# Some Metal-ion Complexes with Ligands Formed by Reaction of Amines with Aliphatic Carbonyl Compounds. Part I. Nickel(II) and Copper(II) Complexes Formed by the Diaminoethane–Acetone Reaction

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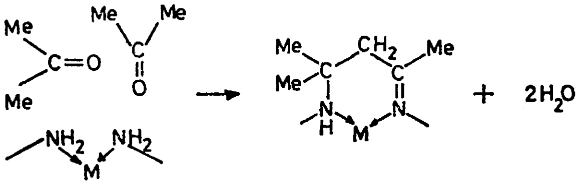
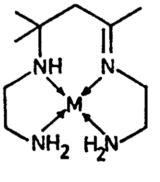
Reaction of acetone with bis(diaminoethane)nickel(II) yields the bis-complex of the β-amino-ketone $NH_2CH_2CH_2NHC(CH_3)_2CH_2COCH_3$, which acts as a tridentate ligand. With bis(diaminoethane)copper(II), the complex of the linear pentadentate ligand $NH_2CH_2CH_2NHC(CH_3)_2CH_2C(CH_3){:}NCH_2CH_2NHC(CH_3)_2CH_2COCH_3$ is formed. Observations on the reaction between the tris(diaminoethane) complexes and acetone, which yield isomeric macrocyclic complexes, and on the reaction between diaminoethane and acetone are reported.

A NUMBER of examples have been reported of a reaction in which a metal–amine complex reacts with an aliphatic carbonyl compound to form a complex in which two amine residues are linked by a three carbon bridge, with imino and secondary amino donor groups.[1-12] With acetone as the carbonyl compound, the reaction can be schematically represented as in Scheme A, the bridging moiety being 2-amino-4-imino-2-methyl-pentane, derived from two acetone molecules. Studies of the course of this reaction with diaminoethane as the amine, acetone as the carbonyl compound and nickel(II) and copper(II) as the metal ions are now reported, and some new compounds isolated from the system are described. In subsequent papers, similar studies with 1,2- and 1,3-diaminopropane and with other carbonyl compounds will be described.

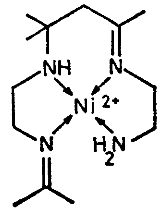


SCHEME A

*Bis(diaminoethane)nickel*(II)*–Acetone Reaction*.—A reaction between bis(diaminoethane)nickel(II) perchlorate and acetone at 110° has been reported.[1] The products, initially formulated as *N*-isopropylidene imino-derivatives are the singlet ground state, square planar complex cations $[Ni(\mathbf{1})]^{2+}$ and $[Ni(\mathbf{2})]^{2+}$, of linear tetradentate ligands formed from two diamino-residues linked by the amine–imine bridging group. The complex $[Ni(\mathbf{2})]^{2+}$ with an additional *N*-isopropylidene group appears to be the initial product, as the yield of $[Ni(\mathbf{2})]^{2+}$ decreases, and that of $[Ni(\mathbf{1})]^{2+}$ increases as the reaction is continued. A preparation of $[Ni(\mathbf{2})]^{2+}$ by reaction of bis(diaminoethane)bis(pyridine)nickel(II) perchlorate with acetone under reflux conditions was later reported.[2] $[Ni(\mathbf{1})]ZnCl_4$ Is formed by reaction of tris(diaminoethane)nickel(II) chloride with acetone in the presence of zinc chloride at 110°.[9]



$[M(\mathbf{1})]^{2+}$



$[Ni(\mathbf{2})]^{2+}$

A solution in acetone of bis(diaminoethane)nickel(II), or the di-aquo or bis(methyl cyanide) adducts, with an anion such as perchlorate † reacts at room temperature over a period of *ca.* 1 day to yield a blue-violet, triplet ground state complex, $[Ni(\mathbf{3})](ClO_4)_2$.

Analysis indicates the composition $[C_{16}H_{36}N_4NiO_2](ClO_4)_2$, *i.e.* with two diamine and four acetone residues condensed by elimination of two molecules of water. The compound is stable to water, but rapidly hydrolysed by dilute mineral acid, and from the hydrolysed solution mesityl oxide was isolated, indicating the presence of the $C_6$ bridging moiety. In pyridine, $[Ni(\mathbf{3})]^{2+}$ is rapidly converted to the macrocyclic complex $[Ni(\mathbf{4})]^{2+}$,[13] with elimination of two moles of water. The i.r. spectrum of $[Ni(\mathbf{3})](ClO_4)_2$ shows bands assigned to co-ordinated primary amino groups [ν($NH_2$): 3342, 3293m, sp; δ($NH_2$): 1593m cm$^{-1}$], and co-ordinated secondary amino-groups [ν(NH): 3197 cm$^{-1}$] *cf.* $[Ni(\mathbf{1})](ClO_4)_2$; ν($NH_2$): 3313, 3260m,sp; δ($NH_2$): 1590m; ν(NH): 3197 cm$^{-1}$. The lower frequencies for this compound result from the change from triplet to singlet ground

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† Salts with other anions which confer solubility in acetone, such as tetrafluoroborate or hexafluorophosphate react similarly, and can generally be used instead of the perchlorate for the reactions described in this paper.

[1] N. F. Curtis, *J. Chem. Soc.*, 1960, 4409.

[2] M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 1204.

[3] M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 3016.

[4] D. A. House and N. F. Curtis, *Chem. and Ind.*, 1961, 1708; *J. Amer. Chem. Soc.*, 1962, **84**, 3248; 1964, **86**, 1331.

[5] D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1964, **86**, 233.

[6] N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc.* (*A*), 1966, 1015.

[7] N. F. Curtis and D. A. House, *J. Chem. Soc.* (*A*), 1967, 537.

[8] V. C. Patel and N. F. Curtis, *J. Chem. Soc.* (*A*), 1968, 1265; 1969, 1607.

[9] T. E. McDermott and D. H. Busch, *J. Amer. Chem. Soc.*, 1967, **89**, 5780.

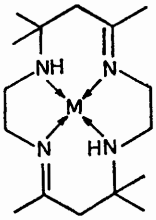
[10] F. I. Urbach and D. H. Busch, p. 21 of D. A. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius Alfred Werner*, 1967, 174.

[11] F. Hanic and M. Serator, *Chem. Zvesti*, 1964, **18**, 572; W. Jehn, *Z. Chem.*, 1964, 307; *Z. anorg. Chem.*, 1967, **351**, 260; N. J. Rose, M. S. Elder, and D. H. Busch, *Inorg. Chem.*, 1967, **6**, 1924; D. E. Goldberg, *J. Chem. Soc.* (*A*), 1968, 2671.

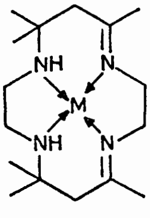
[12] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

[13] M. F. Bailey and I. E. Maxwell, *Chem. Comm.*, 1966, 908; *J.C.S. Dalton*, 1972, 938.

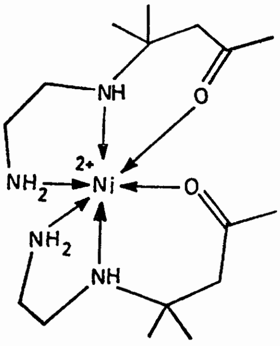
state. Strong bands present for [Ni(**3**)]($ClO_4$)$_2$ at 1690 and 1682 cm$^{-1}$ are more intense, and at a higher frequency than usual for co-ordinated imino groups, *cf.* [Ni(**2**)]($ClO_4$)$_2$; ν(C:N): 1660 cm$^{-1}$, and are assigned as ν(C:O) of co-ordinated keto groups.



[M(4)]$^{2+}$

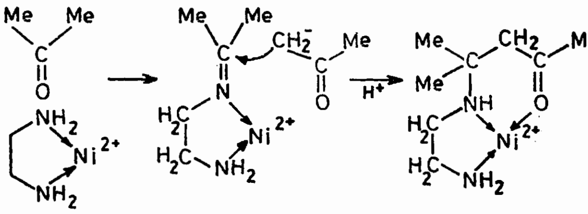


([M(5)]$^{2+}$



[Ni(3)]$^{2+}$

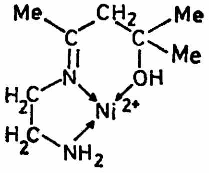
These observations are consistent with the formulation of [Ni(**3**)]$^{2+}$ as the bis-complex of the tridentate β-amino-ketone $NH_2CH_2CH_2NHC(CH_3)_2CH_2COCH_3$. This is considered to be formed by an aldol type reaction between an *N*-isopropylidene imino group and an acetone molecule, as in Scheme B. The β-amino-ketone is stabilized by co-ordination of the keto-group with formation of a six-membered chelate ring. The alternative possible aldol type reaction would lead to an isomeric β-imino-alcohol complex, [Ni(**6**)]$^{2+}$, which could also be stabilized by co-ordination of the hydroxy group.* However, this structure is in poor accord with the observed i.r. spectrum, and there is no mechanism which would explain the easy conversion to [Ni(**4**)]$^{2+}$.



Scheme B

The *d–d* spectrum of [Ni(**3**)]$^{2+}$ in methanol shows three bands at 10,500 (ε 16), 17,400 (ε 12), and 29,400 (ε 50) cm$^{-1}$. The three band spectrum for the $NiN_4O_2$ chromophore suggests a *cis*-arrangement of the oxygen atoms, but co-ordination could be meridional or one of the two facial forms. The observed resistance to intramolecular imine formation yielding the macrocycle Ni(**4**) (below) is most readily understood for the facial form represented in the formula, which places the reacting amine and keto-group *trans*.

[Ni(**3**)]$ClO_4$)$_2$ dissolves in pyridine to form a blue solution which turns yellow over a period of minutes at room temperature, as [Ni(**4**)]$^{2+}$ is formed. The reaction does not appear to be exclusively intramolecular since (*a*) when [Ni(**3**)]($ClO_4$)$_2$ and its 1,2-diaminopropane analogue were dissolved in pyridine, an appreciable amount of the 'mixed diamine' macrocycle[7] was formed, and (*b*) in the presence of $Cu^{2+}$, some [Cu(**4**)]$^{2+}$ was formed.



[Ni(6)]$^{2+}$

*Tris(diaminoethane)nickel*(II)*–Acetone Reaction.*—A solution in acetone of tris(diaminoethane)nickel(II) perchlorate at room temperature forms the macrocycle complexes [Ni(**4**)]$^{2+}$ and [Ni(**5**)]$^{2+}$ [15] over a period of days.[6] The yield of [Ni(**5**)]$^{2+}$ is *ca.* 25% at 25°, but drops to zero at *ca.* 50°, indicating that the two products are formed by distinct mechanisms.

A freshly prepared solution of [Ni(en)$_3$]($ClO_4$)$_2$,0·5$H_2O$ in acetone is mauve, but within minutes the colour starts changing to brown. The spectrum shows the growth of a band near 23,000 cm$^{-1}$ typical of singlet ground state $NiN_4$ species, such as [Ni(**1**)]$^{2+}$ or [Ni(**4**)]$^{2+}$. The colour change is initially reversed by the addition of water, indicating that the species present are readily hydrolysed *N*-isopropylidene imino complexes. [From tris(1,3-diaminopropane)nickel(II) and acetone the bis(*N*-isopropylidene-diamine) complex crystallizes at this stage].[5] Within hours, singlet ground state species which are stable to water, but decomposed by dilute mineral acid appear in the solution and the complex [Ni(**2**)]$^{2+}$ can be isolated from the solution, the yield reaching a maximum of *ca.* 25% after *ca.* 1 day. By this time the acid resistant macrocyclic complexes [Ni(**4**)]$^{2+}$ and [Ni(**5**)]$^{2+}$ are present in the solution, and grow in amount over a period of days, the concentrations of other species, including the [Ni(**2**)]$^{2+}$ decreasing.

A solution of [Ni(**2**)]$^{2+}$ in acetone in the presence of diaminoethane, conveniently as the adduct [Ni(**2**)(en)]($ClO_4$)$_3$, is slowly converted at room temperature to [Ni(**5**)]$^{2+}$; [Ni(**1**)]$^{2+}$ behaves similarly. It is therefore

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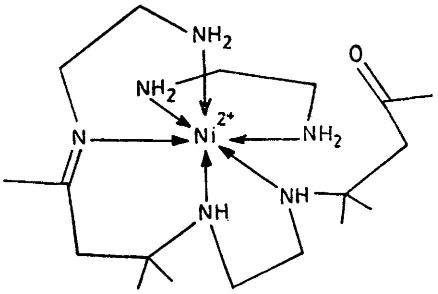
* Related α-imino-alcohol complexes have been reported.[14]

[14] T. E. McDermott, B. E. Sewall, and D. H. Busch, *J. Amer. Chem. Soc.*, 1967, **89**, 5784.

[15] B. T. Kilbourn, R. R. Ryan, and J. D. Dunitz, *Chem. Comm.*, 1966, 910; *J. Chem. Soc.* (*A*), 1969, 2407.

reasonable to conclude that the $[Ni(\mathbf{2})]^{2+}$ observed in the reacting solution of $[Ni(en)_3]^{2+}$ in the early stages, in about the same amount as the final yield of $[Ni(\mathbf{5})]^{2+}$, is the precursor of the $[Ni(\mathbf{5})]^{2+}$. The presence of the chelate diaminoethane is essential for this reaction, other bases, such as pyridine being ineffective. A solution of bis(diaminoethane)bis(pyridine)nickel(II) perchlorate in acetone proceeds *via* the β-amino ketone complex $[Ni(\mathbf{3})]^{2+}$ to $[Ni(\mathbf{2})]^{2+}$, but reaction ceases at this stage.

Co-ordination of diaminoethane to $[Ni(\mathbf{2})]^{2+}$ would force the ligand (**2**) into folded co-ordination, which must be sterically significant. An aldol reaction of $[Ni(\mathbf{2})(en)]^{2+}$ would produce the β-amino ketone complex $[Ni(\mathbf{7})(en)]^{2+}$, which could then undergo intramolecular imine formation to yield $[Ni(\mathbf{5})]^{2+}$. The presence of the nickel(II) in the labile triplet ground state as the octahedral diaminoethane adduct probably facilitates this reaction, which requires the temporary detachment of the amino group from the nickel, a process which may be difficult for singlet ground state nickel(II) species.



$[Ni(\mathbf{7})(en)]^{2+}$

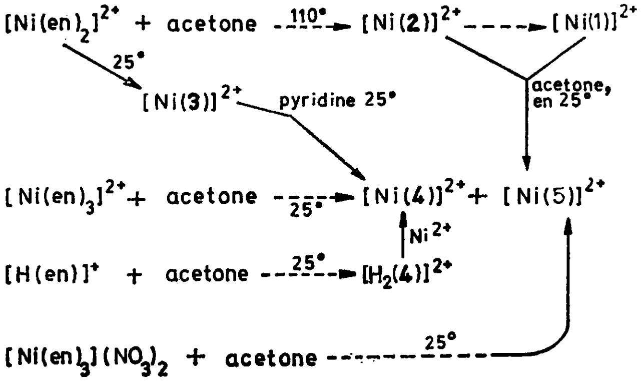
When tris(diaminoethane)nickel(II) nitrate hydrate was allowed to stand under acetone at room temperature, the sparingly soluble salt dissolved over a period of months while the salt $[Ni(\mathbf{5})](NO_3)_2$ crystallized. It is considered that the functioning of the nitrate ion as a bidentate ligand[16] in the low polarity solvent must control the course of the reaction, since the chloride salt, of comparable solubility, yielded exclusively $[Ni(\mathbf{4})]Cl_2$ under these conditions.

The complex cation $[Ni(\mathbf{5})]^{2+}$ can thus be prepared free of $[Ni(\mathbf{4})]^{2+}$ by reaction of $[Ni(en)_3](NO_3)_2$ with acetone, while $[Ni(\mathbf{4})]^{2+}$, free of $[Ni(\mathbf{5})]^{2+}$ can be prepared *via* the ligand,[17] or from the β-amino-ketone complex $[Ni(\mathbf{3})](ClO_4)_2$, avoiding the need for the separation by fractional crystallization of the mixed products formed by reaction of $[Ni(en)_3](ClO_4)_2$ with acetone.[6]

The reactions of the nickel(II)–diaminoethane–acetone system are summarized in Scheme C.

*Bis(diaminoethane)copper*(II)–*Acetone Reaction.*—The reaction between bis(diaminoethane)copper(II) perchlorate and acetone at 110° to yield initially the complex of the linear tetradentate ligand $[Cu(\mathbf{1})]^{2+}$, and finally the macrocyclic complex $[Cu(\mathbf{4})]^{2+}$ has been reported.[3]

A solution of bis(diaminoethane)copper(II) perchlorate (or fluoroborate, *etc.*) in acetone at room temperature slowly changes colour from magenta to blue, and after *ca.* 24 h a blue complex $[Cu(\mathbf{8})](ClO)_2$ was isolated. The same product was isolated after *ca.* 30 min under reflux. Analysis indicates the composition $[C_{16}H_{34}CuN_4O](ClO_4)_2$, *i.e.* one mole of water less than $[Ni(\mathbf{3})]^{2+}$, one more than $[Cu(\mathbf{4})]^{2+}$. $[Cu(\mathbf{8})]^{2+}$ Is stable in water, hydrolysed by dilute mineral acid, mesityl oxide being formed. $[Cu(\mathbf{8})]^{2+}$ is converted slowly in boiling water, more rapidly in aqueous ammonia, and rapidly in pyridine into the macrocyclic complex $[Cu(\mathbf{4})]^{2+}$.



Scheme C

The i.r. spectrum of $[Cu(\mathbf{8})](ClO_4)_2$ shows bands assignable to ν($NH_2$): 3348, 3277m,sp; ν(NH): 3230m,sp; but the intensity of the ν(NH) band is enhanced relative to that of the ν($NH_2$) bands compared to $[Ni(\mathbf{3})]^{2+}$; ν(C:O): 1692s; ν(C:N): 1667; δ($NH_2$): 1597 cm$^{-1}$. The copper(II) *d–d* spectrum in methanol shows a broad band at 15,200 cm$^{-1}$ (ε 127). This band is displaced to lower frequency compared with that for $[Cu(\mathbf{1})]^{2+}$ at 23,000 cm$^{-1}$ and $[Cu(en)_2]^{2+}$ at 18,200 cm$^{-1}$. A displacement to lower frequency in these circumstances is often an indication of tetragonal co-ordination geometry.[8,18]

These observations are compatible with the formulation of $[Cu(\mathbf{8})]^{2+}$ shown, with a linear pentadentate ligand. This could be formed similarly to $[Ni(\mathbf{3})]^{2+}$, above, except that for Cu$^{II}$ the preferred arrangement would place the weaker carbonyl donor groups in *trans*-sites, facilitating one intramolecular imine formation to form $[Cu(\mathbf{8})]^{2+}$. The interaction with the keto-group in the remaining tetragonal site is sufficient to stabilize the structure, although in the presence of ammonia, or pyridine, which could displace the keto-donor group, cyclization occurs rapidly, by an intramolecular mechanism. When the reaction was performed in the presence of nickel ions, no $[Ni(\mathbf{4})]^{2+}$ was formed, *cf.* the equivalent reaction with $[Ni(\mathbf{3})]^{2+}$ and Cu$^{2+}$, above.

When equimolar amounts of $[Cu(\mathbf{8})]^{2+}$ and $[Cu(en)_2]^{2+}$ were dissolved in pyridine, or in methanol with a trace of diaminoethane as catalyst, rapid reaction to form $[Cu(\mathbf{1})]^{2+}$ occurred, providing a convenient method for the preparation of this compound, and providing an

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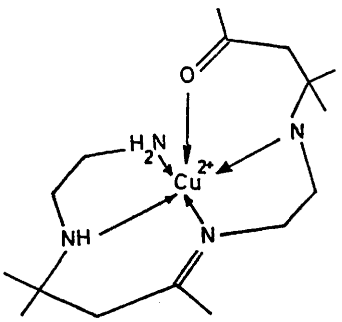
[16] N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, **4**, 804.

[17] N. F. Curtis and R. W. Hay, *Chem. Comm.*, 1966, 524; N. Sadisivan and J. F. Endicott, *J. Amer. Chem. Soc.*, 1966, **88**, 5468.

[18] I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc.* (*A*), 1968, 1678.

indication of a probable mechanism by which the $[Cu(\mathbf{1})]^{2+}$ is formed at higher temperatures.[3]

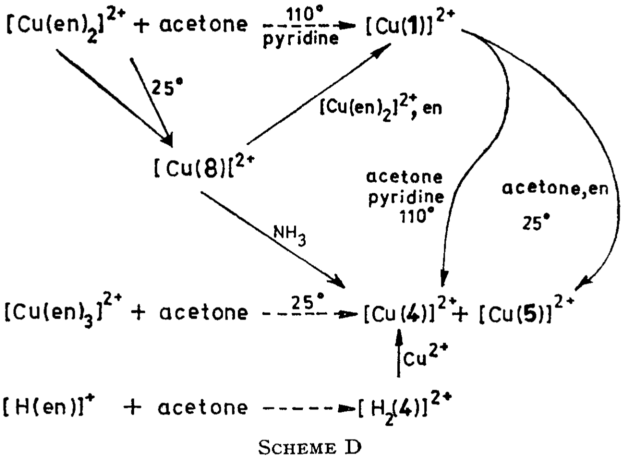


$[Cu(\mathbf{8})]^{2+}$

*Tris(diaminoethane)copper*(II)*-Acetone Reaction*.—A solution of tris(diaminoethane)copper(II) perchlorate in acetone (conveniently prepared by the addition of 1 mole of diaminoethane to a solution of the bis complex) reacted over a period of days at room temperature to yield a mixture of the isomeric macrocyclic complexes $[Cu(\mathbf{4})]^{2+}$ (*ca.* 75%) and $[Cu(\mathbf{5})]^{2+}$ (*ca.* 25%), the less soluble salt $[Cu(\mathbf{5})](ClO_4)_2$ crystallizing first, as for the equivalent reaction with nickel.[6] An indirect preparation of $[Cu(\mathbf{5})]^{2+}$ from $[Ni(\mathbf{5})]^{2+}$ has been reported by Love and Powell.[19] As with the nickel(II) analogue, $[Cu(\mathbf{1})](ClO_4)_2$ in acetone plus 1 mole of diaminoethane is converted slowly at room temperature to $[Cu(\mathbf{5})]^{2+}$.

The reactions of the copper(II)–diaminoethane–acetone system are summarized in Scheme D.

*Diaminoethane–Acetone Reaction*.—In view of the observations that the macrocyclic ligand(**4**), as $[H_2(\mathbf{4})]X_2$, $X = ClO_4^-$, $Br^-$, $NCS^-$, *etc.*, is formed by reaction of $[H(en)]X$ with acetone, diacetone alcohol, or mesityl oxide,[14] it is of interest to know how important the role of the metal ion is in the reaction of the diaminoethane complexes with acetone.



SCHEME D

A solution of diaminoethane in acetone slowly becomes yellow over a period of weeks at room temperature. Solutions of copper perchlorate were added to aliquots of the diaminoethane–acetone solution after varying times ($Cu^{2+}$ : en in 1 : 2 molar proportions), and the main products isolated. For the first three days, $[Cu(en)_2](ClO_4)_2$ was isolated, suggesting that the majority of the diaminoethane was present as readily hydrolysed *N*-isopropylidene imines. After *ca.* 7 days (and for months thereafter), $[Cu(\mathbf{8})](ClO_4)_2$ was isolated, suggesting that the diaminoethane was present as the β-amino-ketone. The fact that the usually rapid-base catalysed polymerization of the acetone is retarded suggests that the β-amino-ketone is stabilized, either as the diazepine by intramolecular imine formation, or as the dimer(**4**). For the period between 3 and 7 days, the main product was $[Cu(\mathbf{1})](ClO_4)_2$, showing the presence of diaminoethane imines and the β-amino-ketone, since $[Cu(en)_2]^{2+}$ and $[Cu(\mathbf{8})]^{2+}$ react together to form $[Cu(\mathbf{1})]^{2+}$, above. The same sequence of reactions occurs in a solution of diaminoethane in acetone under reflux, conversion to the β-amino-ketone taking *ca.* 8 h. Addition of nickel perchlorate to the acetone–diaminoethane solution gave less clear cut results, the immediate result being the formation of a gelatinous precipitate, with crystals of $[Ni(\mathbf{4})](ClO_4)_2$ forming slowly.

Thus, it appears that the metal-ion does not have any critical stereochemical role in these reactions generating the β-amino-ketone, or the macrocycle(**4**). The metal ions catalyse the aldol reaction forming the β-amino-ketone, reaction for the complexes being *ca.* ten times faster than for the free diaminoethane. The macrocycle(**5**) has been formed only during the reaction of the tris(diaminoethane) complexes with acetone, and this remains as a metal-ion ' template reaction.'[20]

## EXPERIMENTAL

*Bis(7-amino-4,4-dimethyl-5-azaheptan-2-one)nickel*(II) *Perchlorate*, $[Ni(\mathbf{3})](ClO_4)_2$.—Bisaquobis(diaminoethane)nickel(II) perchlorate, or bis(diaminoethane)nickel(II) perchlorate (formed by desiccation of the bisaquo-complex), or bis(methyl cyanide)bis(diaminoethane)nickel(II) perchlorate, was dissolved in acetone (10 g in 50 ml) and the solution left at room temperature for 3 days. The acetone was removed using a rotary evaporator, and the residue twice recrystallized from hot ethanol as fine light blue feathery *crystals*. The compound is stable in a desiccator or closed container, but on prolonged exposure to the atmosphere there is superficial conversion to $[Ni(\mathbf{4})](ClO_4)_2$. (Found: C, 33·3; H, 6·6; Ni, 10·1. $C_{16}H_{36}ClN_4NiO_{10}$ requires C, 33·5; H, 6·3; Ni, 10·2%). Magnetic susceptibility: $10^3\chi_g$ (294·4 K) = 3·97 c.g.s.u.; $\mu_{eff}$ = 3·08 B.M., corrected for diamagnetism and T.I.P. (8 $kN\beta^2/\Delta$, where $\Delta$ = 10,700 $cm^{-1}$). The fluoroborate salt was prepared similarly. The most convenient starting material was the bis(methyl cyanide) derivative, prepared by reaction of $[Ni(en)_3](ClO_4)_2,0\cdot5H_2O$ and $[Ni(H_2O)_6](ClO_4)_2$ in 2 : 1 mole proportions in methyl cyanide, and precipitation of the product with propan-2-ol.

(*14-Amino-4,4,9,11,11-pentamethyl-5,8,12-triazatetradec-8-en-2-one*)*copper*(II) *Perchlorate*, $[Cu(\mathbf{8})](ClO_4)_2$.—Bis(diaminoethane)copper(II) perchlorate was dissolved in acetone

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[19] J. L. Love and H. K. J. Powell, *Chem. Comm.*, 1968, 38; G. R. Hedwig, J. L. Love, and H. K. J. Powell, *Austral. J. Chem.*, 1969, **23**, 981.

[20] D. H. Busch, *Rec. Chem. Progr.*, 1964, **25**, 107.

(10 g in 500 ml), and the solution left at room temperature for 3 days, or refluxed for 1 h. The acetone was removed, and the deep blue *product* recrystallized as for the previous compound. The product was desiccated *in vacuo* ($P_2O_5$) before analysis, the crystals obtained from ethanol having variable ethanol and/or water of crystallization (Found: C, 34·1; H, 6·5; Cu, 11·1; N, 10·1. $C_{16}H_{34}Cl_2CuN_4O_7$ requires C, 34·3; H, 6·6; Cu, 11·3; N, 10·0%). The compound crystallizes from water as the dihydrate (Found: C, 32·4; H, 6·5; Cu, 10·8. $C_{16}H_{36}Cl_2CuN_4O_8$ requires C, 32·2; H, 6·4; Cu, 10·7%). The fluoroborate salt was prepared similarly and crystallized as a monohydrate (Found: C, 34·5; H, 6·9; Cu, 11·2. $C_{16}H_{36}B_2CuF_8N_4O_2$ requires C, 34·8; H, 6·5; Cu, 11·5%). Magnetic susceptibility of [Cu(**8**)]$(ClO_4)_2,2H_2O$: $10^3\chi_g(294{\cdot}5\ K) = 1{\cdot}23$ c.g.s.u.; $\mu_{eff} = 1{\cdot}90$ B.M., corrected for diamagnetism but not T.I.P.

*Conversion to the Macrocyclic Complexes*.—[Ni(3)]$(ClO_4)_2$ was dissolved in a small volume of pyridine. The initially blue solution turned yellow after *ca.* 1 h. After several hours the [Ni(**4**)]$(ClO_4)_2$ was precipitated with propan-2-ol, and recrystallized from hot water. The copper complex [Cu(**4**)]$(ClO_4)_2$ was prepared similarly from [Cu(**4**)]$(ClO_4)_2$, or by boiling [Cu(**8**)]$(ClO_4)_2$ in very dilute aqueous ammonia for a few minutes.

*Improved Preparation of* 1,9-*Diamino*-4,6,6-*trimethyl*-3,7-*diazanon*-3-*ene*)*copper*(II) *Perchlorate*, [Cu(**1**)]$(ClO_4)_2$.—This compound [3] is conveniently prepared by mixing methanol solutions of equimolar amounts of [Cu(en)$_2$]$(ClO_4)_2$ and [Cu(**8**)]$(ClO_4)_2$, adding a drop of diaminoethane, and boiling for a few minutes. The product crystallizes on cooling.

*Improved Preparation of* (5,7,7,12,12,14-*Hexamethyl*-1,-4,8,11-*tetra-azacyclotetradeca*-4,14-*diene*)*nickel*(II) *Perchlorate*, [Ni(**5**)]$(ClO_4)_2$.[6]—Tris(diaminoethane)nickel(II) nitrate hydrate (25 g) was allowed to stand under acetone (2 l) at room temperature, with occasional agitation. The solution gradually turned yellow, and after *ca.* 2 months [Ni(**5**)]$(NO_3)_2$ started to crystallize. After *ca.* 1 year the bulk of the starting material had reacted, and the product was filtered from the now brown solution, and recrystallized from methanol as the hygroscopic nitrate, or dissolved in hot water and sodium perchlorate (2 mol) added, when the perchlorate crystallized. Further yield of the nitrate was obtained by evaporation to $\frac{1}{3}$ volume.

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