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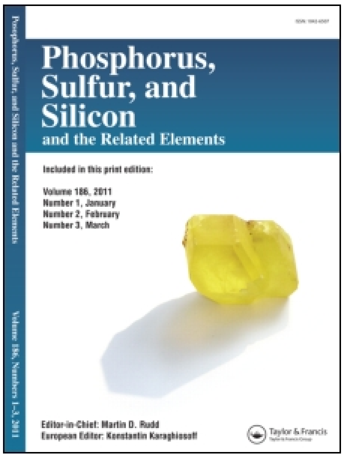

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The Electronic and Magnetic Properties of SSSNCCNSSS(M)$_2$ (M = AsF_6^-,SbF_6^-, $Sb_2F_{11}^-$) and Evidence for the Isostructural Monocation Monoradical (CNSSS)$^{+\bullet}$

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The variable temperature magnetic behaviour of the AsF_6^-, $Sb_2F_{11}^-$ and presently reported SbF_6^- salts of Bis(1,2,3,4-trithiazolium), $^{\bullet+}$SSSNCCNSSS$^{+\bullet}$, 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. ESR spectroscopy confirms the triplet state and also shows a narrow resonance with a similar isotropic g value; possibly due to the presence of a diradical isomer of 1^{2+}. 1^{2+} is readily reduced to the monocation monoradical. Vibrational spectroscopy suggests that 1^+ has a similar geometry to 1^{2+} with some weakening of the bonds within the rings. ESR spectroscopy shows a pentet at -80°C, indicating that the unpaired electron couples with two equivalent N atoms, consistent with the electron delocalized over both rings.

Keywords: trithiazolium; triplet; radical; ESR; Bleany-Bowers; antiferromagnetism; temperature independant paramagnetism (TIP)

INTRODUCTION

The quest for stable organic radicals with interesting electronic and magnetic properties has been a vibrant area of research for several years. The reaction of S_2N^+ with acetylenes and nitriles was found to give $RCSNSCR^+$ and $RCNSNS^+$ respectively, which on reduction gave 7π radicals; characterized by ESR spectroscopy in solution. Although some of these radicals were paramagnetic liquids, all were diamagnetic in the solid state. Similar reactions with a mixture of S_8^{2+} and S_4^{2+} resulted in the formation of the paramagnetic cations $RCSSSCR^{\bullet+}$ and $RCNSSS^{\bullet+}$ ($R = CF_3$) which retained their paramagnetism even in the solid state. Attempting to prepare a stable diradical, $(CN)_2$ was reacted with the S_8^{2+} / S_4^{2+} mixture, leading to the formation of $^{\bullet+}SSSNCCNSSS^{\bullet+}$ (1^{2+}). The brown paramagnetic solids $1(AsF_6)_2$, $1(SbF_6)_2$ and α-$1(Sb_2F_{11})_2$ and green paramagnetic solid β-$1(Sb_2F_{11})_2$ contain the planar centrosymmetric 1^{2+} which contains two 7π rings linked by an sp^2-sp^2 C-C single bond. ESR experiments on frozen solutions of 1^{2+} 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 ($D \approx 500$ MHz, Figure 1b) and $\Delta m_s = \pm 2$ 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 differ from salt to salt. 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 1^{2+} are more complex than those of simple O_2.

1^{2+} is readily reduced to the isostructural 1^+ by reaction of 1^{2+} with $Na_2S_2O_4$. FT-Raman spectroscopy shows a similar spectrum to 1^{2+} but with the peaks shifted significantly to lower wavenumbers, consistent with lengthening of the bonds within the rings. ESR spectroscopy of 1^+ in SO_2 at -90°C shows a single pentet ($g = 2.0152$, $a = 2.0$ G), consistent with weak coupling of a single unpaired electron to two equivalent N atoms.

$(CNSSS)_2(M)_2$ ($M = AsF_6^-$, SbF_6^-, $Sb_2F_{11}^-$)

The preparations of $1(AsF_6)_2$[1] and the two phases of $1(Sb_2F_{11})_2$[2] have been reported previously. $1(SbF_6)_2$ is prepared according to the equations

$$3S_8 + 16SbF_5 \text{ ----------}{>} \ 2S_4(SbF_6)_2 + 2S_8(SbF_6)_2 + 4SbF_3{\bullet}SbF_5 \quad (1)$$
$$S_4(SbF_6)_2 + S_8(SbF_6)_2 + 4(CN)_2 \text{ ---------}{>} \ 4(CNSSS)_2(SbF_6)_2 \quad (2)$$

S_8 (3.250 g / 12.671 mmol) and SbF_5 (14.182 g /65.433 mmol) in SO_2 (18.679 g) solution gave a dark blue solution with a white precipitate after several hours. The blue solution was washed away from the white solid after 24 hours and then $(CN)_2$ (1.813 g / 34.835 mmol) was condensed in slight excess onto the reaction mixture. A green solution with a brown crystalline precipitate formed within minutes. Removal of the volatiles to constant weight after 24 hours gave $1(SbF_6)_2$ quantitatively; characterized by elemental analysis, IR and FT-Raman, and the X-ray crystal structure[3]. The white solid was characterized by FT-Raman spectroscopy and found to be $SbF_3{\bullet}SbF_5$[4].

All salts of 1^{2+} dissolve in liquid SO_2/MF_5 (M=As,Sb) mixtures to give green paramagnetic solutions that have similar ESR spectra over the temperature range -180 to 20°C. The solution spectra (FIGURE 1a) show two components, a broad resonance (A) and a much narrower resonance (**B**).

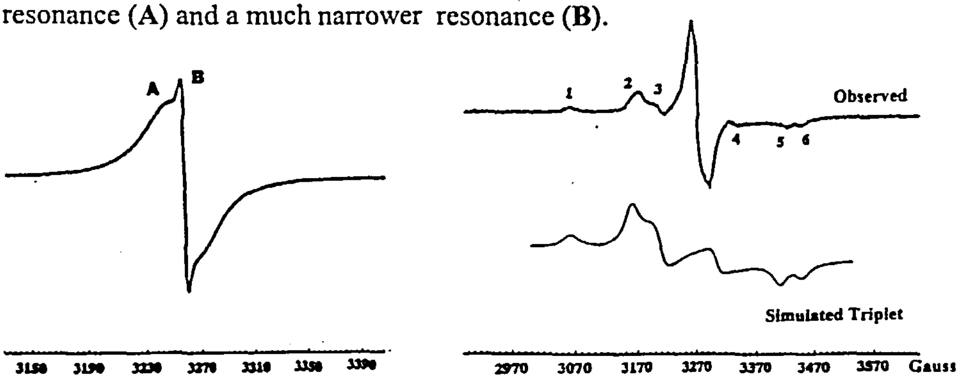
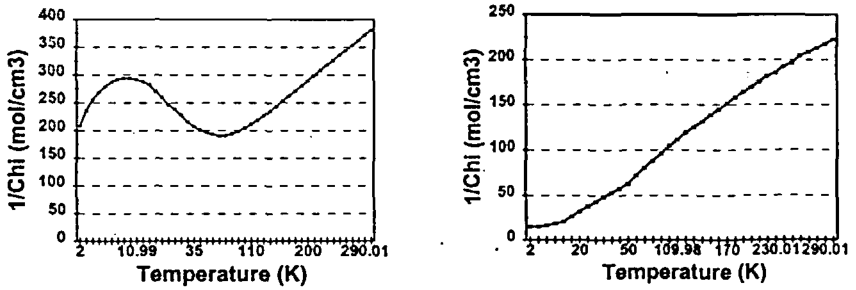


FIGURE 1 ESR spectra of $1(AsF_6)_2$ in SO_2/AsF_5 solution at a) 20°C and b) -165°C

These features are reminiscent of ESR spectra of perchlorotriphenylmethyl diradicals[5]. In the frozen state, **B** remains a single resonance showing slight anisotropy, whereas A shows a powder spectrum characteristic of a triplet with a rhombic g-matrix and a nearly axial zero-field splitting tensor (FIGURE 1b). 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 7π radical[6] in which g_{min} ($\equiv g_{yy}$) is just less than g_e (2.00232) 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[6]. Thus **A** is due to a planar triplet in which each of the unpaired electrons are essentially confined to quasi-isolated π-systems on one of the two rings, separated by a sp^2-sp^2 hybridized C-C single bond (1.462(5) Å for $1(AsF_6)_2$[1]. This description conforms to the detection of the triplet in solution, characteristic of triplets with weakly coupled electrons[7], and the very small values of the intramolecular exchange coupling constant J obtained from solid state magnetic studies (see below). The anisotropic g values and zero-field splitting parameters were determined by simulating the low temperature powder spectrum. It was found that nearly identical simulated spectra could be obtained using two different sets of parameters, but theoretical calculation of the zero-field splitting parameters supports only one of these solutions [FIGURE 1b using line pairs 1,6 2,4 3,5 (theoretical): D = ±555 (-450) MHz, E = ±22.3 (-25) MHz, g_{xx} = 2.0198, g_{yy} = 1.9844, g_{zz} = 2.0211]. The relative intensity of **B** to **A** in $1(AsF_6)_2$ is about 1:1 at 20°C and decreases to about 1:10 at -120°C. Several possibilities for the observance of **B** have been postulated including paramagnetic impurities (either $1^{3+\bullet}$ or $1^{+\bullet}$) or a double quantum transition. It is doubtful that $1^{+\bullet}$ would be present in such highly oxidizing conditions and attempts to oxidize 1^{2+} to $1^{3+\bullet}$ have been unsuccessful. The double quantum transition is formally forbidden (like the $\Delta m_s = \pm 2$ transition) and should therefore be very weak if observed at all. The strong intensity of **B** suggests that it is not likely the cause. Another possibility is that **B** is due to a higher energy diradical rotomer of 1^{2+} having a very small (zero) D value. Although theoretical calculations show no local minima in the rotational energies of 1^{2+} about the C-C bond, it is possible that solvation effects stableize such a geometry. This possibility was also suggested by Ballester et al. for the narrow resonance observed in the ESR spectra of perchlorophenylmethyl diradicals[5]. It is also believed that the diradical rotomer is responsible for the intense green colour observed for solutions of $1(AsF_6)_2$, $1(SbF_6)_2$, and $1(Sb_2F_{11})_2$ in AsF_3, SO_2, and SO_2 / MF_5 (M = As, Sb) solutions as well as in the solid state of β-$1(Sb_2F_{11})_2$. The normally brown solids become green on grinding with a corresponding increase in magnetic moment (2.8 to 3.2 μ_B for $1(AsF_6)_2$), consistent with a change from a triplet to a diradical (spin free moment = 2.83 and 3.46 μ_B respectively).

Variable-temperature magnetic susceptibilities were measured on packed, unground sample of $1(AsF_6)_2$ and $1(SbF_6)_2$ and a lightly ground sample of $1(Sb_2F_{11})_2$ using a Quantum Design (MPMS) SQUID magnetometer (H = 10000 Oe). Magnetic moment values for all salts of 1^{2+} drop significantly from 300K to 2K, consistent with antiferromagnetic exchange interactions. The magnetic susceptibility of $1(AsF_6)_2$ and $1(SbF_6)_2$ (FIGURE 2a) show maxima between 60K and 80K, confirming antiferromagnetism in these samples.



a

b

FIGURE 2 Plot of $1/\chi$ (mol/cm^3) vs. Temperature (K) for a) $1(AsF_6)_2$ and b) $1(Sb_2F_{11})_2$

The plot of $1/\chi$ vs. T for $1(Sb_2F_{11})_2$ (FIGURE 2b) shows deviation of Curie-Weiss behaviour towards the y-axis at 10K, also consistent with antiferromagnetic interactions. The magnetic susceptibility curves were fit using the Bléany-Bowers equation, modified by the molecular field approximation[8] to include the effects of intermolecular antiferromagnetic exchange, a paramagnetic impurity, and temperature-independent paramagnetism; g_{iso} was held fixed at 2.00. The best fit was obtained by fitting only those data above 30K, where effects of paramagnetic impurities are minimized. The fitted parameters are given in Table I.

TABLE I Fitted Magnetic Parameters for the Salts of 1^{2+}

Salt	Intramolecular (2J cm^{-1})[a]	Intermolecular (zJ' cm^{-1})[b]	TIP (cm^3/mol)
AsF_6^-	-60	-11	0.0007
SbF_6^-	-64	-4	0.0007
$Sb_2F_{11}^-$	-3.4	-0.42	0.0022

[a] J is the intramolecular exchange integral and 2J is the energy gap between the singlet ground state and the triplet excited state

[b] z is the number of interacting neighbours and J' is the intermolecular exchange integral

The values for $1(Sb_2F_{11})_2$ are different than for $1(AsF_6)_2$ and $1(SbF_6)_2$. The difference in intermolecular interactions can be explained by the difference in the size in the anions and thus the distance of the intermolecular contacts (Shortest intermolecular interactions: AsF_6^- = 4.08 Å, SbF_6^- = 4.28 Å, α-$Sb_2F_{11}^-$ = 4.37 Å, β-$Sb_2F_{11}^-$ = 5.03 Å). The intramolecular properties must also be somehow dependant on intermolecular interactions; possibly due to perturbations caused by proximity of one dication to another. 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 consistent with the small value of *D* (500 MHz, 0.002 kJ mol^{-1}) obtained from ESR.

Conclusion

1^{2+} is a ground state singlet but the triplet state is nearly degenerate and populated even at low temperatures. As a result even at very low temperatures 3/4 (1 singlet state, 3 equivalent triplet states) of the unpaired electrons occupy the triplet state and 1^{2+} behaves as a characteristic triplet molecule, exhibiting zero-field splitting and a $\Delta m_s = \pm 2$ transition at half field in the ESR spectrum.

Unlike O_2, in which the unpaired electrons are in orthogonal orbitals, the unpaired electrons in 1^{2+} are free to delocalize over both rings and yet the interaction between the spins is very weak. The presence of a significant TIP further differentiates 1^{2+} from O_2 and other main group radicals, making 1^{2+} a novel and unique species.

$(CNSSS)_2AsF_6$

$(CNSSS)_2AsF_6$ ($1AsF_6$) was prepared according to the equation

$$(CNSSS)_2(AsF_6)_2 + \tfrac{1}{2}\, Na_2S_2O_4 \text{ ------> } (CNSSS)_2AsF_6 + NaAsF_6 + SO_2 \quad (3)$$

$1(AsF_6)_2$ (1.024 g / 1.646 mmol) and $Na_2S_2O_4$ (0.138 g / 0.795 mmol; in slight deficite relative to one electron reduction) were combined in SO_2 (12.657 g). The pale green solution of $1(AsF_6)_2$ in SO_2 turned brown within minutes and the insoluble brown solid was consumed within an hour followed by precipitation of a pale brown precipitate. The reaction was allowed to stand for three days to ensure completion of the reaction. There were no further changes observed over this time. The brown solution was washed away from the insoluble pale brown solid and the solvent was removed to constant weight leaving a brown solid behind (0.703 g / 98.6 % yield for $1AsF_6$). The pale brown solid was characterized by FT-Raman spectroscopy and was found to contain some $1AsF_6$. The insoluble is very likely $NaAsF_6$.

The FT-Raman spectra of the brown solid is very similar to that of $1(AsF_6)_2$ except for a significant shift of the non-anion peaks to lower wavenumbers [$1(AsF_6)_2$ (cm^{-1}): 1553.3 (C=N), 1509.4 (C=N), 1480.8 (C=N), 1225.7 (C-C), 1185.1 (C-C), 909.6 (S-N), 643.3 (C-S), 528.0 (S-S), 452.9 (S-S), 416.2 (S-S), 333.4, 222.8; **$1AsF_6$** (cm^{-1}): 1433.3 (C=N), 1417.3 (C=N), 1377.3 (C=N), 1249.7 (C-C), 1190.1 (C-C), 876.5 (S-N), 498.1 (C-S), 472.3 (S-S), 429.7 (S-S), 397.2 (S-S), 218.9, 152.8]. This shift is consistent with a weakening of the bonds within the rings of 1 with little change in the C-C bond. This is supported by theoretical calculations (UHF/STO-3G optimizations) which show lengthening of the bonds within the rings but no significant change in the C-C bond. 1^{2+} and 1^{+} each have 12 Raman active non-anion absorptions out of a total of 24 predicted by group theory for the IR and Raman combined[9]. This is consistent with 1^+ being planar and centrosymmetric like 1^{2+}.

The ESR spectrum at -90°C of 1^+ prepared in-situ as described above shows a single pentet with a = 2.0 G. The hyperfine splitting is consistent with the unpaired electron delocalized over both rings and weak coupling to two equivalent N atoms. The coupling is greater than observed for $CF_3C\underline{N}SSS^{\cdot+}$ ($a(^{14}N)$ = 0 G) but similar to the related $HC\underline{N}SNS^{\cdot}$ ($a(^{14}N)$ = 1.5 G). Delocalization of the unpaired electron suggests that the two rings are co-planar and supports the vibrational evidence.

Conclusion

The evidence suggests that 1^+ is a stable monoradical which can be isolated in the solid state. The ease of the reduction of 1^{2+} to the stable monoradical and thus the oxidation of the monoradical to 1^{2+} means that the chemistry of the monoradical may be exploited further. The choice of a suitable acceptor molecule may allow for the synthesis of donor-acceptor lattices of paramagnetic cations and anions. In some cases[10] this has been shown to lead to materials with interesting magnetic and electronic properties such as ferromagnetism and conductivity.

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