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Synthesis of nitrogen and sulfur macrocycles with *cis* exogenous oxygen and sulfur donor atoms†

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A series of new N_4 and N_8 macrocycles has been prepared, that includes *cis*-exogenous O_2, S_2 and S/O atoms to allow chelation to a metal external to the macrocyclic ring. We found that thioamide units within the macrocycles were unstable to attack by secondary amines and thus alkylated precursors containing only tertiary amines could lead to exogenous-S_2 macrocycles. Cyclisation of alkylated tetraamine precursors with dimethyloxalate or dithiooxamide led to both N_4 and N_8 macrocycles *via* 1 + 1 and 2 + 2 cyclisation reactions with exogenous-O_2 or S_2 respectively. Alkylation of preformed exogenous-O_2 macrocycles was explored and led to alkyl substitution at the secondary amine nitrogens in the ring, however synthesis of these species was overall lower yielding than cyclisation using alkylated tetraamine precursors. Thionation of an exo-O_2 macrocycle using an analogue of Lawesson's Reagent led to formation of the analogous exogenous-S_2 and exogenous-O,S macrocycles. Related S_2N_2 macrocycles with exogenous-O_2 were prepared by a cyclisation route but could not be isolated free of larger ring analogues.

Introduction

Multimetallic transition metal complexes offer an important route for the preparation of magnetic materials,[1] development of catalytic reagents,[2] models of metalloenzymes[3] and in the construction of metallosupramolecular architectures.[4] In such systems, interaction between different metal centres is a key feature and ligand units that can induce and control this are therefore of great importance. We and others have previously reported the synthesis and characterization of cyclam-based macrocyclic ligands that incorporate *cis*-exogenous oxygen atoms (hereafter referred to as exo-O_2) arranged for chelation to a metal atom external to the macrocyclic ring.[5,6] These macrocycles incorporate an oxamide-based bis-bidentate linker with deprotonatable amides and are related to amino acid based ligands.[7] Although bis-amide macrocycles have been widely studied[8–10] generally as precursors to saturated macrocycles (by reduction), only a small minority of those reported contain *cis* amides and the use of exogenous binding groups as bidentate linkers has been seldom utilized for the formation of multinuclear systems in macrocyclic chemistry.[11]

The reports of exo-O_2 macrocycles[5,6] although limited in number, have stimulated much further work involving synthesis of heteropolynuclear complexes and assemblies.[12] Such macrocycles have tremendous potential to form novel functional materials as illustrated by the variety of materials developed from open chain oxamido analogues, including multinuclear complexes[13–17] and coordination polymers,[14,16–18] giving for example ferromagnetic complexes and ferrimagnetic chains. The extension of this approach to macrocyclic complexes offers the possibility to exploit the greater control over ligand selectivity, greater structural rigidity of the ligand framework and greater thermodynamic and kinetic stability typical of macrocyclic complexes.

Although oxamato, oxamide and oxalato linkers for first row transition metals are well known, dithiooxamide-based linkers are much less studied, yet it is expected that diffuse sulfur 3s and 3p valence orbitals will mediate strong electronic communication between coordinated metals. With the use of macrocycles to enforce a *cis* conformation, soft exogenous sulfur-donor atoms may allow complexation of second and third row transition metals. Combined with the hard macrocyclic nitrogen donors coordinating first row transition metals, the result would be novel alternating hard–soft multimetallic complexes.

Results and discussion

We report the preparation of a series of new macrocycles that contains *cis*-exogenous sulfur and oxygen donor atoms (Fig. 1). Compounds **3b–e**, **4a–c**, **5b–c**, **6b**, and **7b** were isolated, purified and fully characterised. Compounds **10b,c** were identified by NMR and mass spectrometry methods, however we were unable to isolate these in a pure form as they remained contaminated with the larger 2 + 2 cyclisation products (**11b,c**). An important target of this work was to extend this field from the known exo-O_2

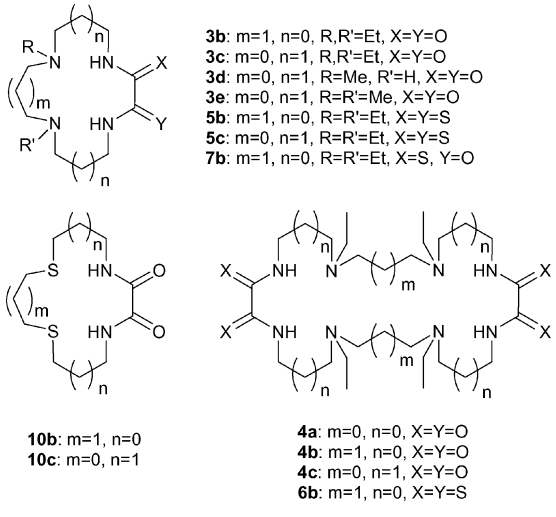

Fig. 1 New macrocycles prepared in this work.

† Electronic supplementary information (ESI) available: synthesis and characterisation of **1a–c**, **2a–c**, **10b,c** and **11b,c**; COSY NMR spectra of **3b**, **5b**, **5c**, **7b**, **10c**. See DOI: 10.1039/b510734b

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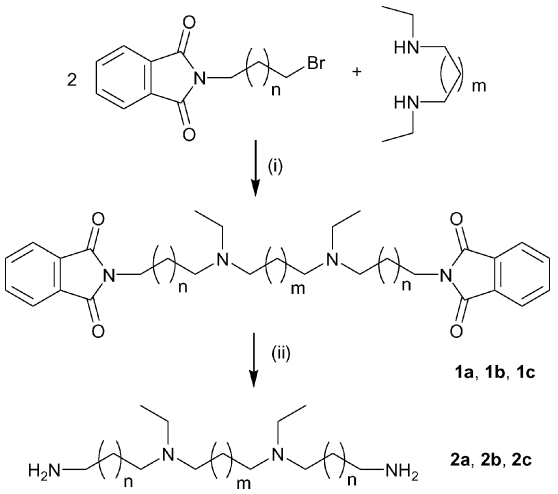
macrocycles to novel exo-S_2 macrocycles. Synthesis of such macrocycles proved difficult as we observed that macrocycles containing the dithiooxamide fragment (*e.g.* **5b–c**, **6b**) are unstable when the macrocycle contains secondary amines that can attack the thioamide functionality. This led us to explore the chemistry of alkylated analogues of the reported exo-O_2 macrocycles[5,6] as these would contain only tertiary amines. Thus we have developed new alkylated exo-O_2 macrocycles and furthermore used this chemistry to prepare novel exo-S_2 and exo-O,S macrocycles.

(i) Cyclisation route to 3b, 3c, 4a–c

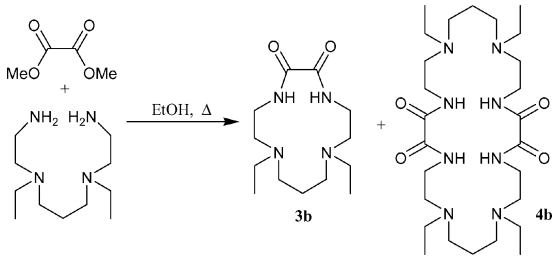
Synthesis of alkylated macrocycles containing tertiary amines was approached in two ways. The first of these, discussed in this section, involved the preparation and cyclisation of alkylated precursors containing both primary and tertiary amines. The most commonly utilized nitrogen protecting groups are the toluenesulfonyl (tosyl) and *tert*-butoxycarbonyl (Boc) groups. Phthalimides are much less frequently used, however we found that phthalimides enabled easier column chromatography and gave crystalline products that aided isolation. Thus we obtained the highest yields of protected tetraamine precursors (**1a–c**) using phthalimide protection for the primary amines (Scheme 1).



Scheme 1 Synthesis of **1a–c** and **2a–c**. n and m defined in Fig. 1 (i) Na_2CO_3, CH_3CN (ii) $NH_2NH_2{\cdot}H_2O$.

The anaerobic reaction of the appropriate secondary diamine and excess *N*-bromo-alkylphthalimide in the presence of sodium carbonate produced diprotected diamine which could be purified by column chromatography in around 50% yield.† The deprotection step of (**1a–c**) (Scheme 1) was chemically clean, facile and high yielding. Although the protected diamines are very stable, the deprotected tetraamines (**2a–c**) are deliquescent and absorb carbon dioxide from the atmosphere. The only literature example concerning phthalimide group protection of a diamine that we are aware of[19] afforded purified yields of only 20% in contrast to the >80% yields obtained here from **1a–c**. The air sensitive compounds **2a–c** were characterised by both positive ion FAB mass spectrometry and ^{1}H NMR.†

The series of tetraaza and octaaza *N*-substituted macrocyclic oxamides (**3b**, **3c**, **4a**, **4b** and **4c**) were synthesized *via* cyclisation reactions utilising **2a–c** with dimethyloxalate (*e.g.* Scheme 2 for **3b** and **4b**) using a method analogous to the synthesis of 2,3-dioxo-1,4,8,11-tetraazacyclotetradecane.[6] The reaction scale, dilution and addition rate were varied to determine the optimal cyclisation conditions and it was found that the slow and simultaneous drop-wise addition of **2a–c** and dimethyl oxalate in degassed ethanol in a precise 1 : 1 ratio, to a refluxing pool of degassed ethanol over ~2–3 days yielded the best results. It is interesting to observe that no product species "**3a**" could be identified and presumably 1 + 1 cyclisation is disfavoured in this case due to the small and poorly flexible ring that would result.



Scheme 2 Synthesis of **3b** and **4b**.

The presence of small amounts of water had little effect on the cyclisation, however exposure of the **2a–c** precursor to carbon dioxide appeared to promote formation of the larger series **4** macrocycles and increased polymeric side product. In all cases, successful reactions generated no precipitate.

The comparison between the **3b** and **4b** ^{1}H NMR peaks revealed a general downfield shift in the spectrum of the larger macrocycle giving rise to diagnostic peaks. These also showed a general downfield shift with increasing macrocycle size and an upfield shift in the $CH_2NC(O)$ peak from tetraaza to octaaza macrocycles with $m = 0$. The former trend is related to ring strain whilst the latter trend relates to amides in a fixed *cis* configuration where the $CH_2NC(O)$ protons are more deshielded relative to more relaxed configurations. The $m = 1$ bridged **3b** and **4b** do not fit the latter trend, suggesting that greater flexibility in the bridge between the tertiary amines opposite the oxamide allows relaxation from the more deshielded configuration.

Equivalent carbon environments in directly related **3** and **4** macrocycles can be distinguished by $^{13}C\{^1H\}$ NMR and a general downfield shift was observed with the decrease in ring size to the smaller macrocycle, **3b**. The amide carbon peaks clearly reflect both the increase in macrocycle size and the relaxation of the *cis* configuration as the octaazamacrocycle amide peaks are upfield relative to the more strained and deshielded tetraaza macrocycle amide peaks. The other influencing factor was the location of *m* or $n = 1$ bridges relative to the oxamide group. When positioned next to the oxamide group such bridges became less shielded in the larger macrocycles.

(ii) Alkylation of N_4 macrocycle

Since 2,3-dioxo-1,4,8,11-tetraazacyclotetradecane is already known from the literature,[6] alkylation of this precursor to prepare new macrocycles was explored. Room temperature reaction with a large amount of methyl iodide produced an inseparable mixture of mono-, bis- and tris-methylated products according to mass spectrometry. To prevent tris-methylated product formation, it was necessary to reduce the excess of methyl iodide used. This in turn increased the probability of unreacted and monomethylated product formation and heating was required to promote the reaction. A mixture of unreacted 2,3-dioxo-1,4,8,11-tetraazacyclotetradecane and macrocycles **3d** and **3e** was produced and isolation of pure **3d** and **3e** was possible *via* column chromatography.

Overall, the high dilution cyclisation route proved to be higher yielding and more flexible than alkylation of the preformed macrocycle despite the extra synthetic step. In both routes, the cyclisation step limits the obtainable yields, however the presence of tertiary rather than secondary amines in the cyclisation step for **3b** and **3c** appeared to generally promote cyclisation over polymerisation.

(iii) Mixed thia-aza macrocycles with exo-O_2

Kimura *et al.*[20] synthesised mixed thia-aza macrocycles by cyclisation of the appropriate dithia diamine with dimethylmalonyl dichloride in the presence of caesium carbonate. We used a

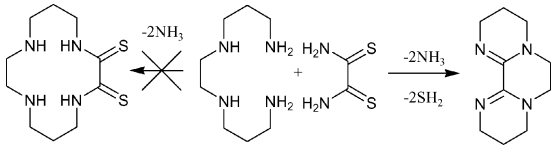
higher dilution variant of the methodology of Kimura *et al.* for the synthesis of macrocycle **10c** using oxalyl chloride (X = Cl) as a rigid unit that should favour cyclisation and lead to the exo-O_2 product. The solid contained both the product macrocycle (**10c**) and an unidentified side product that was neither a larger macrocycle nor a polymer chain. The absence of any connectivity between the macrocyclic peaks and the side product peaks could clearly be seen in the COSY NMR spectrum,† as could the internal connectivity within both sets of peaks. Attempts to isolate **10c** *via* solvent extraction and further column chromatography were unsuccessful, thus only a crude 52% yield of **10c** can be reported.

Cyclisation in degassed absolute ethanol generated various mixtures of **10b**, the 2 + 2 cyclisation product (**11b**) and a side product, however it was not possible to obtain macrocycle **10b** uncombined with either **11b** or the side product. Cyclisation with dimethyl oxalate was also attempted but was very low yielding either with or without addition of caesium carbonate as an ion pair templating agent. Whilst it was not possible to isolate pure macrocyclic product **10b** (or the related **10c**), it is evident that the faster cyclisation reaction with oxalyl chloride in combination with high dilution favoured [1 + 1] cyclisation over polymerisation and formation of larger cycles. Conversely, the slower cyclisation with dimethyl oxalate produced primarily polymeric material.

(iv) Synthesis of exo-S_2 macrocycles by cyclisation

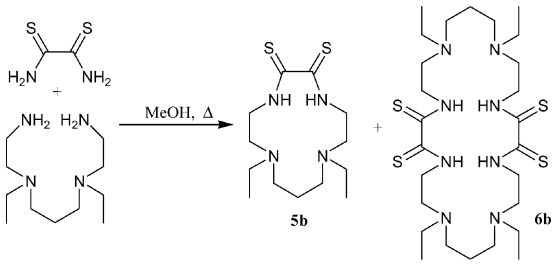
In contrast to the abundant literature examples of macrocyclic amides, very few examples of macrocyclic thioamides are known.[21–24] A recent report (2003) reported a polythioamide macrocycle series designed as anion receptors and described these as "the first thioamide-based macrocycles",[25] emphasising the novel nature of such ligands. It should also be noted that in contrast to our work below, the thioamide groups were not adjacent and thus not positioned for exogenous coordination. Very similar macrocycles with pyridine in place of the benzene rings have subsequently been reported.[26,27] The latter examples were produced by conversion of their amide-based precursors to thioamides *via* a thionation agent such as Lawesson's reagent.

The general reaction of unsubstituted thioamides with primary aliphatic amines *via* elimination of NH_3 is known as the Wallach reaction and dates back to 1891.[28] Since the use of mild reaction temperatures leads to high yields, the Wallach reaction is one of the major routes for the production of *N*,*N*′-disubstituted dithiooxamides. Whilst several species with terminal oxy functional groups have been synthesized,[20,29] for species containing additional non-dithiooxamide nitrogens, only compounds with tertiary amines, amides[30] or bulky alkyl group-protected[31,32] amines are reported. In each of these cases, the absence of available amine protons prevents the elimination of hydrogen sulfide and formation of oxalamidines (in the absence of an external proton source). In keeping with this, our initial attempts to synthesise a novel exo-S_2 macrocycle through reaction of a tetraamine with dithiooxamide (Scheme 3) resulted in the further elimination of two equivalents of H_2S through reaction of the secondary amines giving a non-macrocyclic product. Thus it is apparent that to be stable, macrocycles based on the dithiooxamide unit must not contain additional secondary amines and that our synthetic approach should use the alkylated, tertiary amine precursors **2a–c**.



Scheme 3 Reaction of tetraamine with dithiooxamide to give a non-macrocyclic product.

We prepared the series of tetraaza and octaaza *N*-substituted macrocyclic thioamides *via* cyclisation of the **2a–c** *N*-substituted tetraamine precursor series. Cyclisation was performed in an analogous manner to the synthesis of macrocycles **3** and the primary difference lay in the application of the Wallach reaction to the cyclisation as illustrated in Scheme 4 for the synthesis of macrocycles **5b** and **6b**. The reaction scale, dilution and addition rate were varied to determine the optimum cyclisation conditions and successful reactions generated no precipitate. Isolation of the macrocyclic products was complex since reduction of the reaction mixture to dryness repeatedly resulted in the immediate and irrecoverable decomposition of the mixture into an insoluble brown substance with release of H_2S. This problem was circumvented by addition of degassed distilled water and removal of the lower boiling methanol followed by extraction into chloroform. Column chromatography (silica/methanol) separated the macrocyclic products from the unidentified by-products. In general the ^{1}H NMR spectra were directly comparable with those of the equivalent macrocyles **3** discussed above. The $CH_2NC(S)$ chemical shift values compared well to the 3.88 ppm literature value previously observed for macrocyclic $CH_2NC(S)$.[25]

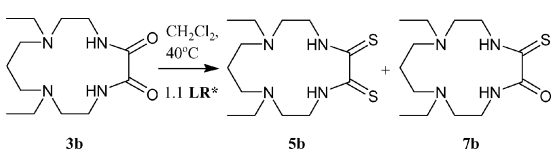


Scheme 4 Synthesis of **5b** and **6b**.

(v) Thionation of preformed macrocycle

Due to the low yields obtained for **5b** and **6b** using the cyclisation route above, we also studied the synthesis of thioamide macrocycles through thionation of the amide macrocycle **3b**. Thioamides were amongst the earliest thiocarbonyl compounds produced, by the reaction of amides and phosphorus pentasulfide at very high temperatures. The development of the more reactive species 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, known as Lawesson's reagent (**LR**),[33] made possible the thionation of a wider range of carbonyl compounds and improved thionation product yields. Lawesson's reagent is easily produced from phosphorus pentasulfide and has the advantage of solubility in boiling organic solvents such as toluene.[34] We found however that the target macrocycles **5** were temperature sensitive and a gentler thionation reagent was required. Woollins *et al.*[35] have produced a Lawesson's reagent analogue (**LR***) allowing the thionation reaction to proceed at lower/room temperatures.

Scheme 5 outlines the thionation reaction of **3b**. Only one equivalent of **LR*** is required to convert two carbonyl/amide groups since thionation is believed to proceed *via* a four-ring intermediate, either akin to the Wittig reaction mechanism or *via* a dithiophosphine ylide.[36]



Scheme 5 Thionation of **3b**.

Macrocycle **5b** was produced in 16% yield whilst **7b** was obtained in 51% yield. The successful synthesis of a finite yield of macrocycle **5b** suggested that all or most of macrocycle **7b**

would be fully converted to **5b** given sufficient time, thionation reagent and energetic input. In an effort to increase the yield of **5b**, the reaction was repeated with a greater excess of **LR*** and a stepwise gradual increase in reaction temperature. TLC monitoring showed little change in the **5b** : **7b** ratio as the temperature increased until it had reached ~100 °C (dry, degassed toluene) whereupon no **5b** was observed. Additionally, the yield of **5b** and the combined yields of **5b** and **7b** obtained with a ~60 °C reaction temperature were both lower than the yields obtained with the <40 °C reaction temperature. Evidently, a much longer reaction time at a low temperature was the only possibility for increasing the yield. The ^{1}H NMR spectrum of the reaction mixture of a larger scale reaction upon three weeks stirring at room temperature contained diagnostic peaks in a 3 H_2NC(S) : 1 CH_2NC(O) ratio suggesting a potential ~50% yield of **5b**. Only an 18% yield of **5b** was recovered after column chromatography and it is likely that some decomposition occurred during isolation of **5b**.

The 1D and 2D COSY ^{1}H NMR spectra† of **5b** and **7b** indicated that the presence of thioamides rather than amides caused a downfield shift in the associated peaks. In other respects, the ^{1}H NMR spectrum of **5b** was almost identical to that of **3b**. The 2D COSY spectrum of **5b** with low level contours is of interest due to the apparent weak connection between the CH_2NC(S) peak and a minor peak at ~1.2 ppm, typical of a thiol. The connection suggested the presence of both the dithiooxaamide and dithiol tautomer forms of **5b**. A similar connection was not observed in the 2D COSY spectrum of **7b** although a thiol peak was present, as the very low level contours were not displayed. In both cases, the thiol peaks are small and do not integrate correctly. This indicates that either **5b** preferentially exists in the thioamide tautomer form or that decomposition *via* loss of hydrogen sulfide is more facile from the thiol tautomer form. The change from exo-O_2 (**3b**) to exo-S,O (**7b**) and exo-S_2 (**5b**) was also evident through observation of the change in the ν(C=O) peak in the IR spectrum, which weakened in intensity in **7b** and disappeared entirely in **5b** as expected.

As an individual reaction step, the thionation reaction proved to be much more efficient and higher yielding than the cyclisation route. Taking into account the previous steps, both routes give similarly low yields of macrocycles **5** however a significant yield of macrocycle **7b** was achieved by this route.

Conclusions

A series of new nitrogen-donor macrocycles with exogenous oxygen and/or sulfur-donor atoms has been synthesised and fully characterised. The syntheses involved both cyclisation reactions and also modification of preformed macrocycles by alkylation or thionation. In all cases, the yield was limited by the cyclisation step. The exo-O_2 macrocycles were air stable whereas macrocycles with exo-S_2 thioamide units were found to be unstable in air. Thionation methods produced better (but still low) yields of the exo-S_2 macrocycle than the analogous cyclisation route, although the yield of the exo-O,S macrocycle was much higher and provides a convenient route to this very novel macrocycle.

The ready formation of **7b** indicates that thionation is simple in principle for these systems, however the difficulty in forming the *bis*-thioamide macrocycle with adjacent thioamide groups suggests an inherent reactivity of this motif, consistent with the isolation difficulties experienced in the preparation of **5b** and **5c** by the cyclisation route. Such instability may arise from the pseudo-*cis* geometry imposed on the sulfur atoms by the rigidity of the macrocycle and suggests that further work should focus on more flexible systems such as the N_8 macrocycles **4a–c** as these may be more readily thionated to give the *cis*-exo-S_2 product. Further work will also explore the coordination chemistry of the new macrocycles in an effort to prepare new multimetallic species.

Experimental

LR* was synthesised according to the literature procedure[35] and the purity determined by ^{1}H and ^{31}P-{^{1}H} NMR. Solvents used were distilled over standard drying agents under nitrogen before use. A Watson-Marlow 300U model peristaltic pump was used for cyclisation reactions. Silica gel for flash chromatography of 30–70 μm particle size was used for chromatographic separations. All NMR spectra were recorded using a Delta upgrade on a Jeol EX 270 MHz spectrometer. Mass spectra were recorded using positive FAB methods on a micromass Autospec Q spectrometer with a 35 keV Cs^+ primary ion beam and a 3-nitrobenzyl alcohol matrix. Infra red spectra were recorded using either a KBr pressed disc or Nujol mull on a Perkin Elmer Spectrum RX FT-IR system spectrometer. The microanalyses were carried out by Mr S Boyer of the Scientific Analysis and Consultancy Services (SACS) at the University of North London.

7,11-Diethyl-2,3-dioxo-1,4,7,11-tetraazacyclotridecane (3b)

Applying standard Schlenk techniques, 4,8-diethyl-1,4,8,11-tetraazaundecane (**2b**) (270 mg, 1.25 mmol) was dissolved in degassed ethanol (150 mL) and placed in an appropriate flask *via* cannular transfer. Dimethyl oxalate (148 mg, 1.25 mmol) was dissolved in degassed ethanol (150 mL). A pool of stirring degassed ethanol (250 mL) was then heated to reflux prior to the simultaneous drop-wise addition of the two reactant solutions *via* peristaltic pump at 40 rpm until addition was complete (~2 days). The mixture was allowed to continue refluxing for a further 4 hours then cooled. The ethanol was removed and recycled. The white residue was extracted into dry acetonitrile and any insoluble polymeric material was filtered off. The acetonitrile filtrate was evaporated to dryness and separation of the products was achieved by column chromatography (silica/methanol). 7,11-Diethyl-2,3-dioxo-1,4,7,11-tetraazacyclotridecane (118 mg, 0.44 mmol, 35%) was eluted as the third fraction (rf 0.375) as a white powder upon removal of the solvent. Analysis, calculated for $C_{13}H_{26}N_4O_2$: C 57.77, H 9.62, N 20.74%. Found: C 57.61, H 9.47, N 20.65%. ^{1}H NMR δ($CDCl_3$) ppm: 0.96 (t, 6H, NCH_2CH_3), 1.35 (m, 2H, $CH_2CH_2CH_2$), 2.29 (t, 4H, $NCH_2(CH_2)_2N$), 2.45 (q, 4H, NCH_2CH_3), 2.57 (t, 4H, $NCH_2CH_2NC(O)$), 3.26 (dt, 4H, $C(O)NHCH_2CH_2$), 9.32 (br, 2H, N*H*amide). ^{13}C{^{1}H} NMR δ($CDCl_3$) ppm: 12.22 (NCH_2CH_3), 28.89 ($NCH_2CH_2CH_2N$), 40.12 ($(O)CNCH_2$), 48.34 ($CH_3CH_2NCH_2$), 51.53 (NCH_2), 53.64 (NCH_2), 162.98 ($OCNH$). ($^+$ve FAB) *m/z*: 271 $(M)^+$, 269 $(M\text{-}2H)^+$. Accurate mass: 271.2138 $(M)^+$; calculated mass for $C_{13}H_{27}N_4O_2$: 271.2134. IR (KBr disk, cm^{-1}): 3412 m, 3012 w, 2971 m, 2938 m, 2812 m, 1675 s, 1508 s, 1466 m, 1350 m, 1270 w, 1220 m, 1189 w, 1067 m, 887 m.

8,11-Diethyl-2,3-dioxo-1,4,8,11-tetraazacyclotetradecane (3c)

5,8-Diethyl-1,5,8,12-tetraazadodecane (**2c**) (206 mg, 0.9 mmol) was cyclised with dimethyl oxalate (106 mg, 0.89 mmol) as described for macrocycle **3b**, except with a faster addition rate (36 hours). 8,11-Diethyl-2,3-dioxo-1,4,8,11-tetraazacyclotetradecane (87 mg, 0.31 mmol, 33%) was eluted as the third fraction (rf 0.42) in column chromatography (silica/methanol) and isolated as an off-white solid. ^{1}H NMR δ($CDCl_3$) ppm: 1.03 (t, 6H, NCH_2CH_3), 1.68 (m, 4H, $CH_2CH_2CH_2$), 2.54 (m, 8H, NCH_2CH_3), 2.62 (t, 4H, $NCH_2(CH_2)_2N$), 3.46 (dt, 4H, $C(O)NHCH_2CH_2$), 9.88 (br, 2H, N*H*amide). ^{13}C{^{1}H} NMR δ($CDCl_3$) ppm: 10.44 (NCH_2CH_3), 23.24 ($NCH_2CH_2CH_2N$), 41.61 ($(O)CNCH_2$), 46.84 ($CH_3CH_2NCH_2$), 50.52 (NCH_2), 55.01 (NCH_2), 161.02 ($OCNH$). ($^+$ve FAB) *m/z*: 285 $(M)^+$. Accurate mass: 285.2310 $(M)^+$; calculated mass for $C_{14}H_{29}N_4O_2$: 285.2291. IR (KBr disk, cm^{-1}): 3252 w, 3006 m, 2974 m, 2828 m, 1686 s, 1560 m, 1508 m, 1472 m, 1385 w, 1346 w, 1258 w, 1220 s, 1132 w, 1063 w, 876 m.

2,3-Dioxo-8-methyl-1,4,8,11-tetraazacyclotetradecane and 8,11-dimethyl-2,3-dioxo-1,4,8,11-tetraazacyclotetradecane (3d and 3e)

2,3-Dioxo-1,4,8,11-tetraazacyclotetradecane (94 mg, 0.4 mmol) was dissolved and stirred in absolute ethanol (3 mL). Methyl iodide (0.06 mL, 0.9 mmol) was then added *via* microsyringe and the mixture stirred at ~50 °C for 24 hours. The reaction mixture was then reduced to dryness. Column chromatography (silica/methanol) of the resultant pale yellow solid enabled separation of the products to yield:

(**3d**) 2,3-dioxo-8-methyl-1,4,8,11-tetraazacyclotetradecane (14.5 mg, 0.06 mmol, 15%) as the second fraction at rf 0.1. ^{1}H NMR δ($CDCl_3$) ppm: 1.69 (m, 4H, $CH_2CH_2CH_2$), 2.15 (s, 3H, NCH_3), 2.40 (dt, 2H, $HNCH_2CH_2N$), 2.53 (t, 2H, $HNCH_2CH_2N$), 2.83 (t, 2H, $CH_3NCH_2CH_2$), 3.47 (dt, 4H, $HNCH_2CH_2$), 8.84 (br, 1H, N*H*amine), 9.45 (br, 2H, N*H*amide). ^{13}C{^{1}H} NMR δ($CDCl_3$) ppm: 24.08 ($CH_3NCH_2CH_2CH_2N$), 27.09 ($HNCH_2CH_2CH_2N$), 40.69 (NCH_3), 41.08 ((O)$CNCH_2$), 41.27 ((O)$CNCH_2$), 46.74 (CH_3NCH_2), 50.12 ($HNCH_2$), 58.45 (NCH_2), 59.74 (NCH_2), 161.04 (O*C*NH), 161.16 (O*C*NH). ($^+$ve FAB) *m/z*: 243/1 $(M)^+$, {265 $(M + Na^+)$}. Accurate mass: 243.1827 $(M)^+$; calculated mass for $C_{11}H_{23}N_4O_2$: 243.1821. IR (KBr disk, cm^{-1}): 3397 m, 3250 w, 3006 m, 2949 m, 2848 m, 1678 s, 1558 m, 1516 m, 1464 w, 1356 w, 1120 w, 889 s.

(**3e**) 8,11-Dimethyl-2,3-dioxo-1,4,8,11-tetraazacyclotetradecane (15 mg, 0.06 mmol, 15%) as the third fraction at rf 0.35. ^{1}H NMR δ($CDCl_3$) ppm: 1.67 (m, 4H, $CH_2CH_2CH_2$), 2.19 (s, 6H, NCH_3), 2.45 (s, 4H, $N(CH_2)_2N$), 2.60 (t, 4H, $CH_3NCH_2CH_2$), 3.48 (dt, 4H, $HNCH_2CH_2$), 9.45 (br, 2H, N*H*amide). ($^+$ve FAB) *m/z*: 257 $(M)^+$. Accurate mass: 257.1972 $(M)^+$; calculated mass for $C_{12}H_{25}N_4O_2$: 257.1977. IR (KBr disk, cm^{-1}): 3251 w, 3006 m, 2899 m, 2823 m, 1684 s, 1558 m, 1508 m, 1464 m, 1348 w, 1239 w, 1129 w, 892 s.

7,10,19,22-Tetraethyl-2,3,14,15,-tetraoxo-1,4,7,10,13,16,29,22-octaazacyclo24ane (4a)

4,7-Diethyl-1,4,7,10-tetraazadecane (**2a**) (162 mg, 0.85 mmol) was cyclised with dimethyl oxalate (102 mg, 0.85 mmol) as described for macrocycles **3b** and **4b**. **4a** (45 mg, 0.086 mmol, 21%) was eluted as the third fraction (rf 0.02) in column chromatography (silica/methanol) and isolated as a pale yellow solid. ^{1}H NMR δ($CDCl_3$) ppm: 1.04 (t, 12H, NCH_2CH_3), 2.56 (s, 8H, NCH_2CH_2N), 2.61 (t, 8H, $NCH_2CH_2NC(O)$), 2.70 (q, 8H, NCH_2CH_3), 3.29 (dt, 8H, $C(O)NHCH_2CH_2$), 8.33 (br, 4H, N*H*amide). ^{13}C{^{1}H} NMR δ($CDCl_3$) ppm: 10.55 (NCH_2CH_3), 37.96 ((O)$CNCH_2$), 48.45 ($CH_3CH_2NCH_2$), 49.43 (NCH_2), 49.90 (NCH_2), 160.59 (O*C*NH). ($^+$ve FAB) *m/z*: 513 $(M)^+$, 511 $(M-2H)^+$. Accurate mass: 513.3895 $(M)^+$; calculated mass for $C_{24}H_{49}N_8O_4$: 513.3877. IR (KBr disk, cm^{-1}): 3348 w, 3255 w, 2973 m, 2812 m, 1669 s, 1518 s, 1466 m, 1350 w, 1189 w, 1094 w, 887 m.

7,11,20,24-Tetraethyl-2,3,15,16-tetraoxo-1,4,7,11,14,17,20,24-octaazacyclo26ane (4b)

4b was obtained as the [2 + 2] cyclisation product in the synthesis of **3b**. **4b** (127 mg, 0.235 mmol, 38%) eluted at rf 0.45 upon changing the chromatography system to (silica/9 MeOH : 1 NH_3 : 20 DCM). Analysis, calculated for $C_{26}H_{52}N_8O_4$: C 57.77, H 9.62, N 20.74%. Found: C 57.63, H 9.51, N 20.64%; ^{1}H NMR δ($CDCl_3$) ppm: 1.01 (t, 12H, NCH_2CH_3), 1.66 (m, 4H, $CH_2CH_2CH_2$), 2.50 (t, 8H, $NCH_2(CH_2)_2N$), 2.56 (m, 8H, NCH_2CH_3), 2.61 (t, 8H, $NCH_2(CH_2)_2NC(O)$), 3.38 (dt, 8H, $C(O)NHCH_2CH_2$), 8.07 (br, 4H, N*H*amide). ^{13}C{^{1}H} NMR δ($CDCl_3$) ppm: 11.73 (NCH_2CH_3), 24.80 ($NCH_2CH_2CH_2N$), 37.24 ((O)$CNCH_2$), 48.08 ($CH_3CH_2NCH_2$), 51.09 (NCH_2), 51.34 (NCH_2), 159.84 (O*C*NH). ($^+$ve FAB) *m/z*: trace 811 $(M [3 + 3])^+$, 541 $(M [2 + 2])^+$, 539 $(M-2H)^+$. Accurate mass: 541.4209 $(M)^+$; calculated mass for $C_{26}H_{53}N_8O_4$: 541.4190. IR (KBr disk, cm^{-1}): 3396 w, 3309 w, 2972 m, 2821 m, 1672 s, 1507 s, 1458 m, 1374 w, 1260 w, 1211 m, 1090 w, 1008 w, 860 s.

8,11,22,25-Tetraethyl-2,3,15,16-tetraoxo-1,4,8,11,15,18,22,25-octaazacyclo28ane (4c)

4c was obtained as the [2 + 2] cyclisation product in the synthesis of **3c**. **4c** (32 mg, 0.058 mmol, 13%) eluted as the first fraction upon changing the chromatography system to (silica/9 MeOH : 1 NH_3). ^{1}H NMR δ($CDCl_3$) ppm: 1.01 (t, 12H, NCH_2CH_3), 1.79 (m, 4H, $CH_2CH_2CH_2$), 2.54 (m, 24H, $NCH_2CH_{2/3}$), 3.32 (dt, 8H, $C(O)NHCH_2CH_2$), 9.47 (br, 4H, N*H*amide). ^{13}C{^{1}H} NMR δ($CDCl_3$) ppm: 10.97 (NCH_2CH_3), 24.52 ($NCH_2CH_2CH_2N$), 40.47 ((O)$CNCH_2$), 47.94 ($CH_3CH_2NCH_2$), 50.97 (NCH_2), 54.63 (NCH_2), 159.65 (O*C*NH). ($^+$ve FAB) *m/z*: 569 $(M)^+$, 567 $(M-2H)^+$. Accurate mass: 569.4490 $(M)^+$; calculated mass for $C_{28}H_{57}N_8O_4$: 569.4502. IR (KBr disk, cm^{-1}): 3395 m, 3328 m, 2971 m, 2820 m, 1668 s, 1517 s, 1471 m, 1374 w, 1212 s, 1184 w, 1071 w, 846 m.

7,11-Diethyl-2,3-dithio-1,4,7,11-tetraazacyclotridecane (5b) (cyclisation route)

Applying standard Schlenk techniques, 4,8-diethyl-1,4,8,11-tetraazanonane (**2b**) (200 mg, 0.926 mmol) was dissolved in degassed dry methanol (140 mL) and placed in an appropriate flask *via* cannular transfer. Dithiooxamide (111 mg, 0.926 mmol) was dissolved in degassed dry methanol (150 mL). A pool of stirring degassed dry methanol (250 mL) was then heated to reflux prior to the simultaneous drop-wise addition of the two reactant solutions *via* peristaltic pump until addition was complete (~24 hours). The mixture was allowed to cool and stirred for a further 3 days. The volume of methanol was reduced to ~30 mL, degassed distilled water (120 mL) added and the remaining methanol removed under vacuum. The products were extracted into chloroform (~300 mL), then the volume of chloroform was reduced to ~5 mL. Separation of the products was achieved by column chromatography (silica/methanol). 7,11-Diethyl-2,3-dithio-1,4,7,11-tetraazacyclotridecane (15.0 mg, 0.05 mmol, 5.4%) was eluted as the third fraction (rf 0.43) as an air sensitive orange powder upon removal of the solvent and drying under vacuum. ^{1}H NMR δ($CDCl_3$) ppm: 0.98 (t, 6H, NCH_2CH_3), 1.32 (m, 2H, $CH_2CH_2CH_2$), 2.24 (t, 4H, $NCH_2(CH_2)_2N$), 2.48 (q, 4H, NCH_2CH_3), 2.73 (t, 4H, $NCH_2CH_2NC(S)$), 3.74 (t, 4H, $C(S)NHCH_2CH_2$). ($^+$ve FAB) *m/z*: 325 $(M + Na)^+$, 303 $(M)^+$. IR (KBr disk, cm^{-1}): 3255 w, 2970 s, 2812 m, 1558 m, 1540 m, 1521 s, 1458 m, 1396 w, 1338 w, 1084 w, 920 m, 898 m.

8,11-Diethyl-2,3-dithio-1,4,8,11-tetraazacyclotetradecane (5c)

5,8-Diethyl-1,5,8,12-tetraazadodecane (**2c**) (150 mg, 0.65 mmol) in degassed absolute ethanol (160 mL) and dithiooxamide (78 mg, 0.65 mmol) in degassed absolute ethanol (160 mL) were cyclised *via* peristaltic pump addition as described for macrocycles **5b** and **6b**. The air sensitive orange-brown solid, 8,11-diethyl-2,3-dithio-1,4,8,11-tetraazacyclotetradecane (12.3 mg, 0.04 mmol, ~7%), was eluted as the first fraction (rf 0.45) in column chromatography (silica/methanol) after elution of unreacted material (silica/ethanol). ^{1}H NMR δ($CDCl_3$) ppm: 1.03 (t, 6H, NCH_2CH_3), 1.68 (m, 4H, $CH_2CH_2CH_2$), 2.52 (s, 4H, NCH_2CH_2N), 2.56 (q, 4H, NCH_2CH_3), 2.61 (t, 4H, $NCH_2(CH_2)_2N$), 3.48 (dt, 4H, $C(S)NHCH_2CH_2$), 9.93 (br, 2H, N*H*thioamide). ($^+$ve FAB) *m/z*: 283 $(M-SH_2)^+$; (CI, ammonium) *m/z*: 421, 285 $(M-S)^+$, 255 $(M-2S)^+$.

7,11,20,24-Tetraethyl-2,3,15,16-tetrathio-1,4,7,11,14,17,20,24-octaazacyclo26ane (6b)

6b was obtained as the [2 + 2] cyclisation product in the synthesis of **5b**. **6b** (19 mg, 0.032 mmol, 7%) eluted as the fourth fraction at rf 0.25 in column chromatographic separation of the product mixture (silica/methanol). Analysis, calculated for $C_{26}H_{52}N_8S_4$:

C 51.66, H 8.61, N 18.54%. Found: C 51.81, H 8.74, N 18.65%. ^{1}H NMR δ($CDCl_3$) ppm: 1.02 (t, 12H, NCH_2CH_3), 1.77 (m, 4H, $CH_2CH_2CH_2$), 2.56 (m, 12H, $NCH_2CH_{2/3}$), 2.61 (t, 8H, $NCH_2CH_2NC(S)$), 3.62 (dt, 8H, $C(S)NHCH_2CH_2$), 10.61 (br, 4H, N*H*thioamide). ($^+$ve FAB) *m*/*z*: 605 $(M)^+$, 603 $(M\text{-}2H)^+$, trace 549. IR (KBr disk, cm^{-1}): 3187 m, 2962 m, 2928 s, 2855 m, 1653 w, 1522 m, 1458 m, 1377 m, 1312 w, 1261 m, 1094 m, 1017 w, 858 m.

7,11-Diethyl-2,3-dithio-1,4,7,11-tetraazacyclotridecane (5b) and 7,11-diethyl-2-oxo-3-thio-1,4,7,11-tetraazacyclotridecane (7b) (thionation route)

Applying standard Schlenk techniques, freshly prepared[35] 2,4-bis(3-*tert*-butyl-4-methoxyphenyl) 1,3,2,4-dithiadiphosphetane-2,4-disulfide (**LR***) (56 mg, 0.1 mmol) and 7,11-diethyl-2,3-dioxo-1,4,7,11-tetraazacyclotridecane (**3b**) (27 mg, 0.1 mmol) were dissolved in dry degassed DCM (3 mL). The mixture was stirred at room temperature for 3 days and monitored by TLC (silica/methanol). The mixture was then heated at 40 °C for 3 hours without causing any apparent change. After a further 24 hours stirring at room temperature, a new spot appeared in the TLC trace. Column chromatography (silica/methanol) of the reaction mixture eluted **5b** (5.1 mg, 0.017 mmol, 16%) at rf 0.48 and **7b** (14.6 mg, 0.051 mmol, 51%) at rf 0.32. Both **5b** and **7b** were air sensitive yellow-orange solids that had to be dried under vacuum and stored under nitrogen.

Both longer periods of heating at <40 °C and longer periods of stirring at room temperature increased the proportion of **5b** produced (acc. to ^{1}H NMR) but higher yields were not obtained due to gradual decomposition with loss of H_2S during column chromatography to generate a reddish band at rf 0.1.

5b. ^{1}H NMR δ($CDCl_3$) ppm: as listed for cyclisation route plus 9.25 (br, 2H, N*H*C(S)) and 1.25 (t, trace, S*H*). ($^+$ve FAB) *m*/*z*: 303 $(M)^+$. Accurate mass: 303.1670 $(M)^+$, calculated mass for $C_{13}H_{26}N_4S_2$: 303.1677

7b. ^{1}H NMR δ($CDCl_3$) ppm: 0.96 (dt, 6H, NCH_2CH_3), 1.25 (s, trace, S*H*), 1.34 (m, 2H, $CH_2CH_2CH_2$), 2.27 (t, 4H, $NCH_2(CH_2)_2N$), 2.43 (dq, 4H, NCH_2CH_3), 2.60 (t, 4H, $NCH_2CH_2NC(O)$), 2.73 (t, 4H, $NCH_2CH_2NC(S)$), 3.27 (dt, 4H, $C(O)NHCH_2CH_2$), 3.74 (t, 4H, $C(S)NHCH_2CH_2$), 7.67 (br, 2H, N*H*C(O)), 9.26 (br, 2H, N*H*C(S)). ($^+$ve FAB) *m*/*z*: 287 $(M)^+$. Accurate mass: 287.1912 $(M)^+$, calculated mass for $C_{13}H_{26}N_4OS$: 287.1906. IR (KBr disk, cm^{-1}): 3429 w, 3350 w, 3255 w, 2968 m, 2812 m, 1676 m, 1514 m, 1460 w, 1396 w, 1350 w, 1262 s, 1097 m, 1016 m, 909 m.

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