}$, $C_{44}H_{90}$, $C_{50}H_{102}$, Aldrich) were used as received. Solutions of neat PACs ($1.3\times10^{-3}\,\mathrm{g\,L^{-1}}$) or mixtures of PAC ($1.3\times10^{-3}\,\mathrm{g\,L^{-1}}$) with $C_{32}H_{66}$, $C_{44}H_{90}$, $C_{50}H_{102}$ ($1.3\times10^{-2}\,\mathrm{g\,L^{-1}}$) were spin-coated onto the basal plane of highly oriented pyrolytic graphite (HOPG, Advanced Ceramics Co., USA, quality ZYH at 40 rps). The coated graphite samples were dried for 10 min at 40 °C before SFM investigations were carried out with a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in the tapping mode. An E-scanner over a range of scan lengths from 5 to 0.3 μm, and commercial Si cantilevers (length 125 μm and width 30 μm) with spring constants between 17 and 64 $\mathrm{N\,m^{-1}}$ were used.

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$(C_2H_{10}N_2)[Cr(HPO_3)F_3]$: The First Organically Templated Fluorochromium(III) Phosphite**

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In recent years the search for new open-framework materials with transition metal elements has become the focus of much interest due to the potential application of these materials as absorbents, ion exchangers, solid-state electrolytes, and catalysts in heterogeneous catalysis.[1] Such applications are not possible with main group systems of tetrahedral framework zeolites. The syntheses of these materials usually involve organic templates, for example organic diamines, for generating large cavities and are performed under mild hydrothermal conditions to avoid the formation of dense phases.

Microporous behavior has been successfully extended to the phosphate and arsenate systems of at least 14 elements of the periodic table, but examples dealing with chromium have not been reported.[1b,2] The pattern of behavior of these kinds of compounds is underpinned by the strength of the P–O

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bond, which is broadly comparable with that of Si–O and Al–O bonds. Therefore, the relative stabilities within this family of M-P-O materials are probably determined by the M–O bond strengths. However, less work has been carried out on the anionic part of the inorganic network. The possibility of incorporating the pyramidal $(HPO_3)^{2-}$ hydrogen phosphite group into extended structures templated by inorganic alkaline earth cations was explored a few years ago.[3] Recently we prepared several phosphite compounds templated by alkyldiamine molecules,[4] which incorporate 3d transition metal cations.

At a first glance it appears that the Cr^{III}-P-O system would surely show excellent kinetic and thermodynamic stability, given the large ligand field stabilization energy of the octahedrally coordinated Cr^{III} cation. However, the particular behavior of Cr^{III} in solution, with many condensation steps between the octahedra, can make the attainment of Cr^{III} phosphate systems difficult.[5] Recently, a chromium(III) dicarboxylate compound exhibiting a microporous structure was formed.[6] To date, neither inorganic–organic hybrid phosphate nor phosphite materials containing the Cr^{III} cation have been reported. Here we describe the synthesis and crystal structure of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$, the first organically templated M-P-O compound containing Cr^{III}.

The crystal structure of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$ consists of $[Cr(HPO_3)F_3]^{2-}$ chains running along the [001] direction, in which the fluoride anions stabilize the +3 oxidation state of chromium. The ethylenediammonium cations are in the cavities of the structure delimited by three different chains (Figure 1). These organic cations establish both ionic interactions and hydrogen bonds with the anionic chains.

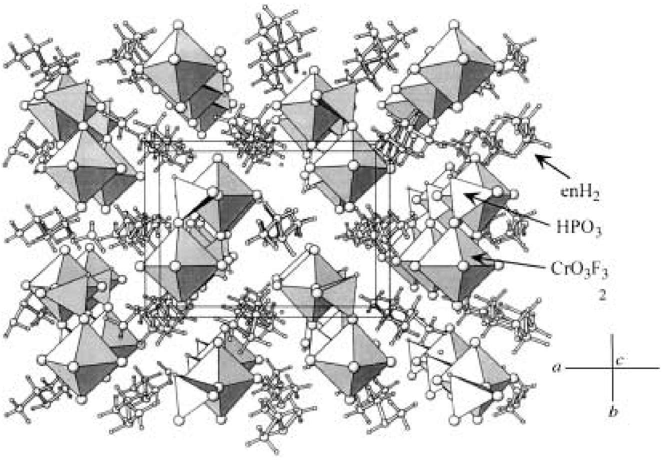

Figure 1. Crystal structure of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$.

The $[Cr(HPO_3)F_3]^{2-}$ chains are constructed from isolated CrO_3F_3 octahedra and pseudopyramidal $(HPO_3)^{2-}$ phosphite oxoanions (Figure 2). The CrO_3F_3 octahedra share the *trans* O(1) and O(3) atoms with the HPO_3 tetrahedra, forming an infinite chain of alternating octahedra and tetrahedra. Each octahedron also shares its O(2) atom with another HPO_3 tetrahedron belonging to a parallel chain, giving rise to infinite double chains as shown in Figure 2. A remarkable feature of this compound is the absence of covalent Cr-O-Cr intrachain interactions.

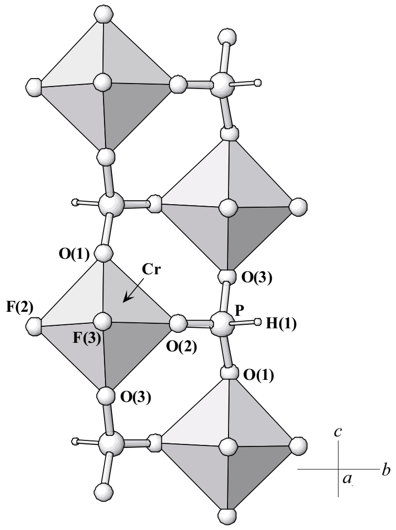

Figure 2. Representation of the chains in $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$. The Cr–O and Cr–F distances range from 1.880(3) to 1.974(4) Å. The *cis* and *trans* angles are between 86.3(2)–94.7(2)° and 175.7(2)–176.4(2)°, respectively. The Cr^{III}–Cr^{III} intrachain bond distances are 4.883(2) and 6.508(2) Å. The mean P–O bond distance is 1.55(8) Å.

The reflectance diffuse spectrum of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$ is characteristic of Cr^{III} with octahedral coordination.[7] The values of the D_q and Racah parameters are $D_q = 1535\ cm^{-1}$, $B = 720\ cm^{-1}$, and $C = 3280\ cm^{-1}$. The B parameter is approximately 75% of that corresponding to the Cr^{III} ion (918 cm^{-1}), which indicates the existence of significant covalent character in the Cr–O bonds.

The molar magnetic susceptibility χ_m increases with decreasing temperature in the range studied (Figure 3). The thermal evolution of χ_m follows the Curie–Weiss law at temperatures above 10 K, with $C_m = 1.88\ cm^3\,K\,mol^{-1}$ and $\theta = -5.4$ K. The value for $\chi_m T$ decreases from 1.84 cm^3 K mol^{-1} at 300 K to 0.88 cm^3 K mol^{-1} at 5.0 K, indicating the existence of antiferromagnetic interactions.

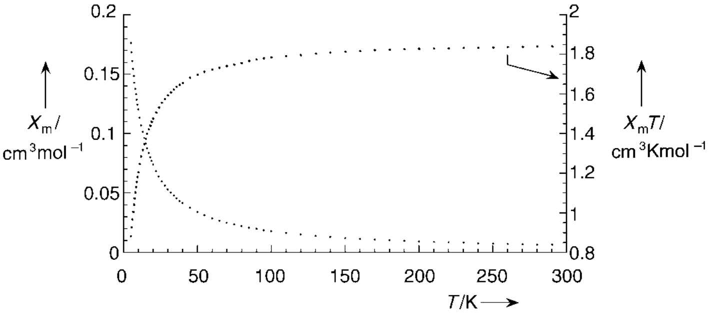

Figure 3. Thermal evolution of the molar magetic susceptibility χ_m and the product $\chi_m T$ for $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$. The arrow in the figure indicates that the curve corresponds to the $\chi_m T$ versus T representation.

Experimental Section

$(C_2H_{10}N_2)[Cr(HPO_3)F_3]$: A mixture of $Cr(NO_3)_3 \cdot 9H_2O$ (1.00 g, 2.51 mmol), H_3PO_3 (1.23 g, 15.00 mmol), HF (1.0 mL, 27.59 mmol), and ethylenediamine (up to pH 2.0) in 20 mL of water/ethanol (1/1) was stirred until homogeneous, and sealed in a PTFE-lined (PTFE = poly(tetrafluoroethy-

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lene) stainless-steel pressure vessel (fill factor 75%). The reagents were heated at 170°C for 5 d, and then the mixture was slowly cooled to room temperature. The pH value did not show any appreciable change during the hydrothermal reaction. Small, well-formed, green single crystals were formed. Elemental analysis calcd for $C_2H_{11}CrF_3N_2O_3P$: C 9.5, H 4.3, N 11.1, P 12.2, Cr 20.5, F 22.5; found: C 9.3, H 4.1, N 10.8, P 12.0, Cr 20.1, F 22.0. The IR spectrum does not show any bands above 3500 cm^{-1}, in accordance with the absence of $(OH)^-$ groups.[8] A density of 2.11(1) $g\,cm^{-3}$ was measured by flotation in $CHCl_3/CHBr_3$ (60/40).

Physical measurements: The diffuse reflectance spectrum was recorded at room temperature on a Cary 2415 spectrometer from 210–2000 nm. Magnetic measurements on powdered samples were performed at temperatures between 5.0–300 K, using a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field was 0.1 T, a value in the range of linear dependence of magnetization vs. magnetic field, even at 5.0 K.

Structure determination of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$: $0.08 \times 0.035 \times 0.03$ mm, $M_r = 251.10$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 12.801(2)$, $b = 9.337(1)$, $c = 6.508(1)$ Å, $V = 777.9(2)$ Å^3, $Z = 4$, $\mu = 1.703$ mm^{-1}, $\rho_{calcd} = 2.144$ $g\,cm^{-3}$, $F(000) = 508$. The data were collected on a BRUKER SMART-APEX CCD automated diffractometer (graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 100$ K). Of 4588 measured reflections ($2.70° \leq \theta \leq 28.45°$), 1176 were independent ($R_{int} = 0.0521$) and 1100 observed ($I > 2\sigma(I)$). An absorption correction based on symmetry-equivalent reflections was applied using SADABS.[9] The structure was solved by direct methods (SHELXS 97)[10] and refined by the full-matrix least-squares method based on F^2, using the SHELXL 97 computer program[11] belonging to the WINGX V1.63.02 software package.[12] All non-hydrogen atoms were assigned anisotropic thermal parameters. The atomic coordinates of the hydrogen atoms of the phosphite anions were calculated from difference Fourier maps, the hydrogen atoms of the ethylenediammonium cations were geometrically placed. Final R factors: $R1 = 0.088$ (all data), $wR2 = 0.127$; max./min. electron density 0.673/–0.976 e Å^{-3}; goodness of fit on F^2: 0.879. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-412497. A simulation based on the single-crystal structure of $(C_2H_{10}N_2)[Cr(HPO_3)F_3]$ was in excellent agreement with the X-ray powder data, indicating phase purity and high crystallinity.

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Tuning Electronic Behavior of Carbonyl Metal Clusters by Substitution of Interstitial and Capping Atoms[**]

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Ligand-stabilized, nanosized metal clusters have been proposed as an ultimate solution for nanolithography and microelectronics.[1] In this context metal carbonyl clusters could also play a role as they are potential nanocapacitors. However, for the cluster to truly function as a capacitor, its CO shell should effectively insulate the metal core, and it should be able to reversibly accept and donate electrons. At present there is no evidence of intermolecular exchange of electrons between differently charged carbonyl clusters, at least on the EPR timescale. They act as quantum dots, in which the cluster valence electrons are confined.[2] However, most metal carbonyl clusters displaying redox behavior have fortuitously been obtained.[3]

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