



This is a repository copy of *Nitrogen-rich complexes of p-block elements : highly endothermic polytetrazolates and polyazides.*

White Rose Research Online URL for this paper:  
<http://eprints.whiterose.ac.uk/142144/>

Version: Submitted Version

---

**Proceedings Paper:**

Portius, P. [orcid.org/0000-0001-8133-8860](https://orcid.org/0000-0001-8133-8860), Crozier, B., James, L. et al. (2 more authors) (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 .

---

© 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](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.



[eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk)  
<https://eprints.whiterose.ac.uk/>

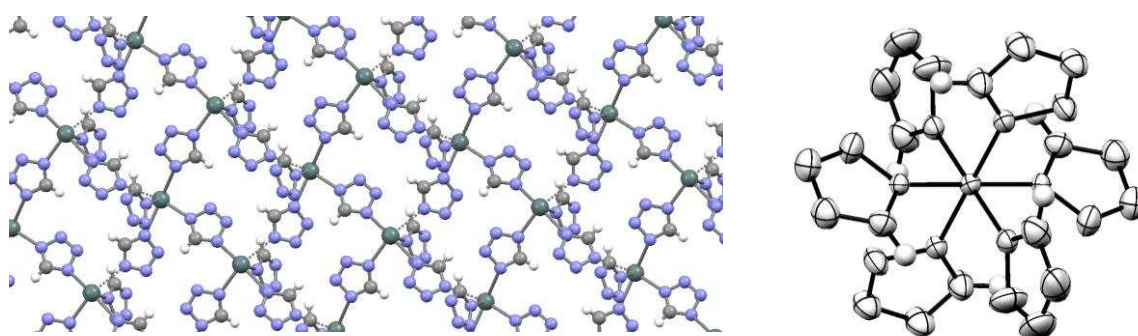
## Nitrogen-rich complexes of p-block elements: Highly endothermic polytetrazolates and polyazides

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  $N_2$  - ideal for smokeless,  $CO_2$ -free, “green” energetic materials as replacement for conventional propellants, explosives & pyrotechnics.<sup>1</sup> 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.<sup>4</sup> These include Lewis base adducts,<sup>3,6</sup> homoleptic azido complexes,<sup>2,5</sup> covalent, binary azides  $E(N_3)_n$ ,<sup>3</sup> the first homoleptic p-block element tetrazolates  $E(T)_6^{2-}$  and  $E(T)_3^-$  ( $E$  = Si - Sn,  $T$  =  $N_4CH$ , 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  $\{Sn(CHN_4)_3\}^-_\infty$  (blue N, turquoise Sn, white H), right  $[Si(\kappa-N(1)-N_4CH)_6]^{2-}$  (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.