

Nickel macrocycles with complex hydrides—new avenues for hydrogen storage research†‡

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As part of an investigation into Ni(macrocycle) complexes as a new class of complex hydride hydrogen store catalysts, two isomers of the unusually stable nickel borohydride, Ni(cyclam)(BH₄)₂ (cyclam = 1,4,8,11-tetraazacyclotetradecane), have been isolated and characterised by means of single crystal X-ray diffraction, infrared spectroscopy, thermogravimetry and calorimetry. *trans*-Ni(cyclam)(BH₄)₂ crystallizes monoclinic (*P*2₁/*c*, *a* = 7.1397(5) Å, *b* = 12.8109(7) Å, *c* = 8.7041(5) Å, β = 109.948(6)°, *V* = 748.36(8) Å³, *Z* = 2); *cis*-Ni(cyclam)(BH₄)₂ crystallizes orthorhombic (*Pnma*, *a* = 14.4512(7) Å, *b* = 9.4625(6) Å, *c* = 11.7824(7) Å, *V* = 1611.18(16) Å³, *Z* = 4, with static disorder). The compounds were found to be considerably more thermally stable than the unchelated relative, Ni(BH₄)₂, with the onset of decomposition for the *trans* isomer at 170 °C, thus nearly 200 °C higher than the decomposition temperature of Ni(BH₄)₂. This spectacular stabilisation holds promise for related macrocycle complexes of late transition metals to be used as hydrogenation catalysts on an equal footing with their unligated early transition metal counterparts.

Introduction

A key barrier to the widespread adoption of hydrogen as an energy carrier is the problem of how to store it efficiently. Storage materials that chemically bind the hydrogen, and one type in particular, the complex hydrides, are highly worthy of investigation

as they offer high volumetric capacity and the lighter members also provide a reasonable gravimetric range.

Though many complex hydrides will evolve hydrogen by simple reaction with water, this causes problems for refuelling the store (effectively requiring off-site regeneration which is expensive and often impractical¹). Rather, heating the hydrogen store to release its hydrogen with an entropic driving force is the preferred method and the one which, if the thermodynamics are nicely balanced, allows reversible re-fuelling via lower-temperature, higher-pressure enthalpic stabilisation.² However, the thermal decomposition (hydrogen evolving) temperature (*T*_{dec}) of the most attractive stores is too high for efficient use with a polymer–electrolyte fuel cell, which requires a *T*_{dec} range of about 60–90 °C to enable the use of waste heat from the fuel cell. The refuelling (hydrogenation) temperatures and pressures are also too high.

Where the problem lies in the kinetics rather than the thermodynamics, catalysts may present a solution, and much work has been done on developing suitable candidates. After Bogdanović and Schwickardi's breakthrough,³ considerable attention turned to Ti,⁴ but many other transition metals have also been investigated.⁵ The platinum group metals find abundant

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† Electronic supplementary information (ESI) available: Additional experimental information, detailed crystal refinement data, further analysis of FTIR spectroscopy, Raman spectroscopy, further analysis of TGA/DSC data including evolved gas analysis, milling of Ni(cyclam)(BH₄)₂ with NaBH₄, particle size effects and DFT calculations. CCDC reference numbers 773705 and 773706. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ee00051e

‡ This work is dedicated to Professor Bogdan Baranowski and commemorates the first synthesis of nickel hydride half a century ago.

Broader context

If the West is to wean itself off fossil fuel dependency and towards renewable sources, a suitable vector to transport the energy from the place of production to place of use is required. Hydrogen is a much-touted candidate for such a carrier but despite considerable investment in research significant barriers are still to be overcome, not least that of hydrogen storage. Releasing the potential of the thermodynamically favourable but kinetically slow complex hydride hydrogen stores is a valuable goal. Catalysis of such stores has been heavily investigated, but we present here the early results of a different approach, using the flexibility of the transition metals and the multitude of ligands to which they may be connected to design a suitable catalyst. We have used a macrocycle complex to tune the properties of a nickel(II) centre such that it may remain intact in the highly reducing atmosphere of a hydrogen store and bind borohydride ligands, while showing an enhanced thermal stability to 170 °C.

applications as hydrogenation catalysts in other areas of chemistry, but Pd and Pt present considerable practical problems in terms of cost and availability. Ni, however, is cheap, abundant, and lighter than Pd or Pt and seems worthy of further investigation.

Unfortunately, the hydride connections of nickel are much less stable than their Pd and Pt siblings. For example, binary nickel hydride of the form NiH_x ($0.1 \leq x \leq 0.2$) is thermodynamically unstable under ambient (p , T) conditions, establishing an equilibrium pressure with H_2 of approximately 3400 atm.⁷ Similarly, $\text{Ni}(\text{BH}_4)_2$ decomposes at temperatures below -20°C ⁸ and $\text{Ni}(\text{AlH}_4)_2$ below -125°C ,⁹ preventing their use directly as doping agents (which is perhaps of little consequence, as both compounds must be thermodynamically unstable at ambient conditions, disqualifying them from use as catalysts on a purely thermodynamic basis, *cf.* Fig. 1).

Recently, Ni nano-particles were found to reduce the decomposition temperature of $\text{LiMn}(\text{BH}_4)_3$, but do not perform well with hydrogenation/dehydrogenation cycling,¹⁰ and Ni nano-particles (~ 20 nm diameter) were also found to be significantly better dehydrogenation catalysts for LiAlH_4 than Ni micro-particles (~ 0.8 μm diameter).¹¹ Simple nickel(II) salts such as NiCl_2 have also been found to reduce T_{dec} of LiAlH_4 ,¹² with the most effective system being that with the smallest and most dispersed NiCl_2 particles; the size and distribution of the initial dopant are therefore important, as would be expected in solid reactions where mass-transport is likely to be a rate-limiting factor. However, the true nature of the catalyst is unclear since ionic nickel(II) salts are easily reduced to metallic nickel(0).

These results confirm that Ni and its derivatives may indeed catalyse hydrogenation reactions, albeit with neither mechanism nor role of different oxidation states known. But they also point to the main disadvantage of these systems: the limited options for improving them beyond their inherent level.

Rather than using bald nickel or its simple salts, we have chosen to investigate Ni complexes due to the considerable advantages afforded by the ability to tune the properties of the metal centre by choice of ligand type and geometry. In particular we are investigating Ni coordinated to macrocycles as these ligands provide greater stability to the complex relative to

separate monodentate groups and even open-chain polydentate ligands, thanks to the macrocyclic effect.¹³ In addition, these bulky complexes typically form molecular rather than ionic or covalent crystals, that is, the bonding between molecular entities in the crystal is relatively weak compared to the bonding within each molecule (complex). These molecular crystals should more readily break-up and disperse under mechanical stress during milling, reducing the milling time required.

Recently two groups have published structures of Ni-borohydride complexes, one involving a tri-dentate BH_4^- group and a chelating, tridentate N-donor ligand, hydrotris(3,5-dimethylpyrazolyl)borate,¹⁴ and the second a dinuclear, hexaaza-dithiophenolate macrocycle complex,¹⁵ where the BH_4^- group bridges the two Ni atoms. These studies, documenting two complexes quite different from those described here, emphasise the abundant possibilities for designing transition metal borohydride complexes.

Regarding the desired catalytic role, it doesn't seem unreasonable (though recognising this as speculation in the absence of a definite mechanism) that when either discharging or recharging the hydridic hydrogen store the reaction pathway will at some point involve a higher oxidation state of nickel bound to a hydride.¹⁶ Stabilisation of the Ni^{II} hydride derivative will require donation of additional electron density to the metal centre. As such we decided to make our first attempt with the well-known tetra-aza macrocycle, cyclam (1,4,8,11-tetraazacyclotetradecane, $\text{C}_{10}\text{H}_{24}\text{N}_4$). This ligand is commercially available and readily forms strongly bound complexes with Ni^{II} species,¹⁷ coordinating through all four secondary amine groups, with a cavity size very well suited to Ni^{II} .

The mass of the $\text{Ni}(\text{cyclam})(\text{BH}_4)_2$ complex, weighing in at 289 g mol^{-1} , must also be considered. If we take a hypothetical storage material capable of reversibly storing 10% hydrogen by mass but showing poor kinetics, the revised DOE ultimate targets¹⁸ (7.5% by weight) would still allow $\frac{1}{4}$ of the store by mass to be catalyst. This would require each catalytic centre to 'process' around 40–50 molecules of H_2 in each cycle. Whilst not underestimating the challenges of mass transport in solids, we do not think this is unreasonable.

Here we present the details of two remarkably stable isomers of a borohydride complex of $\text{Ni}^{\text{II}}(\text{cyclam})$, which are of particular interest for hydrogenation catalysis due to the presence of a Ni^{II} centre susceptible to reduction. Stolzenberg and Zhang have previously reported one of the syntheses we give here and its suspected result,¹⁹ but were not able to give a crystal structure of their product as we do. In addition, we present the findings of our investigation into the thermal decomposition profile of both $\text{Ni}^{\text{II}}(\text{cyclam})(\text{BH}_4)_2$ isomers and show that the thermal stability of $\text{Ni}(\text{BH}_4)_2$ is significantly enhanced *via* ligation of a macrocyclic ligand. Finally, we discuss the potential for macrocycle complexes of Ni and other late transition metals to form useful catalysts for complex hydride hydrogen stores.

Experimental

Unless otherwise noted, all operations were carried out in a glovebox in an argon atmosphere with typical working values of $\text{O}_2 < 0.1$ ppm and $\text{H}_2\text{O} < 1$ ppm. Reagents were used as received and

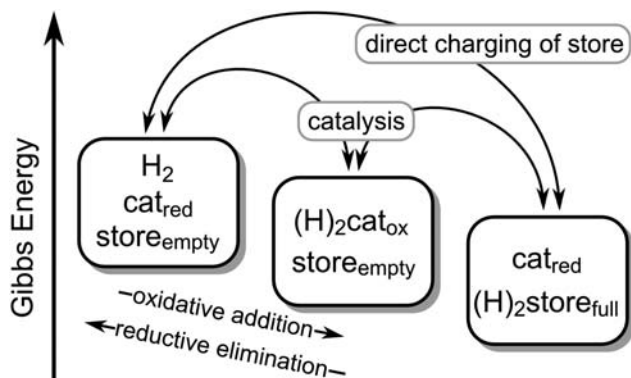


Fig. 1 Relationship between the thermodynamic stabilities of a hydrogen store (store) and a potential hydrogenation catalyst (cat) during charging and discharging with hydrogen (H_2). Modified after ref. 6.

not further purified, except dehydration of solvents where stated. Considerable additional information may be found in the ESI†.

Reactions of [Ni(cyclam)L_x] with LiBH₄

Typically, approximately 80 mg of Ni(cyclam)L_x (L_x = SO₄, (ClO₄)₂ or (BF₄)₂) were reacted with approximately 2 ml of 0.1 M LiBH₄ in tetrahydrofuran (THF, from a 2 M solution (Aldrich) diluted with THF (Aldrich) distilled over Na), the solid–liquid reaction mixture being ground in an agate mortar to ensure complete reaction. The resulting solid (*trans*-Ni(cyclam)(BH₄)₂) was separated and washed with dry THF. If FTIR analysis showed any remaining solvent the product was heated for 1 hour at 150 °C to drive off solvent residue.

The reaction of any of the precursors with LiBH₄ was found to be the easiest synthetic route to *trans*-Ni(cyclam)(BH₄)₂. Alternative reaction pathways are described in the ESI†. Deuterated BD₄[−] analogues were prepared from such an alternative pathway using NaBD₄ with a typical isotopic purity of 95%.

Attention! Use of perchlorate complexes of Ni(II) in this synthetic procedure is discouraged due to risk of explosion.

Conversion of *trans*-Ni(cyclam)(BH₄)₂ to *cis*-Ni(cyclam)(BH₄)₂

cis-Ni(cyclam)(BH₄)₂ readily forms during synthesis of the *trans* isomer, evident as a pink colour that slowly develops in the solution above the solid *trans*. *cis*-Ni(cyclam)(BH₄)₂ formed in this manner is, however, contaminated with the excess metal–borohydride reagent, purification of which is not simple. Rather, the *cis* isomer was prepared by taking a sample of the *trans*-isomer and mixing with acetonitrile (Aldrich, distilled over CaH₂), forming a pink solution of *cis*-Ni(cyclam)(BH₄)₂ over a period of several hours, from which the solvent could simply be evaporated.

Results

Single crystal X-ray diffraction data proved unambiguously the existence of two stable isomers (*cis* and *trans*) of Ni(cyclam)(BH₄)₂, with a BH₄ group coordinated to a Ni^{II} centre. The structures are shown in Fig. 2 and important parameters in Table 1 (for more detailed data see ESI†).

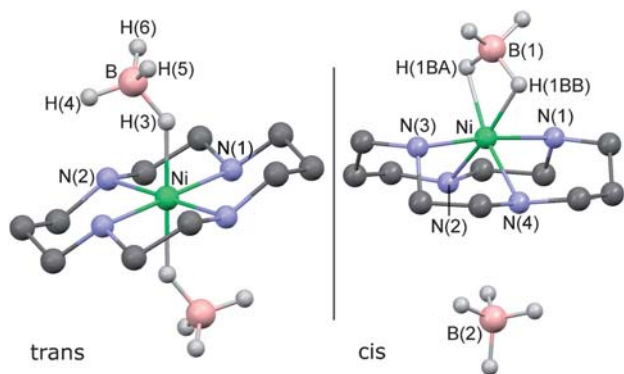


Fig. 2 The crystal structures of *trans*- and *cis*-Ni(cyclam)(BH₄)₂. Note, for the *cis* isomer only one of two symmetry related parts is shown. Please see ESI† for more figures, especially on the disorder in the *cis* structure.

Table 1 Crystal data for Ni(cyclam)(BH₄)₂

	<i>trans</i>	<i>cis</i>
Empirical formula	C ₁₀ H ₃₂ B ₂ N ₄ Ni	C ₁₀ H ₃₂ B ₂ N ₄ Ni
<i>M</i>	288.73	288.73
<i>T</i> /K	100(2)	100(2)
<i>λ</i> /Å	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No 14)	<i>Pnma</i> (No 62)
Unit cell dimensions/Å, °	<i>a</i> = 7.1397(5) <i>b</i> = 12.8109(7) <i>c</i> = 8.7041(5) <i>β</i> = 109.948(6)	<i>a</i> = 14.4512(7) <i>b</i> = 9.4625(6) <i>c</i> = 11.7824(7)
<i>V</i> /Å ³	748.36(8)	1611.18(16)

Table 2 Selected interatomic distances (Å) and angles (°) for both isomers of Ni(cyclam)(BH₄)₂

<i>trans</i> -Ni(cyclam)(BH ₄) ₂			
Ni(1)–N(1)	2.0676(10)	Ni(1)–H(3)–B(1)	142(1)
Ni(1)–N(2)	2.0654(10)	H(3)–B(1)–H(4)	110(1)
Ni(1)–H(3)	1.829(15)	H(3)–B(1)–H(5)	104(1)
Ni(1)–B(1)	2.8691(13)	H(3)–B(1)–H(6)	108(2)
B(1)–H(3)	1.184(15)		
B(1)–H(4)	1.101(15)		
B(1)–H(5)	1.085(15)		
B(1)–H(6)	1.054(18)		
<i>cis</i> -Ni(cyclam)(BH ₄) ₂			
Ni(1)–N(1)	2.182(7)	H(1BA)–Ni(1)–H(1BB)	60.8
Ni(1)–N(2)	2.107(6)	N(3)–Ni(1)–N(1)	170.9(3)
Ni(1)–N(3)	2.021(7)	N(4)–Ni(1)–N(2)	98.1(2)
Ni(1)–N(4)	2.033(6)		
Ni(1)–H(1BA)	1.800		
Ni(1)–H(1BB)	1.736		
Ni(1)–B(1)	2.202(6)		
Ni(1)–B(2)	4.4325(2)		
B(1)–H(1BA)	1.087		
B(1)–H(1BB)	1.166		
B(1)–H(1BC)	1.112		
B(1)–H(1BD)	1.069		

Crystal structure of *trans*-Ni(cyclam)(BH₄)₂

Single crystal X-ray diffraction reveals an octahedral geometry of Ni(II) (thus pointing to high-spin d⁸ Ni(II), in agreement with DFT calculations) with the *trans* BH₄[−] groups in equivalent chemical environments (Fig. 2). The central Ni atom is located at the centre of symmetry thus only half of the complex constitutes a symmetrically independent part of the unit cell. Selected geometrical parameters are given in Table 2. The NiN₄ unit is close to square planar with four comparable Ni–N distances of ca. 2.07 Å. The H(3)–B(1) bond, formed by Ni⋯B-bridging H(3) atom, is considerably elongated (1.184 Å) compared to the other B–H bonds (their bond lengths range from 1.054 to 1.101 Å) and not perpendicular to the plane made by the four N atoms, but slightly bent.

Crystal structure of *cis*-Ni(cyclam)(BH₄)₂

The crystal structure of the *cis* isomer of Ni(cyclam)(BH₄)₂ is of the ionic type and consists of weakly interacting [cis-Ni(cyclam)(BH₄)]⁺ and BH₄[−] moieties (for selected geometrical parameters see Table 2). There is insufficient room for the two rather large BH₄[−] anions to coordinate to the Ni^{II} centre on the

same side of the cyclam ring resulting in the *cis* conformation adopting a very deformed pseudo-octahedral geometry around Ni^{II} with four N atoms arranged in a butterfly fashion and a bidentate BH₄[−] anion. This bidentate coordination leads to a small [H(1BA)]–Ni–ligand[H(1BB)] angle of about 61° and a close Ni(1)–B(1) contact of 2.202(6) Å in contrast to 2.869(2) Å for the *trans* isomer.

The structure is severely disordered, similar to its *trans*-perchlorate analogue.²⁰ The [*cis*-Ni(cyclam)(BH₄)]⁺ cation is located on a mirror plane passing through Ni(1), B(1) and B(2) atoms. Because the single *cis*-Ni(cyclam) moiety is chiral this operation generates two overplayed species with ½ occupancy each. Such disorder is of the static type. Moreover, because of the rather loose packing of moieties—the difference in the calculated crystal densities of the *trans* and *cis* structures is 7.3%—the independent *cis*-Ni(cyclam) fragment reveals large atomic displacement parameters. However, this could be the effect of either averaging out of slightly different geometries or thermal motion. It is evident that the *cis* isomer shows much broader NH stretching bands than the *trans*, which, we think, could be linked to the static disorder present in the crystal structure of the *cis* isomer.

Additional comments on both crystal structures and figures illustrating the *cis* isomer's disorder may be found in the ESI†.

Thus, we now have two distinct isomers of a Ni^{II} complex with the divalent metal center sufficiently resistant to reduction that it may be bound to a BH₄[−] group under ambient conditions. This stability is in contrast to the poor thermal stability of the unchelated Ni(BH₄)₂⁸ and also demonstrates that such Ni complexes may indeed be used in a hydrogen store without being reduced to Ni metal. Let us now inspect how the coordination of the borohydride anions influences the vibrational spectra of both isomers.

Infrared absorption spectra

The FTIR spectra are shown in Fig. 3, with an indication of which regions correspond to the cyclam ring (N–H and C–H stretches) and to B–H stretches. A list of the main peaks for the *cis* and *trans* isomers is reported.†

Relative to bulk NaBH₄ (with its lowest energy BH stretch at 2233 cm^{−1}) both isomers show lower energy BH stretches (2126 cm^{−1} *trans*, 2063 cm^{−1} *cis*), and therefore weakened B–H bonding, a desirable trait for lowering of the thermal decomposition temperatures. This supposition is nicely corroborated by our TGA/DSC studies (see section below). A notable difference between the two isomers is the greater range in the BH stretching region of the *cis* isomer than the *trans*. The lowest energy BH stretches arise from the further weakened B–H bonds of the *cis* bridging hydrogens, whilst the highest energy stretches arise from the uncoordinated BH₄[−] counterion.

Comparison of the IR spectrum of *trans*-Ni(cyclam)(BH₄)₂ after 3 months in air (Fig. 3c) with that of the freshly prepared

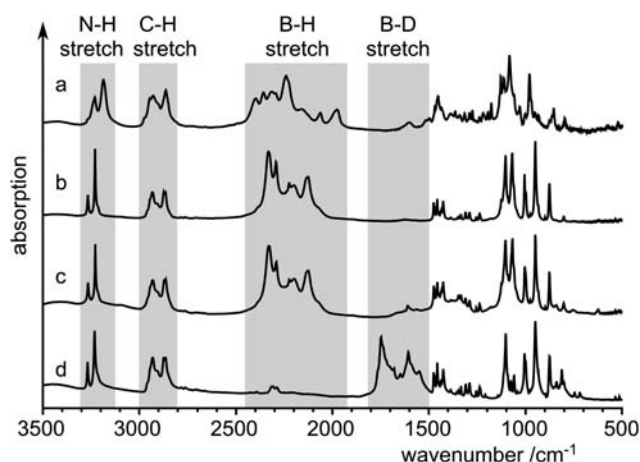


Fig. 3 IR spectra of (from top) (a) *cis*-Ni(cyclam)(BH₄)₂, (b) *trans*-Ni(cyclam)(BH₄)₂, (c) *trans*-Ni(cyclam)(BH₄)₂ after 3 months in air, (d) *trans*-Ni(cyclam)(BD₄)₂.

compound (Fig. 3b) shows no decomposition of the complex and the presence of only traces of water, again indicating the remarkable stability of this Ni macrocycle borohydride complex.

Further discussion of these data and that from deuterated analogues and Raman spectroscopy, can be found in the ESI†.

TGA/DSC and evolved gas analysis

The thermogravimetric and simultaneous differential scanning calorimetry results are shown in Fig. 4. *trans* differs from that of the *cis* isomer calculated at 140 °C, though this value should be treated with care as the onset is considerably less well defined than for *trans*. Since Ni(BH₄)₂ decomposes at temperatures below −20 °C,⁸ the thermal stability afforded by the macrocyclic ligand results in decomposition temperatures for *trans* of more than 190 °C higher than its unchelated relative. The *cis* isomer's broad onset for *T*_{dec} makes precise quantification harder, but is nevertheless substantially stabilised as well. This result clearly demonstrates that manipulation of the coordination environment allows a Ni^{II} centre bound to a BH₄[−] moiety to survive to temperatures relevant for use in an on-board hydrogen store. It

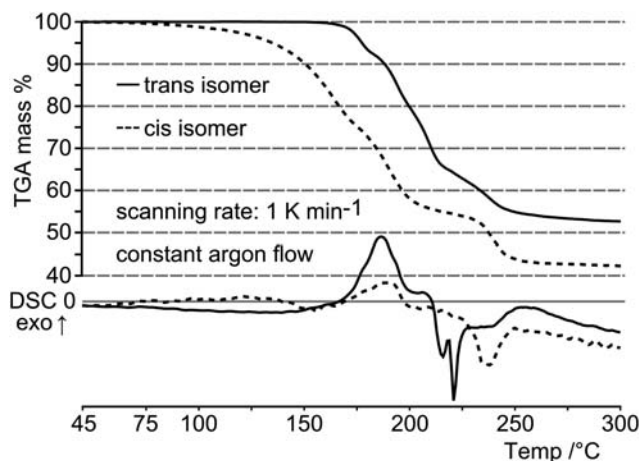


Fig. 4 TGA/DSC curves of *cis*- and *trans*-Ni(cyclam)(BH₄)₂.

† List of main IR absorption peaks. *trans*-Ni(cyclam)(BH₄)₂: 3267 and 3229 (NH), 2993 and 2865 (CH), 2327, 2292, 2199 and 2126 (BH), 1447, 1459, 1428, 1312, 1291, 1240, 1108, 1067, 1005, 951, 877. *cis*-Ni(cyclam)(BH₄)₂: 3231 and 3187 (NH), 2924 and 2865 (CH), 2397, 2358, 2293, 2240, 2063 and 1977 (BH), 1498, 1453, 1342, 1318, 1221, 1178, 1128, 1113, 1084, 981, 855.

is, unfortunately, an over-achievement though, as it takes these borohydrides beyond the T_{dec} range required for practical applications (60–90 °C).

The DSC traces indicate that the initial stages of thermal decomposition of both complexes are mildly exothermic. This precludes them from acting as catalysts as the decomposition must be slightly endothermic to allow for enthalpy driven hydrogenation and entropy driven dehydrogenation (*cf.* Fig. 1). Further modifications to the metal center and/or the chelating ligand are needed to achieve the modest thermodynamic stability necessary for the transition metal complex to act as a hydrogenation catalyst.

The combined TGA/DSC results show that the thermal decomposition pathway is convoluted, involving many steps, which unfortunately evolved gas analysis does not provide much insight into. Given these complexities, and that these first-run compounds are not suited to catalysis, this pathway was not investigated in detail (for more analysis see ESI†).

Assessment of potential of macrocyclic compounds as hydrogen store catalysts: Ni^{II} and beyond

The use of ligands, in particular macrocycles, to stabilise the higher oxidation state of Ni in a reducing environment is clearly demonstrated by the coordination of BH₄[−] groups to a high-spin Ni^{II} centre, similar to the remarkably stable complexes described in ref. 14 and 15. In this case, the use of cyclam has apparently stabilised the complex beyond what we would like, resulting in a decomposition temperature higher than the 60–90 °C range required for use with fuel cell waste heat. Unfortunately, the exothermic nature of the decomposition is also unfavourable to its use in an on-board rechargeable store, effectively ruling these particular complexes out of this application.

Nevertheless, the family of macrocycles is large, and the resulting possibilities for tuning the environment of the metal centre is considerable, precisely the reason for our initial investigation of these complexes. Use of different ring size and geometry, bridging groups to enforce *cis* geometry, judicious positioning of different donor atoms (for example strongly donating P or S in place of N), and of course the choice of metal center, are some of the methods available for altering the thermal and thermodynamic properties of the final borohydride product. We are now extending our investigations to new complexes of Ni^{II}, looking to improve upon the results presented here. One particularly promising pathway involves ligation of phosphamacrocyces since even the non-macrocyclic analogues are capable of the impressive stabilisation of low-spin derivatives of Fe(II), active for organic hydrogenations.²¹

Conclusions

Successful manipulation of the chemical environment of Ni *via* ligation with an N₄-macrocyclic has resulted in two isomers of a metastable borohydride complex, in which a formally high-spin Ni(II) centre is directly coordinated to at least one BH₄[−] group as confirmed by single crystal X-ray diffraction. Detailed characterisation has revealed that the ‘covalent’ *trans* isomer is thermally stable to 170 °C, slightly outperforming the ‘ionic’ *cis* isomer in thermal stability and over 190 °C higher than the

unchelated Ni(BH₄)₂. However, these complexes are unsuitable for application as catalysts in automotive hydrogen stores as they are actually too stable and show exothermic decomposition. Nevertheless, the successful stabilisation of Ni by macrocycle-ligation represents an intriguing new avenue for catalyst research, bringing with it as it does, the many possibilities for tuning the properties of the metal centre (and in particular achieving low-spin Ni(II) in an appropriate ligand environment). We are further encouraged by the success of Morris *et al.*²¹ in tuning Fe centres using tetradentate, mixed N,P ligands, hydrogenation reactions. More generally, stabilisation of the inherently unstable Ni–BH₄ connection *via* ligation holds promise for related macrocycle complexes of late transition metals to be utilized as hydrogenation catalysts on an equal footing with their unligated early transition metal counterparts.^{3–5}

Acknowledgements

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Notes and references

- 1 US Department of Energy, *Gol/No-Go Recommendation for Sodium Borohydride for On-Board Vehicular Hydrogen Storage*, National Renewable Energy Laboratory Report, NREL/MP-150-42220.
- 2 W. Grochala and P. P. Edwards, *Chem. Rev.*, 2004, **104**, 1283–1316.
- 3 B. Bogdanović and M. Schwickardi, *J. Alloys Compd.*, 1997, **253**, 1–9.
- 4 B. Bogdanović, M. Felderhoff, S. Kaskel, A. Pommerin, K. Schlichte and F. Schüth, *Adv. Mater.*, 2003, **15**, 1012–1015; J. Chen, N. Kuriyama, Q. Xu, H. T. Takeshita and T. Sakai, *J. Phys. Chem. B*, 2001, **105**, 11214–11220; T. Vegge, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4853–4861; J. Graetz, J. J. Reilly, J. Johnson, A. Y. Ignatov and T. A. Tyson, *Appl. Phys. Lett.*, 2004, **85**, 500–502.
- 5 D. Blanchard, H. Brinks, B. Hauback and P. Norby, *Mater. Sci. Eng., B*, 2004, **108**, 54–59; R. Zidan, *J. Alloys Compd.*, 1999, **285**, 119–122; B. Bogdanović, R. A. Brand, A. Marjanovic, M. Schwickardi and J. Tolle, *J. Alloys Compd.*, 2000, **302**, 36–58; M. Naik, S. Rather, C. S. So, S. W. Hwang, A. R. Kim and K. S. Nahm, *Int. J. Hydrogen Energy*, 2009, **34**, 8937–8943; Z. Xueping, L. Shenglin and L. Donglin, *Int. J. Hydrogen Energy*, 2009, **34**, 2701–2704.
- 6 W. Grochala, *Pol. J. Chem.*, 2005, **79**, 1087–1092.
- 7 B. Baranowski and K. Bocheńska, *Z. Phys. Chem., Neue Folge*, 1965, **45**, 140–152.
- 8 J. Aubry and G. Monnier, *Bull. Soc. Chim. Fr.*, 1955, **4**, 482–482.
- 9 G. Monnier, *Bull. Soc. Chim. Fr.*, 1955, (10), 1138–1139.
- 10 P. Choudhury, S. S. Srinivasan, V. R. Bhethanabotla, Y. Goswami, K. McGrath and E. K. Stefanakos, *Int. J. Hydrogen Energy*, 2009, **34**, 6325–6334.
- 11 Y. Kojima, Y. Kawai, M. Matsumoto and T. Haga, *J. Alloys Compd.*, 2008, **462**, 275–278.
- 12 T. Sun, C. Huang, H. Wang, L. Sun and M. Zhu, *Int. J. Hydrogen Energy*, 2008, **33**, 6216–6221.
- 13 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, 1969, **91**, 6540–6541.
- 14 P. J. Desrochers, S. LeLievre, R. J. Johnson, B. T. Lamb, A. L. Phelps, A. W. Cordes, W. Gu and S. P. Cramer, *Inorg. Chem.*, 2003, **42**, 7945–7950.

-
- 15 Y. Journaux, V. Lozan, J. Klingele and B. Kersting, *Chem. Commun.*, 2006, 83–84.
- 16 W. Grochala, *J. Mol. Model.*, 2007, **13**, 757–767.
- 17 B. Bosnich, M. L. Tobe and G. A. Webb, *Inorg. Chem.*, 1965, **4**, 1109–1112; E. Y. Lee and M. P. Suh, *Angew. Chem., Int. Ed.*, 2004, **43**, 2798–2801; J. Collin, M. Beley, J. Sauvage and R. Ruppert, *J. Am. Chem. Soc.*, 1986, **108**, 7461–7467; M. A. Donnelly and M. Zimmer, *Inorg. Chem.*, 1999, **38**, 1650–1658; A. McAuley and S. Subramanian, *Coord. Chem. Rev.*, 2000, **200–202**, 75–103.
- 18 US Department of Energy, *Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles*, Office of Energy Efficiency and Renewable Energy and The FreedomCAR and Fuel Partnership, Revision 4, September 2009.
- 19 A. M. Stolzenberg and Z. Zhang, *Inorg. Chem.*, 1997, **36**, 593–600.
- 20 L. Prasad, S. C. Nyburg and A. McAuley, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1987, **43**, 1038–1042.
- 21 C. Sui-Seng, F. N. Haque, A. Hadzovic, A. Pütz, V. Reuss, N. Meyer, A. J. Lough, M. Zimmer-De Iuliis and R. H. Morris, *Inorg. Chem.*, 2009, **48**, 735–743; C. Sui-Seng, F. Freutel, A. J. Lough and R. H. Morris, *Angew. Chem., Int. Ed.*, 2008, **47**, 940–943; A. Mikhailine, A. J. Lough and R. H. Morris, *J. Am. Chem. Soc.*, 2009, **131**, 1394–1395.