The Preparation and Characterization of the Paramagnetic Solid Bis(1,2,3,4-trithiazolium)bis(hexafluoroarsenate) containing the Dioxygen-like Dication Diradical $^{\bullet+}\mathrm{\overline{SSSNC}\overline{CNSSS}}^{+\bullet}$

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The hexafluoroarsenate salt of $^{\bullet+}\mathrm{\overline{SSSNC}\overline{CNSSS}}^{+\bullet}$ **1**, prepared by the reaction of $S_8(AsF_6)_2$, $S_4(AsF_6)_2$ and $(CN)_2$ in SO_2, is the only known sterically unhindered non-metal diradical, other than dioxygen, that contains two unpaired electrons in the solid state ($\mu = 2.81\ \mu_B$ at room temp.).

'Organic' or non-metal radicals that are stable as pure materials are rare. There are numerous examples of non-sterically hindered non-metal radicals in dilute solution or in the gas phase, but few can be isolated as pure *paramagnetic liquids*, and even fewer as pure paramagnetic solids. Examples of *paramagnetic liquids* include $\mathrm{CF_3\overline{CSNSC}CF_3}^{\bullet}$,[1] which is a green liquid under a blue gas at room temperature. However, it and other related *paramagnetic liquids* (*e.g.* $\mathrm{Bu^t\overline{CNSNS}}^{\bullet}$,[2] $\mathrm{CF_3\overline{CNSSN}}^{\bullet}$[3]) become diamagnetic on solidification with the formation of weak π^*–π^* dimers.† Examples of *paramagnetic solids* include O_2^+ salts,[4] $I_2Sb_2F_{11}$[5] and more recently AsF_6^- salts of $\mathrm{CF_3\overline{CSSSC}CF_3}^{+\bullet}$[6] and $\mathrm{CF_3\overline{CSSSN}}^{+\bullet}$[7] **2**. Research has sought to exploit the properties of these compounds in the synthesis of novel materials such as organic magnets.[8a,b] In this regard, stable organic multiradicals are clearly of interest, but they are even rarer. Oakley and Banister have recently reported the syntheses of several dithiadiazolyl- or diselenadiazolyl-based multiradical systems including *o*-, *m*- and *p*-$\mathrm{C_6H_4(\overline{CNSNS})_2}^{\bullet\bullet}$[9a] and *o*-, *m*- and *p*-$\mathrm{C_6H_4(\overline{CNEEN})_2}^{\bullet\bullet}$[10a,b] (E = S or Se), although some of these have been shown to be paramagnetic in solution, they are essentially diamagnetic‡ in the solid state, forming either dimers or extended structures *via* π^*–π^* interactions in both cases. In fact, although other diradical species have been detected in very dilute solutions, the only known sterically unhindered, non-metal diradical to exhibit paramagnetism in the solid state is dioxygen.[11] We now report the synthesis, characterization and X-ray crystal structure of $\mathrm{(\overline{CNSSS})_2(AsF_6)_2}$, containing $^{\bullet+}\mathrm{\overline{SSSNC}\overline{CNSSS}}^{+\bullet}$ **1**, the only sterically unhindered, non-metal diradical other than O_2 to retain its paramagnetism in all states.

The salt **1**$(AsF_6)_2$ was prepared in quantitative yield according to eqn. (1) by condensing $(CN)_2$ (0.204 g, 3.92 mmol) onto a mixture of $S_4(AsF_6)_2$ and $S_8(AsF_6)_2$ prepared *in situ* from S_8 (0.742 g, 2.90 mmol), AsF_5 (2.332 g, 13.27 mmol),

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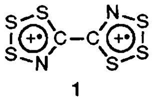
† These materials, although essentially diamagnetic solids often show a weak paramagnetism. The magnetic susceptibilities of solid $\mathrm{CF_3\overline{CSNSC}CF_3}^{\bullet}$,[1,3] $\mathrm{CF_3\overline{CNSSN}}^{\bullet}$[3] and $C_6H_4SNS^{\bullet}$[16] are 0.03 μ_B (at −25 °C), 0.21 μ_B (at 20 °C) and 0.51 μ_B (at 25 °C), respectively. However, these values fall far short of that corresponding to one unpaired electron and the residual paramagnetism may arise from a variety of causes including the presence of 'trapped' radicals. We define *paramagnetic liquids* or *paramagnetic solids* as those substances that show substantial paramagnetism in the stated phase.

‡ Several of these[9a,10a,b] have, like the monoradicals† been shown to interact *via* π^*–π^* bonds and yet retain some paramagnetism in the solid state. Banister has reported that *p*-$\mathrm{C_6H_4(\overline{CNSNS})_2}^{\bullet\bullet}$ (which stacks via π^*–π^* interactions in the solid state) was 'strongly paramagnetic' although an actual value was not provided.



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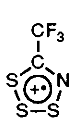

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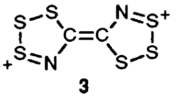

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$S_8(AsF_6)_2 + S_4(AsF_6)_2 + 2\,(CN)_2 \xrightarrow{SO_2} 2\,(\overline{CNSSS})_2(AsF_6)_2$

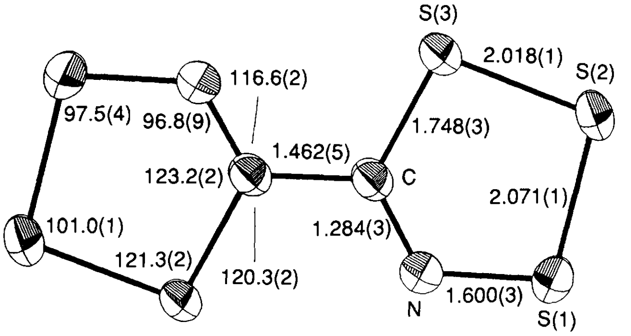

Fig. 1 Bond distances (Å) and angles (°) in planar 1^{2+}

Br_2 (15 mg) in SO_2 (8.128 g). A brown precipitate gradually formed on stirring, and a brown solid [$1(AsF_6)_2$] was isolated after one week; this was washed continuously by SO_2 under reflux[9b] at 50 °C for two days, giving an analytically pure product (isolated yield of the less soluble purified product = 82%).

$$S_8(AsF_6)_2 + S_4(AsF_6)_2 + 2(CN)_2 \xrightarrow{SO_2} 2(\overline{CNSSS})_2(AsF_6)_2 \quad (1)$$

The IR and FT Raman spectra of $1(AsF_6)_2$ were similar to those of the related $2AsF_6$.[7] The mass spectrum of a sample ground with CsF (to facilitate volatilization in the probe and removal of AsF_5) exhibited a fragmentation pattern consistent with the formation of $1F_2$ (*i.e.* $1F^+$ and other fluorides) although no molecular ion was observed. The magnetic susceptibility at room temperature, determined by the Guoy method, was 2.81 μ_B indicating the presence of two unpaired electrons (ideal spin only value = 2.83 μ_B). We were unable to obtain an ESR spectrum of $1(AsF_6)_2$ in dilute AsF_3 solution at room temperature.

Crystals§ of $1(AsF_6)_2$ were obtained by slow evaporation of a solution of $1(AsF_6)_2$ in AsF_3 over six weeks at 5 °C. The X-ray structure consists of alternating layers of non-interacting [minimum cation–cation distance S(2)–S(2) = 5.716(1) Å] planar **1** dications (Fig. 1), and AsF_6^- anions parallel to the *ab* plane (Fig. 2). The dications are tilted with respect to the plane and lie in channels along the *c*-axis. The dication and anion coordination numbers are 12 and 6, respectively, as predicted by the radius-ratio rule.[12] The midpoint of the C–C bond in the cation lies on a crystallographic inversion centre, consistent with the mutual exclusion of bands observed in the IR and FT-Raman spectra of this cation. The C–C distance, 1.462(5) Å, implies a C(sp^2)–C(sp^2) single bond.[13] The bond distances within the rings are similar to those in **2**, consistent with the presence of an unpaired electron in each of the rings (*i.e.* $^{\bullet+}\overline{SSSNC}\text{–}\overline{CNSSS}^{+\bullet}$).

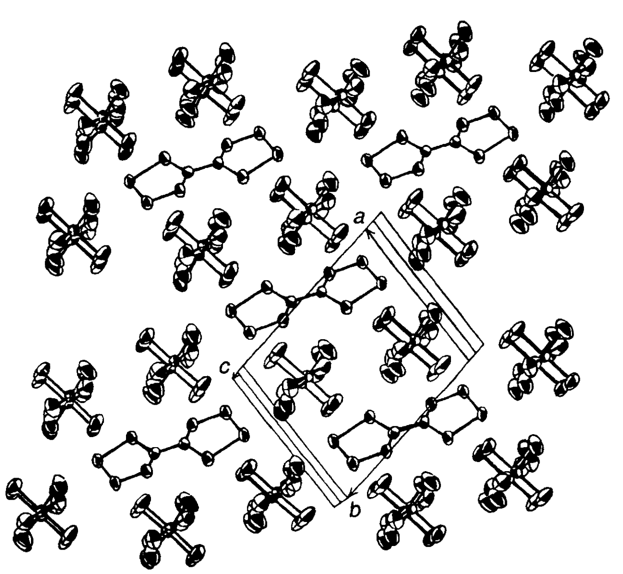

Fig. 2 The crystal packing of $1(AsF_6)_2$. Alternating sheets of anions and dications in the *ab*-plane with the dications tilted out of the plane and lying in channels along the *c*-axis.

Compound **1** and O_2 are unique in non-metal chemistry because they retain their diradical character in all states. The weakness of O–O σ bonds precludes the formation of $(O_2)_2$, while **1** does not dimerize owing to the electrostatic repulsion associated with its positive charge. Hund's rule prevents 'internal' electron pairing in O_2, and similarly ROHF/STO-3G//MNDO¶ calculations suggest that in **1** the unpaired electrons reside in two almost degenerate SOMOs (ΔE = 6 kcal mol^{-1}) (1 cal = 4.184 J). We initially anticipated that the spin-paired state for **1** would correspond to the quinoidal configuration **3**, and that the observed structure of **1** mostly reflects the preferred formation of two 2pπ–2pπ C=N bonds over one 2pπ–2pπ C=C bond. In fact, we were unable to optimize a quinoidal geometry at the MNDO level, and in all calculations planar singlets optimized to a structure incorporating significant C=N character, which is 99 kcal mol^{-1} higher in energy than the planar triplet **1**. A single-point STO-3G calculation on an assumed quinoidal geometry **3**‖ suggested that this state lies *ca.* 300 kcal mol^{-1} higher than the observed planar triplet **1**.

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§ *Crystal data:* $C_2N_2S_6(AsF_6)_2$, M_r = 622.21, triclinic, space group $P\bar{1}$, a = 5.716(1), b = 7.658(2), c = 9.170(2) Å, α = 98.52(2), β = 91.79(1), γ = 102.25(2)° R = 0.028, R_w = 0.039, V = 387.1(2) Å^3, Z = 1, D_c = 2.669 g cm^{-3}, Mo-Kα radiation (graphite monochromator), λ = 0.70930 Å, $F(000)$ = 296, 1530 observed reflections with $I > 1\sigma(I)$. The data, 1686 unique reflections, were collected at 295 K with an ω–2θ scan. The data were reduced and brought to a common scale; Lorentz-polarization and empirical absorption corrections were applied. The position of the As atom was derived from a Patterson map. All other atom positions were obtained from Fourier and difference-Fourier maps. The atomic scattering factors were taken from ref. 14 and the effects of anomalous dispersion were included in F_c using the values of Cromer.[15] The structure was refined using full-matrix least-squares analysis, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. All atoms were refined using anisotropic displacement parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ All geometry optimizations assumed C_{2h} symmetry and were performed at the MNDO level, while all energies refer to STO-3G calculations using the MNDO geometries. Calculations used the ROHF procedure for triplets, and the RHF procedure for singlets; all were carried out using the GAUSSIAN-86 suite of programs. Optimized geometry of planar single: C–C 1.4238, C–N 1.3624, N–S(1) 1.5444, S(1)–S(2) 1.9813, S(2)–S(3) 1.9692, and C–S(3) 1.6996 Å. Optimized geometry of planar triplet **1**: C–C 1.4791, C–N 1.3157, N–S(1) 1.5920, S(1)–S(2) 1.9785, S(2)–S(3) 1.9479, C–S(3) 1.7003 Å.

‖ Geometry used for the single-point calculation on a quinoidal singlet: C–C 1.3303, C–N 1.5120, N–S(1) 1.5463, S(1)–S(2) 2.0400, S(2)–S(3) 2.0400, C–S(3) 1.7920 Å.

The facile preparation of the paramagnetic solids $CF_3\overline{CNSSS}^{+\cdot}$, $CF_3\overline{CSSSC}CF_3^{+\cdot}$ and the multiradical **1** has been demonstrated using the reagent '$S_3^{+\cdot}$'. It is likely that multiradicals of higher spin possessing novel electronic and magnetic properties can be prepared using this synthetic strategy.

We thank Dr E. G. Awere (UNB) for helpful technical assistance, Dr F. Grein (UNB) for use of computational facilities and helpful discussion, the NSERC (Canada) for an operating grant (J.P.), and UNB (D.J.W.) and the Canadian Commonwealth Scholarship and Fellowship Committee (S.P.) for assistantships.

Received, 30th September 1992; Com. 2/05264D

References

1 E. G. Awere, N. Burford, C. Mailer, J. Passmore, M. J. Schriver, P. S. White, A. J. Banister, H. Oberhammer and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 66.
2 W. V. F. Brooks, N. Burford, J. Passmore, M. J. Schriver and L. H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 69.
3 M. J. Schriver, PhD Thesis, University of New Brunswick, 1988; R. C. Haddon, personal communication.
4 *From Atoms to Polymers: Isoelectronic Analogies*, ed. J. F. Liebman and A. Greenberg, VCH Publishers Inc., New York, 1989, p. 55 and references cited therein.
5 W. W. Wilson, R. C. Thompson and F. Aubke, *Inorg. Chem.*, 1980, **19**, 1489.
6 T. S. Cameron, R. C. Haddon, S. M. Mattar, S. Parsons, J. Passmore and A. P. Ramirez, *J. Chem. Soc., Dalton Trans.*, 1992, **9**, 1563.
7 T. S. Cameron, R. C. Haddon, S. M. Mattar, S. Parsons and J. Passmore, *Inorg. Chem.*, 1992, **31**, 2274.
8 (*a*) Z. Yoshida and T. Sugimoto, *Angew. Chem., Int. Ed. Engl.*, 1988, **11**, 1573; (*b*) J. S. Miller, A. J. Epstein and W. M. Reiff, *Acc. Chem. Res.*, 1988, **21**, 114.
9 (*a*) A. J. Banister, J. M. Rawson, W. Clegg and S. L. Birkby, *J. Chem. Soc., Dalton Trans.*, 1991, 1099; (*b*) R. W. Small, A. J. Banister and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1984, 1377.
10 (*a*) A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley and T. T. M. Palstra, *Inorg. Chem.*, 1992, **31**, 1802; (*b*) M. P. Andrews, A. W. Cordes, D. C. Douglass, R. M. Fleming, S. H. Glarum, R. C. Haddon, P. Marsh, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, G. W. Trucks, R. Tycko, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 3559; A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 582.
11 E. Muller, A. Rieker, K. Scheffler and A. Moosmayer, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 6.
12 J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, Harper and Row Publishers Inc., New York, 3rd edn., 1983, p. 83.
13 H. A. Bent, *Chem. Rev.*, 1961, **61**, 283.
14 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Kynoch, Birmingham, England, 1974, vol. IV, Table 2.2.A.
15 D. T. Cromer, *International Tables for X-ray Crystallography*, Kynoch, Birmingham, England, 1974, vol. IV, Table 2.3.1.
16 E. G. Awere, N. Burford, R. C. Haddon, S. Parsons, J. Passmore, J. V. Waszczak and P. S. White, *Inorg. Chem.*, 1990, 29.