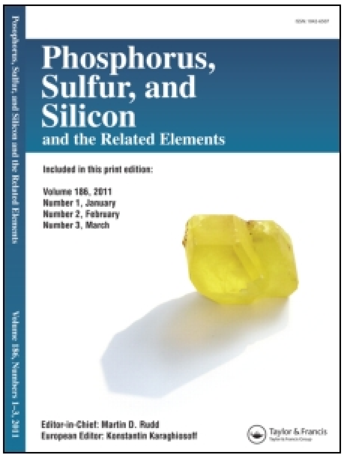

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A New Type of Dithiadiaziolylium Salt:

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A NEW TYPE OF DITHIADIAZIOLYLIUM SALT: $[p\text{Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]_6\text{Cl}_2$.

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Abstract The title salt has been characterised by x-ray crystallography which shows that the chloride anions hold the dithiadiazolyl/ium rings in an unusual structural array.

INTRODUCTION

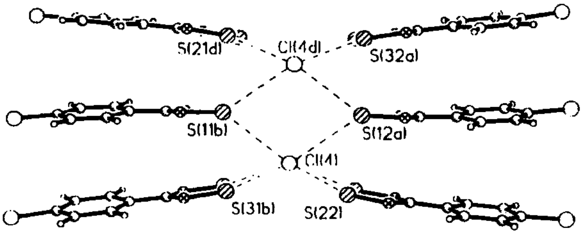
Ring systems based on the p-block elements have attracted considerable interest recently in the search for materials possessing unusual magnetic/electrical properties [1]. The 7π heterocyclic dithiadiazolyl radical, $[\text{R-}\overline{\text{CNSSN}}]$, is one such system since changes in the R functionality significantly affect the degree of association of the radical at room temperature. In order to improve our understanding of the electronic and geometric factors which affect these systems in the solid state, we have undertaken a crystallographic study of compounds containing the 1,2,3,5-dithiadiazolyl/ium ring. These have included $[\text{p-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]\text{Cl}$, $[\text{p-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]_2$, and the previously unknown $[\text{p-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]_6\text{Cl}_2$.

RESULTS

Compound (I), $[\text{p-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]\text{Cl}$, crystallises in the space-group $P2_1/m$ [2]. The chloride anion is held in a 3-centre 2-electron triangular S...Cl...S arrangement with the associated cation and there are "chain" Cl..S–S...Cl...S–S...Cl interactions with neighbouring cations, leading to a layer lattice remarkably similar to that seen for 4-phenyl-1,2-dithiolium chloride monohydrate [3].

Compound (II), $[\text{p-Cl.C}_6\text{H}_4.\overline{\text{CNSSN}}]_2$, crystallises in the space group C2/c [4] with the radical species being dimerised in the usual manner in the solid state through S...S interactions perpendicular to the plane of the heterocyclic ring. There are also significant S...N and S...Cl interactions between dimer units.

Compound (III), $[p\text{-}Cl.C_6H_4.\overline{CNSSN}]_6Cl_2$, is of a new structural type; it crystallises in the $P\bar{1}$ space group [2]. The molecule contains two stacks of three dithiadiazolyl/ium units linked by S...Cl interactions with two chloride anions (see Figure below). The anions are arranged so as to maximise the number of S...Cl contacts present. The stacks are held together by S...S interactions perpendicular to the rings, in a similar fashion to compound (II).



DISCUSSION

The length of the S-S bond can give useful information about the electronic environment of the $[\overline{CNSSN}]$ ring [5]. This is because the LUMO possesses anti-bonding character along the S-S bond; placing an electron in the LUMO (to form the 7π radical species) leads to an increase in the length of the S-S bond. This is confirmed by the structures outlined above; the S-S distances (Å) are 2.007(3) for (I), 2.085(2) and 2.091(2) for (II). For (III) they are 2.064(4), 2.066(4) and 2.079(4)Å. Since the S-S bond lengths for (III) are the same within experimental error the structure can be said to contain segregated stacks of three $[\overline{CNSSN}]$ rings in an very similar electronic environment. This is in marked contrast to $[CF_3\overline{CNSSN}]_3Cl$, which contains the chloride salt co-crystallised with the radical [6]. Thus, (III) is the first mono-substituted dithiadiazolyl/ium system containing $[\overline{CNSSN}]$ rings with a charge intermediate between the 6π cation and the 7π radical species.

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