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PAPER

Chemo-switched chromatic, magnetic and structural changes with retention of molecular crystallinity, \(\text{Ni(12aneS}_4\text{)(BF}_4\text{)}_2\)

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The molecular crystal \([\text{Ni(12aneS}_4\text{)}\text{(BF}_4\text{)}_2\text{]}\) displays the uncommon ability to retain its crystallinity on facile reversible hydration/dehydration without requiring polymeric bonding and despite the significant structural changes required. The flexibility of the 12aneS 4 ring facilitates rearrangement of the complex in the solid state upon absorption of two equivalents of water, with the crystal structures showing a clear topotactic relationship. The well defined chromatic, structural and magnetic changes that are both highly sensitive and easily reversed makes this complex of interest as an environmentally responsive material and as a contrasting example to the commonly reported coordination polymers.

Introduction

Materials capable of binding small molecules are of interest for their potential as functional materials responsive to their environment. Various characteristics of a solid may be altered upon attachment of a small molecule, with common examples including optical properties, conductivity and magnetism. Uses include catalysis, separation and purification, storage, sensing and switching. Additionally, the study of such materials can provide fundamental insights into complex processes such as solid state decomposition reactions.

Ni complexes, readily capable of forming various geometries, are well-known for their ability to detach small molecules, for example the Lifschitz salts based on ethylene diamine derivatives and the similar substituted acetylacetone. Reports in the literature reflect nickel’s affinity for N- and O-donors, and studies involving other donors, such as S reported here, are somewhat rarer, as are those demonstrating reversible uptake from the atmosphere rather than precipitation from solution.

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In functional materials structural integrity is often desirable for example when using a chemical sensor or switch, and the retention of crystallinity is one way to accomplish this. In almost all cases this is achieved using a robust polymeric structure with extensive strong bonds that can withstand the strains of structural reorganisation. For this reason coordination polymers have received a lot of attention with many good reviews covering this wide-ranging subject.

In the course of our recent investigations into macrocyclic complexes of nickel, \(\text{Ni(12aneS}_4\text{)}\text{(BF}_4\text{)}_2\) (1) was found to easily absorb and then desorb two equivalents of water (Fig. 1). It differs, however, from the vast majority of such reported systems in being a molecular crystal. Rather than the brute force of strong bonds linking throughout the structure, this complex uses the subtle flexibility of the macrocyclic 12aneS 4 ligand to

![Fig. 1](https://example.com/image1)

A 0.3 mm capillary was filled with 1 (purple, bottom) and exposed to air, which converted it to \(\text{12H}_2\text{O}\) (light blue, top): a microscope photograph of the diffusion front.
allow the transition metal complex to reversibly undergo the significant structural changes required upon hydration/dehydration in the solid phase yet remain crystalline. This makes these systems a complementary alternative to the bulk of research made on their polymeric cousins, whilst allowing us to draw parallels with the research terminology already in place. Such polymers have been classified according to many schemes, including whether they are reversible, the dimensionality of the polymer (0D isolated molecules, 1D chains, 2D sheets, or 3D networks), the nature of the small molecule interaction (coordination to a metal, or weaker intermolecular bonds, as in host–guest systems) and the porosity of the desorbed structure (whether the pores remain or not). As will be further described below, the hydration/dehydration of Ni(12aneS₄) may be considered a reversible 0D ↔ 0D transition, involving direct coordination to the metal centre and a non-porous structure.

Results and discussion

Complete hydration of 1 was achieved in a matter of minutes by simple exposure to atmospheric moisture, with surface effects visible in seconds. Desorption could be achieved in either a few seconds on heating to 120 °C, a few minutes on lowering the pressure to ~1 mbar, or several hours at room temperature and pressure in an argon filled glovebox (H₂O < 1 ppm). (In contrast, however, exposure to liquid water results in hydrolysis of the complex and liberation of the 12aneS₄ ligand.) The conversion is readily apparent as 1 is deep purple, while 1·2H₂O is light blue (Fig. 1) and time-resolved UV/vis spectra of the transformation show clear differences between the two phases. Upon hydration, the UV/vis reflectance spectrum (see ESI, Fig. S4†) shows reduced broad absorption features in the 460 nm and 630 nm regions and increased absorption in the 590 nm and 390 nm regions, associated with the colour change.

Crystal structure

The crystal structures of both 1 and 1·2H₂O (Fig. 2) were solved from powder synchrotron X-ray diffraction patterns collected at 100 K (further patterns collected over the temperature range 100 K to room temperature showed no phase changes). Crystal data for 1: orthorhombic, space group Pbca, a = 16.1254(3) Å, b = 15.2621(3) Å, c = 13.2577(3) Å, Z = 8 for B₂C₆H₁₂NiS₂, Mᵣ = 472.8 g mol⁻¹, ρ_calcd = 1.924 g cm⁻³, λ = 0.80035 Å, T = 100 K, R_p = 1.68%, R_w = 1.28%, GoF = 1.36, CCDC 846504; for 1·2H₂O: powder sample measured in 1.0 mm capillary, orthorhombic, space group Pbca, a = 18.5287(5) Å, b = 15.2433 (4) Å, c = 13.3682(3) Å, Z = 8 for B₂C₆H₁₂NiO₂S₂, Mᵣ = 508.8 g mol⁻¹, ρ_calcd = 1.789 g cm⁻³, λ = 0.80035 Å, T = 100 K, R_p = 3.52%, R_w = 2.89%, GoF = 4.35, CCDC 846503.

These crystal structures reveal the molecular crystal nature of this reversible process. 1 shows an almost square-planar configuration, with Ni slightly above the plane of the four S atoms, as expected given that the 12aneS₄ cavity is generally too small for the low-spin Ni(II) ion.¹¹ Though one F atom from a BF₄⁻ group points towards the Ni centre, the distance is 2.813(3) Å, far too long to be considered a covalent bond. Hydration results in two water molecules attaching directly to the Ni(II) cation in a cis fashion to form an octahedral complex, typical for high-spin Ni(II).

The structures of 1 and 1·2H₂O are closely related as they both crystallise in the Pbca space group, such that (unbonded) planes of Ni atoms may be chosen that divide the unit cell into four slabs (Fig. 2). Upon hydration, the crystal structure expands to accommodate 16 water molecules per unit cell (Z = 8), with the lattice expansion being highly anisotropic: a (perpendicular to the Ni planes) increasing by 14.9%, whilst those without water increase by 18% (Fig. 2). This is explained by the rearrangement of the flexible 12aneS₄ ring which folds back to accommodate the new water ligands and form the [NiS₄] butterfly geometry, resulting in increased steric repulsion in the slabs not bearing water. Animations visualizing this transformation are available in the ESI.† It is not possible to determine the H locations from the powder X-ray diffraction data, but inferring their positions to give closest proximity to F atoms (thus maximizing hydrogen bonding) would give a ring of 8 such contacts, with H⋯F distances of around 1.8–1.9 Å.

Fig. 2 Top: structure of the molecular components extracted from the unit cells, showing the slightly distorted square planar arrangement of 1 and the quasi-octahedral arrangement of 1·2H₂O. Bottom: crystal packing diagrams of the two compounds looking along the b axis. The anisotropic elongation of the a axis is readily apparent. The thick grey lines show the planes of Ni atoms with interplanar distances given. Asterisks mark the S atoms that move most upon hydration/dehydration.

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Thermogravimetric analysis and differential scanning calorimetry

Gravimetric analysis (using a bulk sample and a standard laboratory analytical balance) showed a 7.3% mass increase on conversion of 1 to 1-$\text{H}_2\text{O}$ (calculated: 7.6%). Differential scanning calorimetry (DSC) for the dehydration of 1-$\text{H}_2\text{O}$ to 1 gave an endothermic signal composed of two overlapping processes that are well resolved only at very low scanning rates (Fig. 3). We interpret the two events as the sequential loss of first one water molecule and then the second, but due to the moisture sensitivity of the dehydrated complex it was not possible to analyse the intermediate phase, supposed to be 1-$\text{H}_2\text{O}$, to confirm this. A similar double-peak feature is also seen in the DSC profile for hydration of 1 (see ESI, Fig. S2†).

Integration of the combined peak gives an enthalpy change of 139 ± 3 kJ (mol $\text{H}_2\text{O}$)$^{-1}$; DFT calculations corroborate the experimental findings yielding a marginally larger energy of dehydration of 144 kJ (mol 1-$\text{H}_2\text{O}$)$^{-1}$ at 0 K (ESI†). However, the heat effect is not evenly split across the two steps. The first step on dehydration and second on hydration show a larger enthalpy change which, from the slow speed DSC hydration (ESI, Fig. S2†), we estimate accounts for about 57% of the total change, or 79 kJ (mol H$_2$O)$^{-1}$, vs. 60 kJ (mol H$_2$O)$^{-1}$ for the other step. The measured reaction heats are about $\frac{3}{2}$ and $\frac{1}{2}$ larger than the enthalpy change associated with a hypothetical ice → water vapour transformation (46.7 kJ mol$^{-1}$), and other reported values for solids which reversibly absorb and desorb water at temperatures not exceeding 100 °C (32.0 kJ (mol H$_2$O)$^{-1}$ and 44.7 kJ (mol H$_2$O)$^{-1}$; 44 kJ (mol H$_2$O)$^{-1}$). (See ESI† for further discussion of thermodynamics.)

We performed DSC measurements for a series of dehydration reactions at scanning speeds of 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07 K min$^{-1}$, from which the peaks were sufficiently well resolved to allow determination of their individual maxima. Using Kissinger’s equation$^{15}$ we calculated approximate values for the activation energy of the steps to be 400 kJ mol$^{-1}$ for the first dehydration step and 340 kJ mol$^{-1}$ for the second dehydration step (Fig. 4). The considerable complexity of solid state kinetics means care must always be taken when interpreting such data.$^{16}$ Nevertheless, if similar mechanisms are at work in each dehydration step (e.g., breaking of the Ni–O bond), the more endothermic enthalpy change for the first water lost would likely also result in a higher activation energy, which is what we see.

Cycling experiments show excellent durability of the complex on repeated hydration/dehydration (see ESI† for details).

Magnetic susceptibility

The 1 → 1-$\text{H}_2\text{O}$ conversion brings about clear changes in magnetic susceptibility. Despite the seemingly simple near square-planar coordination of Ni(II), typical for a low-spin diamagnetic d$^8$ system, 1 shows complex magnetic behaviour (Fig. 5). Magnetic susceptibility data were fitted to the Curie–Weiss law in the $T$ range 260–373 K, giving a weakly paramagnetic behaviour with a Curie constant (C) of 0.31 emu K mol$^{-1}$ from which $\mu$$_{\text{eff}}$ = 1.6 $\mu$$_B$ can be derived. Below 250 K, $\mu$$_{\text{eff}}$ (inferred from the product $\chi$($\infty$)$T$) is seen to steadily decrease to a value of 1.3 $\mu$$_B$ ($\chi$($\infty$)$T$ = 0.21 emu K mol$^{-1}$) at 12 K, and then drop rapidly ( inset, Fig. 5). This weak, temperature-dependent effective magnetic moment likely arises from the slight deviation away from the ideal square-planar geometry and the resulting incomplete quenching of the orbital angular momentum; though ‘anomalous’, its magnitude is not without precedent.$^{17}$

In contrast, the magnetic susceptibility of 1-$\text{H}_2\text{O}$ indicates the presence of high-spin Ni(II), as expected for the octahedral geometry, with C = 1.3 emu K mol$^{-1}$, $\mu$$_{\text{eff}}$ = 3.2 $\mu$$_B$, within the normal range (3.0–3.3 $\mu$$_B$) for such complexes.$^{18}$ The 1/$\chi$ vs. $T$ plot in Fig. 5b shows very close to the origin, indicating no significant magnetic coupling, as expected for a molecular crystal with no obvious pathway for through-bond intermolecular magnetic superexchange.$^{18}$ The low temperature fall in $\chi$($\infty$)$T$ is likely due to zero-field splitting. The magnetic susceptibility of 1 in the paramagnetic regime ($T$ > 250 K) is less than 30% that of

Fig. 3 DSC signal for dehydration of 1-$\text{H}_2\text{O}$ to 1 in static atmospheric air, at various scanning rates.

Fig. 4 Kissinger plot to determine the activation energy of the two dehydration steps evident in very slow speed DSC. The activation energy is obtained by multiplying the slope by the gas constant, 8.314 J K$^{-1}$ mol$^{-1}$, $T_m$ = temperature of peak maximum, $\Phi$ = scanning rate.

(ESI†), notably shorter than those reported by Strauss et al. (2.116–2.180 Å) in their K$_3$(H$_2$O)$_2$B$_2$F$_{12}$ system.$^{6d}$

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of the slight change in the slope of the FC curve above 365 K. The change is small but is repeatable across different samples (though the onset temperature varies from 240 K to 260 K), including with syntheses using excess 12aneS4. Though the effect is more subtle, there is also a change in the signal for the FC measurement occurring in the same temperature range. This is evident from the first derivatives of the $X_m T$ vs. $T$ plot (Fig. 6), and points to a real event occurring around this temperature.

We have performed sensitive heat capacity measurements using a Quantum Design, Inc. Physical Properties Measurement System (PPMS), but see no change in signal in this region. Synchrotron X-ray diffraction patterns measured at 200 K and room temperature show only lattice parameter changes, with no significant structural rearrangement. Thus, the origin of this effect is currently unknown.

The zero-field cooled data of 1·2H2O are essentially identical to those of the field cooled experiment except for a very slight deviation below 4 K.

Fig. 5 Comparison of the magnetic susceptibility of 1 and 1·2H2O in a field cooled experiment. The dotted line in b is a linear extrapolation of the Curie–Weiss law fitted in the $T$ range of 260–373 K. Inset, top right, is magnified low temperature region for 1.

Fig. 6 Magnetic susceptibility plots for 1 in both field cooled and zero-field cooled experiments. Smoothed first derivatives are also shown (scale on right axis). Note, the ZFC measurement was performed first, with the FC measurement immediately after, which causes the ZFC and FC signals to meet at 373 K (the maximum temperature measured), thus the convergence at this temperature is likely artificial and also the cause of the slight change in the slope of the FC curve above 365 K. 1·2H2O, a readily detectable difference between the complexes even at room temperature.

Zero-field cooled (ZFC) measurements reveal further interesting behaviour for 1: at low temperature the plot of $X_m T$ vs. $T$ for a ZFC measurement (Fig. 6) lies below that of the FC measurement, indicating a lower value for $\mu_{eff}$ and suggesting some randomization of the spins is frozen into the structure on zero-field cooling. At about 240 K, the slope of the ZFC $X_m T$ vs. $T$ plot changes, causing the value of $\mu_{eff}$ for the ZFC measurement to rise above that of the FC measurement, with the intersection at 275 K. Thus, the ZFC measurement has a lower $\mu_{eff}$ at low temperatures which switches to a higher $\mu_{eff}$ at higher temperatures, around 275 K. The difference is small but is repeatable across different samples (though the onset temperature varies from 240 K to 260 K), including with syntheses using excess 12aneS4. Though the effect is more subtle, there is also a change in the signal for the FC measurement occurring in the same temperature range. This is evident from the first derivatives of the $X_m T$ vs. $T$ plot (Fig. 6), and points to a real event occurring around this temperature.

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Experimental

1 was synthesised by refluxing a 1:1 mole ratio of Ni(BF4)2·6H2O with 12aneS4 in acetone for 30 minutes and removing the solvent on a rotary evaporator to yield a dark purple solid. No further purification was made. Elemental analysis for 1: C 20.13% (calc. 20.32%), H 3.39% (3.41%); for 1·2H2O C 18.55% (18.88%), H 3.92% (3.96%).

UV/vis spectra were recorded on a Shimadzu UV-2401PC spectrometer fitted with a specular reflectance attachment.

Powder synchrotron X-ray diffraction patterns for 1 and 1·2H2O were recorded on the MS beamline of the Swiss Light Source, Paul Scherrer Institute, using a 15.5 keV beam (the exact wavelength was determined by Rietveld refinement on a NIST 640C Si standard, and found to be 0.80035 Å). Both complexes were indexed using the nTreor algorithm implemented in Expo2009 software, and found to have very similar unit cells. For 1, Pbca was the most likely space group. For 1·2H2O, the choice of space group was not as clear and both Pcca and Pbca were tested in Fox (see below), with Pbca (the same as for 1) giving considerably better agreement between model and experiment.

Initial structures were found using the parallel tempering algorithm implemented in the Fox program. For 1, three ‘molecules’ were introduced: two BF4 groups and one for the Ni-12aneS4 group, with starting structures optimised using a molecular dynamics algorithm in the Avogadro program. These were allowed to refine in Fox with the automatic flexibility mode and a small anti-bump penalty. Additionally, the ring was restructured using molecular dynamics on average every 10 configurations to allow new conformations to be tested, which the ring structure’s lack of torsional freedom might otherwise prevent. It was found that soft restrictions on the Ni–S distance were necessary to prevent the ring from deforming unrealistically. 1·2H2O was refined in the same way, except that two O atoms were added (H was not used), and a higher anti-bump cost was needed to prevent O from colliding with S.
Though these initial structures were used for Rietveld refinement as implemented by the Jana2006 program. Soft restraints (based on an extensive survey of related structures in the Cambridge Structural Database, see ESIF) on most bond lengths and angles were applied. These refined structures were then used for DFT calculations (ESI†). The results of the DFT calculations were then used as starting structures for another Rietveld refinement.

For I, the Rietveld refinement after the DFT calculations was limited to adjusting B–F bond lengths, then moving the BF₃ groups and the Ni-12aneS₄ group as rigid bodies. The most important change in refining the DFT structure of I was the lengthening of the shortest Ni–F distance from 2.547 Å to 2.813 Å (i.e. from a weak Ni–F bond to essentially no bonding). For 1·2H₂O, a similar approach was taken, with B–F bond lengths slightly corrected, then the following four rigid bodies allowed to refine separately: two BF₃ groups, 12aneS₄ ring (this time without Ni) and the NiO₂ group. H positions were not refined.

TGA and DSC measurements were carried out on a Netzsch STA 409 PG instrument, using approximately 7 mg of sample in a alumina crucible.

Magnetic susceptibility was measured on a MPMS vibrating sample magnetometer made by Quantum Design, Inc. To exclude the possibility that the slight paramagnetism observed in I was due to remnant hydrated species, I was fully dehydrated in the magnetometer before measurement by heating to 100 °C for 4 hours at 10⁻⁵ Torr. Data were corrected for the diamagnetic contribution of the sample holder by subtracting a ‘blank’ measurement and the core electrons using Pascal’s constants, for which a value of ₱3.0 × 10⁻⁴ emu mol⁻¹ was used for I and ₱3.3 × 10⁻⁴ emu mol⁻¹ for 1·2H₂O.

See ESIF† for further experimental details.

Conclusions
We have demonstrated the extremely facile interconversion of a non-porous, molecularly crystalline Ni(ii) complex in the solid phase displaying clearly defined chromatic, structural and magnetic changes upon reversible water vapour uptake and release. The ability of Ni(12aneS₄)(BF₃)₂ to retain its crystallinity whilst undergoing such significant structural changes is rare for a molecular crystal and provides an alternative to the much studied coordination polymers. It remains to be investigated whether the title complex is similarly sensitive to other small molecules and whether thin layers could be used as moisture sensors. ¹²⁴

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Notes and references
12 If A is not porous, the molar volume of 1·2H₂O corresponds very closely to the sum of the volumes of I and two water molecules of hexagonal ice (see ESIF for more details).
18 The complex does show hydrogen bonding, but only providing very long (eight bond) paths between metal centres.