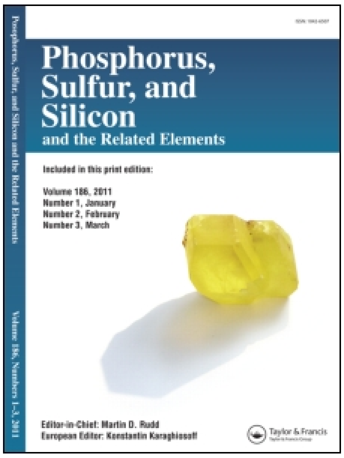
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Recent Advances in the Synthesis and Characterisation of the O_2-Like Paramagnetic Solid $(M)_2$ [M = $AsF_6$$^{(1)}$, Sb_2F_{11}] Containing the Diradical

Paul D. Boyle[a]; Jack Passmore[a]; Dale J. Wood[a]
[a] Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick

To cite this Article Boyle, Paul D. , Passmore, Jack and Wood, Dale J.(1994) 'Recent Advances in the Synthesis and Characterisation of the O_2-Like Paramagnetic Solid $(M)_2$ [M = $AsF_6$$^{(1)}$, Sb_2F_{11}] Containing the Diradical ', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 227 — 230

To link to this Article: DOI: 10.1080/10426509408021822

URL: http://dx.doi.org/10.1080/10426509408021822

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93-94, pp. 227–230
Reprints available directly from the publisher
Photocopying permitted by license only

© 1994 OPA (Overseas Publishers Association) Amsterdam B. V.
Published under license by Gordon and Breach Science Publishers SA
Printed in the United States of America

Downloaded At: 11:27 29 January 2011

RECENT ADVANCES IN THE SYNTHESIS AND CHARACTERISATION OF THE O_2-LIKE PARAMAGNETIC SOLID $\mathrm{SSSNCCNSSS(M)_2[M{=}AsF_6^{(1)}, Sb_2F_{11}]}$ CONTAINING THE DIRADICAL $\mathrm{^{\cdot+}SSSNCCNSSS^{+\cdot}}$.

Paul D. Boyle, Jack Passmore, Dale J. Wood
Department of Chemistry, University of New Brunswick,
Fredericton, New Brunswick E3B 6E2

Abstract. The AsF_6^- and $Sb_2F_{11}^-$ salts of $\mathrm{^{\cdot+}SSSNCCNSSS^{+\cdot}}$(1), prepared by the reaction of $S_8(AsF_6)$, $S_4(AsF_6)$, and $(CN)_2$ in liquid SO_2 and (1)$(AsF)_2$ and an excess of antimony pentafluoride in liquid SO_2 respectively, is the only known sterically unhindered non-metal triplet state species other than dioxygen, that contains two unpaired electrons in the solid state ($\mu=2.6\ \mu_B$ both salts) at room temperature.

We have been able to essentially quantitatively prepare various stable radicals by the reaction of SNS^+ ($SNSAsF_6$) with C-C and C-N containing molecules followed by reduction of the cationic cycloadduct. These include the *paramagnetic liquids* $F_3CCSNSCCF_3^{\cdot}$ and $Bu^tCNSNS^{\cdot}$ that as pure isolated materials are paramagnetic, but become diamagnetic in the solid state.[2] More recently we have prepared the *paramagnetic solids* $F_3CCSSSCCF_3AsF_6$ and $CF_3CNSSSAsF_6$ containing radical cations that are paramagnetic in all states, by the reaction of "S_3^+" (a mixture of $S_8(AsF_6)$ and $S_4(AsF_6)$) with F_3CCCCF_3 and CF_3CN respectively. Stable sterically unhindered compounds that contain two unpaired electrons are even less common than stable sterically unhindered radicals. However SNS^+ undergoes a double cycloaddition with $(CN)_2$ to give $\overline{SNSNC}\overline{CNSNS}^{2+}$ quantitatively, which on reduction gives $\overline{SNSNC}\overline{CNSNS}^{\cdot\cdot}$ in high yield[3]. Surprisingly the analagous reaction of $(CN)_2$ with "S_3^{+}" in liquid SO_2 gave (1) according to equation 1. Reaction of $(1)(AsF_6)_2$ with SbF_5 in liquid SO_2 lead to $(1)(Sb_2F_{11})_2$ (equation 2).

$$S_4(AsF_6)_2+S_8(AsF_6)_2+2(CN)_2 \longrightarrow 2(\overline{CNSSS})_2(AsF_6)_2 \quad (1)$$

$$(\overline{CNSSS})_2(AsF_6)_2+4SbF_5 \longrightarrow (\overline{CNSSS})_2(Sb_2F_{11})_2+2AsF_5 \quad (2)$$

The arsenic salt is dark brown and the antimony salt green although both had elemental analyses that were in excellent agreement with the given formulations. The structure of the cations are identical in both salts and are shown in fig 1.

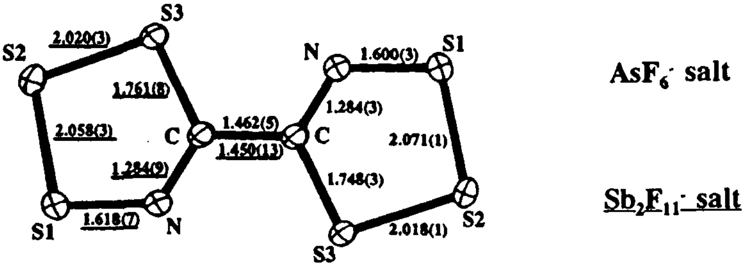


FIGURE 1. Structure of (1)

The cations lie in stacks down the a-axis and sheets in the bc plane with no cation-cation interaction. The coordination numbers of cation and anion fit with those calculated by the radius ratio rules. The structure of (1)

Downloaded At: 11:27 29 January 2011

Downloaded At: 11:27 29 January 2011

is planar with a centre of symmetry on the C-C bond. Consistent with the structure, the IR and FT-Raman spectra of the cations of both salts obey the mutual exclusion rule. The C-C bond length of 1.46 Å is consistent with an sp^2-sp^2 hybridized C-C single bond. The magnetic moment of (1), determined by the Guoy method, is 2.6 μ_B in the solid state consistent with the presence of two unpaired electrons. On the basis of bond energy estimates, the diamagnetic quinoidal form of (1) ((2) shown in fig 2) is slightly less stable by a small amount plus the energy needed to localise the positive charge on the sulfur atoms. Thus the two unpaired electrons in (1) like in O_2 do not pair up, either by intra- or inter-molecular interactions.

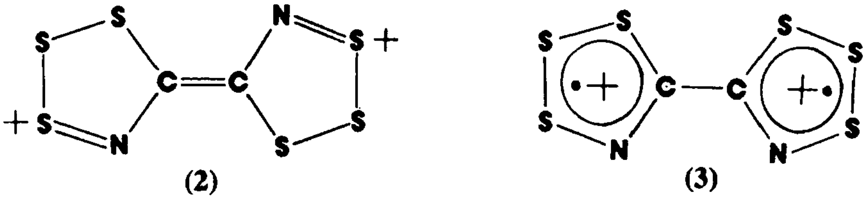


FIGURE 2. Quinoidal geometry (2) and 135° rotomer (3)

The esr of (1) in a frozen matrix of SO_2 at -175°C shows signals corresponding to both the Δm_s = +/- 1 transition (H = 3254.7 G, g = 2.0186) and Δm_s = +/- 2 transition (H = 1612.7 G, g = 4.0738). This shows unambiguously that (1) like oxygen is a triplet state species. The similarities are furthur supported by a comparison of the relative energies of the their first and second excited states with respect to their ground states shown in fig 3. The values for O_2 are experimental and those for (1) are ROHF/STO-3G energy calculations on UHF/MNDO optimized geometries.

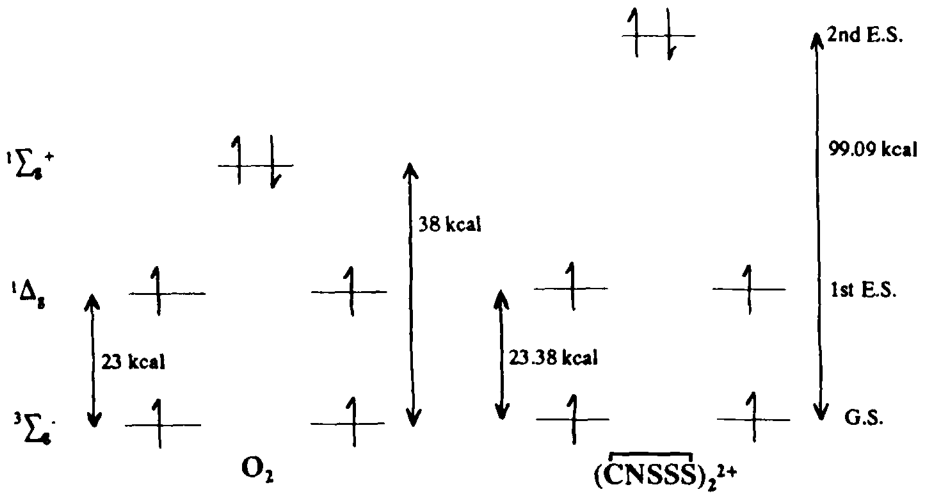


FIGURE 3. Electronic states of O_2 and $(\overline{CNSSS})_2^{2+}$

The difference in colour of the two salts was puzzling (ie. AsF_6^- salt dark brown, $Sb_2F_{11}^-$ salt green, both dissolving to give green solutions). The antimony salt gave a temperature dependent esr spectrum that showed the presence of two radicals, the broad peak decreasing in intensity as the temperature was lowered. The energy of (1) was calculated (ROHF/STO-3G) as the rings were rotated about the C-C bond, showing the presence of a rotational isomer in a shallow potential energy well only 29.8 kJ/mol higher in energy than the trans planar form. We hypothesize that this rotomer (3) exists in equilibrium with (1) in solution and in small amounts in the solid antimony salt and may be the source of the green colour and the broad peak in the esr spectrum.

REFERENCES

1. P.D. Boyle, S. Parsons, J. Passmore and D.J. Wood; J. Chem. Soc., Chem. Commun., 199 (1993).
2. S. Parsons and J. Passmore, Acc. Chem. Res., 27(4), 101 (1994).
3. S. Parsons, J. Passmore and P.S. White; J. Chem. Soc., Dalton Trans.; 1499 (1993).
S. Brownridge, poster at 7th Inorganic Ring Systems (IRIS) Conference (1994)

Downloaded At: 11:27 29 January 2011