A microporous framework from a magnetic molecular square: $[Co(HAT)Cl_2]_4$ (HAT = 1,4,5,8,9,11-hexaazatriphenylene)

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The neutral, paramagnetic molecular square $[Co(HAT)Cl_2]$ 1,4,5,8,9,11-hexaazatriphenylene (HAT) form stacks with large open, water-filled channels that constitute approximately 37% of the void space in the crystal.

The nitrogen heterocyclic molecule, 1,4,5,8,9,11-hexaazatriphenylene (HAT) and its derivatives have been studied in the context of supramolecular chemistry,[1] photochemistry[2] and organometallic chemistry.[3] The HAT molecule exhibits a symmetrical arrangement of three bidentate binding sites that resemble three fused 1,10-phenanthroline units. The topology of the coordination sites renders HAT an especially interesting ligand for paramagnetic metals due to the fact that the triangular geometries promote spin-frustration if the magnetic interactions between paramagnetic metals are antiferromagnetic. Given that superexchange through similar molecules such as pyrazine, bipyrimidine and pyrazino[2,3-*f*][4,7]phenanthroline (pap)[4] bridges are typically antiferromagnetic, we expect that HAT bridges will also promote antiferromagnetic exchange between paramagnetic metal centers. In terms of HAT coordination chemistry, one can envision the elaboration of a three-dimensional framework, *e.g.* the fascinating chiral compound $[Ag(HAT)ClO_4{\bullet}2MeNO_2]_\infty$,[5] but if fewer than three binding sites are occupied by metal ions, it is conceivable that cyclic oligomers such as molecular squares[6] or one-dimensional polymers will ensue.

In spite of the interest in the HAT molecule, its chemistry has not been widely explored. Presumably, this is due to the fact that it is not commercially available and is insoluble in nearly all common solvents. Two main synthetic approaches to HAT have been reported, one of which employs triaminotrinitrobenzene, a compound that is used as a mild explosive in military applications.[7] We have elected to use an alternative six-step procedure beginning with commercially available precursors that leads to HAT in low overall yields.[8] Colorless, prismatic crystals of HAT were grown from hot water and subjected to a single-crystal X-ray study.† As Fig. 1 clearly shows, HAT forms one-dimensional zigzag chains that run along the *c* axis. Adjacent HAT molecules in the same chain are rotated 180° from each other and engage in π–π interactions at distances of *ca.* 3.25 Å (sum of the van der Waals radii is 3.54 Å).[9] The orientations of HAT molecules between chains are tilted by *ca.* 38° from a parallel arrangement. The packing of the chains is pseudo-tetragonal, with vacancies between the chains being occupied by water molecules that assume close contacts to the nitrogen atoms of the HAT molecules (*ca.* 2.8–3.0 Å).

The title compound was prepared from the addition of aqueous solutions of HAT and $CoCl_2$ in a 1:1 ratio. Slow evaporation of the water led to the formation of orange prismatic crystals of the product in 65% yield.† The solid-state structure of $[Co(HAT)Cl_2]_4{\bullet}27H_2O$ revealed that the compound is a molecular square with four distorted octahedral Co(II) ions coordinated to *cis* HAT molecules (Fig. 2). Each HAT bridge is bound to only two Co atoms and forms an angle of 105° with respect to the plane of the metal atoms. The remaining coordination sites of the Co ions are occupied by two terminal Cl^- ligands. The distortion from a regular octahedron is evident from an examination of the Co–N distances [two each at 2.177(10) and 2.145(9) Å] and the Co–Cl distances [2.397(4) Å]. The angles about the Co atoms are *ca.* 90° with the exception of the chelating N–Co–N which is 77.8(3)°. The $CoCl_2(L–L)_2$ corners exhibit alternating chirality (Δ,Λ,Δ,Λ) which allows for the formation of a square rather than the open-chain analog. The individual squares pack in an eclipsed fashion along the *c* axis (Fig. 3) which results in the formation of large, open channels of 6 Å in diameter. The interactions between the stacks are dominated by π–π interactions between HAT ligands at 3.40 Å, a distance that is slightly longer than the interaction observed in $HAT{\bullet}2H_2O$, but shorter than the sum of the van der Waals radii.

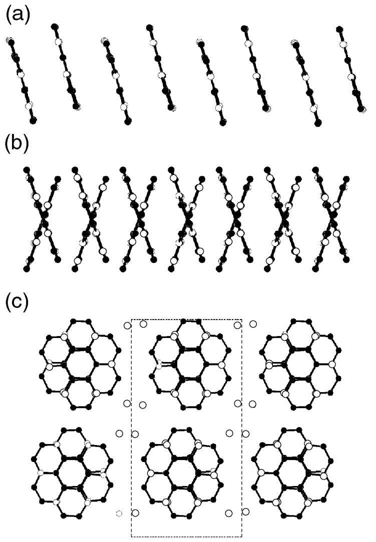

Fig. 1 Structure of $HAT{\bullet}2H_2O$: (a) side view of a dimerized chain, (b) side view of two adjacent chains and (c) projection in the *bc* plane.

It is worth mentioning at this point that the void space in this structure occupied by water molecules represents *ca.* 37%[10] of

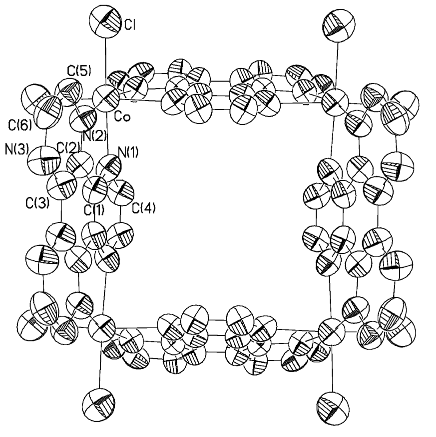

Fig. 2 Molecular structure of the $[Co(HAT)Cl_2]_4$ molecule.

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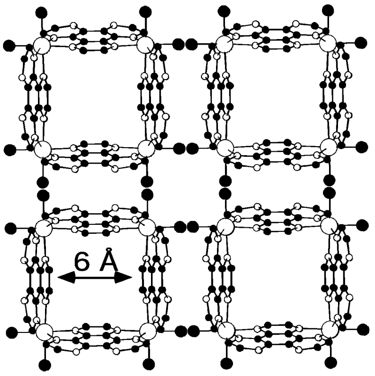

Fig. 3 Projection of the $[Co(HAT)Cl_2]_4•27H_2O$ structure on the *ab* plane, showing the channels created by eclipsed stacking of the $[Co(HAT)Cl_2]_4$ squares (solvent molecules are omitted).

the total volume, which places this compound in the category of a microporous material. As many as 27 disordered water molecules were located in the channels created by the stacking of the squares and in the interstices between the stacks. The ability of this material to reversibly absorb and desorb water molecules and other molecules in the solid state is under investigation.

The magnetic properties of $[Co(HAT)Cl_2]_4•27H_2O$ were investigated over the temperature range 2–300 K. The behavior of $\chi_m T$ is shown in Fig. 4. The room-temperature value of $\chi_m T$ is 10.41 emu K mol^{-1} which corresponds to four magnetically isolated Co ions ($S = 3/2$; $g = 2.34$). Below 150 K and down to 2 K, $\chi_m T$ steadily decreases which can be attributed to the well known zero-field splitting of high-spin Co(II) ions and also, possibly, to antiferromagnetic exchange between the Co centers. The anisotropy of these Co(II) systems precludes a quantitative analysis of these data, but it is possible to compare these data to the corresponding behavior of the model compound $Co(bpy)_2Cl_2$ with isolated Co ($S = 3/2$) centers. As indicated in Fig. 4, the decrease in χT observed for $Co(bpy)_2Cl_2$ below 150 K is essentially identical to that observed for $[Co(HAT)Cl_2]_4$, thus it must be concluded that the moment decrease is due exclusively to the zero-field splitting of the Co ions. Magnetic exchange through the HAT ligand in this particular case is negligible compared to the ZFS.

In conclusion, a novel magnetic molecular square composed of Co^{II} ions and HAT ligands has been prepared and characterized in the solid state. Several aspects of this molecular structure are particularly noteworthy. It is one of the few neutral molecular squares known to date, and it forms a microporous solid with channels of 6 Å diameter and 37% void space. Efforts to use the HAT ligand to produce new clusters as well as polymeric structures with paramagnetic metal centers are in progress.

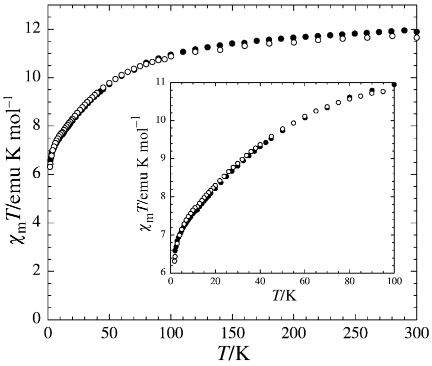

Fig. 4 The $\chi_m T$ *vs.* T plot ($H = 1000$ G) for $[Co(HAT)Cl_2]_4$ (●) compared to 4 × ($\chi_m T$) product for the model compound $Co(bpy)_2Cl_2$ (○).

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Notes and references

† *Crystal data*: for $[C_{12}N_6H_6]•2H_2O$: $C_{12}H_{10}N_6O_2$, $M_w = 270.26$, monoclinic space group Pc, $a = 6.9260(14)$, $b = 9.242(2)$, $c = 18.158(4)$ Å, $\beta = 90.04°$, $V = 1162.3(4)$ Å^3, $T = 110(2)$ K, $Z = 4$, $D_c = 1.544$ Mg m^{-3}, Graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å), Bruker CCD diffractometer, $F(000) = 560$, $\mu = 0.112$ mm^{-1}, 0.07 × 0.04 × 0.04 mm, 8715 reflections measured, 4374 of which were unique ($R_{int} = 0.0673$). The structure was solved by direct methods (SIR97)[11] followed by Fourier synthesis, and refined on F^2 (SHELX-97. G. M. Sheldrick, University of Göttingen, 1997). The isotropic thermal parameters of equivalent hydrogen atoms were constrained to be identical. All other atoms were refined anisotropically. The final refinement gave $R(F^2) = 0.0522$ and $R^2_w(F^2) = 0.0958$, by using 2601 reflections ($I > 2\sigma$).

For $[Co(HAT)Cl_2]_4•27H_2O$: $C_{48}H_{78}Cl_8Co_4N_{24}O_{27}$, $M_w = 1942.64$, tetragonal, space group $P42/nnm$, $a = 17.663(3)$, $c = 12.171(3)$ Å, $V = 3797.1(13)$ Å^3, $T = 110(2)$ K, $Z = 2$, $D_c = 1.699$ Mg m^{-3}, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å), Bruker CCD diffractometer, $F(000) = 1988$, $\mu = 1.233$ mm^{-1}, 0.05 × 0.04 × 0.02 mm, 32898 reflections measured, 2469 of which were unique ($R_{int} = 0.0925$). The structure was solved by direct methods (SIR97) followed by Fourier synthesis, and refined on F^2 (SHELX-97). The solvent molecules are disordered, and were modeled as 16 crystallographically independent oxygen atoms all of them with occupancy factors less than one. All other non-hydrogen atoms were refined anisotropically. The final refinement gave $R(F^2) = 0.0824$ and $R^2_w(F^2) = 0.2056$, by using 783 reflections ($I > 4\sigma$).

CCDC 182/0000. See http://www.rsc.org/suppdata/cc/b0/b008209k/ for crystallographic files in .cif format

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