

507. *Some Cyclic Tetra-amines and their Metal-ion Complexes. Part I.
Two Isomeric Hexamethyltetra-azacyclotetradecanes and their Copper(II)
and Nickel(II) Complexes.*

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A cyclic Schiff base-amine complex of nickel(II), formed by condensation of nickel(II)-ethylenediamine complexes with acetone, can be reduced to form two isomeric cyclic tetra-amine-nickel(II) complexes. These are decomposed by cyanide ions, releasing the isomeric cyclic tetra-amines, which re-form the original nickel(II) complexes on reaction with nickel(II) salts, and form isomeric complexes with other metal ions. The amines, hydrochloride salts, and copper(II) and nickel(II) complexes are described.

THE cyclic Schiff base-amine complex of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) (I) formed by the reaction of ethylenediaminenickel complexes with acetone,^{1,2} is readily reduced, to give two isomeric cyclic tetra-amine-nickel

¹ Curtis, *J.*, 1960, 4409.

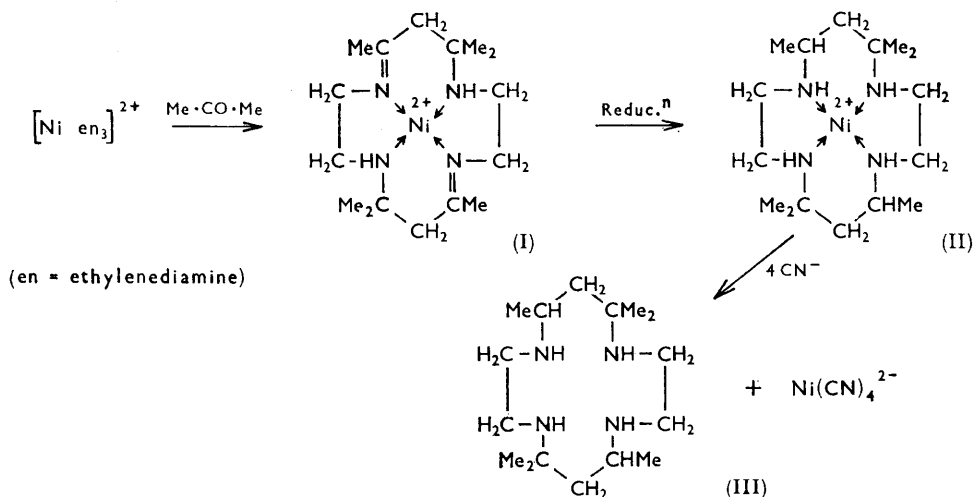
² Blight and Curtis, *J.*, 1962, 3016.

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complexes (II). Reduction can be effected by catalytic hydrogenation (with platinum or nickel), by nickel-aluminium alloy in alkaline solution, by sodium borohydride in aqueous solution, electrolytically, etc. Metals in acid, and sodium in alcohol, were ineffective. When the complex (I) was hydrogenated over platinum at room temperature and atmospheric pressure, four moles (2H_2) were absorbed, indicating that both C:N groups were reduced. This was confirmed by the absence in the infrared spectrum of (II) of the strong C:N stretching band (1660 cm^{-1}) present in the spectrum of (I). Reduction of (I) yields



two isomeric nickel complexes, (IIa) and (IIb). The yield of the minor constituent varies from 22% when nickel-aluminium alloy in sodium hydroxide solution is used, to about 45% with sodium borohydride in aqueous solution. The isomers can readily be separated, since their salts have different solubilities. They are decomposed by cyanide solutions, forming the tetracyanonickelate(II) ion and liberating the cyclic tetra-amines (IIIa) and (IIIb). The isomerism of the nickel complexes persists in the amines, which have different physical properties, and the original nickel complexes are re-formed by reaction of the amines with a nickel salt.

In this Paper the cyclic tetra-amines, some of their ammonium salts, and their complexes with nickel(II) and copper(II) are described. Compounds formed with other metal ions will be described later.

The cyclic tetra-amine, 1,4,8,11-tetra-azacyclotetradecane (IV), had previously been prepared by standard techniques.^{3,4} The preparation of cyclic tetra-amines by the method here described is an example of the "template" action of a metal ion. The usual reaction of acetone with ethylenediamine produces tarry polymeric material. In the presence of the nickel(II) ion, the cyclic Schiff base-amine-nickel complex (II) is produced by a complicated series of reactions in which the nickel ion holds the diamine molecules in suitable orientation for the cyclic condensation.⁵ The cyclic Schiff base-amine is stabilised by co-ordination (since removal of the nickel ion by reaction with cyanide ion yields ethylenediamine and mesityl oxide^{2,6}), permitting reduction to the cyclic tetra-amine complex. Other cyclic tetra-amines have been prepared by the reduction of cyclic Schiff base-amine complexes of nickel(II) formed by the condensation of various nickel di- and

³ Van Alphen, *Rec. Trav. chim.*, 1937, **56**, 1343.

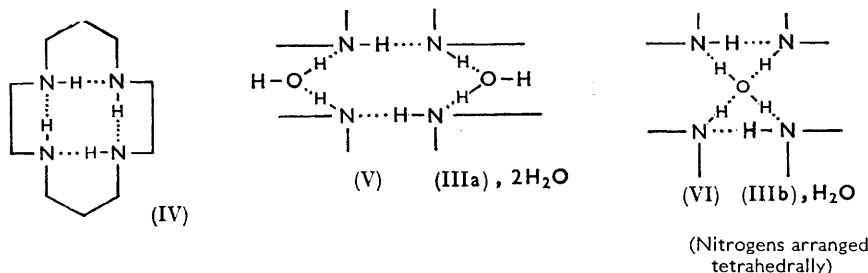
⁴ Stetter and Mayer, *Chem. Ber.*, 1961, **94**, 1410.

⁵ Powell, Thesis, University of New Zealand, 1961.

⁶ Curtis and House, *Chem. and Ind.*, 1961, **42**, 1708.

poly-amine complexes with various carbonyl compounds,⁷ and these will be described subsequently.

Cyclic Tetra-amines.—As it is not known if the complex (I) has the C:N groups in the *cis*- or *trans*-configuration, the configurations of the reduced complex (II) and the free amine (III) are uncertain. For convenience, the *trans*-configuration is assumed for (I), (II), and (III).



The isomers (IIIa) and (IIIb) are probably the *racemic* and *meso* modifications which arise from the introduction of two asymmetric carbon centres when (I) is reduced, although attempts to resolve the isomers by fractional crystallisation of the diammonium (+)-tartrates were unsuccessful. It is considered unlikely that the isomers of (II) and (III) could be geometrical isomers resulting from the fact that (I) is a mixture of *cis*- and *trans*-isomers, since the relative yields of the isomers of (II) varied with the reducing agent, whilst the relative yield with a specific reducing agent (nickel-aluminium alloy in alkali) was unaffected by repeated fractional crystallisation of (I).

The amines crystallise as the hydrates; (IIIa), 2H₂O, m. p. 146–148°; and (IIIb), H₂O, m. p. 97–105°. Isomer (IIIa) is insoluble in cold water, and very sparingly soluble in ether, light petroleum, etc. It can be recrystallised readily from ethanol or aqueous ethanol. Isomer (IIIb) is appreciably soluble in cold water, and more so in hot water, from which it can be crystallised, although it has a tendency to separate as an oil. It is extremely soluble in alcohols, and appreciably soluble in ether, light petroleum, etc. It can be extracted from alkaline aqueous solution by ether, and recrystallised from ether or light petroleum.

Base Strength of Amines.—pH titrations of aqueous solutions of the amine (IIIb), H₂O, and the hydrochlorides [(IIIa)H₄]Cl₄ and [(IIIb)H₄]Cl₄·½H₂O {(IIIa), 2H₂O was not sufficiently soluble in water}, showed that both amines function as tetra-acidic bases. The pH titration curves show a sharp change, of about 5 pH units, after the addition of two moles of acid, or of base in the case of the hydrochlorides. Approximate values for the base constants are: (IIIa) pK_{a1} > 11, pK_{a2} = 10.5, pK_{a3} = 2.2, pK_{a4} < 2; (IIIb) pK_{a1} = 11.6, pK_{a2} = 10.7, pK_{a3} = 2.7, pK_{a4} = 2.3. These values differ considerably from those (9.9, 9.4, 6.8, 3.8) shown by the non-cyclic triethylenetetramine.⁸ The difference is attributed to intramolecular hydrogen bonding in the cyclic amine.

Ammonium Salts.—The amines form tetra-hydrochlorides which can be recrystallised from methanol containing a few drops of concentrated hydrochloric acid. Recrystallisation from methanol alone yielded a crystalline tri-hydrochloride for amine (IIIa), and a very hygroscopic substance, presumably the tri-hydrochloride, for amine (IIIb).

Nickel(II) Complexes.—The isomeric nickel(II) complexes are formed directly by the reduction of the cyclic Schiff base-amine-nickel(II) complex (I). They can be formed from the amines by reaction in alcoholic or aqueous solution with one mole of a nickel salt. The

⁷ Blight and Curtis, *J.*, 1962, 1204; House and Curtis, *J. Amer. Chem. Soc.*, 1962, **84**, 3248; 1964, **86**, 223, 1331, and unpublished work.

⁸ *Chem. Soc. Special Publ.* No. 6, p. 42.

preparation of the orange perchlorate of (IIa), and the blue hemioxalate perchlorate of (IIb) (analogous to other nickel amine hemioxalate perchlorates⁹) are described.

The nickel complexes of both amines form orange diamagnetic salts with anions of low co-ordinating ability, such as perchlorate, and green-blue-violet paramagnetic compounds with anions which have a tendency to co-ordinate. The properties of the salts of the two isomers are usually dissimilar, and they can readily be separated because of their different solubilities. Other compounds of complexes (IIa) and (IIb) will be described subsequently.

The complex ions (IIa) and (IIb) are stable to acid, alkali, ammoniacal dimethylglyoxime, etc. They are slowly decomposed by cyanide, and very slowly by hot concentrated acid or alkali solution. They are also decomposed by powerful oxidising agents, such as acid permanganate or boiling peroxydisulphate solutions.

Copper(II) Complexes.—The copper(II) complexes (IIa,Cu) and (IIb,Cu) are prepared by reaction of the amines with one mole of a copper salt in alcoholic or aqueous solution. The complexes are conveniently isolated as the maroon perchlorates, which are sparingly soluble in water [(IIb,Cu)(ClO₄)₂ less soluble than (IIa,Cu)(ClO₄)₂]. The copper compounds are stable to acid and alkali, but are slowly decomposed by powerful oxidising agents, hot concentrated acids or alkali, and by sulphide or cyanide ions. They cannot be satisfactorily prepared by reduction of the copper analogue of (I),¹⁰ as extensive decomposition occurs with formation of metallic copper.

Infrared Spectra (Table I).—The infrared spectra of the tetra-hydrochlorides show the normal features of secondary amine salts,^{10,11} with strong complex NH₂⁺ stretching bands

TABLE I.
Infrared spectra (cm.⁻¹).

Assignment	(IIIa), 2H ₂ O	(IIIb), H ₂ O	[(IIIa)H ₄]Cl ₄	[(IIIb)H ₄]Cl ₄ · ½H ₂ O	(IIIa)H ₃ Cl ₉ · H ₂ O	1,4,8,11-Tetra-azacyclotetra-decane *
ν(NH)	3275s,sp 3240s,sp	3310sh 3280s,sp 3240s 3330s,sp			3240s,sp	3260s,sp 3170s,sp
ν(NH ₂ ⁺)	2830s,sp 2840s,sp †	2870m,sp 2825s,sp 2780m,sp †	2850— 2550vs	2850—2550vs 2510m 2450m †	2830s † 2570s 2500s 2460m 2410s 2380s †	2810s,sp 2700m 2650w
ν(NH ··· H)						
δ(NH ₂ ⁺)	1500vw	1510vw 1480m	1590m,sp 1578w	1585m	1597m,sp 1530w,br 1500w	1520m
δ(NH ··· H)						
ν(OH)	3400m,br	3400m,br		3450m,br	3330s,sp 3370s,sp	
δ etc. (H ₂ O)	2270w,br 1690w,br	1713m,br		1625w,br	1625m	

sp = sharp. * Frequencies estimated from published spectrum.⁴ † Plus other bands in the CH stretching region. ‡ Plus weak bands at lower frequency.

in the 2800—2200 cm.⁻¹ region, and deformation bands near 1600 cm.⁻¹. The hydrated hydrochloride of (IIIb) also shows bands due to water, at 3450 and 1625 cm.⁻¹. The trihydrochloride of (IIIa) shows bands due to the NH₂⁺ groups similar to those of the tetrahydrochloride, and also a strong sharp band at 3240 cm.⁻¹ due to the NH group. Weak bands at 1500 and 1530 cm.⁻¹ may also be due to this group (below). The compound shows water bands at 3330, 3370, and 1625 cm.⁻¹.

The amine hydrates show absorption, due to the NH groups, near 3300 cm.⁻¹, as is usual

⁹ Curtis, *J.*, 1963, 4109.

¹⁰ Bellamy, "Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

¹¹ Heacock and Marion, *Canad. J. Chem.*, 1956, **34**, 1782; Nakanishi, Goto, and Ohashi, *Bull. Chem. Soc. Japan*, 1957, **30**, 403.

for secondary amines.¹⁰⁻¹² The compounds also show bands in the 2800—2600 cm^{-1} region, and near 1500 cm^{-1} . Bands in these regions have been reported for other secondary amines,¹¹ including the related compound, 1,4,8,11-tetra-azacyclotetradecane.⁴ These bands are probably due to the hydrogen-bonded $\text{NH} \cdots \text{H}$ group. The hydrogen-bonded structure (IV) was suggested for 1,4,8,11-tetra-azacyclotetradecane.⁴ The infrared spectra of the water molecules in the hydrates are also indicative of hydrogen bonding. The OH stretching bands are broad, and centred at about 3400 cm^{-1} . (IIIa), $2\text{H}_2\text{O}$ shows a weak deformation band at 1690 and a weak combination band at 2270 cm^{-1} . These values are similar to those observed for the H_3O^+ ion,¹³ suggesting that hydrogen-bonded structures of the $\text{H}_2\text{O} \cdots \text{H}$ type are present, as for example in structure (V). The deformation band of (IIIb), H_2O is much stronger than usual, and, at 1713 cm^{-1} , is shifted to even higher frequency than for (IIIa), $2\text{H}_2\text{O}$. The deformation frequency would increase in the sequence H_2O , $\text{H}_2\text{O} \cdots \text{H}$, H_3O^+ , $\text{H}_2\text{O}(\cdots \text{H})_2$, suggesting that a structure of the latter type is present. The nickel(II) complex of this amine occurs in forms (to be described subsequently) in which the tetra-amine occupies four adjacent positions of an octahedral complex, with, for example, ethylenediamine occupying the remaining positions. Compounds of this type are not observed with the amine (IIIa). If the amine (IIIb) were to adopt a similar conformation in the hydrate, the water molecule could be surrounded tetrahedrally by, and hydrogen-bonded to, the four nitrogen atoms, as in structure (VI).

The perchlorate salts of the copper(II) complexes (IIa,Cu) and (IIb,Cu) show sharp NH stretching bands at 3220 cm^{-1} . The position of the NH bands for the nickel(II) complexes are very variable, depending upon the anion, hydration, etc., and the spectra of these compounds will be described subsequently.

TABLE 2.

Absorption spectra in aqueous solution (band maxima in 10^3cm^{-1} ; molar extinction coefficients in parentheses).

Compound	Charge-transfer bands	π -Electron band	Metal-ion band
(IIa)	48.6 (10,500), 42.5 (15,600)	—	21.65 (79)
(IIb α) *	49 (9300), 43.8 (12,700)	—	22.57 (70)
(IIb β) *	49.0 (10,200), 43.2 (10,600)	—	22.20 (104)
(I)	47 (complex) (17,000)	35.7 (5400)	22.9 (104)
(IIa,Cu)	37.1 (5200)	—	19.6 (132)
(IIb,Cu)	37.0 (5000)	—	19.6 (184)
(I,Cu)	38.2 (5900)	> 50 (>10,000)	19.7 (110)

* The ion (IIb), as the perchlorate, occurs in two interconvertible forms, α and β . This phenomenon, attributed to configurational isomerism caused by steric hindrance, will subsequently be described in detail.

Visible and Ultraviolet Absorption Spectra.—The spectra of the nickel(II) and copper(II) tetra-amine complexes, as the perchlorate salts in aqueous solution, are shown in Table 2, together with data for the unreduced complex (I) and its copper analogue (I,Cu).

The visible spectra show the single band ($\epsilon \sim 100$) and the broad asymmetric band ($\epsilon \sim 150$), characteristic of singlet ground-state nickel(II) and copper(II) square-planar compounds, respectively.

The band at 280 $m\mu$, present in the spectrum of the Schiff base-amine complex (I) and absent from the spectra of the tetra-amine complexes (IIa) and (IIb), is probably a transition involving the π -electrons of the C:N groups. The remaining bands, near 220 $m\mu$, are similar for the reduced and unreduced compounds, and are probably due to charge-transfer transitions. For the copper compounds, the band near 200 $m\mu$ in the spectrum of (I,Cu) is absent from the spectra of the tetra-amine complexes, and is therefore assigned to the π -electron transition, whilst the 260 $m\mu$ band remains and is assigned to the charge-transfer transition.

¹² Russell and Thompson, *J.*, 1955, 483.

¹³ Curtis, *J. Inorg. Nuclear Chem.*, 1961, 19, 208, and references therein.

EXPERIMENTAL

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-dienenickel(II) perchlorate was prepared as previously described.¹

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecanenickel(II) (Isomer b) Hemioxalate Perchlorate.—The perchlorate (I) $(\text{ClO}_4)_2$ (30 g.), in water (800 ml.) was maintained at about 60° and stirred vigorously. Sodium hydroxide (8 g.) and powdered nickel-aluminium alloy (50% nickel; 10 g.) were added in small portions during about 30 min., keeping the alkali addition slightly ahead of the alloy addition. The solution was stirred for a further 15 min., filter aid was added, and the aluminium precipitated as the hydroxide by the addition of concentrated hydrochloric acid until the pH was 8–9. The suspension was heated to boiling, and filtered hot. The residue was boiled with a little water and refiltered. The combined filtrates were cooled, and the precipitated perchlorate of (IIa) was filtered off and washed with a little cold ethanol. The filtrate was heated to boiling, and sodium oxalate (10 g.) was added. The resulting suspension was maintained near boiling for 30 min., allowed to cool slowly, filtered while still warm, and the precipitate of the blue hemioxalate perchlorate washed well with cold water (6 g., 22%) (Found: C, 41.9; H, 7.7; Ni, 12.1. $\text{C}_{16}\text{H}_{36}\text{N}_4\text{Ni}(\text{C}_2\text{O}_4)_2\text{ClO}_4$ requires C, 42.0; H, 7.7; Ni, 12.1%).

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecanenickel(II) (Isomer a) Perchlorate.—The filtrate from the previous preparation was evaporated to half volume, and filter aid and calcium chloride (15 g.) were added to the boiling solution. The precipitated calcium oxalate was filtered off hot, and washed with a little warm water. The filtrate was acidified with perchloric acid, and the product which separated on cooling was filtered and washed with ethanol. A further crop was obtained by evaporating the filtrate to small volume. This final, impure material was purified by dissolving it in a small volume of boiling acetone containing 5% of water, filtering, and adding concentrated hydrochloric acid (10% of the volume of the filtrate). The chloride of (IIa) separated, and was filtered off, boiled with propan-2-ol, and refiltered, this process being repeated until the washings were colourless. [The filtrate contains a cyclic Schiff base-amine-nickel complex, formed in about 10% yield by reduction of one of the C:N groups of (I), which will be described subsequently]. The combined perchlorate and chloride of (IIa) were recrystallised from hot water, to which sodium perchlorate was added after filtration, to give the pure perchlorate (50–60%) [Found: C, 35.4; H, 7.0; N, 9.8; Ni, 10.9. $\text{C}_{16}\text{H}_{36}\text{N}_4\text{Ni}(\text{ClO}_4)_2$ requires C, 35.5; H, 6.7; N, 10.4; Ni, 10.8].

(Alternate preparation). The perchlorate (I) $(\text{ClO}_4)_2$ (10 g.) and platinum oxide catalyst (0.3 g.) in water (300 ml.) were treated with hydrogen at 50 atm. for 1 day, or 3 atm. for about 4 days. The suspension was heated to boiling, the catalyst was filtered off, and the filtrate treated as previously described. The yield of isomer b was about 33%. Reduction of (II) using sodium borohydride will be described subsequently (yield of isomer b about 43%). Amine a was prepared more simply when isomer b was not required, by filtering the nickel metal residue from the original reduction solution, and decomposing the mixed nickel complexes by digestion with cyanide, as above. Amine a was filtered from the cold solution and recrystallised. The more soluble isomer b, and the amine from the half-reduced material, remain in the filtrates.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane (Isomer a) Dihydrate (IIIa).—(IIa) $(\text{ClO}_4)_2$ and sodium cyanide (6 moles) in 30% ethanol were heated on a water-bath for several hours, until the mauve colour of the initially formed cyanide adduct had faded to the yellow colour of the tetracyanonickelate ion, and most of the ethanol had evaporated. The solution was rendered strongly alkaline with sodium hydroxide, cooled (ice), and the colourless product filtered off, washed with ice-water and recrystallised from aqueous ethanol (>90%) [Found: C, 60.1; H, 12.4; N, 17.2%; Equiv. (titration with acid), 161. $\text{C}_{16}\text{H}_{36}\text{N}_4 \cdot 2\text{H}_2\text{O}$ requires C, 60.0; H, 12.6; N, 17.5%; (Equiv. calc. for formation of diammonium salt), 160.3]. The presence of water was confirmed from the infrared spectrum.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane (Isomer b) Hydrate (IIIb).—The hemioxalate perchlorate of (IIb) was decomposed as in the previous preparation. The solution was rendered strongly alkaline, and cooled in ice, and the product was filtered off and washed with a small volume of ice-water. A further crop was obtained by continuous ether extraction of the filtrate for several hours, the product separating as colourless needles on cooling. It was recrystallised from light petroleum (>90%) [Found: C, 63.8; H, 13.2; N, 18.2%; Equiv.

(titration with acid), 152.5. $C_{16}H_{32}N_4 \cdot H_2O$ requires C, 63.5; H, 12.7; N, 18.5%; Equiv. (calc. for formation of diammonium salt), 151.3]. The presence of water was confirmed from the infrared spectrum.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecanecopper(II) Perchlorate.—The amine hydrate and 1 mole of copper(II) acetate dihydrate were heated in ethanol for about 15 min. Sodium perchlorate was added to the hot solution and the maroon *product* recrystallised from hot water (90%) [Found, for the derivative of isomer a: C, 35.0; H, 6.6; Cu, 11.7. Found, for the derivative of isomer b: C, 35.4; H, 6.9; Cu, 11.7. $C_{16}H_{36}CuN_4 \cdot (ClO_4)_2$ requires C, 35.1; H, 6.6; Cu, 11.6%].

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane (Isomer a) Tetra-hydrochloride.—Concentrated hydrochloric acid was added to the amine dissolved in propan-2-ol, and the *product* was recrystallised from methanol containing a few drops of concentrated hydrochloric acid [Found: C, 44.8; H, 9.1; Cl, 32.9%; Equiv. (titration with alkali), 215.1. $C_{16}H_{40}Cl_4N_4$ requires C, 44.6; H, 9.4; Cl, 32.9%; Equiv., 216]. The infrared spectrum showed no bands attributable to water.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane (Isomer b) Tetra-hydrochloride Hemihydrate.—Concentrated hydrochloric acid was added to a solution of the amine in methanol, and the solution evaporated to dryness under reduced pressure. The *residue* was recrystallised as for the previous compound [Found: C, 43.8; H, 9.6; Cl, 32.1; N, 12.3%; Equiv. (titration with alkali), 225. $C_{16}H_{40}Cl_4N_4 \cdot \frac{1}{2}H_2O$ requires C, 43.7; H, 9.4; Cl, 32.3; N, 12.8%; Equiv., 220]. The presence of water was confirmed from the infrared spectrum.

5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane (Isomer a) Tri-hydrochloride Hydrate.—This *compound* was prepared by recrystallisation of the tetrahydrochloride from methanol [Found: C, 46.6; H, 10.6; Cl, 25.9%; Equiv. (titration with alkali), 417. $C_{16}H_{39}Cl_3N_4 \cdot H_2O$ requires C, 46.7; H, 10.1; Cl, 26.0%; Equiv., 412]. The presence of water was confirmed from the infrared spectrum.

Infrared spectra were measured on mulls, using a Perkin-Elmer 221 spectrophotometer with sodium chloride-grating interchange. Electronic spectra were measured using a Unicam S.P. 700 spectrophotometer.

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