ized ^{1}H MAS spin-echo NMR spectrum of B-ZSM-5, which exhibits two maxima at $\delta = 1.7$ and 2.0 and a broad shoulder at $\delta = 3.0$. The corresponding ^{1}H{^{11}B} REDOR spectrum (evolution time 16.8 ms) is displayed in Figure 2b and shows a substantial decrease in the intensity of the maximum at $\delta = 2.0$ and the shoulder at $\delta = 3.0$. This is also evident in the difference spectrum (Figure 2c), in which the relatively weak change in the intensity of the signal at $\delta = 1.7$ can be seen. Although further work is necessary to clarify the detailed assignment of these three signals, it is clear that they arise from protons near to ($\delta = 3.0$, 2.0) or remote from ($\delta = 1.7$) framework boron atoms. We assign the signal at $\delta = 1.7$ to defect silanol groups, and the signals at $\delta = 3.0$ and $\delta = 2.0$ to the SiOH $\cdots$ B[3] groups in the zeolite framework. The observation of two different chemical shifts for these sites is similar to findings for analogous zeolites that contain aluminum instead of boron.[9] The weak REDOR effect of the defect silanol groups is explained by their remoteness from boron atoms in the next nearest tetrahedral framework positions (B[3] or B[4]). Consistent with this model, we expect the B[3] units to be closely associated with the protons, since the charge of the B[4] units is balanced by sodium cations (see above). This conjecture is confirmed by the ^{11}B{^{1}H} REDOR curve in Figure 2d. The initial slope of the curve for B[3] is much steeper than for B[4], and this proves that the B[3] units are significantly closer to protons than the B[4] units. This suggests the formation of SiOH $\cdots$ B[3] groups, whereas the B[4] units are fairly remote from protons. Although it should be possible in principle to estimate an approximate B–H distance from such experiments, we refrain from doing so here, because the presence of long-range interactions means that no isolated spin pairs are present.

Our ^{11}B{^{23}Na}, ^{11}B{^{1}H}, and ^{1}H{^{11}B} REDOR results provide the first direct evidence that tetrahedral B[4] units are associated with charge-balancing sodium cations in dehydrated B-ZSM-5. Trigonal B[3] units are located in SiOH $\cdots$ B[3] groups, as predicted by the theoretical calculations of Sauer.[5] Two proton NMR signals at $\delta = 2.0$ and 3.0 are observed for these sites. The results from experiments with other Na/H ratios are consistent with the data presented here.

Experimental Section

Zeolite B-ZSM-5 was hydrothermally crystallized at 423 K from a gel of molar composition H_3BO_3:NaOH:TPABr:TPAOH:H_2O:SiO_2 = 0.084:0.08:0.06:0.04:36:1. Calcination was carried out in air at 923 K, and the resulting zeolite powder was carefully dehydrated in vacuum at 623 K. The sample was initially heated to 353 K at 5 K min^{-1} and held at this temperature for 2 h. Subsequently the temperature was raised at 10 K min^{-1} to 623 K and kept at this temperature for 4 h. Solid-state double resonance NMR experiments on the dry samples were carried out on a Bruker DSX-500 spectrometer with a 4 mm triple resonance probe operating at 10 kHz spinning speed. The rotor speed was maintained by a standard automatic control unit. The resonance frequencies for ^{1}H, ^{11}B, and ^{23}Na are 500.11, 160.45, and 132.29 MHz, respectively.

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An Unexpected Layered Structure in Inorganic Cyanide Clusters: $[Cu_4(\mu_3\text{-}OH)_4][Re_4(\mu_3\text{-}Te)_4(CN)_{12}]$**

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Cyanide compounds have been known for nearly three centuries.[1–3] New complex transition metal cyanides have been described recently that promise to have a variety of useful applications.[4–7] Complex cyanides demonstrate unique structures, properties, and reactivity.[1–7] The ambidentate nature of the CN^- ligand, its terminal and bridging binding modes, its wide variety of coordination number, and arrangement of metal centers favor the formation of amazing and unusual structures both for binary and for complex cyanides of transition metals. The last few years have made available the cyanide clusters.[8–14] The availability of these compounds gave us the possibility to begin the study of their chemistry systematically.

We have recently prepared and structurally characterized caesium and potassium salts containing the new cyanide cluster anion $[Re_4(\mu_3\text{-}Te)_4(CN)_{12}]^{4-}$.[13, 14] Here we report the new complex, polymeric inorganic cluster compound $[Cu_4(\mu_3\text{-}OH)_4][Re_4(\mu_3\text{-}Te)_4(CN)_{12}]$ (**1**) built from these cluster anions.

Compound **1** was prepared by adding a solution of $CuCl_2$ to $K_4[Re_4Te_4(CN)_{12}]$ in silica gel at about pH 7. The structure of **1** was solved by X-ray single-crystal analysis.[15] The structure consists of layers built from the tetranuclear copper(II) cations

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$[Cu_4(\mu_3\text{-}OH)_4]^{4+}$ (Figure 1a) and the cluster anions $[Re_4Te_4(CN)_{12}]^{4-}$ (Figure 1b). Eight of the twelve CN^- ligands of each anion are bonded to copper atoms in the layer (Figure 2). The remaining four CN^- ligands are directed perpendicular to the

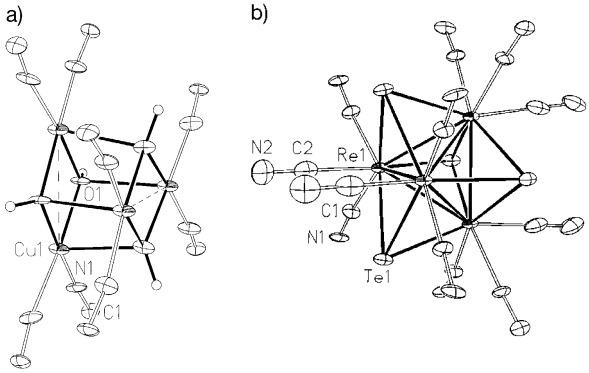

Figure 1. The structures of the $[Cu_4(\mu_3\text{-}OH)_4]^{4+}$ cation (a) and the cluster anion $[Re_4(\mu_3\text{-}Te)_4(CN)_{12}]^{4-}$ (b); the thermal ellipsoids are at the 50% probability level. Selected bond length [Å]: Re–Re 2.834(1) (3×), 2.857(1)(3×), Re–Te 2.632(2), 2.636(1) (2×), Re–C 2.04(2), 2.10(2) (2×), Cu–O 1.934(7) (2×), 2.31(1), Cu–N 1.96(1) (2×).

layer and form hydrogen bonds with hydroxyl groups from cations belonging to the neighboring layers (Figure 3); the N–O distances are 2.82 Å.

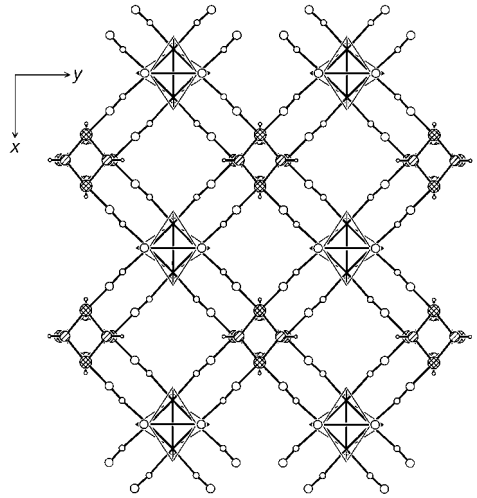

Figure 2. The covalent layer in **1** (projection along the *xy* plane). The Re–(μ_3-Te) bonds are shown by thin lines.

The geometrical characteristics of the cluster anion are close to those previously reported.[13, 14] The structure of the Re_4Te_4 core is typical of metal–chalcogen cubane clusters. In the cation $[Cu_4(\mu_3\text{-}OH)_4]^{4+}$ four Cu atoms and four OH groups also form a cubane-like complex, elongated along the direction *z* axis, with two short and four long Cu–Cu contacts of 2.99 and 3.18 Å, respectively (Figure 1a). The coordination polyhedron of the Cu^{2+} ions is a distorted square pyramid with two oxygen and two nitrogen atoms in the basal plane and one oxygen atom in the axial position. The cubane-like $Cu_4(\mu_3\text{-}O)_4$ fragment was found previously in many Cu^{2+} complexes. But

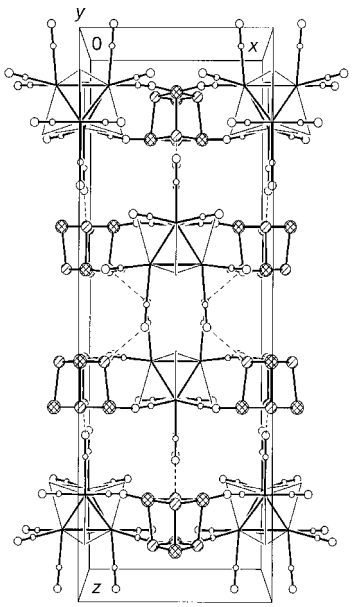

Figure 3. The packing of the layers (projection along the *xz* plane). The hydrogen bonds are shown by dashed lines.

there are only two known compounds with the $\{Cu_4(\mu_3\text{-}OH)_4\}$ core: $[Cu_4(OH)_4(SO_3CF_3)_2\{N(py)_3\}_4]\cdot[SO_3CF_3]_2\cdot C_3H_6O$[17] (**2**, py = pyridine) and $[Cu(bpy)OH]_4(PF_6)_4$[18] (**3**, bpy = 2,2′-bipyridine). In many other cases the O atoms in the Cu_4O_4 fragment belong to the organic ligands. The $Cu_4(\mu_3\text{-}OH)_4$ fragments in both **2** and **3** appear to be similar to that **1**. The main difference is that the copper atoms in compounds **2** and **3** are coordinated by six donor atoms, not by five as in **1**. Also, the distortions of the Cu_4 clusters from an ideal tetrahedral geometry in compounds **2** and **3** are larger than in **1** (the mean bond distances Cu–Cu are 2.970 and 3.32 Å in **2**[17], 2.914 and 3.408 Å in **3**,[18] and 2.99 and 3.18 Å in **1**).

The layers in the structure of **1** are arranged in such a way that the classical four-layered packing (···ABCDA···) is formed (Figure 3). The crystals do not have the plate shape usually expected for covalent layered structures. In our case prismatic and even cylindrically shaped crystals have been obtained. The single crystal used for structure analysis was elongated in the direction perpendicular to the layers. In the infrared spectrum[19] the O–H stretching vibration occurs at 3360 cm^{-1}, which is close to that found for **2** (3470 cm^{-1}).[17] Two bands at 2191 and 2145 cm^{-1} correspond to the two different CN groups, namely, the bridging and terminal ones, respectively. Preliminary magnetic measurements of the title compound between room temperature and 78 K showed a complex antiferromagnetic interaction of copper(II) ions; a maximum in χ_M occurs at about 260 K. Detailed magnetic and EPR studies are in progress.

Experimental Section

Preparation of single crystals of **1**: A solution of commercial waterglass (10 mL) in water (100 mL) was titrated with acetic acid (0.5 M) to produce pH ≈ 7. After titration the mixture was placed into a U-tube, and the gel allowed to set for one day. Diffusion in the opposite direction of aqueous solutions of $K_4[Re_4Te_4(CN)_{12}]$ (0.1 mmol L^{-1}) and $CuCl_2$ (0.5 mmol L^{-1}) through the silica gel for four weeks resulted in single crystals, some of

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which were suitable for single-crystal X-ray determination. The crystals were separated from the silica gel manually. Yield: ≈70%. Our attempts to obtain the title compound by simply mixing the solutions of starting materials were unsuccessful. However, the compound can be prepared by slow diffusion of reagents through a fritted glass filter (pore size several microns).

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Reactions of Selected Bismuth Oxide Cluster Cations with Propene**

Markus Kinne, Andreas Heidenreich, and Klaus Rademann*

Many chemical and physical properties of metal clusters have been determined over the past few years.[1] One of the main reasons for studying these compounds—in addition to carrying out fundamental research in itself—is the hope of obtaining a deeper insight into the sequence of events involved in catalytic processes.[2] To this end, the reactions of pure metal clusters deposited on surfaces and of free particles in the gas phase were studied.[3] Moreover, a great number of experiments on the formation and stability of metal oxide clusters have been carried out, but very little is known about the reactions themselves.[4] This is all the more astonishing when one considers that metal oxides in particular are widely employed as catalysts in the chemical industry. Bismuth oxide compounds are used, for example, in the oxidation of propene and butene.

We prepared bismuth oxide clusters with a modified gas aggregation source and carried out reactions with them. In order to do this, the pure metal was vaporized directly into a stream of cooled helium, whereupon clusters were formed due to oversaturation. Bismuth oxide clusters were formed by adding oxygen to the bismuth vapor. These were then ionized by using a short-pulse excimer laser (ATL, pulse length 2–4 ns, wave length 248 nm, laser energy 10 mJ) and identified by using a Wiley-McLaren mass spectrometer. The oxidation did not lead to a broad distribution of different mixed oxides, but rather to a cluster series with the general formula $BiO^+(Bi_2O_3)_n$.[5] The structures of the $Bi_3O_4^+$ and $Bi_5O_7^+$ isomers obtained from ab initio geometry optimizations at the MP2 level are shown in Figures 1a–c and 2a, b.[6] Two closed isomers were found for $Bi_3O_4^+$ (Figures 1a, b). Attempts to formulate structures with terminal O atoms—in as far as any local minima on the potential hypersurface could be found for them—always led to considerably higher energies. The formation of structures with terminal O atoms can thus be excluded under experimental conditions. The open isomer (Figure 1c) is, at 4.6 eV, higher in energy than the isomer in Figure 1a. The ground state in all three structures is a singlet and the corresponding vertical singlet–triplet splittings are 4.6, 3.5, and 1.8 eV. Two isomer types are observed for the closed structures $Bi_3O_4^+$ and $Bi_5O_7^+$. In type 1 (Figures 1a and

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