Coordination Chemistry Reviews
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

MACROCYCLIC COORDINATION COMPOUNDS FORMED BY CONDENSATION OF METAL-AMINE COMPLEXES WITH ALIPHATIC CARBONYL COMPOUNDS

N. F. CURTIS

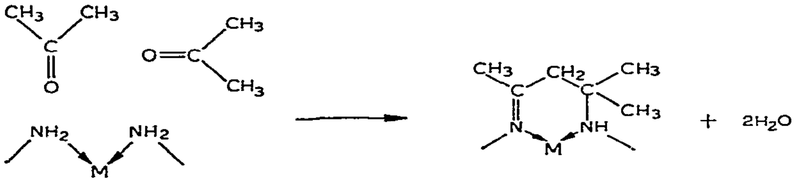
Chemistry Department, Victoria University of Wellington, Wellington (New Zealand)

(Received September 25th, 1967)

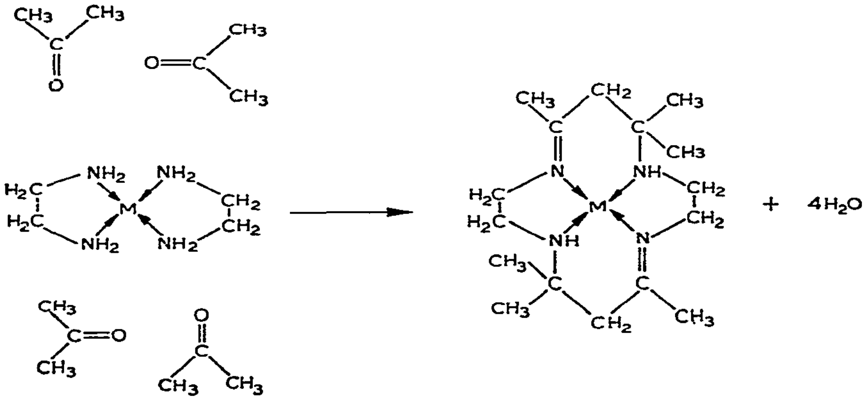
CONTENTS

A. INTRODUCTION

This review describes metal-ion complexes which are formed by reaction of certain amine complexes with aliphatic carbonyl compounds. The characteristic feature of the reaction is the linking of coordinated amine groups by a three carbon bridge. With acetone as the carbonyl compound, the bridging group is diacetone-amine-imine, formed from two acetone molecules.



With diamines, formation of a second bridge gives a cyclic complex (*e.g.* with diaminoethane a complex of a hexamethyltetra-azacyclotetradecadiene is obtained).



This reaction provides a convenient route to complexes of macrocyclic ligands with for nitrogen donor atoms. The macrocycle ring size can be changed by replacing one or both of the diaminoethane residues by 1,3-diaminopropane residues, or by cyclisation of triethylenetetramine complexes by a single amine-imine bridge. The ring substituents can be changed by replacement of *e.g.* diaminoethane by a C substituted diaminoethane, or by replacement of acetone by some other aliphatic carbonyl compound.

The macrocyclic complexes formed by cyclisation with diamines have two imine and two secondary amine donor groups, but it is possible to vary the unsaturation of the macrocycle, by oxidation or reduction, from the tetra-imine to the tetra-amine.

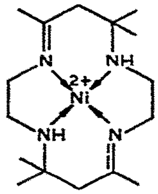
The direct condensation between metal-amine complexes and carbonyl compounds is satisfactory only for nickel(II) and copper(II), but by isolation of some of the macrocycles from the nickel(II) complexes it has been possible to prepare complexes of other metal ions. Recently, a method of preparing some of the macrocycles by direct condensation of diamines and carbonyl compounds in the absence of metal ions has been devised, and can be used to prepare complexes of metal ions.

The majority of this review refers to the cyclic complexes, particularly the most extensively studied hexamethyltetraazacyclotetradecadienenickel(II) complexes formed by condensation of (diaminoethane)nickel(II) complexes with acetone. Complexes of macrocycles derived by oxidation or reduction, and complexes of related but non-cyclic ligands, will only be mentioned briefly. Much of the work has been carried out in these laboratories and some unpublished material is included to clarify the discussion.

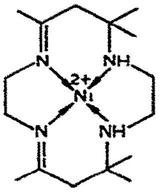
B. NOMENCLATURE

Systematic names for these compounds are cumbersome and abbreviations will be used. The majority of the compounds discussed are formed with acetone as the carbonyl compound and the presence of the six methyl substituents from the acetone residues is assumed unless otherwise stated. The bridging group derived from acetone is 2-methyl-2-amino-4-iminopentane (diacetone-amine-imine), which will be abbreviated to "aib". Thus the square planar nickel complex cation IX with the linear tetradentate ligand formed from two diaminoethane residues linked by a single amine-imine bridge will be referred to as $[\mathrm{Ni(en\text{-}aib)}]^{2+}$, and extension of this nomenclature to other non-cyclic tetradentate complexes will be made as required.

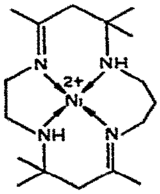
The cyclic complexes will be distinguished by ring size and degree of unsaturation *e.g.* a tetra-azacyclotetradecadienenickel(II) complex will be referred to as $[\mathrm{Ni([14]diene)}]^{2+}$ and the hexadecadiene analogue with two 1,3-diaminopropane residues as [Ni([16]diene)]$^{2+}$. The tetra-imine and tetra-amine complexes derived from [Ni([14]diene)]$^{2+}$ become [Ni([14]tetene)]$^{2+}$ and [Ni([14]tetramine)]$^{2+}$ etc. The macrocycle derived from triethylenetetramine will for convenience be referred to as ([13]monene) even though it has only three ring methyl substituents. Various forms of isomerism are possible with these macrocyclic complexes. Thus the amine-imine bridge components can be *cis* or *trans* with respect to the nickel ion, giving [Ni(*cis*[14]diene)]$^{2+}$, II, and [Ni(*trans*[14]diene)]$^{2+}$, I. Restricted inversion about the secondary amine centres distinguishes [Ni(*rac trans*[14]diene)]$^{2+}$ and [Ni(*meso trans*[14]diene)]$^{2+}$, etc. The more general abbreviations will be used where the configuration of the macrocycle has not been established and when referring to all known isomers. Formulae, systematic names and abbreviations for the simplest members of the various types of macrocyclic complexes formed by condensation of nickel-amine complexes and acetone are represented in formulae I–V.



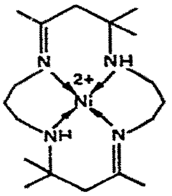
I



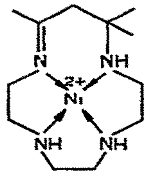
II



III



IV



V

I [Ni(*trans*[14]diene)]$^{2+}$ (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)-nickel(II)

II [Ni(*cis*[14]diene)]$^{2+}$ (5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,14-diene)-nickel(II)

III [Ni([15]diene)]$^{2+}$ (5,7,7,13,15,15-Hexamethyl-1,4,8,12-tetra-azacyclopentadeca-4,12-diene)-nickel(II)

IV [Ni([16]diene)]$^{2+}$ (6,8,8,14,16,16-Hexamethyl-1,5,9,13-tetra-azacyclohexadeca-5,13-diene)-nickel(II)

V [Ni([13]monene)]$^{2+}$ (11,13,13-Trimethyl-1,4,7,10-tetra-azacyclotrideca-10-ene)nickel(II)

C. REACTIONS OF NICKEL(II) AMINE COMPLEXES WITH ALIPHATIC CARBONYL COMPOUNDS

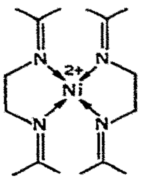
(i) Reaction of various nickel(II) amine complexes with acetone

Addition of acetone to non-aqueous solutions of (diaminoethane)nickel(II) complexes results in a slow colour change from blue-violet to brown. This reaction had undoubtedly been observed previously but the fortuitous combination of perchlorate diamine complex salts and acetone as a solvent resulted in the formation of crystalline reaction products and opened a wide field to investigation[1].

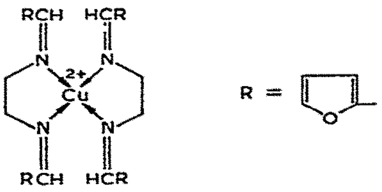
Reaction of tris(diaminoethane)nickel(II) perchlorate with acetone at room temperature yields a yellow crystalline product[1]. The stoichiometry of the reaction can be represented as

$$[\mathrm{Ni(NH_2.CH_2.CH_2.NH_2)_3}]^{2+} + 4\mathrm{CH_3.CO.CH_3} \longrightarrow [\mathrm{Ni(C_{16}H_{32}N_4)}]^{2+} + \mathrm{NH_2.CH_2.CH_2.NH_2} + 4\mathrm{H_2O}$$

i.e. the product is a nickel complex containing two diaminoethane residues and four acetone residues, condensed by elimination of four moles of water. (The mechanism of the reaction is discussed in section F, i)The product is diamagnetic, and the infrared spectrum shows that all NH_2 groups have been eliminated and C:N groups introduced. The tetra N-isopropylidene (Schiff base) structure VI was suggested[1], but this formulation failed to account for the observed resistance to hydrolysis (H, i), as apparently analogous Schiff base complexes (such as VII described by Hoyer), are readily hydrolysed[2].



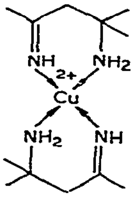
VI



VII

When the product was decomposed by cyanide, (H, iv), mesityl oxide (4-methyl-3-pentene-2-one) was the only carbonyl compound isolated, indicating that the acetone was present in the complex as C_6 units[3]. The cyclic structure [Ni(*trans*[14]-diene)]$^{2+}$, I, isomeric with VI, was therefore proposed[3]. The chemical inertness of the product was more easily understandable with this macrocyclic ligand, and a band at ~3200 cm^{-1} in the infrared spectrum, unaccounted for by formula VI was now assignable as ν(NH) of the secondary amine groups. Moreover, the C:N groups of the compound were completely reduced by the uptake of two moles of hydrogen with a platinum catalyst indicating the presence of only two imino groups (H, ii)[4].

This formulation received support from work by Hanic and Serator[5] who reported a slow reaction between copper(II) nitrate, acetone and ammonia to yield *trans* bis(2-methyl-2-amino-4-imino-pentane)copper(II) nitrate, VIII, the structure of which was confirmed by an X-ray crystallographic investigation (J, v). This compound can be considered analogous to the nickel/diaminoethane/acetone product, with the diamienoethane replaced by ammonia. (Analogous nickel(II) compounds are described below.)



VIII

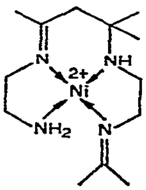
The product of the tris(diaminoethane)nickel(II) perchlorate/acetone condensation reaction was observed to have a somewhat variable infrared spectrum, particularly in the "finger print" region and gave non-reproducible X-ray diffraction patterns, although the analytical data always fitted the expected formula. It was later observed that the tris(diaminoethane)nickel(II)/acetone condensation reaction yielded two chemically distinct products, and these were considered to have the amine-imine bridging components *cis*, [Ni(*cis*[14]diene)]$^{2+}$, II, or *trans*, [Ni(*trans*[14]diene)]$^{2+}$,I with respect to the nickel. Furthermore, the *trans* isomer can exist in two forms which are interconvertible in solution, but form distinct salts, so that three isomeric perchlorate salts were isolated from the reaction[6]. The isomerism of the *trans* complex was attributed to restricted inversion about the asymmetric nitrogen atoms (G). These assignments have since been verified by X-ray crystallographic studies (J,v).

Similar reactions, yielding analogous products, occur with other tris(diaminoethane)nickel(II) salts which are soluble in acetone, *e.g.* the fluoroborate and fluorophosphate[7]. Salts of other anions will react under reflux with acetone, *e.g.* the thiocyanate[8], or in mixed solvents such as acetone/methanol.

At higher temperatures (*e.g.* sealed tube at 100°) tris(diaminoethane)nickel(II) complexes react with acetone, diacetone alcohol (4-methyl-4-hydroxy-pentane-2-one) or with mesityl oxide to yield[9a] only [Ni(*trans*[14]diene)]$^{2+}$.

Bis(diaminoethane)nickel(II) perchlorate reacts with acetone under reflux or in a sealed tube at 100° to yield a mixture of two products, both square planar nickel(II) complexes of non-cyclic tetradentate ligands. The products are [Ni(en-aib)]$^{2+}$, with two diaminoethane residues linked by a single amine-imine bridge, IX, and [Ni(en-aib-N-iprop)]$^{2+}$ which has in addition a coordinated N-isopropylidene imino group, assumed *trans* with respect to the other imino group, X[1,10] These compounds were initially formulated as N-isopropylidene Schiff bases[1], but isolation of mesityl oxide from the products of acid hydrolysis indicated the

IX

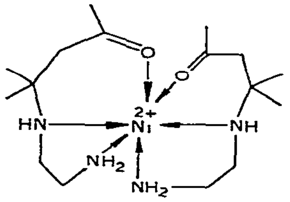


X

IX [Ni(en-aib)]$^{2+}$ (4,6,6-Trimethyl-1,9-diamino-3,7-di-aza-nona-3-ene)nickel(II)
X [Ni(en-aib-N-iprop)]$^{2+}$ (4,6,6,11-Tetramethyl-1-amino-5,7,10-tri-azaduodeca-3,10-diene)-nickel(II)

presence of the C_6 amine-imine bridging unit[4]. The same condensation reaction occurs with the more conveniently prepared bis(pyridine)bis(diaminoethane)-nickel(II) perchlorate and acetone[10] (at room temperature this reaction yields [Ni(en-aib-N-iprop)$^{2+}$ only)[9]. The perchlorate of [Ni(en-aib)]$^{2+}$ is very soluble in water and this cation is conveniently isolated as the tetrachlorozincate, prepared by reaction of tris(diaminoethane)nickel(II) chloride dihydrate with acetone and zinc chloride at 100° in a sealed tube.

Bis(diaminoethane)nickel(II) perchlorate reacts over a period of days with acetone at room temperature to yield the bis-nickel complex of the β amino ketone $NH_2.CH_2.CH_2.NH.C(CH_3)_2.CH.CO.CH_3$, [Ni(en-βak)$_2$](ClO$_4$)$_2$, XI, which is stabilised as the octahedral complex, with the coordinated ketone groups probably in *cis* positions. This compound is decomposed by aqueous acids or bases, but in pyridine is rapidly converted[11] to [Ni(*trans*[14]diene)]$^{2+}$.



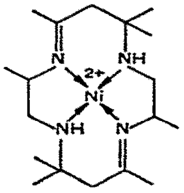
XI

XI [Ni(en-βak)$_2$]$^{2+}$ Bis(4,4-dimethyl-8-amino-5-azahepta-2-one)-nickel(II)

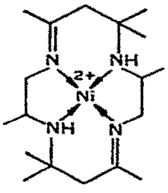
The reaction of tris(*rac* 1,2-diaminopropane)nickel(II) perchlorate with acetone yields a mixture of non-interconvertible orange and yellow crystalline products. These were initially formulated as simple N-isopropylidene imino complexes, as for the (diaminoethane)nickel/acetone products[10]. However, the chemical and physical properties resemble those of the macrocyclic nickel complexes and they are now formulated as dimethyl analogues of the [Ni([14]diene)]$^{2+}$ complexes. With 1,2-diaminopropane there are several possible sources of isomerism. *Cis* and *trans* arrangements are possible for both the amine-imine bridge components and for the diamine residue methyl groups. For the *trans trans* arrangement the diamine residue methyl groups could be adjacent to either the amino or imino groups.

Optical isomerism associated with the asymmetric carbon centres (noninterconvertible) or the asymmetric nitrogen centres (interconvertible) is also possible. The space group of the "orange" perchlorate salt (J,v)) requires that the complex cation be centrosymmetric, *i.e.* that the bridge components and the diamine methyl groups be *trans* and the asymmetric carbon and nitrogen centres be *meso*. The N.M.R. spectrum of the "orange" isomer resembles that of [Ni(*meso trans*[14]-diene)]$^{2+}$ and the spectrum of the "yellow" isomer resembles that of [Ni(*rac trans*[14]diene)]$^{2+}$, in each case with additional bands indicating the presence of an equivalent pair of methyl groups, thus excluding structures with *cis* amine-imine bridging units[12]. Reaction of tris(*d* or *l* 1,2-diaminopropane)nickel(II) perchlorate with acetone yields, in each case, an orange and yellow pair of complexes, the orange pair being formed in low yield. The yellow pair (and presumably also the orange pair) are enantiomorphs and their racemic mixture has a crystal structure different from that of the yellow product from *rac* diaminopropane[9]. This indicates that the latter compound is C *meso*, *i.e.* both products from *rac* diaminopropane are C *meso*.

The tetra-imine complexes formed by oxidation of these compounds (H, iii) both give green products on treatment with base (like [Ni(*trans*[14]tetene)]$^{2+}$ and unlike [Ni(*cis*[14]tetene)]$^{2+}$ which gives a violet product), supporting the assignment of *trans* structures to both isomers. The infrared spectrum of the tetra-imine complex from the "yellow" isomer, but not that from the "orange" isomer, has a weak band[9] at 3070 cm^{-1}. For the [Ni([14]tetene)]$^{2+}$ complexes this band was assigned to ν(CH) of the vinyl hydrogen[13]. The presence of vinyl hydrogens for the "yellow" tetra-imine complex would indicate that the methyl groups of the diamine residues are in the 3,10 positions, XII, and their absence for the "orange" compound would indicate they are in the 2,9 position, XIII.



XII



XIII

XII yellow [Ni(Me$_2$*trans*[14]diene)]$^{2+}$ (3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)nickel(II)

XIII orange [Ni(Me$_2$*trans*[14]diene)]$^{2+}$ (2,5,7,7,9,12,14,14-Octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)nickel(II)

The orange isomer can be prepared from the macrocycle perchlorate formed by reaction of 1,2-diaminopropane hydroperchlorate with acetone or mesityl oxide, (F, ii, iii).

Bis(1,2-diaminopropane)nickel(II) perchlorate reacts with acetone at room temperature to yield blue $[Ni(pn\text{-}\beta ak)_2](ClO_4)_2$, analogous to XI. In pyridine this is converted to the "orange" isomer of the macrocyclic complex and therefore the tridentate ligand has the structure

$$NH_2.CH_2\text{-}CH(CH_3).NH.C(CH_3)_2.CH_2.CO.CH_3,$$

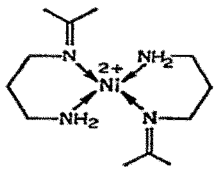
assuming XIII is correct[9].

At 110° bis(1,2-diaminopropane)nickel(II) perchlorate reacts with acetone to yield the non cyclic, singly bridged complexes $[Ni(pn\text{-}aib)]^{2+}$ and $[Ni(pn\text{-}aib\text{-}N\text{-}iprop)]^{2+}$, analogous to IX and X[10].

Tris or bis(2-methyl-2,3-diaminopropane)nickel(II) perchlorate both react readily with acetone to give the non-cyclic, singly bridged product, $[Ni(ibn\text{-}aib)]^{2+}$, presumably with the methyl substituents adjacent to the primary amine groups. Attempts to prepare cyclic complexes by prolonged heating or ultraviolet irradiation of acetone solutions were unsuccessful[10].

Neither tris nor bis complexes of *meso* or racemic 2,3-diaminobutanenickel(II) reacted with acetone under any conditions tried[9].

Tris(1,3-diaminopropane)nickel(II) perchlorate reacts rapidly with acetone, particularly if heated, to yield a yellow crystalline product. Analysis indicates the presence of two diamine and two acetone residues, but the compound is hydrolysed in aqueous solution yielding acetone as the carbonyl product and the infrared spectrum shows no ν(NH) band. It was therefore concluded that no amine-imine bridge is present and the compound was assigned structure XIV with two coordinated N-isopropylidene groups[14].



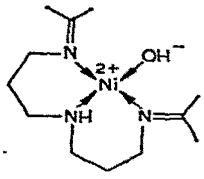
XIV

XIV $[Ni(1,3\text{-}pn\text{-}N\text{-}iprop)_2]^{2+}$ Bis(2-methyl-6-amino-3-azahexa-2-ene)nickel(II) *or* Bis(N-isopropylidene-1,3-diaminopropane)nickel(II)

If the tris(1,3-diaminopropane)nickel(II) perchlorate/acetone reaction mixture is allowed to stand for several days the macrocyclic complex $[Ni[16]diene)]^{2+}$, IV, is formed (*trans* structure assumed). The reacting solution should be tightly stoppered as much tarry polymeric material is formed if it is exposed to the atmosphere[14].

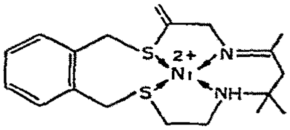
Triethylenetetraminenickel(II) complexes react with acetone at 100° to yield the cyclic complex $[Ni([13]monene)]^{2+}$, V[15]. This complex is similar to the cyclic products obtained from diamines, but it has three secondary amine and one imine donor groups in place of two of each. As for the non-cyclic singly bridged diamine cations *e.g.* $[Ni(en\text{-}aib)]^{2+}$, the perchlorate salt is very soluble, and the product is conveniently isolated as the tetrachlorozincate salt, prepared by reaction of $Ni_2trien_3Cl_4,2H_2O$, acetone and zinc chloride in a sealed tube at 110°[15].

No reaction was observed with bis(diethylenetriamine)nickel(II) and acetone under any condition studied[9]. Bis(dipropylenetriamine)nickel(II) perchlorate reacts rapidly with acetone at room temperature to yield the paramagnetic complex XV with two N-isopropylidene Schiff base groups and with coordinated hydroxide, considered to be dimerised by hydroxy-bridging[16].



XV

XV Hydroxo(2,12-dimethyl-3,7,11-tri-azatrideca-2,11-diene)nickel(II) perchlorate *or* Hydroxo-(di-(3-isopropylidene-aminopropyl)amine)-nickel(II) perchlorate



XVI

Equimolar mixtures of tris(diaminoethane) and tris(1,3-diaminopropane)-nickel(II) perchlorates react with acetone to yield the macrocyclic complex $[Ni([15]diene)]^{2+}$, III, with one diaminoethane and one diaminopropane residue[22], (a preparation of a *cis* analogue, XXV, is described in section(F, iii). Similarly when equimolar mixtures of tris(diaminoethane)nickel(II) and tris(1,2-diaminopropane)nickel(II) perchlorates react with acetone, the major product is [Ni(Me-*trans*[14]diene)]$^{2+}$ with one diaminoethane and one 1,2-diaminopropane residue[17]. This compound is conveniently prepared from [H_2(Me*trans*[14]diene)]$(ClO_4)_2$ formed by reaction of equimolar amounts of diaminoethane and 1,2-diaminopropane hydroperchlorates with acetone or mesityl oxide (F, ii, iii). (A preparation of a *cis* copper(II) analogue, XXIV, is described in section (F, iii). When mixtures of tris(diaminoethane) and tris(2-methyl-2,3-diaminopropane)nickel(II) perchlorates were reacted with acetone, only the products formed by the amine complexes reacting separately were isolated[9].

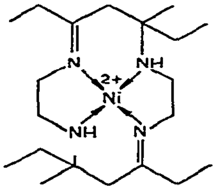
Nickel(II) ammine salts with a variety of anions react with acetone to yield the bis(2-methyl-2-amino-4-iminopentane)nickel(II) salts analogous to VIII[8,18,19]. In the case of $Ni(NH_3)_6PF_6$, triplet ground state (TGS) tris(2-methyl-2-amino-4-iminopentane)nickel(II) hexafluorophosphate is formed[19].

Busch and Urbach describe the preparation of macrocyclic complexes with two sulphur and two nitrogen donor atoms, XVI, by bridging the coordinated amine groups of the dithio diamine, by reaction with acetone[20,21].

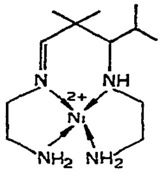
(ii) Reactions of nickel(II) amine complexes with aliphatic carbonyl compounds other than acetone

Tris(diaminoethane)nickel(II) reacts with a variety of aliphatic aldehydes and ketones to yield analogues of $[Ni(en\text{-}aib)]^{2+}$, with a single amine-imine bridge linking two diamine residues[9,9a,22,23]. Further reaction to yield the cyclic complexes analogous to $[Ni([14]diene)]^{2+}$, is extremely slow and the product has been isolated only for butanone-2 (methyl ethyl ketone), XVII. In this case the reaction to yield the singly bridged product took several hours at 100°, while only a small yield of the cyclic product was obtained after many weeks at this temperature[22]. $[Ni(\textit{trans}[14]diene)]^{2+}$ analogues formed from carbonyl compounds other than acetone are usually more conveniently prepared via the appropriate macrocycle perchlorate (F, ii). MacDermott and Busch have prepared $[Ni(en\text{-}aib)]^{2+}$, and various analogues, by reaction of $[Ni(en)_3]^{2+}$ salts with β hydroxy ketones and β hydroxy aldehydes[9a].

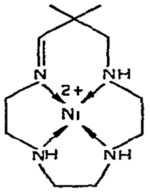
With triethylenetetramine, which needs only a single amine-imine bridge to form a cyclic complex, reaction occurs readily with a variety of aldehydes and ketones to yield analogues of $[Ni([13]monene)]^{2+}$ with different ring substituents[23].



XVII



XVIII



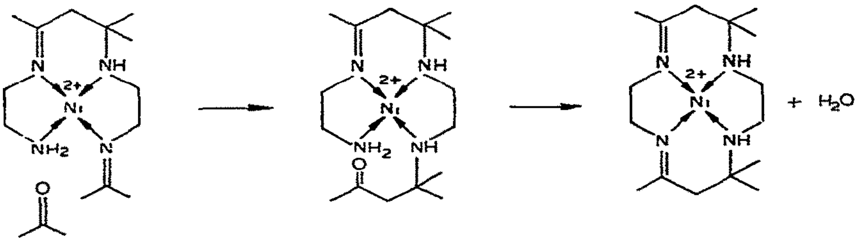
XIX

XVII (7,14-Dimethyl-5,7,12,14-tetra-ethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)nickel(II)
XVIII (5,5-Dimethyl-6-isopropyl-1,9-diamino-5,7-di-azanona-3-ene)-nickel(II)
XIX (12,12-Dimethyl-1,4,7,10-tetra-azatrideca-10-ene)nickel(II)

The perchlorate salts of these analogues of $[Ni(en\text{-}aib)]^{2+}$ and $[Ni([13]monene)]^{2+}$ tend to be very water soluble and the complexes are conveniently isolated as the tetrachlorozincates[23].

One distinction between the reactions of diaminoethane and triethylenetetramine has been observed. With isobutyraldehyde and diaminoethane the expected product XVIII is obtained, while with triethylenetetramine the symmetrical cyclic complex XIX, minus one isopropyl group is formed[23].

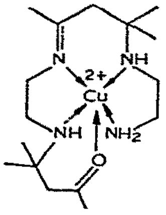
Formation of the amine-imine bridge requires a carbonyl compound with at least one α hydrogen. There is no such restriction on the formation of simple imino groups and tris(1,3-diaminopropane)nickel(II) perchlorate reacts with a wider range of carbonyl compounds, including cyclohexanone and furfuraldehyde to form di-imino analogues of XIV[9].



D. REACTIONS OF COPPER(II) AMINE COMPLEXES WITH ALIPHATIC CARBONYL COMPOUNDS

(i) Reaction of various copper(II) amine complexes with acetone

Bis(diaminoethane)copper(II) perchlorate reacts with acetone at room temperature over a period of 1–2 days, or under reflux for about 30 minutes, the colour of the solution changing from magenta to blue as the copper(II) complex of the pentadentate ligand $NH_2.CH_2.CH_2.NH.C(CH_3)_2.CH_2.C(CH_3)$: $N.CH_2.CH_2.NH.C(CH_3)_2.CH_2.CO.CH_3$ $[Cu(en\text{-}aib\text{-}\beta ak)]^{2+}$, XX, is formed[11]. Under basic conditions this compound is rapidly converted[11] to $[Cu(\mathit{trans}[14]diene)]^{2+}$.



XX

XX $[Cu(en\text{-}aib\text{-}\beta ak)]^{2+}$ (4,4,9,11,11-Pentamethyl-14-amino-5,8,12-tri-azatetradeca-8-ene-3-one)-copper(II)

Bis(diaminoethane)copper(II) perchlorate reacts slowly with acetone at room temperature in the presence of diaminoethane to yield a mixture of $[Cu(\mathit{cis}[14]diene)]^{2+}$ and $[Cu(\mathit{trans}[14]diene)]^{2+}$. As with the equivalent nickel(II) reaction the less soluble perchlorate of the *cis* complex crystallises first[11]. The mechanism of the room temperature reactions are discussed in section (F,i).

In a sealed tube at 110°, bis(diaminoethane)copper(II) perchlorate reacts with acetone yielding first the singly bridged complex $[Cu(en\text{-}aib)]^{2+}$ and then the cyclic[4] complex $[Cu(\mathit{trans}[14]diene)]^{2+}$. The reaction is catalysed by diaminoethane. If the heating is continued too long much dark polymeric material is formed and copper metal is deposited. Yields are reported to be improved and polymer formation reduced if the dehydrating agent 2,2-dimethoxypropane is present[25]. The cation $[Cu(en\text{-}aib)]^{2+}$ is also prepared by reaction of equimolar amounts of $[Cu(en\text{-}aib\text{-}\beta ak)]^{2+}$ and $[Cu(en)_2]^{2+}$ in the presence of a trace of diaminoethane[11], or as the tetrachlorozincate by reaction of bis(diaminoethane)-copper(II) chloride with 1:1 acetone:methanol at 100° in the presence of zinc chloride[9].

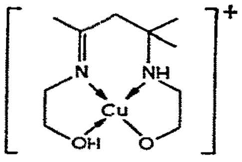
$[Cu(\textit{trans}[14]diene)](ClO_4)_2$ occurs in two crystalline forms, because of restricted inversion about the coordinated secondary amine centres. The "orange" form of Curtis and Blight is N *meso* and their "red" form N racemic (Section G).

Bis(1,2-diaminopropane)copper(II) reacts with acetone at 100° in the presence of 1,2-diaminopropane as catalyst, yielding first the singly bridged product $[Cu(pn\text{-}aib)]^{2+}$ and then the cyclic[4] complex $[Cu(Me_2\textit{trans}[14]diene)]^{2+}$. A single cyclic product was observed (*cf.* the nickel(II) reaction (C, i), but the yield was low and a minor product may have escaped detection. The same product is formed from the macrocycle dihydroperchlorate (F, ii) which gives the "orange" nickel complex and hence the copper(II) and the "orange" nickel(II) complexes are assigned[9] the same structure (C, i).

Reaction of the copper(II) complexes of 2-methyl-2,3-diaminopropane[4] (isobutylenediamine), 1,3-diaminopropane[13], triethylenetetramine[15] and dipropylenetriamine[16] with acetone yields products analogous to those formed by the nickel(II) complexes of the amines, *i.e.* $[Cu(ibn\text{-}aib)]^{2+}$, $[Cu(1,3\text{-}pn\text{-}N\text{-}iprop)_2]^{2+}$, $[Cu([16]diene)]^{2+}$, $[Cu([13]monene)]^{2+}$ and the Cu analogue of XV, respectively. $[Cu(Me\textit{trans}[14]diene)]^{2+}$ has been prepared from the macrocycle (F,ii, iii). As with nickel(II) no reaction was observed with the copper(II) complexes of *meso* or *rac* 2,3-diaminobutane.

Copper(II) nitrate, acetone and ammonia react slowly to form the complex VIII, which has the same amine-imine bridge system as the other amine-acetone[5] condensation products (J, v).

The 2-hydroxyethylamine (ethanolamine) complex of copper(II) perchlorate or nitrate reacts with acetone to form a complex of the linear tetradentate ligand XXI in which the amino groups have been linked by an amine-imine bridge[24].



XXI

XXI (4,6,6,-Trimethyl-1-hydroxy-9-oxy-3,7-di-azanon-3-ene) copper(II) (or -1-oxy-9-hydroxy-)

(ii) Reaction of various copper(II) amine complexes with aliphatic carbonyl compounds other than acetone

Copper(II) amine complexes, like their nickel(II) analogues react most rapidly with acetone. The methyl ethyl ketone analogue of $[Cu(\textit{trans}[14]diene)]^{2+}$ has been described[4]. Attempts to react copper(II) triethylenetetramine complexes with aldehydes led to extensive reduction of the copper and no cyclic complexes were isolated[23].

E. REACTIONS OF AMINE COMPLEXES OF METAL IONS OTHER THAN NICKEL(II) AND COPPER(II) WITH ACETONE

Complexes of metal ions other than nickel(II) and copper(II) are conveniently prepared from $[H_2(\textit{trans}[14]diene)](ClO_4)_2$ or from (*cis*[14]diene) (Section (F, ii, iii). The following reactions of diaminoethane complexes with acetone have been reported.

(i) Cobalt(II)

Sadasivan and Endicott report a very air and water sensitive reaction between tris(diaminoethane)cobalt(II) perchlorate and acetone to yield initially a very readily hydrolysed crystalline product which was dehydrated by treatment with 1,1,1-trifluoro-acetone to yield $[Co(\textit{trans}[14]diene)](ClO_4)_2$[25]. The initial product showed a ν(OH) band in the infrared spectrum and may have been a carbinolamine intermediate.

(ii) Cobalt(III)

Tris(diaminoethane)cobalt(III) and a wide variety of bis(diaminoethane)-cobalt(III) complexes have been heated with acetone for periods of months, without any indication of reaction[9].

(iii) Platinum(II) and palladium(II)

There is some indication of an extremely slow reaction between acetone and the bis(diaminoethane) complex perchlorates to yield ([14]diene) complexes[26].

(iv) Iron(II) and magnesium(II)

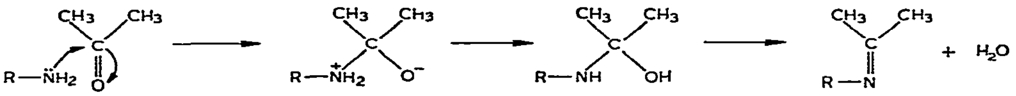
The reactions of tris(diaminoethane)iron(II) perchlorate and of bis(diaminoethane)magnesium(II) perchlorate with acetone are discussed in section (F, ii).

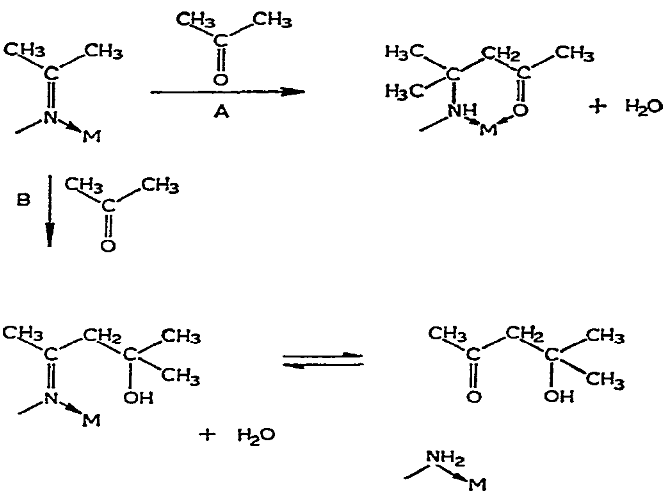
F. REACTIONS YIELDING TETRA-AZA-DIENE MACROCYCLES

(i) Mechanism of the reactions of diaminoethane complexes with acetone

Bis(diaminoethane)nickel(II) perchlorate dissolves in acetone to form an orange, diamagnetic solution which rapidly changes to blue, over a period of hours, forming the β-amino ketone complex [Ni(en-βak)$_2$] (ClO$_4$)$_2$, XI, (C, i). Bis(diaminoethane)copper(II) perchlorate forms a magenta solution in acetone which changes to blue, again over a period of hours, as the complex [Cu(en-aib-βak)]-(ClO$_4$)$_2$, (XX), is formed (D, i).

The initial reaction of a primary amine complex with acetone would form an N-isopropylidene imine. Imine formation occurs by the mechanism shown (elucidated with the more stable aromatic Schiff bases), the carbinolamine intermediate often having appreciable stability[27]. Imine formation could not occur with the amino group coordinated (for steric reasons and because of the reduced nucleophilic character of the coordinated amino nitrogen), and this is supported by the observed lack of reaction with non labile diamine complexes *e. g.* of cobalt(III)[9]. Reaction probably occurs with transient species which have one amino group of the diamine detached from the metal ion, the imino group then recoordinating. (Reaction of free diaminoethane is discussed below.) The next stage of the reaction appears to be formation of β amino ketones by an aldol reaction





between the coordinated N-isopropylidene imino group and an acetone molecule (reaction A). This species, which is fairly resistant to hydrolysis, would be stabilised by coordination of the ketone group. The alternative reaction B would lead to a β imino alcohol, which would be readily hydrolysed and effectively catalyse the formation of diacetone alcohol. In the case of bis(diaminoethane)nickel(II) the bis(β-aminoketone) complex $[Ni(en\text{-}\beta ak)_2]^{2+}$ is stabilised as a six coordinate complex by coordination of the two ketone groups. The metal-ion spectrum suggests a structure with the oxygens in *cis* position, such as XI, which prevents cyclisation by intra-molecular imine formation. Cyclisation to yield [Ni(*trans*[14]diene)]$^{2+}$ occurs rapidly in pyridine solution, but the formation of some [Cu(*trans*[14]diene)]$^{2+}$ when the reaction was carried out in the presence of copper(II) indicates that it is not a simple intra-molecular reaction[9]. In the case of bis(diaminoethane)copper(II), the tendency to form tetragonal complexes probably restricts the four nitrogen atoms, with stronger donor properties, to a planar arrangement, with the ketones weakly coordinated in the axial positions. One imino group is formed readily, giving $[Cu(en\text{-}aib\text{-}\beta ak)]^{2+}$ and the remaining ketone group is more firmly held in an axial position. Formation of the second imino group occurs readily under basic conditions, yielding [Cu(*trans*[14]diene)]$^{2+}$.

It is a possibility that the reaction forming these complexes occurs via the small equilibrium concentration of free diaminoethane, the metal ions taking no part in the significant reactions, but merely coordinating the products. Reaction of diaminoethane with acetone at room temperature is very slow, a faint yellow colouration appearing in a 10% solution after a week, and gradually becoming darker. Initial reaction yields N-isopropylidene imines and these undergo further aldol reactions, analogous to those of the coordinated imino groups discussed above. For diaminoethane the more resistant β amino ketone is probably stabilised by formation of the cyclic imine, dihydro diazapine, XXII. However, reaction of ammonia with acetone yields[27] the β-amino ketone $(CH_3)_2C \cdot NH_2 \cdot CO \cdot CH_3$, so this reaction may be general. A diaminoethane-acetone solution which has reacted for about a week at room temperature or for eight hours under reflux, reacts with copper(II) to yield the complex $[Cu(en\text{-}aib\text{-}\beta ak)]^{2+}$ which is also formed by reaction of bis(diaminoethane)copper(II) with acetone after one day at room temperature or 30 minutes under reflux. Thus reaction of copper-coordinated diaminoethane with acetone yields the same products, but is faster than reaction of free diaminoethane by a factor of the order of 10.

When tris(diaminoethane)nickel(II) is dissolved in acetone the violet solution initially formed rapidly (minutes) turns brown. This colour change is caused by a decrease in intensity of the three band spectrum of the $[Ni(en)_3]^{2+}$ cation and the growth of a band at 23,000 cm^{-1} characteristic of singlet ground state (SGS) NiN_4 complexes (Table 1). The product formed is probably the di-imine (the diaminoethane analogue of XIV), since with 1,3-diaminopropane the di-imine complex crystallises at this stage (C, i). The colour changes are reversed by the addition of water, supporting the proposition that readily hydrolysed coordinated imino groups are present. Thus in the solution there will be coordinated diamino-ethane-imino groups, which will react further to form the β-amino ketone and free diaminoethane, which will react much more slowly. Similarly for tris(diaminoethane)-copper(II), the third mole of diaminoethane is probably largely "free". Water resistant, but acid hydrolysed SGS species appear in the reacting solutions after about 30 minutes and steadily increase in concentration. The singly bridged species [Ni(en-aib-N-iprop)]$^{2+}$ and [Cu(en-aib)]$^{2+}$ can be isolated from the solution at this stage [28]. These are considered to be formed by raction of a coordinated β-amino ketone molecule with diaminoethane. This is supported by the observation that equimolar amounts of [Cu(en-aib-βak)]$^{2+}$ and [Cu(en)$_2$]$^{2+}$ react together in the presence of a trace of diaminoethane to form [Cu(en-aib)]$^{2+}$, and that diaminoethane will displace the β-amino ketone from [Ni(en-βak)$_2$]$^{2+}$ to form [Ni(en)$_3$]$^{3+}$. Reaction of [Ni(en-aib)]$^{2+}$ with acetone to form [Ni(en-aib-N-iprop)]$^{2+}$ is extremely slow and water sensitive[28], but is probably more rapid for the TGS diaminoethane adduct, since diaminoethane catalyses the reverse reaction.

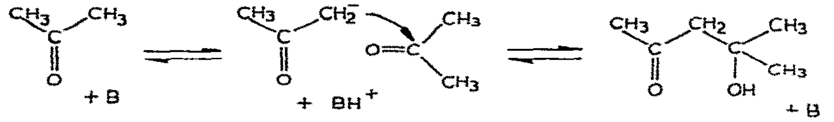
The non cyclic complexes [Ni(en-aib)]$^{2+}$, [Ni(en-aib-N-iprop)]$^{2+}$ and [Cu(en-aib)]$^{2+}$ react with acetone in the presence of diaminoethane to form the (*cis*[14]diene) complexes and it is reasonable to conclude that the *cis* macrocyclic complexes formed in the reaction of the tris(diaminoethane) complexes are formed via these species. When tris(diaminoethane)nickel(II) reacts with acetone in the presence a of molecular sieve [Ni(en-aib-N-iprop)](ClO$_4$)$_2$ crystallises in about 30% yield, about the same as the normal yield of the *cis* macrocyclic complex. (The molecular sieve apparently acts by removal of diaminoethane from the adduct [Ni(en-aib-N-iprop)en]$^{2+}$ causing the sparingly soluble [Ni(en-aib-N-iprop)]-(ClO$_4$)$_2$ to crystallise[9].) Only one complex [Ni(en-aib-N-iprop)]$^{2+}$ has been isolated and this probably has the imino grouping in *trans* positions as this arrangement is adopted by other di-imine complexes of copper(II) and nickel(II) where possible. An aldol reaction of the *trans* complex to form the β-amino ketone, which then cyclises, would yield the *cis* macrocycle.

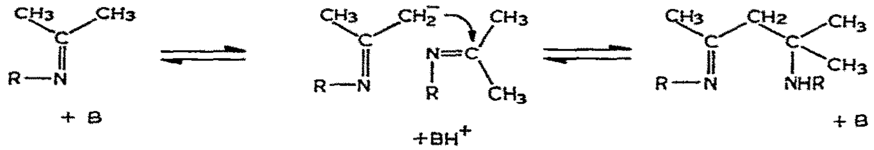
The major products of these reactions are the (*trans*[14]diene) complexes, probably formed from the β aminoketone complexes [Ni(en-βak)$_2$]$^{2+}$ and [Cu(en-aib-βak)]$^{2+}$, which are converted to the (*trans*[14]diene) complexes in the presence of diaminoethane.

It has been suggested that the reactions forming the (*trans*[14]diene) macrocyclic complexes are examples of "metal-ion template" reactions[29]. However, the preparation of the critical β-amino ketone species by reaction of diaminoethane and acetone and the isolation of the macrocyclic salts (F, ii) shows that the metal ions are not necessary. The (*cis*[14]diene) macrocycle is formed only in the presence of metal ions, and this does appear to be a metal-ion template reaction.

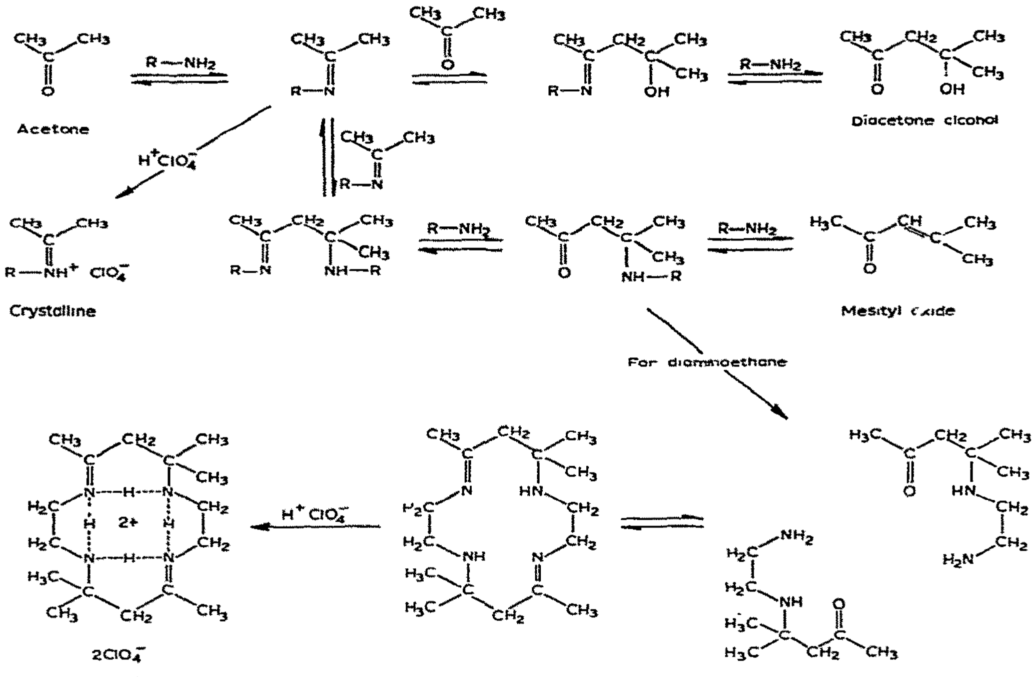
(ii) Reactions of non-coordinated amines with acetone

Acetone undergoes base catalysed aldol dimerisation by the mechanism shown. In the presence of large amounts of amine, aldol type condensations will occur between imines, leading to β amino imines. For example, acetone reacts with ammonia to form 2-methyl-2-amino-4-imino pentane (the imine of diacetone-amine)[30]. αβ Unsaturated ketones (*e.g.* mesityl oxide) readily undergo Michael addition with amines, yielding β amino ketones[30]. The whole series of compounds, ketones, carbinolamines, imines, β keto amines, etc., are linked by reversible processes, with many equilibrium steps. Removal of any species from solution as a solid, or as a complex of some sort, may give high yields of that species by displacement of successive equilibria, regardless of the equilibrium concentration. Thus amine hydroperchlorates react rapidly with acetone to give the crystalline imonium perchlorate, usually in high yield—the reaction is fast because of the near optimum acidity, and the yield is high because of the insolubility of the product[31]. Mesityl oxide and diacetone alcohol are linked to the reaction system as shown, and the same product is obtained starting with acetone, diacetone alcohol or mesityl oxide (or even with higher polymers such as phorone).



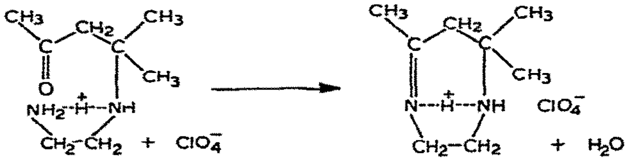


The di-hydroperchlorate of diaminoethane yields the di-imonium perchlorate $(CH_3)_2C{:}NH \cdot CH_2 \cdot CH_2 \cdot NH{:}C(CH_3)_2(ClO_4)_2$ by this reaction. The mono-hydroperchlorate reacts exothermally with acetone, diacetone alcohol or mesityl oxide, to yield a different product, formulated as $[H_2($*trans*[14]diene$)(ClO_4)_2$[32]. This product is considered to be formed because of the insolubility of the perchlorate salt, *i.e.* to be a function of the lattice energy of this salt, rather than any special inherent stability of the (*trans*[14]diene) macrocycle (see later for discussion of the stability of the macrocycle). Similar reactions occur with bromide, iodide or thiocyanate replacing the perchlorate ions. The high lattice energy of the salts of the doubly protonated macrocycle is possibly related to an optimum conformation of this macrocycle for inter-nitrogen hydrogen bonding. An analogous macrocycle dihydroperchlorate, is formed with 1,2-diaminopropane, but not with 1,3-diaminopropane which would form the (*trans*[16]diene) macrocycle[9].

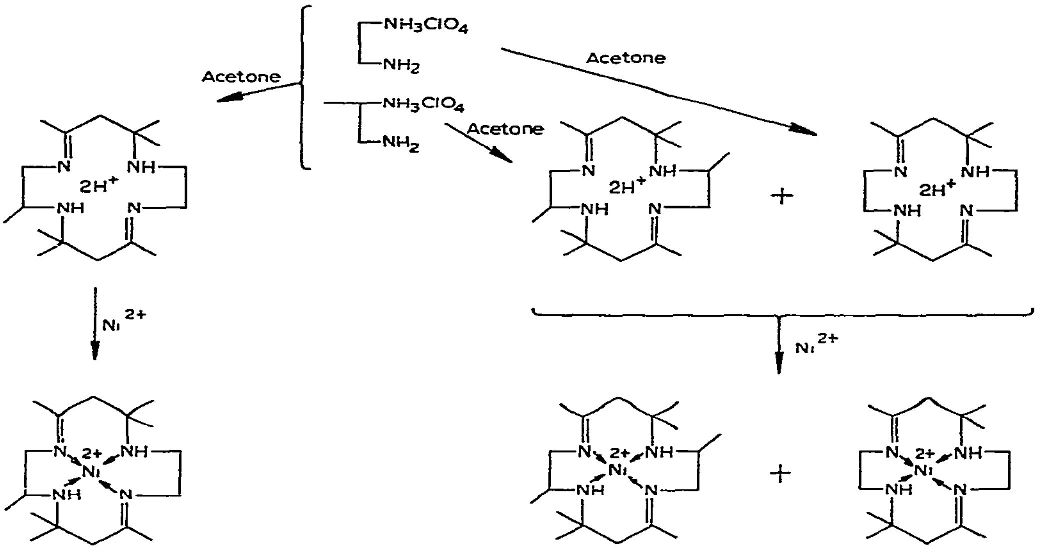


Protonation equilibria and carbinolamine-type intermediates omitted

The product of the diaminoethane HX/acetone condensation reaction could conceivably be the substituted dihydrodiazapine salt, formed by mono-molecular cyclisation of the diaminoethane β amino ketone. The diaminoethane hydroperchlorate/acetone condensation product yields [Ni(*trans*[14]diene)]$^{2+}$ and the *rac*



1,2-diaminopropane hydroperchlorate/acetone condensation product yields the orange dimethyl analogue [Ni(Me$_2$*trans*[14]diene)]$^{2+}$, XIII. These reactions do not exclude the possibility of dimerisation of the diazapine about the metal ion as the complex is formed. However, reaction of equimolar amounts of diaminoethane and *rac* 1,2-diaminopropane hydroperchlorates with acetone yielded a perchlorate salt which exclusively formed [Ni(Me *trans*[14]diene)]$^{2+}$, (with one diaminoethane and one diaminopropane residue), whereas reaction of equal amounts of the separately formed diaminoethane and 1,2-diaminopropane condensation products yielded a mixture[9] of [Ni(*trans*[14]diene)]$^{2+}$ and orange [Ni(Me$_2$*trans*[14]diene)]$^{2+}$. This series of reactions confirms that the diamine hydroperchlorate/acetone condensation reaction described by Curtis and Hay yields the (*trans*[14]diene) macrocycle, which does not dissociate during the metal-ion insertion reaction.



The condensation reaction proceeds with diaminoethane and mono-C-substituted diaminoethanes, such as 1,2-diaminopropane, with acetone and with various methyl and α methylene ketones. It does not proceed with 1,3-diaminopropane, and no equivalent reaction was observed with diethylenetriamine, dipropylenetriamine or triethylenetetramine[9].

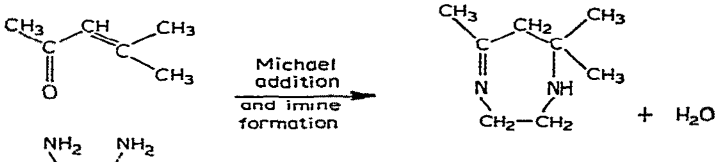
Sadasivan and Endicott report a reaction between acetone and anhydrous tris(diaminoethane)iron(II) perchlorate to yield $[H_2(trans[14]diene)](ClO_4)_2$[25]. The product commenced to separate within a few hours and simultaneously a black precipitate formed. Access of air appears to be necessary for the reaction to proceed, suggesting that the iron(III) diaminoethane complex may be the reacting species.

$$Fe(en)_3(ClO_4)_2 + \text{acetone} + \text{air} \longrightarrow [H_2(trans[14]\text{diene})]\,(ClO_4)_2 + \text{oxide of iron} + \text{water}$$

It appears probable that the ferrous perchlorate in this reaction is serving as a buffered source of perchloric acid, and that the reaction should be classified with the acetone/diamine perchlorate reaction, rather than with the cobalt(II), nickel(II) or copper(II) diaminoethane complex/acetone reactions.

When two moles of diaminoethane were added to anhydrous magnesium perchlorate dissolved in acetone a rapid, exothermic reaction occured and a mixture of magnesium hydroxide and $[H_2(trans[14]diene)]\,(ClO_4)_2$ crystallised[9]. A mechanism similar to that proposed for the iron(II) perchlorate/acetone reaction is suggested. Addition of tris(diaminoethane)nickel(II) perchlorate to an acetone solution of magnesium perchlorate resulted in the crystallisation of $[H_2$(*trans*[14]-diene)] $(ClO_4)_2$.

Mushkalo and Shokol report a reaction between diaminoethane and mesityl oxide (equimolar quantities) when heated at 100° for 15 minutes. A product was separated by fractional distillation (b. 60°/3 mm) in 56% yield and formulated as the substituted dihydro diazapine, XXII[30,33]. From the base they prepared the perchlorate, picrate and quaternized derivatives. The melting point of the perchlorate is the same as the product of the diaminoethane hydroperchlorate/acetone condensation and it appears that these salts are identical. It is therefore possible that the free base also exists as the (*trans*[14]diene) dimer, although dimerisation of the diazapine upon salt formation could occur.



XXII

The dihydroperchlorate of (*trans*[14]diene) is remarkably resistant to hydrolysis, and can be recrystallised unchanged from aqueous methanol or dilute aqueous ammonia[25]. It is hydrolysed by concentrated hydrobromic acid in two stages yielding first the dibromide of the β amino ketone $NH \cdot CH_2 \cdot CH_2 \cdot NH_2 \cdot C(CH_3)_2 \cdot CH_2 \cdot CO \cdot CH_3$ and finally diaminoethane (as the dihydrobromide)[25]. Hydrolysis of (*cis*[14]diene) by dilute perchloric acid yields the dihydroperchlorate salt of the di-β-ketodiamine[34] XXIII, (F, iii).

Sodium borohydride reduces the cyclic diene to the cyclic tetramine[25] (presumably yielding a mixture of the optical isomers (tet *a*) and (tet *b*)).

It should be noted that diamine di-hydroperchlorates can detonate extremely violently when heated to about 200°, and care should always be exercised in their preparation. The macrocycle perchlorates decompose non-violently when heated.

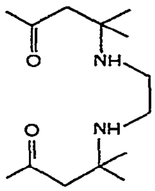
Powell has described the preparation of solutions of the free base (*cis*[14]-diene) by treatment of [Ni(*cis*[14]diene)] $(ClO_4)_2$ with potassium cyanide in dry methanol. Ether was added and the precipitated $KClO_4$ and $K_2Ni(CN)_4$ filtered off, leaving a solution of the free base[34]. (*trans*[14]diene) can be prepared similarly[60].

(iii) Preparation of metal-ion complexes from the macrocyclic ligand

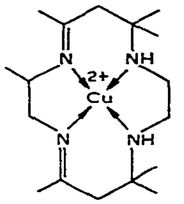
Metal ion complexes of (*trans*[14]diene) can readily be prepared from $[H_2$(*trans*[14]diene)] $(ClO_4)_2$. Sadasivan and Endicott reacted the macrocycle perchlorate with the carbonates of cobalt(II), nickel(II), copper(II) and zinc(II) in methanol/water[25]. Higher yields have been obtained by reaction with the metal acetates in methanol[7]. Cobalt(III) complexes have been prepared by reaction with $Na_3Co(CO_3)_3$, and by oxidation of solutions prepared by reaction with cobalt(II) acetate or carbonate. [Pd(*trans*[14]diene)] $(ClO_4)_2$ has been prepared by reaction of the macrocycle perchlorate and H_2PdCl_4[9] and there appears no reason why the range of complexes should not be extended.

The direct preparation of the (*trans*[14]diene) complex by reaction of the metal diamine complexes with acetone is applicable only for nickel(II) and copper(II), but even here the preparation via the macrocycle is often advantageous, as the need for separation from the *cis* isomer is avoided. For complexes of macrocycles derived from carbonyl compounds other than acetone the direct reaction is extremely slow and preparation from the appropriate macrocycle perchlorate is preferable.

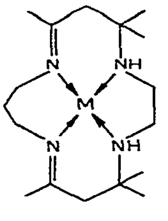
Metal ion complexes of the ([14]diene)s can also be prepared from the macrocycle, released from the nickel(II) complex by reaction with cyanide (H, iv). For (*trans*[14]diene) complexes this method is less convenient than preparation from the macrocycle perchlorate. For (*cis*[14]diene) complexes, preparation via the free base is the only method available, since only for the diaminoethane-nickel(II) (or copper(II))/acetone condensation is the *cis* isomer formed. Love and Powell describe the preparation of [Zn(*cis*[14]diene)]$ZnCl_4$, CH_3OH, [Fe(*cis*[14]-



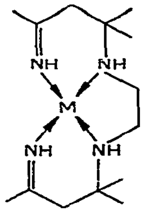
XXIII



XXIV



XXV



XXVI

XXIII 4,4,9,9-Tetramethyl-5,8-di-aza-duodeca-2,11-dione

XXIV 3,5,7,7,12,12,14 Septamethyl-1,4,8,11-tetra-azacycltetradeca-4,14-diene copper(II)

XXV (6,8,8,13,13,15-Hexamethyl-1,5,9,12-tetra-azacyclopentadeca-5,15-diene)nickel(II) (or copper(II))

XXVI (4,4,9,9-Tetramethyl-2,11-di-imino-5,8-di-azaduodecane) nickel(II) (or copper (II)) diene)] $FeCl_4$, H_2O[34], and cobalt(II) (*cis*[14]diene) complexes with the stable [(*cis*[14]diene)Co^{II}–Co^{II}(*cis*[14]diene)]$^{4+}$ moiety[35] (I, iii).

Love and Powell report the isolation of the di β-keto diamine XXIII as the perchlorate salt, by treatment of (*cis*[14]diene), or its Fe^{III} or Zn^{II} complexes, with dilute perchloric acid. By reaction of this compound with diaminoethane in the presence of metal ions they were able to reform (*cis*[14]diene) complexes. Reaction with 1,2-diaminopropane in the presence of copper(II) gave Cu(Me*cis*[14]diene) XXIV, and reaction with copper(II) or nickel(II) plus 1,3-diaminopropane gave the M(*cis*[15]diene) complexes, XXV. With ammonia the linear tetradentate complexes XXVI of copper(II) and nickel(II) were formed[34].

G. ISOMERISM ASSOCIATED WITH RESTRICTED INVERSION ABOUT THE COORDINATED SECONDARY AMINE CENTRES

Each of [Ni(*trans*[14]diene)]$^{2+}$ and [Cu(*trans*[14]diene)]$^{2+}$ exists as a pair of interconvertible isomers. For [Cu(*trans*[14]diene)] $(ClO_4)_2$ the phenomenon was originally attributed to polymorphism[4]. For [Ni(*trans*[14]diene)]$^{2+}$ the isomerism was shown to persist in solution and the perchlorates, tetrachlorozincates, thiocyanates, etc. of the isomers were isolated[6,7,36]. By X-ray crystallographic studies of the perchlorates (J, v) Bailey and Maxwell showed that the isomerism was attributable to restricted inversion about the secondary amine centres, the α modification of reference 6 being the racemic form and the β modification the *meso* form[37]. Rose, Warner and Busch came to the same conclusion by N.M.R. studies (J, iv) and by partial resolution of the racemic form on a starch column[7,36]. [Ni(*meso trans*[14]diene)] $(ClO_4)_2$ and the "orange" modification of [Cu(*trans*[14]diene)] $(ClO_4)_2$ are isostructural and therefore the "orange" form is considered to be *meso*, the "red" form racemic[6]. Other examples of isomerism attributed to restricted inversion about coordinated secondary amine centres have been reported[38].

In solution the rate of isomerisation depends on the solvent, temperature, anion (or added electrolytes) and on the pH. In aqueous solution the rate of equilibration of [Ni(*trans*[14]diene)]$^{2+}$ is very slow (days) at room temperature, rapid at 100° and retarded by acid.

Only the racemic forms of [Ni(*cis*[14]diene)]$^{2+}$ and [Cu(*cis*[14]diene)]$^{2+}$ have been observed, in line with the suggestion of Bailey and Maxwell that a *cis meso* arrangement, with both *gem* methyl groups on the same side of the molecular plane, would be very crowded[37].

Orange [Ni(Me_2*trans*[14]diene)] $(ClO_4)_2$, formed by reaction of tris(*rac* 1,2-diaminopropane)nickel(II) perchlorate with acetone, or from the macrocycle prepared by reaction of *rac* 1,2-diaminopropane hydroperchlorate with acetone (F, ii) is centrosymmetric (J, v) and therefore must have *meso* arrangements of both the asymmetric carbon and nitrogen centres. The copper(II) analogue, prepared by similar reactions (D, i) forms a red perchlorate salt, very similar to the racemic modification of [Cu(*trans*[14]diene)] $(ClO_4)_2$ and is therefore probably racemic. (The copper and nickel compounds have dissimilar X-ray powder diffraction patterns)[9].

The two forms of *trans* [Co(*trans*[14]diene)Cl_2]$^+$ reported by Endicott and co-workers[39] are presumably complexes of the *meso* and racemic forms of the macrocycle (I, v).

Similar isomerism, attributed to restricted inversion about coordinated secondary amine groups, has been observed for *cis* and *trans* [Ni([14]monene)]$^{2+}$, and complexes of the four ([14]tetramines)[9].

H. CHEMICAL REACTIVITY OF THE METAL ION COMPLEXES

(i) *Acid hydrolysis*

Nickel(II) and copper(II) complexes with coordinated N-isopropylidene imino groups such as the non-cyclic complexes formed by reaction of the 1,3-diaminopropane (XIV) or dipropylenetriamine (XV) complexes with acetone (C, i and D, i) are readily hydrolysed by water, as observed for analogous complexes formed by other ketones such as VII. The N-isopropylidene imino groups of complexes such as [Ni(en-aib-N-iprop)]$^{2+}$ are hydrolysed extremely slowly in aqueous solution, yielding *e.g.* [Ni(en-aib)]$^{2+}$ and acetone. The reaction is so slow that [Ni(en-aib-N-iprop)] $(ClO_4)_2$ can be recrystallised from boiling water without appreciable loss[1]. The rate of hydrolysis is much increased in the presence of diaminoethane, probably indicating greater lability of the imino group for the TGS octahedral diaminoethane adduct[28]. These complexes are hydrolysed slowly by dilute acetic acid (but more rapidly than amine-imine bridged compounds without the N-isopropylidene group) yielding acetone and mesityl oxide as the carbonyl compounds.

Amine-imine bridged complex cations such as [Ni(en-aib)]$^{2+}$ are stable to water, but are slowly hydrolysed by dilute acetic acid and rapidly by dilute mineral acids. The TGS diaminoethane adduct [Ni(en-aib)en)$^{2+}$ is slowly hydrolysed in aqueous solution[28]. In view of the resistance to acid hydrolysis of the cyclic complexes, below, it seems probable that acid hydrolysis occurs by stepwise protonation and unrolling of the linear tetradentate ligand, rather than by attack on the imino groups, yielding the protonated *β* amino ketone $NH_3.CH_2.CH_2.NH_2.C(CH_3)_2.CH.CO.CH_3$. *β* Amino ketones are hydrolysed by an acid catalysed reversal of the Michael addition yielding the protonated amine plus as *αβ* unsaturated carbonyl compound (*e.g.* mesityl oxide from acetone condensation products)[40]. For the singly bridged nickel(II) analogue of IX formed with diaminoethane and isobutyraldehyde (C, ii), the *β* amino ketone formed by hydrolysis cannot form an $\alpha\beta$ unsaturated carbonyl compound by amine elimination. Hydrolysis yields isobutyraldehyde, possibly via the non-conjugated unsaturated aldehyde $\alpha\alpha$-dimethyl-β-isopropylidene acrolein, which is readily hydrolysed to isobutyraldehyde[23].

The complexes $[\mathrm{Ni}(\textit{trans}[14]\mathrm{diene})]^{2+}$ and $[\mathrm{Ni}(\textit{cis}[14]\mathrm{diene})]^{2+}$ are very resistant to hydrolysis, being unaffected by boiling dilute mineral acids. (They are oxidized by nitric acid (H, iii). They are slowly decomposed by boiling concentrated sulphuric and perchloric acids, but this is probably a result of the oxidising ability of the acids. Boiling dilute mineral acids hydrolyse the other heterocyclic nickel complexes, $[\mathrm{Ni}([13]\mathrm{monene})]^{2+}$ over a period of hours, $[\mathrm{Ni}([15]\mathrm{diene})]^{2+}$ and $[\mathrm{Ni}([16]\mathrm{diene})]^{2+}$ in minutes[17].

One explanation for the readier hydrolysis of the [15] and [16]diene complexes is that the C:N groups are not as effectively shielded by the remainder of the compact "doughnut" macrocyle. It is perhaps significant that the rate of hydrolysis for $[\mathrm{Ni}([16]\mathrm{diene})]^{2+}$ which has both diaminoethane residues replaced by 1,3-diaminopropane residues, is approximately twice as great as that for $[\mathrm{Ni}([15]\mathrm{diene})]^{2+}$. The suggestion that the reactivity is a consequence of the lack of shielding of the imine groups receives some support from the hydrolytic properties of some $[\mathrm{Ni}([13]\mathrm{monene})]^{2+}$ analogues formed with various aldehydes. The compounds which have no methyl groups adjacent to the C:N groups are hydrolysed by acid more rapidly than their acetone-condensation analogues which have an adjacent methyl group[17]. The ([14]diene) cyclic ligand with a 5,6,5,6 chelate ring system is a less strained system than ([13]monene) (5,5,5,6), [15]diene) (5,6,6,6) or ([16]diene) (6,6,6,6) and this factor may contribute to the ease of hydrolysis of the complexes of the latter macrocycles by making the complexes thermodynamically less stable

The ([15]diene) and ([16]diene) nickel(II) complexes are also hydrolysed by hot dilute base. The ([14]diene) complexes are not hydrolysed by base, but in strongly basic media red deprotonated species are formed[9].

The copper(II) compounds are hydrolysed slightly more readily than their nickel(II) analogues and in particular the cyclic complexes are specifically attacked by concentrated hydrochloric and hydrobromic acids, apparently via an intermediate with coordinated halide, since a dark colouration develops when the acid is added[4].

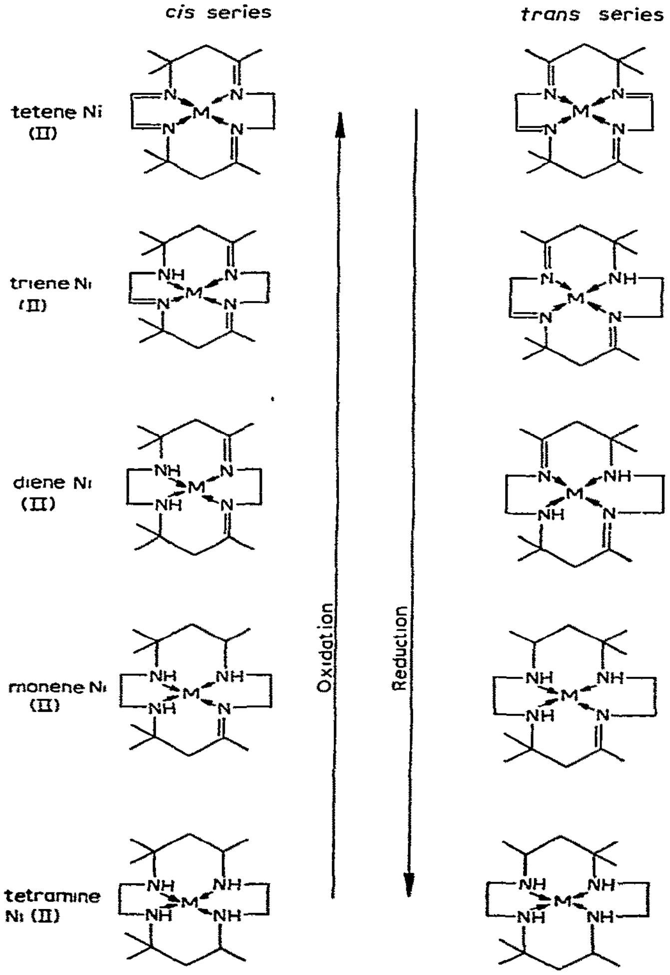
The imine groups of the macrocycle in trans $[\mathrm{Co}(\textit{trans}[14]\mathrm{diene})\mathrm{Cl}_2]^+$ are. reported to be slowly hydrolysed in hydrochloric acid solution[39].

(ii) Reduction

The coordinated imino groups of the macrocyclic nickel(II) complexes can be reduced to give coordinated secondary amine groups. For the fourteen membered macrocycles, hydrogen (platinum catalyst), sodium borohydride, nickel aluminium alloy in basic solution and cathodic reduction have been found effective[41–43].

For [Ni([13]monene)]$^{2+}$, [Ni([15]diene)]$^{2+}$ and [Ni([16]diene)]$^{2+}$ catalytic hydrogenation is the only satisfactory method[44]. Under carefully controlled conditions the diene complexes can be half reduced yielding cyclic triamine-monimine complexe[13] *e.g.* [Ni(*trans*[14]monene)]$^{2+}$.

Reduction of each of the [Ni([14]diene)]$^{2+}$ complexes yields two isomeric cyclic tetramine complexes (the products from [Ni(*trans*[14]diene)]$^{2+}$ have been designated [Ni(tet *a*)]$^{2+}$ and [Ni(tet *b*)]$^{2+}$[41] and the pair from [Ni(*cis*[14]diene)]$^{2+}$, [Ni(tet *c*)]$^{2+}$ and [Ni(tet *d*)]$^{2+}$[42], and this less cumbersome nomenclature will be used). The attribution of this isomerism to the introduction of two asymmetric carbon centres during reduction[41] has been confirmed by X-ray crystallography for the (tet *a*)-(tet *b*) pair, (tet *a*) being (C *meso trans*[14]tetramine) and (tet *b*) being (C *rac trans*[14]tetramine) (J, v). The pair of cyclic amines (tet *b*) and (tet *d*) are able to form *cis* octahedral complexes (I, i) and it appears probable that (tet *d*)



like (tet *b*) is asymmetrical about the molecular plane *i.e.* (tet *d*) is (C *meso cis*-[14]tetramine) while (tet *c*) is (C *rac cis*[14]tetramine). The relative yields of the two isomers varies with the reducing agent *e.g.* for $[Ni(trans[14]diene)]^{2+}$, 22% $[Ni(tet\ b)]^{2+}$ was obtained with alkali and nickel aluminium alloy, 33% with hydrogen and platinum catalyst, and about 40% with borohydride[41,43]. When $[Ni([15]diene)]^{2+}$ and $[Ni([16]diene)]^{2+}$ were reduced only one product was obtained, but these reductions were carried out on a small scale and a second isomer produced in low yield may have escaped detection[44].

The $[Ni([14]tetramine)]^{2+}$ complexes are chemically very stable, *e.g.* being extremely resistant to acid attack, but react with cyanide to yield the free cyclic amine, plus the tetracyanonickelate ion[41,42]. The four isomeric ([14]tetramines) crystallise as hydrates, but the other amines have not been obtained crystalline. A similar phenomenon was observed for the nonsubstituted cyclic tetramines, prepared by standard organic techniques by Stetter and Mayer[45]. 1,4,8,11-Tetraazacyclotetradecane, cyclam, (the analogue of the ([14]tetramines) without the six methyl substituents) crystallised readily but amines with other ring sizes had much lower melting points. It was suggested that N . . . H-N intermolecular hydrogen bonding is most efficient for the fourteen membered cyclam ring[45,46]. The cyclic tetramines, prepared by decomposition of the nickel complexes with cyanide, can be used to form complexes with a variety of metal ions[41,47,48].

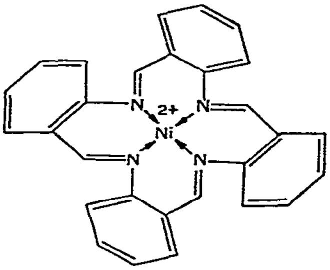
Attempts to reduce the copper(II) analogues have been unsuccessful, decomposition occurring with deposition of copper metal. Since the copper cyclic tetramine complexes can be prepared readily from the free amines these reductions have not been studied in detail. The cobalt(III) complexes $[Co(trans[14]diene)X_2]^+$ are usually reduced by Zn/H^+ or by BH_4^- to yield the cobalt(II) (*trans*[14]diene) complexes. $[Co(trans[14]diene)(CN)_2]^+$ is exceptional, BH_4^- reducing the imino groups yielding $[Co^{III}(tet\ a)(CN)_2]^+$[39].

(iii) Oxidation

Strong oxidising agents such as acid permanganate and peroxydisulphate completely destroy the ligand of these macrocyclic complexes. The $[Ni([14]diene)]^{2+}$ complexes are oxidised by nitric acid to give cyclic tetra-imine "tetene" complexes, *e.g.* $[Ni(trans[14]tetene)]^{2+}$ and $[Ni(cis[14]tetene)]^{2+}$[13]. The crystal structure of one modification of $[Ni(cis[14]tetene)](ClO_4)_2$ has been determined by Bailey and Maxwell, confirming the structure shown (J, v). The tetene complexes are readily reduced by borohydride or hydrogen (platinum catalyst), to give first the original diene complexes and finally the tetramine complexes. Milder reducing agents, such as sulphurous acid yield the triene complexes and hypophosphorous acid yields first the triene and finally the diene complexes. The tetene complexes are stable to acids, but in basic solutions undergo an irreversible slow reaction to yield intensely coloured products, violet for $[Ni(cis[14]tetene)]^{2+}$ and green for [Ni(*trans*[14]-

tetene)]$^{2+}$. The violet *cis* compound is stable, but the green material in solution is slowly oxidised on exposure to the air. From the increase in intensity of visible light absorption some of the C:N groups may have migrated to increase the conjugation, or addition of hydroxide to the C:N bonds may have occurred, as suggested for the related compound XXVII (below).

The ([14]tetene) complexes are closely related to the macrocyclic complex XXVII, described by Melson and Busch, formed by the self condensation of four moles of *o*-aminobenzaldehyde in the presence of nickel(II) ions. This complex is also stable to acids, but reacts with bases[49].



XXVII

The [Ni([14]tetene)]$^{2+}$ complexes can also be prepared by nitric acid oxidation of the [Ni([14]tetramine)]$^{2+}$ complexes. Under mild conditions (warm dilute, or cold concentrated nitric acid) nickel(III) tetramine complexes can be isolated, *e.g.* [Ni(tet *a*) $(NO_3)_2$] (ClO_4)[50]. It thus appears probable that the oxidation reactions yielding the tetene complexes occur via the Ni^{III} complex as intermediate.

The complexes [Ni([13]monene)]$^{2+}$, [Ni([15]diene)]$^{2+}$, [Ni([16]diene)]$^{2+}$ and all copper(II) analogues are apparently destroyed by the rather violent conditions of the nitric acid oxidation[9].

(iv) Reactions with cyanide ion

The macrocyclic nickel(II) and copper(II) complexes react with cyanide to yield the tetracyanonickelate(II) or cyanocuprate(I) ions plus the macrocycle[41,42,51] The macrocycles with imino groups are readily hydrolysed and the products isolated depend on the conditions. Thus under anhydrous conditions the reaction of cyanide with the [Ni([14]diene)]$^{2+}$ complexes yields solutions of the macrocycle which can be used to prepare complexes of other metal ions (F, iii). The addition of acetic acid to the solution resulting from the reaction of [Ni(*trans*14]diene)] $(ClO_4)_2$ and sodium cyanide in methanol causes crystallisation of [H_2(*trans*[14]diene)] $(CN)_2$ (sparingly soluble dihydrocyanides are formed by the ([14]tetramines) also[9]). In water, the diene macrocycles are hydrolysed, yielding first the β amino ketone and finally diaminoethane plus mesityl oxide[3,9].

Addition of cyanide to aqueous solutions of [Ni(*rac trans*[14]diene)]$^{2+}$ causes a colour change from orange to pink, the colour then fading over a period of minutes as pale yellow $[Ni(CN)_4]^{2-}$ is formed. The pink colouration was shown to be due to a TGS monocyanide adduct, formation constant of the order[51] of 10. The racemic isomer is less hindered on one side of the molecular plane and is thus suited to formation of five-coordinate adducts. No TGS adducts were observed with $[Ni($*meso trans*$[14]diene)]^{2+}$ or $[Ni($*cis*$[14]diene)]^{2+}$ but the overall decomposition reaction occurs at about the same rate for the three isomers[6]. Solutions of $[Ni([15]diene)]^{2+}$ and $[Ni([16]diene)]^{2+}$ both change from orange to pink in colour on addition of cyanide (the formation constants of the cyanide adducts appearing to be larger than for $[Ni($*rac trans*$[14]diene)]^{2+}$), the colour then fading as for the ([14] diene) complexes[17].

Addition of cyanide to solutions of a variety of macrocyclic copper(II) complexes causes a colour change from magenta to blue, the colour then fading over about a day as colourless cyanocuprate(I) complexes are formed. For several cases the blue colour was found to be due to the formation of monocyanide adducts with formation constants[51] ranging from 300–900.

(v) Reactions with ammonia

The non-cyclic nickel(II) complexes $[Ni(en\text{-}aib)]^{2+}$ and $[Ni(en\text{-}aib\text{-}N\text{-}iprop)]^{2+}$ undergo a variety of reactions with ammonia. In the solid state the powdered perchlorate salts absorb two moles of ammonia gas to form violet TGS di-ammine adducts[9,52]. The ammonia is rapidly lost on exposure to the atmosphere. In dilute aqueous solution violet TGS ammine adducts are formed. In concentrated aqueous ammonia a "disproportionation" type reaction occurs, yielding $[Ni($*trans*$[14]diene)]^{2+}$ [6]. When ammonia gas is passed into a solution of the perchlorate salts in methanol a complex series of colour changes occurs, and $[Ni(NH_3)_6](ClO_4)_2$ crystallises[52].

(vi) Isotopic exchange

Burns found no exchange of nickel ion between several of the amine-imine complexes and Ni_{aq}^{2+} labelled with ^{63}Ni in aqueous solution[52]. Very slow exchange occurred between the complexes and $[Ni(en)_3]^{2+}$ similarly labelled in aqueous ammonia solution. The non-cyclic complexes $[Ni(en\text{-}aib)]^{2+}$, $[Ni(pn\text{-}aib)]^{2+}$ and $[Ni(ibn\text{-}aib)]^{2+}$ exchanged much more rapidly than $[Ni([14]diene)]^{2+}$ in the presence of ammonia but slow decomposition of the non-cyclic complexes under these conditions complicated the reaction[52]. The studies on $[Ni([14])diene)]^{2+}$ were carried out before the existence of the *cis* and *trans* isomers was realised and hence it is not known whether the studies were on a single isomer or a mixture of the two.

The secondary amine protons exchange rapidly with deuterium in basic D_2O, the exchange being inhibited by acid. Warner, Rose and Busch report that the methyl and methylene protons adjacent to the imino group of the isomers of $[Ni([14]diene)]^{2+}$ exchange for deuterium in basic D_2O[7,36].

I. COMPLEXES OF THE TETRA-AZA CYCLIC DIENES WITH COORDINATION NUMBERS ABOVE FOUR

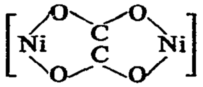
(i) Nickel(II) compounds

Almost all the salts of the ([13]monene), ([14], [15] and [16]diene)nickel(II) complex cations are square planar, (diamagnetic, SGS), as are their solutions even in solvents of high coordinating ability. For small ligands, SGS square planar nickel(II) complexes are formed by high ligand field ligands, such as cyanide, but spectroscopic measurements (J, iii) show that these macrocycles have ligand field strengths comparable with bis(diaminoethane), which forms mainly octahedral TGS derivatives.

The two main factors determining the relative stability of SGS square planar and TGS octahedral arrangements by tetra-amines are the blocking of the axial coordination sites by substituents, and the extent of strain in poly-chelate ring systems. For bis(C-methyldiaminoethane)nickel(II) complexes the tendency to form SGS salts and SGS species in solution increases with increasing "bulk" of the ligand, but axial methyl groups have a much greater effect than equatorial ones. Hence this tendency increases in the sequence: diaminoethane < 1,2-diaminopropane < *rac* 2,3-diaminobutane(0) $\ll$ 1-methyl-2,3-diaminopropane $\sim$ *meso* 2,3-diaminobutane (2) $\ll$ 2,3-dimethyl-2,3-diaminobutane (4). (Number of axial methyl groups for the bis complexes in parenthesis). These observations indicate that for these diamines crowding of the axial sites is the factor determining the relative stability of the SGS planar and TGS octahedral species, the latter with *e.g.* water or an anion coordinated in two sites. The $[Ni([14]diene)]^{2+}$ structures reported (J, v) reveal considerable crowding of the axial sites by methyl groups, indicating that this is an important factor for these macrocyclic complexes.

Models suggest that for the cyclic amine cyclam with a 5,6,5,6 chelate ring system there should be little difference in total strain between planar (square planar or *trans* octahedral) and folded (*cis* octahedral) arrangements, but the former are most common[53]. The ([14]tetramines) have the cyclam chelate ring system but interactions involving the six methyl substituents affect the arrangements adopted. The C *meso trans* isomer (tet *a*) has the more symmetrical structure and only square planar and *trans* octahedral derivatives have been prepared[41,43,54–56]. Most derivatives have a centrosymmetric C *meso* N *meso* N *meso* arrangement (similar to that found for $Ni(cyclam)Cl_2$) (J, v) but isomeric forms with different arrangements of the asymmetric nitrogen centres have been observed. The C racemic isomer (tet *b*) is unsymmetrical about the molecular plane, and commonly adopts a *cis* octahedral arrangement with the macrocycle folded[41,43,48,54] (*e.g.* [Ni(tet *b*)-CH_3COO]ClO_4, (J, v).

The (*trans*[14]diene) macrocycle is symmetrical about the molecular plane for the N *meso* isomer and more crowded on one side of the molecular plane for the N racemic isomer. The only TGS octahedral derivatives known for the racemic isomer is {[Ni(*rac trans*[14]diene)]$_2C_2O_4$} $(ClO_4)_2$, with the macrocycle folded and with the oxalate ion functioning as a bridging bichelate[57]. A recent crystallographic study of a bis(diaminoethane) analogue, {[Ni(en$_2$]C_2O_4} $(NO_3)_2$, has confirmed the structure with



groups as postulated in reference 57[58]. The only known TGS derivatives of the *meso* isomer are metastable N-coordinated Ni(*meso trans*[14]diene) $(NCS)_2$ (prepared by recrystallisation from chloroform and reverting to the stable SGS form on exposure to the atmosphere)[7,36] and [Ni(*meso trans*[14]diene)]Ni$(CN)_4$, H_2O[9], (a polymer with cyanide bridges) both presumably with *trans* arrangements. No TGS derivatives of Ni(*cis*[14]diene)$^{2+}$ are known[9]. The occurrence of many TGS derivatives of the tetramines and so few of the cyclic dienes is probably a consequence of the greater flexibility of the saturated tetramine macrocycle, which permits distortion to accommodate additional ligands with less strain (J,v).

Both [Ni([15]diene)]$^{2+}$ and [Ni([16]diene)]$^{2+}$ form TGS thiocyanates and tetracyanonickelates[23], while no TGS derivatives of [Ni([13]monene)]$^{2+}$ are known[9].

The linear tetradentate amine-imine complex [Ni(en-aib)]$^{2+}$ and [Ni(en-aib-N-iprop)]$^{2+}$ occur as SGS perchlorates and aqueous solutions, but form a variety of TGS salts (*e.g.* []NO_2ClO_4, []$_2C_2O_4(ClO_4)_2$[57], []BH_4ClO_4[43], []$(NCS)_2$ etc., and form amine adducts such as []$(NH_3)_2(ClO_4)_2$ and []en$(ClO_4)_2$[9]. The bis nickel(II) complexes of the bidentate ligand 2-amino-2-methyl-4-iminopentane, formed by reaction of nickel ammine complexes with acetone, occurs as SGS salts with most anions. The thiocyanate has a TGS, and TGS adducts are formed with some aromatic bases[8,59].

(ii) Copper(II) compounds

Solution spectra of the [Cu([14]diene)]$^{2+}$ perchlorates vary with the solvent, the characteristic single band of the Cu^{II} ion shifting from 20,400 cm^{-1} in acetone (magenta) to 19,500 cm^{-1} in dimethylformamide (blue)[4]. This shift of the band to lower energy is indicative of axial interactions with the solvent, and in confirmation, blue di-aquo and dimethylsulphoxide adducts can be isolated for the *trans* isomer[4,9]. Addition of ammonia to aqueous solutions causes a colour change from magenta to blue, and a blue di-ammine can be isolated, for the *trans* isomer.

These adducts provide a convenient source of the isomers, the di-ammine, like the di-hydrate, yielding the racemic (red) form on heating, while the dimethylsulphoxide adduct yields the *meso* (orange) form when washed with ethanol.

Interaction can occur with anions also, and blue mono cyanide adducts are formed in aqueous solution (H, iv). A crystalline cyanide derivative $\{[Cu(\textit{trans}[14]diene)]_2CN\}(ClO_4)_3$ was isolated and assigned a dimeric structure with a cyanide bridging group[56]. For $[Cu(\textit{trans}[14]diene)]^{2+}$ the blue chloride, bromide, chloride perchlorate and bromide perchlorate have been prepared, and are considered to have five coordinate structures[9]. The mauve di-thiocyanate has S bonded thiocyanate (ν(CS) at 727 cm^{-1}, cf. S bonded $Cu(en)_2(SCN)_2$)[9]. Similar, but more soluble, derivatives with coordinated anions are formed by $[Cu(\textit{cis}[14]diene)]^{2+}$[9].

(iii) Cobalt(II) compounds

Love and Powell prepared cobalt(II) (*cis*[14]diene) complexes by reaction of the free base (F, ii) with cobalt(II) salts[35]. Dimeric formulae with a cobalt-cobalt single bond were proposed for orange brown $[(H_2O)(\textit{cis}[14]diene)Co\text{-}Co(\textit{cis}[14]diene)(H_2O)](ClO_4)_4, H_2O$ ($\mu_{eff} = 4.7$ B.M.); green $[(SCN)(\textit{cis}[14]diene)Co\text{-}Co(\textit{cis}[14]diene)(NCS)]Co(NCS)_4, H_2O$; yellow $[(CN)(\textit{cis}[14]diene)Co\text{-}Co(\textit{cis}[14]diene)(CN)](ClO_4)_2$, ($\mu_{eff} = 0.84$ B.M.); and $(X_3CoX)(\textit{cis}[14]diene)\text{-}Co\text{-}Co(\textit{cis}[14]diene)(XCoX_3), 2H_2O$ ($X = Cl^-$, blue-green, $X = Br$, yellow green). The moiety $[(\textit{cis}[14]diene)Co\text{-}Co(\textit{cis}[14]diene)]^{4+}$ is reported to have high chemical stability towards acid, alkali and metal ion reagents[35]. An X-ray crystallographic study of the cyanide derivative is in progress[60]. These compounds, unlike the cobalt(II) (*trans*[14]diene) derivatives, are resistant towards oxidation to cobalt(III).

(iv) Cobalt(III) compounds

Cobalt(III) complexes of (*trans*[14]diene) reported by Endicott and co-workers include the *cis* complex with chelate carbonate, and various *trans* complexes[25,39]. $\textit{Trans}[Co(\textit{trans}[14]diene)Cl_2](ClO_4)$ was obtained in two forms, designated "a" and "b"[39]. The *cis* derivative $[Co(\textit{trans}[14]diene)(CO_3)](ClO_4)$, by analogy with the *cis* nickel(II) oxalato derivative, probably contains the N racemic isomer of the macrocycle (Section G). Treatment of this carbonato derivative with hydrochloric acid yields the "a" dichloro derivative and hence the "a" series is probably N racemic and the "b" series N *meso*[9].

(v) Zinc(II) compound

Sadasivan and Endicott report the preparation of the zinc(II) complex $[Zn(\textit{trans}[14]diene)(Cl)(H_2O)](ClO_4)$ from $H_2(\textit{trans}[14]diene)](ClO_4)_2$ (formulated as hexacoordinate without experimental justification)[25].

J. PHYSICAL PROPERTIES

(i) Ultraviolet Spectra

The nickel(II) complexes have a strong band near 49,000 cm^{-1}, $\varepsilon \sim$ 20,000 and a weaker band near 36,000 cm^{-1}, $\varepsilon \sim$ 5,000[1,10]. The 36,000 cm^{-1} band is lost when the imino groups of the cyclic complexes are reduced, forming cyclic amine complexes, and was therefore assigned to transitions involving the azomethine chromophore, and the 49,000 cm^{-1} band which remained was assigned as a charge transfer transition[41]. The copper(II) complexes show similar ultraviolet spectra, with bands at 38,000 cm^{-1}, $\varepsilon \sim$ 6,000, and at $\sim$50,000 cm^{-1}, $\varepsilon \sim$ 10,000, but in this case it is the lower frequency band which remains in the spectrum of the cyclic amine complex and therefore was assigned as the charge transfer transition[4,41]. The cobalt(III) (*trans*[14]diene) complexes have charge transfer bands near 46,000 cm^{-1} [25,39].

(ii) Infrared Spectra

The infrared spectra of the macrocyclic ligands are complex. The complexes which have coordinated secondary amine groups have band/bands in the vicinity of 3,200 cm^{-1} assigned as ν(NH). The frequencies are raised by increasing the coordination number, and decreased by hydrogen bonding interactions, (*e.g.* for [Ni(*rac trans*[14]diene)]$^{2+}$; $\{[\,]_2C_2O_4\}(ClO_4)_2$, 3255, 3250[57]; $[\,](ClO_4)_2$, 3170[6]; $[\,]ZnCl_4,H_2O$, 3110 (hydrogen bonded to a water molecule?)[6]; $[\,](NCS)_2$, 3085. 2870 (hydrogen bonded to NCS$^-$)[61]; and for [Cu(*rac trans*[14]diene)]$^{2+}$; $[\,](ClO_4)_2$, 3205; $\{[\,]Cl\}ClO_4$, 3242 cm^{-1} [9]. The frequencies observed for Co^{III} derivatives, $\sim$3200 cm^{-1} [39], are similar to those observed with derivatives of divalent ions, not showing the usually observed displacement to lower frequency with increasing charge on the central ion. A similar effect has been observed for the complexes of the cyclic tetramine (tet *a*)[47].

The coordinated methyl imino groups absorb at $\sim$1660 cm^{-1} while the α hydrogen imino groups of ([14]triene) and ([14]tetene) complexes absorb at $\sim$1675 cm^{-1} [13]. The ([14]triene) and ([14]tetene) complexes are also distinguished by sharp bands at $\sim$3070 cm^{-1} assigned to ν(CH) of vinyl hydrogen atoms[13]. The remainder of the spectra are complex and vary with the anion. Marked changes occur with different ring conformations and the infrared spectra in the region 1350–750 cm^{-1} provide a convenient method of identifying isomeric compounds (*e.g. rac* and *meso* [Ni(*trans*[14]diene)]$^{2+}$ and [Ni(*cis*[14]diene)]$^{2+}$ [6]. Band positions for some (*trans*[14]diene) complexes of Co^{II}, Co^{III}, Ni^{II}, Cu^{II} and Zn^{II} are tabulated (together with some spectra), by Endicott and co-workers[25,39]. Warner, Rose and Busch report the spectra of deuterated [Ni(*trans*[14]diene)]$^{2+}$ cations[36].

TABLE 1

SOLUTION SPECTRA OF SOME SINGLET GROUND STATE $[Ni(N_4)]^{2+}$ COMPLEXES[a]

N_4	*Band Maximum*[b]	*Reference*
(*meso trans* [14]diene)	23.0 (101)	6
(*rac trans* [14]diene)	23.2 (93)	6
(*rac cis* [14]diene)	23.0 (108)	6
(tet *a*)	21.7 (79)	41
(α tet *b*)[c]	22.6 (70)	41
(β tet *b*)	22.2 (104)	41
(tet *c*)	22.5 (111)	9
(cyclam)	22.1 (68)	53
(Me_2 *trans*[14]diene) "orange"	22.9 (78)	10
(Me_2 *trans*[14]diene) "yellow"	23.7 (95)	10
([15]diene)	22.1 (131)	17
([16]diene)	22.8 (100)	14
([16]tetramine)	22.2 (106)	44
([13]monene)	23.8 (110)	15
([13]tetramine)	23.3 (119)	44
(*cis* [14]monene)	22.9 (85)	9
(*trans* [14]tetene)	22.6 (159)	9
(en–aib)	23.0 (70)	10
(en–aib–N–iprop)	23.0 (105)	10
$(Me_4en)_2$[d]	23.0 (64)	62
(2-methyl-2-amino-4-iminopentane)$_2$	23.1 (100)	18
$(ibn)_2$[ef]	22.5 (59)	26
(*meso* sbn)$_2$[fg]	22.5 (55)	26
(beap)[hi]	22.2 (?)	63

[a] Spectra of related compounds quoted in references 1, 10, 14–16, 30.

[b] In 10^3 cm^{-1}. Extinction coefficient in parenthesis.

[c] N *meso* N *meso* isomer.

[d] Me_4en = tetra-C-methyldiaminoethane (2,3-dimethyl-2,3-diaminobutane).

[e] ibn = isobutylenediamine (2-methyl-2,3-diaminopropane).

[f] Singlet ground state form (the perchlorate salt in acetone).

[g] *meso* sbn = *meso* sym. butylenediamine (2,3-diaminobutane).

[i] Singlet ground state form. triethylenetetramine complex has a similar band[64].

[h] beap = 1,9-diamino-3,7-di-azanonane.

(iii) Metal ion spectra

Singlet ground state nickel(II) complexes in 4 N square planar coordination typically have a single metal-ion absorption band near 22,000 cm^{-1}, $\varepsilon \sim 100$.

For amine-imine ligands the energy of this transition is relatively insensitive to changes in the ligand. Reduction of the ([14]diene) complexes to yield the tetramine complexes, or oxidation to yield the tetra-imine complexes, causes little change in the absorption spectrum. The spectra of SGS nickel(II) complexes with a variety of bis diamines, linear and cyclic tetramines, linear and cyclic amine-imines are listed in Table 1. The similarity of the band positions for these complexes indicates a similarity in ligand field strength of the ligands. The solution spectra are the same in solvents of widely varying donor strength (*cf.* the copper(II) complexes, (J, iii). The colours of salts often vary slightly with the anion, remaining in the general colour range yellow-orange. The molar extinction coefficients are approximately 100 and in general are higher for less symmetrical arrangements. For example the extinction coefficient is higher for (*cis*[14]diene) than for (*trans*[14]diene), and is higher for ([15]diene) than for ([14]diene) or ([16]diene).

The spectra of TGS octahedral nickel(II) complexes show three main bands, corresponding to the transitions $^3T_{1g} \leftarrow {}^3A_{2g}$, $^3T_{2g}(F) \leftarrow {}^3A_{2g}$ and $^3T_{2g}(P) \leftarrow {}^3A_{2g}$. The lowest energy transition $^3T_{1g} \leftarrow {}^3A_{2g}$ gives an approximate value for the ligand field parameter Δ.

The [Ni(*trans*[14]diene)]$^{2+}$ cation forms two pseudo-octahedral TGS derivatives, the dithiocyanate[7,36], and the oxalato perchlorate[57]. Analogous compounds are formed by a variety of nickel-tetramine cations, making comparison of the ligand field strengths of the amines ligands possible. Both series of compounds have "three-band" reflectance spectra; for the *trans* thiocyanates the difference between the ligand field strengths of the nitrogen atoms of the amine-imines and of the thiocyanate ions are too small to cause splitting of the lowest energy band (ν_1) commonly observed with tetragonal distortion[65], while for *cis* NiN_4O_2 complexes (such as the oxalato derivatives) splitting of this band does not usually occur[54]. Within each of these series of compounds, the energy of the ν_1 band probably gives a reliable indication of the relative ligand field strengths of the tetramines. Most of these compounds dissociate in solution, and hence the data in Tables 2 and 3 refer to the reflectance spectra and therefore too much should not be inferred from minor variations.

TABLE 2

REFLECTANCE SPECTRA OF SOME $\{[Ni(N_4)]_2C_2O_4\}(ClO_4)_2$ COMPLEXES[a]

N_4	ν_1[b]	ν_2[c]	ν_3[d]
(*rac trans*[14]diene)[e]	10.8	17.8	28.6
(α tet *b*)	10.1	17.2	27.2
(*cis*[14]triene)	11.2	18.2	28.5
(*cis*[14]monene)[f]	10.3	17.1	27.0
(α tet *d*)	10.6	17.5	27.6
$(en)_2$	10.8	17.6	27.2
(trien)	11.0	18.0	27.6
$(1,3\ pn)_2$	10.7	17.5	27.7
(en-aib)	10.7	17.7	27.9

[a] In order to make comparisons valid the spectra were all measured using the same apparatus, a Unicam S.P.700 spectrophotometer calibrated using the 15273 cm^{-1} hydrogen line and with $MgCO_3$ as reference.

[b] $^3T_{2g} \leftarrow {}^3A_{2g}$ in O_h symmetry.

[c] $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ in O_h symmetry.

[d] $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ in O_h symmetry.

[e] Violet anhydrous salt. Forms a blue hydrate also.

[f] Hydrated.

TABLE 3

REFLECTANCE SPECTRA OF SOME $Ni(N_4)(NCS)_2$ COMPLEXES[a]

N_4	ν_1[b]	ν_2[c]	ν_3[d]
(*meso trans*[14]diene)[e]	10.8	20.5	28.5
([15]diene)	10sh, 11.8	17.7	28.7
([16]diene)	10.5	17.6	?
(tet *a*)	10.5	19.0	28.6
(α tet *b*)[f]	9.7	16.6	26.0
(tet *c*)	10.9	19.2	28.9
(α tet *d*)[g]	9.4	16.8	27.5
(β tet *d*)[h]	10.6	19.2	28.7
(*cis*[14]tetene)	11.0	21	26.6
(TAAB)[i]	10.5	18.2	—
(en-aib)	10.5	18.6	27.9
$(en)_2$	10.0,11.5sh	18.0	27.8
$(1,3\ pn)_2$	10.6	17.3	27.0
(trien)	11.0	18.1	27.4
$(2\text{-methyl-2-amino-4-iminopentane})_2$	[j]10.7	18.7	—
$(2\text{-methyl-2-amino-4-iminopentane})_2$	[k]10.6	18.1	—

[a] See footnote a to table 2

[b] $({}^3E_g{}^a, {}^3B_{2g}) \leftarrow {}^3B_{1g}$ (from ${}^3T_{2g} \leftarrow {}^3A_{2g}$ in O_h).

[c] $({}^3E_g{}^b, {}^3A_{2g}) \leftarrow {}^3B_{1g}$ (from ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ in O_h).

[d] $({}^3E_g{}^c, {}^3A_{2g}) \leftarrow {}^3B_{1g}$ (from ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$ in O_h).

[e] Metastable TGS compound crystallized from chloroform. Values from ref. 36.

[f] Same isomer as the oxalate-perchlorate, probably N *meso* N *meso*.

[g] Same isomer as the oxalate perchlorate.

[h] Produced by recrystallization of the previous (g) compound from hot methanol.

[i] Tetrabenzo b, f, j, n 1,5,9,13 tetra-azacyclohexadecine. Values from ref. 49.

[j] Nujol mull Values from ref. 19.

[k] Acetone solution. Values from ref. 18.

For the *cis* oxalato compounds (Table 2) the derivatives of (*trans*[14]diene), (C *meso trans*[14]tetramine), diaminoethane, 1,2- and 1,3-diaminopropane and (en-aib) have similar spectra and ν_1 values. For the *trans* dithiocyanato derivatives (Table 3) the values cover a range of values near that of the dithiocyanato bis-(diaminoethane) complex. For the dithiocyanato derivatives, expanding the diene macrocycle has no clear cut effect—the energy of ν_1 increases from [14] to [15] but falls again to [16]diene.

Increasing the degree of unsaturation of the macrocycle (*i.e.* replacing amine by imine donor groups appears to cause a slight increase in the ligand field strength, but the effect is masked by the variability associated with differing ring configurations, *e.g. cis*[14]-oxalato series: tetramine, $\nu_1 = 10.4$; monene, 10.1; triene, 11.2. *trans*[14]-oxalato series: tetramine, 10.1; diene, 10.8, *trans*[14]-thiocyanato series: tetramine, 9.7, and 10.5; diene, 10.8, tetene, 11.2 (10^3 cm^{-1}). This effect is possibly a consequence of the slightly shorter Ni-N bond lengths for imino compared with amino donor groups and does not necessarily indicate any significant degree of

π bonding by the imino groups (J, v). The spectra of the nickel(II) complexes of a number of macrocyclic ligands are discussed by Busch[21].

The spectra of the copper(II) complexes show the single band near 19000 cm^{-1}, $\varepsilon \sim 150$ characteristic of square planar copper(II) complexes[4]. The band position and intensity are very susceptible to axial interactions, the band being displaced to lower frequency in coordinating solvents, with a corresponding colour change from magenta to blue. For [Cu(*trans*[14]diene)]$^{2+}$ the highest frequency was observed in acetone (20,400 cm^{-1}) and the lowest in dimethylformamide (19,500 cm^{-1})[4]. Addition of ligands such as ammonia or cyanide to aqueous solutions causes colour changes from magenta to blue, with displacement of the band to lower frequencies. A variety of solid five and six coordinated derivatives can be isolated (I, ii) and these are characteristically blue in colour.

The spectra of octahedral cobalt(III) complexes show two main bands assigned to the transitions $^1T_1 \leftarrow {}^1A_1$ (Band I) and $^1T_2 \leftarrow {}^1A_1$ (Band II). Values of Δ can be calculated from the energies of these transitions only for arbitrarily assigned values of the electronic repulsion parameters B and C.

For *cis* tetramine complexes, $Co(N_4)X_2^+$, the two band spectrum remains and Δ_{avge} values can be calculated, which should be sufficiently reliable for comparison purposes with a series of analogous compounds. Table 4 lists details of the spectra of a series of carbonato tetramine complexes $[Co(N_4)CO_3]^+$, with

TABLE 4

SPECTRA OF SOME $[Co(N_4)CO_3]^+$ COMPLEXES[a]

N_4	I[b]	II[c]	Δ_{avge}[d]	B[d]	C[d]	Δ_{amine}[e]
(*trans*[14]diene-*b*)[fg]	19.4	26.8	22.8	0.472	3.3	24.7
(tet *b*)[g]	18.2	25.9	21.6	0.487	3.4	22.9
cyclen[h]	18.9	27.2	22.6	0.518	3.7	24.4
$(en)_2$[gh]	19.4	27.6	23.2	0.515	3.6	25.3
α trien[i]	19.9	28.0	23.5	0.515	3.6	25.5
β trien[i]	19.7	27.9	23.3	0.518	3.7	25.8
$(NH_3)_4$[h]	19.0	27.6	22.9	0.543	3.8	24.4

Order of Δ_{avge} and Δ_{amine} trien > en > (*trans*[14]diene-b)NH_3 ~ cyclen > (tet *b*)

[a] All energies in 10^3 cm^{-1}.

[b] $^1T_1 \leftarrow {}^1A_1$ in O_h symmetry.

[c] $^1T_2 \leftarrow {}^1A_1$ in O_h symmetry.

[d] Calculated from $II = 16B - C$; $I = \Delta - C$, assuming $C/B = 7.0$. This ratio gives values of B and C similar to those obtained by Wentworth and Piper in calculations making use of the energy of the $^3T_1 \leftarrow {}^1A_1$ transition. Other reasonable values of the ratio give only slightly different values of Δ_{avge}.

[e] Calculated using the "average environment" approximation, the Δ value for chelate CO_3^{2-} being obtained from the Δ_{avge} values for the en and NH_3 complexes, assuming $\Delta_{en} = 25.3$ and $\Delta_{NH_3} = 24.9$ which both give Δ values of $\Delta_{CO_3^{2-}} = 9.5 \times 10^3$ cm^{-1}.

[f] Differing values quoted in reference 39 are in error[70].

[g] Measured in methanol.

[h] From reference 67.

[i] From reference 68.

TABLE 5

SPECTRA OF SOME *trans* $[Co(N_4)Cl_2]^+$ COMPLEXES[a]

N_4	*Ia*[b]	*Ib*[ce]	*II*[de]	Δ *amine*[f]
(*trans*[14]diene-b)[gh]	15.9	22.3	29.3	24.8
(*trans*[14]diene-a)[g]	15.9	?	?	24.8
(tet *a*)[h]	15.7	20.5	24.3	24.4
(tet *b*)[h]	15.5	20.7	24.3	24.0
cyclam[i]	15.7	22.7	?	24.4
trien[j]	16.3	22.2	?	25.6
beap[jk]	16.1	23.4	?	25.2
$(en)_2$[l]	16.1	21.9	25.0	25.2
$(NH_3)_4$[l]	15.9	21.0	24.9	24.8

Order of Δ_{amine}: trien > beap ~ en > NH_3 ~ (*trans*[14]diene) > (tet *a*) ~ cyclam > (tet *b*)

[a] All energies in 10^3 cm^{-1}.

[b] $^1E \leftarrow {}^1A_1$ in D_{4h} derived from $^1T_1 \leftarrow {}^1A_1$ in O_h.

[c] $^1A_2 \leftarrow {}^1A_1$ in D_{4h} derived from $^1T_1 \leftarrow {}^1A_1$ in O_h.

[d] $(^1E, {}^1B_2) \leftarrow {}^1A_1$ in D_{4h} derived from $^1T_2 \leftarrow {}^1A_1$ in O_h.

[e] Often shoulders on, or obscured by charge transfer bands.

[f] Calculated by the procedure of Wentworth and Piper[66] as modified by Sadasivan, Kernohan and Endicott[39], $\Delta_{amine} = 2Ia - 2C - \Delta_{Cl^-}$, where C is given the value 3800 cm^{-1} and Δ_{Cl^-} the value 14600 cm^{-1}, *i.e.* $\Delta_{amine} = (2Ia - 700) cm^{-1}$.

[g] Differing values quoted in reference 39 are in error[70].

[h] Methanol solutions of perchlorate salts.

[i] Estimated from the published spectrum – values approximate – reference 46.

[j] From reference 69.

[k] beap = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$.

[l] From reference 66.

values of Δ_{avge} (calculated assuming C/B = 7.0), and values of Δ_{amine} (Δ_{amine} is the Δ value for an octahedral complex with six donor groups of the same average ligand field strength as the tetramine—see footnote to Table 4). The order of ligand field strength obtained is trien > en > (*trans*[14]diene) > (tet *b*).

For *trans* tetramine complexes, $[Co(N_4)X_2]^+$ the $^1T_1$ level is appreciably split, resulting in the splitting of band I into two components, Ia and Ib. The intensities are much lower than for *cis* complexes and bands Ib and II often occur as shoulders on, or are obscured by, charge transfer bands. From the energy of the Ib band, using a procedure described by Wentworth and Piper[66], as modified by Sadasivan, Kernohan and Endicott[39] (see footnote to Table 5) values of Δ_{amine} can be calculated. Spectral data and Δ_{amine} values for some *trans*$[Co(N_4)Cl_2]^+$ complexes are listed in Table 5. The order obtained is much the same as observed for the carbonato complexes; trien > en > NH_3 ~ (*trans*[14]diene) >(tet *a*) ~ cyclam > (tet *b*). Sadasivan, Kernohan and Endicott calculate values for Δ_{amine} of (*trans*[14]diene) well above the other amines, but spectral values used in the calculations have since been shown to be in error[9,70]. They also list spectra for *trans* di-aquo and other *trans* di-acido complexes[39]. The spectra of tetragonal complexes of cobalt(III) with a number of macrocyclic ligands have been discussed by Busch[21].

The various macrocycles have four nitrogen donor atoms which can be present as secondary amino or as imino groups, depending on the level of oxidation. Although imines appear to have lower base strengths than related amines (few have been measured[27a]), the aliphatic imino groups in these compounds have higher ligand field strengths than their secondary amine equivalents. (The difference is larger for cobalt(III) than for nickel(II) presumably a consequence of the smaller size of the trivalent ion). The higher ligand field strengths of the imino groups compared with the secondary amino groups is reflected in a slightly shorter nickel(II)-nitrogen bond length (J, v). Imino groups can in principle from π bonds by overlap of filled d orbitals on the metal ion and π antibonding orbitals of the ligand. The ligand field strengths observed suggest that this effect is not of much significance for these first row transition elements, the ligand field strengths all being lower than for triethylenetetramine which is incapable of π bonding. The effective ligand field strengths of the various optical isomers of the macrocycles can vary appreciably (*cf.* α and β Ni(tet *d*) $(NCS)_2$, Table 3) presumably because the isomers (particularly those associated with asymmetric nitrogen centres) may have quite different conformations of the chelate rings. Secondary amines generally have ligand field strengths lower than primary amines[71]—the base strengths are higher, but crowding is more serious for secondary amines. Overall, the average ligand field strengths for the cyclic dienes appear comparable with bis(diaminoethane) for nickel(II), and rather less than bis(diaminoethane) for cobalt(III).

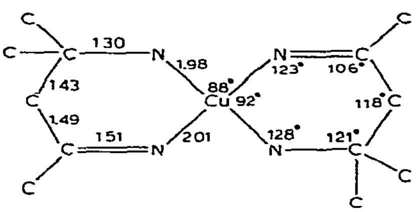
(iv) N.M.R. spectra

The N.M.R. spectra in acidic D_2O of *rac* and *meso* $[\mathrm{Ni}(\textit{trans}[14]\mathrm{diene})]^{2+}$ and *rac*$[\mathrm{Ni}(\textit{cis}[14]\mathrm{diene})]^{2+}$ are described by Warner, Rose and Busch[7,36]. The spectra show three equally intense methyl resonances, indicating that the methyls are pairwise equivalent, *i.e.* that the two six membered chelate rings have equivalent conformation and that the secondary amine centres are configurationally stable towards inversion, thus producing an axial-equatorial distinction between the *gem* methyl groups. Under basic conditions inversion of the nitrogen centres is rapid and the *gem* methyl resonances collapse into a single band at 100°. The methylene resonances can be used to distinguish *cis* and *trans* isomers[7,36]. Rose, Elder and Busch describe the N.M.R. spectrum of tris(2-methyl-2-amino-4-iminopentane)-nickel(II) hexafluorophosphate (C, i) in deutero-acetone[19]. (The N.M.R. spectra of the 1,2-diaminopropane/nickel/acetone condensation products $[\mathrm{Ni}(\mathrm{Me}_2\textit{trans}[14]\text{-}\mathrm{diene})]^{2+}$ are discussed in section C).

(v) X-ray crystallographic studies

The first structural determination of a complex with the diacetone-amine-imine bridge was reported by Hanic and Serator[5] (Fig. 1). The compound was the copper nitrate/acetone/ammonia condensation product, *trans* bis(2-methyl-2 amino-4-imino-pentane)copper(II) nitrate (C, i; D, i). Monoclinic; $P2_1/c$; a = 7.10 ± 0.03 Å, b = 14.63 ± 0.04 Å, c = 9.24 ± 0.02 Å, β = 99°21′; Z = 2).

Structural investigations have been reported on the three isomeric forms of the [Ni([14]diene)] $(ClO_4)_2$ complexes (C, i), confirming the *cis* (4,14-) and *trans* (4,11-) arrangements of the imine groups, and that the interconvertible pair of *trans* isomers are the *meso* and racemic forms associated with restricted inversion about the secondary amine centres (G). Bailey and Maxwell report[37] that crystals of the "A$\alpha(ClO_4)_2$" form described by Curtis, Curtis and Powell[6] are orthorhombic, space group Pbca (a = 19.73 Å, b = 17.01 Å, C = 13.69 Å; Z = 8) and describe in preliminary form the results of a structural investigation confirming the racemic *trans* arrangement. Refined parameters are shown in Fig. 2. Crystals of the isomer "A$\beta(ClO_4)_2$" are monoclinic, with the centrosymmetric space group $P2_1/c$ (a = 9.65 Å, b = 10.76 Å, C = 10.90 Å; β = 99°55′; Z = 2) requiring that the nickel atom be on a centre of symmetry *i.e.* the complex must have the *meso trans* arrangement[37]. Bailey and Maxwell also predicted from stereochemical considerations that the *cis* isomer "$B(ClO_4)_2$" would exist in the racemic form and this was confirmed by Ryan, Kilbourn and Dunitz who give a preliminary report of a structural investigation[72]. (Orthorhombic, space group Pbcn with Ni on the dyad axes; a = 10.60 Å, b = 11.11 Å, c = 19.16Å; Z = 4).



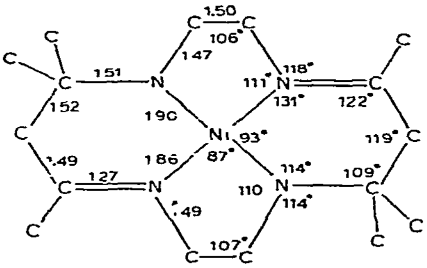


Fig. 1. Dimensions for *trans* bis(2-methyl-2-amino-4-iminopentane)copper(II) nitrate. Centrosymmetric structure, NO_3^- in axial sites, Cu—O = 2.75 Å.

Fig. 2. Dimensions for [Ni(*rac trans*[14]diene)]$(ClO_4)_2$. Dimensions quoted are the averages for the pairs of *chemically* equivalent sites.

The space group has also been determined by Maxwell for the orange cyclic nickel-1,2-diaminopropane-acetone condensation product as the perchlorate salt[12] "orange [Ni(Me_2*trans*[14]diene)] $(ClO_4)_2$". (Monoclinic, $P2_1/c$; a = 11.22 Å, b = 8.44 Å, C = 14.0 Å, β = 99°40′; Z = 2). Again the nickel atom lies on a centre of symmetry, showing that the imino groups are *trans* (*i.e.* the compound is the dimethyl analogue of [Ni(*meso trans*[14]diene)] $(ClO_4)_2$, that the methyl groups of the diaminopropane residues are in *trans* (2,9 or 3,10) arrangements, and that the cation contains one *d* and one *l* diaminopropane residues (Section C).

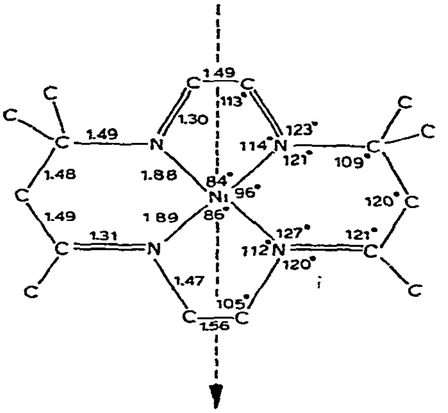
Robinson and Ireland in a preliminary study of [NC(*cis*[14]diene)Co-

Co(*cis*[14]diene)CN] $(ClO_4)_2$ (I, (*iii*)) have determined the space group[73]. (Orthorhombic; Pbca; a = 12.2 Å, b = 21.3 Å, c = 18.5 Å; Z = 4).

Structural determinations of related compounds include:

(a) [Ni(*cis*[14]tetene)] $(ClO_4)_2$ (α modification) (H, iii) by Maxwell and Bailey, reported in preliminary form[74]. The structure confirms the 4,8,10,14-tetraimine arrangement. Refined parameters are shown in Fig. 3.

[Ni(*cis*[14]diene)] $(ClO_4)_2$, [Ni(*cis*[14]tetene)] $(ClO_4)_2$ and [Ni(*cis*[14]triene)]-$(ClO_4)_2$ are isostructural (the triene derivative from powder diffraction data)[9].



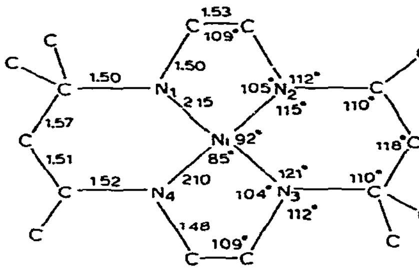


Fig. 3. Dimensions for α[Ni(*cis*[14]tetene)] $(ClO_4)_2$.

Fig. 4. Dimensions for [Ni(C *rac* N *meso* N *meso trans*[14]tetramine)CH_3COO] ClO_4. Chelate acetate group dimensions: Ni—O = 2.12 Å, O—C = 1.26 Å, $\widehat{ONiO}$ = 62°, $\widehat{OCO}$ = 120°, $\widehat{NiOC}$ = 89°. Dimensions quoted are the averages for the pairs of *chemically* equivalent sites. N_2 and N_4 are in the same (approximate) plane as the acetate oxygen atoms. The macrocycle is folded along N_1NiN_3, with N_2, N_4 and the two acetate oxygen atoms approximately in a plane. N_1NiN_3 = 175°, N_2NiN_4 = 103°.

(b) [Ni(tet *b*) (CH_3COO)] (ClO_4), (H, ii) by Whimp and Bailey. The structure indicates that (tet *b*) is the (C *rac trans*[14] tetramine), with both pairs of asymmetric nitrogen centres *meso* and that the acetate ion is functioning as a chelate[75]. Refined parameters are shown in Fig. 4.

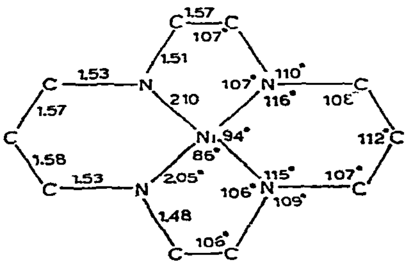


Fig. 5. Dimensions for Ni(cyclam)Cl_2. Centrosymmetric structure, Cl^- in axial sites, Ni—Cl = 2.49 Å.

(c) Ni(cyclam)Cl_2 by Bosnich, Mason, Pauling, Robertson and Tobe[76] (Fig. 5).

The space group has also been determined for Cu(tet *a*)I_2 (violet modification) by Maxwell. This requires that the copper ion lie on a centre of symmetry *i.e.* that the complex contains a (C *meso* N *meso* N *meso* *trans*[14]tetramine)[12]. The space group of Co(tet *b*) (C_2O_4) (ClO_4), determined by Whimp, confirms the C racemic *trans* configuration of (tet *b*) (H, ii)[75].

For comparison, details of completed relevant structures are shown (Figs. 1–5). The additional strain in the 1,4,8,11-tetra-azacyclotetradecadiene ring system through the linking of the separate chelate groups appears to be minimal. Thus five membered diaminoethane chelate rings have very similar bond angles to those observed for simple nickel(II) diaminoethane complexes and the six membered chelate ring system has very similar angles to those observed for the bis(diacetone-amine-imine)copper(II) complex (Fig. 1). Ring strain in the five membered chelate rings causes a slight contraction of the central (N-Ni-N) bond angle from the optimum 90° and a slight expansion in the six membered chelate ring system. The strain in the six membered ring system also results in considerable distortion about the central methylene group, this bond angle being near 120°. Reduction to form the cyclic tetramine causes changes in the bond angles about the "ex-imino" groups. Two tetramine structures have been reported, *trans* Ni(cyclam)Cl_2 and *cis*[Ni(tet *b*)CH_3COO]ClO_4. The bond lengths and angles within the macrocycle are similar for the planar cyclam derivative and the folded (tet *b*) derivatives, although the angle at the central methylene of the six membered chelate ring is larger for (tet *b*) than for cyclam suggesting that the ring strain may be greater for the folded arrangement, explaining why only *trans* derivatives of cyclam have been prepared. With the ([14]tetramines) the interactions of the six methyl substituents alter the relative stability of the two arrangements, the more symmetrical C *meso* isomer (tet *a*) forming only *trans* derivatives, while (tet *b*) (C racemic), which is asymmetric about the molecular plane, forms *trans* derivatives with monodentate ligands and *cis* derivatives with chelates. For [Ni(tet *b*)CH_3COO]ClO_4 the macrocycle has folded with the more crowded side outward, *i.e.* with the *gem* dimethyl groups pointing towards the chelate acetate group. In view of the structure of this compound, it seems probable that the *cis* derivatives {[Ni(*rac trans*[14]diene)]$_2$-C_2O_4} $(ClO_4)_2$ and [Co(*trans*[14]diene)CO_3]ClO_4 have the macrocycle similarly folded.

The Ni-N (and Cu-N) bond lengths are slightly, (but significantly) shorter for the imino nitrogens than for the amino nitrogens. This small difference is most probably a consequence of the change from tetrahedral to trigonal arrangement about the nitrogen atom producing a decrease in repulsion, together with a change in orbital hybridisation, and does not imply any significant degree of π bonding between metal ion d orbitals and the imino π orbitals. The Ni-N bond lengths are appreciably longer for the TGS octahedral complexes than for the SGS square planar complexes.

K. POSTCRIPT

There are a number of amine-imine macrocyclic complexes which are similar to those described in this review, but which are outside its field. These include the series of complexes discovered by Curry and Busch, formed by reaction of 2,6-diacetyl pyridine with various polyamines in the presence of metal ions[77]. The nickel(II) complex formed with dipropylenetriamine which has a tetra-aza macrocycle with one secondary amino, one pyridine nitrogen and two imino donor groups, can be reduced to form the cyclic tetramine complex. Others include complexes of the cyclic tetramer of *o*-amino benzaldehyde, XXVII, and the nickel(II) complex reported by Jager[78].

The complexes of the tetra-aza macrocycles described in this review, formed by reactions between metal-amine complexes and aliphatic carbonyl compounds, are related to complexes of biological significance such as the porphyrins and corrins (and more distantly to a wider group of metal-ion macrocyclic derivatives such as the phthalocyanines)[21,29]. There are two major features distinguishing the complexes described from these other classes of macrocyclic complexes: the absence of conjugation involving the donor atom, and the absence of fused ring systems. The complexes can serve as models for the biological system to the extent that their properties are characteristic of metal ions coordinated to tetra-aza macrocycles, but the greater flexibility of the macrocycles and the inability to transmit electronic effects through the ligand because of the absence of conjugation limit their usefulness in this regard.

The condensation reaction provides series of compounds in which macrocycle size, degree of unsaturation, and ring substituents can be varied, and the effects on the properties of the complexes studied. The macrocycle-metal-ion moiety is non-labile, simplifying studies of the reactivity at additional coordination sites. The compounds illustrate the importance of stereochemical considerations in determining the properties of complexes of macrocycles, for example the ability of the macrocycle to buckle to accommodate a chelate depends on the configuration about coordinated secondary amine centres.

The most useful feature of the metal-amine carbonyl condensation is the facility with which a variety of macrocyclic complexes can be prepared. The condensation is an interesting example of the reaction of coordinated ligands, and of the steric control of an organic reaction by a coordination centre.

ACKNOWLEDGMENTS

The author gratefully acknowledges all prepublication information, and the assistance of Y. M. Curtis in the preparation of the manuscript.

REFERENCES

1 N. F. CURTIS, *J. Chem. Soc.*, (1960) 4409.
2 E. HOYER, *Naturwiss.*, 46 (1959) 14.
3 N. F. CURTIS AND D. A. HOUSE, *Chem. and Ind.*, (1961) 1708.
4 M. M. BLIGHT AND N. F. CURTIS, *J. Chem. Soc.*, (1962) 3016.
5 F. HANIC AND M. SERATOR, *Chem. Zvesti.*, 18 (1964) 572.
6 N. F. CURTIS, Y. M. CURTIS AND H. K. J. POWELL, *J. Chem. Soc. A*, (1966) 1015.
7 L. G. WARNER, N. J. ROSE AND D. H. BUSCH, *Abstracts, 152nd National Meeting of the American Chemical Society, N.Y.*, 1966.
8 W. JEHN, *Z. Anorg. Chem.*, 351 (1967) 260.
9 N. F. CURTIS, unpublished results.
9a T. E. MACDERMOTT AND D. H. BUSCH, *J. Am. Chem. Soc.*, *89* (1967) 5780.
10 M. M. BLIGHT AND N. F. CURTIS, *J. Chem. Soc.*, (1962) 1204.
11 N. F. CURTIS, *A.N.Z.A.A.S. Conference*, Christchurch, 1968.
12 I. E. MAXWELL, private communication.
13 N. F. CURTIS, *Chem. Commun.*, (1966) 882.
14 D. A. HOUSE AND N. F. CURTIS, *J. Am. Chem. Soc.*, 86 (1964) 223.
15 D. A. HOUSE AND N. F. CURTIS, *J. Am. Chem. Soc.*, 84 (1962) 3248.
16 N. F. CURTIS AND D. A. HOUSE, *J. Chem. Soc.*, (1965) 5502.
17 N. F. CURTIS AND D. A. HOUSE, *J. Chem. Soc. A*, (1967) 537.
18 W. JEHN, *Z. Chem.*, 4 (1964) 307.
19 N. J. ROSE, M. S. ELDER AND D. H. BUSCH, *Inorg. Chem.*, 6 (1967) 1924.
20 F. I. URBACH AND D. H. BUSCH, page 176 of ref. 21.
21 D. H. BUSCH, *Helv. Chim. Acta., Fasciculus Extraordinarius* ALFRED WERNER, (1967) 174.
22 M. M. BLIGHT, thesis, university of Wellington, 1959.
23 D. A. HOUSE AND N. F. CURTIS, *J. Am. Chem. Soc.*, 86 (1964) 1331.
24 V. C. PATEL AND N. F. CURTIS, *J. Chem. Soc.*, to be published.
25 N. SADASIVAN AND J. F. ENDICOTT, *J. Am. Chem. Soc.*, 88 (1966) 5468.
26 D. J. GALLOP, thesis, university of Wellington, 1962.
27 (a) E. H. CORDES AND W. P. JENCKS, *J. Am. Chem. Soc.*, 84 (1962) 832.
(b) T. C. BRUCE AND S. BENKOVIC, *Bioorganic Mechanisms*, Vol. II, p. 227 et. seq., Benjamin, New York, 1966.
28 H. K. J. POWELL, thesis, university of Wellington, 1961.
29 D. H. BUSCH, *Record of Chemical Progress*, 25 (1964) 107.
30 M. HAUSER, *Chem. Rev.*, 63 (1963) 311.
31 N. J. LEONARD AND J. V. PAUTSKELIS, *J. Org. Chem.*, 28 (1963) 3021.
32 N. F. CURTIS AND R. W. HAY, *Chem. Commun.*, (1966) 524.
33 L. K. MUSHKALO AND Z. I. SHOKOL, *Zhur. Obschchei. Khim.*, 30 (1960) 1023, *Chem. Abstr.*, 55 (1961) 563.
34 J. L. LOVE AND H. K. J. POWELL, *Chem. Commun.*, To be published.
35 J. L. LOVE AND H. K. J. POWELL, *Inorg. Nucl. Chem. Letters*, 3 (1967) 113.
36 L. G. WARNER, N. J. ROSE AND D. H. BUSCH, *J. Am. Chem. Soc.*, 89 (1967) 703.
37 M. F. BAILEY AND I. E. MAXWELL, *Chem. Commun.*, (1966) 908.
38 D. A. BUCKINGHAM, L. G. MARZILLI AND A. M. SARGESON, *J. Am. Chem. Soc.*, 89 (1967) 825, and references therein; D. A. BUCKINGHAM, P. A. MARZILLI AND A. M. SARGESON, *Inorg. Chem.*, 6 (1967) 1032; H. G. HAMILTON AND M. D. ALEXANDER, *J. Am. Chem. Soc.*, 89 (1967) 5065.
39 N. SADASIVAN, J. A. KERNOHAN AND J. F. ENDICOTT, *Inorg. Chem.*, 6 (1967) 770.
40 N. H. CROMWELL, *Chem. Rev.*, 38 (1946) 83.
41 N. F. CURTIS, *J. Chem. Soc.*, (1964) 2644.
42 N. F. CURTIS, *J. Chem. Soc. C*, (1967) 1979.
43 N. F. CURTIS, *J. Chem. Soc.*, (1965) 924.
44 G. J. GORDON, thesis, university of Wellington, 1964.
45 H. STETTER AND K. H. MAYER, *Chem. Ber.*, 94 (1961) 1410.

46 B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 4 (1965) 1102.
47 P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A*, (1966) 867.
48 P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A*, (1966) 1827.
49 G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, 86 (1964) 4834.
50 N. F. Curtis and D. F. Cook, *Chem. Commun.*, (1967) 962.
51 Y. M. Curtis and N. F. Curtis, *Australian J. Chem.*, 18 (1965) 1933.
52 G. R. Burns, thesis, university of Wellington, 1961.
53 B. Bosnich, M. L. Tobe and G. A. Webb, *Inorg. Chem.*, 4 (1965) 1109.
54 N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 4 (1965) 804.
55 N. F. Curtis and Y. M. Curtis, *Australian J. Chem.*, 19 (1966) 1423.
56 Y. M. Curtis and N. F. Curtis, *Australian J. Chem.*, 19 (1966) 609.
57 N. F. Curtis, *J. Chem. Soc.*, (1963) 4109.
58 R. McKormick and T. N. Waters, private communication.
59 W. Jehn, *Z. Chem.*, 7 (1967) 279.
60 H. K. J. Powell, private communication.
61 N. F. Curtis and Y. M. Curtis, *J. Chem. Soc. A*, (1966) 1653.
62 F. Basolo, Y. T. Chen and R. K. Murmann, *J. Am. Chem. Soc.*, 76 (1954) 956.
63 B. Bosnich, R. D. Gillard, E. D. McKenzie and G. A. Webb, *J. Chem. Soc. A*, (1966) 1331.
64 N. F. Curtis and D. A. House, *J. Chem. Soc.*, (1965) 6194.
65 D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 6 (1967) 1092.
66 R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4 (1965) 709.
67 J. P. Collman and P. W. Schneider, *Inorg. Chem.*, 5 (1966) 1380.
68 A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6 (1967) 787.
69 H. G. Hamilton and M. D. Alexander, *Inorg. Chem.* 5 (1966) 2060.
70 J. F. Endicott, private communication.
71 S. P. Pavkovic and D. W. Meek, *Inorg. Chem.*, 4 (1965) 20.
72 R. R. Ryan, B. T. Kilbourn and J. D. Dunitz, *Chem. Commun.*, (1966) 910.
73 W. T. Robinson and P. R. Ireland, private communication.
74 I. E. Maxwell and M. F. Bailey, *Chem. Commun.*, (1966) 883.
75 P. O. Whimp, thesis, university of Wellington, 1967.
76 B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson and M. L. Tobe, *Chem. Commun.*, (1965) 97.
77 Ref. 21, page 179 for references.
78 E. G. Jäger, *Z. Chem.*, 4 (1964) 437.