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

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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.[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 $E(N_3)_n$,[3] 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.

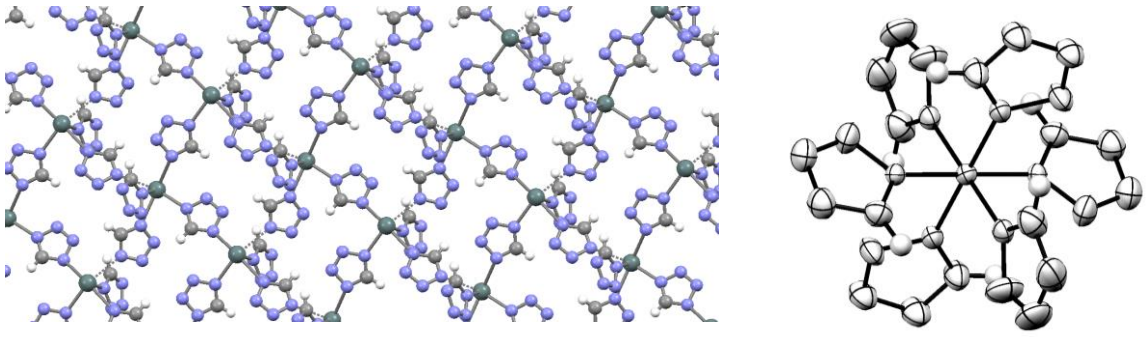

Figure 1 Tetrazole-based N-rich coordination networks and complexes: left $\{Sn(CHN_4)_3^-\}_\infty$ (blue N, turquois Sn, white H), right $[Si(\kappa\text{-}N(1)\text{-}N_4CH)_6]^{2-}$(thermal ellipsoid plot, 50%).

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.