



Deposited via The University of Sheffield.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/142144/>

Version: Submitted Version

Proceedings Paper:

Portius, P., Crozier, B., James, L. et al. (2016) Nitrogen-rich complexes of p-block elements : highly endothermic polytetrazolates and polyazides. In: Abstracts of Papers of the American Chemical Society. 252nd ACS National Meeting & Exposition, 21-25 Aug 2016, Philadelphia, PA, USA. ACS Publications. ISSN: 0065-7727.

© 2016 The American Chemical Society. This is an author-produced abstract subsequently published in Abstracts of Papers of the ACS. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

Nitrogen-rich complexes of *p*-block elements: Highly endothermic polytetrazolates and polyazides

R. Campbell, B. F. Crozier, L. James, Z. Smallwood, P. Portius

Department of Chemistry, The University of Sheffield, Brook Hill, S3 7HF, UK;

p.portius@sheffield.ac.uk

Our aim is to stabilise and control the reactivity of N-rich coordination compounds. Upon decomposition, N-rich compounds generate mainly N₂ - ideal for smokeless, CO₂-free, “green” energetic materials as replacement for conventional propellants, explosives & pyrotechnics.¹ Low barriers toward decomposition pose major challenges in their preparation and characterisation. Here we discuss E(Y)_n complexes with E = group 13, 14 or 15 coordination centre in low or high oxidation state, Y = N-rich ligand, n = 2-6. We apply synthetic methods novel to energetic chemistry, which involves a combination of hypercoordination, bulky counterions, and ligand exchanges, to achieve the synthesis and isolation of new classes of complexes as candidates for efficient & controllable energy storage.⁴ These include Lewis base adducts,^{3,6} homoleptic azido complexes,^{2,5} covalent, binary azides E(N₃)_n,³ the first homoleptic *p*-block element tetrazolates E(T)₆²⁻ and E(T)₃⁻ (E = Si - Sn, T = N₄CH, Fig. 1). These complexes have a unique chemistry – reactions with nitriles and phosphines afford unusual *poly*(tetrazolato) and *poly*(phosphiniminato) complexes. Syntheses, reactivity, structures, and thermal and spectroscopic properties of the new species, including the application of fast time-resolved IR spectroscopy to study photoreactivity, will be described.

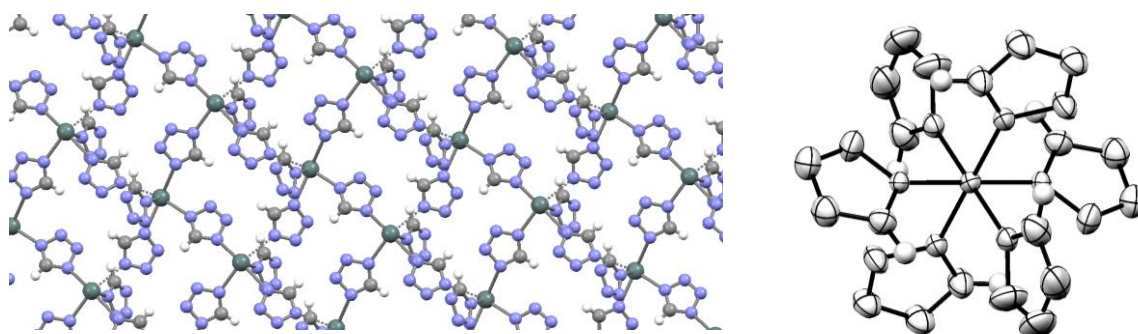


Figure 1 Tetrazole-based N-rich coordination networks and complexes: left {Sn(CHN₄)₃}⁻_∞ (blue N, turquoise Sn, white H), right [Si(κ-N(1)-N₄CH)₆]²⁻ (thermal ellipsoid plot, 50%).

1) G. Steinhauser, T. M. Klapoetke *Angew. Chem.* **2008**, *47*, 3330; 2) P. Portius, P. W. Fowler et al. *Inorg. Chem.* **2008**, *47*, 12004; 3) P. Portius, A. C. Filippou et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 8013; 4) M. Davis, P. Portius *Coord. Chem. Rev.* **2013**, *257*, 1011; 5) B. Peerless, T. Keane et al. *Chem. Commun.* **2015**, *51*, 7435; 6) R. M. Campbell, M. Davis, M. Fazakerley, P. Portius *Chemistry-Eur. J.* **2015**, *21*, 16898.