Some Copper and Cobalt Complexes of Schiff-Base Macrocycles Containing Pyridazine Head Units[‡]

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Keywords: N ligands / Schiff bases / Macrocyclic ligands / Electrochemistry / Magnetic properties

The Schiff-base macrocycle L14, formed by the [2+2] condensation of 3,6-diformylpyridazine and 1,3-diaminopropane, has facilitated the preparation of the first extensive family of pyridazine-bridged macrocyclic complexes. The structural, magnetic and electrochemical behaviour of these complexes is of considerable interest. This microreview provides an overview of prior relevant studies and then describes some of the recent copper and cobalt chemistry of the macrocyclic ligand L14.

Contents

1. Scope

This microreview covers some aspects of the recent introduction of a new head unit, 3,6-diformylpyridazine (Figure 1), into Schiff-base macrocyclic chemistry,[1,2] focussing on the interesting copper and cobalt chemistry that it has generated to date.[3−11] The reader is referred to earlier reviews on Schiff-base macrocycles for excellent introductions to this general area and in-depth reviews of Schiff-base macrocycles incorporating pyridine- and phenol-based head units (e.g. $L2^{2-}$, Figure 2).[12−17] Recently, an overview of

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MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

[‡] The advice, enthusiasm and encouragement of Professor Karl Wieghardt (MPI für Strahlenchemie) is gratefully acknowledged on the occasion of his 60th birthday

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those which incorporate thiophenolate-based head units has been published (e.g. $L3^{2-}$, Figure 2),[18] and macrobicycles, or cryptands, have been comprehensively reviewed.[19]

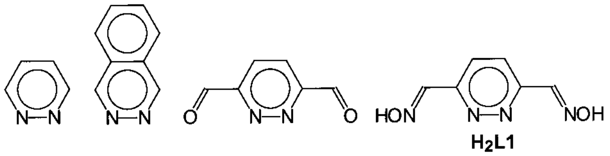


Figure 1. From left to right: pyridazine, phthalazine, 3,6-diformylpyridazine, H_2L1

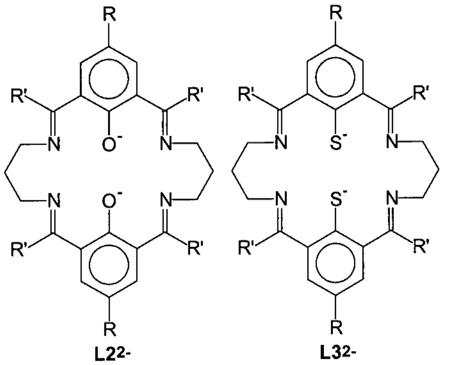


Figure 2. Phenolate macrocycles $L2^{2-}$ (e.g. R = CH_3, *tert*-butyl, CF_3; R′ = H, CH_3, phenyl) and thiophenolate macrocycles $L3^{2-}$ (R = CH_3, *tert*-butyl; R′ = H)

2. Background

2.1 Acyclic Pyridazine and Phthalazine Ligands

Aromatic nitrogen heterocycles such as diazines have been extensively and effectively employed as bridging ligands.[20] In keeping with this, pyridazine- and phthalazine-based acyclic ligands and their complexes are numerous and well-known. The earliest studies relevant to our work are those by Blake and co-workers[21−24] and Lever and co-workers,[25,26] concerning structural and magnetic studies of acyclic pyridazine- and phthalazine-bridged dimetallic complexes of first row transition metal ions. Since the 1980's Thompson and co-workers have been the key players in the development of, in particular, magnetostructural data on pyridazine- and phthalazine-bridged acyclic dicopper(II) complexes.[27−75]

However, of all the acyclic studies reported in the literature, the paper that most caught our attention was one by Bremard and co-workers, in 1991, in which the observation of antiferromagnetic coupling in the dicopper(II) complex of the acyclic dioxime ligand H_2L1 derived from 3,6-diformylpyridazine was reported (Figure 1).[76] As coordination chemists with a strong background in Schiff-base ligand chemistry, the possibility of incorporating the interesting pyridazine bridging unit into Schiff-base macrocycles, using 3,6-diformylpyridazine as a head unit (see Section 3), was a natural extension of the chemistry reported by Bremard and co-workers. Before focussing on studies of pyridazine- and phthalazine-containing macrocycles, a short overview is presented of the — more numerous — copper and cobalt complexes of acyclic pyridazine- and phthalazine-containing ligands.

2.1.1 Copper Complexes of Acyclic Pyridazine and Phthalazine Ligands

There are many reports of copper complexes containing a Cu−N(pyridazine moiety) bond (SciFinder Scholar[77] indicates that there are 943 such complexes in 218 papers, as of 12.2.02). Many of these complexes have been structurally characterised, as a search of the Cambridge Crystallographic Database[78] (CSD version 5.22 October 2001) shows: there are 130 entries for crystallographically characterised copper complexes containing a Cu−N(pyridazine moiety) bond. Of these, other than the structures of our pyridazine-bridged copper complexes (only three of which are in the CSD[78] version 5.22 October 2001 as the others were published after this version was released),[3,6,7] there are 93 entries which contain copper ions bridged by a pyridazine or phthalazine moiety: the majority of these structures are of di- or polycopper(II) complexes (69 entries), with a smaller number of di- or polycopper(I) complexes (26 entries), and no examples of mixed-valent complexes other than one of ours[6] (Table 1). Narrowing the field still further, relatively few of these complexes contain copper ions doubly or triply bridged by pyridazine or phthalazine, with only seven dicopper(II) examples (none of these involve triple pyridazine or phthalazine bridges) and 17 di- or polycopper(I) compounds (Table 1).

Studies on acyclic pyridazine- and phthalazine-bridged dicopper(II) complexes have clearly shown that these moieties are capable of mediating moderate to strong antiferromagnetic coupling, although it should be remembered that, with only one structurally characterised exception,[76] hydroxide, halide, azide, alkoxide, nitrate or sulfate exogenous bridges are always present in addition to the diazine bridge(s) in these acyclic copper complexes.[30−34,36−39,41,42,44,45,47,48,50,52,53,57,60−62,67,68,70−73,79,80] Another point to note in this regard is that on coordination of two metal ions these acyclic ligands form either two five-membered chelate rings (as in the case of complexes of H_2L1) or two six-membered chelate rings, and this affects the planarity of the ligand in the complex, the number and type of exogenous bridging groups bound to the copper atoms, and hence the magnetic properties of the complexes.

As expected, the bridging π-acceptor pyridazine moiety has been shown to be able to stabilise copper ions in the +1 oxidation state, with Cu^I/Cu^{II} couples commonly observed at positive potentials relative to SCE,[37,39,42,44−46,60−62,73] with very few exceptions.[41] Generally pyridazine- and phthalazine-bridged dicopper complexes undergo a single — albeit sometimes quite broad — two-electron process $Cu_2^{II} \rightleftarrows Cu_2^{I}$.[37,42,44,45,60−62,73] There are very few examples of two well-separated one-electron waves being observed,[39,46,81] which is in stark contrast to the dicopper(II) complexes of related phenolate ligands,

Table 1. Entries (given as Refcodes with the associated literature reference) from the Cambridge Crystallographic Database[78] (CSD version 5.22 October 2001) which contain pyridazine- or phthalazine-bridged copper ions; $x \geq 2$

Cu_x^{II}	Single pyridazine (or related) bridge (30 entries)	BEGNOQ;[122] BITQEA;[123] BITQIE;[123] BUKXIO;[124] CAPJUY;[125] CERCUX;[126] CICPIN;[127] COTCET;[128] DIMQIZ;[75] DOGLUG;[38] DOGMAN;[38] FAGXOA;[43] FEKZAW;[44] FEKZEA;[44] FODHOV;[45] GALBUQ;[47] HENTOJ;[129] NIHWUW;[72] NIHXAD;[72] NOWVAW;[80] NOWVEA;[80] PAHGUA;[58] PECJEM;[130] PECJOW;[130] TAZWUM;[73] VEHKAU;[131] YETZIG;[67] YETZOM;[67] YETZUS;[67] YUBKUB[68]
	Single phthalazine (or related) bridge (32 entries)	BAYZOQ;[132] BITQOK;[123] BUCJOY;[31] COLDOW;[34] COLDUC;[34] DEKWIZ;[37] DETCUA;[32] DURXET;[39] DUTCIE;[41] DUTCIE10;[52] FAGXEQ;[43] FEKZIE;[44] FURSAM;[50] HAHNEJ;[62] HAHNIN;[62] HAHNOT;[62] HODXED;[74] JODNIZ;[54] JODNIZ10;[58] LASZUA;[60] LASZUA10;[70] NIHWOQ;[72] YETZAY;[67] YETZEC;[67] YEVBAC;[67] YUBKAH;[68] YUBKEL;[68] YUBKIP;[68] YUBKOV;[68] ZIGQEL;[69] ZIMWOH;[70] ZOFVOF[61]
	Double pyridazine (or related) bridge (6 entries)	GAGMUW;[51] HENTUP;[79] HENTUP01;[114] RAPCAM;[3] [a] VIVHOX;[76] VIVHOZ[76]
	Double phthalazine (or related) bridge (1 entry)	PAGWOJ[57]
	Triple pyridazine or phthalazine (or related) bridge (0 entries)	No examples
Cu_x^{I}	Single pyridazine (or related) bridge (9 entries)	CAQXIB;[115] FEDBIZ;[119] JUGBES;[110] KIKBEL;[113] MEHJUE;[6] [a] RETPOV;[116] RIXHOV;[117] RIXHUB;[117] YOYFOH[118]
	Single phthalazine (or related) bridge (0 entries)	No examples
	Double pyridazine (or related) bridge (10 entries)	CAQXAT;[115] CAQXEX;[115] CAQXOH;[115] FUPREN;[133] GABYIR;[46] GONSAD;[134] [b] LIFKIU;[135] PILTOT;[136] PYAZCU10;[137] SOJGUT[81]
	Double phthalazine (or related) bridge (1 entry)	ZOFVUL[61]
	Triple pyridazine (or related) bridge (6 entries)	COCQEQ;[111] COCQIU;[111] COCQOA;[111] COCROB;[111] LIFKOA;[135] PILTIN[136]
	Triple phthalazine (or related) bridge (0 entries)	No examples
$Cu^{I}Cu^{II}$	Double pyridazine (or related) bridge (1 entry)	MEHJOY[6] [a][c]

[a] Macrocyclic-pyridazine bridging (our work). [b] Valence sum calculations indicate that the average oxidation state of copper is +1 in this mixed metal complex. [c] The only pyridazine- or phthalazine-bridged mixed-valent copper complex of any kind reported to date.

such as $L2^{2-}$ (Figure 2), in which this is commonly observed (albeit at negative potentials vs. SCE).[82] Consistent with these observations, there are some examples of di- and polycopper(I) complexes of bridging pyridazine and phthalazine acyclic ligands which have been isolated and fully characterised (including single crystal X-ray structure determination, Table 1), but, prior to our work, no example of a pyridazine- or phthalazine-bridged copper(I)/copper(II) mixed-valent complex.

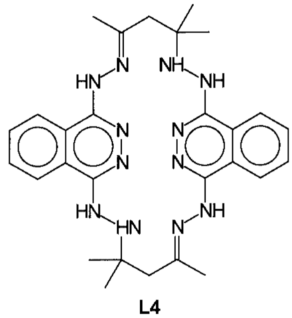
2.1.2 Cobalt Complexes of Acyclic Pyridazine and Phthalazine Ligands

Whilst less common than copper pyridazine and phthalazine complexes, there are still numerous reports of cobalt complexes containing a Co−N(pyridazine moiety) bond (SciFinder Scholar[77] indicates that there are 192 such complexes, with a variety of oxidation states of cobalt, in 77 papers, as of 12.2.02). Of these, those concerned with cobalt(II) complexes are of some relevance to the studies described herein,[21,24,26,35,40,48,49,83−89] with those di- or polycobalt(II) complexes in which pyridazine[21,24,40,84,85] or phthalazine[21,24,26,35,49,89] bridging is observed being of most relevance. Focussing in on these pyridazine- or phthalazine-bridged cobalt(II) complexes: (a) for all cases in which magnetic data are reported the cobalt(II) ions are in the high-spin state and are only weakly antiferromagnetically coupled;[21,24,26,40,49,84] (b) only two of the complexes contain macrocyclic ligands and neither of these complexes are fully characterised;[88,89] (c) whilst aerobic oxidation leads to the production of dicobalt(III) complexes in some cases,[28] no electrochemical studies have been reported, other than a brief mention of the interesting fact that a macrocyclic dicobalt complex with double phthalazine bridges catalyses the four-electron reduction of O_2 in alkaline solutions when absorbed onto graphite.[89,90]

Very few such complexes have been structurally characterised, as a search of the Cambridge Crystallographic Database[78] (CSD version 5.22 October 2001) shows. There are still — other than our own cobalt pyridazine complexes[4,5,8,9,11] — only four other crystallographically characterised cobalt complexes containing a Co−N(pyridazine moiety) bond.[49,83,91,92] The first structurally characterised example was a red-brown high-spin phthalazine-bridged dicobalt(II) complex [Co$_2^{II}${1,4-bis[(6-methylpyridine-2-carboxaldimino)amino]phthalazine}Cl](H$_2$O)$_4$Cl$_3$ [av. Co−N(phthalazine ligand) 2.151(5) Å].[49] Haupt and co-workers then reported two structurally characterised complexes, a dicobalt(I) complex [Co$_2^{I}${μ_2-benzo[*c*]cinnoline-*N*,*N′*}-bis(η^5-cyclopentadienyl)trimethylphosphane],[91] and a monocobalt(0) complex, [Co^0{η^2-benzo[*c*]cinnoline-*N*,*N′*}tris(trimethylphosphane)].[92] Finally, an orange high-spin monocobalt(II) complex [Co^{II}(pyridazine)$_4$(NCS)$_2$] was reported in 1998 [Co−N(NCS) 2.057(2), av. Co−N(monodentate pyridazine) 2.204(2) Å].[83]

2.2 Macrocyclic Pyridazine and Phthalazine Ligands

Prior to our studies,[1−11] very little pyridazine- or phthalazine-based macrocyclic chemistry had been reported in the literature, despite an isolated but interesting example described early on by Rosen.[93] This 1971 publication described one of the earliest macrocycles to completely encircle *two* metal ions (following on from the independent breakthroughs in 1970 by Robson and co-workers[94] and by Busch and co-workers[95] in encircling two metal ions with a macrocycle), in this case two nickel(II) ions.[93] The macrocycle synthesis is reminiscent of the Curtis macrocycles,[96] being prepared from 1,4-dihydrazinophthalazine (expensive but commercially available as the dihydrochloride salt) and 2,2-dimethoxypropane in the presence of an acid and the metal salt. It was, quite reasonably, proposed that the phthalazine groups of L4 (Figure 3) bridge the nickel ions, but this was not confirmed by a single crystal X-ray structure determination.

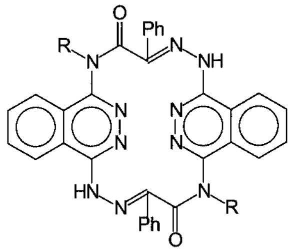


L4

Figure 3. Phthalazine-containing macrocyclic ligand L4

A dicobalt complex of the Rosen phthalazine-containing macrocycle L4 is also mentioned in the literature, in the context that it catalyses the four-electron reduction of O_2 in alkaline solutions when absorbed onto graphite.[89][90] No synthetic detail or further characterisation information was provided for this complex.

There is one further isolated case of a phthalazine-containing macrocycle, H$_2$L5 (Figure 4), being prepared. In this case it is proposed by Okur that the macrocyclic cavity only incorporates a single metal ion (paramagnetic Co^{II} or diamagnetic Ni^{II}); again no structural information is available for either of these complexes.[88]



H$_2$L5

Figure 4. Phthalazine-containing macrocyclic ligand H$_2$L5

In addition to their extensive studies of complexes of acyclic pyridazine- and phthalazine- containing ligands (Section 2.1), Thompson and co-workers have also prepared a range of pyridazine- and phthalazine-containing macrocyclic thioether ligands, by reacting commercially available 3,6-dichloropyridazine (affordable) and 1,4-dichlorophthalazine (relatively expensive) with appropriate dithiolate reagents (e.g. L6 to H$_2$L12, Figure 5).[55,56,59,64−66]

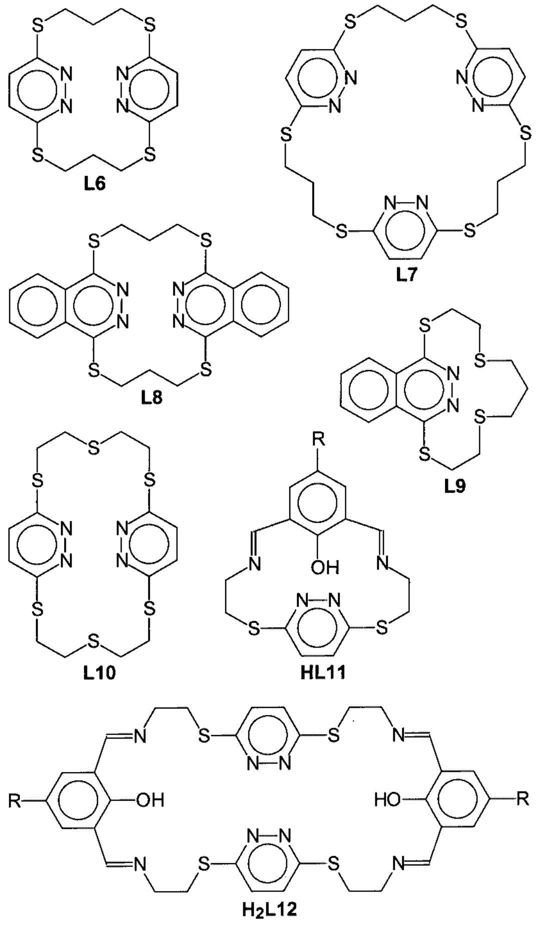
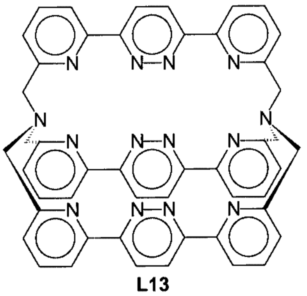


Figure 5. A selection of thioether pyridazine- and phthalazine-containing macrocycles

Initially both [2+2] and [3+3] thioether macrocycles were obtained from the reaction of 3,6-dichloropyridazine and 1,3-propanedithiol (L6 and L7, Figure 5): these macrocycles were separated from one another readily on the basis of solubility.[56] Other dithiols employed in the cyclisation with 3,6-dichloropyridazine included 3,7-dithianonane-1,9-dithiol,[55] 2,2′-thiodiethanethiol (L10, Figure 5),[64,65] and 1,4,7,10-tetrathiadecane.[65] Some [2+2] phthalazine analogues were prepared by reaction of 1,4-dichlorophthalazine with 1,3-propanedithiol (L8, Figure 5), 3,7-dithianonane-1,9-dithiol (L9, Figure 5) or 2,2′-thiodiethanethiol.[65] A series of copper(II), copper(I) and silver(I) complexes were characterised,[55,56,64,65] including an example of a mixed-valent copper(I)/copper(II) complex $[Cu_2(L10)Br_3]$, which was not structurally characterised, but which was proposed to have a polymeric structure with the copper(II) ion bound within the macrocycle and the copper(I) ion, involved in bridging the macrocyclic rings, bound in an exocyclic manner.[64] In none of these complexes did the pyridazine rings bridge the metal ions.

The next development was the preparation of a “two armed pyridazine diamine”, 3,6-bis[(2-aminoethyl)thio]pyridazine, from 3,6-dichloropyridazine, in 87% yield, which opened up the possibility of using metal ions to template the formation of Schiff base macrocycles.[66] Copper(II) template ions were employed in the reactions of this diamine with 2,6-diformyl-4-methylphenol or with 2,6-diformyl-4-*tert*-butylphenol (e.g. HL11 and H_2L12, Figure 5) and this resulted in a range of mono-, di- and tetranuclear copper complexes,[59,66] including examples of mixed valent copper(II)/copper(I) complexes.[66] However, once again, pyridazine bridging is not a feature of these complexes.[59,66] Rather, they contain phenolate bridge(s) so they are actually more closely related to the dicopper complexes of phenolate-containing macrocycles such as $L2^{2-}$ (Figure 2).[82]

More recently, Lehn and co-workers have reported a pyridazine-containing cryptand ligand, L13 (Figure 6), that can accommodate two sodium ions which are believed to be triply bridged by the pyridazine moieties, although no details are provided.[97]



L13

Figure 6. Pyridazine-containing cryptand ligand L13

To summarise, despite the construction of some pyridazine- and phthalazine-containing macrocycles,[55,56,59,64–66,88–90,93,97] in only three isolated cases was bridging of the incorporated metal ions by these moieties proposed (for L4 and L13, Figure 3 and 6 respectively).[89,90,93,97] Therefore we set out to carefully design and construct pyridazine-containing macrocycles in which bridging by this 1,2-diazine moiety was facilitated, and to subsequently thoroughly examine the resulting families of complexes to determine whether or not special features had resulted from incorporating this interesting diazine bridging unit into a macrocyclic framework.

3. Macrocycles Built from 3,6-Diformylpyridazine

3,6-Diformylpyridazine was targeted (Section 2.1, Figure 1) as a suitable macrocycle precursor to achieve the initial aim of producing a family of macrocycles capable of binding two metal ions and providing two pyridazine bridges. Initially this dialdehyde was prepared from 3,6-bis(hydroxymethyl)furan by the four-step method reported by Bremard and co-workers [Figure 7, steps (i)−(iv)],[76] modifying the final step from the reported Swern oxidation to an MnO_2 oxidation[98] in order to readily isolate the dialdehyde.[2] However this route[99,100] was less than satisfactory because: (a) the starting material, whilst not particularly expensive, was not cheap, (b) step (ii) was found to be unreliable, and (c) it was found that an extra step was necessary [step (iii) was replaced with steps (v) and (vi)] making it a five-step synthesis.[2] Hence a more convenient synthesis was sought. Wiley[101] has described a three step synthesis [Figure 7, steps (1)−(3)], starting from cheap starting materials, and this was found to be a good alternative route to 3,6-diformylpyridazine. The first two steps are reported as moderately large scale reactions which is advantageous, whilst the third and final step, being an ozonolysis reaction, must be done on a small scale for safety reasons.[2,101]

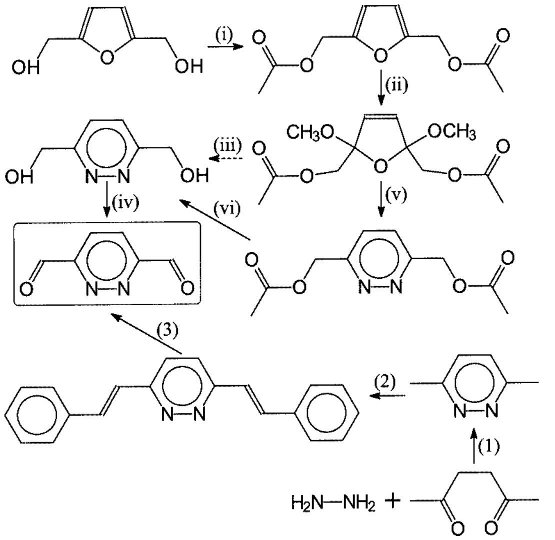


Figure 7. Syntheses of 3,6-diformylpyridazine from 2,5-bis(hydroxymethyl)furan [steps (i)−(v)] or from acetonylacetone and hydrazine hydrate [steps (1)−(3)]; reagents and conditions: (i) acetic anhydride/pyridine; (ii) Br_2/CH_3OH; (iii) 1% acetic acid/CH_3OH/$H_2NNH_2 \cdot H_2O$; (iv) activated Amberlite IRA400 resin/CH_3OH; (v) oxalyl chloride/dmso or MnO_2/dioxane; (1) Pd/C-benzene; (2) $ZnCl_2$; (3) O_3/MeOH

With a good synthesis of 3,6-diformylpyridazine in hand, attention turned to preparing Schiff-base macrocyclic, and related acyclic, ligands and complexes from them. Whilst the condensation of this dialdehyde head unit is being explored with a wide range of amines,[11] this microreview will focus entirely on the results obtained using 1,3-diaminopropane.

3.1. Macrocycles L14 and L14′ from 3,6-Diformylpyridazine and 1,3-Diaminopropane

Models indicated that a [2+2] condensation of 1,3-diaminopropane with 3,6-diformylpyridazine would produce a macrocycle which would bind two first row transition metal ions well. Hence this was the diamine used initially, and the resulting [2+2] and [4+4] macrocycles, L14 and L14′ (Figure 8), are the focus of this section.

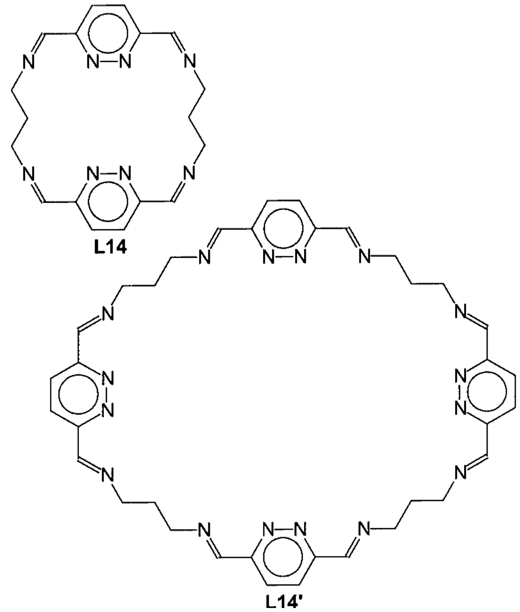


Figure 8. Pyridazine-containing [2+2] and [4+4] Schiff-base macrocycles L14 and L14′

It is relevant to note that many interesting complexes have been prepared from the [2+2] macrocycles formed by condensing 1,3-diaminopropane with either 2,6-diformylphenols[82,102] or 2,6-diformylthiophenols[18] (the $L2^{2-}$ and $L3^{2-}$ families of macrocycles, Figure 2). There are clearly both similarities and differences between phenolate and pyridazine moieties. Features they share include the well-established ability to bridge metal ions and to mediate magnetic exchange. However, they are also very different in that phenolate has a negative charge whilst pyridazine is neutral and is a π-acceptor ligand. Another key difference is that phenolate provides a one-atom bridge whereas pyridazine provides a two-atom bridge. These differences are significant and should impact on the properties of the complexes, in particular on the magnetic and redox chemistry, hence the interest in incorporating bridging pyridazines into Schiff base macrocycles for the first time.

Success came with a lead(II) templated cyclisation reaction of 3,6-diformylpyridazine and 1,3-diaminopropane, the results of which were published as a communication in 1994.[1] An unexpected [4+4] cyclisation occurred (confirmed by single crystal X-ray structural analysis, Figure 9) producing what was at the time only the second example of a [4+4] Schiff-base macrocycle.[103,104] Subsequently it was found that, depending on the reaction stoichiometry, one could produce either the [4+4] or the [2+2] macrocycle, as $[Pb_2L14'](ClO_4)_4$ or $[Pb_2L14](ClO_4)_4$ respectively, in good yields (Figure 8).[2] This ability to control the ring size of the product macrocycle by stoichiometry alone is unique to the best of our knowledge.

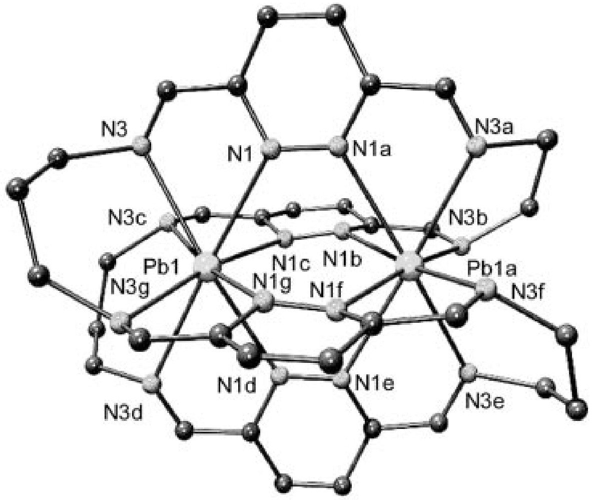


Figure 9. Perspective view of the cation of $[Pb_2L14']^{4+}$

Transmetallation reactions, starting from either $[Pb_2L14'](ClO_4)_4$ or $[Pb_2L14](ClO_4)_4$, allowed the preparation of the first row transition metal complexes of interest. Alternatively, these complexes could, in principle, have been prepared by using the transition metal ions as template ions, but in practice this was unsuccessful for most of the metal ions studied, including copper(II) and cobalt(II) ions. One of the key exceptions to this generalisation is that copper(I) ions could be used as template ions for the formation of L14 (see below).

Usually, for reasons of ease of synthesis of clean samples, $[Pb_2L14'](ClO_4)_4$ was the preferred precursor complex for the transmetallation reactions. The use of this precursor complex immediately raised the question as to whether the transition metal complexes would be of the [4+4] macrocycle L14′ or of the [2+2] macrocycle L14. The answer to this question is that, to date, all of the products obtained have been of the [2+2] macrocycle L14.[11] Hence the [4+4] Schiff-base macrocycle L14′ rearranges during the transmetallation reaction to form the [2+2] macrocycles L14, in contrast to the first known example of a [4+4] Schiff-base macrocycle in which the reverse was believed to be occurring (the [4+4] macrocycle was proposed to form from two [2+2] macrocycles coming together).[104] Interestingly, this substantial ring-size change from L14′ to L14 occurs successfully even when inserting transition metal ions which cannot be used to template the macrocycle formation from 3,6-diformylpyridazine and 1,3-diaminopropane. Relatively minor changes to the size of Schiff-base macrocycles can occur during transmetallation reactions by the nucleophilic addition of solvent alcohol[105] to the imine bond(s) or by intramolecular attack of an alcohol[106] or amine[107] moiety on the imine bond(s), but a change in the actual number of head and lateral units making up the macrocyclic framework, such as is occurring here, is very uncommon.[104][108]

The metal ions incorporated into L14 to date include manganese, iron, cobalt, nickel, copper and zinc: here we will focus on the results obtained with copper and cobalt.

3.1.1 Copper Complexes of the L14 Schiff-Base Macrocycle

Direct reactions, employing copper(II) as a template ion for the cyclisation, were unsuccessful, presumably due to the tendency of the copper(II) ions to participate to some extent in redox chemistry in the presence of the ligand components.[3,7] Rather, the transmetallation route from $[Pb_2L14'](ClO_4)_4$ was followed and this yielded single crystals of an emerald green complex, $[Cu^{II}_2L14(CH_3CN)_4](ClO_4)_4$, in good yield.[3,7] The single crystal structure determination (Figure 10) shows that the macrocycle conformation is somewhat bent, with an angle of 29.67(7) ° between the planes of the two pyridazine rings. The copper(II) ions are square pyramidal with a weak interaction to a perchlorate ion in the otherwise vacant sixth site of the distorted octahedron. As expected (Section 2.1.1), strong antiferromagnetic coupling was observed between the doubly pyridazine-bridged copper(II) ions, with $-2J = 482\ cm^{-1}$. This value is similar to the $-2J$ values of 536 cm^{-1} and 489 cm^{-1} obtained for the only two closely related acyclic complexes known: orange-red $[Cu^{II}_2(HL1)_2(H_2O)_2(ClO_4)_2]$ and olive-green $[Cu^{II}(DHPH)_2(H_2O)_2](ClO_4)_2$ (where DHPH = 1,4-dihydrazinophthalazine), in which the copper(II) ions are doubly bridged by pyridazine[76] and phthalazine[57] moieties, respectively, and there are no other bridging moieties present.

Electrochemical experiments revealed the presence of two well-separated reversible one electron processes at positive potentials vs. SCE, which correspond to $Cu^{II}_2 \rightleftarrows Cu^{II}Cu^{I} \rightleftarrows Cu^{I}_2$. This result contrasts with the previous studies on acyclic pyridazine complexes in which the norm was the observation of a single two-electron process of varying reversibility (Section 2.1.1). The observation of two well-separated reversible processes is more reminiscent of the analogous doubly phenolate-bridged dicopper(II) macrocyclic complexes (e.g. $L2^{2-}$, Figure 2), however, in that case, the processes occur at negative potentials (Section 2.1.1), in contrast to the positive potentials observed in the case of dicopper(II) complexes of the pyridazine macrocycle L14. These redox properties opened up a unique opportunity to access not only the mixed valent copper(I)/copper(II) complex but also the dicopper(I) complex.

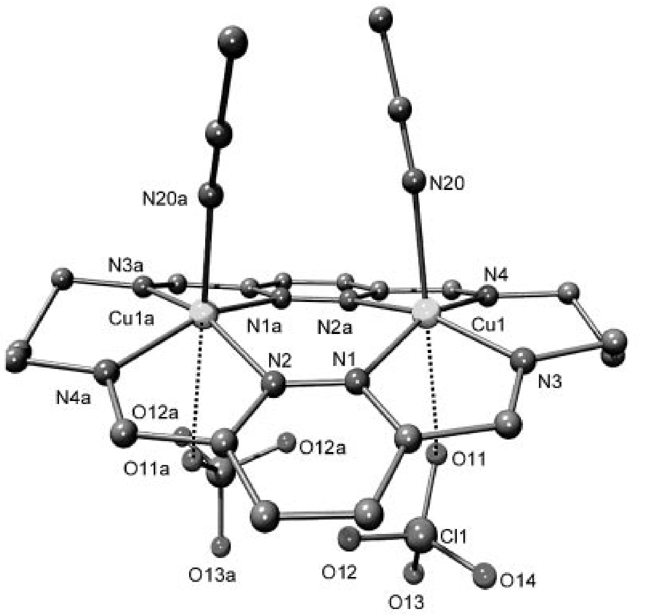


Figure 10. Perspective view of the cation of $[Cu^{II}_2L14(CH_3CN)_2(ClO_4)_2]^{2+}$

As a first attempt to prepare the dicopper(I) complex a transmetallation reaction was carried out with $[Cu^{I}(CH_3CN)_4](PF_6)$ in acetonitrile under argon. For ease of workup, vapour diffusion of diethyl ether into the resulting red-brown solution was carried out in air. This resulted in the isolation of red-brown single crystals of the mixed valent complex, $[Cu^{I}Cu^{II}L14(CH_3CN)_2](ClO_4)_2(PF_6)$, in 41% yield, due to the in situ air oxidation of the dicopper(I) complex, which was presumably the initial product of the transmetallation reaction.[6] A structure determination carried out on one of these crystals at low temperature clearly showed that this is a valence-localised compound: longer bond lengths are observed to the copper(I) atom and it is further out of the N_4 plane (Figure 11; Cu1 0.72 Å out-of-plane, Cu2 0.26 Å out-of-plane). The observation of a four-line EPR spectrum is consistent with this

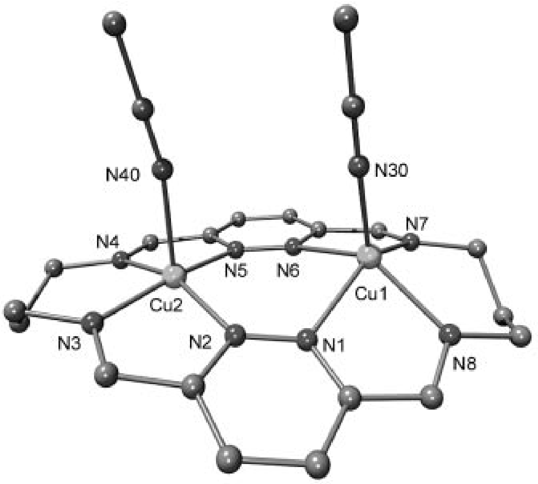


Figure 11. Perspective view of the cation of $[Cu^{I}Cu^{II}L14(CH_3CN)_2]^{3+}$

assignment.[7] It is also interesting to note that this is a relatively rare example of five coordinate copper(I).[109]

The use of copper(I) ions as template ions seemed an improbable route to clean L14 macrocycle formation given the preference of copper(I) for a tetrahedral (not square-based) geometry and the demands of L14 macrocycle formation. However, this experiment was attempted because related acyclic ligands have, in this laboratory[11] and elsewhere,[110] given grid complexes with tetrahedral copper(I) ions. Therefore an interesting and unusual result was possible, providing the propylene lateral units were capable of linking up the pyridazine head units which would be expected to be held perpendicular to one another by the copper(I) template ions. Fortunately this was the case, and brown single crystals of $[Cu^{I}_4(L14)_2](PF_6)_4$ were formed, in 61% yield, on diffusing diethyl ether vapour into the acetonitrile reaction solution, in air. The complex does have a grid structure, where each of the two parallel strands are linked together in a single macrocycle, and the two macrocycles approach each other at right angles to give rise to the perpendicular strands of the grid structure (Figure 12).[6] Thus the copper(I) atoms have distorted tetrahedral geometries, with each macrocycle providing a bidentate donor set at right angles to that supplied by the other macrocycle.

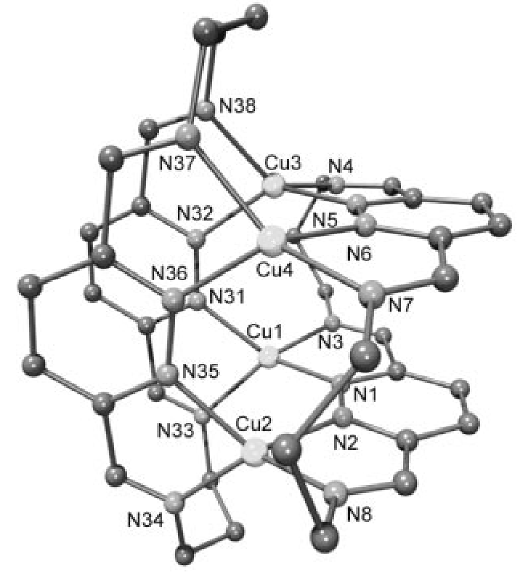


Figure 12. Perspective view of the cation of $[Cu^{I}_4(L14)_2]^{4+}$

In noncoordinating solvents, for example nitromethane and acetone, this tetracopper complex is stable in air. However, there is evidence, from both NMR spectroscopy and cyclic voltammetry, that when this complex is dissolved in coordinating solvents, such as acetonitrile, that it is then in equilibrium with an open form that looks like the dicopper(II) and mixed valent forms (Figure 10, 11 and 13).[7] In this "open" form (Figure 13) it is expected to be air sensitive, as it has already been observed that the transmetallation of the lead complex with copper(I), on air workup, yielded the mixed valent complex $[Cu^{I}Cu^{II}L14(CH_3CN)_2](ClO_4)_2(PF_6)$. Therefore, in order to improve the 61% yield one should presumably carry out the template synthesis completely under argon or in a noncoordinating solvent (but not acetone,[96] or nitromethane which makes explosive mixtures with amines). More importantly though, the presence of this equilibrium mixture in acetonitrile solution provides an easy route to cleanly isolate the dicopper(I) complex.

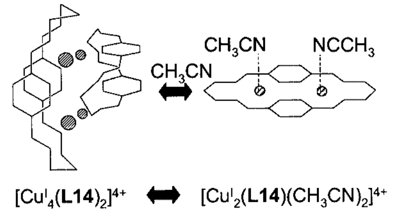


Figure 13. Proposed equilibrium formed between $[Cu^{I}_4(L14)_2]^{4+}$ and $[Cu^{I}_2L14(CH_3CN)_2]^{2+}$ in acetonitrile solution; reprinted from *Coord. Chem. Rev.* **2001**, *216−217*, 3−30, S. Brooker *et al.*, Doubly pyridazine-bridged macrocyclic complexes of copper in +1, +2 and mixed valent oxidation states, with permission from Elsevier Science

The reaction of $[Cu^{I}_4(L14)_2](PF_6)_4$ in acetonitrile with two equivalents of PPh_3 yields brown single crystals of $[Cu^{I}_2L14(PPh_3)_2](PF_6)_2$ in 51% yield.[7] PPh_3 was used in order to provide a donor that was better able to stabilise copper(I) than acetonitrile.[111−113] As expected, the steric bulk of the triphenylphosphane groups leads to the observation of a trans arrangement of the two PPh_3 groups relative to the macrocycle plane (Figure 14).[7] The five-coordinate copper(I) atoms are even further displaced from the N_4 plane [0.822(1) Å] than in the previous complexes. Despite the unusual five coordination of the copper(I) atoms the $Cu-PPh_3$ bond length [2.2239(8) Å] is at the lower end of

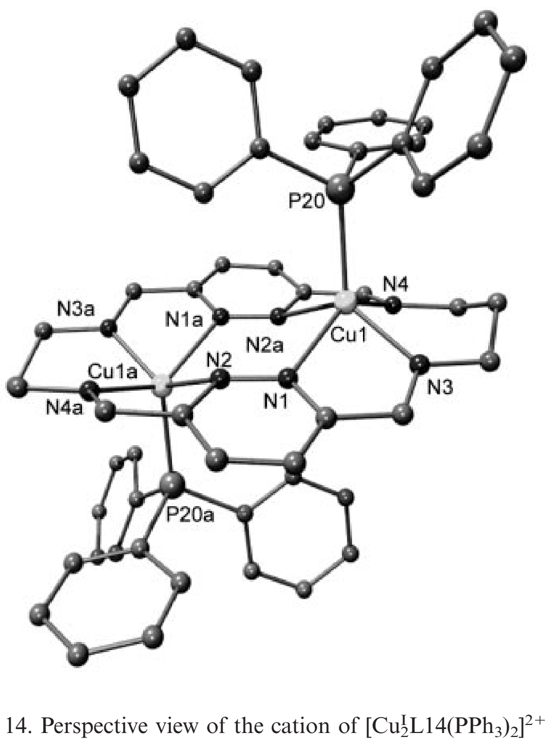


Figure 14. Perspective view of the cation of $[Cu^{I}_2L14(PPh_3)_2]^{2+}$

the range observed for the four copper(I) pyridazine phosphane complexes which have been structurally characterised to date, all of which contain copper(I) atoms in a distorted tetrahedral geometry [two monocopper(I) complexes $\mathrm{Cu^{I}-PPh_3}$ 2.244–2.293 Å;[111,112] one singly pyridazine-bridged dicopper(I) complex with double bis(diphenylphosphanyl)methane bridging $\mathrm{Cu^{I}-P}$ 2.23–2.29 Å;[113] one triply-pyridazine-bridged dicopper(I) complex $\mathrm{Cu^{I}-PPh_3}$ 2.217 and 2.208 Å;[111]].

An expected difference between these doubly pyridazine-bridged macrocyclic complexes and those of the doubly phenolate-bridged macrocyclic complexes of $\mathrm{L2^{2-}}$ was the metal ion separation (Section 3.1, Figure 2). The Cu···Cu separation in the dicopper(II) complexes of $\mathrm{L2^{2-}}$ is typically 3.06–3.22 Å[82] whereas in the dicopper(II) complexes of L14 it is 3.805(3) Å in $\mathrm{[Cu^{II}_2L14(CH_3CN)_4](ClO_4)_4}$ [3] and 3.888(3) Å in $\mathrm{[Cu^{II}_2L14(H_2O)_2](ClO_4)_4}$.[7] The impact of the two-atom pyridazine bridge, as opposed to the one-atom phenolate bridge, is therefore clear. These Cu···Cu separations can also be usefully compared with the six acyclic structurally characterised doubly pyridazine- or phthalazine-bridged copper(II) complexes (Table 1). In three out of the six entries only double pyridazine/phthalazine bridging is present and the Cu···Cu separations are somewhat shorter than those observed in the macrocyclic complexes, at 3.760 Å (VIVHOX)[76] and 3.729 Å (PAGWOJ);[57] no detailed information is available for VIVHOZ.[76] In the other three entries an additional one-atom exogenous bridge is present (chloride or nitrate) and this results in a significant shortening of the Cu···Cu separation, to 3.269–3.406 Å.[51,79,114]

In the mixed-valent complexes the $\mathrm{Cu^{I}\cdots Cu^{II}}$ separations are 3.8986(9) Å in $\mathrm{[Cu^{I}Cu^{II}L14(NCS)_4Cu^{I}]}$[7] and 3.9599(4) Å in $\mathrm{[Cu^{I}Cu^{II}L14(CH_3CN)_2](ClO_4)_2(PF_6)}$.[6] The Cu···Cu separation is a large 4.4316(12) Å for the dicopper(I) triphenylphosphane complex $\mathrm{[Cu^{I}_2L14(PPh_3)_2](PF_6)_2}$, due primarily to the fact that the copper ions are displaced from the macrocyclic plane in opposite directions.[7] Double pyridazine or phthalazine bridging of copper(I) ions (Table 1) by acyclic ligands usually results in Cu···Cu separations in the range 2.970–3.679 Å, with a mean value of 3.261 Å which is significantly lower than the 4.4316(12) Å observed here.

Interestingly the shortest Cu···Cu separations observed in this series of macrocyclic pyridazine-bridged copper complexes are found in the tetracopper(I) complex $\mathrm{[Cu^{I}_4(L14)_2](PF_6)_4}$, in which only one pyridazine bridge, not two, is observed between neighbouring copper atoms. In this case the nearest copper(I) atoms are separated by just 3.711(3)–3.738(3) Å.[6] The other eight entries of singly pyridazine- or phthalazine-bridged copper(I) complexes (Table 1) have shorter Cu···Cu separations, in the range 3.438–3.688 Å,[110,113,115–118] with the exception of FEDBIZ in which the separation is even shorter (2.788 Å).[119] The structure of the $\mathrm{[Cu^{I}_4(dppn)_4]^{4+}}$ complex [dppn = 3,6-bis(2′-pyridyl)pyridazine], described by Youinou and co-workers,[110] is particularly closely related to that of $\mathrm{[Cu^{I}_4(L14)_2](PF_6)_4}$ so the difference in Cu···Cu separations [3.566(1) and 3.582(1) Å vs. 3.711(3)–3.738(3) Å] is presumably due to the restrictions imposed by the macrocyclic nature of the two coordinated L14 ligands as opposed to the relative freedom of the four coordinated acyclic ligands in that study.

3.1.2 Cobalt Complexes of the L14 Schiff-Base Macrocycle

Direct reactions, employing cobalt(II) as a template ion for the cyclisation, were unsuccessful.[9] Instead, the transmetallation route was followed and this gave single crystals of a deep red complex, $\mathrm{[Co^{II}_2L14(CH_3CN)_4](ClO_4)_4}$, in good yield.[4] This dicobalt(II) complex was prepared in air so clearly it does not react spontaneously with oxygen, unlike the cobalt complexes of the large unsymmetrical phenolate macrocycles described by Okawa and co-workers which must be prepared carefully under an inert atmosphere.[120] In this sense, $\mathrm{[Co^{II}_2L14(CH_3CN)_4](ClO_4)_4}$ is more similar to the dicobalt(II) complexes of the phenolate macrocycle $\mathrm{L2^{2-}}$, $\mathrm{[Co^{II}_2L2X_2]\cdot}y\mathrm{CH_3OH}$ (where $\mathrm{X = Cl^-}$ and $y = 2$; or $\mathrm{X = Br^-}$ and $y = 1$), which are air stable even in solution.[121]

The deep red colour indicates that $\mathrm{[Co^{II}_2L14(CH_3CN)_4](ClO_4)_4}$ is a low-spin cobalt(II) complex and a careful analysis of the parameters obtained from the low temperature single crystal structure analysis (Figure 15)[4] was consistent with this prediction. For example, the average Co–N(macrocycle) bond length is 1.983(4) Å, which strongly indicates that the cobalt(II) ion is low spin as the bond lengths are typically ca. 0.15 Å shorter for low-spin complexes than they are for high-spin complexes (Section 2.1.2).[9,120] The cobalt ions are in distorted octahedral environments and the macrocycle adopts a remarkably flat conformation. Detailed magnetic studies have subsequently confirmed the low-spin state of this complex at the temperature of the X-ray data collection.[9]

This complex, $\mathrm{[Co^{II}_2L14(CH_3CN)_4](ClO_4)_4}$, was the first pyridazine-bridged cobalt complex[21,24,40,84] established to

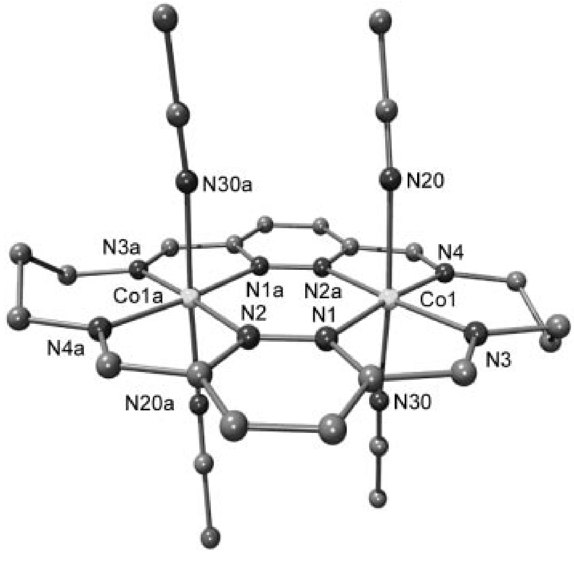


Figure 15. Perspective view of the cation of $\mathrm{[Co^{II}_2L14(CH_3CN)_4]^{4+}}$

be low spin (Section 2.1.2). This implies that building the pyridazine moiety into a macrocyclic ligand has resulted in a unique and rather special environment for the encircled cobalt ions. Four reversible one-electron processes are a feature of the electrochemistry of this complex,[4] however, the magnetic properties have been the focus of attention to date. Given that the macrocycle encircles the two cobalt ions, providing each with a planar N_4 donor set, this leaves two axial sites on each cobalt ion available to be occupied by exogenous ligands. In the $[Co_2^{II}L14(CH_3CN)_4](ClO_4)_4$ complex the axial sites are occupied by solvent acetonitrile molecules. The next question was therefore: can the spin state be tuned by altering the group occupying the axial sites?

The first clue to the answer of this question was provided by the observation that on adding water to the deep red residues left on the glassware used to make $[Co_2^{II}L14(CH_3CN)_4](ClO_4)_4$ (i.e. washing up), an orange solution, indicative of high spin cobalt(II), was obtained. When this was repeated and optimised in a scientific manner it was found that the recrystallisation of $[Co_2^{II}L14(CH_3CN)_4](ClO_4)_4$ from 9% water (by volume) in acetonitrile by vapour diffusion of diethyl ether, yielded orange single crystals of the tetra-aquo adduct $[Co_2^{II}L14(H_2O)_4](ClO_4)_4$.[9] The low temperature crystal structure determination reveals a very similar overall structure (Figure 16) to that of the tetra-acetonitrile adduct, however the bond lengths are, as expected for this high-spin complex, significantly longer [av. $Co-N_{macro}$ 2.104(4) Å] than those in the low-spin tetra-acetonitrile adduct [av. $Co-N_{macro}$ 1.992(4) Å] and the bond angles are somewhat more distorted from those expected for an octahedron [tetra-aquo adduct 76.6−110.6°; vs. tetra-acetonitrile adduct 80.8−103.7°].[9]

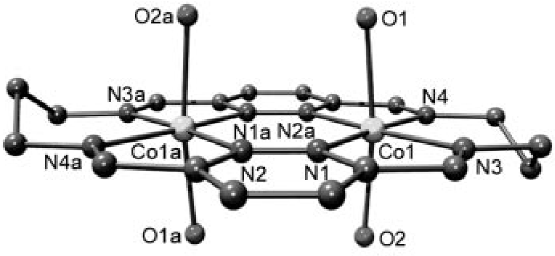


Figure 16. Perspective view of the cation of $[Co_2^{II}L14(H_2O)_4]^{4+}$

Sodium thiocyanate is often found to be useful when exogenous ligands are required in macrocyclic chemistry so this was the next reagent used in attempts to vary the nature of the axial ligands. In this case dark red-black single crystals of $[Co_2^{II}L14(NCS)_2(SCN)_2]$ formed when acetonitrile solutions of $[Co_2^{II}L14(CH_3CN)_4](ClO_4)_4$ and NaSCN were slowly diffused together. The colour indicated that the complex was low spin.[5] The low temperature single crystal structure determination revealed the same very flat macrocycle conformation seen in the previous two structures, and once again the presence of octahedral cobalt ions (Figure 17). Of note in this structure is that each cobalt ion has one N-bound and one S-bound thiocyanate ion, the latter being a first for cobalt(II). The bond lengths are consistent with the low spin configuration [av. $Co-N_{macro}$ 1.951(3) Å], and the angles at cobalt approach 90° more closely [86.8−92.8°] than they do in the high-spin complexes. The magnetic behaviour of this complex is even more interesting than the previous two complexes as it turns out that it is

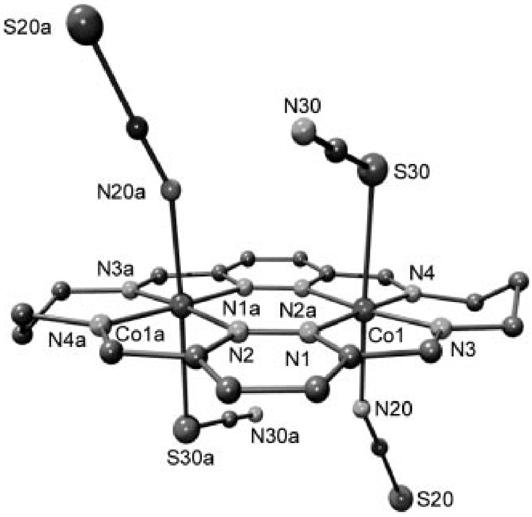


Figure 17. Perspective view of $[Co_2^{II}L14(NCS)_2(SCN)_2]$

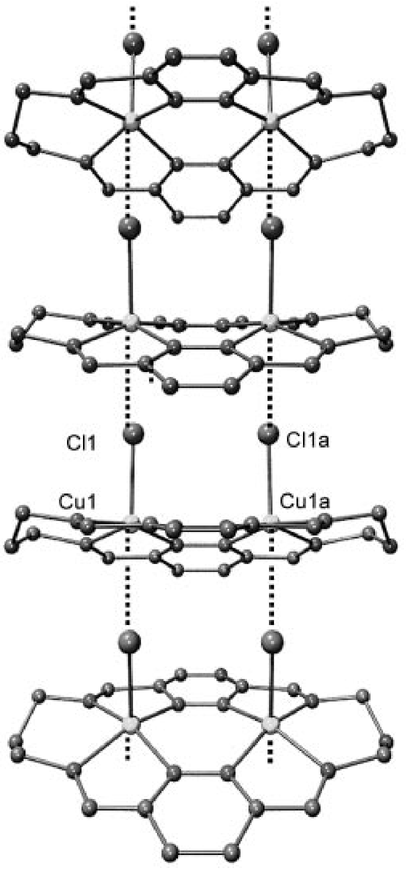


Figure 18. Perspective view of the cation of $[Cu_2^{II}L14(Cl)_2]^{2+}$

the first cobalt complex to exhibit both exchange coupling and spin-crossover effects.

Further variations have been made to the groups occupying the axial sites.[9] Attempts, unsuccessful to date, have also been made to insert bridging ligands in these sites in order to stack these complexes,[9] as has been seen before in the case of the "ladder" complex observed for copper(II), $[\mathrm{Cu}^{\mathrm{II}}_2\mathrm{L14Cl}_2]^{2+}_{\infty}$ (Figure 18).[7]

4. Conclusions and Outlook

The incorporation of 3,6-diformylpyridazine into Schiff-base macrocycles has resulted in a novel coordination chemistry and a rich structural diversity. The first examples of complexes in which Schiff-base macrocyclic pyridazine bridging of encapsulated metal ions is observed have been isolated and fully characterised. A rare example of a [4+4] macrocycle, L14′, has been prepared and structurally characterised as a dilead(II) complex: in all cases transmetallation of this complex with first row transition metal ions has resulted in ring-size alteration to form complexes of the [2+2] macrocycle L14. Both $[\mathrm{M}_2\{2+2\}]^{x+}$ and $[\mathrm{M}_4\{2+2\}_2]^{y+}$ complexes have been formed and both flat and folded macrocycle conformations have been observed. Coordination numbers for metal ions encapsulated in either the [2+2] or [4+4] macrocycle range from 4−8 (examples of seven coordination are not discussed here[2]).

A rich and reversible electrochemistry is a feature of these complexes of L14. The macrocyclic framework has led to increased stability of the redox products over that generally observed for related acyclic complexes. This also led to the isolation of the first mixed-valent pyridazine-bridged complex (of copper), due to significant stabilisation of the mixed-valent oxidation state, in marked contrast to the acyclic analogues.

Exciting magnetochemistry is a feature of the cobalt(II) complexes. Incorporation of the bridging pyridazine moiety into this macrocyclic framework has resulted in the first examples of low-spin and spin-crossover cobalt(II) for pyridazine-bridged complexes of any type.

Many new and interesting avenues remain to be explored. These include the condensation of 3,6-diformylpyridazine with other mono-, di- and triamines.[11] For example, the reaction of this head unit with tris(2-aminoethyl)amine (tren) has provided ready access to a new cryptand and the coordination chemistry of this cryptand, and the amine analogue, is well underway.[8,10,11] The incorporation of related heterocycles into macrocyclic frameworks,[11] and the design and synthesis of polydentate acyclic ligands for use in extending and developing the grid-like behaviour observed in some of the macrocyclic complexes described above (e.g. Figure 12)[6,7] are other areas of considerable and ongoing interest to us.[11]

Acknowledgments

I am extremely grateful to the following research students and assistants, postdoctoral and research fellows, and collaborators who have "made things happen": Dr. Robert J. Kelly (research assistant and PhD student), Dr. Paul G. Plieger (PhD student), Janna D. Ewing [BSc(Hons) student], Dr. Duncan J. de Geest, Dr. Dietmar K. Kennepohl, Dr. David S. Larsen (organic synthesis advice), Dr. Eckhard Bill (EPR, MPI für Strahlenchemie), Dr. Eberhard Bothe (electrochemistry, MPI für Strahlenchemie), Dr. Boujemaa Moubaraki (magnetism, Monash University), Professor Keith S. Murray (magnetism, Monash University) and Professor Jane Nelson (pyridazine cryptates, Queens University of Belfast). This research program gained momentum thanks in large part to a small grant from the Public Good Science Fund (Foundation for Research, Science and Technology, NZ) in 1993 which meant I could employ RJK (research assistant) full time for seven months. Support from a variety of grants from the University of Otago has been vital throughout, and we are very fortunate that we currently have a three year grant from the Marsden Fund (Royal Society of New Zealand).

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Received March 17, 2002
[I02137]