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Figure-of-eight Shaped Metal-free Amide-containing Schiff-base Macrocycles and Two Dicobalt(III) Amide Complexes

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Two 36-membered (2+2) Schiff-base macrocycles have been prepared and characterised without the use of template ions or high dilution techniques. Rather, intramolecular hydrogen-bonding and $\pi-\pi$ interactions promote the isolation of these 'figure-of-eight' products in good yields. Two cobalt(III) complexes of the 18-membered (1+1) Schiff-base macrocycles are formed when cobalt(II) is used as a template. The structures of one 'figure-of-eight' metal-free (2+2) macrocycle and of one dicobalt(III) complex of a (1+1) macrocycle, in which the cobalt centres are octahedral, are presented. $[H_4L1tBu]_2$: $C_{70}H_{70}N_8O_9$, space group P−1, $a = 7.747(1)$, $b = 17.106(3)$, $c = 23.662(4)$ Å, $\alpha = 104.83(3)$, $\beta = 95.86(3)$, $\gamma = 97.80(3)°$, $U = 2972.4(8)$ Å^3, $Z = 2$, $D_c = 1.30$ g cm^{-3}, T = 100 K, 554 parameters, R1 = 0.072 [for 4137 reflections having F > 4[(F)], wR2 = 0.191 and goodness of fit 0.97 (for all 8343 independent F^2 data). $[Co_2(L1tBu)(OAc)_2(pyridine)]$ 1.5DMF 0.5MeCN, $C_{47.5}H_{49}N_7O_{9.5}Co_2$, space group P2(1)/n, $a = 13.067(2)$, $b = 26.071(4)$, $c = 14.023(3)$ Å, $\beta = 93.02(1)°$, $U = 4770.6(15)$ Å^3, $Z = 4$, $D_c = 1.38$ g cm^{-3}, T = 168 K, 622 parameters, R1 = 0.075 [for 5233 reflections having F > 4[(F)], wR2 = 0.133 and goodness of fit 1.08 (for all 8512 independent F^2 data).

Keywords: Amide; Imine; Metal-free; Cobalt; Hydrogen-bonding; $\pi-\pi$ interactions

INTRODUCTION

Schiff-base macrocycles are not generally stable metal-free so the vast majority are formed around a metal template ion and isolated as the resulting metal complex [1]. On occasion, as demonstrated by Robson and co-workers [2], protons can used as the template moiety in the Schiff-base condensation, and the protonated macrocycle isolated [3]. It is not common to isolate neutral metal-free Schiff-base macrocycles [4], as this usually relies on the presence of special factors, for example intramolecular hydrogen-bonding, controlling the conformational preferences [5]. The use of hydrogen-bonding and/or $\pi-\pi$ interactions to control molecular architecture is now widespread [6]. Here we employ both of these types of interactions to facilitate the formation and isolation of two new, large Schiff-base macrocycles, from 'head' and 'lateral' groups which contain both aromatic moieties and hydrogen bond

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acceptors/donors. The macrocycles have been designed to contain a combination of interesting donor atoms for the coordination of two or more metal ions. Specifically, both amide [7] and phenol groups, both of which are well known to stabilise metal ions in high oxidation states, are provided [8].

We have previously reported the copper and nickel coordination chemistry of the dinucleating acyclic and (1 + 1) macrocyclic ligands, **H_3L1**, **H_3L2**, **H_4L1*t*Bu**, **H_4L2*t*Bu** and **H_4L2DFPh** (Fig. 1) [9]. This paper details the synthesis and characterisation of two large (2 + 2), potentially tetranucleating, metal-free amide macrocycles **$[H_4L1tBu]_2$** and **$[H_4L2tBu]_2$** and the cobalt coordination chemistry of the smaller (1 + 1) ligands **[H_4L1*t*Bu]** and **[H_4L2DFPh]** (Fig. 1). The cyclisation of the **H_3L1** or **H_3L2** ligands with several different dicarbonyl head units, either in the absence or presence of metal ions gives rise to the macrocycles or to their bimetallic complexes respectively (Fig. 1). These macrocycles have amide and phenolate donors and thus provide an opportunity to stabilise metal ions in high oxidation states. The synthesis and characterisation of these macrocycles and complexes is discussed and the results obtained are compared to other systems. In addition the

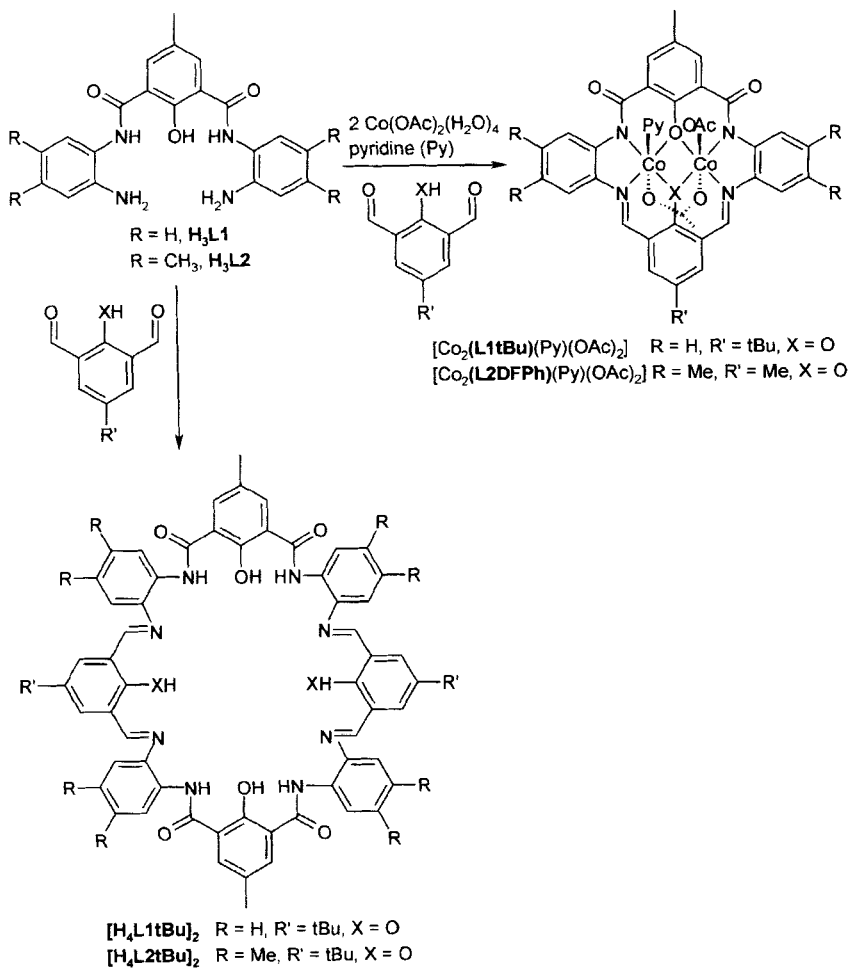

FIGURE 1 Synthesis of the ligands and complexes.

crystal structure of a metal-free macrocycle **[H_4L1*t*Bu]$_2$** and a dicobalt(III) macrocyclic complex [Co_2(**L1*t*Bu**)(OAc)$_2$(pyridine)] are presented.

RESULTS AND DISCUSSION

Non-template Synthesis of Macrocycles Derived from H_3L1 and H_3L2

The direct reaction of the acyclic **H_3Lj** (j = 1 or 2) 'lateral' components [9] with the 'head' units 2,6-diformyl-4-methylphenol, 4-*t*-butyl-2,6-diformylphenol and S-(2,6-diformyl-4-methylphenyl)-dimethylthiocarbamate respectively, in IPA, yielded six yellow solid products (Fig. 1). Of these, only the two obtained by using 4-*t*-butyl-2,6-diformylphenol showed any appreciable solubility in common organic solvents, so only these products, **[H_4L1*t*Bu]$_2$** and **[H_4L2*t*Bu]$_2$**, were investigated further. Cyclisations were also attempted with the diketones 2,6-diacetyl-4-methylphenol and 2,6-dibenzoyl-4-methylphenol with the aim of preparing macrocycles of greater solubility. However, when the cyclisations were carried out with these ketones, under exactly the same conditions as those used for the aldehydes, no reaction occurred. This is not an unusual observation and is probably due to a combination of unfavourable steric interactions and the differing reactivity of aldehydes *vs.* ketones leading to differing stability of the resulting imine bonds [10].

The large (2 + 2) Schiff-base macrocycles **[H_4L1*t*Bu]$_2$** and **[H_4L2*t*Bu]$_2$** (Fig. 1) are prepared, in good yields (70–80%), without the use of a template metal ion(s) or high dilution conditions. The success of these two cyclisation reactions can attributed to the preorganisation of the components and to the low solubility of the desired macrocyclic product (draining the reaction equilibrium in the desired direction). Hydrogen-bonding within the **H_3Lj** (j = 1 or 2) 'lateral' components is expected to hold these components in a fairly flat conformation ready for cyclisation with the 4-*t*-butyl-2,6-diformylphenol 'head' units.

The infrared spectra of the two macrocycles, **[H_4L1*t*Bu]$_2$** and **[H_4L2*t*Bu]$_2$**, were consistent with successful cyclisation: in both cases the carbonyl stretch of the aldehyde precursor is absent and a new band present at $\sim 1630\,cm^{-1}$ is consistent with imine formation. In addition the amide and amine N–H stretch region ($3100-3400\,cm^{-1}$) has simplified upon cyclisation with only one sharp band, at $\sim 3280\,cm^{-1}$, remaining, due to the amide N–H stretch. The Amide I band is $10-20\,cm^{-1}$ higher in energy for the macrocycles than for the acyclic precursors, **H_3Lj** (j = 1, 2).

Both (2 + 2) macrocycles have interesting NMR spectra in that the symmetry is reduced, consistent with a folded structure, as opposed to the relatively flat (and hence likely higher symmetry) structure that would be expected for the (1 + 1) analogues [11, 12]. The ^{1}H NMR spectrum of **[H_4L2*t*Bu]$_2$** in $CDCl_3$ is shown as a representative example (Fig. 2). It can be seen that there are separate signals for half, rather than a quarter, of the atoms in the **[H_4L2*t*Bu]$_2$** macrocycle. This reduced symmetry, which contrasts with the symmetry seen in the NMR spectra of the **H_3Lj** (j = 1, 2) precursors [9], is also observed in the ^{13}C NMR spectra, and is consistent with the 'figure-of-eight' conformation observed in the solid state (vide infra) being maintained in chloroform solution. This also indicates that both complexes are (2 + 2) macrocycles, as opposed to (1 + 1) macrocycles, as the smaller systems would not be expected to be able to exist in such a conformation.

A vapour pressure osmometry measurement carried out on **[H_4L2*t*Bu]$_2$**, in chloroform, found the molar mass to be ca. 1300, indicating that the (2 + 2) macrocycle was present in solution. **[H_4L1*t*Bu]$_2$** was too insoluble in suitable volatile solvents (it is soluble in both pyridine and DMF but unfortunately these solvents are unsuitable for this technique for two reasons: their low

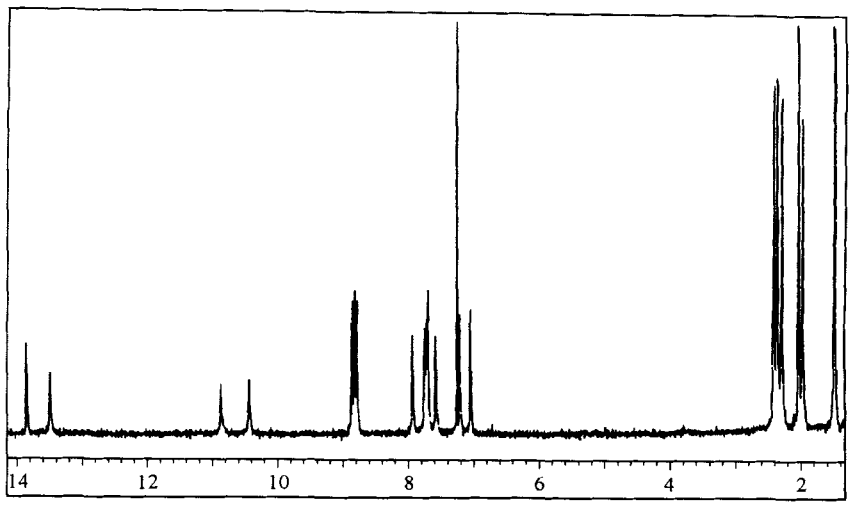

FIGURE 2 ^{1}H NMR spectrum of **[H$_4$L2*t*Bu]$_2$** in $CDCl_3$.

vapour pressures and the fact that they dissolve the rubber seals of the equipment) for its molar mass to be estimated by this method.

The solution and solid state (vide infra) evidence is consistent with these being (2 + 2), not (1 + 1), macrocycles. However, the FAB mass spectra of the macrocycles are inconsistent with this, instead indicating that they are (1 + 1) macrocycles. This conflicts with both the NMR data and the definitive crystal structure obtained for **[H$_4$L1*t*Bu]$_2$**, both of which show the compound to be a (2 + 2) macrocycle. The inconsistent FAB mass spectra results are therefore presumed to be due to the macrocycles fragmenting substantially before detection.

Structure of [H$_4$L1*t*Bu]$_2$

The X-ray structure of **[H$_4$L1*t*Bu]$_2$** revealed that it is indeed a (2 + 2) macrocycle (Figs. 3 and 4). Instead of one molecule of **H$_3$L1** having condensed with one molecule of 4-*t*-butyl-2,6-diformylphenol to form a (1 + 1) diphenol macrocycle, rather *two* molecules of **H$_3$L1** had condensed with *two* molecules of 4-*t*-butyl-2,6-diformylphenol to form a (2 + 2) tetraphenol macrocycle. The overall structure of the macrocycle resembles a 'figure-of-eight'. The key to this conformation is that within each phenol diamide moiety of the macrocycle (shown with solid bonds; the 'head' units are shown with hollow bonds) the two amide groups are in two different conformations; one has a *cis* relationship between the amide oxygen atom and the phenol oxygen atom whilst the other has a *trans* relationship. This feature facilitates an extensive hydrogen-bonding array and also allows the macrocycle to fold back over itself to form favorable $\pi - \pi$ interactions (Fig. 4).

The hydrogen-bonding network within the macrocycle **[H$_4$L1*t*Bu]$_2$** is of particular interest as it plays an important role in templating the formation of this macrocycle. All of the phenol and amide protons were located from a difference map and each of these protons is hydrogen bonded to an adjacent nitrogen or oxygen atom (Figs. 3 and 4). The phenol proton on O(7) of the 4-*t*-butyl-2,6-diiminophenol group is hydrogen bonded to N(6), an imine nitrogen atom, whilst the other imine nitrogen atom of this group, N(7), is hydrogen bonded to the amide proton of N8. To facilitate this, the amide nitrogen atom, N(8), is *trans* to the phenol oxygen atom, O(1). The oxygen atom of this *trans* amide, O(8), is hydrogen bonded to the phenol proton on O(1). In turn, this oxygen

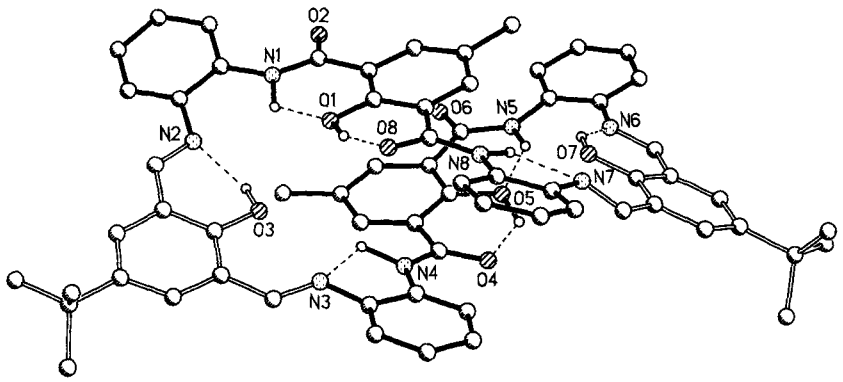

FIGURE 3 Perspective view of the $[H_4L1tBu]_2$ macrocycle. Only the hydrogen atoms involved in the hydrogen-bonding network are shown. Selected interatomic distances (Å) and angles (°): O(1)—C(1) 1.354(5), C(2)—C(79) 1.486(6), C(6)—C(8) 1.502(6), C(8)—O(2) 1.229(5), C(8)—N(1) 1.371(6), N(1)—C(9) 1.416(6), C(10)—N(2) 1.428(6), N(2)—C(17) 1.291(6), O(3)—C(19) 1.357(6), C(29)—N(3) 1.273(6), N(3)—C(31) 1.423(6), C(32)—N(4) 1.407(6), N(4)—C(39)1.363(6), C(39)—O(4) 1.254(6), C(39)—C(42)1.479(6), O(5)—C(41) 1.359(5), C(46)—C(48) 1.520(7), C(48)—O(6) 1.221(5), C(48)—N(5) 1.365(6), N(5)—C(49) 1.416(6), C(50)—N(6) 1.432(6), N(6)—C(57) 1.295(6), O(7)—C(59) 1.352(5), C(69)—N(7) 1.281(5), N(7)—C(71) 1.425(6), C(72)—N(8) 1.401(6), N(8)—C(79) 1.364(6), C(79)—O(8) 1.241(5), O(1)···O(8) 2.4962(45), O(1)···N(1) 2.683(49), O(3)···N(2) 2.6852(49), N(3)···N(4) 2.5796(55), O(4)···O(5) 2.4965(48), O(5)···N(5) 2.6221(51), O(7)···N(6) 2.6696(49), N(7)···N(8) 2.5876(55), O(2)—C(8)—N(1) 123.0(5), O(2)—C(8)—C(6) 120.9(5), N(1)—C(8)—C(6) 116.1(4), C(8)—N(1)—C(9) 126.1(4), C(17)—N(2)—C(10) 120.2(4), C(29)—N(3)—C(31) 121.2(4), C(39)—N(4)—C(32) 128.8(4), O(4)—C(39)—N(4) 121.1(5), O(4)—C(39)—C(42) 122.1(5), N(4)—C(39)—C(42) 116.8(4), O(6)—C(48)—N(5) 124.5(5), O(6)—C(48)—C(46) 120.6(5), N(5)—C(48)—C(46) 114.9(5), C(48)—N(5)—C(49)127.7(4), C(57)—N(6)—C(50) 119.1(4), C(69)—N(7)—C(71) 120.0(4), C(79)—N(8)—C(72) 128.9(4), O(8)—C(79)—N(8) 120.9(5), O(8)—C(79)—C(2) 121.3(5), N(8)—C(79)—C(2) 117.8(4).

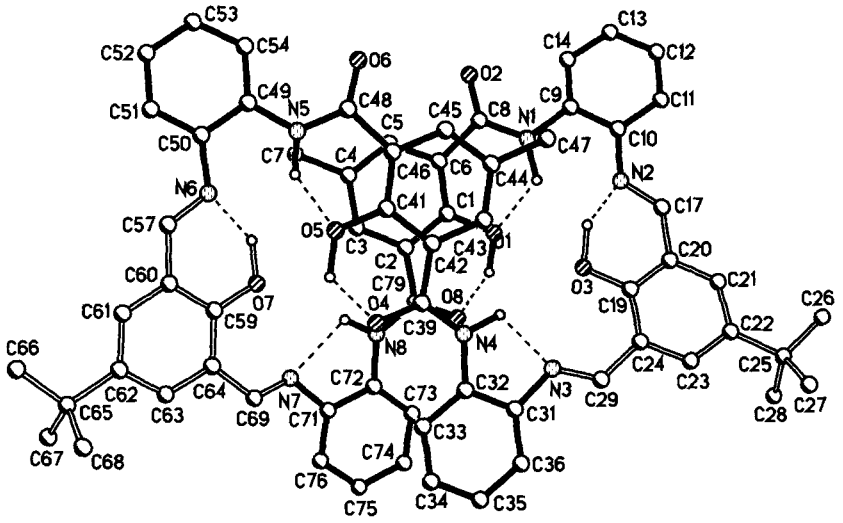

FIGURE 4 Perspective view of $[H_4L1tBu]_2$ through the mean plane of the C1-to-C6 aromatic ring.

atom, O(1), is hydrogen bonded to the amide proton of N(1). The same pattern of hydrogen-bonding is observed in the other half of the macrocycle.

There are $\pi-\pi$ interactions within the macrocycle (Fig. 4) and also between stacked macrocycles in the crystal lattice. The intramolecular π-bonding occurs between the two

diamidophenol units: the phenyl ring mean planes (C1 to C6 *vs.* C41 to C46) intersect at 2.0(2)° and they are separated by 3.294(7)–3.350(7) Å, typical values for a parallel offset $\pi-\pi$ interaction [6].

The 'figure-of-eight' conformation of the macrocycle is different to the structures of other previously characterised tetraphenol macrocycles which usually have the phenol groups pointing into the centre of a bowl-like structure. For example, a (4+4) octaamine macrocycle, prepared from the magnesium templated condensation of four equivalents of 1,2-diaminoethane and four equivalents of 2,6-diformyl-4-methylphenol followed by reduction of the imine bonds with sodium borohydride, had a calculated minimum energy conformation in which the four phenol groups were pointing towards each other in a bowl-like conformation [13]. However, in this octaamine macrocycle the links between each phenol ring are very flexible, as is shown by the uncomplicated ^{1}H NMR spectrum of the molecule, so there are many conformations which are energetically possible for this macrocycle. Another example of a tetraphenol macrocycle is the calixarenes in which there is only a methylene spacer between the phenol groups [14]. The calixarenes also have a bowl-like conformation. In **[H_4L1*t*Bu]$_2$**, the planarity of the *o*-phenylene linkages and the amide/imine groups, along with the hydrogen-bonding and $\pi-\pi$ interactions, determines the conformation and size of **[H_4L1*t*Bu]$_2$**. Together these three factors prevent the macrocycle having a bowl-like conformation, and in the absence of metal ions disfavour (1+1) macrocycle formation. Consistent with this is the fact that a macrocycle related to **[H_4L1*t*Bu]$_2$**, with the key differences being that it has 1,3-diaminopropane groups instead of 1,2-diaminobenzene groups and that the imine bonds have been reduced to amine bonds, does have a (1+1) structure [15].

Dicobalt(III) Macrocyclic Complexes

Two dicobalt(III) macrocyclic complexes with amide and phenolate donors, [Co_2(**L1*t*Bu**)(OAc)$_2$(pyridine)] · 2DMF and [Co_2(**L2DFPh**)(OAc)$_2$(pyridine)] · 2H_2O, have been successfully isolated and characterised (Fig. 1). The method used to synthesise these complexes was similar to that used to make the dicopper(II) and dinickel(II) macrocyclic complexes [9], and involved the dropwise addition of a pyridine solution of **H_3L1** or **H_3L2** to a green refluxing pyridine solution of cobalt(II) acetate and the appropriate dialdehyde 'head' unit, in air. A brown solution immediately formed but unlike the copper(II) and nickel(II) ion reactions the product did not precipitate from the reaction solution. Removal of the solvent *in vacuo* gave a red-brown residue which was taken up in DMF and diffused with diethylether to give the desired complex. Whilst similar observations were obtained for the reactions involving the template synthesis of the other ligands, **H_4L1DFPh** and **H_4L2*t*Bu**, no pure products were isolated. The only other dicarbonyl 'head' unit which was tried was S-(2,6-diformyl-4-methyl)-dimethylthiocarbamate and while encouraging colour changes were observed again no pure products were isolated.

The infrared spectra of the dicobalt complexes show that there are no amine or amide N–H stretches and no carbonyl stretches, that an imine stretch is present ($\sim$1616 cm^{-1}) and that the Amide I band has moved to lower wavenumbers than in the **H_3Lj** (j = 1 or 2) precursors. Thus there has been amide deprotonation and coordination, as well as ring closure. Both complexes contained solvent: [Co_2(**L1*t*Bu**)(OAc)$_2$(pyridine)] · 2DMF had a band at 1669 cm^{-1} which is consistent with the presence of DMF whilst [Co_2(**L2DFPh**)(OAc)$_2$(pyridine)] · 2H_2O had a broad band centred at 3420 cm^{-1} which is consistent with the presence of water. In both cases this was subsequently

confirmed by microanalysis results. The binding modes of the acetate ions could not be distinguished from the infrared spectra as there are too many bands in the region of interest, 1300–1600 cm^{-1} [16].

Both complexes contain cobalt in the +3 oxidation state and not the +2 oxidation state that was present initially. The cobalt(III)/(II) redox couple is very sensitive to the ligands coordinated to the metal centre. With amine and/or amide donors the redox potential is usually sufficiently low to allow aerial oxidation of cobalt(II) to cobalt(III) [17].

The FAB mass spectrum of $[Co_2(\mathbf{L1}t\mathbf{Bu})(OAc)_2(pyridine)] \cdot 2DMF$ is consistent with the complex being of the (1+1), and not the (2+2), macrocycle, as observed for the analogous dinickel(II) and dicopper(II) complexes [9]. Although this data can not be taken as conclusive evidence regarding macrocycle size (see above), in this case the results are consistent with the solid state structure (vide infra).

The UV/vis spectra of both cobalt(III) complexes, $[Co_2(\mathbf{L1}t\mathbf{Bu})(OAc)_2(pyridine)]$ and $[Co_2(\mathbf{L2DFPh})(OAc)_2(pyridine)]$, are totally dominated by intense charge transfer bands. Two intense bands are observed at 422 nm (13600) and 322 nm (34000) for the former complex and 430 nm (15200) and 325 nm (38000) for the latter complex. For low spin cobalt(III) ions two spin allowed d–d transitions are expected in the visible region [8], however the bands observed are too intense to be d–d transitions. The d–d bands, with an expected intensity of less than 100 $dm^3 mol^{-1} cm^{-1}$, are presumed to be obscured by these intense charge transfer bands.

The ^1H NMR spectra of these diamagnetic dicobalt(III) complexes, $[Co_2(\mathbf{L1}t\mathbf{Bu})(OAc)_2(pyridine)]$ and $[Co_2(\mathbf{L2DFPh})(OAc)_2(pyridine)]$, were investigated in d_7-DMF. The ^1H NMR spectra for the two complexes are very similar: the most interesting feature is that in both cases two different signals are observed for the methyl groups of the acetate groups {$\delta = 1.35$ ppm and $\delta = 0.72$ ppm in $[Co_2(\mathbf{L1}t\mathbf{Bu})(OAc)_2(pyridine)]$; $\delta = 1.36$ ppm and $\delta = 0.72$ ppm in $[Co_2(\mathbf{L2DFPh})(OAc)_2(pyridine)]$}. This shows that the two complexes have very similar structures in solution, and that there are two different binding modes for the two acetate groups in each complex [18,19].

Structure of $[Co_2(\mathbf{L1}t\mathbf{Bu})(OAc)_2(pyridine)]$

The X-ray structure of $[Co_2(\mathbf{L1}t\mathbf{Bu})(OAc)_2(pyridine)]$ shows that the macrocycle is indeed a (1+1) macrocycle (Fig. 5). That is, it is half the size of the (2+2) macrocycle $\mathbf{[H_4L1}t\mathbf{Bu]_2}$ (Figs. 3 and 4). Within the macrocycle cavity are two octahedral cobalt(III) ions which are bridged by the two phenolate oxygen atoms: the Co(1)···Co(2) distance is 2.8115(14) Å. Each cobalt(III) ion is also coordinated to an imine nitrogen atom and a deprotonated amide nitrogen atom from the macrocycle. The $Co-N_{amide}$ bond lengths are similar to those observed in a complex which has the same five-atom *o*-phenylene diamine containing chelate ring [$Co-N_{amide} = 1.877(4)$ Å] [20] and are shorter than those observed in complex which does not have these conformationally constrained rings [$Co-N_{amide} = 1.917(4)$ Å] [17]. Other ligands to the cobalt(III) ions are a 1,3-bridging acetate ion, a monodentate acetate ion and a pyridine molecule. The two cobalt(III) ions have different coordination environments with Co(1) being coordinated to the four macrocyclic donors, a pyridine nitrogen atom and an oxygen atom from the bidentate acetate while Co(2) is coordinated to the four macrocyclic donors and two oxygen atoms, one from the 1,3-bridging bidentate acetate and one from the monodentate acetate ion. The pyridine molecule and the non-bridging acetate ion occupy one side of the macrocycle while the 1,3-bridging acetate ion occupies the other side. The two acetate anions are different as expected from the

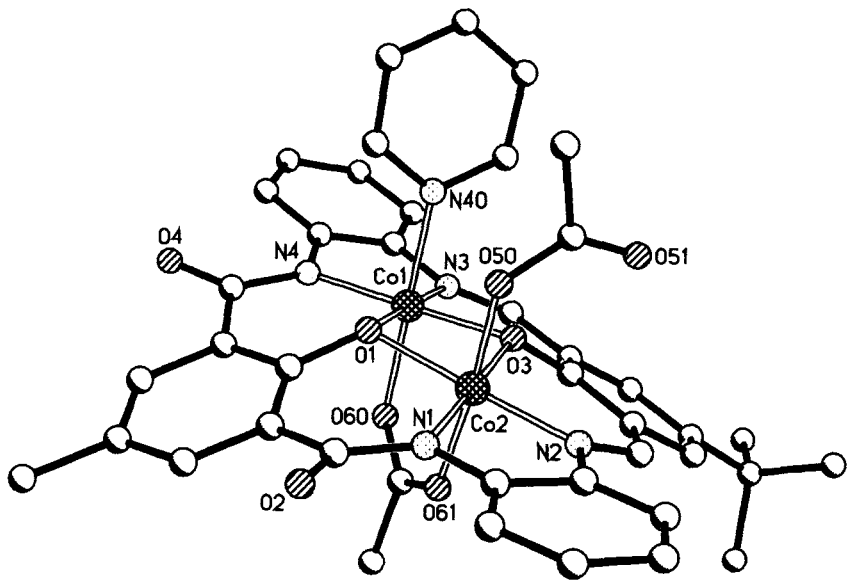

FIGURE 5 Perspective view of $[Co_2(\mathbf{L1}t\mathbf{Bu})(OAc)_2(pyridine)]$. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Co(1)—N(4) 1.853(5), Co(1)—O(3) 1.881(4), Co(1)—N(3) 1.885(5), Co(1)—O(1) 1.903(4), Co(1)—O(60) 1.909(5), Co(1)—N(40) 1.943(6), Co(1)···Co(2) 2.8115(14), Co(2)—N(2) 1.838(6), Co(2)—N(1) 1.877(6), Co(2)—O(1) 1.892(4), Co(2)—O(50) 1.898(5), Co(2)—O(3) 1.906(5), Co(2)—O(61) 1.919(5), O(3)—Co(1)—O(1) 83.12(19), O(3)—Co(2)—O(3) 82.76(19), Co(1)—O(1)—Co(2) 95.6(2), Co(1)—O(3)—Co(2) 95.9(2).

^{1}H NMR study; one is monodentate whilst the other is bidentate and bridges the two cobalt(III) ions. The Co—O bond lengths to the bridging acetate oxygen atoms are longer than those for the non-bridging acetate oxygens. The compromise required of the bridging acetate ion is also mirrored in the O—C=O bond angles, *viz.* O(60)—C(60)—O(61) = 127.8(6)° compared to O(50)—C(50)—O(51) = 112.2(6)°.

The macrocycle is quite bent, despite the extensive conjugation (Figs. 1 and 5). Presumably this is caused by the constraint of the 1,2-diaminobenzene groups holding the macrocycle components in very close proximity to one another, causing a range of unfavorable steric interactions which are alleviated by adopting this non-planar conformation. This strain is reflected in the fact that, when this macrocycle is prepared free of the metal ions a (2+2), not (1+1), macrocycle is formed (Figs. 1,3 and 4).

CONCLUSIONS

The diamide-containing two armed ligands $\mathbf{H_3L1}$ and $\mathbf{H_3L2}$ have been used as building blocks for the synthesis of two 36-membered metal-free macrocycles, and of two dicobalt(III) macrocyclic complexes which contain deprotonated amide and phenol donors. As anticipated these octahedral cobalt complexes are more soluble than the square planar nickel and copper complexes were [9]. The coordination of these macrocycles to other transition metal ions such as manganese and vanadium (which have well known higher oxidation states) [21] should be explored.

The formation of the large metal-free macrocycles, $\mathbf{[H_4L1}t\mathbf{Bu]_2}$ and $\mathbf{[H_4L3}t\mathbf{Bu]_2}$, without using high dilution conditions or a metal template ion(s) is a very promising development. These ligands should readily afford tetranuclear transition metal complexes once the hydrolysable imine bonds have been reduced

to amine bonds. The combination of strongly electron-donating amides and phenolates may well enhance the properties and chemistry of the resulting complexes over that observed for their non-amide-containing analogues.

EXPERIMENTAL SECTION

2,6-Diformyl-4-methylphenol [22], 2,6-diacetyl-4-methylphenol [23], 2,6-dibenzyl-4-methylphenol [23], 4-*t*-butyl-2,6-diformylphenol [24], and S-(2,6-diformyl-4-methylphenyl)-dimethylthiocarbamate [24, 25], **H_3L1** and **H_3L2** [9] were made according to literature methods. *o*-Phenylenediamine and 4,5-dimethyl-*o*-phenylenediamine were purchased from the Aldrich Chemical Company and were used as received unless the compound was discoloured in which case it was sublimed under vacuum before use. Isopropanol (IPA) was stored over CaO, then decanted and distilled. Pyridine was refluxed over, and then distilled from, KOH.

[H_4L1*t*Bu]$_2$

In a 100 mL round bottomed flask was placed **H_3L1** (100 mg, 0.27 mmol), 4-*t*-butyl-2,6-diformylphenol (58 mg, 0.28 mmol) and dry *iso*-propanol (50 mL) and the resultant suspension was heated to reflux and refluxed for 2 hours. The mixture was then filtered to yield an orange/yellow solid of **[H_4L1*t*Bu]$_2$** (115 mg, 78%). The compound could be recrystallised from either chloroform/diethyl ether or chloroform/pentane, with crystals suitable for an X-ray structure determination being obtained from the former solvent combination by the diffusion of diethyl ether vapour into a chloroform solution of **[H_4L1*t*Bu]$_2$**. M.P. > 250°C; (Found C, 70.56; H, 5.71; N, 9.76. Expect for $C_{33}H_{30}N_4O_4 \cdot H_2O$: C, 70.24; H, 5.71; N, 9.92%); I.R. (KBr disk, *inter alia*) υ/cm^{-1} 3282, 2956, 2864, 1663, 1633, 1611, 1580, 1522, 1451, 746; ^{1}H NMR (300 MHz, solvent $CDCl_3$, reference TMS) δ 13.84(s, 1H), 13.55(s, 1H), 10.91(s, 1H), 10.57 (s, 1H), 8.92(s, 1H), 8.82(s, 1H), 8.02(d, 1H), 7.95 (s, 1H), 7.78(t, 3H), 7.60(s, 1H), 7.42(t, 2H), 7.28 (d, 1H), 7.18(t, 1H), 6.93(t, 1H), 6.62(t, 1H), 1.99 (s, 3H), 1.44(s, 9H); ^{13}C NMR (75 MHz, solvent $CDCl_3$, reference TMS) δ 168.1, 163.9, 162.4, 158.5, 157.1, 155.6, 142.0, 137.8, 137.6, 135.6, 134.2, 134.1, 132.8, 131.0, 128.7, 128.3, 127.9, 123.8, 123.6, 121.2, 120.4, 120.3, 118.8, 117.9, 115.5, 113.5, 34.2, 31.5, 20.0; F.A.B. mass spectrum, m/z (fragment): 547 **[H_4L1*t*Bu]**H^+, 383 [(**H_4L1*t*Bu**-$C_9H_8O_3$]H^+; λ_{max}/nm (DMF) 381 nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$ 16100), 320 nm (20500).

[H_4L2*t*Bu]$_2$

In a 100 mL round bottomed flask was placed **H_3L2** (82 mg, 0.19 mmol), 4-*t*-butyl-2,6-diformylphenol (40 mg, 0.19 mmol) and dry *iso*-propanol (50 mL) and the resultant suspension was heated to reflux and refluxed for 1.5 hours. The mixture was then filtered to yield an orange/yellow solid of **[H_4L2*t*Bu]$_2$** (81 mg, 71%). The compound could be recrystallised from chloroform/diethyl ether. M.P. > 250°C. (Found C, 71.93; H, 6.16; N, 8.90. Expect for $C_{37}H_{38}N_4O_4 \cdot H_2O$: C, 71.60; H, 6.50; N, 9.03%); I.R. (KBr disk, *inter alia*) υ/cm^{-1} 3279, 2957, 2862, 1671, 1631, 1611, 1580, 1522, 1451, 1048, 791, 708; ^{1}H NMR (300 MHz, solvent $CDCl_3$, reference TMS) δ 13.95(s, 1H), 13.56(s, 1H), 10.93(s, 1H), 10.48(s, 1H), 8.89(s, 1H), 8.84(s, 1H), 8.81(s, 1H), 7.94(s, 1H), 7.76(s, 1H), 7.72(s, 1H), 7.70(s, 2H), 7.58(s, 1H), 7.21(s, 1H), 7.05(s, 1H), 2.39(s, 3H), 2.33(s, 3H), 2.26(s, 3H), 2.01(s, 3H), 1.94(s, 3H), 1.45(s, 9H); ^{13}C NMR (75 MHz, solvent $CDCl_3$, reference TMS) δ 167.7, 162.6, 162.3, 158.3, 157.0, 154.4, 141.9, 137.4, 137.3, 136.0, 135.7, 135.4, 135.1, 132.4, 132.2, 132.1, 131.8, 131.2, 130.7, 128.2, 123.7, 122.2, 120.5, 120.2, 119.8, 118.5, 115.5, 114.2, 34.2, 31.5, 20.2, 20.1, 19.9, 19.8, 19.6; F.A.B. mass spectrum, m/z (fragment): 603 **[H_4L2*t*Bu]**H^+, 439 **[H_4L2*t*Bu** – $C_9H_8O_3$]H^+; λ_{max}/nm (DMF) 385 nm (ε/$dm^3\,mol^{-1}\,cm^{-1}$ 16000), 328 nm (5400).

[Co_2(L1*t*Bu)(OAc)$_2$(pyridine)]

4-*t*-Butyl-2,6-diformylphenol (103 mg, 0.50 mmol) and cobalt(II) acetate tetrahydrate (262 mg, 1.1 mmol) were dissolved in dry pyridine (20 mL) forming a brown solution. To this solution was added a dry pyridine (30 mL) solution of **H_3L1** (188 mg, 0.50 mmol) in a dropwise fashion. The resultant brown solution was brought to reflux and refluxed for a further 1.5 hours before being allowed to cool. Once cool the pyridine was removed on a rotary evaporator to leave a red/brown residue. The residue was dissolved in DMF and the diffusion of diethyl ether vapour into this solution resulted in the formation of red/brown crystals of [Co_2(**L1tBu**)(OAc)$_2$(pyridine)] · 2DMF (222 mg, 44%). The crystal which was used for X-ray crystallography had been recrystallised initially from acetonitrile/ether and then from DMF/ether, and had the formula: [Co_2(**L1tBu**)(OAc)$_2$(pyridine)] · 1.5DMF · 0.5MeCN. (Found C, 57.25; H, 5.06; N, 9.71. Expect for $Co_2C_{33}H_{26}N_4O_4 \cdot 2CH_3COO \cdot C_5H_5N \cdot 2C_3H_7NO$: C, 57.43; H, 5.12; N, 9.77%); I.R. (KBr disk, *inter alia*) υ/cm^{-1} 1663, 1615, 1571, 1556, 1471, 1437, 1360, 752; ^{1}H NMR (200 MHz, solvent d$_7$-DMF, reference DMF) δ 9.5–7.0 (19H, aromatics, imines, pyridine), 2.37 (3H, s), 1.48 (9H, s), 1.35 (3H, s), 0.72 (3H, s); F.A.B. mass spectrum, m/z (fragment): 858 [Co_2(**L1*t*Bu**)(OAc)$_2$(pyridine)]H$^+$, 798 [Co_2(**L1*t*Bu**)(OAc)(pyridine)]$^+$, 778 [Co_2(**L1*t*Bu**)(OAc)]H$^+$, 719 [Co_2(**L1*t*Bu**)(OAc)]$^+$, 661 [Co_2(**L1*t*Bu**)]H$^+$; λ_{max}/nm (DMF) 422 nm (ε/dm^3 mol^{-1} cm^{-1} 13600), 322 nm (34000).

[Co_2(L2DFPh)(OAc)$_2$(pyridine)] · 2H_2O

2,6-Diformyl-4-methylphenol (81 mg, 0.49 mmol) and cobalt(II) acetate tetrahydrate (256 mg, 1.0 mmol) were dissolved in dry pyridine (30 mL). The resultant brown solution was heated to reflux and to it was added **H_3L2** (215 mg, 0.50 mmol) in dry pyridine (40 mL) in a dropwise fashion. The red/brown reaction mixture was refluxed for 2 hours and then allowed to cool. The solvent was removed on a rotary evaporator to leave a red/brown residue. The desired compound was obtained by the diffusion of diethyl ether vapour into a DMF solution of this residue (68 mg, 18%). (Found C, 56.97; H, 4.77; N, 7.91. Expect for $Co_2C_{34}H_{28}N_4O_4 \cdot 2CH_3COO \cdot C_5H_5N \cdot 2H_2O$: C, 56.90; H, 4.77; N, 7.72%); I.R. (KBr disk, *inter alia*) υ/cm^{-1} 3420, 1616, 1563, 1548, 1484, 1438, 1361; ^{1}H (200 MHz, solvent d$_7$-DMF, reference DMF) δ 9.3–7.4 (15H, aromatics, imines, pyridine), 2.50 (3H,s), 2.37 (3H,s), 2.31 (6H,s), 2.27 (6H,s), 1.36 (3H,s), 0.72 (3H,s); λ_{max}/nm (DMF) 430 nm (ε/dm^3 mol^{-1} cm^{-1} 15200), 325 nm (38000).

X-ray Crystallography

Data were collected on a Siemens P4 four-circle diffractometer for [Co_2(**L1*t*Bu**)(OAc)$_2$(pyridine)]1.5DMF 0.5MeCN, and on a Bruker SMART diffractometer for **[H_4L1*t*Bu]$_2$**, using graphite-monochromated Mo-Kα radiation (λ = 0.71013 Å). Hydrogen atoms were inserted at calculated positions except where noted otherwise, and rode on the atoms to which they are attached (including isotropic thermal parameters which were equal to 1.2 times the equivalent isotropic displacement parameter for the attached non-hydrogen atom). Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 150155 and 150156.

Crystal Data for [H_4L1*t*Bu]$_2$

$C_{70}H_{70}N_8O_9$, pale yellow plate, dimensions 0.63 × 0.39 × 0.07 mm, triclinic, space group P–1, a = 7.747(1), b = 17.106(3), c = 23.662(4) Å, α = 104.83(3), β = 95.86(3), γ = 97.80(3)°, U = 2972.4(8) Å^3, μ = 0.09 mm^{-1}, Z = 2, D_c = 1.30 g cm^{-3}, F(000) = 1236, T = 100 K. 11887 Reflections were collected, on a Bruker SMART diffractometer, in the range $2 < 2\theta < 47°$. The 8343 independent reflections were used to solve

the structure in P1 by direct methods (SHELXS86) [26,27] which resulted in the location of most of the two macrocycles. The centre of symmetry was then located, one macrocycle deleted and the other macrocycle moved to allow refinement in P−1. All non-hydrogen atoms except the ring carbon atoms were anisotropic. The hydrogen atoms on the nitrogen and oxygen atoms were located from a difference map and their positions fixed during subsequent refinements. The refinement (SHELXL97) [28] of 554 parameters converged to R1 = 0.072 [for 4137 reflections having F > 4[(F)], wR2 = 0.191 and goodness of fit 0.97 (for all 8343 F^2 data). The function minimised in the F^2 refinement was $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w\,[\sigma^2(F_o^2) + (0.0755\,P)^2]^{-1}$ and $P = [\max(F_o^2, 0) + 2F_c^2)/3$. Peak/hole 0.40/−0.38 eÅ^{-3}.

Crystal data for [Co_2(**L1*t*Bu**)(OAc)$_2$(pyridine)]1.5DMF 0.5MeCN. $C_{47.5}H_{49}N_7O_{9.5}Co_2$, dark red rectangular block, dimensions 0.92 × 0.40 × 0.24 mm, monoclinic, space group $P2_1/n$, $a = 13.067(2)$, $b = 26.071(4)$, $c = 14.023(3)$ Å, $\beta = 93.02(1)°$, $U = 4770.6(15)$ Å^3, $\mu = 0.76$ mm^{-1}, $Z = 4$, $D_c = 1.38$ g cm^{-3}, F(000) = 2052, T = 168 K. The unit cell parameters were determined by least squares refinement of 21 accurately centred reflections ($9 < 2\theta < 25°$). Using 1.40° ω-scans, at a fixed scan rate of 100 min^{-1}, 9450 reflections were collected in the range $4 < 2\theta < 51°$. Crystal stability was monitored by recording three check reflections every 97 and no significant variations were observed. An empirical absorption correction was applied based on Ψ-scan data ($T_{min} = 0.24$, $T_{max} = 0.27$). The 8512 independent reflections were used to solve the structure by Patterson methods (SHELXS86) [26,27]. All full occupancy non-hydrogen atoms and the disordered *t*Bu carbons were anisotropic. The *t*Bu substituent was rotationally disordered and modeled and restrained accordingly. The half occupancy DMF molecule was disordered 50 : 50 over two superimposed sites. The refinement (SHELXL97) [28] of 622 parameters converged to R1 = 0.075 [for 5233 reflections having F > 4[(F)], wR2 = 0.133 and goodness of fit 1.08 (for all 8512 F^2 data). The function minimised in the F^2 refinement was $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = [\sigma^2(F_o^2) + (0.1181P)^2 + 8.64P]^{-1}$ and $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Peak/hole 1.15/−0.39 eÅ^{-3}.

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