The novel magnetic properties of $\overline{\mathrm{SSSNC}}\,\overline{\mathrm{CNSSS}}(\mathrm{M})_2$ (M = AsF_6, Sb_2F_{11}) and the electronic properties of $^{\cdot+}\overline{\mathrm{SSSNC}}\,\overline{\mathrm{CNSSS}}^{+\cdot}$

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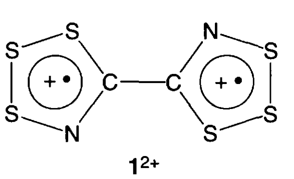
The variable-temperature magnetic behaviour of the previously reported AsF_6^- and presently reported $Sb_2F_{11}^-$ salts of bis(1,2,3,4-trithiazolium), $^{\cdot+}\overline{\mathrm{SSSNC}}\,\overline{\mathrm{CNSSS}}^{+\cdot}$ (1^{2+}), are complex but indicate intermolecular antiferromagnetic interactions and temperature-independent paramagnetism, as well as intramolecular antiferromagnetic coupling leading to a singlet ground state, with a nearly degenerate thermally accessible triplet excited state, which is confirmed by EPR spectroscopy.

The brown, paramagnetic solid $\mathbf{1}(AsF_6)_2$ (**1a**) contains the planar centrosymmetric $\mathbf{1}^{2+}$ which resembles O_2 in that it retains its paramagnetism in the solid state.[1] We now report the preparation of green, paramagnetic $\mathbf{1}(Sb_2F_{11})_2$ (**1b**) containing dications that are essentially identical to those in **1a**. EPR experiments on frozen solutions of **1a** and **1b** in SO_2–MF_5 (M = As, Sb) provide spectroscopic proof of the presence of a triplet state from observation of the characteristic zero-field splittings [D = 555 MHz, Fig. 1(*b*)] and a $\Delta m_s = \pm 2$ resonance at half field. Variable-temperature solid-state magnetic studies imply a singlet ground state with a nearly degenerate triplet excited state, as well as intermolecular (dication–dication) antiferromagnetic interactions and temperature-independent paramagnetism (TIP), although their contributions are different in the two salts. Antiferromagnetic intramolecular and intermolecular interactions and TIP are not uncommon solid-state properties, but the salts of $\mathbf{1}^{2+}$ are unique in that they incorporate all of these electronic and magnetic properties. $\mathbf{1}^{2+}$ and O_2 are the only main group non-sterically hindered diradicals to retain their paramagnetism in the solid state; however, the electronic and magnetic properties of $\mathbf{1}^{2+}$ are more complex than those of simple O_2.



$\mathbf{1}^{2+}$

1a (1.461 g, 2.438 mmol) and an excess of SbF_5 (4.794 g, 22.11 mmol) in SO_2 (10.133 g) solution gave green **1b** quantitatively; characterized by elemental analyses, IR and FT-Raman, and the X-ray crystal structures of two phases[2] of **1b**.

Both salts of $\mathbf{1}^{2+}$ dissolve in liquid SO_2–MF_5 (M = As, Sb) to give green paramagnetic solutions that have similar EPR spectra over the temperature range −180 to 20 °C. The solution spectra [Fig. 1(*a*)] show two components, a broad resonance (**A**) and a much narrower resonance (**B**). These features are reminiscent of EPR spectra of perchlorotriphenylmethyl diradicals.[3] In the frozen state, **B** remains a single resonance, whereas **A** shows a powder-spectrum characteristic of a triplet with a rhombic g-matrix and a nearly axial zero-field splitting tensor [Fig. 1(*b*)]. In addition a resonance at half field is observed corresponding to the $\Delta m_s = \pm 2$ transition. The principal values of g ($\Delta m_s = \pm 1$) are typical of a 7 π radical[4] in which $g_{\min}$ ($= g_{yy}$) is just less than g_e and lies parallel to the component p orbitals, *i.e.* perpendicular to the molecular plane. The maximum component of the dipolar tensor D_{zz} ($= 2/3\ D$) must then lie in the molecular plane. Its value corresponds to a separation between 'point electrons' of 5.2 Å which is commensurate with the distance between the ring centres. Thus **A** is a planar diradical in which each of the unpaired electrons is essentially confined to quasi-isolated π systems on each of the two rings, separated by a sp^2–sp^2 hybridized C–C single bond [1.462(5) Å for **1a**].[1] This description conforms to the detection of the $\Delta m_s = \pm 2$ resonance, the triplet in solution which is characteristic of biradicals with weakly coupled electrons,[5] and the very small values of the intramolecular exchange coupling constant J obtained from solid-state magnetic studies (see below). The relative intensity of **B** to **A** is about 1 : 1 at 20 °C and decreases to about 1 : 10 at −120 °C. We tentatively assign **B**, and the green colour of solutions of brown **1a** and green **1b**, to a higher energy non-planar diradical rotomer of $\mathbf{1}^{2+}$ having a very small D value.

Variable-temperature magnetic susceptibilities were measured on a packed, unground sample of **1a** and a lightly ground sample of **1b** using a Quantum Design (MPMS) SQUID magnetometer (H = 10 000 Oe). Magnetic moment values for **1a** and **1b** decrease from 2.36 and 3.27 μ_B at 300 K to 0.23 and 1.04 μ_B at 2 K, respectively, consistent with antiferromagnetic exchange interactions that are significantly greater in the former compound. The magnetic susceptibility of **1a** shows a maximum at *ca.* 60 K, confirming antiferromagnetism in this sample. The curve shown as a dashed line in Fig. 2(*a*) was calculated from the Bleaney–Bowers equation [singlet–triplet separation, $2J = -42\ \mathrm{cm}^{-1}$ ($0.50\ \mathrm{kJ\ mol}^{-1}$) for $g_{\mathrm{iso}} = 2.00$, where J is the intramolecular exchange coupling constant] modified by the molecular-field approximation[6] to include the effects of intermolecular antiferromagnetic exchange ($zJ' = -18\ \mathrm{cm}^{-1}$, where z is the number of interacting neighbours and J' is the intermolecular exchange coupling constant), a paramagnetic impurity (% P) of 2.3%, and TIP ($0.0010\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$). The best fit [solid line, $2J = -60\ \mathrm{cm}^{-1}$ ($0.72\ \mathrm{kJ\ mol}^{-1}$), $zJ' = -11\ \mathrm{cm}^{-1}$ and TIP = $0.0007\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ for $g_{\mathrm{iso}} = 2.00$ and % P = 0] was obtained by fitting only those data above 30 K, where effects of paramagnetic impurities are minimized. The theoretical curves only approximate the experimental findings, so that the parameter values should be treated with caution. In particular, the molecular-field approximation has quantitative validity only when the intermolecular exchange is weak[6] and this is not the case here. Qualitatively, this analysis supports the presence of significant TIP and intermolecular antiferromagnetic exchange, as well as intramolecular exchange leading to a ground-state singlet, the small value of J ($0.36\ \mathrm{kJ\ mol}^{-1}$)

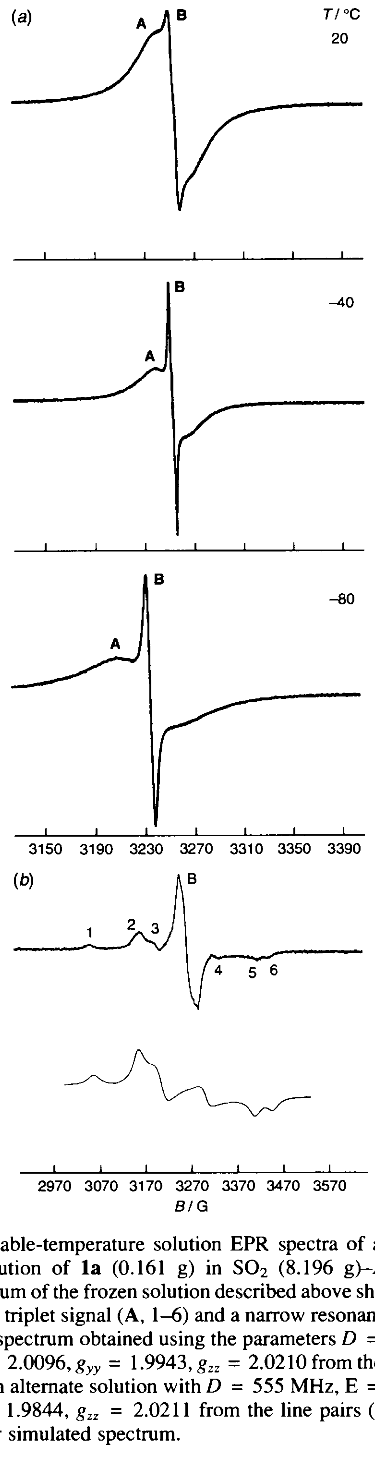


Fig. 1(*a*) Variable-temperature solution EPR spectra of a 4.193 × 10^{-4} mol dm^{-3} solution of **1a** (0.161 g) in SO_2 (8.196 g)–AsF_5 (0.980 g); (*b*) EPR spectrum of the frozen solution described above showing zero-field splitting of the triplet signal (**A**, 1–6) and a narrow resonance (**B**). Below is the simulated spectrum obtained using the parameters D = 555 MHz, E = 54 MHz, g_{xx} = 2.0096, g_{yy} = 1.9943, g_{zz} = 2.0210 from the line pairs (1,6), (2,5), (3,4). An alternate solution with D = 555 MHz, E = 22 MHz, g_{xx} = 2.0198, g_{yy} = 1.9844, g_{zz} = 2.0211 from the line pairs (1,6), (2,4), (3,5) gives a similar simulated spectrum.

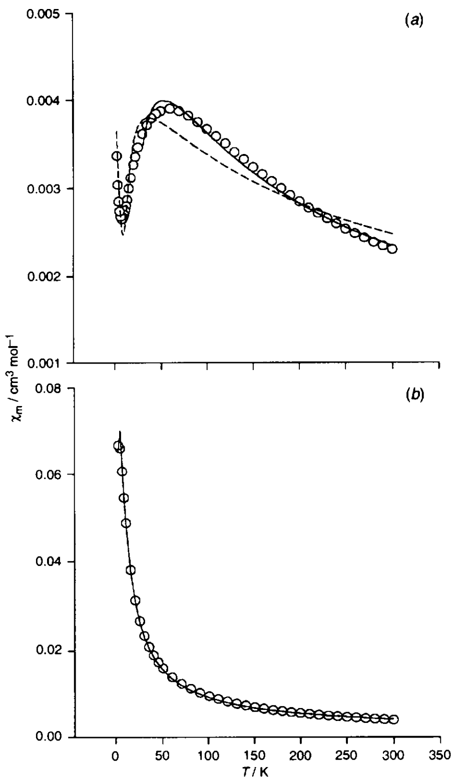


Fig. 2(*a*) χ_M *vs.* T data for an unground sample of **1a** and (*b*) a lightly ground sample of **1b**. Lines calculated from theory as described in the text.

consistent with the small value of D (555 MHz, 0.0002 kJ mol^{-1}) obtained from EPR.

The near degeneracy of the singlet and triplet states is supported by theoretical calculations.[7]† The magnetic results for **1b** are shown in Fig. 2(*b*) where the solid line was calculated as above with $2J = -3.4$ cm^{-1} (0.041 kJ mol^{-1}), $zJ' = -0.42$ cm^{-1}, TIP = 0.0022 cm^3 mol^{-1} (for g_{iso} = 2.00 and % P = 0). Both intra- and inter-molecular exchange appear to be much weaker in this compound. There appears to be significant TIP in both samples, implying a low-lying but thermally unoccupied excited state supported by the theoretical results.[7] The anti-ferromagnetic intercationic interactions estimated by the zJ' values are strong in **1a** and weaker in **1b** where the distances between dications are much larger.[2]

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Footnote

† Open-shell singlet (GVB Perfect Pairing/CEP-31G*) and triplet (ROHF/CEP-31G*) state calculations[7] give a singlet 0.88 kJ mol^{-1} higher in energy than the triplet.

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