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A π-stacked 1,2,3-dithiazolyl radical. Preparation and solid state characterization of $(Cl_2C_3NS)(ClC_2NS_2)$

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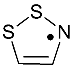
Crystals of $(Cl_2C_3NS)(ClC_2NS_2)$, an isothiazolyl-substituted 1,2,3-dithiazolyl radical, consist of evenly spaced, slipped π-stacks; magnetic and conductivity measurements indicate the material is a Mott insulator with $\sigma_{RT} = 2 \times 10^{-7}$ S cm^{-1}.

In our pursuit of conductive molecular materials based on neutral heterocyclic radicals we have recently focused on derivatives of the 1,2,3-dithiazolyl framework **1**. While such radicals have been known for many years,[1] their isolation and solid state characterization have proven difficult. Heavy spin density at the 5-position (resonance form **1b**) favours dimerization at carbon[2] and while association at the 5-position can be inhibited by the use of sterically bulky substituents, as in **2**,[3] or by adding 4,5-fused rings, as in **3**,[4] such modifications have to date only altered the mode of dimerization rather than preventing it. We now report the preparation of the 5-isothiazolyl derivative **4**, the first example of an unassociated 1,2,3-dithiazolyl.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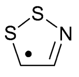
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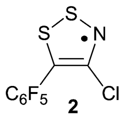
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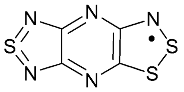
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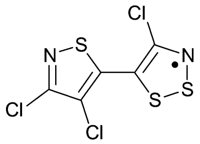
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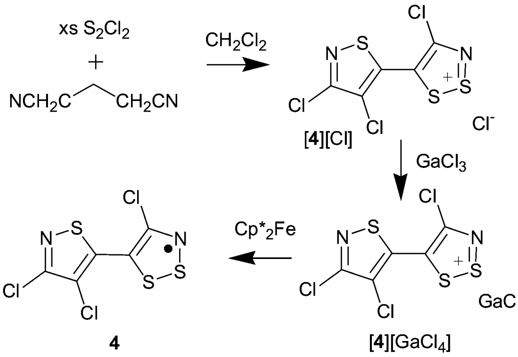
The most common synthetic route to monocyclic 1,2,3-dithiazoles involves the Appel cyclization[5] of an aliphatic nitrile RCH_2CN with S_2Cl_2. While exploring the behaviour of α,ω-dinitriles under similar conditions we have discovered that glutaronitrile $NC(CH_2)_3CN$ (3.0 g, 31.7 mmol) reacts with S_2Cl_2 (25 mL) and $Bu^n{}_4NCl$ (0.5 g) in 30 mL CH_2Cl_2 to afford the chloride salt of the isothiazolyl-dithiazolylium cation $\mathbf{4}^+$ (Scheme 1) as a green microcrystalline precipitate (8.10 g, 24.8 mmol, 78%). Canary yellow crystals, mp 147–49 °C, of the corresponding tetrachlorogallate salt [**4**][$GaCl_4$] can be prepared by treatment of [**4**][Cl] with gallium trichloride in SO_2(l). Subsequent reduction of [**4**][$GaCl_4$] (1.00 g, 1.9 mmol) with $Cp^*{}_2Fe$ (0.62 g, 1.9 mmol) in 15 mL degassed CH_3CN then affords **4** (0.50 g, 1.7 mmol, 86%) as a green precipitate. Lustrous green/black needles of **4**, dec. >90 °C, were grown from degassed chloroform.†

Green/brown solutions of **4** in CH_2Cl_2 exhibit a strong and persistent EPR signal characteristic of a 1,2,3-dithiazolyl radical.[6] In addition to the expected triplet (a_N = 0.498 mT) arising from hyperfine coupling to the dithiazole nitrogen, the spectrum (Fig. 1) also displays appreciable (a_N = 0.135 mT) coupling to the isothiazolyl nitrogen, as well as smaller coupling to two of the three chlorines present in the molecule. This is indicative of substantial spin delocalization away from the dithiazolyl ring. Spin delocalization is also reflected in the electrochemical behaviour of **4**. Cyclic voltammetry on solutions of [**4**][$GaCl_4$] in MeCN (Pt electrodes, $Bu^n{}_4NPF_6$ supporting electrolyte) reveals a reversible reduction wave ($\mathbf{4}^{+/0}$) with $E_{½}$ = 0.565 V (*vs.* SCE) and an irreversible reduction ($\mathbf{4}^{0/-1}$) with E_{pc} = −0.389 V (*vs.* SCE). While the appearance of these waves is typical of a 1,2,3-dithiazolyl, the separation $E_{pc}(\mathbf{4}^{+/0}) - E_{pc}(\mathbf{4}^{0/-1})$ = 0.935 V is substantially less than, for example, that seen for **2** (1.5 V), and even smaller than that observed for the tricyclic system **3** (0.99 V).



Scheme 1

The EPR and CV data above suggest improved solid state charge transfer characteristics for **4**, *i.e.*, a low on-site coulomb repulsion parameter *U* for **4**.[7] Density functional calculations (B3LYP/6-31G** with Cs geometry optimisation) on the triad of oxidation states available to **4** (cation, radical and anion) provide estimates (△SCF) of its ionisation potential (IP) and electron affinity (EA) which echo the electrochemical results. Thus, the calculated disproportionation enthalpy $\triangle H_{disp}$ = IP

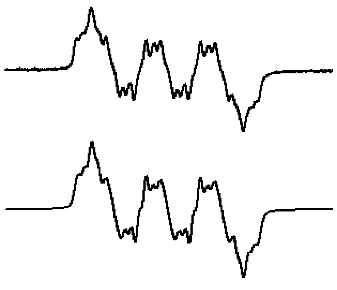


Fig. 1 EPR spectrum (293 K, CH_2Cl_2, SW = 3 mT, *g* = 2.00875) of radical **4** (above) and simulation (below). Hyperfine coupling constants are a_N = 0.498 and 0.135, a_{Cl} = 0.066/0.054 ($^{35/37}$Cl), 0.052/0.042 ($^{35/37}$Cl) mT , lw = 0.058 mT, L/G = 0.6.

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− EA = 7.08 − 2.11 = 4.97 eV is much lower than that of the prototypal 1,2,3-dithiazolyl **1** (6.67 eV), and even smaller than that found for the tricyclic compound **3** (5.32 eV).[8,9]

The crystal structures of both **4** and [**4**][$GaCl_4$] have been determined.‡ Crystals of [**4**][$GaCl_4$] contain discrete **4**$^+$ cations (planar to within 0.24 Å) and $GaCl_4^-$ anions, with no short intercation contacts. Crystals of **4** consist of planar (to within 0.03 Å) undimerized radicals aligned in a slipped π-stack arrangement running parallel to the *x* axis. Fig. 2 illustrates the packing in the *yz* plane, and Fig. 3 shows the slipped π-stacks. The mean interplanar separation is 3.488 Å.

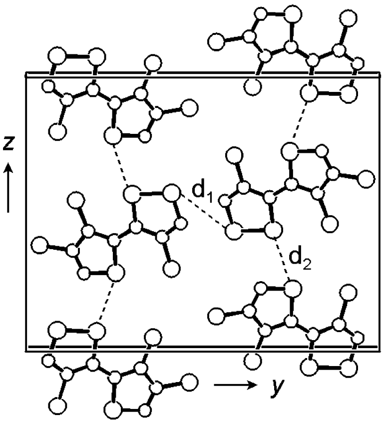

Fig. 2 Unit cell diagram of **4**, viewed perpendicular to the *yz* plane.

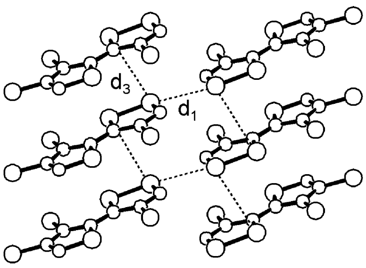

Fig. 3 Slipped π-stacks of **4**, running parallel to the *x* axis.

Comparison of the intramolecular features§ of the cation and radical reveal the expected lengthening of the S–S, S–N, S–C and N–C linkages occasioned by addition of an electron to the antibonding LUMO of the cation (SOMO of the radical).[10] There are no S···S intermolecular interactions between the radicals that are inside the normal van der Waals contact of 3.6 Å.[11] The closest S···S interactions outside this range are the head-to-head contact d_1 (3.843(3) Å), the head-to-tail contact d_2 (3.626(2) Å), and the π-stacking contact d_3 (3.707(2) Å).

Variable temperature magnetic susceptibility measurements on **4** indicate a Curie–Weiss temperature dependence for χ above 100 K (Fig. 4), with derived values of $\chi_0 = -144.5 \times 10^{-6}$ emu mol^{-1}, $C = 0.345$ and $\Theta = -45$ K.[12] The Curie spin count is near 0.92 at 300 K, as expected for a $S = \frac{1}{2}$ paramagnet, but drops rapidly below 100 K, indicative of strong intermolecular antiferromagnetic interactions. There is, however, no indication down to 5 K of a phase transition to a dimerized (and diamagnetic) state.

A single crystal conductivity measurement on **4** reveals a room temperature conductivity $\sigma_{RT} = 2 \times 10^{-7}$ S cm^{-1}. Presumably, intermolecular overlap along the π-stacks is insufficient to offset the magnitude of *U*, and the material thus remains a Mott insulator. The conductivity of **4** is nonetheless much better than that seen for π-stacked dithiadiazolyls.

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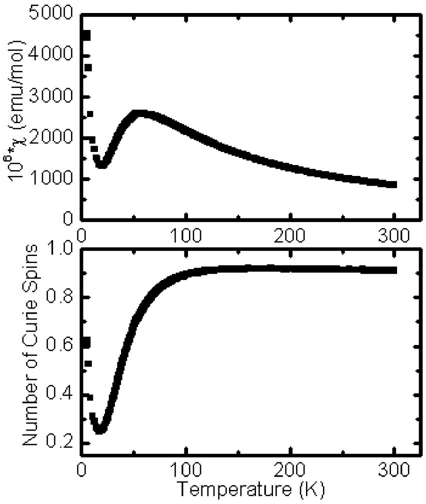

Fig. 4 Magnetic susceptibility χ *vs T* for **4** (above) and number of Curie spins *vs T* (below).

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Notes and references

† Satisfactory chemical analyses were obtained for **4** and [**4**][$GaCl_4$]. The IUPAC name for **4** is 4-chloro-5-(3,4-dichloroisothiazol-5-yl)-1,2,3-dithiazol-3-yl.

‡ *Crystal data*: X-ray data were collected at 293 K on a Rigaku Mercury CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.7107 Å) using ω scans. The structures were solved and refined by full matrix least-squares analysis which minimized $\Sigma w(\Delta F)^2$. Compound [**4**][$GaCl_4$]: $C_5N_2S_3Cl_7Ga$, M = 502.12, monoclinic, space group $P2_1/n$, with a = 7.8222(8), b = 14.0812(14), c = 14.4301(15) Å, β = 98.882(5)°, V = 1570.4(3) Å^3, Z = 4, D_c = 2.124 g cm^{-3}, μ = 3.321 mm^{-1}. 164 parameters were refined using 2907 (all) unique reflections to give R = 0.051 and R_w = 0.170. Compound **4**: $C_5N_2S_3Cl_3$, M = 290.60, monoclinic, space group $P2_1/c$, with a = 3.8833(6), b = 17.557(3), c = 13.668(2) Å, β = 93.428(9)°, V = 930.2(3) Å^3, Z = 4, D_c = 2.075 g cm^{-3}, μ = 1.603 mm^{-1}. 118 parameters were refined using 1737 (all) unique reflections to give R = 0.068 and R_w = 0.102. CCDC 186279–186280. See http://www.rsc.org/suppdata/cc/b2/b204855h/ for crystallographic files in .cif or other electronic format.

§ Summary of intramolecular distances in the C_2NS_2 rings. Compound [**4**][$GaCl_4$]: S–S, 2.0283(16); S–N, 1.593(4); N–C, 1.303(7); S–C, 1.689(5) Å. Compound **4**: S–S, 2.0862(18); S–N, 1.641(4); N–C, 1.298(6); S–C, 1.748(4) Å.

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