ChemComm

COMMUNICATION

View Article Online
View Journal

Check for updates

Cite this: DOI: 10.1039/c7cc06678c

Received 25th August 2017,
Accepted 21st September 2017

DOI: 10.1039/c7cc06678c

rsc.li/chemcomm

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

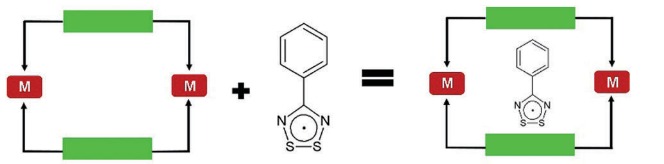
Varvara I. Nikolayenko, [a] Leonard J. Barbour, [a] Ana Arauzo, [b] Javier Campo, [b] Jeremy M. Rawson [c] and Delia A. Haynes *[a]

Inclusion of the dithiadiazolyl radical PhCNSSN• into the dynamically porous metallocycle $[Cu_2(L1)_2Cl_4]$, 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 antiferromagnetic coupling between the paramagnetic host and guest species. The radical guest is readily released by heating or by the addition of solvent (CH_2Cl_2).

The evolution and exploitation of host–guest interactions for use in gas sequestration and storage,[1,2] chemical sensing,[3–5] and heterogeneous catalysis[6–8] 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 focusing 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 metallocycles) 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 group[21] have shown the copper metallocycle $[Cu_2(L1)_2Cl_4]$ (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 metallocyclic 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



Scheme 1 Schematic representation of the synthesis of **12** from **1a** ($[Cu_2(L1)_2Cl_4]$ where L = 1,3-bis(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene) and phenyl-1,2,3,5-dithiadiazolyl.

[a] *Department of Chemistry and Polymer Science, Stellenbosch University, P. Bag X1 Matieland, 7602, Stellenbosch, South Africa. E-mail: dhaynes@sun.ac.za*
[b] *Aragón Materials Science Institute (CSIC-University of Zaragoza) and Condensed Matter Physics Dept. Facultad de Ciencias, 50009 Zaragoza, Spain*
[c] *Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue, Windsor, ON, N9B 3P4, Canada*

† Electronic supplementary information (ESI) available: Full experimental details, synthesis, TGA, DSC, EPR SQUID and DFT. CCDC 1566860–1566863. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc06678c

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 **1**, following the previously reported synthesis,[21] 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 (Fig. S2, ESI†). 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.[19,21,22] This is also possible for metallocycles such as **1a**.[21] The volatility of **PhCNSSN•** permitted its inclusion into the apohost **1a** when the two species were heated together *in vacuo* at 80 °C (Fig. S1, ESI†). 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), **12** (Fig. 1). The UV absorption spectra of the two samples (Fig. S9, ESI†) 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** (Fig. S3, ESI†), 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, ESI†). 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 (Fig. 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 (Fig. 2). Guest inclusion results in two cavities within the host merging, analogous to the behaviour of the host on inclusion of naphthalene.[21] 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_4 parameter (defined as $[360 - (\alpha + \beta)]/141$ where α and β are the two largest angles subtended at Cu[23]) is 0.37, intermediate between square-planar ($\tau_4 = 0$) and tetrahedral ($\tau_4 = 1$) geometries. In **12** the geometry at Cu is slightly more compressed towards square planar ($\tau_4 = 0.32$).

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 (Fig. S4, ESI†). 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

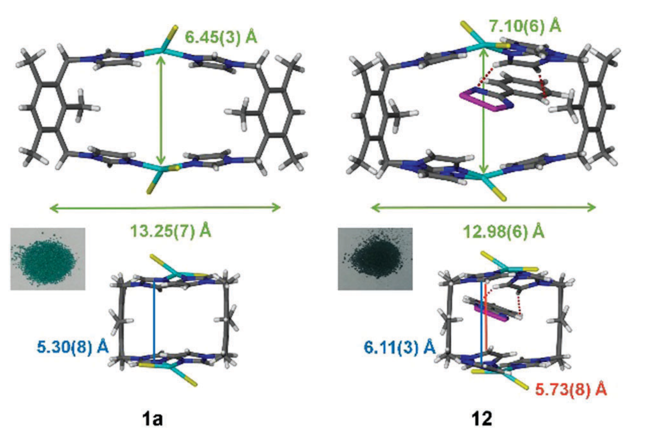


Fig. 1 Comparison of the structures of **1a** (left, 100 K) and **12** (right, 100 K). Vertical green arrows show Cu···Cu distances. Horizontal green arrows show distances between the centroids of the phenyl rings on the ligands in the metallocycle. Vertical blue and red lines show the distances between the centroids on the imidazole rings, where red and blue relate to the two components of the disorder. The insets show photographs of solid **1a** and **12**.

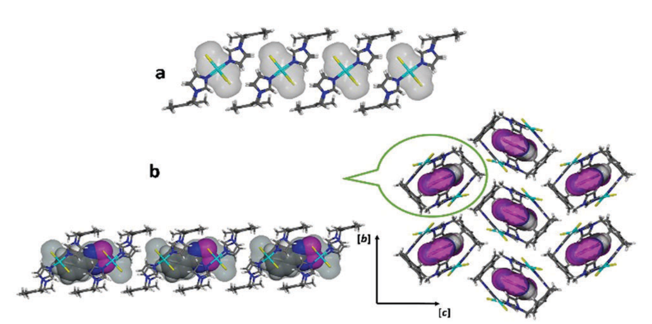


Fig. 2 (a) A perspective view of a column of **1a** metallocycles showing the discrete guest-accessible voids as a grey transparent surface (V = 97 Å^3 per ASU). (b) A perspective view of a column of **12** showing merged guest-filled voids (V = 145 Å^3 per host). Metallocycles stack with a 40° slant relative to the *a* axis.

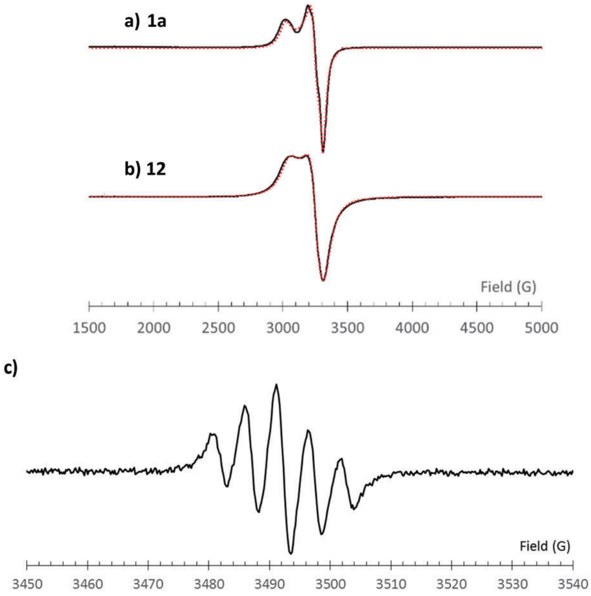


Fig. 3 Solid-state EPR spectra of (a) **1a** and (b) **12** at room temperature (solid lines = experimental data, dotted line = simulation); (c) solution EPR spectrum of dithiadiazolyl radical recovered from **12** by immersion in CH_2Cl_2.

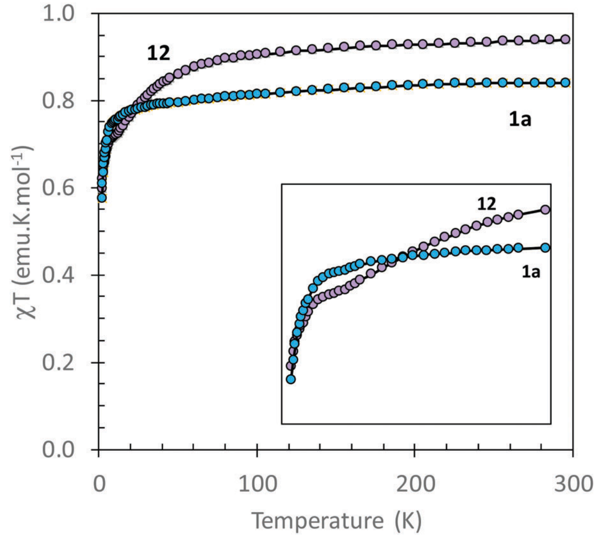


Fig. 4 Temperature dependence of χT for **1a** (blue circles) and **12** (purple circles). The inset is an expansion of the data between 0 and 50 K.

loss for **12** up to 100 °C (Fig. S5, ESI†). These findings are consistent 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 and ESI†). Previous EPR studies on distorted $CuCl_4^{2-}$ anions ($0.72 > \tau_4 > 0.61$) produce rhombic spectra with $g_{\parallel} > g_{\perp}$ 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 $g_{\parallel} > g_{\perp}$, 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 $CuCl_4^{2-}$, consistent with geometries significantly closer to square planar (τ_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 = 1/2 spin system. The presence of the radical in the host framework was confirmed by displacement of the guest by addition of CH_2Cl_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 θ = −2.0 K, consistent with very weak antiferromagnetic interactions between two S = 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 = 1/2 ions using g = 2.12 and a mean field correction term to take into account weak anti-ferromagnetic interactions (θ = −0.95 K, see ESI†). Radical inclusion leads to a marked change in the paramagnetism of the sample (Fig. 4). 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 = 1/2 (based on TGA data on the same sample recorded after the SQUID measurements) with g = 2.0 and two S = 1/2 Cu^{2+} centres with g = 2.15. The Weiss constant (θ = −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}, θ = −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 −10 and −11 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.

We thank the National Research Foundation of South Africa and Stellenbosch University for funding. J. M. R. acknowledges the support of the Canada Research Chair Program. J. C. acknowledges the Grant No. MAT2015-68200-C2-2-P from the Spanish Ministry of Economy and Competitiveness.

Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

1 H. Wu, W. Zhou and T. Yildirim, *J. Am. Chem. Soc.*, 2007, **129**, 5314.
2 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald., D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724.
3 X. Xu, J. Wang and Y. Long, *Sensors*, 2006, **6**, 1751.
4 M. Xue, L. Fan, Z. Kang, W. Zhang, H. Li and S. Qiu, *J. Mater. Chem.*, 2012, **22**, 17644.
5 L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2011, **112**, 1105.
6 H.-L. Jiang, T. Akita, T. Ishida, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 1304.
7 A. K. Cheetham, G. Ferey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.
8 M. E. Davis, *Nature*, 2002, **417**, 813.
9 A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, *Chem. Soc. Rev.*, 2014, **43**, 6062.
10 X. Tang, J. Provenzano, Z. Xu, J. Dong, H. Duan and H. Xiao, *J. Mater. Chem.*, 2011, **21**, 181.
11 *Supramolecular Photochemistry: Controlling Photochemical Processes*, ed. V. Ramamurthy and Y. Inoue, Wiley, 2011.
12 H. Kobayashi, T. Ueda, K. Miyakubo, J. Toyoda, T. Eguchi and A. Tani, *J. Mater. Chem.*, 2005, **15**, 872.
13 H. Kobayashi, T. Ueda, K. Miyakubo, T. Eguchi and A. Tani, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 711.
14 H. Kobayashi, T. Ueda, K. Miyakubo, T. Eguchi and A. Tani, *Mol. Cryst. Liq. Cryst.*, 2009, **506**, 150.
15 H. Kobayashi, T. Asaji and A. Tani, *Materials*, 2010, **3**, 3625.
16 P. J. Langley, J. M. Rawson, J. N. B. Smith, M. Schuler, R. Bachmann, A. Schweiger, F. Palacio, G. Antorrena, G. Gescheidt, A. Quintel, P. Rechsteiner and J. Hulliger, *J. Mater. Chem.*, 1999, **9**, 1431.
17 H. I. Süss, T. Wuest, A. Sieber, R. Althaus, F. Budde, H.-P. Lüthi, G. D. McManus, J. M. Rawson and J. Hulliger, *CrystEngComm*, 2002, **4**, 432.
18 T. B. Faust and D. M. D'Alessandro, *RSC Adv.*, 2014, **4**, 17498.
19 S. V. Potts, L. J. Barbour, D. A. Haynes, J. M. Rawson and G. O. Lloyd, *J. Am. Chem. Soc.*, 2011, **133**, 12948.
20 H. J. Cowley, J. J. Hayward, D. R. Pratt and J. M. Rawson, *Dalton Trans.*, 2014, **43**, 1332.
21 L. Dobrzańska, G. O. Lloyd, H. G. Raubenheimer and L. J. Barbour, *J. Am. Chem. Soc.*, 2006, **128**, 698; A. Heyns, PhD thesis, Stellenbosch University, 2012; V. I. Nikolayenko, A. Heyns and L. J. Barbour, DOI: 10.1039/C7CC06676G.
22 H. Wahl, T. Le Roux and D. A. Haynes, *Cryst. Growth Des.*, 2017, **2017**, 4377.
23 L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.*, 2007, 955.
24 A. Winter, K. Thiel, A. Zabel, T. Klamroth, A. Pöppl, A. Kelling, U. Schilde, A. Taubert and P. Strauch, *New J. Chem.*, 2014, **38**, 1019.

