Characterisation of the thermally accessible spin triplet state in dimers of the 7π $ClCNSSS^{+\bullet}$ in the solid state†

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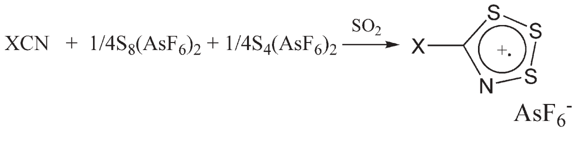
$[ClCNSSS]_2^{2+}$ is the first example of a thiazyl radical dimer where population of a thermally excited spin triplet state has been detected, as is proved by VT-powder and single-crystal EPR spectroscopy.

Stable non-metal radicals such as the thiazyls, for example RCNSSN, RCSNSCR and RCSSNCR, are of interest in their own right and as building blocks of materials possessing important physical properties *e.g.* electrical conduction, ferromagnetism, or magnetic switches. It is important to have general, simple synthetic routes to these radicals and to understand the factors governing their solid state properties. To this end we have extended the synthesis of the rare (only two previous examples) $RCNSSS^{+\bullet}$ family,[1] previously restricted to those derived from RCN with high IPs, to $XCNSSS^{+\bullet}$ with X = halide. Like many thiazyl radicals, but in contrast to the previously known $RCNSSS^{+\bullet}$, these dimerise in the solid state to form $[XCNSSS]_2[AsF_6]_2$ solids containing 7π $XCNSSS^{+\bullet}$ radicals dimerised *via* four-center–two-electron π*–π* bonds. Thiazyl π-dimers are generally considered to be diamagnetic, as probed by magnetic susceptibility techniques, owing to large spin singlet–triplet (S–T) energy gaps. Here we show *via* powder and single-crystal EPR spectroscopy on the X = Cl derivative that there is a small percentage of dimers in the thermally excited spin triplet state even at room temperature (r.t.). Although triplet excitons have been observed in organic π-radical pairs,[2] this is their first observation in *any* thiazyl π-radical dimer. EPR also allows determination of the S–T separation, the relationship between the triplet electronic and geometric structures *via* single crystal studies, and characterization and quantification of lattice defects.



Scheme 1 Preparation of **1(Cl)**$[AsF_6]$, **1(Br)**$[AsF_6]$ and **1(I)**$[AsF_6]$.

The only previously known $[RCNSSS]^{+\bullet}$ (R = CF_3, $CNSSS^{+\bullet}$ as AsF_6^- salts)[1] are derived from RCN with high IPs, prepared by reaction of a 4:1 ratio of RCN and $S_n(AsF_6)_2$ (n = 4, 8).[1] With RCN of low IPs this reaction instead gives 1,2,4-thiadiazoles.[3] However, by reacting the nitrile in aliquots with an excess of $S_n(AsF_6)_2$ (n = 4, 8) we have now extended this reaction to a wider range of nitriles with intermediate IPs (ClCN, 12.4 eV; BrCN, 11.8 eV; ICN, 10.9 eV). Thus, $[XCNSSS][AsF_6]$ were isolated in yields ranging from 40% (**1(I)**$[AsF_6]$) to 60% ([**1(Cl)**, **1(Br)**]$[AsF_6]$) (Scheme 1).‡

Crystals of [**1(Cl)**, **1(Br)**, **1(I)**]$[AsF_6]$ are isomorphous.§ In contrast to the previous $RCNSSS^{+\bullet}$ derivatives, which do not dimerise, all three radical-cations form centrosymmetric π*–π* dimers *via* weak S···S contacts in the range 3.150(6)–3.167(2) Å at 200 K (Fig. 1). The *trans*-antarafacial mode of association has previously been observed for the well-known $[S_3N_2^{+\bullet}]_2$,[4a,b] the β-phase of *m*-$NCC_6H_4CNSSN^{\bullet}$,[4c] and *m*-$[(S_2N_2C)C_6H_4(CN_2S_2)][Cl]_3$.[4d] Dimerisation does not appear to have an effect on the heterocyclic bond lengths and angles which are similar to those reported previously.[1]

Polycrystalline $[\mathbf{1(Cl)}]_2[AsF_6]_2$ (as a representative example) has a small negative magnetic susceptibility χ at r.t. (Fig. S2, ESI†), and hence could be classed diamagnetic, consistent with the strong π*–π* bonding interaction between radicals. Despite this, solid-state samples have rich EPR spectra at r.t. The X-band powder

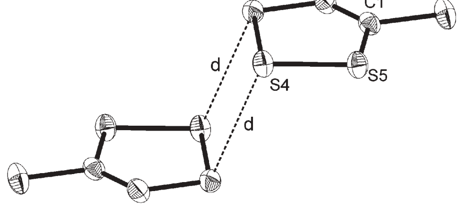


Fig. 1 DIAMOND depiction of the π*–π* dimer $[XCNSSS^{+\bullet}]_2$ (T = 200 K): d = 3.167(2), 3.161(2), 3.150(6) Å for X = Cl, Br, I, respectively.

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† Electronic supplementary information (ESI) available: Experimental details. Fig. S1: Packing diagram of [**1(Cl)**]$[AsF_6]$ with the nearest interdimeric contacts illustrated. Fig. S2: Temperature dependence of magnetic susceptibility of **1(Cl)**AsF_6. Fig. S3: Room-temperature EPR spectra (S- and K-band) of a powdered sample of $[ClCNSSS^{+\bullet}]_2[AsF_6^-]_2$. Fig. S4: Representative EPR spectra of $[\mathbf{1(Cl)}]_2[AsF_6]_2$ at 200, 240 and 290 K. Table S1: Experimental and calculated vibrational frequencies for $\mathbf{1(Cl)}^{+\bullet}$, $\mathbf{1(Br)}^{+\bullet}$ and $\mathbf{1(I)}^{+\bullet}$. Fig. S5: Calculated and solid state (RT) geometries of $[ClCNSSS]_2^{2+}$ and $[HCNSSN]_2$ at MPW1PW91/6-31G* level of theory. Table S2: Compilation of experimental and calculated bond dictances of $[ClCNSSS]_2^{2+}$, $[S_3N_2]_2^{2+}$ and $[HCNSSN]_2$. Table S3: Angular relation between atoms of the dimer and principal axes of *g*-matrix and *D*-tensor. Table S4: Direction cosines between principal axes of *g*-matrix and *D*-tensor. See DOI: 10.1039/b602843h

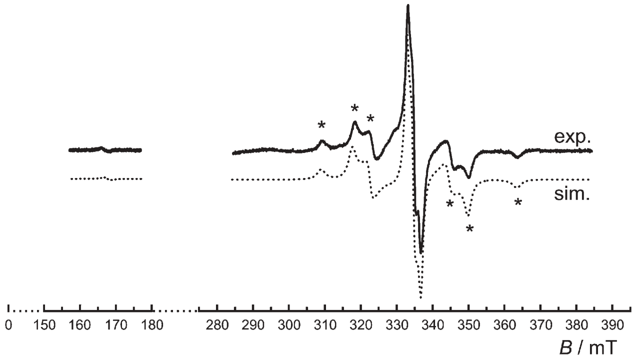

Fig. 2 Room-temperature experimental (solid line) and simulated (doted line) X-band EPR spectra of a powdered sample of $[ClCNSSS^{+\bullet}]_2[AsF_6^-]_2$. *Spin allowed resonances of the spin triplet.

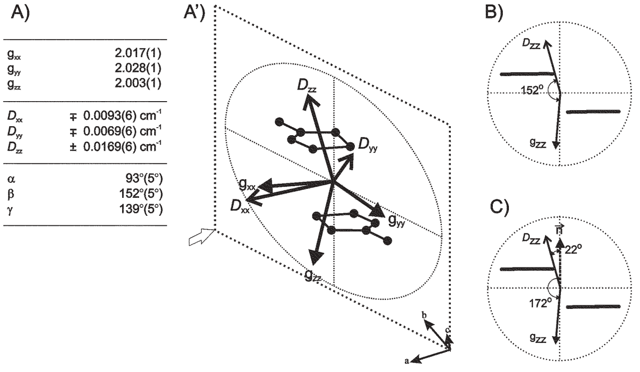

Fig. 3 (A) Principal values of the g-matrix and D-tensor in the triplet state of the dimer. The axis systems are interconverted by the set of Euler angles α, β, γ. (A′) Schematic representation of the principal directions of g and D. (B) and (C) Cross sections depicting the relation between g_{zz} and D_{zz} with each other (B) and with the normal to the plane of the radical (C).

spectra (Fig. 2; S- and K-band spectra are in Fig. S3, ESI†) show features due to two distinct paramagnetic species: (i) a six-line spectrum (spread over *ca.* 55 mT) with a further weak, formally forbidden ($\Delta M_s = \pm 2$) transition at "half-field", characteristic of a rhombic $S = 1$ species, and (ii) a central narrow signal with the appearance of a rhombic $S = ½$ species. Good simulations of these spectra were obtained at all frequencies (Fig. 2 and S3, ESI†) by assuming two independent paramagnetic species ($S = ½$ and 1) with the parameters in Table 1. The relative weighting of the spectral intensities of the two signals (*i.e.* the total double integrals of the EPR transitions from each species) at r.t. was determined by simulation as 1 : 1 with an estimated error of $\pm 10\%$.

The $S = 1$ spectrum must be due to thermal population of the excited state of the $[\mathbf{1(Cl)}]_2^{2+}$ dimer, and the axial zero-field splitting (ZFS) parameter $|D|$ of the triplet is comparable to those observed in organic π-radical ion pairs.[2] Furthermore, single-crystal studies at X-band (Tables S3 and S4, ESI†) reveal that the smallest g-value ($g_{zz} \approx g_e$) of the triplet is near perpendicular to the plane of the radicals in the centrosymmetric dimer, consistent with a π-radical, and that the principal (largest) component of the ZFS (D_{zz}) is approximately along the long S···S inter-monomer bonds (Fig. 3) which suggests that the ZFS is predominantly due to the dipolar interaction between unpaired electrons within the dimer.

The intensity of the $S = 1$ signal decreases rapidly on cooling, as the triplet is depopulated, and disappears below *ca.* 200 K (Fig. S4, ESI†). Fitting this behaviour to the Bleaney–Bowers equation[5] gives the S–T gap for the dimer as $2J = -1900 \pm 100$ cm^{-1}. This large energy gap implies that only 0.03% of the dimers are in the triplet state at 300 K, 99.97% being in the diamagnetic singlet state, consistent with the measured diamagnetic susceptibility.

The $S = ½$ signal is also observed in spectra of single crystals which implies that this species is intrinsic to the sample and not an impurity. Its g-values are identical to those of the dimer and also to those of frozen solutions (SO_2) of $\mathbf{1(Cl)}^{+\bullet}$ (Table 1). These data suggest inherent $S = ½$ defects in the crystal lattice arising from the occasional absence of one half of a radical cation pair. This is also consistent with the observed Curie Law temperature dependence of this signal, as expected for isolated paramagnets. The defect concentration is very low and can be estimated from the approximate 1 : 1 relative intensities *at r.t.* of the triplet and doublet EPR signals (see above). Since only 0.03% of dimers are in the thermally excited triplet state at r.t., the concentration of monomeric $S = ½$ defects must be *ca.* 0.03%. Both the defects and the small fraction of dimers in the triplet state are dilute in an effectively diamagnetic host (dimers in the singlet ground state) at r.t. and hence give sharp solid state EPR spectra.

Table 1 Spin-Hamiltonian parameters of the paramagnetic centres in the EPR spectra of $[\mathbf{1(Cl)}]_2^{2+}$ at room temperature

S		g_{xx}	g_{yy}	g_{zz}	$\|D\|$/cm^{-1}	$\|E\|$/cm^{-1}
½	Powder	2.017(1)	2.026(1)	2.004(1)	n.a.	n.a.
	Frozen solution	2.017(1)	2.027(1)	2.002(1)		
1	Powder	2.018(1)	2.026(1)	2.003(1)	0.0250(6)	0.0012(6)
	Single crystal	2.017(1)	2.028(1)	2.003(1)	0.0255(6)	0.0014(6)

A slight hysteresis is observed in the triplet intensity on heating and cooling (Fig. 4(A)). Thermal hysteresis has been observed in a number of (non-dimeric) thiazyl radicals in the solid state,[6] associated with first-order phase transitions. Single-crystal X-ray structures of $[\mathbf{1(Cl)}]_2[AsF_6]_2$ determined at six different temperatures in the range 168–353 K (Table 2) reveal *no* first order phase-transitions. However there was a very notable shortening of the intra-dimer S···S contacts on cooling, from 3.318(4) Å at 353 K to 3.154(10) Å at 168 K, and a small change in the site occupancy ratios of the disordered AsF_6^- (0.816(18) : 0.183(18) at 353 K to 0.924(6) : 0.076(6) at 168 K), suggesting the hysteresis might be associated with this second-order phase transition. The shortening of the S···S contacts on cooling is consistent with an observed slight increase in $|D|$ (from 0.025 to 0.027 cm^{-1} between 300 and

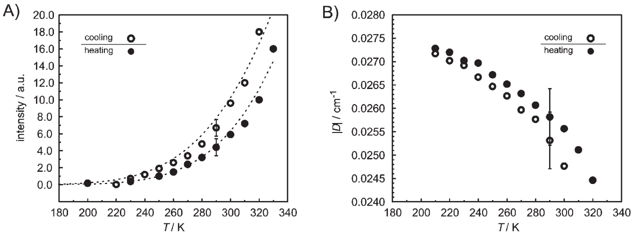

Fig. 4 Temperature dependence of EPR intensity of the triplet spectrum (A) and the magnitude of the triplet ZFS, $|D|$ (B) of a powder sample of $[\mathbf{1(Cl)}]_2[AsF_6]_2$ on a cooling–heating cycle, measured after equilibration times of 30 min at each data point. Experimental errors at r.t. are presented.

Table 2 Temperature dependence of intradimer S···S contacts in $[\mathbf{1(Cl)}]_2^{2+}$ as derived from X-ray crystallography

T/K	168	203	243	293	303	353
S···S/Å	3.154(10)	3.167(2)	3.194(6)	3.249(6)	3.237(6)	3.318(4)

200 K) where *D* is predominantly dipolar in nature. There is also a slight hysteresis in these changes in *D* (Fig. 4(B)).

The dication $[ClCNSSS]_2^{2+}$ is calculated (MPW1PW91/6-31G*) to be 280 kJ mol^{-1} more unstable in the gas phase than two isolated radical cations (note there is a minimum corresponding to a fully optimized structure, Fig. 5). This unfavorable term is only one of the components of the overall lattice enthalpy. Thus the dimerization is *lattice enforced*[7] in the solid state. Our calculations (CASSCF/6-31G*) of the ΔE_{ST} (-2400 cm^{-1}) are in good agreement with the experimental EPR value (-1900 ± 100 cm^{-1}). Calculated ΔE_{ST} values are much higher for the related $[S_3N_2]_2^{2+}$ and $[HCNSSN]_2$ dimers (-3500 and -13000 cm^{-1}, respectively), although thermally accessible triplet states might be observable at higher temperatures.

In summary, by EPR we have detected triplet excited state population in a thiazyl radical dimer for the first time, and have determined the large S–T energy gap. Hence, the usual description of thiazyl radical dimers as "diamagnetic" is clearly inadequate in this case. We have also detected and quantified defect sites in this material by EPR spectroscopy. Neither of these observations are possible by susceptibility techniques. This implies that EPR investigations of the numerous and structurally diverse known S,N-radical dimers with varying inter-radical S···S distances (and thus varying ΔE_{ST}), and related non-metal radical dimers,[8] warrant investigation. Since the S–T gap is proportional to the local dimer dissociation energy, such studies should provide important experimental thermodynamic data towards the understanding of solid-state properties.

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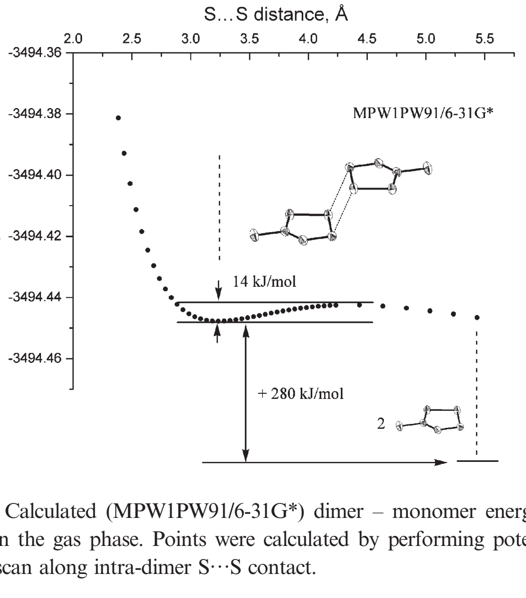

Fig. 5 Calculated (MPW1PW91/6-31G*) dimer – monomer energetics of $\mathbf{1}^{+\bullet}$ in the gas phase. Points were calculated by performing potential energy scan along intra-dimer S···S contact.

Notes and references

‡ ClCN (0.5217 g, 0.008483 mol) in SO_2 (15.36 g) was poured onto a solid (2.3311 g, 0.002045 mol) 1 : 1 mixture of $S_4(AsF_6)_2$ and $S_8(AsF_6)_2$ ("S_3AsF_6") in 6 aliquots during 18 h with stirring. After recrystallizing from SO_2, 1.703 g (60% yield based on sulfur cations) of green crystalline solid $ClCNSSSAsF_6$ was collected in a dry-box.

§ *Crystal data*: for **1(Cl)** at 168 K: $CAsClF_6NS_3$, triclinic, space group $P\bar{1}$, $a = 7.8360(5)$, $b = 9.851(2)$, $c = 6.12(1)$ Å, $\alpha = 95.7(7)$, $\beta = 109.7(5)$, $\gamma = 89.33(8)°$, $V = 442.5(7)$ Å^3, $Z = 2$, 5445 reflections collected, 2595 unique; $R1 = 0.0433$, $wR2 = 0.1179$ refined on F^2. AsF_6^- anions are disordered with the occupancy ratio 0.924(6) : 0.076(6). Crystal data for **1(Cl)** at 353 K: triclinic, space group $P\bar{1}$, $a = 7.964(6)$, $b = 9.900(3)$, $c = 6.147(5)$ Å, $\alpha = 95.32(4)$, $\beta = 109.05(5)$, $\gamma = 88.83(4)°$, $V = 456.1(5)$ Å^3, $Z = 2$, 2858 reflections collected, 2680 unique; $R1 = 0.0398$, $wR2 = 0.1014$ refined on F^2. AsF_6^- anions disordered with occupancy ratio 0.816(18) : 0.183(18). For **1(Br)**: $CAsBrF_6NS_3$, triclinic, space group $P\bar{1}$, $a = 6.1479(4)$, $b = 7.9522(5)$, $c = 9.9240(6)$ Å, $\alpha = 88.7910(10)$, $\beta = 84.4210(10)$, $\gamma = 70.5080(10)°$, $V = 455.17(5)$ Å^3, $T = 198$ K, $Z = 2$, 3186 reflections collected, 1989 unique ($R_{int} = 0.0168$ (1σ)); $R1 = 0.0234$, $wR2 = 0.0640$ refined on F^2. For **1(I)**: $CAsIF_6NS_3$, triclinic, space group $P\bar{1}$, $a = 6.2389(10)$, $b = 8.0343(12)$, $c = 10.1430(16)$ Å, $\alpha = 87.847(2)$, $\beta = 84.629(2)$, $\gamma = 70.804(2)°$, $V = 478.03(13)$ Å^3, $T = 198$ K, $Z = 2$, 2385 reflections collected, 1550 unique ($R_{int} = 0.0235$ (1σ)); $R1 = 0.0566$, $wR2 = 0.1483$ refined on F^2. CCDC 273159–273162. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602843h

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