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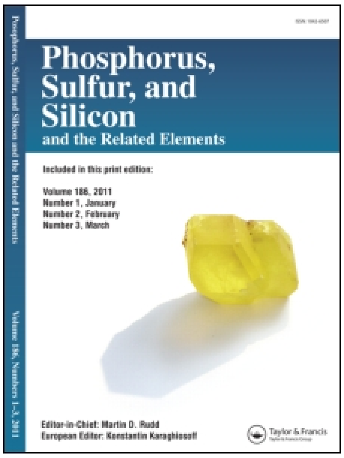

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
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To cite this Article Feeder, Neil , Less, Robert J. , Rawson, Jeremy M. , Palacio, Fernando , Novoa, Juan and Oliete, Patricia(2001) 'Structures of Novel Diselenadiazolyls', Phosphorus, Sulfur, and Silicon and the Related Elements, 169: 1, 43 — 46

To link to this Article: DOI: 10.1080/10426500108546586

URL: http://dx.doi.org/10.1080/10426500108546586

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Phosphorus, Sulfur and Silicon, 2001, Vol. 169, pp. 43–46
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Structures of Novel Diselenadiazolyls

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A series of fluorinated diselenadiazolyls (p-$XC_6F_4CNSeSeN$, X = NC, F, Cl, Br) have been synthesised and show an unusual mode of association (X = Cl, Br) in the solid state which has been investigated by Density Functional Theory. Their magnetic behaviour has also been investigated and have been shown to be essentially diamagnetic.

Keywords: diselenadiazolyl; density functional theory; magnetism; platinum; palladium; complexes; disproportionation; abstraction

INTRODUCTION

Recently, our group has synthesised a number of organic magnets based on the dithiadiazolyl ring system (p-XC_6F_4CNSSN, X = NC, O_2N, Br).[1] As a natural extension of this work, we have prepared a series of fluorinated diselenadiazolys[2] (p-$XC_6F_4CNSeSeN$, X = NC **1**, F **2**, Cl **3**, Br **4**) in the anticipation that similar or improved magnetic properties would be obtained.

RESULTS

Synthesis

Radicals **1**, **2**, **3** and **4** were all prepared using a one-pot procedure based on a variation of the literature method.[3] Crystals suitable for X-Ray diffraction were all grown by vacuum sublimation in sealed glass tubes.

Solid-State Structures

The radicals **1** and **2** associate as closed-shell, diamagnetic, cofacial dimers in the solid state. **3** and **4** associate in a novel manner where the N_2Se_2 portion of one ring interacts with the Se_2 portion of the next (FIGURE 1).

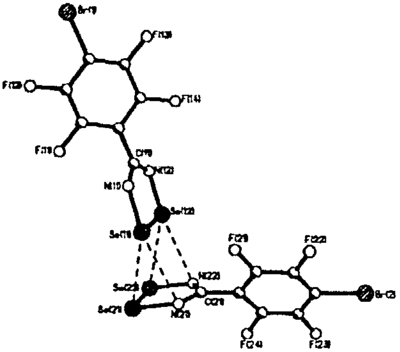

FIGURE 1. Crystal structure of 4.

Theoretical Studies

Density Functional Theory calculations show that the ground-state electronic configuration is an open-shell singlet. The difference between open shell singlet and triplet states gives a value for the magnetic exchange interaction, J, as 3779 cm^{-1} (~45 $kJ.mol^{-1}$).

Magnetic Studies

Susceptibility measurements as a function of temperature and the magnetisation behaviour as a feature of applied field were measured at 1.8 and 3K.

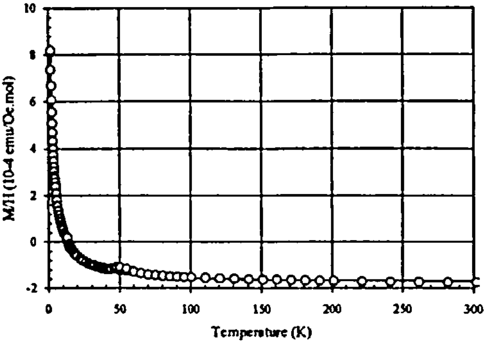

FIGURE 2. Magnetic susceptibility as a function of temperature of 4. The solid line is the fit of the Curie-Weiss law and a diamagnetic contribution.

Magnetic data clearly indicate that both 3 and 4 are essentially diamagnetic. The magnitude of the exchange interaction ($J = -3779\ cm^{-1}$) indicates that the open-shell singlet-triplet separation is so large that the triplet state is not significantly populated even at room temperature

Discussion

It is clearly evident from the structures of 1 and 4 that fluorinated diselenadiazolyls are not isostructural with the corresponding dithiadiazolyls and monomeric radicals are not obtained. Instead the higher dimerisation enthalpy of diselenadiazolyls compared to dithiadiazolyls favours association in the solid-state and consequently the formation of diamagnetic materials.

Conclusion

Structures of fluorinated diselenadiazolys (p-$XC_6F_4CNSeSeN$, X = NC, F, Cl, Br) are reported where chloro and bromo derivatives show a novel mode of association. All materials, however are diamagnetic.

ACKNOWLEDGEMENTS

We would like to thank the EPSRC for a studentship (RJL), CICYT (Grant. No. MAT97-0951) for financial support (FP).

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