(C–O 2.36–2.66 Å), and 3) π-stacking interactions between the electron-rich catechol rings of the crown ether and the electron-poor aromatic rings and ester group of the pyridinium salt.

The new binding motif for the formation of [2]pseudorotaxanes presented herein demonstrates for the first time that simple crown ethers can be used to form [2]pseudorotaxanes. The ability to easily tune the interaction strength and the availability of these simple components bodes well for the extension of this motif to more complex supramolecular systems with interlocked [*n*]rotaxanes and [*n*]catenanes.

Experimental Section

All pyridinium bromide salts were prepared by the literature method.[14] The BF_4^- salts were precipitated from water by the addition of $NaBF_4$ or NH_4BF_4 and recrystallized before use. DB24C8 was purchased from Aldrich and used as received. B24C8 and 24C8 were prepared by literature methods.[15] In a typical experiment, [2]pseudorotaxanes were formed in solution by mixing equimolar solutions of **2a**$(BF_4)_2$–**d**$(BF_4)_2$ and crown ether in MeCN. Typical data for [2]pseudorotaxanes in which $X = CO_2Et$: **3d**: ^1H NMR (300 MHz, CD_3CN, 298 K): $\delta = 9.27$ (d, 4H, $J = 5.3$ Hz; α-pyH), 8.56 (d, 4H, $J = 5.3$ Hz; β-pyH), 5.40 (s, 4H; NCH_2), 4.50 (q, 4H, $J = 7.1$ Hz; $C(O)OCH_2$), 3.50 (s, 32H; OCH_2), 1.44 (t, 6H, $J = 7.1$ Hz; CH_3); ES-MS *m*/*z* (%): 770 (5) $[M - BF_4]^+$, 341 (100) $[M - 2BF_4]^{2+}$. **4d**: ^1H NMR (300 MHz, CD_3CN, 298 K): $\delta = 9.24$ (d, 4H, $J = 6.4$ Hz; α-pyH), 8.36 (d, 4H, $J = 6.4$ Hz; β-pyH), 6.80 (m, 4H; Ar), 5.46 (s, 4H; NCH_2), 4.47 (q, 4H, $J = 7.1$ Hz; $C(O)OCH_2$), 4.02 (m, 4H; $ArOCH_2$), 3.94 (m, 4H; OCH_2), 4.83 (m, 8H; OCH_2), 3.63 (m, 4H; OCH_2), 3.43 (m, 4H; OCH_2), 3.18 (m, 4H; OCH_2), 1.44 (t, 6H, $J = 7.1$ Hz; CH_3); ES-MS *m*/*z* (%): 818 (7) $[M - BF_4]^+$, 365 (100) $[M - 2BF_4]^{2+}$. **5d**: ^1H NMR (300 MHz, CD_3CN, 298 K): $\delta = 9.24$ (d, 4H, $J = 6.7$ Hz; α-pyH), 8.14 (d, 4H, $J = 6.7$ Hz; β-pyH), 6.74 (m, 8H; Ar), 5.58 (s, 4H; NCH_2), 4.40 (q, 4H, $J = 7.1$ Hz; $C(O)OCH_2$), 4.00 (m, 24H; OCH_2) 1.44 (t, 6H, $J = 7.1$ Hz; CH_3); ES-MS *m*/*z* (%): 865 (12) $[M - BF_4]^+$, 389 (100) $[M - 2BF_4]^{2+}$.

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[13] Crystal structure data for **5d**$(BF_4)_2$: monoclinic, space group $P2_1/c$, $a = 13.2421(4)$, $b = 15.7037(5)$, $c = 12.1739(4)$ Å, $\beta = 94.909(1)°$, $V = 2522.3(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.308\ g\,cm^{-3}$, $2\theta_{max} = 45.0°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 296$ K. A pale yellow crystal with dimensions $0.2 \times 0.2 \times 0.3$ mm was grown by vapor diffusion of isopropyl ether into a solution of **5d** in MeCN and mounted on a fibre. The 3280 unique reflections ($R_{int} = 0.0715$) were integrated from frame data obtained from programmed hemisphere scan routine on a Siemens SMART CCD diffractometer. Decay (<1%) was monitored by 50 standard data frames measured at the beginning and end of data collection. Systematic absences in the diffraction data and determined unit-cell parameters were consistent with the space group $P2_1/c$. Lorentzian-polarization correction and semi-empirical absorption correction, based on redundant data at varying effective azimuthal angles, were applied to the data ($\mu = 0.112\ cm^{-1}$, min./max. transmission = 0.221/0.492). The structure was solved by direct methods, with Fourier syntheses, and refined with full-matrix least-squares methods against $|F^2|$ data to give $R(F) = 0.0815$, $wR(F^2) = 0.2271$, GOF = 1.033, $N_o/N_v = 3275/354$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (Sheldrick, G. M., Madison, WI). 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-101459. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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$[Te_6N_8(TeCl_4)_4]$—Tellurium Nitride Stabilized by Tellurium Tetrachloride

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Exactly 100 years ago tellurium nitride was first obtained by the reaction of tellurium tetrabromide with liquid ammonia.[1] The composition TeN was ascribed to this yellow, extremely poorly soluble, and highly exlosive substance. Considering the analogy to the crystallographically well characterized homologues S_4N_4[2] and Se_4N_4,[3] this assignment has not been entirely ruled out to this day.[4] However, later analytical work made the composition Te_3N_4 with tetravalent tellurium probable.[5–7] The tellurium compounds with nitride functionalities which were characterized in recent years also derive from tellurium(+IV). Among these are the complexes of type **1** with X = Cl[8] and F,[9] which correspond to the structure motif **A** with pyramidal nitride functionality, and the nitride

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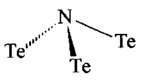
halides **2**[10] and **3**[11] with the structure motif **B** and trigonal-planar nitride functionality, which is also realized in **4** with the structure motif **C**.

$N[Te(NSN)X]_3$ **1**
$(X = F,Cl)$

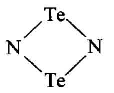
$[Te_4N_2Cl_8](AsF_6)_2$ **2**

$[Te_3N_2Cl_5(SbCl_5)]SbCl_6$ **3**

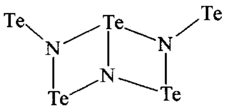
$Te_{11}N_6Cl_{26}$ **4**



A



B



C

We now found a method of approach to tellurium nitride stabilized by $TeCl_4$ molecules in the reaction of tellurium tetrachloride with tris(trimethylsilyl)amine in THF [Eq. (1)]. This tellurium nitride can be obtained in more than 80% yield.

$$10\,TeCl_4 + 8\,N(SiMe_3)_3 \xrightarrow{THF} \underset{\mathbf{5}}{[Te_6N_8(TeCl_4)_4]} + 24\,ClSiMe_3 \qquad (1)$$

Compound **5** forms pale yellow, moisture-sensitive, non-explosive crystals. According to the crystal structure analysis[13] these crystals still contain 7.5 equivalents of THF per formula unit, four of which enter into weak bonding interactions with the atoms Te1 and Te2. With 271.3 pm their Te–O distances agree with the Te–O bond lengths of 273.1 pm in $[TeCl_4(OPCl_3)]_2$.[16] The core of the structure of $[\mathbf{5}\cdot 4\,THF]\cdot 3.5\,THF$ consists of the rhombic dodecahedral unit Te_6N_8, in which the tellurium atoms form the corners of a distorted octahedron and the nitrogen atoms occupy the faces of the octahedron as μ_3 ligands (Figure 1). Four of these nitrogen atoms are coordinated with $TeCl_4$ molecules, the chlorine atoms of which adjust themselves well to the shape of the Te_6N_8 core due to the steric effect of the free electron pair at the tellurium atom (Figure 2). At the same time, with 304–331 pm the distances of the chlorine ligands of the $TeCl_4$ molecules to the Te atoms of the core which are not coordinated with THF are clearly below the van der Waals sum of radii (381 pm). Since the shielding of the Te_6N_8 core obtained thereby is not yet perfect, the tellurium atoms Te1 and Te2 which are facing each other are solvated by THF molecules. This results in Te_6N_8 molecules which are isolated from one another in the crystal lattice because of their jacket and thus lose their explosive character. Upon heating under argon $\mathbf{5}\cdot 7.5\,THF$ loses tetrahydrofuran at 83 °C. From 141 °C onwards **5** is intrinsically unstable with dinitrogen evolution and blackening under separation of tellurium beginning. At 168 °C, finally, $TeCl_4$ can be observed as yellow sublimate.

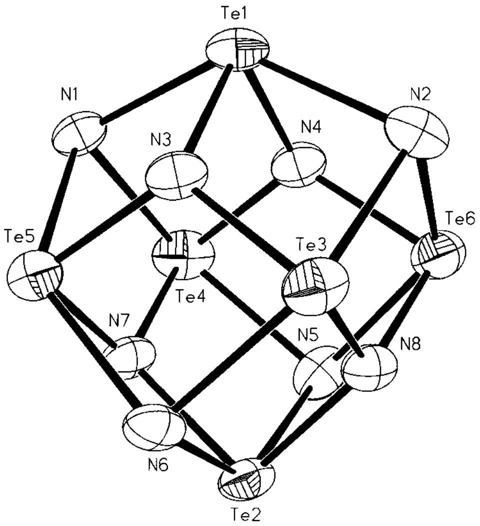


Figure 1. View of the Te_6N_8 core in the structure of $[\mathbf{5}\cdot 4\,THF]\cdot 3.5\,THF$. Displacement ellipsoids are at the 30% probability level at 223 K.

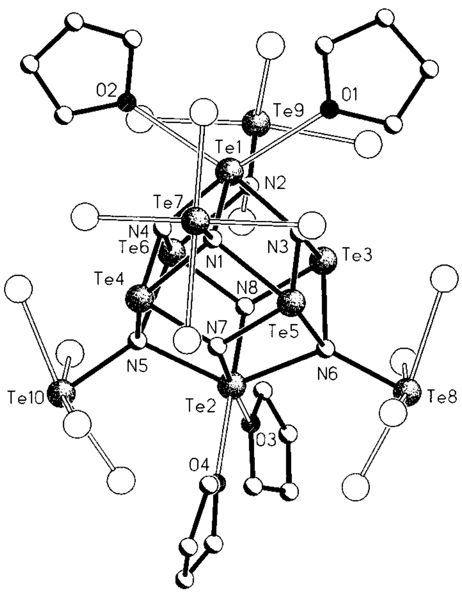


Figure 2. Molecular structure of $[\mathbf{5}\cdot 4\,THF]$ in the crystal. In the disordered $TeCl_4$ groups at Te(8–10) only the more strongly occupied orientations are shown. Selected average bond lengths [pm] and angles [°] (standard deviations taken from the mean of the single values): Te(1–6)–N(1,2,5,6) 228.5(6), Te(7–10)–N(1,2,5,6) 204.0(6), Te(1–6)–N(3,4,7,8) 201.3(6), Te(1,2)–O(1–4) 271.3(8), Te–Cl 251.6(4); Te-N(1,2,5,6)-Te 95.5(2), Te-N(3,4,7,8)-Te 114.4(2), Te-N(1,2,5,6)-Te(7–10) 121.0(2).

The $TeCl_4$ molecules bonded to the nitrogen atoms N(1,2,5,6) cause not only a restriction of the Te-N-Te bond angles of the Te_6N_8 skeleton from 114.4° to 95.5° at N(3,4,7,8), but also a stretching of the affected Te–N bonds of the Te_6N_8 core to 228.5 pm on average; all the other Te–N distances are only 201.3 pm. As a result, the latter are only a bit shorter than the Te–N bonds of the nitride functionality in the molecular complex **1** with 203.1 pm for X = F[9] and 206.1 pm for X = Cl.[8] Almost the same length is also shown by the Te–N bonds of the $TeCl_4$ molecules which are connected to the Te_6N_8 skeleton (av 204.0 pm). Te–N bonds which are a little shorter with an approximate length of 198 pm were observed in the cationic complexes **2** and **3**.[10, 11] In all cases these distances approximately meet the value of 199 pm for Te–N single bonds.[17] An approximately planar surrounding of the tellurium atoms by the four chlorine atoms as given in **5** is also observed in the polymeric structure of phenyltellurium trichloride.[18]

In THF **5** shows dynamic behavior in the ^{125}Te NMR spectrum. Only two signals of different intensities are observed at $\delta = 716$ for the coordinated $TeCl_4$ molecules and at $\delta = 567$ for the tellurium atoms of the Te_6N_8 core. This is in accord with the idea of a synchronized change of location for the four $TeCl_4$ molecules on the Te_6N_8 surface. Detachment of the $TeCl_4$ molecules does not take place in this process; the ^{125}Te NMR signal of $TeCl_4$ in THF is at $\delta = 1036$.[19] Because of their disorder behavior the change of location of the $TeCl_4$ molecules is also indicated in the crystalline state, even at 223 K. In contrast, the THF molecules which are only loosely bonded are subject to quick exchange according to the ^{1}H NMR spectrum.

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[13] Crystal structure determination of [**5**·4THF]·3.5THF ($C_{30}H_{60}Cl_{16}N_8O_{7.5}Te_{10}$, $M_r = 2496.06$): A colorless crystal (ca. $0.54 \times 0.54 \times 0.45$ mm) was analyzed with an area detector system (IPDS, Stoe) at −50 °C with $Mo_{K\alpha}$ radiation ($\lambda = 71.069$ pm, graphite monochromator). Unit cell monoclinic, $a = 2291.7(2)$, $b = 1222.7(1)$, $c = 5356.0(5)$ pm, $\beta = 101.74(1)°$; $V = 14694 \times 10^{-30}$ m^3, space group $I2/a$, $Z = 8$, $\rho_{calcd} = 2.257$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 4.53$ mm^{-1}, $F(000) = 9184$. Because of a rapid decline in intensity at increasing diffraction angle, data were only collected up to $\theta = 24°$, $\Phi = 0-250°$, $\Delta\Phi = 1°$, $t = 1$ min per record. Of 55355 reflections collected, 11290 were independent ($R_{int} = 0.060$) and 7648 observed ($I \geq 2\sigma(I)$). Measurement at even lower temperature was not possible, since a phase transition apparently occurs at approximately 220 K. Below this temperature diffuse streaks occur along the nevertheless very long c axis with maxima corresponding to a double superstructure. Semiempirical absorption corrections (from equivalent reflections) were carried out, and the structure was solved by direct methods and refined against all F^2 data[14] by full matrix. The $TeCl_4$ molecules bonded to the Te_6N_8 core showed strong disorder. Three of them had to be described by split atom models, which in two cases showed also a shift component in addition to a rotational component. All atoms, just as those of the core, could be refined with individual anisotropic displacement parameters. The four THF molecules coordinated at the core could be refined without using split positions, but with large anisotropic displacement parameters. The 3.5 THF molecules per molecule additionally fitted into gaps of the packing, one of which was situated on a twofold axis, and showed very strong motion and/or disorder. A model refined with split positions for two THF molecules converged at $wR_2 = 0.1182$ (all reflections) and $R = 0.0404$ (observed reflections). Because of the less than satisfactory possibility of describing the electron density blurred over this solvent range, its contribution to the structure factors was calculated by way of Back-Fourier transformation[15] and subtracted from the data set. Thereafter, the main structure [**5**·4THF] could be refined with clearly improved accuracy ($wR_2 = 0.0901$, $R = 0.0348$, residual electron density 0.95/−0.79 e Å^{-3}). The geometrical details documented here refer to this refinement. The structure determined at 223 K has the character of a high-temperature form in which the solvate molecules and $TeCl_4$ groups show high mobility or disorder. As documented in the quite physically meaningful shapes of displacement ellipsoids ($U_{eq} = 0.054-0.083$ Å^2) of all atoms of the Te_6N_8 core, its orientation is not noticeably involved. Thus, no significant influence on the geometry is expected. Crystallographic data (excluding structure factors) for the structure reported in this paper (those obtained by Back-Fourier transformation as well as those obtained according to the disorder model) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101663 and CCDC-101664. 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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Langmuir–Blodgett Films of Single-Molecule Nanomagnets**

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The discovery that individual molecules can act as magnets of nanometer size is a very recent one.[1, 2] The most thoroughly studied single-molecule magnets are the mixed-valence manganese clusters $[Mn_{12}O_{12}(carboxylate)_{16}]$ (carboxylate = acetate,[1, 3] propionate,[4] benzoate,[5] and 4-methylbenzoate[6]), referred to here as Mn_{12}. The current excitement for this kind of magnetic cluster is primarily due to

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