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Isolation of chloride- and hydride-bridged tri-iron and -zinc clusters in a tris(β-oxo-δ-diimine) cyclophane ligand†

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A cyclophane ligand (H_6L) bearing three β-oxo-δ-diimine arms and the corresponding tri-iron and -zinc complexes in which the metal ions are bridged by either chlorides, *viz.* $Fe_3Cl_3(H_3L)$ (1) and $Zn_3Cl_3(H_3L)$ (2), or hydrides, *viz.* $Fe_3H_3(H_3L)$ (3), $Zn_3H_3(H_3L)$ (4), were synthesized and characterized. 1 adopts a chair-shaped C_{3v}-symmetric $[Fe_3(\mu\text{-}Cl)_3]^{3+}$ cluster wherein only one hemisphere of the ligand is metallated and the other three ketoimine sites remain protonated as evidenced by single crystal X-ray diffraction and vibrational and NMR spectroscopic analyses. 3 and 4 were synthesized by substitution of the bridging chlorides in 1 and 2 using $KBEt_3H$ and are accessed with retention of the three protonated ketoimine sites.

Introduction

Active sites of the enzymes that catalyse multielectron redox reactions utilize metal cluster cofactors in conjunction with secondary coordination sphere interactions (*e.g.*, hydrogen bonding interactions) to facilitate bond activation.[1–7] As an initial approach to understanding and replicating such reactivity, several groups have employed ligands to template the spatial and electronic environment of multiple metal centres, thereby accessing polynuclear metal complexes with *a priori* control.[8–14] As part of those efforts, our group has reported a number of trimetallic complexes supported by a tris (β-diketimine) cyclophane (H_3**L**) for which the metal ion type and the identity of the bridging ligands can be varied.[14–21] Members of this trimetallic cyclophanate family are capable of supporting low-valent high spin metal centres, can readily undergo substitution of bridging ligands, and can reductively activate small molecules. One challenge, however, is that the internal space within the cavity limits substrate binding and product egress and these compounds are limited to trimetallic species. Expansion of the internal void space of the ligand by utilizing linking arms that are longer than acetylacetone as well as arms capable of coordinating more than one metal centre provides a straightforward and complementary route to address these issues.

Gerlach and Holm first reported the use of deprotonated β-ketoiminates as ligands in which the ligand sterics preclude polymer formation and allow access to four-coordinate metal species,[22] and reports by others have since been communicated.[23,24] As an extension, β-oxo-δ-diimine can be accessed by Schiff base condensation of a triketone with amines. Once fully deprotonated, the corresponding β-oxo-δ-diiminate can coordinate two metal centers with each metal ion held within a monoanionic *N*,*O*-chelate.[25,26] In addition to the dimetallic species, others have reported selective and exclusive monometalation of this β-oxo-δ-diimine; the resultant complexes retain the N–H proton on one half of the ligand.[25,27,28] We reasoned then that employing β-oxo-δ-diimine as arms in a cyclophane could simultaneously allow access to hexanuclear metal complexes under one metalation condition or trimetallic complexes by minor changes to the synthetic approach. For the latter, the internal cavity of one hemisphere of the complex would be decorated with N–H protons, providing a large internal cavity for substrate access and also template secondary coordination sphere hydrogen bond donors. To our knowledge, there are only a few examples of dimetallic complexes in which secondary coordination sphere interactions are incorporated by design, and no examples for higher nuclearity compounds. Herein, we report the synthesis and characterization of a tris(β-oxo-δ-diimine) bis(1,3,5-triethylbenzene) cyclophane and its tri-iron and tri-zinc complexes with bridging chlorides or hydrides (Scheme 1). These trimetallic complexes comprise monometallation of each β-oxo-δ-diimine arm and retention of the N–H at the unmetallated site.

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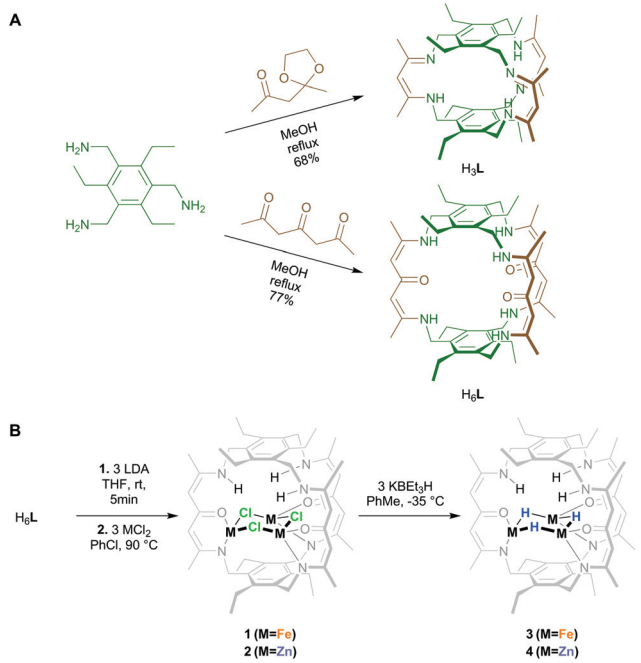

Scheme 1 Synthesis of tri- or hexa-nucleating ligands and coordination complexes of H_6**L**.

Experimental section

Synthetic procedures

General considerations. All manipulations except ligand synthesis were performed inside an N_2-filled Innovative Technologies glovebox. Tetrahydrofuran (THF), benzene, toluene, and *n*-hexane were purchased from Sigma-Aldrich, dried under Ar using a solvent purification system (Innovative Technologies), transferred to the glovebox, and stored over activated 3A molecular sieves. Benzene-d_6, toluene-d_8, and THF-d_8 (Cambridge Isotope Laboratories) were distilled over CaH_2 or with Na/benzophenone and then degassed and stored over 3A molecular sieves. ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded on a 500 MHz Varian Inova spectrometer or a 300 MHz Mercury spectrometer equipped with a three-channel 5 mm indirect detection probe with *z*-axis gradients. Chemical shifts were reported in δ (ppm) and were referenced to solvent resonances: δ_H = 7.26 ppm ($CDCl_3$), 7.16 ppm (C_6D_6), 2.09 ppm (C_7D_8), and 3.58 ppm (C_4D_8O). Fourier Transform Infrared (FT-IR) spectra were recorded as solids on a Thermo Fisher iS5 instrument equipped with an ATR diamond crystal stage using OMNIC software package. 2,4,6-Heptatrione was synthesized following the literature procedure.[29]

H_6L. A methanolic (60 mL) solution of 2,4,6-heptatrion (3.40 g, 23.9 mmol) and 1,3,5-tri(aminomethyl)-2,4,6-triethylbenzene (5.15 g, 20.6 mmol) was heated at 50 °C for 6 h. Resulting beige solid was collected by filtration and dried under reduced pressure (yield = 5.00 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 9.56 (s, br, 6H), 4.72 (s, 6H), 4.29 (s, 12H), 2.73 (d, J = 7.1 Hz, 12H), 2.02 (s, 18H), 1.17 (t, J = 6.9 Hz, 18H). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 189.6, 157.3, 144.1, 131.6, 95.7, 41.2, 23.0, 20.0, 16.3. IR (cm^{-1}): 3060, 2931, 1620, 1560, 1427, 1296, 1080, 790, 710. ESI-MS calcd for $C_{51}H_{73}N_6O_3$ $[M + H]^+$ 817.5739, found 817.5725.

$Fe_3Cl_3(H_3L)$ (1). A THF solution (12 mL) of H_6**L** (1.16 g, 1.42 mmol) and LiN^iPr_2 (LDA, 0.470 g, 4.27 mmol) was stirred at r.t. for 5–10 min. After formation of a green solution, the solvent was removed under vacuum at 50 °C. The residue was suspended in chlorobenzene (24 mL) and $FeCl_2$ (0.555 g, 4.37 mmol) added. The reaction mixture was stirred at 90 °C overnight, then filtered, and the filtrate dried *in vacuo* at 50 °C to yield analytically pure orange solid (1.43 g, 92%). Crystals suitable for diffraction were grown by cooling toluene solution from 80 °C to r.t. $C_{51}H_{69}Cl_3Fe_3N_6O_3{\cdot}0.5C_6H_5Cl$ (calcd): C, 56.48 (56.68); H, 6.33 (6.30); N, 7.04 (7.34). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 141.31, 77.17, −10.05, −11.81, −13.38, −13.58, −18.52, −32.72, −33.59. IR (cm^{-1}): 3280, 2963, 1599, 1494, 1324, 1066, 781. μ_{eff} ($CDCl_3$, 298 K) = 5.6μ_B. UV–Vis (THF, 25 °C, M^{-1} cm^{-1}): ε_{535} = 644.

$Zn_3Cl_3(H_3L)$ (2). A THF solution (4 mL) of H_6**L** (323 mg, 0.395 mmol) and LDA (134 mg, 1.22 mmol) was stirred at r.t. for 5–10 min. After the formation of a green solution, the solvent was removed under vacuum at 50 °C. A suspension of the deprotonated ligand and $ZnCl_2$ (166 mg, 1.22 mmol) in chlorobenzene (8 mL) was stirred at 90 °C overnight. The reaction mixture was then filtered and, the filtrate was evaporated under vacuum at 50 °C to afford **2** as a yellow solid (362 mg, 82%). $C_{51}H_{69}Cl_3N_6O_3Zn_3$ (calcd): C, 54.33 (54.86); H, 6.11 (6.23); N, 7.16 (7.53). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 9.53 (s, 3H), 4.55 (d, 6H), 4.33 (d, 12H), 2.68 (dd, 12H), 2.03 (d, 18H), 1.18 (dt, 18H). IR (cm^{-1}): 3244, 2981, 1599, 1503, 1397, 1333, 1074, 782.

$Fe_3H_3(H_3L)$ (3). To a toluene solution (1 mL) of **1** (33.5 mg, 0.0308 mmol) was added a toluene solution (1 mL) of $KBEt_3H$ (12.5 mg, 0.0292 mmol) at −35 °C and the mixture stirred overnight. Then, the reaction was filtered through toluene-rinsed Celite, and the filtrate was evaporated under vacuum to yield **3** as a red-brown solid (28.8 mg, 95%). $C_{51}H_{72}Fe_3N_6O_3{\cdot}0.5C_4H_{10}O$ (calcd): C, 61.76 (62.30); H, 7.67 (7.60); N, 7.83 (8.23). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 58.34, 43.37, 15.71, 4.41, −0.93, −3.33, −5.24, −6.36, −7.85, −44.24. IR (cm^{-1}): 3295, 2963, 1612, 1501, 1398, 1337, 1067, 787. UV–Vis (THF, 25 °C, M^{-1} cm^{-1}): ε_{533} = 1410, ε_{582} = 857.

$Zn_3H_3(H_3L)$ (4). The procedure is as described for **3** employing **2** (111 mg, 0.0998 mmol) instead of the triiron congener and yields **4** as a yellow solid in good yield (78.6 mg, 78%). $C_{51}H_{72}N_6O_3Zn_3{\cdot}C_6H_6$ (calcd): C, 62.66 (62.73); H, 7.37 (7.20); N, 7.26 (7.70). ^{1}H NMR (500 MHz, C_6D_6, 298 K): δ 8.38 (s, 2H), 5.01 (d, 6H), 4.23 (d, 12H), 3.38 (s, 2H), 2.56 (q, 6H), 2.40 (q, 6H), 1.87 (s, 9H), 1.78 (s, 9H), 1.09 (t, 9H), 1.02 (t, 9H). IR (cm^{-1}): 2869, 1612, 1507, 1405, 1341, 1068, 782.

Results and discussion

The target ligand (H_6**L**) comprising three β-oxo-δ-diimine sites was synthesized in 77% yield from the condensation of 2,4,6-

heptatrione with the previously used 1,3,5-triaminomethyl-2,4,6-triethylbenzene (Scheme 1). As anticipated from our prior work with the tris(β-diketimine) cyclophane, this ligand is a solution averaged D_{3h} symmetric compound at ambient temperature with only six resonances observed in the ^{1}H-NMR spectrum (Fig. S1†). The β-oxo-δ-diimine has been previously reported to adopt the keto-di(enamine) tautomer; similarly, the integral singlet α-hydrogens at 4.72 ppm and that of the downfield shifted amine protons at 9.56 ppm are indicative of the keto-di(enamine) tautomer in H_6**L**. Notably, a weak absorbance is observed at 3060 cm^{-1} in IR spectra of solid samples of H_6**L** is assigned to N–H stretching mode (Fig. S2†); these data together with the NMR resonance at 9.56 ppm are the diagnostic markers for successful deprotonation at a given site.

Deprotonation of H_6**L** in THF with 3 equiv. LiN^{i}Pr$_2$ (LDA) results in a reduction of the molecular symmetry and, likely, a distribution of slowly equilibrating conformers of $Li_3(H_3$**L**$)$ species in solution. For example, the ^{1}H-NMR resonances corresponding to the backbone C–**H** protons of the β-oxo-δ-diimine arms and the aminomethyl protons broaden from well-resolved singlets to multiplets (Fig. S3†). Mono-deprotonation of each arm also affords observable changes in the IR spectrum, with a hypsochromic shift of the absorption at 1560 cm^{-1} to 1577 cm^{-1} and loss of the absorption associated with the N–H vibration (Fig. S4†). In contrast to the deprotonation with 3 equiv. LDA, ^{1}H-NMR resonances in spectra from reactions of H_6**L** with 6 equiv. LDA are broad and through bond couplings are unresolved. For both the proposed $Li_3(H_3$**L**$)$ and Li_6**L**, the NMR spectra of the deprotonated species could reflect a distribution of slowly equilibrating isomers in solution, which is consistent with the decrease or absence of a discernible IR absorption for the N–H vibration in the partially deprotonated ligand. In addition, we observe a loss of absorptions between 1560–1620 cm^{-1} (Fig. S5, Fig. S6†). The changes to the IR spectrum upon deprotonation are reminiscent of our observations for deprotonation of our tris(β-diketimine) cyclophane; we observe an almost complete loss in the absorption at ~1617 cm^{-1} upon complete deprotonation of the free base ligand. Attempts to access the hexametalllic complexes have been unsuccessful with reaction of putative Li_6**L** with excess $FeCl_2$ resulting in intractable products that are insoluble in all solvents tested. Comparable results were obtained for a survey of other metalating agents in which metal ion type and counteranion were varied. In contrast, treatment of a chlorobenzene suspension of $Li_3(H_3$**L**$)$ with 3 equiv. $FeCl_2$ or $ZnCl_2$ readily affords the orange-red tri-iron ($Fe_3(\mu\text{-}Cl)_3(H_3$**L**$)$, **1**) or yellow tri-zinc ($Zn_3(\mu\text{-}Cl)_3(H_3$**L**$)$, **2**) complexes, respectively. The paramagnetic ^{1}H-NMR spectrum of **1** comprises ten resonances between 144.26 and −36.04 ppm (Fig. S7†). Similarly, we observe five doublets for the aliphatic protons and a singlet for N–**H** protons in ^{1}H-NMR spectra of **2** (Fig. S9†). Taken together, we conclude that **1** and **2** both have C_{3v}-symmetry in solution, hinting at selective metalation of only one hemisphere of the ligand and μ-chloride donors.[17,19] Notably, a new absorption is observed in IR spectra of **1** and **2** in the O/N–H region of the IR spectrum (*viz.* 3280 cm^{-1} for **1** and 3244 cm^{-1} for **2**) as compared to spectra of $Li_3(H_3$**L**$)$ (Fig. S8 and S10†). These absorptions support retention of three N–H protons in the isolated compounds, with incorporation of the d-block metal ions resulting in one preferred conformer and loss of the fluxionality observed for the Li derivatives. In addition, metalation results in a hypsochromic shift of the absorption at 1577 cm^{-1} in the $Li_3(H_3$**L**$)$ to 1599 cm^{-1} in **1** and **2**. Taken together, we surmise that **1** and **2** are isostructural and are C_{3v} symmetric.

The solid-state structure of **1** determined by single crystal X-ray diffraction qualitatively corroborate our IR and NMR analysis: the average stoichiometry is $Fe_3Cl_3(H_3$**L**$)$.‡ In this structure solution, the three iron centres are positionally disordered over the six β-ketoiminate sites with occupancies ranging from 0.46–0.54 (Fig. 1). The three bridging chlorides are on the same plane of carbonyl oxygens (rms distance of 0.160 Å for 3Cl atoms from the O_3 plane); the elongated thermal ellipsoids of the O and Cl atoms are consistent with the Fe positional disorder and site averaging of the iron atom in one half of each arm. The average result together with the solution C_{3v} symmetry deduced from our ^{1}H NMR data implies a chair-shaped $[Fe_3Cl_3]^{3+}$ cluster within the internal cavity of the cyclophane. This chair motif has substantial precedent in d-block chemistry with analogous $[M_3Cl_3]^{n+}$-type clusters have been reported

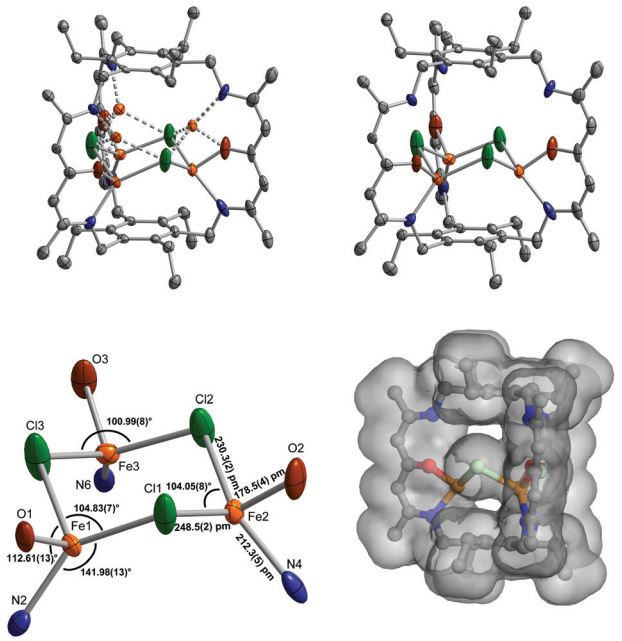

Fig. 1 Single-crystal structure of **1** at 50% thermal ellipsoid (top-left). Bonds with disordered iron atoms are displayed as a dashed line. The chair-shaped $[Fe_3Cl_3]^{3+}$ cluster occupies the lower hemisphere of the ligand with each iron atom adopting a trigonal pyramidal geometry (top-right). Expanded view of the donor atoms for each metal centre in the cluster highlights the local coordination geometry (bottom-left). Connolly surface map drawn with no diameter of probe provides insight into the access to the internal cavity (bottom-right). H atoms and solvent molecules have been omitted for clarity. C, N, O, Fe, and Cl are depicted as grey, blue, red, orange, and green ellipsoid, respectively.

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for rhodium,[30–32] platinum,[33,34] copper,[35,36] and palladium.[37] However, to our knowledge based on search of the Cambridge Structural Database, this complex represents the first case of crystallographic structure of chair-shaped triiron cluster bridged by chlorides. The average Fe–Fe distance in the cluster is 3.759(1) Å, which is the second largest value from chloride bridged Fe(II) compound reported so far.[38] The largest Fe–Fe distance is found from the parallel diiron β-diiminato complex, two iminate groups of which are separated by xanthene moiety.[39] The Fe–Fe lengths and Fe–Cl–Fe angles (θ) are well correlated by the following equation: $d_{\mathrm{Fe-Fe}} = 2d_{\mathrm{Fe-Cl}}\sin(\theta/2)$, giving an average bond length of bridging Fe–Cl as 2.392(5) Å (Fig. S11†). Based on the angle dependence on coupling proposed by Goodenough, Kanamori, and Anderson, we anticipate that the iron centres in $Fe_3Cl_3(H_3\mathbf{L})$ are antiferromagnetically coupled as in our previous trimetallic complex.[14,40–43]

There are differences for coordinating halides between **1** and our previous β-diketiminate complex with $[Fe_3Br_3]^{3+}$ cluster.[14] For our previously reported trinucleating ligand, the ancillary ligands (*e.g.*, chloride) lie in the M_3 plane, whereas the μ-halides in **1** and **2** are out of the M_3 plane. Such a change in the structure is expected based on the preferred bonding interactions for halides in metal halide clusters. Such an assertion is supported by the prevalence of self-assembled chair-like clusters as compared to the dearth of analogous planar clusters. Thus, the larger cavity size of $H_6\mathbf{L}$ *versus* to the more compressed tris(β-diketiminine) cyclophane allows the M_3X_3 cluster to adopt the preferred chair orientation. Arguably, the ligand fields differ slightly between the *O*,*N*-chelate afforded by $H_6\mathbf{L}$ as opposed to the *N*,*N*-chelate in our previous work; given precedent, such changes are not expected to be the driving force for loss of planarity of the M_3X_3 unit.

Each iron centre in **1** adopts a pseudotrigonal pyramidal coordination geometry with τ_4 values between 0.72 and 0.75 (τ_4 = 0.85 for trigonal pyramidal).[44] Here, the trigonal plane is defined by the two chlorides and the nitrogen donor coordinated to a given Fe centre with the sum of these L–M–L angles being 359°. The plane is composed of two large N–Fe–Cl bond angles, which give rise to relatively small τ_4, and small Cl–Fe–Cl angle (103.29(4)°). Given the similarity of this chair motif to the synthetic 3Fe-4S clusters, we note that these Cl–Fe–Cl angles are comparable to the average S–Fe–S angle of 103.64(2)° in synthetic examples.[8] Future directions aim to leverage these structural similarities to access high nuclearity compounds.

With the trichloride complexes in hand, we then sought to derivatize these complexes as previously demonstrated for the trimetallic complexes of our tris(β-diketiminate) cyclophane. Reaction of **1** or **2** with 3 equiv. of KEt_3BH at −35 °C effected the desired substitution, affording the triiron (**3**) or trizinc (**4**) complexes of $[H_3\mathbf{L}]^{3-}$ in excellent yield (95% or 89%, respectively). Unlike the reported result for monometallic β-diketiminatoiron(II) complexes, we do not observe transmetalation and adventitious formation of iron-alkyl species.[17,45] A total of ten resonances are observed in ^{1}H-NMR spectra of **3**, consistent with the expected retention of C_{3v} molecular symmetry (Fig. S12†). Retention of the enamine protons within the cavity is evidenced by the IR absorption at 3295 cm^{-1}, which we assign as the N–H stretching mode based on deuteration experiments (Fig. S13†). Further corroboration for retention of the protonated state of the unmetalated enamines is provided by analysis of **4**. NMR spectra recorded on samples of **4** comprise a sharp resonance at 3.38 ppm assigned to the Zn–**H** as well as ten resonances corresponding to the ligand protons and one singlet at 8.39 ppm for amine protons (Fig. S14†). We note for **4**, however, that the integrals for the hydride and amine proton peak were smaller than expected, and the absorption corresponding to the N–H stretching frequency was not well-resolved from baseline in IR spectra (Fig. S15†). Both iron complexes showed two irreversible reduction events (*viz.* −2.25 and −2.58 V *vs.* Fc/Fc$^+$ for **1** and −1.66 and −2.33 V *vs.* Fc/Fc$^+$ for **3**) from cyclic voltammograms measured in THF and using ^{n}Bu$_4$NPF$_6$ as the electrolyte (Fig. S16 and S17†). As we will mention about the stability of the complex below, data suggest that these complexes are significantly more labile as compared to our tris(β-diketiminate) cyclophane complexes and this lack of stability likely contributes to irreversibility of these redox processes.

The stability of **1** was significantly affected by the presence of added chloride, solvent, and temperature. Despite the initial synthesis in an aromatic solvent, dissolution of isolated **1** in toluene or benzene followed by heating at 90 °C over the course of 24 h results in decomposition of the complex to the free base ligand as well as species with apparent C_{2v} symmetry, which are consistent with that expected for partially metalated complexes (*e.g.*, di- and monometallic complexes). Surprisingly, demetalation was also apparent in the solid state even at −35 °C over the course of several weeks as evidenced by NMR and IR. The stability of **1** could be enhanced if THF was used as the solvent instead of toluene or benzene, if the bridging ligand was exchanged from chloride to hydride as in **3**, or an exogenous halide source was added. The instability in aromatic solvents and enhanced stability in THF suggests the chloride donors in **1** may sample modes in which solvent can coordinate to the iron centres, increasing the metal coordination number and stabilizing the metal centres. One distinct difference between complexes **1–4** and our prior trimetallic species is the presence of the three reasonably acidic enamine protons in the upper hemisphere of the ligand. We posit then that one possible mechanism for demetalation may be triggered by proton transfer from the N–H to the coordinating carbonyl O atom, thereby labilizing the Fe centre. Alternatively, one can envision a pathway in which formal loss of HCl leads to a dianionic chelate for one metal centre; the liberated HCl may facilitate protonation and demetalation of remaining **1** in solution.

Consistent with hydridic reactivity expected for **3**, the triiron trihydride reaction with chloroform at ambient temperature in near quantitative (based on ^{1}H-NMR spectra) to generate **1**, and a mixture of dichloromethane and chloromethane. Contrastingly, **1** is stable indefinitely in chloroform.

As might be expected based on the facile demetallation of **1**, this complex is unstable to water affording the free ligand, whereas **3** reacts readily with water to afford a mixture of a new C_{3v} symmetric species with a strong IR absorption consistent with O–H ligands as well as the protonated ligand (Fig. S18 and S19†). This reactivity contrasts the reactivity of the trimetallic trihydride complexes reported previously by our group; those compounds demonstrated unusually slow reactivity towards water as well as specific reactivity towards CO_2. Here, we surmise that the greater accessibility of the cavity as well as the presence of hydrogen bonding donors allows for the more facile approach of water, enhancing reactivity towards proton sources.

Conclusions

In summary, we report the synthesis and metalation with iron (II) and zinc(II) chloride of a tris(β-oxo-δ-diimine) cyclophane. The resultant trimetallic compounds contain $[M_3Cl_3]^{3+}$ clusters, in which each metal centre is ligated by a monoanionic *N*,*O* chelate and two halides and with retention of one N–H proton per ligand arm. Facile derivatization of the chloride complexes to the corresponding hydride bridged compounds was readily effected using KEt_3BH, generating complexes bearing both hydridic and protic groups. In addition, complexes **1–4** represent rare examples of the complexes in which secondary coordination sphere interactions are templated in a designed multimetallic system, and the first example for trimetallic systems to our knowledge. The possible redox and H^+/H^- transfer reactivities are the subject of future and ongoing work.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

‡ **Crystal data for $Fe_3Cl_3(H_3L)\cdot(PhMe)_3$:** $C_{72}H_{90}Cl_3Fe_3N_6O_3$, M = 1361.39, monoclinic, space group $P2_1/n$, a = 12.9148(13) Å, b = 22.857(2) Å, c = 23.150(2) Å, β = 98.891(2)°, V = 6571.9(12) Å^3, Z = 4, T = 100(2) K. 66 004 reflections collected, 11 889 independent reflections with R_1 ($I > 2\sigma(I)$) = 0.0829, wR_2 (all data) = 0.1646.

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