Copper(II), Nickel(II), Cobalt(III), Rhodium(III) and Chromium(III) Complexes of 1,4,7,10-Tetra-azacyclotridecane([13]aneN$_4$) and Kinetic Studies of the Conversion of *cis*-[Ni([13]ane N$_4$)(OH$_2$)$_2$]$^{2+}$ to the Planar Complex

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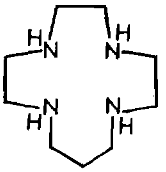
Abstract

A variety of complexes of 1,4,7,10-tetra-azacyclotridecane ([13]aneN$_4$ = L) have been prepared and characterised. These complexes include [CuL](ClO$_4$)$_2$, [CuL](CuBr$_4$), [CuL](CuCl$_4$)·H$_2$O, [NiL](ClO$_4$)$_2$, *cis*-[CoBr$_2$L]Br, *cis*-[CoCl$_2$L]ClO$_4$, *trans*-[CoCl(Br)L]Br,O·5H$_2$O, *trans*-[CoCl$_2$L]Cl, *cis*-[CrCl$_2$L]Cl·H$_2$O and *cis*-[Rh$_2$LCl$_6$]. The syntheses, properties, IR and electronic spectra of the complexes are discussed.

The blue octahedral complex *cis*-[Ni([13]aneN$_4$)(en)](ClO$_4$)$_2$ has been characterised and the isomerisation of *cis*-[Ni([13]aneN$_4$)(OH$_2$)$_2$]$^{2+}$ to the planar yellow [Ni([13]aneN$_4$)]$^{2+}$ studied kinetically. The reaction follows the rate law, rate = k_{OH}[complex][OH$^-$] with k_{OH} = 2.4 × 10^3 dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.1 mol dm^{-3}. The blue folded *cis*-complexes are likely intermediates in the formation of nickel(II) complexes of tetra-aza macrocycles in aqueous solution.

Introduction

Although a considerable volume of data is available on transition metal complexes of cyclen ([12] aneN$_4$) and cyclam([14]aneN$_4$) much less information is available on complexes of 1,4,7,10-tetra-azacyclotridecane([13]aneN$_4$) (I). The complexes [Cu([13]aneN$_4$)](PF$_6$)$_2$ [1], [RhCl$_2$([13]aneN$_4$)]PF$_6$ [2] and *cis*- and *trans*-[CoCl$_2$([13]aneN$_4$)]Cl [3] have been prepared. The chemistry of [Ni([13]aneN$_4$)](ClO$_4$)$_2$ has been briefly discussed, and its oxidation to the corresponding nickel(III) complex investigated [4].



I

Experimental

1,4,7,10-Tetra-azacyclotridecane was prepared as previously described [3], and was isolated as [13]-aneN$_4$·4HBr. The ^{1}H NMR spectrum of the tetrahydrobromide salt in D$_2$O with NaTMS as internal reference has the expected quintet at 2.26 δ (J ≃ 6 Hz) (2H) due to the bridgehead methylene group. The ^{13}C spectrum has the expected five carbon signals at 48.03; 46.31; 45.98, 45.62 and 23.72 ppm. The latter signal is assigned to the bridgehead methylene carbon (spectrum in D$_2$O with NaTMS reference). The free ligand was prepared from [13]aneN$_4$·4HBr essentially as previously described [3].

[Ni([13]aneN$_4$)](ClO$_4$)$_2$

To a slurry of basic nickel(II) carbonate (0.50 g) in water (200 cm^3) was added with stirring, the ligand tetrahydrobromide (0.52 g) and the mixture heated on a water bath for *ca.* 30 min. The solution was filtered hot and the filtrate reduced to *ca.* 5 cm^3 by evaporation. Perchloric acid (6–8 drops) was added giving a gummy yellow precipitate. Addition of acetone (10 cm^3) and ethanol (10 cm^3) followed by scratching gave yellow crystals which were filtered off, washed with ethanol and dried *in vacuo* over silica gel (yield 0.15 g). *Anal.* Calc. for C$_9$H$_{22}$Cl$_2$-NiN$_4$O$_8$; C, 24.35; H, 5.00; N, 12.62. Found: C, 24.63; H, 5.06; N, 12.26%.

[Cu([13]aneN$_4$)](CuBr$_4$)

A mixture of copper(II) carbonate (0.4 g, excess) and the ligand tetrahydrobromide (0.26 g) in methanol–water (60 cm^3, 2 to 1 v/v) was heated on a water bath for *ca.* 20 min and filtered hot to remove unreacted copper(II) carbonate. The blue–

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violet filtrate was concentrated to *ca.* 20 cm^3. Addition of methanol (20 cm^3) to the cooled solution resulted in the precipitation of a grey–green product which was filtered off and discarded. The blue–violet filtrate was slowly evaporated to dryness. Addition of acetone (5 cm^3) initiated crystallisation of the dark blue complex, which was filtered off, washed with acetone and dried (yield 0.25 g). *Anal.* Calc. for $C_9H_{22}Br_4Cu_2N_4$; C, 17.08; H, 3.50; N, 8.85. Found: C, 16.81; H, 3.27; N, 8.6%.

[Cu([13]aneN$_4$)](CuCl$_4$)·H$_2$O

The ligand tetrahydrobromide (0.5 g) was added with stirring, to a solution of potassium hydroxide (0.24 g) in water (20 cm^3). The free ligand was then extracted four times with 20 cm^3 portions of chloroform and the combined chloroform extracts were rotary evaporated to give an oil (0.2 g). The oil was added with stirring, to a solution of copper(II) chloride dihydrate (0.5 g) in methanol (20 cm^3) and the mixture heated on a water bath for *ca.* 1 min during which time a brown compound formed. The mixture was then heated on a water bath for a further five minutes and allowed to cool. The complex was filtered off, washed with methanol, then ethanol and dried *in vacuo* over silica gel. *Anal.* Calc. for $C_9H_{24}N_4OCu_2Cl_4$; C, 22.84; H, 5.11; N, 11.83. Found: C, 23.01; H, 4.72; N, 11.69%.

[Cu([13]aneN$_4$)](ClO$_4$)$_2$

The free ligand (0.20 g) was added to a filtered solution of copper(II) perchlorate hexahydrate (0.40 g) in methanol (20 cm^3) and the solution heated under reflux for 10 min. The solution was slowly evaporated to *ca.* 5 cm^3 when purple crystals of the complex separated. The crystals were washed with ethanol then ether and dried *in vacuo* over silica gel. *Anal.* Calc. for $C_9H_{22}Cl_2CuN_4O_8$ C, 24.09; H, 4.94; N, 12.49. Found: C, 23.85; H, 4.81; N, 12.24%.

cis-[CoBr$_2$([13]aneN$_4$)]Br

A suspension of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (0.4 g) in methanol (40 cm^3) was mixed with the ligand tetrahydrobromide (0.52 g) in methanol–water (30 cm^2, 2:1 v/v) and the mixture stirred and heated on a steam bath for 40 min. The red solution was filtered and cooled. Conc. HBr (2–3 cm^3) was added to the filtrate, which was then concentrated to *ca.* 5 cm^3. Olive green crystals were obtained and these were washed with ethanol, methanol then diethyl ether and dried *in vacuo* over silica gel (yield 0.4 g). *Anal.* Calc. for $C_9H_{22}Br_3CoN_4$: C, 22.29; H, 4.57; N, 11.56. Found: C, 22.16; H, 4.50; N, 11.28%.

cis-[CoCl$_2$([13]aneN$_4$)]ClO$_4$

A mixture of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (0.4 g) and the ligand tetrahydrobromide (0.5 g) in methanol–water (100 cm^3, 3:1 v/v) was stirred and heated on a water bath for 15 min., then filtered. The resulting wine–red filtrate was evaporated to *ca.* 10 cm^3. Conc. HCl (10 cm^3) was added and the mixture evaporated to *ca.* 5 cm^3. When the solution became deep green, methanol (10 cm^3) was added. Addition of a few drops of conc. $HClO_4$ resulted in the crystallisation of dark red shining crystals which were filtered off and recrystallised from dilute (2 M) hydrochloric acid–methanol. *Anal.* Calc. for $C_9H_{22}Cl_3CoN_4O_4$; C, 25.99; H, 5.33; N, 13.47. Found: C, 25.85; H, 5.20; N, 13.51%.

trans-[CoCl$_2$([13]aneN$_4$)]Cl

The free ligand (0.40 g) was added with stirring to a solution of $CoCl_2\cdot 6H_2O$ (0.50 g) in methanol and the resulting mixture warmed to *ca.* 60 °C on a water bath, after some 20 min, the colour had changed from brown to green. Conc. HCl (1 cm^3) was added and the mixture was aerated for 2 h, when some green crystals formed. The volume was reduced to 10 cm^3 and the green product was filtered off and recrystallised from methanol (yield 0.25 g). *Anal.* Calc. for $C_9H_{22}Cl_3CoN_4$; C, 30.75; H, 6.31; N, 15.94. Found: C, 30.30; H, 6.23; N, 15.61%.

trans-[CoCl([13]aneN$_4$]Br]Br·0.5H$_2$O

Concentrated HBr (5 cm^3) was added to a solution of *trans*-[CoCl$_2$([13])aneN$_4$)]Cl (0.20 g) in boiling methanol (50 cm^3) and the mixture heated on a steam bath for 30 min. The solution was then concentrated to *ca.* 10 cm^3, when green crystals of the complex separated. The crystals were collected and washed with a little methanol, followed by ethanol then ether. *Anal.* Calc. for $C_9H_{23}Br_2ClCoN_4O_{0.5}$; C, 24.04; H, 5.15; N, 12.46%.

cis-[Rh$_2$([13]aneN$_4$)Cl$_6$]

A solution of the free ligand (0.5 g) in methanol (50 cm^3) was mixed with a solution of $RhCl_3\cdot 3H_2O$ (0.5 g) in methanol (50 cm^3). The mixture was refluxed for *ca.* 3 h and then allowed to stand overnight. The orange product which formed was filtered off, washed with methanol and dried *in vacuo* over silica gel (0.2 g). *Anal.* Calc. for $C_9H_{22}N_4Rh_2Cl_6$; C, 17.87; H, 3.67; N, 9.26. Found: C, 17.57; H, 3.89; N, 9.22%.

cis-[CrCl$_2$([13]aneN$_4$)]Cl·H$_2$O

A solution of $CrCl_3\cdot 3H_2O$ (0.52 g) in a mixture of N,N-dimethylformamide and 2,2-dimethoxypropane (30 cm^3, 1:1 v/v) was heated under reflux for 30 min. The free ligand (0.40 g) was then added. The mixture was heated on a hot plate with constant stirring for *ca.* 15 min, when violet crystals deposited. The product was filtered off after cooling in an ice bath, washed with DMF, then ether and dried *in vacuo* over silica gel. Fractionation from hot methanol solutions gave no indication of any ***trans***-isomer. *Anal.* Calc. for $C_9H_{24}Cl_3CrN_4O$; C, 29.81; H, 6.67; N, 15.45. Found: C,29.63; H, 6.41; N, 15.85%.

cis-[Ni([13]aneN$_4$)en](ClO$_4$)$_2$

Ethylenediamine (0.2 g) was added dropwise with constant stirring to a solution of $[Ni([13]aneN_4)](ClO_4)_2$ (0.2 g) in warm water (10 cm^3). The solution became violet and on slow evaporation gave purple–violet needle shaped crystals of the complex. The compound was recrystallised from the minimum volume of hot water. *Anal.* Calc. for $C_{11}H_{30}N_6Cl_2O_8Ni$; C, 26.22; H, 6.00; N, 16.67. Found: C, 26.41; H, 6.22; N, 16.80%.

Kinetics

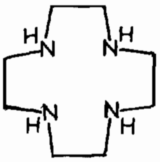
The kinetics of the conversion of the *cis*-$[Ni([13]aneN_4)(OH_2)_2]^{2+}$ to the planar yellow complex was monitored spectrophotometrically at 425 nm, corresponding to λ_{max} for the planar complex. Absorbance changes were logged using a Gilford 2400S spectrophotometer interfaced with an Apple II computing system. Plots of $\ln(A_\infty - A_t)$ *vs.* time were linear for at least four halves. Measurements were made using tris(hydroxymethyl)aminomethane buffers adjusted to $I = 0.1$ M with $NaClO_4$. All pH measurements were made using a Radiometer PHM64 Research pH meter, which was standardised using 0.05 M potassium hydrogen phthalate (pH 4.008) and phosphate buffer (0.025 M), pH 6.86 at 25 °C. Hydroxide ion concentrations were determined from the pH using $pK_W = 13.996_5$ at 25 °C and a molar activity coefficient of 0.774.

General

Infrared spectra were determined as KBr discs using a Perkin Elmer 577 instrument. Electronic spectra were obtained using a Perkin Elmer 402 instrument or a Beckman 24 spectrophotometer. Carbon-13 NMR spectra were obtained using a Bruker WP80 instrument. Interval scan spectra were determined with a Perkin Elmer Lambda 5 instrument.

Results and Discussion

The ligand cyclen (**II**) gives only *cis*- complexes with cobalt(III) and rhodium(III) due to the small 'hole size' of the ligand [5]. The 14-membered macrocycle cyclam (**III**) gives both *cis* and *trans* complexes with cobalt(III) [6] rhodium(III) [7] and chromium(III) [8]. As a result, *cis* and *trans* complexes of the type $[CoLX_2]^+$ are expected with cobalt(III) and [13]aneN$_4$. Chromium(III) gives predominantly *cis*-complexes with cyclam, unlike cobalt(III) where the *trans*-isomers tend to be the most thermodynamically stable. Both *cis* and *trans* isomers of $[Rh(cyclam)X_2]^+$ can be readily prepared [7].



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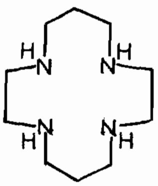
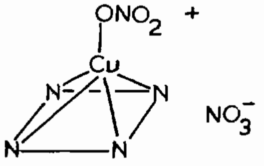


III

Copper(II) Complexes

Copper(II) complexes of cyclen have been prepared [9] including $Cu(cyclen)X_2$ ($X = Cl^-, Br^-, NO_3^-$). Chemical substitution reactions, conductivity, ESR spectra and electronic spectra indicate a five coordinate structure with a square pyramidal stereochemistry [9]. This view is confirmed by the crystal structure of $[Cu(cyclen)NO_3](NO_3)$ [10] where the copper(II) ion lies out of the plane of the macrocyclic ring in a distorted square pyramidal stereochemistry (**IV**).



IV

Three complexes of copper(II) with [13]aneN$_4$ have been characterised in the present work, $[CuL](ClO_4)_2$, $[CuL](CuCl_4)\cdot H_2O$ and $[CuL](CuBr_4)$. The IR spectrum of the perchlorate salt is consistent with ionic perchlorate with bands at 620 cm^{-1} and the characteristic broad perchlorate band near 1100 cm^{-1}. The complex has λ_{max} 532 nm ($\epsilon = 214$ M^{-1} cm^{-1}) in water, but a stronger ligand field occurs in the solid state where λ_{max} is 510 nm, Table I. This result may be indicative of weak ClO_4^- interactions with copper(II) in the solid. The tetrahalocuprate(II) complexes $[CuL](CuCl_4)\cdot H_2O$ and $[CuL](CuBr_4)$ were also isolated. A characteristic feature of the electronic spectrum of the $[CuCl_4]^{2-}$ ion is the strong $Cl(\pi) \rightarrow Cu(d)$ charge transfer band near 400 nm [11]. This band occurs in the solid state spectrum of $[CuL](CuCl_4)\cdot H_2O$ at 420 nm, and as expected this band is absent in the aqueous solution spectrum where $\lambda_{max} = 538$ nm ($\epsilon = 124$ M^{-1} cm^{-1}), Table I. Bhattacharya [1] has previously characterised $[CuL](PF_6)_2$. This complex is a 1:2 electrolyte in nitromethane and in aqueous solution ($\Lambda_M = 174$ ohm^{-1} cm^2 mol^{-1} and 182 ohm^{-1} cm^2 mol^{-1} respectively). The compound has λ_{max} 540 nm in water ($\epsilon = 286$ M^{-1} cm^{-1}) and 525 nm ($\epsilon = 175$ M^{-1} cm^{-1}) in nitromethane. The λ_{max} value of the broad band gives the approximate value of 10 Dq (xy). In the case of

TABLE I. Electronic Spectra of Complexes of [13]aneN_4.

Complex	Solvent	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
[NiL]$(ClO_4)_2$	H_2O	422	96
		210(sh)	
		200	1.4×10^4
[CuL]$(ClO_4)_2$	H_2O	532	214
		262	5.2×10^3
	Nujol mull	510	
		275	
[CuL]$(CuCl_4)\cdot H_2O$	H_2O	538	124
		262	3.1×10^4
	Nujol mull	540sh	
		420	
		310	
[CuL]$(CuBr_4)$	Nujol mull	630sh	
		555	
		350	
		288	
	H_2O	555	194
		260	5.7×10^3
Trans-[$CoCl_2L$]Cl	MeOH	600	35
		300sh	*ca.* 3.1×10^3
		248	2.4×10^4
Trans-[CoCl(Br)L]Br$\cdot 0.5H_2O$	MeOH	627	43
		262	1.9×10^4
		202	1.9×10^4
Cis-[$CoCl_2L$]ClO_4	DMSO	540	149
		390sh	210
		258	*ca.* 1.2×10^4
Cis-[$CoBr_2L$]Br	DMSO	560	140
		262	1.4×10^4
cis-[$CrCl_2L$]Cl$\cdot H_2O$	H_2O	532	147
		398	88
		212	9.4×10^3
Rh_2LCl_6	Nujol	350sh	

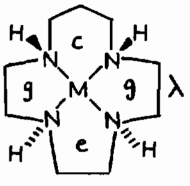
[Cu([13]aneN_4)]$(PF_6)_2$ in nitromethane, there will be no axial ligand and λ_{max} corresponds to the field caused by the ligand in the square plane. The 10 Dq(xy) value in [CuL]$(PF_6)_2$ (19,050 cm^{-1}) is somewhat less than in [Cu(cyclam)]$(PF_6)_2$ (20,200 cm^{-1}) and it may well be that the copper ion lies somewhat out of the plane of the four nitrogens giving a square pyramidal structure.

Cobalt Complexes

The reaction of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ with the ligand tetrahydrobromide in methanol–water solution, followed by treatment with HCl then $HClO_4$ gives the dark red *cis*-[$CoCl_2$([13]aneN_4)]ClO_4, which has λ_{max} 540 nm (ϵ = 149 M^{-1} cm^{-1}) with a shoulder at 390 nm (ϵ = 210 M^{-1} cm^{-1}), in DMSO solvent fully consistent with the *cis*-configuration.

Aeration of a mixture of the free ligand and $CoCl_2\cdot 6H_2O$ in methanol gave the green *trans*-isomer, which has λ_{max} 600 nm (ϵ = 35 M^{-1} cm^{-1}) in methanol. The IR spectrum of the *trans*-isomer has a single sharp νNH band at 3150 cm^{-1} (Cl^- salt), while the *cis*-isomer (ClO_4^- salt) has two νNH bands at 3180 cm^{-1} and 3255 cm^{-1}. The *trans*-chloro–bromo complex *trans*-[CoCl([13]aneN_4)Br]Br$\cdot$ $0.5H_2O$ can be obtained by heating the *trans*-dichloro complex with concentrated HBr in boiling methanol. This complex is green in colour with λ_{max} 627 nm (ϵ = 43 M^{-1} cm^{-1}) in methanol solvent. The IR spectrum has a single sharp NH band at 3150 cm^{-1} consistent with the *trans*-configuration. The olive–green *cis*-[$CoBr_2$([13]aneN_4)]Br was prepared by reaction of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ with the ligand tetrahydrobromide in methanol–water followed by treatment with conc. HBr. This complex has λ_{max} 560 nm (ϵ = 140 M^{-1} cm^{-1}) and the IR spectrum displays two νNH bands at 3075 and 3150 cm^{-1} as expected for the *cis*-configuration.

As predicted [12] the *cis*-complexes undergo rapid base hydrolysis and kinetic studies will be reported in detail in a subsequent paper. Hung and Busch [3] have previously studied the aquation of *cis* and *trans*-$[CoCl_2([13]aneN_4)]^+$. For the loss of the first halide ligand $k_{aq} = 9.5 \times 10^{-4}$ s^{-1} (*cis*) and 6.8×10^{-4} s^{-1} (*trans*) at 25 °C. The *trans*-diaquo complex isomerises to the *cis*-diaquo complex with a rate constant for isomerisation of 5.4×10^{-4} s^{-1} at 25 °C. The *trans*-complexes are expected to have the configuration (V) with a chair (c) six membered ring, two gauche (g) five-membered rings and an eclipsed (e) five-membered ring with the chirality (δ or λ) indicated.



V

Rhodium(III)

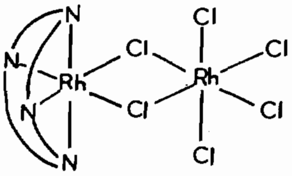
Rhodium(III) complexes of $[13]aneN_4$ with the formulations $[RhCl_2L]Cl$ and $[RhCl_2L]PF_6$ have been previously characterised [2]. These complexes were prepared by heating $RhCl_3 \cdot 3H_2O$ with the ligand in methanol for 2 days, the PF_6^- salt being crystallised by the addition of NH_4PF_6. The chloride derivative has λ_{max} 350 nm (ϵ 443 M^{-1} cm^{-1}) and 300 nm (ϵ = 538) with $\Lambda_M = 96$ ohm^{-1} cm^2 mol^{-1} in water, indicating a 1:1 electrolyte. Both complexes were assigned a *cis*-configuration. In the present work we have found that reaction of the free ligand with $RhCl_3 \cdot 3H_2O$ in methanol for 3 h gives an orange–yellow complex which can be formulated Rh_2LCl_6. The *cis*-configuration of the macrocycle in this complex is consistent with the observation of two νNH bands at 3162 and 3310 cm^{-1} [7]. *Trans*-complexes normally show a single νNH band [7, 13]; The solid state spectrum has λ_{max} 350 nm occurring as a distinct shoulder on an intense charge transfer band; a result consistent with a *cis*-configuration. Rhodium(III) and cobalt(III) give only *cis*-complexes with $[12]aneN_4$ [14]. However, $[13]aneN_4$ gives both *cis* and *trans*-complexes with Co(III), but only *cis*-complexes with Rh(III). This is a result of the respective ionic radii of Co(III) and Rh(III) which are 53 and 67 pm, respectively [15]. The ligand $[13]aneN_4$ cannot encompass Rh(III) to form a *trans* complex. Trends in the stereochemistries of cobalt(III) and rhodium(III) complexes of tetra-aza macrocycles are summarised in Table II.

A possible structure for Rh_2LCl_6 is shown in (VI) in which the macrocycle adopts a *cis*-configuration.

TABLE II. The Stereochemistry of Macrocyclic Complexes of Cobalt(III) and Rhodium(III).[a]

L	Rh(III)	Co(III)
$[12]aneN_4$	*cis*	*cis*
$[13]aneN_4$	*cis*	*cis* and *trans*
$[14]aneN_4$	*cis* and *trans*	*cis* and *trans*
$[15]aneN_4$	*trans*	*trans*
$[16]aneN_4$	*trans*	*trans*

[a] For Co(III) and Rh(III) complexes of $[12]aneN_4$ see ref. 5. For Rh(III) complexes of $[14]aneN_4$ see ref. 7. Other Rh(III) complexes see ref. 2. For the cobalt(III) complexes see ref. 3.



VI

In addition to the two νNH stretching vibrations at 3310 and 3162 cm^{-1}, there are two strong sharp bands at 555 and 480 cm^{-1} which can be assigned to Rh–N stretching vibrations. Two Rh–N stretching vibrations are indicative of a *cis*-configuration, only one band being observed with *trans*- complexes [7]. A medium intensity band at 300 cm^{-1} is probably due to νRh–Cl. The structure (VI) must be regarded as tentative, but may well represent an intermediate in the formation of monomeric $[RhCl_2L]^+$ species.

Nickel(II)

The nickel(II) complex was isolated as a yellow square planar species, with λ_{max} = 422 nm (ϵ = 96 M^{-1} cm^{-1}) in water solvent. The visible spectrum was not affected by increasing the temperature or by increasing concentrations of sodium perchlorate. There was therefore no evidence for a square planar ⇌ octahedral equilibrium of the type:

$$[NiL]^{2+} + 2H_2O \rightleftharpoons [NiL(H_2O)_2]^{2+}$$

which has been observed with a variety of nickel(II) complexes of tetra-azamacrocycles [16]. Similar observations have been made by Bencini, Fabbrizzi and Poggi [4] who found that $[Ni([13]aneN_4]^{2+}$ is 100% square planar in acetonitrile.

The $[13]aneN_4$ ligand appears to be unique in forming exclusively low spin square nickel(II) complexes. The 12-, 14-, 15- and 16-membered tetra-azamacrocycles form nickel(II) complexes which exhibit square planar ⇌ octahedral equilibria [4].

Busch *et al.* [17] have estimated an average ideal M–N bond length for various tetra-azamacrocycles. A metal ion having this ideal M–N distance would chelate with minimum strain of the macrocyclic ligand. For 12-, 13- and 14-membered rings the ideal metal nitrogen bond lengths are 1.83, 1.92 and 2.07 Å respectively.

Crystallographic measurements [18] have established that in 14-membered rings the Ni–N bond lengths are 1.96–1.97 Å for the low spin complexes and 2.06–2.08 Å for the high spin octahedral species. The larger high spin nickel(II) which has a Ni–N distance of 2.12 Å in $[Ni(en)_3]^{2+}$ [19] provides a much poorer fit to the [13]aneN$_4$ ligand than the smaller low spin ion for which the fit is almost ideal.

Addition of ethylenediamine to an aqueous solution of the yellow planar $[Ni([13]aneN_4)](ClO_4)_2$ leads to an immediate colour change to blue. The blue folded *cis*-$[Ni([13]aneN_4)(en)](ClO_4)_2$ can be readily isolated from solution. The macrocycle is likely to have the *trans* (V) configuration (RRRR, SSSS) which allows two fold axes (VII) giving the blue *cis* complex (VIII). Treatment of the chelate ethylenediamine complex with HBr gives the *cis*-$[Ni([13]aneN_4)Br_2]$ which gives the blue *cis*-$[Ni([13]aneN_4)(OH_2)_2]^{2+}$ cation in aqueous solution.

Conversion of *cis*-$[Ni([13]aneN_4)(OH_2)_2]^{2+}$ to the yellow planar complex $[Ni([13]aneN_4)]^{2+}$ having the RSSR chiral nitrogen configuration readily occurs in basic solution, Fig. 1. Detailed kinetic studies establish that the reaction is first order in hydroxide and first order in the complex with rate = k_{OH^-} [Complex] [OH$^-$]. At 25 °C and $I = 0.1$ M, the value of $k_{OH} = (2.4 \pm 0.2) \times 10^3$ M^{-1} s^{-1}, Table III. This value of k_{OH} is some four fold greater than that for *cis*-$[Ni(cyclam)(H_2O)_2]^{2+}$ where k_{OH} = 560 M^{-1} s^{-1} at 25 °C and I = 0.1 M [22]. Base catalysed isomerisation is surprisingly rapid, and is faster than for *cis*-$[Ni(2,3,2\text{-tet})(OH_2)_2]^{2+}$ where k_{OH} = 450 M^{-1} s^{-1} at 25 °C [22]. Such *cis*-macrocyclic complexes are likely to be intermediates in the formation of Ni(II) complexes of tetra-azamacrocycles, and some evidence for such intermediates has been presented [23]. The formation reaction is expected to proceed by initial coordination of the ligand in a folded configuration, in order to allow sequential replacement of coordinated water molecules. In the reaction of copper(II) with tet *a* (tet *a* = C-*racemic*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), an unstable complex containing tet *a* in a folded configuration is initially formed and slowly reverts to a planar red complex [24, 25]. Similar results have been observed with copper(II) and tet *b* (the C-*racemic* ligand) [26].

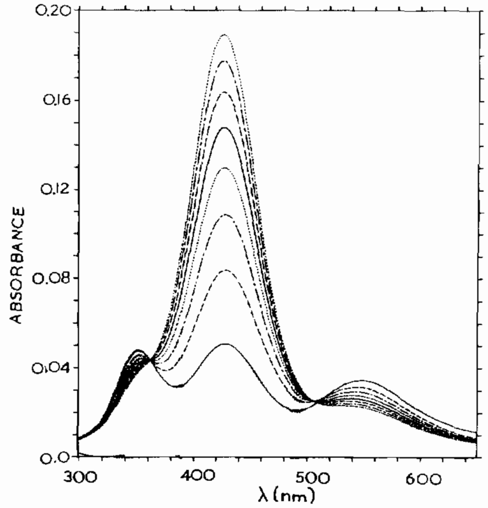
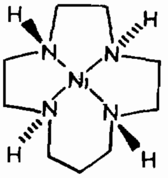


Fig. 1. Spectral changes during the conversion of *cis*-$[Ni([13]aneN_4)(OH_2)_2]^{2+}$ to the planar complex $[Ni([13]aneN_4)]^{2+}$ at pH 7.61 and 25 °C. The time interval between scans is 2 min.

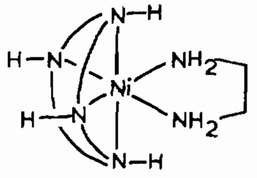
TABLE III. Kinetics of Conversion of *cis*-$[Ni([13]aneN_4)(OH_2)_2]^{2+}$ to Planar $[Ni([13]aneN_4)]^{2+}$ at 25 °C and I = 0.1 M (NaClO$_4$).[a]

pH	$10^6[OH^-]$ (M)	$10^3 k_{obs}$ (s^{-1})	$10^{-3} k_{OH}$ (M^{-1} s^{-1})
8.22	2.17	5.08	2.3
8.91	1.06	2.53	2.4
7.82	0.86	2.21	2.5
7.71	0.67	1.75	2.6
7.55	0.46	1.07	2.2

[a] Reactions in tris(hydroxymethyl)aminomethane buffers adjusted to I = 0.1 M with NaClO$_4$.



VII



VIII

Chromium(III)

Chromium(III) complexes of [12]aneN$_4$, [14]aneN$_4$ and [15]aneN$_4$ have been previously characterised [8, 20]. Only the *cis*-isomer $[Cr([12]aneN_4)X_2]^+$ was obtained with [12]aneN$_4$, while with [15]aneN$_4$ only the *trans*-isomer was isolated. The ligand [14]aneN$_4$ gives both *cis*- and *trans* isomers with the *cis*-isomer predominating [8]. The reaction of $[CrCl_3(DMF)_3]$, (prepared *in situ* by dehydration of $CrCl_3 \cdot 6H_2O$ in DMF solution) with the [13]aneN$_4$ gives the violet *cis*-[CrCl$_2$-

([13]aneN$_4$)]Cl. No evidence for the *trans*-isomer was found. The *cis*-configuration of the complex is confirmed by the electronic spectrum which has λ_{max} 532 nm (ϵ = 147) and 398 nm (ϵ = 88), values which are very comparable to those of *cis*-[CrCl$_2$([14]aneN$_4$)]$^+$ with λ_{max} 529 nm (ϵ = 111) and 404 nm (ϵ = 106 M^{-1} cm^{-1}) [8]. In O$_h$ symmetry three ligand field bands are expected for a d^3 ion $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and the two electron transition $^4A_{2g} \rightarrow {}^4T_{1g}(P)$. The more symmetrical *trans*-isomers of [CrN$_4$Cl$_2$]$^+$ normally have extinction coefficients of <30 and the lowest energy d–d band ($^4A_{2g} \rightarrow {}^4T_{2g}$) occurs in the range 570–580 nm [21]. The less symmetrical *cis*-isomers have much higher extinction coefficients (*ca.* 70–140 M^{-1} cm^{-1}) and the lowest energy d–d band occurs in the region 530–560 nm. The IR spectrum of *cis*-[Cr([13]aneN$_4$)Cl$_2$]Cl·H$_2$O has a broad band due to water at *ca.* 3450 cm^{-1} and a strong νNH band at 3090 cm^{-1} with a shoulder at 3130 cm^{-1}.

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