Pure & Appl. Chem., Vol. 58, No. 11, pp. 1437–1444, 1986.
Printed in Great Britain.

Tetraimine Schiff base macrocycles derived from heterocyclic dicarbonyls †

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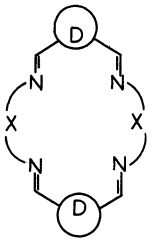
Abstract - The coordination chemistry of tetraimine Schiff base macrocycles derived from heterocyclic dicarbonyls and primary diamines is reviewed in outline.

INTRODUCTION

It is the purpose of this review to consider the coordination chemistry of tetraimine Schiff base macrocycles which result from [2+2] condensation reactions of heterocyclic dicarbonyl-containing species with 1,n-diamines (Fig. 1). Serious exploitation of tetraimine Schiff base macrocycles as binucleating ligands commenced in 1970 with Robson's work on the template synthesis of transition metal complexes of macrocycles derived from the condensation of 2,6-diformyl-4-methylphenol with 1,3-diaminopropane (ref. 1). The subsequent exploitation of such phenol-containing systems has been extensive and the subject of review (ref. 2). It was not possible to isolate metal-free macrocycles from the phenolic systems. Interestingly Steinkopf had reported, in 1939 (ref. 3), that metal-free macrocycles were available from the condensations of 3,4-di-bromothiophene-2,5-dicarbaldehyde with a range of primary diamines. The intense colour and amorphous nature of these materials led to the suggestion that they were likely to be polymers rather than discrete tetraimine Schiff base macrocycles (ref. 4). During the course of an investigation into the coordination chemistry of some pentadentate Schiff base macrocycles (ref. 5), Martin Nelson and his co-workers found that, in the presence of lead(II) cations, a condensation occurred beween 2,6-diacetylpyridine and 3,6-dioxooctane-1,8-diamine to give not the anticipated mononuclear complex of the pentadentate macrocycle (L^1) but a bimetallic complex of a 30-membered decadentate macrocyclic ligand (L^5) (ref. 6). This observation led on to a seminal study of tetraimine Schiff base macrocyclic complexes derived from heterocyclic dicarbonyl head-units (refs. 7-10). Two key steps facilitated the development of this area of macrocyclic chemistry. The first, the utilisation of alkaline earth and main group elements as templating devices, and the second, transmetallation reactions to give transition metal complexes which were inaccessible by other routes.



Head unit: D = pyridine, furan, thiophen, pyrrole
Lateral unit: X = 1, n-diamine

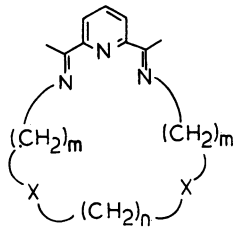
Fig. 1. Schematic representation of tetraimine Schiff base macrocycle

DERIVATIVATION OF [2+2] MACROCYCLES

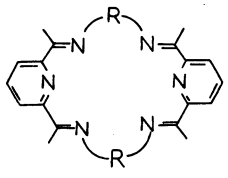
Metal ion control in macrocycle synthesis

One general synthetic route to macrocycles (L^1-L^4) has been through the application of metal template procedures; equimolar amounts of the organic precursors are reacted in the presence of a transition metal salt in alcoholic solution. Extension of the nature of the templating cation to include the alkaline earth metals and main group elements such as tin and lead was established in Belfast (refs. 6,11,12) and in Sheffield (refs. 12-15). The compatability between the radius of the templating cation and the 'hole' of the macrocycle contributes to the effectiveness of the synthetic pathway, and to the geometry of the product complex. For example cations of radii less than ca. 0.80 Å appear not to generate macrocyclic complexes with L . Furthermore neither Cu(II) nor Ni(II) act as templates for this group of

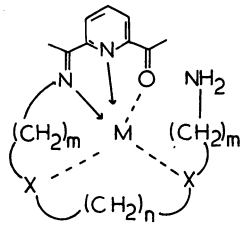
† This lecture is presented in memoriam Martin Nelson (1928-1985)



L^1, m = n = 2, X = O
L^2, m = n = 2, X = NH
L^3, m = 2, n = 3, X = NH
L^4, m = 3, n = 2, X = NH



L^5, R = $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$
L^6, R = $-CH_2CH_2NHCH_2CH_2NHCH_2CH_2-$
L^7, R = $-C_6H_4-$
L^8, R = $-CH_2CH(OH)CH_2-$
L^9, R = $-CH_2CH_2CH_2-$
L^{10}, R = $-CH_2CH_2SCH_2CH_2-$
L^{11}, R = $-CH_2CH_2CH_2NHCH_2CH_2CH_2-$



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macrocycles yet are commonly used to template tetradentate 'N_4' macrocycles (ref. 16); this probably arises from the preference of these cations for stereochemistries in which the bonding orbitals are in orthogonal arrangements as opposed to being pentagonally based. If the cation radius is too large for the 'hole' then a [2+2] rather than a [1+1] condensation can occur. Mg^{++} (r = 0.72 Å) acts as a template for L^1 (ref. 12) but Sr^{++} (r = 1.16 Å), Ba^{++} (r = 1.36 Å), Ag^{+} (r = 1.15 Å) and Pb^{++} (r = 1.18 Å) lead to complexes of L^5 (ref. 6,7,17). The nature of the donor atom is also important as although use of Pb^{++} yields L^5, in the corresponding all nitrogen system the [1+1] product L^2 is obtained. The Pb^{++} lies significantly closer to the nitrogen donors than to the oxygen donors in the complex $Pb_2L^5(SCN)_4$ (ref. 6) and in a related mononuclear 'N_3O_3' macrocycle (ref. 13). This suggests that if a strong interaction occurs between the metal and the donor atoms X then the terminal NH_2 and C=O groups of the probable intermediate (1) can be brought into cis-alignment as required for ring closure to the [1+1] product. With weakly coordinating donors then the constraint leading to close proximity of the terminal units is raised and a [2+2] product results.

Mechanistic aspects of the syntheses

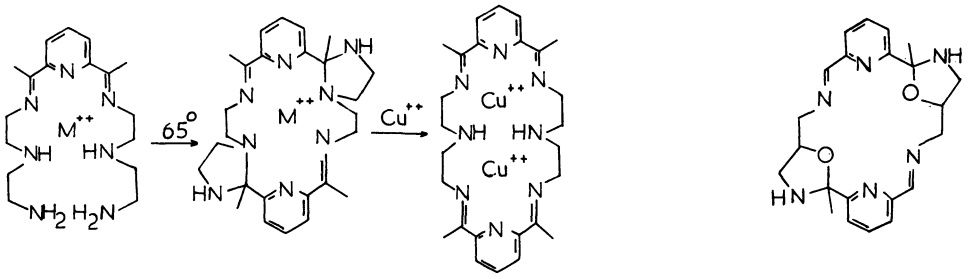
Possible routes to the formation of [1+1] or [2+2] macrocycles are indicated in Scheme 1 (refs. 7,17). It has been proposed that in the presence of Ba^{++} the formation of the macrocycle L^5 proceeds via the open chain intermediate (3) derived from one molecule of dicarbonyl and two molecules of diamine. The intermediates, isolated as their Ba^{++} complexes, were shown to undergo ring closure in anhydrous MeOH on treatment with a further molecule of dicarbonyl. Both symmetric and nonsymmetric (containing both pyridyl and furanyl head units) macrocycles were obtained. The formation of a Ba^{++} complex of type (4) derived from two molecules of 2,6-diacetylpyridine and one molecule of 3,6-diazaoctane-1,8-diamine has been found not to ring close on reaction with a range of diamines (ref. 18). This is because there is an unfavoured mutual positioning of the two carbonyl units inhibiting further reaction. Ring closure of (3) has been achieved by merely warming (3) in dry solvents: elimination of diamine via a bimolecular transmination reaction has been proposed to occur (ref. 17).

Transmetallation reactions

The alkaline earth metal and lead(II) complexes have been found to be unusually kinetically labile in that the complexed template ion may be readily exchanged for another metal ion in solution (refs. 5,7,15,19,20). This process makes available a range of metal complexes, particularly those of Cu(II), which were not accessible using direct template synthesis.

Metal-induced ring contraction

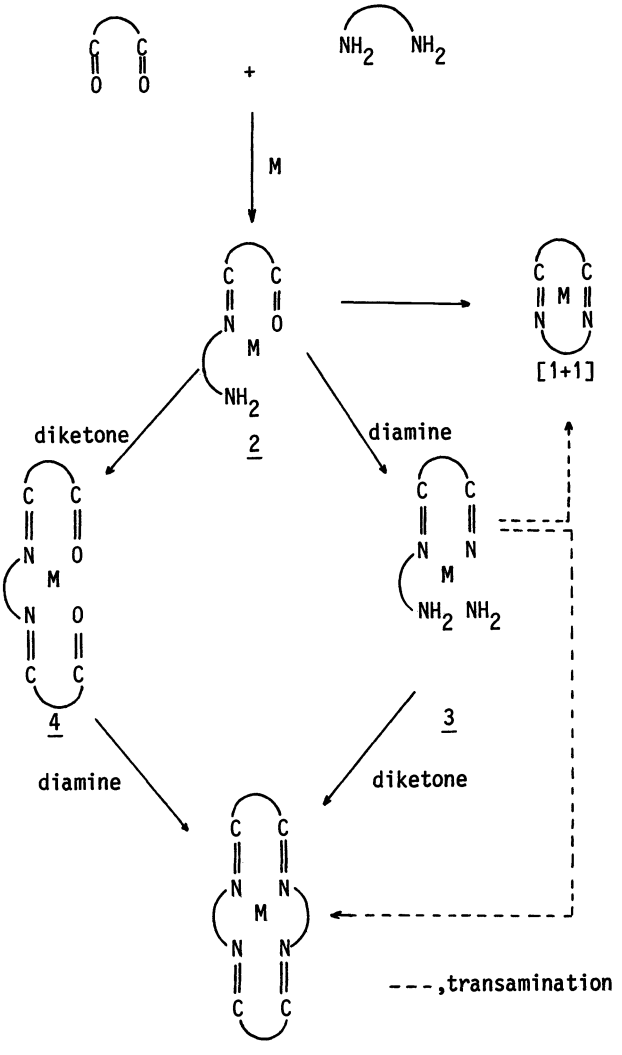
The reaction of 2,6-diacetylpyridine with diethylenetriamine in the presence of Ca^{++}, Sr^{++} or Ba^{++} in 1:1:1 molar ratio in MeOH at room temperature gave the complexes (5), (ref. 21). If the reaction was carried out at higher temperature the macrocyclic complexes (6) were obtained; the intermediacy of (5) in the formation of (6) can be shown by ring-closure reactions both in the presence and absence of added diketone. The structure of the barium complex (6, M = Ba) has been solved and clearly established that the secondary amine groups have added across neighbouring imine bonds with expulsion of two imidazolidone rings from the inner ring of the macrocycle. The thermodynamic driving force for the ring contraction, [24] → [18], can be attributed to a mismatch of macrocyclic cavity size in the extended L^6 form and the alkaline earth metal ion radius. Treatment of (6) with $Cu(ClO_4)_2$, $6H_2O$ gave the homobinuclear complex (7) with accompanying ring expansion; a similar reversal was noted on transmetallation with $AgClO_4$.



5 6 7 8

The above ring contraction is entirely analogous to an [18] → [15] contraction observed on replacement of alkaline earth metal cations by smaller transition metal ions in the related macrocycle L^7, (ref. 22). The reaction of 1,3-diamino-2-propanol with 2,6-diacetylpyridine provides further evidence for the metal-ion control of ring contraction (ref. 23). In the presence of Ba^{++} the macrocycle L^8 was produced as its Ba^{++} complex whereas with the smaller Pb^{++} cation as template a [20] → [18] ring contraction occurred to give the Pb^{++} complex of the oxazolidone-containing macrocycle (8). Both products give a dinuclear complex of L^8 on reaction with copper(II) (refs. 23,24).

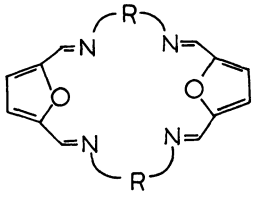
Scheme 1



UTILISATION OF [2+2] MACROCYCLES

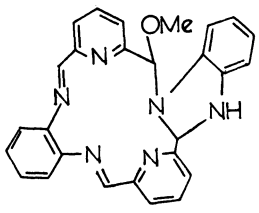
Mononuclear complexes

Mononuclear alkaline earth metal complexes of the [2+2] macrocycles provide interesting chemical features in their own right as well as serving, through the transmetallation reaction, as useful synthetic reagents. Macrocycles such as L^7, L^{12} and L^{13} are readily generated in the presence of Ca^{++}, Sr^{++}, Ba^{++} or Pb^{++} (refs. 25-28). The influence of cation size is noted in that Mg^{++} is ineffective as a templating device as are the transition metal ions Mn^{++}-Zn^{++}. The complexes have 1:1 stoicheiometry with hexagonally-based geometries (refs. 25,26), with the exception of the Ba^{++} complexes of L^{12} and L^{13} where a 1:2 metal:ligand ratio is observed (refs. 27,28). X-Ray crystallographic studies reveal that these complexes have 'sandwich' structures, the Ba^{++} being too large to sit within the macrocyclic cavity. In the complex $[Ba(L^{12})_2(H_2O)_2][Co(NSC)_4]$ the Ba^{++} is bound to all six donor atoms from one macrocycle but only three donors from the second. There is a severe folding of this latter macrocycle such that one furan group is not coordinated (ref. 27). The hexahapto-trihapto structure is retained in solution (CD_3CN) at low temperatures; ^1H n.m.r. studies reveal that as the temperature is raised there is a coalescence of resonances indicating a fluxional interconversion between the four available, equivalent configurations of the complex. The complex $[Ba(L^{13})_2][BPh_4]_2$ shows a true sandwich structure with two almost parallel donor ring planes (ref. 28). The macrocycle L^{13} can also be prepared in the presence of K^+, but the smaller alkali cations do not induce cyclisation. The Na^+ complex may be synthesised via neutralisation of the diacid salt $[H_2L^{13}][ClO_4]_2$ and the ^{23}Na n.m.r. spectrum shows slow exchange of Na^+ between $[NaL^{13}][ClO_4]$ and $[Na(^2H_6\text{-dmso})_n]^+$. The free macrocycle was not isolated but recrystallisation of the Na^+ complex gave the metal-free alcohol addition products L^{13}.2MeOH and L^{13}.EtOH. These may be compared with similar products found during the template generation of related diimine macrocycles containing α-aminoether units (ref. 29).



L^{12}, R = $-CH_2CH_2CH_2-$
L^{13}, R = $-C_6H_4-$
L^{14}, R = $-CH_2C(CH_3)_2CH_2-$

Although the transition metal ions are not effective templating agents for the above macrocycles, it was found that transmetallation reactions with the alkaline earth complexes of L^7 gave Mn(II), Fe(II), Co(II) and Zn(II) complexes of the ring-contracted ligand (9), (ref. 22). This ring contraction is consistent with the observed poor templating properties of transition metal ions. Mononuclear transition metal complexes (Fe(II), Co(II), Co(III), Ni(II) and Cu(II)) have been prepared via transmetallation routes for the macrocycle L^5. The complexes are octahedral and only the six methine N atoms are coordinated. In the case of the Fe and Co complexes the large crystal field stabilisation energy accompanying the formation of the spin-paired, approximately octahedral structure is suggested as the driving force for the macrocycle adopting this mode of coordination (ref. 30). The copper complex can be treated with excess metal to generate a binuclear complex; this is in contrast with the Fe, Co and Ni complexes (ref. 31).



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Binuclear complexes

Binuclear complexes of macrocyclic ligands have been the focus of much attention (ref. 32). They are of importance in several areas including the study of ferro- and anti-ferromagnetic exchange coupling, electron transfer properties, the binding and activation of small substrate molecules and as small molecule models for bimetallobiosites. Homodinuclear complexes of [2+2] tetraimine Schiff base macrocycles have been readily obtained but, to date, heterobinuclear complexes are restricted to a CuNi complex of L^5 (ref. 31).

Homodinuclear complexes as hosts

Homodinuclear complexes of [2+2] macrocycles are ideally suited to act as hosts for small bridging ligands (refs. 8-10). The copper(II) complex $[Cu_2L^5](ClO_4)_4$, $2H_2O$ serves as the starting point for the preparation of several derivatives in which small substrate anions may be bound between the metal centres (OH^-, imidazolate, N_3^-, NCS^-), (refs. 31,33). The crystal structures of the OH^-, imidazolate (ref. 31) and N_3^- (ref. 33) derivatives show the copper(II) atoms held by the methine N atoms and bridged by the anion, (Fig. 2). The N_3^- and imidazolate bridge in μ-1,3-modes. Magnetic exchange studies on μ-OH and μ-imidazolate show antiferromagnetic coupling to occur with respective J values of -120 cm^{-1} and -21 cm^{-1}. The latter value corresponds with a value of -23 cm^{-1} found for the related dinuclear copper(II) μ-imidazolate complex derived from L^{10} (ref. 34) and is close to that (-26 cm^{-1}) found from temperature dependent e.p.r. studies of the $Cu(II)_4$ derivative of bovine superoxide dismutase (ref. 35), in which bridging imidazolates span each pair of Cu(II) atoms by analogy with the known structure of the native CuZn form (ref. 36).

The Ba^{++} in $[BaL^9](ClO_4)_2$ may be replaced by two copper(II) atoms to give $[Cu_2L^9(OH)](ClO_4)_3$, $2H_2O$ and $[Cu_2L^9(OMe)](ClO_4)_3$, $2H_2O$ (ref. 37). The X-ray structure of the former established the presence of the bridging hydroxy-group and magnetic studies show antiferromagnetic coupling with J values of -32 and -53 cm^{-1} respectively. The e.p.r. spectra indicate a retention of the bridge in solution. Treatment of the μ-OH complex with NaN_3 yields an azido-complex which, from its i.r. spectrum, probably has present an μ-1,1-azide. Electrochemical studies have been reported for the μ-OH and μ-imidazolate complexes; all showed two district reduction processes to occur, and no evidence for a cooperative, two-electron process, as found in Type 3 copper proteins, was observed (ref. 38).

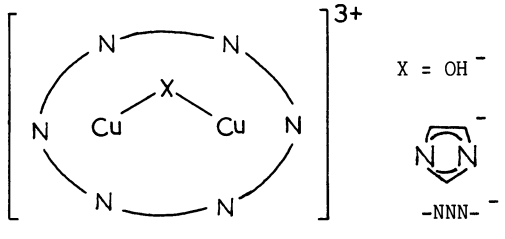


Fig. 2. Schematic representation of bridging substrates

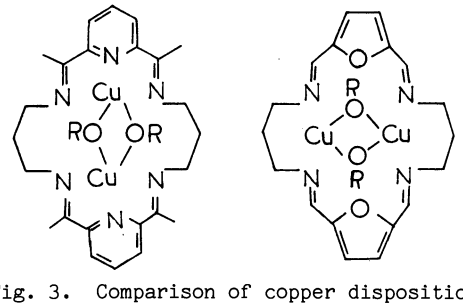


Fig. 3. Comparison of copper disposition in pyridine and furan headed macrocycles

μ-Hydroxy and μ-alkoxy dicopper(II) complexes are also available for furan-containing ligands. The structure of $[Cu_2L^{12}(OEt)_2](NCS)_2$, (ref. 39), shows that the copper(II) atoms are bound to the imine N atoms but not to the furan, and so a lateral Cu...Cu disposition is found in contrast to the head-to-head disposition found in the corresponding pyridine complexes (Fig. 3). The copper(II) atoms in the furan-headed macrocycles are strongly antiferromagnetically coupled having J values of -300 to -350 cm^{-1}.

Dicopper(I) complexes of L^5 and L^{12} have been prepared by transmetallation reactions, or by the reduction of copper(II) present in the macrocycle (refs. 31,39). The latter route can be accomplished by reduction of dicopper(II) complexes of L^5 using $NaBPh_4$ (ref. 31), or by simply heating dicopper(II) complexes of L^{12} in MeCN to yield the dicopper(I) complex (ref. 39). The ease of reduction in the latter case has been traced to geometrical factors (ref. 10) as when the 'Cu_2L^{12}' moiety is in the planar configuration preferred by Cu(II) severe steric hindrance occurs between the bridging groups and the noncoordinated furan oxygens. This is effectively removed if a tetrahedral geometry is attained; this is less acceptable to Cu(II) so the facile reduction is promoted.

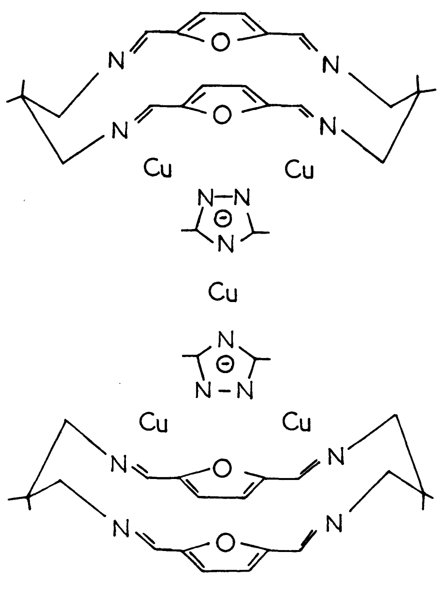
The first observation of thiocyanate bridging through the S-atom only was made through the X-ray structure of $[Cu_2L^{12}](SCN)_2$ prepared by reduction of $[Cu_2L^{12}(OEt)_2](NCS)_2$ (ref. 40). A series of dicobalt(II) complexes of L^{12}, having present hydroxo-, alkoxo-, phenoxo-, thiolato-, halogeno- and pseudohalogeno-bridges has been reported (ref. 41).

Substrate oxidation

In the presence of certain substrates the reduction of the $[Cu(II)_2L^{12}]$ moiety in $[Cu_2L^{12}(OH)_2](ClO_4)_2$, $2H_2O$ or $[Cu_2L^{12}(OR)_2(MeCN)_2]BPh_4$ is accompanied by substrate oxidation (refs. 10,39,42). For example PhSH, PhC≡CH, hydrazobenzene, catechols, hydroquinones and ascorbic acid gave respectively PhSSPh, PhC≡CC≡CPh, azobenzene, o-quinones, p-quinone and dehydroascorbic acid. The latter reactions may be compared with the behaviour of Type III cuproproteins. Several of the oxidations proved to be catalytic in '$Cu(II)_2L^{12}$' when

carried out in dimethylformamide solution in the presence of O_2. The complex $[Cu_2L^{12}(OEt)_2](NCS)_2$ was inactive, however, illustrating a requirement for coordinative unsaturation at the metal centres in the reduced state. The very poor activity of mononuclear $Cu(ClO_4)_2$, $6H_2O$ in the above reactions is indicative of the need for a dicopper site.

The oxidation of acetonitrile to 3,5-dimethyl-1,2,4-triazole has been found to occur when $[Cu_2L^{14}(MeCN)_2][ClO_4]_2$ is heated in a MeCN/EtOH solvent mixture containing a little water, and in the presence of air. The complex $[Cu_5(L^{14})_2(TAZ)_2][ClO_4]_3$, EtOH (<u>10</u>) (TAZ = the 3,5-dimethyl-1,2,4-triazole anion) was recovered and identified through the X-ray crystal structure (ref. 43). A possible mechanism for the reaction is illustrated in Scheme 2; the ammonia required for ring closure is probably generated by a metal-promoted hydrolysis of MeCN. The Cu_5 complex can also be synthesised via spontaneous self-assembly from



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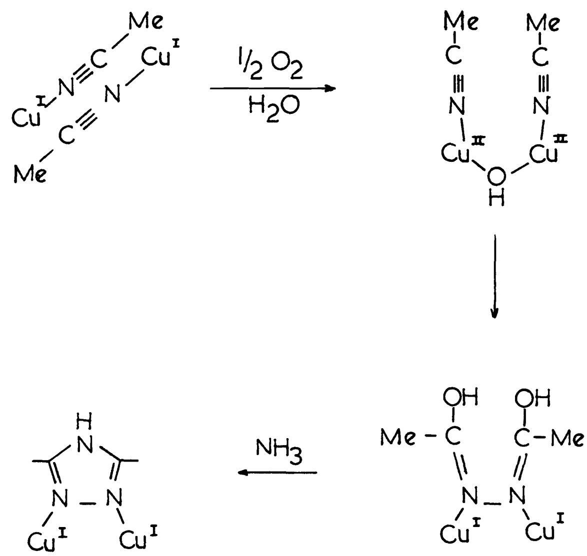
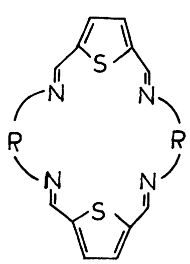
Scheme 2



pre-prepared 3,5-dimethyl-1,2,4-tetrazole. Aggregate structures in copper complexes of L^{12} have also been found. The tetranuclear cation $[Cu_4(L^{12})_2(C{\equiv}CPh)]^{3+}$, containing a Cu_4-phenylacetylide core has been isolated during the oxidative coupling of phenylacetylene (ref. 42) and $[Cu_6(L^{12})_3(SPh)_2]^{4+}$ is isolated as a by-product in the catalytic oxidation of PhSH to PhSSPh (ref. 10). Spectrophotometric monitoring of the reaction of $[Cu_2L^{12}(MeCN)_2]$-$(ClO_4)_2$ with O_2 in dimethylacetamide provides further demonstration of molecular association of the dinuclear units. It can be established that the concentration of a reddish brown intermediate complex is optimised when 0.25 moles of O_2 per di-Cu(I) complex is consumed. The stoicheiometry of the intermediate is probably 'Cu_4O' and an aggregation has occurred. From these and related observations of O uptake it is proposed that the di-Cu(I) complexes promote a four-electron reduction of O via a μ-peroxo-di-Cu(II) stage. In the presence of a substrate further reduction occurs through substrate dehydrogenation whereas in the absence of substrate it occurs via association with a second unit of di-Cu(I) (ref. 10).

Metal-free [2+2] macrocycles

Although in general it has been found necessary to use template procedures in the synthesis of [2+2] macrocycles derived from heterocyclic dicarbonyls, metal-free macrocycles (L^{15}) were obtained by non-template procedures when thiophen-2,5-dicarbaldehyde was reacted with primary diamines (ref. 44). The integrity of the macrocycles was deduced through i.r.,



L^{15}

n.m.r., and m.s., and verified by the X-ray structure of L^{15} (R = $-CH_2CH_2OCH_2CH_2-$). These syntheses, and the template procedures referred to throughout, have been carried out in alcohols. When 2,6-diacetylpyridine was reacted with bis(aminopropyl)amine in thf the metal-free macrocycle L^{11} was obtained (ref. 45). The metal-free macrocycles may be reduced with $NaBH_4$ to give the corresponding tetramines. Reduction of the lead complexes of tetraimine Schiff bases also provides a route to the metal-free tetramines; the lead(II) being reduced to lead(0) (ref. 20).

Recent developments

Pyrrole-2,5-dicarbaldehyde (ref. 46) and 5,5'-diformyldipyrrole (ref. 47) have been used to promote the synthesis of tetraimine Schiff bases, and so extend the range of available head-units. Functionalised lateral-units have been incorporated introducing hydroxyl (refs. 23,24), dimethylaminoethyl (ref. 45), aminoethyl and pyridylmethyl (ref. 48) moieties and giving 'opened cryptands'. The cyclisation process itself does not stop at the [2+2] stage. This has been evidenced through the crystal structure of a tetranuclear Schiff base complex in which a novel cubane-like $Mn_4(alkoxy)_4$ core is incorporated into a [4+4] macrocycle derived from 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane (ref. 49). Extension of the range of templating metal ions to include lanthanides (ref. 50) and actinides (ref. 51) has also been achieved.

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