Inclusion of a dithiadiazolyl radical in a seemingly non-porous solid

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Inclusion of the dithiadiazolyl radical PhCNSSN• into the
dynamically porous metalallocycle [Cu₂(L1)₂Cl₄], where L1 is the
bidentate ligand 1,3-bis(imidazol-1-ylmethyl)-2,4,6-
trimethylbenzene, has been achieved by gas phase diffusion. Single
crystal X-ray diffraction, powder X-ray diffraction, UV-visible
spectroscopy, EPR and SQUID magnetometry studies confirm
inclusion of the radical into this seemingly non-porous material,
and illustrate the presence of antiferromagnetic coupling between
the paramagnetic host and guest species. The radical guest is
readily released by heating or by the addition of solvent (CH₃Cl₂).

The evolution and exploitation of host–guest interactions for
use in gas sequestration and storage,1,2 chemical sensing,3,5 and
heterogeneous catalysis6–8 have garnered considerable interest
in recent years owing to the rapid expansion of the number of
known dynamically porous solid-state materials.9 As this field of
chemistry becomes more established, researchers are focussing
on property development, including magnetic behaviour, light
modulation, spin-state bistability, electron, hole and ion
mobility, ferroelectricity and luminescence. Each of the
aforementioned properties is governed by host–guest
interactions: sensors require one entity to impose some
measurable change on the other, for example,10 while orientation-specific binding can lead to regio- and/or
enantioselective transformations in catalysis.11 The inclusion of
radical guest molecules into porous materials such as hydrogen-bonded frameworks (HOFs), metal-organic
frameworks (MOFs) or discrete cavities (such as those found in
metalallocycles) offers the potential for strong host-guest and
guest-guest electronic interactions, potentially resulting in
interesting magnetic or transport properties.

The majority of known HOF-radical inclusion compounds
were obtained by co-crystallisation of the guest with an organic
host from solution or the gas phase.12–17 A recent review by
D’Alessandro et al. illustrates the increase in reports of MOFs
containing radical moieties, either incorporated into the host
backbone or as encapsulated guests.18 However, the number of
reported inclusion compounds containing paramagnetic guests
still remains low. In fact, there are only two reports of the
inclusion of thiazyl radicals into metal-containing frameworks,
both arising from our groups, and both involving diamagnetic
host frameworks. One study reports the inclusion of
benzodithiazolyl and methylbenzodithiazolyl into MIL-53(Al),19
while the other reports the inclusion of PhCNSSN• into
Faujasite.20 Notably, in the former complex the walls of the host
cavity rotate to accommodate the guest, indicating a responsive
relationship between the host and the guest.

Previous studies in the Barbour group21 have shown the
copper metalallocycle [Cu₂(L1)₂Cl₄] (Scheme 1, hereafter 1a)
to be a dynamic material, capable of undergoing multiple single
crystal-to-single crystal (SC-SC) guest-inclusion reactions. A
variety of guests have been included in the metalallocyclic host,
yielding host-guest systems 1–11, where the host adapts the size
of the cavity to best suit a particular guest via rotation of the
imidazole rings.21 Since 1a is a highly stable, dynamic host that
is inherently paramagnetic, we decided to investigate inclusion
of a thiazyl radical (4-phenyl-1,2,3,5-dithiadiazolyl, PhCNSSN•,
Scheme 1) into this material, with the aim of inducing
communication between the spin on the host and the spin on
the guest.

Since guest encapsulation is accompanied by cooperative
motion of the host, inducing a highly specific change in the
solvent-accessible space and in turn in the chemical
environment of the metal, single-crystal (SC) X-ray data in
conjunction with variable temperature solid-state EPR were
employed to obtain a clearer understanding of the host-guest
interaction.
The host was prepared as its methanol solvate, following the previously reported synthesis, and was activated by heating under dynamic vacuum at 100 °C for 24 hours to eliminate the included methanol, yielding the apohost 1a. Bulk phase purity was established using powder X-ray diffraction (Figure S2). Previous work conducted by Barbour, Haynes and co-workers has shown that materials that are solid but sufficiently volatile at room temperature can be included into framework hosts by sorption of the guest directly from the gas phase. This is also possible for metallocycles such as 1a.

The volatility of PhCNSSN permitted its inclusion into the apohost 1a when the two species were heated together in vacuo at 80 °C (Figure S1). After 24 hours of exposure to vapours of the radical, crystals of 1a had undergone a distinct colour change from green to deep red (almost black), (Figure 1). The UV absorption spectra of the two samples (Figure S9) confirm the observed colour change, with 1a absorbing the majority of the visible spectrum except in the green region, while 12 does not transmit any light.

The powder pattern of bulk 12 is similar to that of 1a (Figure S3), albeit with some small differences in peak positions/intensities, indicating that the radical has been included in the host without significant structural changes to the crystal structure. Notably there is no evidence for neat PhCNSSN in the PXRD, confirming that the observed colour change is not as a result of crystallisation of the radical on the surface of the host crystals.

The structure of 12 was elucidated by means of single-crystal X-ray diffraction, as inclusion of the radical is a SC-SC process (Table S1). The structure shows that the space group of the host (P2_1/c) is maintained in 12, but there is an increase in the length of the b axis, with a corresponding increase in the unit cell volume. In addition to the metal, ligand and chloride counterions present in the asymmetric unit of 1a, the asymmetric unit of 12 also contains one dithiadiazolyl radical, which is disordered across an inversion centre with a site occupancy of ca. 30%, resulting in a guest occupancy of ca. 60%.

Closer examination of the two crystal structures determined at 100 K (Figure 1) shows notable differences in the Cu—Cu distances, as well in the phenyl(centroid)—phenyl(centroid) and imidazole(centroid)—imidazole(centroid) distances. In order to accommodate the radical guest, the copper metallocycle expands along the shorter dimension (Cu-Cu), while contracting along the longer dimension (phenyl-phenyl). In 12, one of the two imidazole moieties is disordered over two positions with the minor fragment having a site occupancy of 30%. This disorder is attributed to weak hydrogen bonding between the nitrogen atom of the radical guest and the hydrogen atom of the host imidazole. Extension of the ASU shows the radicals encapsulated within stacks of metallocycles (Figure 2). Guest inclusion results in two cavities within the host merging, analogous to the behaviour of the host on inclusion of naphthalene. Merged cavities are separated from one another because the radical guest is too large to be included between every metallocycle pair. however, the Cu…Cu distances between metallocycles remain constant along the metallocycle stack (Fig. 2b). The distortion of the host lattice is manifested in a subtle change in the coordination geometry at the four-coordinate copper(II) centre. For the host complex, the τ parameter (defined as \[\tau = \frac{360 - (\alpha + \beta)}{141}\]) where \(\alpha\) and \(\beta\) are the two largest angles subtended at Cu) is 0.37, intermediate between square-planar (\(\tau = 0\)) and tetrahedral (\(\tau = 1\)) geometries. In 12 the geometry at Cu is slightly more compressed towards square planar (\(\tau = 0.32\)).

No degradation of 12 was noted using PXRD or EPR, even when samples had been exposed to air in ambient conditions for extended periods of time (Figure S4). This enhanced stability of the radical within the metallocycle is in stark contrast to the pure radical, which degrades when not kept under an inert atmosphere. In addition, TGA data show no significant mass loss for 12 up to 100 °C (Figure S5). These findings are consistent
are the two largest angles subtended at Cu
β structures of both materials were shown to be stable for up to a month.

with previous studies, where thiazyl radicals included in porous materials were shown to be stable for up to a month.19

Solid-state EPR spectroscopy was used to further probe the structures of both 1a and the new radical-containing paramagnetic hybrid material 12. Both 1a and 12 yield essentially axial spectra with a small rhombic distortion (Fig. 3, ESI). Previous EPR studies on distorted CuCl$_2$ anions (0.72 > $\tau_4$ > 0.61; where $\tau_4$ is defined as $[360 - (\alpha + \beta)]/141$ where $\alpha$ and $\beta$ are the two largest angles subtended at Cu$^{2+}$) produce rhombic spectra with $g_{||} > g_\perp$ with increasing distortions towards square planar, leading to a reduction in the magnitude of the g-tensor.24 In this context it is notable that both 1a and 12 also exhibit $g_{||} > g_\perp$, with smaller g-values for 12, which is closer to square planar. The average g-values for 1a and 12 (2.12 and 2.11, respectively) are smaller than those for CuCl$_2$-Cl$^-$, consistent with geometries significantly closer to square planar ($\tau_4 = 0.37$ and 0.32). Notably the EPR spectrum of 12 does not exhibit an observable component associated with the PhCNSSN radical ($g = 2.01$).

The EPR linewidth of the radical inclusion complex is substantially greater than that of the host framework, which can be attributed to dipolar broadening between radical and host, or through some exchange interaction, such that the radical no longer behaves as an isolated S = $\frac{1}{2}$ spin system. The presence of the radical in the host framework was confirmed by displacement of the guest by addition of CH$_2$Cl$_2$ (Fig. 3c).

To examine the nature of the host-guest interaction, variable temperature dc SQUID magnetometry measurements were made on 1a and 12. The parent host framework was found to exhibit Curie-Weiss paramagnetism across the range 1.8 – 300 K with $C = 0.842$ emu K mol$^{-1}$ and $\theta = -2.0$ K, consistent with very weak antiferromagnetic interactions between two S = $\frac{1}{2}$ ions with $g = 2.12$, in agreement with the value determined by EPR spectroscopy (2.12). $M$ vs $H$ studies at 1.8 and 10 K are nicely replicated with two S = $\frac{1}{2}$ ions using $g = 2.12$ and a mean field correction term to take into account weak antiferromagnetic interactions ($\theta = -0.95$ K, see ESI). Radical inclusion leads to a marked change in the paramagnetism of the sample. Down to 50 K the magnetism once again follows Curie-Weiss behaviour but the Curie constant is a little larger ($C = 0.954$ emu K mol$^{-1}$), consistent with an increase in the total number of spin centres in the sample. The Curie constant equates to 24% S = $\frac{1}{2}$ (based on TGA data on the same sample recorded after the SQUID measurements) with $g = 2.0$ and two S = $\frac{1}{2}$ Cu$^{2+}$ centres with $g = 2.15$. The Weiss constant ($\theta = -5.7$ K), reflects weak antiferromagnetic interactions which could comprise both host-host and host-guest interactions. A subtle change in gradient is observed below 20 K ($C = 0.772$ emu K mol$^{-1}$, $\theta = -0.63$ K), consistent with antiferromagnetic coupling between host Cu$^{2+}$ ions and the guest PhCNSSN radicals. This interpretation is supported by DFT calculations (see ESI), which reveal exchange couplings between the radical and Cu$^{2+}$ of -11 and -12 cm$^{-1}$ for the two copper atoms in the metallocycle.

In conclusion, the incorporation of a dithiadiazolyl radical into the dynamic paramagnetic metallocycle 1a results in an unusual paramagnetic hybrid material, 12, in which SQUID and DFT studies support the presence of exchange coupling between host and guest. The stability of the radical is significantly enhanced by inclusion in the metallocyclic host.
Notes and references