Contribution from the Department of Chemistry,
University of York, Heslington, York, United Kingdom.

Catalytic Formation of Cyclic Schiff's Bases By Metal Ions. A Template Process

Michael Green, J. Smith, and P. A. Tasker

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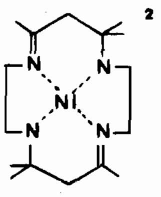
The reactions of diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane and 1,2-diaminobenzene with 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione in the presence of metal ions and Lewis acids are investigated. Both cyclization and polymerisation can occur. Evidence is presented for a template reaction and for Lewis acid catalysis. The following compounds have been synthesized and their physical properties are described: 3,4:9,10-dibenzo-1,5,8,12-tetra-azacyclotetradecane-1, 11-diene, (*V*, *R* = $-CH_2CH_2-$), *3,4:9,10-dibenzo-1,5, 8,12-tetra-azacyclopentadecane-1,11-diene,* (*V*, *R* = $-(CH_2)_3-$), *3,4:9,10-dibenzo-1,5,8,12-tetra-azacyclohexadecane-1,11-diene,* (*V*,*R* = $-(CH_2)_4-$), *1,5,8,12-tetra-aza-3,4:9,10:13,14-tribenzocyclotetradecane-1,11-diene,* (*V*, *R* = o-*phenylene*), *N,N'-bis-*(o-*carbomethoxyphenyl*)*-1,2-diaminoethane,* (*XIII*), *4,7-diaza-2,3:8,9-dibenzodecane-1,10-diol,* (*XIV*), *4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione,* (*II*).

Introduction

Cyclic compounds can often be formed in the presence of a metal ion.[1,2,3] However it is frequently not clear whether the metal ion is a template or not. In this Paper, an investigation is made of the mechanism of a Schiff's base condensation which under some conditions leads to a cyclic product, in order to see whether the metal ions which catalyse the reaction behave as Lewis acids, as controls on the concentration of free amine, or as genuine templates.

In related condensation reactions involving carbonyls and amines and leading to cyclic products, the metal may appear in the final compound as a complex. House and Curtis[3,4] have shown that acetone and diaminoethane yield(I) in the presence of nickel perchlorate.

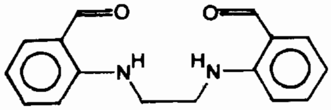


(I)

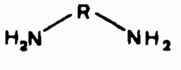
In the presence of either nickel(II) or copper(II), several condensations between simple aldehydes and polyamines take place to give similar products.[3,5] Analogous reactions have been effected by Busch and his co-workers[2] using β-hydroxycarbonyls,[6] α,β-unsaturated carbonyls[6] and α-diketones[7] with diamines using nickel(II). The ultimate products in the self condensation of *o*-aminobenzaldehyde are affected by the presence of cobalt(II), nickel(II) and copper(II),[2,8] while 2,6-diacetylpyridine, which normally condenses with polyamines to form resins, reacts in the presence of nickel(II), copper(II) and iron(II) to give cyclic complexes.[2,9]

The cyclic condensation product need not necessarily appear as a metal complex, however. If nickel is replaced by iron(II) in the reaction of acetone and diaminoethane leading to (I), the corresponding free ligand is formed.[10] In this case an obvious role for the iron(II) is that of a template. The same product, however, can also be formed in the absence of a metal ion, merely by starting with diaminoethane half neutralized with perchloric acid.[11] It is now difficult to see how a similar mechanism can occur, unless « H^+ » can act as a template.

In this Paper a study is made of some of the condensation reactions (of Schiff's Base type) of the dialdehyde (II), 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione. This dialdehyde is treated with various diamines (III, R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, *o*-phenylene) in the absence of catalysts and in the presence of various metal ions and Lewis acids such as aluminium trichloride. When cyclization occurs, to give products such as (IV) and (V), particular attention is paid to the role of the catalyst to see whether or not it is behaving as a template.



(II)



(III)

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(1) D. H. Busch, *Rec. Chem. Progr.* *25*, 107 (1964) *Adv. Chem. Series* *1*, 37 (1963); E. I. Ochiai, *Coord. Chem. Rev.*, 3, 49 (1968); J. P. Collman, Transition Metal Chemistry, ed. Carlin, *2*, 1 (1966).

(2) D. H. Busch, *Helv. Chim. Acta*, Fasc. Extraord., 174 (1966).

(3) N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

(4) D. A. House and N. F. Curtis, *Chem. Ind.* (London), *42*, 1708 (1961).

(5) D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, *86*, 1331 (1964), and references therein.

(6) T. E. MacDermott and D. H. Busch, *J. Amer. Chem. Soc.*, *89*, 5780 (1967).

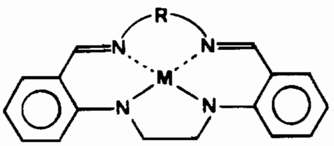
(7) L. T. Taylor, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, *7*, 785 (1968).

(8) G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963); *J. Amer. Chem. Soc.*, *86*, 4834 (1964), *87*, 1706 (1965).

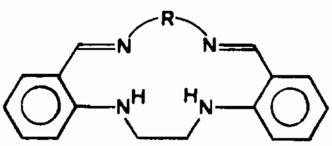
(9) J. L. Karn and D. H. Busch, *Nature*, *211*, 160 (1966), Inorg. Chem., *8*, 1149 (1969); R. L. Rich and G. L. Stucky, *Inorg. Nucl. Chem. Letters*, *1*, 85 (1965); J. D. Curry and D. H. Busch, *J. Amer. Chem. Soc.*, *86*, 592 (1964).

(10) N. Sadasivan and J. F. Endicott, *J. Amer. Chem. Soc.*, *88*, 5468 (1966).

(11) N. F. Curtis and R. W. Hay, *Chem. Comm.*, 524 (1966).

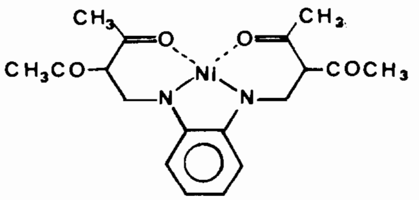


(IV)

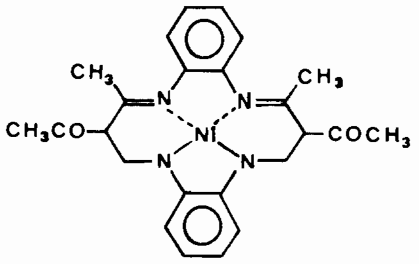


(V)

A somewhat similar reaction has been observed by Jaeger,[12] who finds that the nickel complex (VI) reacts with 1.2-diaminobenzene to form (VII) (amongst other products).



(VI)

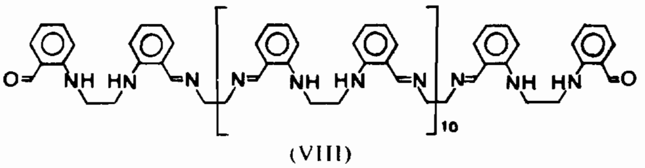


(VII)

Results

The dialdehyde (II) reacts with four diamines (III, R = —$(CH_2)_2$—, —$(CH_2)_3$—, —$(CH_2)_4$—, *o*-phenylene) and nickel(II) or cobalt(II) acetates to produce the corresponding cyclic metal complex (IV, M = Ni, Co) in good yield. Diaminoethane and 1,3-diaminopropane react similarly in the presence of copper(II) acetate. When R is aliphatic, the reactions are complete after refluxing in methanol for six hours, but 16-20 hours were needed for 1,2-diaminobenzene.

When the dialdehyde (II) is treated with diaminoethane in the absence of metal cation under analogous conditions a white material is produced, with a much higher melting point than the metal-free cyclic compound (V, R=—$(CH_2)_2$—, m.wt=292). The lack of a mass peak at m/e = 292 and of carbonyl and amino infra-red frequencies in the white material point to an absence of the free cyclic ligand even in trace quantities. Analysis of the white material fits (VIII) moderately well but this may be coincidence (see Experimental Section). (Hereafter the white material will be referred to as the polymer).

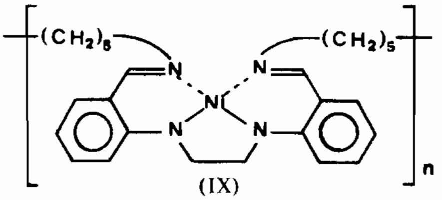


(VIII)

In contrast, when the dialdehyde and diaminoethane are allowed to react under conditions of «high dilution», the metal-free cyclic compound (V, R = —$(CH_2)_2$—) is formed in about 50% yield. The metal-free compound reacts with nickel(II) acetate in a few minutes in boiling methanol to form the nickel complex (IV, M = Ni, R = —$(CH_2)_2$—). In contrast the polymer is only converted to (IV, M = Ni, R = —$(CH_2)_2$—) after boiling with methanolic nickel acetate for 7 days.

Unlike diaminoethane 1,3-diaminopropane and 1,4-diaminobutane react with (II) in the absence of metal ions under conditions of normal concentration to form the metal-free cyclic compounds (V, R = –$(CH_2)_3$–, –$(CH_2)_4$–), no material of higher molecular weight being detected. 1,2-Diaminobenzene does not react with (II) in boiling methanol over a period of six days.

When 1,10-diaminodecane, the dialdehyde and nickel acetate are refluxed in boiling methanol, a solid of low solubility is obtained. As its infra-red, near infra-red and visible spectra resemble those of the other nickel complexes (IV, M=Ni, R= –$(CH_2)_2$–, –$(CH_2)_3$–, –$(CH_2)_4$–), and as it is diamagnetic just as they are, this compond could be the polymer (IX).



(IX)

The reaction between the dialdehyde (II) and diaminoethane is effected by metal ions besides cobalt(II), nickel(II) and copper(II). In the presence of iron(II), zinc(II) and cadmium(II), a mixture of metal-free cyclic compound (V, R = –$(CH_2)_2$–) and polymer is produced, but no metal complex like (IV). Only polymer is formed in the presence of magnesium(II), manganese(II) and silver(I). Aluminium trichloride, a typical Lewis Acid, also leads only to the formation of polymer.

In contrast to the behaviour of the dialdehyde (II) and 1,2-diaminobenzene in the absence of catalyst or in the presence of nickel(II), zinc(II) brings about the production of the free cyclic system (V, R = *o*-phenylene), as do the Lewis acids, the pyridinium ion, aluminium trichloride and antimony trifluoride. The effectiveness of the last two compounds as catalysts can be seen from Table I.

Table I. Time taken for disappearance of solid dialdehyde (II) in the reaction between it and 1,2-diaminobenzene in the presence of different catalyst

Nickel(II) acetate[a]	>10 hr
Zinc(II) acetate	6
Pyridinium perchlorate	5
Aluminium trichloride	1
Antimony trifluoride	<1

[a] Not strictly comparable, as metal complex formed.

The products of the various reactions described are summarized in Tables II and III.

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(12) E. G. Jaeger, *Z. Chemie*, *4*, 437 (1964).

Table II. Products of reaction between the dialdehyde (II) and diaminoethane (en) in the presence of different catalysts, M, together with cumulative stability constants for M en_2 and M en_3

M [a]	Mg^{II}	Mn^{II}	Fe^{II}	Co^{II}	Ni^{II}	Cu^{II}	Zn^{II}	Ag^{I}	Cd^{II}	$AlCl_3$	No Catalyst
Metal complex (IV, R = $-(CH_2)_2-$)				*	*	*					
Cyclic compound (V, R = $(CH_2)_2-$)			*				*		*		High diln. only
« Polymer » [b]	*	*	*				*	*	*	*	*
β_2 [c]	<0.7 [d]	4.9	7.6	10.7	14.1	20.0	11.1	7.1	10.2		
β_3	<1.1 [d]	5.8	9.7	14.0	18.4	19-21	12.9	$\ll$7.1 [e]	12.3		

[a] Details of salts used etc. given in the Experimental Section. [b] *i.e.* white insoluble material with high melting point, see text. [c] $\beta_n = \log K_n$ for $M + n\,en \rightleftharpoons M(en)_n$ in water at 25°C ($\mu = 1$); values from ref. 13. [d] Assuming that $\beta_n < n\beta_1$. [e] There does not appear to be any evidence for $Ag(en)_3^+$.[13,14]

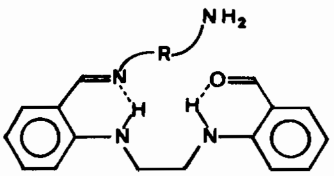
Table III. Products of reaction between the dialdehyde (II) and 1,3-diaminopropane(tn), 1,4-diaminobutane(buten) or 1,2-diaminobenzene(phen) in the presence of different catalysts

	No catalyst	Co^{II}, Ni^{II}	Cu^{II}	Zn^{II}	$AlCl_3$, SbF_3
Metal complex(IV)		tn, buten, phen	tn [a]		
Cyclic compound(V)	tn, buten			phen [b]	phen [b]
No reaction	phen				

[a] Buten and phen not examined. [b] Presumably also for tn and buten.

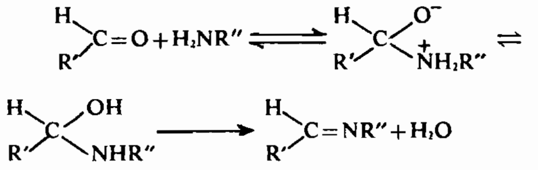
Discussion

The observations, that in the absence of catalyst the dialdehyde (II) and diaminoethane form the cyclic system (V, R = $-CH_2CH_2-$) under conditions of «high dilution» and polymer at larger concentrations, is readily accounted for in terms of probability. At first sight it seems strange that 1,3-diaminopropane and 1,4-diaminobutane should react with the dialdehyde only to form cyclic product (V, R = $-(CH_2)_3-$ and $-(CH_2)_4-$). However once the first imino linkage has been formed as in (X), the hydrogen bonding shown will tend to produce two planar units, so that the probability is quite large of the C=O and NH_2 groups getting close enough to react merely by rotation in one of the C–C bonds in R. Presumably the cyclization step (and also formation of the first imino link) involves a nucleophilic attack by the lone pair on the nitrogen of the NH_2 group on the carbon atom of the carbonyl. This is easy sterically when R is $-(CH_2)_3-$ or $-(CH_2)_4-$. However, a rotation in the C–C bond when R is $-CH_2CH_2-$ superimposes (very nearly) the N from the amine group on the O from the carbonyl group, which illustrates that the lone pair on the nitrogen atom is less favourably placed for the nucleophilic attack on the carbon. This helps to rationalize why cyclization takes place less readily when R is $-CH_2CH_2-$, but does not explain the complete absence of polymerisation in the cases of 1,3-diaminopropane and 1,4-diaminobutane. If only entropy factors were involved some polymerisation would be expected. Is it possible that some form of multicentred hydrogen bonding can help to stabilize the N_4 portion of the cyclic systems?



(X)

The complete failure of the dialdehyde and 1,2-diaminobenzene to react in the absence of catalyst probably arises from the weaker basicity of aromatic amines compared with aliphatic, as the formation of the initial imino group (as well as any subsequent ones) must involve a nucleophilic attack by the amine (like that mentioned in the previous paragraph in connection with cyclization):



(1)

In deciding the role of the catalysts in the reactions between diaminethane and diaminobenzene with the dialdehyde, three effects could be relevant:

(i) the metal ions act as templates, *e.g.*

$$\text{diamine}^{*} \xrightarrow{Zn^{2+}} Zn(\text{diamine})^{2+} \xrightarrow{(II)} (IV) \longrightarrow (V)$$

$$\text{diamine}^{*} \xrightarrow{Ni^{2+}} Ni(\text{diamine})^{2+} \xrightarrow{(II)} (IV)$$

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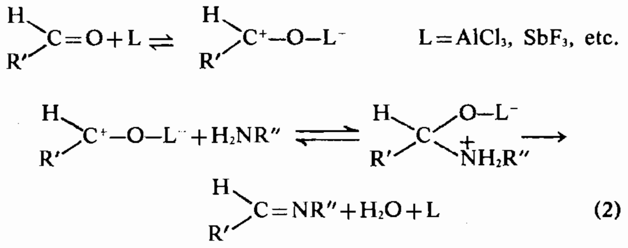
[13] Stability Constants of Metal-Ion Complex, *Spec. Pub. Chem. Soc.*, *17*, (1964).

[14] G. Schwarzenbach, H. Ackermann, B. Maissen, G. Anderegg, *Helv. Chim. Acta*, *35*, 2337 (1952).

(*)The dialdehyde is also a diamine. However it will be a considerably weaker base than diaminoethane because of the acceptor character both of the aromatic and *o*-carbonyl groups. The following β- values[13] (where $\beta = \log K$ for, $H^+ + \text{amine} \rightleftharpoons \text{amine} . H^+$): CH_3NH_2, 10.7; $PhNHCH_3$, 4.8; *o*—$MeOCOC_6H_4NH_2$, 2.2 suggest that $[M(\text{dialdehyde})^{2+}][en]/[M(en)^{2+}][\text{dialdehyde}]$ will be very small. Nevertheless the arguments are still valid if analogous reactions involving the dialdehyde (behaving as a diamine) are introduced at points marked*. At† one must consider the molar ratio of diaminoethane and dialdehyde to zinc ion being greater or less than six.

(ii) catalysis by Lewis acids occurs, *e.g.*



$$\mathrm{HR'C{=}O} + \mathrm{L} \rightleftharpoons \mathrm{HR'C^{+}{-}O{-}L^{-}} \qquad \mathrm{L{=}AlCl_3,\ SbF_3,\ etc.}$$

$$\mathrm{HR'C^{+}{-}O{-}L^{-}} + \mathrm{H_2NR''} \rightleftharpoons \mathrm{HR'C(O{-}L^{-})(\overset{+}{N}H_2R'')} \longrightarrow \mathrm{HR'C{=}NR''} + \mathrm{H_2O} + \mathrm{L} \qquad (2)$$

(iii) complexing between metal ion and diamine* reduces the concentration of the latter so that «high dilution» conditions exist, *e.g.*

$$\mathrm{Mn(en)}_x \underset{\mathrm{Mn^{2+}}}{\rightleftharpoons} \mathrm{en} \xrightarrow{\mathrm{(II)}} (\mathrm{IV}, R = -CH_2CH_2-)$$

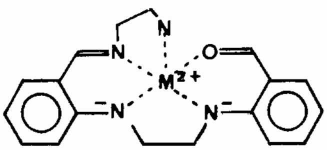
Taking the reaction of diaminoethane first. One can exclude the possibility that the metal ions act just as Lewis acids as in (ii), since aluminium trichloride, which is a better catalyst than metal ions are in promoting reaction of ketones, does not bring about cyclization here. Presumably diaminoethane is sufficiently basic for process (2) to be relatively unimportant compared with (1). At first sight the behaviour of the metal ions (see Table II) can be rationalized in terms of either (i) or (iii). The ions which bring about cyclization all have a strong tendency to form complexes containing four (or more) amine groups, as can be seen from the β_2 values for coordination to diaminoethane quoted in Table II. These ions should be ideal as templates therefore. Although the β_2 values for the formation of the tetramines, $Fe(en)_2^{2+}$ and $Ag(en)_2^{+}$, are almost equal, silver(I) prefers to form tetrahedral rather than square planar (or pseudo-octahedral) complexes.[15] Thus although silver(I) seems to have sufficient affinity to coordinate four amine groups, the geometry would not be satisfactory for cyclization to occur in a template process.

The «high dilution» explanation is supported by the fact the ions which cause cyclization all have large values of β_3 (see Table II). Although the figures quoted refer to aqueous solution at 25°C, they suggest that in boiling methanol the concentration of free, as opposed to complexed, diaminoethane will be small.

Where (i) or (iii) is operating can be determined from the results using zinc(II). The cyclic product is formed both when the molar ratio of diaminoethane† to zinc ion is both greater than and less than three (see Table IV), that is when the concentration of free diaminoethane is both relatively large and very small: high dilution conditions cannot exist when the ratio is greater than three. Therefore the cyclization of the dialdehyde and diaminoethane must involve a template reaction.

It is interesting to note that cadmium(II) is as effective as zinc(II) in bringing about cyclization. Presumably the size of the metal template is not particularly critical.

The metal ion template must operate by formation of a complex such as (XI) in which the carbonyl and crucial amine groups are held close together for a longer time than occurs in the absence of catalyst (c.f. X, R = $-CH_2CH_2-$), so that the probability of condensation is increased. Presumably the aluminium system has insufficient affinity for nitrogen to form anything resembling (XI). Once (XI) is formed the metal ion could act as a Lewis acid as in (ii). However the crucial role of the metal ion has to be that of a template.



(XI)

In contrast to diaminoethane, diaminodecane reacts in the presence of nickel(II) to give a polymeric complex. Presumably condensation of the first amine and carbonyl groups occurs in the same way in each case. However the probability of producing of a complex analogous to (XI) will be very much smaller in the case of diaminodecane, because of a lower chance of formation of a thirteen membered ring compared with one containing five atoms.

The reaction of diaminobenzene with the dialdehyde is rather different from that of diaminoethane, as nothing at all happens in the absence of a catalyst, and as Lewis acids can cause cyclization. Because of the first difference the high dilution suggestion, (iii), is no longer relevant. The question remaining is whether (i) and (ii) are both important, whether metal ions such as nickel(II) and zinc(II) can act as Lewis acids so that only (ii) is relevant, or whether aluminium trichloride, antimony trifluoride and the pyridinum ion can behave as templates so only (i) need be invoked.

Aluminium trichloride and antimony trifluoride are obvious Lewis acids. Though in theory any metal ion can be regarded similarly, it does not follow that zinc(II) and nickel(II) will necessarily be good catalysts as Lewis acids. A sequence of increasing efficiency as catalysts for the reaction between the dialdehyde and diaminobenzene is shown going down Table I. This sequence corresponds roughly to a rise in class B character. Moreover it is class B acceptors that would be expected to coordinate most readily to polarizable donors such as the C=O group. It seems therefore most reasonable to attribute the high catalytic power of aluminium trichloride and antimony trifluoride to Lewis acid character thus invoking hypothesis (ii). Nevertheless if this were their only role and each molecule of catalyst coordinated with only one carbonyl group, the condensation reactions would be expected to result in the formation of polymeric material as well as the cyclic product, as there does not appear to be any steric preference for one rather than the other. Therefore aluminium trichloride and antimony trifluoride must have a secondary role acting as templates. Maybe they can coordinate with both carbonyl groups of the dialdehyde in a bidentate manner as in (XII). In this, the distinction between (ii) and (i) becomes blurred, as Lewis acid catalysis as in (ii) also includes template interaction.

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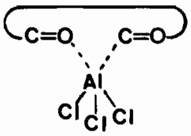
(15) A. F. Wells, Structural Inorganic Chemistry, Oxford, p. 862 (1962).



(XII)

The role of the zinc and nickel ions is more difficult to analyse. The sequence, going down Table I, of catalytic efficiency bears no direct relationship to the ability to form amine complexes. It is difficult to vizualize class A acceptors such as Zn_{aq}^{2+} and Ni_{aq}^{2+} coordinating to carbonyl groups rather than amines. On the other hand the species produced from the respective acetates in methanol could be more polarizable and hence perhaps more class B in nature than the aquo ions. However in view of the fact that zinc acetate and nickel acetate act in the case of diaminoethane by a template process, it seems unreasonable to exclude this possibility for diaminobenzene.

The pyridinium ion could readily act as a source for protonation of carbonyl groups, which would catalyse condensation. However as in the case of aluminium trichloride some template process must also operate in order for cyclization to occur exclusively. (The condensation and cyclization of acetone and half-neutralized diaminoethane[11] mentioned in the Introduction provides an interesting parallel). However the fact that the pyridinium ion is a better catalyst than nickel(II) and zinc(II), which ought to be rather better than the proton in acting as templates, suggests that acid catalysis is more important of the two roles.

Experimental Section

The preparations and properties of the dialdehyde (II) and the cyclic compounds (V) are described in the Appendix, and those of the nickel(II), cobalt(II) and copper(II) complexes in the following paper.[16] As full experimental details can be found there, only an outline of the experimental procedure leading to cyclization (or polymerisation) will be given here.

The reactions of the dialdehyde(II) and the diamines(III) in the presence of nickel(II), cobalt(II) and copper(II) were carried out as follows. About 2.5 mole of (I) and an equal number of moles of metal acetate (hydrated, where more convenient) were stirred in about 20 ml of refluxing methanol in a stream of nitrogen. About 6 m mole of diamine was added in 10 ml methanol. After several hours of refluxing, the desired complex (IV) separated as solid and was removed when the infra-red spectrum indicated that (II) had completely disappeared (IV; M = Ni, Co; R = —(CH_2)—, —$(CH_2)_3$—, —$(CH_2)_4$—, *o*-phenylene; M = Cu, R = —$(CH_2)_2$—, —$(CH_2)_3$—). (The reactions of (II) with 1,4-diaminobutane and 1,2-diaminobenzene in the presence of copper(II) were not studied).

In all the reactions of (II) with diaminoethane, except those in the presence of nickel, cobalt and copper ions, both the cyclic compound (V, R = —$(CH_2)_2$—) and the high-melting white material (*i.e.* the polymer, maybe (VIII)) are formed. Unfortunately the cyclic compound and polymer have very similar infrared spectra. However they can be distinguished by (i) their different melting points, (ii) their different retention times in thin layer chromatography, and (iii) the presence of a small peak at m/e = 208 in the mass spectrum of the polymer, and a large one at m/e = 292 in that of the cyclic compound due to its molecular ion. The chromatograms in (ii) were prepared on a 300 micron thick layer of silica gel (using calcium sulphate as a binder), eluting with a 30:70 (by volume) mixture of petrol (60-80°) and chloroform.

The reaction of (II) with diaminoethane in the absence of catalyst and formation of the so-called polymer were studied by stirring 0.75 m mole of (II) with 1.5 m mole diaminoethane in 30 ml refluxing methanol. The white solid formed was an amorphous powder (m.p. 280-288°) which showed a transition to a more crystalline form just below its melting point. An analysis sample was prepared by solution in tetrahydrofuran, filtration and precipitation by reduction of volume under reduced pressure. (Found, C, 72.74; H, 6.74; N, 19.01%; (V, R= $-CH_2CH_2-$) requires C, 73.94; H, 6.89; N, 19.16%; (VIII) requires C, 73.9; H, 6.87; N, 19.01%). ν(nujol) 3240 (m, b), 3090 (w), 3060 (w), 1634 (s), 1604 (w), 1580 (s), 1565 (sh), 1512 (s), 1465 (s) cm^{-1}. The same product was obtained when the reactants were allowed to stand at room temperature for 4 weeks. This white high melting material is referred to as the polymer. Its formulation as (VIII) is very tentative. Its mass spectrum is very diffuse apart from the small peak at m/e = 208. The similarity of its infra-red spectrum to that of (V, R = $-CH_2CH_2-$) suggests a closely related compound. Terminal groups are frequently difficult to detect in the infra-red spectra of polymers which could account for the absence of any C=O stretching band here. The important point in the present context is that the white high melting material has properties which indicate that it has an appreciably larger molecular weight than (V, R = $-CH_2CH_2-$).

A stirred refluxing mixture of 100 mg polymer and 150 mg nickel(II) acetate in 30 ml methanol slowly turned red. After 7 days a red-brown amorphous solid and a white solid were detected in the reaction flask. After 10 days only the brown solid was obtained on filtration. After washing with a little water and methanol the dried solid showed the same infrared and electronic absorption spectra bands as an authentic sample of (IV, M = Ni, R = $-(CH_2)_2$).

«High dilution» conditions were realized by adding very slowly over a period of 8 hr to a vigorously stirred solution of 1.8 m mole of (II) in 1 l refluxing methanol, a solution of 1.8 mmole of diaminoethane in 250 ml methanol. After refluxing for 36 hr the mixture was cooled and the volume reduced to 150 ml by evaporation under reduced pressure at approximately 10°, when a white solid, m.p. 155-174°, was obtained. This solid was extracted with a small volume of tetrahydrofuran; evaporation gave impure prisms of (IV, R = $-(CH_2)_2-$), m.p. 172-176°. Recrystallization from chloroform improved the melting point (175-177°) giving pale pink crystals.

The reactions of (II) with diaminoethane in the presence of further metal ions and aluminium trichloride were followed by the same general method. The

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(16) M. Green and P. A. Tasker, *Inorg. Chim. Acta*, 5, 65 (1971).

Table IV. Reactions of dialdehyde (II) and diaminoethane in the presence of various catalysts

Catalyst	$Mg^{II\,a}$	$Mn^{II\,a}$	$Fe^{II\,b}$	$Fe^{II\,c}$	$Zn^{II\,a}$	$Zn^{II\,a}$	$Ag^{I\,d}$	$Cd^{II\,a}$	$AlCl_3$
M mole of catalyst	2.0	2.0	1.3	2.6	2.3	0.5	2.9	1.7	7.5
M mole of dialdehyde(II)	1.6	2.0	1.2	2.1	1.7	2.0	1.5	1.5	2.0
M mole of diaminoethane	3.6	3.8	2.3	3.8	3.0	3.0	3.0	3.0	3.0
M litres of methanol	30	25	20	50	80	50	30	30	50
M.P. of product (°C)	289—293	287—292	170—175	170—180	175—177	179—186	288—292	170—175	286—289

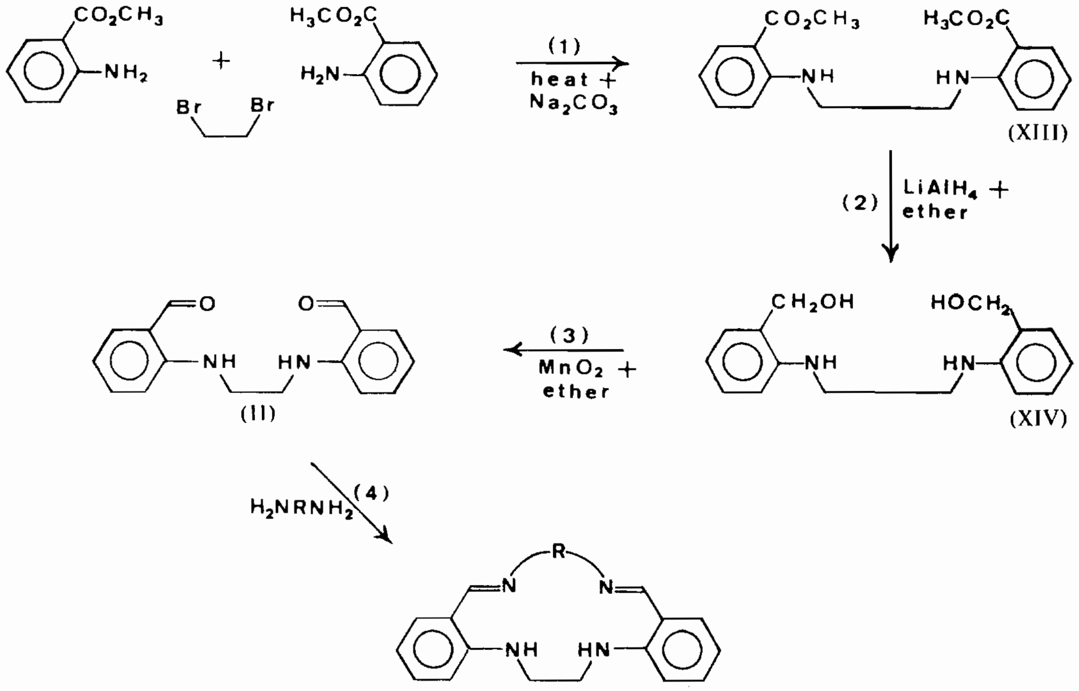
[a] Hydrated metal acetate, [b] hydrated oxalate, [c] ferrous ammonium sulphate + sodium acetate, [d] acetate.

quantities of compounds taken are shown in Table IV. To a stirred suspension of (II) in methanol containing the metal salt was added a methanolic solution of 1,2-diaminoethane. The mixture was refluxed under nitrogen for six hours. The resulting solid was collected by filtration, washed with a little methanol, followed by water, then another small quantity of methanol and finally dried. The melting point, mass spectrum and thin layer chromatogram of the solid were obtained in order to determine whether it was the monomer (V, R= $-(CH_2)_2-$), the polymer or a mixture of both. Further details of the reaction in the presence of zinc acetate can be found elsewhere in the Appendix.

The reaction of (II) and 1,2-diaminobenzene in the presence of catalyst was studied in the same way as that of (II) and diaminoethane just described. About 1 mmole of (II) and an equimolar quantity of diaminobenzene were refluxed in 40 ml of methanol under nitrogen in the presence of between 0.5 and 1 mmole of catalyst until the infra red spectrum of the solid in the bottom of the flask showed (II) had been replaced by (V, R= *o*-phenylene). A full description of the reaction in which zinc acetate is catalyst is given in the Appendix.

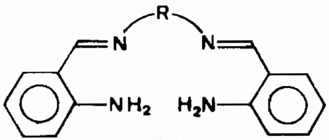
When no catalyst was present, the infra red spectrum remained unchanged even after refluxing for six days, no sign of (V, R=*o*-phenylene) being observed. (Traces of dirt could act as catalysts, however).

Appendix: Synthesis and Properties of the Organic Compounds. The following scheme was used to synthesize compounds (II) and (V):



(V)

If no solid sodium carbonate is present in step (1), N,N'-diphenylpiperazine is produced. (XIII), (XIV), and (II) are new compounds, as are (V, R = $-(CH_2)_{2,3,4}-$ and *o*-phenylene). In many ways (V) resemble their acyclic analogues[17] (XV).



(XV)

N,N'-Bis-(o-carbomethoxyphenyl)1,2-diaminoethane (XIII). Methyl anthranilate (292 g) and 1,2-dibromoethane (181 g) were heated under gentle reflux in the presence of anhydrous sodium carbonate (500 g) for 2 days. The mixture was stirred constantly, and periodically the solid dislodged from the sides of the

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(17) M. Green and P. A. Tasker, *J. Chem. Soc., A*, 2531, 3105 (1970.)

flask. On cooling the mixture solidified and was extracted with boiling chloroform (3×500 ml). On evaporation the extract gave a transparent oil wich was crystallized from a 5:1 petrol (80-100°): chloroform mixture. N,N'-bis-(*o*-carbomethoxyphenyl)-1,2-diaminoethane (105 g, 34%) was obtained as large white needles, m.p. 118-120°, (Found: C, 65.72; H, 6.52; N, 8.68. $C_{18}H_{20}N_2O_4$ requires C, 65.84; H, 6.14; N, 8.53%); τ(chloroform-d) 1.95-3.55 (aromatics, complex), 6.18 (methoxy, singlet), 6.50 (methylene, complex); m/e (molecular ion and principal peaks only) 328 (18%) (molecular ion), 165 (56%), 164 (60%), 132 (100%); ν_{max} (KBr disc) 3345m, 3030w, 2945m, 2935m, 1670s, 1497m, 1572s, 1510s, 1498sh, 1462m, 1448s, 1432s cm^{-1}.

When methyl anthranilate (117 g) and dibromoethane (28 g) were heated in the absence of sodium carbonate a violent reaction set in, producing large quantities of white fumes. The mixture solidified on cooling, and was triturated with methanol. The resulting product was recrystallized from 90% ethanol when N,N'-diphenylpiperazine was obtained as white plates, m.p. 162-164° (lit,[18] m.p. 163°), (Found: C, 80.63; H, 7.43; N, 11.87. Calcd for $C_{16}H_{18}N_4$ C, 80.63; H, 7.61; N, 11.75%); τ(chloroform-d) 2.50-3.42 (aromatics, complex), 6.71 (methylene, singlet); m/e (molecular ion and principal peaks only) 238 (35%), 132 (48%), 105 (100%), 104 (38%), 77 (44%).

4,7 - Diaza-2,3 : 8,9-dibenzodecane-1,10-diol (*XIV*). N,N' - Bis - (o-carbomethoxyphenyl)-1,2-diaminoethane (73 g) was packed into Soxhlet thimbles and extracted with diethyl ether from a refluxing suspension of lithium aluminium hydride (22 g) in ether (1 l). After six hours all the N,N-bis-(o-carbomethoxyphenyl)1,2-diaminoethane had been introduced into the flask and the excess lithium aluminium hydride was destroyed using the conditions which give a granular precipitate[19] (i.e. successive additions of water (22 ml), 15% sodium hydroxide solution (22 ml) and water (67 ml)). The mixture was filtered and the residue extracted with boiling chloroform (4×500 ml). The extracts and filtrate were combined, dried over magnesium sulphate and exaporated under reduced pressure to give a white solid which was recrystallized from a 50% chloroform-petrol (80-100°) mixture. Long white needles of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-diol (58 g, 95%) were obtained, m.p. 124-126°, (Found: C, 69.96; H, 6.96; N, 10.37. $C_{16}H_{20}N_2O_2$ requires C, 70.56; H, 7.40; N, 10.28%); τ(chloroform-d) 2.65-3.55) (aromatics, complex), 4.76 (NH or OH, broad), 5.46 ('benzyl' methylene, singlet), 6.57 ('anilino' methylene, broad); m/e (molecular ion and principal peaks only) 272 (15%) (molecular ion), 137 (45%), 136 (30%), 118 (100%); ν_{max}(nujol) 3395s, 3200m,b, 1612s, 1585s, 1516s, 1400w cm^{-8}.

4,7-Diaza-2,3: *8,9-dibenzodecane-1,10-dione* (*II*). To a solution of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-diol (14 g) in diethyl ether (500 ml) was added active manganese dioxide 'type MnO_2 (B)'[20] (115 g). The suspension was stirred vigorously and the ether gently refluxed for 6 hr. The manganese dioxide was removed by filtration and extracted with boiling chloroform (4×500 ml). The filtrate and extracts deposited a yellow solid on evaporation under reduced pressure, which was dried in a desiccator and recrystallized from chloroform to give 4,7-diaza-2,3-8,9-dibenzodecane-1,10-dione (9.4 g, 67) as large yellow plates m.p. 177-179°, (Found: C, 71.74; H, 5.85; N, 10.19. $C_{16}H_{16}N_2O_2$ requires C, 71.62; H, 6.01; N, 10.44%); τ (in dilute solution in chloroform-d, containing a little DMSO-d_6) 0.02 (methine, singlet), 1.40 (NH, broad), 2.1-3.5 (aromatics, complex), 6.34 ('anilino' methylene, broad); m/e (molecular ion and principal peaks only) 268 (17%) (molecular ion), 135 (37%), 134 (100%); ν_{max} (nujol) 3335m, 2755m, 1660s, 1610m, 1572s, 1528m, 1465m, 1435m cm^{-1}.

3,4: *9,10-dibenzo-1,5,8,12-tetra-azacyclotetradecane-1,11-diene* (*V*, $R = -CH_2CH_2-$). To a stirred suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (450 mg) in refluxing methanol 80 ml containing zinc(II) acetate (500 mg), was added 1,2-diamioethane (0.2 ml). After refluxing for a short time the mixture was allowed to stand for several days. The solid was removed and extracted with hot chloroform (most dissolves). The extract was dried over magneisum sulphate and evaporated under reduced pressure when 3.4:9,10-dibenzo-1,5,8,12 - tetra-azacyclotetradecane-1, 11-diene (282 mg 58%) was obtained as pale pink crystals, m.p. 175-177°. Recrystallization from chloroform produced no increase in m.p. (Found: C, 73.12; H, 7.12; N, 19.53. $C_{18}H_{20}N_4$ requires C, 73.94; H, 6.89; N, 19.16%); m.wt in chloroform 299, theoret 292; τ(chloroform-d) −0.38 (NH, broad), 1.54 (methine, singlet), 2.6-3.5 (aromatics, complex), 6.17 («imino» methylene, singlet), 6.45 («anilino» methylene, broad)*; m/e (molecular ion and principal peaks only) 292 (31%) (molecular ion), 176 (23%) (molecular ion), 176 (23%), 146 (22%), 145 (31%), 133 (26%), 132 (61%), 131 (100%), 130 (21%), 188 (130%) 117 (47%), 104 (30%), 91 (37%); ν_{max}(nujol) 3230w, b, 1638 s, 1606s, 1580sh, 1520m, 1502w, 1460s, 1332m, b, 1272w, 1263m, 1225sh, 1205s, 1165m, 1158m, 1139m, 1092w, 1052w, 1043w, 1035m, 979w, 968w, 919m, 878w, 850w, 795w, 756sh, 748s, 700m, b cm^{-1} $\lambda_{max}(\varepsilon)$ 348(8720), 260(13300), 232(63900) mμ.

3,4: *9,10-Dibenzo-1,5,8,12-tetra-azacyclopentadecane-1,11-diene* (*V*, $R = -(CH_2)_3-$). To a suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (200 mg) in methanol (20 ml) was added a solution of 1,3-diaminopropane (0,13 ml) in methanol (10 ml). The mixture was maintaind at approximately 60° for 6 hours in a stoppered flask. The resulting long white needles were recrystallized from a mixture of methanol (50%) and dichloromethane to give 3,4:9,10-dibenzo-1,5,8,-12-tetra-azacyclopentadecane-1,11-diene (150 mg, 65%) as white needles, m.p. 187-188°, (Found: C, 73.91; H, 7.21; N, 18.98. $C_{19}H_{22}N_4$ requires C, 74.47; H, 7.24; N, 18.29%); m.wt. in chloroform 306, theoret 306; τ(chloroform-d) 0.45 (NH, broad), 1.80 (methine, singlet), 2.7-3.6 (aromatics, complex), 6.30 («imino» α-methylene, triplet, $J = 5$ c./sec.), 6.51

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[18] J. F. Thorpe and A. S. Wood, *J. Chem. Soc.*, *103*, 1608 (1913).

[19] V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, *18*, 1953

[20] M. Harfenist, A. Bavley, and W. A. Lazier, *J. Org. Chem.*, *19*, 1954 (1608).

(*) Sharpens on addition of D_2O.

(«anilino» methylene, complex), 7.99 («imino» β-methylene, quintet, $J = 5$ c./sec.); m/e (molecular ion and principal peaks only) 306 (60%) (molecular ion), 190 (29%), 189 (32%), 188 (29%), 154 (79)%, 146 (34%), 145 (34%), 139 (84%), 131 (37%), 118 (100%), 117 (37%), 91 (31%); ν_{max}(nujol) 3220m, b, 3080m, 3020w, 1632s, 1598s, 1578sh, 1532m, b, 1460s, 1380s, 1352m, 1342s, 1330m, 1282w, 1270w, 1252w, 1210s, 1169m, 1139m, 1112m, 1185w, 1168s, 1144m, 976w, 968w, 930m, 920m, 898w, 875m, 831m, 750s, 744s, 734w, 698s cm^{-1}; $\lambda_{max}(\varepsilon)$ 349 (10300), 278sh (8570), 264(12600), 228(68800) mμ.

3,4:9,10-Dibenzo-1,5,8,12-tetra-azacyclohexadecane-1,11-diene (*V*, *R* = $-(CH_2)_4-$). To a suspension of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (200 mg) in methanol (20 ml) was added a solution of 1,4-diaminobutane (0.15 ml) in methanol (5 ml). The mixture was maintained at approximately 60° for 6 hours in a stoppered flask. 3,4:9,10-dibenzo-1,5,8,12-tetra-azacyclohexadecane-1,11-diene (130 mg, 55%) was collected at a sinter and recrystallized from methanol containing a litle dichloromethane to give long white needles m.p. 149-151°, (Found: C, 74.88; H, 7.60, N, 17.35. $C_{20}H_{24}N_4$ requires C, 74.96; H, 7.55; N, 17.48%); m.wt. in acetone 319-325, theoret 320; τ(carbon tetrachloride) 0.68 (NH, broad), 1.81 (methine, singlet), 2.8-3.7 (aromatics, complex), 6.50 («imino» and «anilino» methylene, broad*), 8.27 («imino» β-methylene, broad); m/e (molecular ion and principal peaks only) 320 (55%) (molecular ion), 202 (32%), 133 (35%), 132 (28%), 131 (62%), 118 (100%), 117 (45%), 91 (32%); ν_{max}(nujol) 3201m, 3150sh, 3080sh, 3010sh, 1630s, 1604sh, 1592s, 1584sh, 1570sh, 1520s, 1514sh, 1460s, 1381s, 1332s, 1283m, 1252w, 1210m, 1198m, 1160s, 1130s, 1111w, 1078m, 1048m, 999m, 983m, 972m, 927w, 919w, 837w, 747s, 735m cm^{-1}; $\lambda_{max}(\varepsilon)$ 352(10400), 275sh (9460), 265(11900), 228(62700) mμ.

1,5,8,12-tetra-aza-3,4:9,10:13,14-tribenzocyclotetradecane-1,11-diene (*V*, *R* = o-*phenylene*). A solution of zinc(II) acetate (0.5 g) in methanol (10 ml) was added to a mixture of 4,7-diaza-2,3:8,9-dibenzodecane-1,10-dione (300 mg) and 1,2-diaminobenzene (121 mg) in methanol (20 ml). After refluxing under nitrogen for six hours the 1,5,8,12-tetra-aza-3,4:9,10:13,14-tribenzotetradecane-1,11-diene (307 mg, 81%) was collected and recrystallized from diisopropyl ether, when fine yellow needless, m.p. 175-176° were obtained. (Found: C, 76.99; H, 5.78; N, 15.99. $C_{22}H_{20}N_4$ requires C, 77.62; H, 5.92; N, 16.46%); τ(dimethylsulphoxide-d$_3$), −0.32 (NH, broad), 1.16 (methine, singlet), 2.3-3.6 (aromatics, complex), 6.42 («anilino» methylene, complex*) ν_{max}(nujol), 3160m, b, 3080sh, 3060sh, 3020sh, 1615s, 1597m, 1585m, 1573m, 1563m, 1520s, 1502w, 1483s, 1462s, 1378s, 1338s, 1325m, 1275w, 1235w, 1225w, 1186s, 1168s, 1159sh, 1149m, 1104w, 1095w, 1082w, 1043m, 978m, 972sh, 938m, 925m, 891m, 883m, 858w, 850w, 830m, 755sh, 742s, 710s cm^{-1}; $\lambda_{max}(\varepsilon)$ 378(13500), 337(11600), 275sh, (25500), 246(52300) mμ.

Analyses were performed by Dr. A. Bernhardt in Mülheim. Molecular weights were determined using the so-called «Osmometer 301A» of Mechrolab by Miss A. Wariss. Melting points were determined on a Reichert hot stage apparatus. Infrared spectra were recorded on a Unicam 200G instrument, and electronic spectra on a Cary 14 Spectrophotometer. Mass spectra were determined on an A.E.I. MS9 instrument by Dr. B. Thomas, using a direct insertion probe. The NMR spectra were recorded by Mrs. M. Sutherland using a Perkin-Elmer R10 instrument. Chemical shifts are quoted with reference to tetramethylsilane as internal standard.

Acknowledgments. We thank Dr. Thomas, Miss Hainsworth, Mrs. Sutherland and Miss Warriss for their help. P.A.T. acknowledges with gratitude a research studentship from the Science Research Council of the United Kingdom.