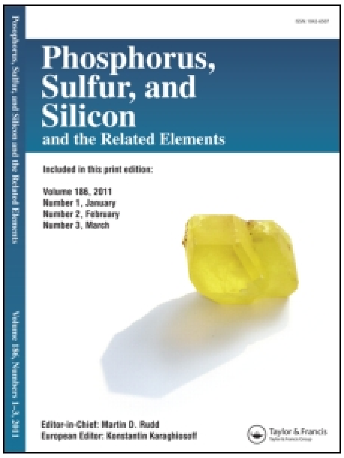

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X-ray Crystal Structure of $(CNSSS)_2(M)_2$ ($M = AsF_6^-, SbF_6^-, Sb_2F_{11}^-$)

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The crystal structures of $(CNSSS)_2(AsF_6)_2$, $(CNSSS)_2(SbF_6)_2$, and two phases of $(CNSSS)_2(Sb_2F_{11})_2$ have been determined. The AsF_6^-, SbF_6^-, and α-$Sb_2F_{11}^-$ salts crystallize as reddish-brown plates whereas the β-$Sb_2F_{11}^-$ salt crystallizes as green rods. The dication $^{\bullet+}SSSNCCNSSS^{+\bullet}$ (1^{2+}) is the same in all four structures and consists of two 7π rings linked by a sp^2-sp^2 C-C bond (1.462 Å in $1(AsF_6)_2$). The packing in the four structures is similar with stacks of dications along the a-axis and alternating sheets of dications and anions lying in the bc-plane. The differences in the dication-dication contacts is reflected in the variable temperature magnetic data.

Keywords: trithiazolium; dication; AsF_6^-; SbF_6^-; $Sb_2F_{11}^-$

INTRODUCTION

Compounds containing unpaired electrons are of interest for their potential as ferromagnetic and/or conductive materials. In order to properly understand these properties it is essential to understand the structures of radicals and multiradicals; how they pack in the solid state and what kinds of interactions are present. By studying the structures of such materials it may even be possible to design and prepare others with specific properties.

The triplet dication 1^{2+} is the only main group diradical other than O_2 to be sterically unhindered from dimerizing and still retain its paramagnetism in the solid state. The magnetic properties of 1^{2+} are unique for a main group radical and they differ significantly as the size of the anion is increased. The characterization, structure and packing of the three salts of 1^{2+} is discussed below where it is shown that the magnetic properties can be explained on the basis of the structure.

The FT-Raman and IR of the three salts of 1^{2+} are mutually exclusive for the absorptions attributed to the dication, consistent with a centrosymmetric geometry. The X-ray structure confirms that the two $CNSSS^{+•}$ rings are joined by a C-C single bond upon which lies a center of symmetry. 1^{2+} has been prepared as the AsF_6^-[1], $Sb_2F_{11}^-$[2] and SbF_6^- (α and β phases)[3] salts; crystallizing as reddish-brown plates in the AsF_6^-, SbF_6^-, and α-$Sb_2F_{11}^-$ salts and as green rods in the β-$Sb_2F_{11}^-$ salt. Elemental analyses indicate that the materials are prepared as pure compounds, the $Sb_2F_6^-$ salt containing small amounts of the $Sb_2F_{11}^-$ salt. The Gouy (all three salts, $\mu_B = 2.81$, 2.72, and 2.80 μ_B for AsF_6^-, SbF_6^-, and $Sb_2F_{11}^-$ salts respectively vs. spin free value of 2.83 μ_B for a triplet) and Evans method (on $1(AsF_6)_2$ in SO_2 / AsF_5, $\mu_B = 2.92$ μ_B at 25°C) magnetic measurements and ESR spectroscopy[2] confirm the triplet state of 1^{2+}. Unlike O_2, variable temperature magnetic measurements[2] indicate that 1^{2+} is actually a ground state singlet with a nearly degenerate, thermally populated triplet excited state. It also exhibits intermolecular antiferromagnetic interactions and a significant temperature independant paramagnetism (TIP).

STRUCTURE AND PACKING OF $1(M)_2$ ($M = AsF_6^-, SbF_6^-, Sb_2F_{11}^-$)

The X-ray structure of 1^{2+} (FIGURE 1) consists of two co-planar centrosymmetric 7π rings joined by a sp^2-sp^2 C-C single bond (see TABLE I vs. 1.462 Å given by [4]).

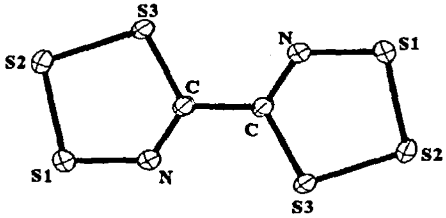

FIGURE 1 X-ray crystal structure of 1^{2+}
(See Colour Plate at back of issue)

The bond distances and angles in 1^{2+} for all four structure are given in TABLE I.

TABLE I Bond distances (Å) and angles (°) in 1^{2+}

Bonds	$1(AsF_6)_2$	$1(SbF_6)_2$	α-$1(Sb_2F_{11})_2$	β-$1(Sb_2F_{11})_2$
C-C	1.462(5)	1.465(9)	1.46(1)	1.46(2)

C-N	1.284(3)	1.279(6)	1.277(8)	1.28(1)
N-S1	1.600(3)	1.600(5)	1.605(5)	1.611(7)
S1-S2	2.070(1)	2.068(2)	2.058(2)	2.071(3)
S2-S3	2.018(1)	2.020(2)	2.012(2)	2.020(3)
S3-C	1.748(3)	1.745(5)	1.748(6)	1.757(8)
Angles				
C-C-N	120.3(2)	120.2(5)	120.1(7)	120.6(9)
C-C-S3	116.6(2)	116.4(5)	116.9(6)	116.8(8)
S3-C-N	123.2(2)	123.3(4)	123.0(5)	122.7(6)
C-N-S1	121.3(2)	121.3(3)	121.3(5)	122.0(6)
N-S1-S2	101.02(9)	101.0(2)	101.1(2)	100.7(3)
S1-S2-S3	97.52(4)	97.42(7)	97.6(1)	97.6(1)
S2-S3-C	96.83(9)	96.8(2)	97.0(2)	97.0(3)

The bond distances and angles are the same within 3σ and are therefore not significantly different.

The packing in all four structures is similar. They consist of alternating sheets of dications and anions in the bc-plane with distinct stacking of the dications along the a-axis (FIGURE 2).

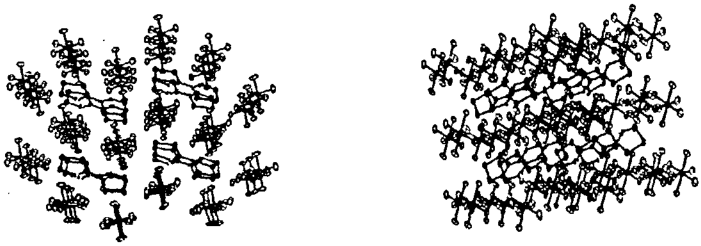

FIGURE 2 Packing in 1$(AsF_6)_2$ (See Colour Plate at back of issue)

The anions are arranged about the dications such that there are no anions situated between dications in either the bc-plane or along the a-axis. This packing allows for unrestricted dication-dication interactions in three dimensions. The dication-dication contact distances for the four structures are given in TABLE II.

TABLE II Dication-dication (S-S) contact distances (Å) in $1(M)_2$ ($M = AsF_6^-$, SbF_6^-, $Sb_2F_{11}^-$)

	Between Planes (bc-plane)	In-Plane (bc-plane)
$1(AsF_6)_2$	4.33 Å	4.08 Å
$1(SbF_6)_2$	4.28 Å	4.33 Å
α-$1(Sb_2F_{11})_2$	5.52 Å	4.37 Å
β-$1(Sb_2F_{11})_2$	5.67 Å	5.03 Å

The the antiferromagnetic intermolecular magnetic interactions observed in 1^{2+} as determined by variable temperature magnetic measurements[3] differ significantly with different anions. This is due to an increase in the length of dication-dication contacts as the size of the anion is increased. The dication-dication contacts in α-$1(Sb_2F_{11})_2$ are shorter than those in β-$1(Sb_2F_{11})_2$. This is due to the fact that the dications in the β structure are alligned in chains while the dications in the α structure are staggered allowing the dications in the latter to be closer to one-another. Variable temperature magnetic measurements on the α structure should reflect this.

CONCLUSION

The four structures of the salts of 1^{2+} consist of alternating stacks of dications and anions lying in the bc-plane and discrete stacks of dications along the a-axis without anions interposed between dications along any of the three crystallographic axes. This packing allows for unrestricted three dimensional intermolecular dication-dication interactions and this is reflected by the strong intermolecular antiferromagnetic interactions.

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