Some Cyclic Tetra-amines and Their Metal-ion Complexes. Part VIII.[1] Cobalt(III) Complexes of 3,3-Dimethyl-1,5,8,11-tetra-azacyclotridecane

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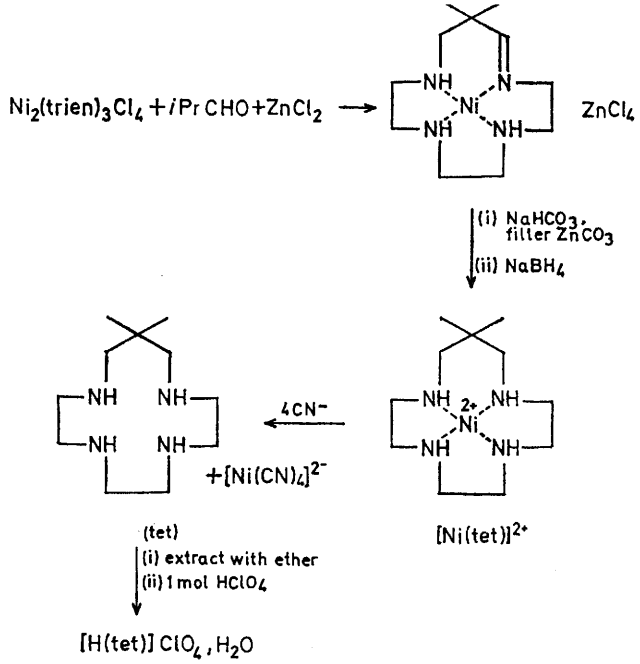
The preparation of the cyclic tetra-secondary amine 3,3-dimethyl-1,5,8,11-tetra-azacyclotridecane from the previously reported nickel(II) complex is described. Cobalt(III) complexes of the amine were prepared with the amine in planar (*bcde*-octahedral) and folded (*abcd*-octahedral) co-ordination. Derivatives of the complex cobalt cation in three configurations arising from restricted inversion at the four chiral co-ordinated secondary amino-groups were prepared. The relative stabilities of the possible configurations in planar and folded co-ordination are discussed, and assignments of configuration of the observed forms are made, based on chemical and physical (particularly ^1H n.m.r. spectral) properties.

THE preparation of the nickel(II) complexes of the cyclic tetra-amine 3,3-dimethyl-1,5,8,11-tetra-azacyclotridecane (tet), by the procedure outlined in the Scheme, has been reported.[1] Here the release of the free amine from the complex nickel(II) cation by reaction with cyanide, and the preparation and properties of some cobalt(III) complexes of the amine are described.

Isolation of Amine.—The complex cation $[Ni(tet)]^{2+}$ reacts rapidly with cyanide ions to form the tetracyanonickelate ion with liberation of the amine. This is conveniently separated by ether extraction, and isolated as the crystalline monohydroperchlorate hydrate. pH Titration showed the presence of a pair of strongly basic and a pair of weakly basic amino-groups, as has been observed for other cyclic tetra-amines[2] (see Experimental section).

Preparation of Cobalt(III) *Complexes.*—Cobalt(III) complexes of (tet) were prepared by two general procedures. (i) A solution of the amine was added to a solution of the appropriate cobalt(II) salt. A brown colouration immediately formed, and oxidation was completed by bubbling air through the solution, or by addition of hydrogen peroxide. The resulting peroxo-derivative was decomposed by acid to yield the desired *trans*-diacido(tet)cobalt(III) derivative. Yields were *ca.* 60%. (ii) The amine hydroperchlorate reacted rapidly with $Na_3Co(CO_3)_3,3H_2O$ in water or methanol to yield a red solution containing the *cis*-product $[Co(tet)CO_3]^+$, from which other *cis*- and also *trans*-compounds were prepared. Yields were almost quantitative.



Chemical Properties of Cobalt(III) *Complexes.*—The chemistry of the cobalt(III)(tet) system generally resembles that of 1,4,8,11-tetra-azacyclotetradecane,

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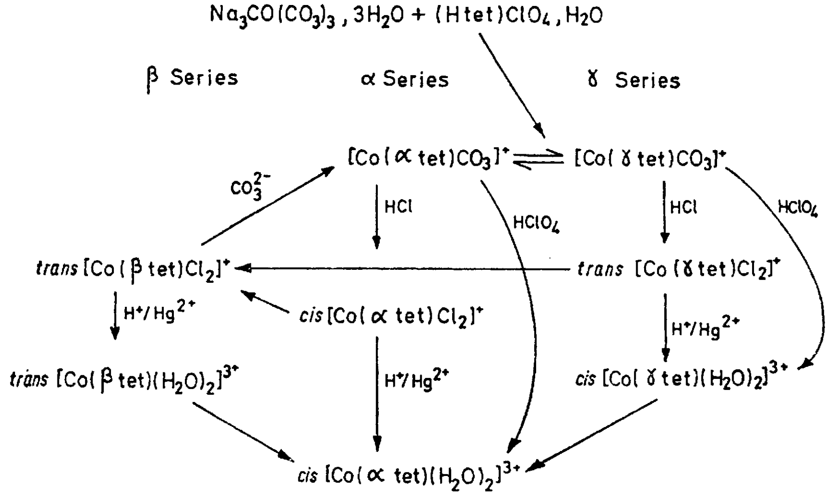
[1] Part VII, N. F. Curtis and G. W. Reader, *J. Chem. Soc.* (*A*), 1971, 1771.

[2] N. F. Curtis, *J. Chem. Soc.*, 1964, 2644.

cyclam,[3] and its *C-rac*-5,5,7,12,12,14-hexamethyl derivative (tet *b*).[4] Derivatives were prepared with the amine in both planar (*bcde*) and in folded (*abcd*) co-ordination, and with the amine in three configurations of the chiral nitrogen centres (below), represented as (α tet), (β tet), and (γ tet). Interconversion of these configurations requires inversion at one or more co-ordinated secondary amino-groups, a process which is very slow under acidic conditions, but rapid under basic conditions.

The chemistry of the chloroaquocarbonato-derivatives of the Co^{III}(tet) moiety is shown in the Scheme. In acid solution β-*trans*-dichloro-complexes aquate to an equilibrium mixture of the *trans*-dichloro- and *trans*-chloroaquo-species, as for the cyclam analogue.[3] Aquation of the α-*cis*-dichloro-complex is more extensive, again as for the cyclam analogue.[3] Removal of chloride ions from solution (by ion exchange, precipitation with Ag^{2+}, or complexation with Hg^{2+}) causes aquation to proceed to the di-aquo species, *trans* for β, *cis* for α and γ. The two latter species are also formed from the appropriate carbonato-complexes in acid solution. In acid (pH 0) at room temperature the inversion reaction which leads to interconversion of the isomeric aquo-complexes is very slow, but at 100° it is quite rapid, and the *trans*-β and *cis*-γ forms are converted to the *cis*-α-diaquo-complex (detectable by the formation of the violet *cis*-α-dichloro-complex when the solution is diluted by an equal volume of concentrated hydrochloric acid). The aquo-complexes were all very soluble and crystalline derivatives were not isolated.

Under basic conditions, hydrolysis of the chloro-complexes, and the inversion reactions are rapid. *trans*-$[Co(\beta\,tet)Cl_2]^+$ is rapidly hydrolysed to *trans*-$[Co(\beta\,tet)(OH)_2]^+$ which absorbs carbon dioxide to form the *cis*-carbonato-complex (*trans*-$[Co(tet\,b)Cl_2]^+$ behaves similarly).[4] The carbonato-complex can also be prepared directly from the dichloro-complex by reaction with carbonate. The carbonato-complex occurs in solution as an equilibrium mixture of the α and γ isomeric forms. In water, the crimson γ form predominates at equilibrium, which is achieved fairly rapidly, but the less soluble vermilion α perchlorate crystallises. In methanol the equilibrium again favours the γ isomer, and the crimson γ perchlorate crystallises.



SCHEME

The α carbonato-complex dissolves in hydrochloric acid to yield a mauve solution, from which mauve *cis*-$[Co(\alpha\,tet)Cl_2]Cl$ crystallises ($[Co(cyclam)CO_3]^+$ behaves similarly).[3] The γ carbonato-complex dissolves in hydrochloric acid to give a transient bluish colouration, which is probably the *cis*-dichloro-complex, but this rapidly isomerises to green *trans*-$[Co(\gamma\,tet)Cl_2]^+$, metastable with respect to *trans*-$[Co(\beta\,tet)Cl_2]^+$($[Co(tet\,b)CO_3]^+$ behaves similarly, reacting with HCl to form *trans*-Co(α tet *b*)Cl_2, metastable with respect to the β isomer).

Reaction of $[Co(\alpha\,tet)CO_3]^+$ with hydrobromic acid yielded a brown solution, from which brown *cis*-$[Co(\alpha\,tet)Br_2]Br$ was isolated. This formed brown solutions in low polarity solvents, or in the presence of high concentrations of bromide ions, but violet solutions, with spectra typical of *cis*-dibromo-tetra-amine cobalt(III) complexes in more polar solvents. The *trans* β and γ dibromo-complexes resembled their dichloro-analogues.

Other cis *Derivatives*.—Derivatives of the complexes, which must have structures with the tetra-amine in folded co-ordination, were prepared with oxalate, acetylacetonate, and diaminoethane. A *cis*-structure for the diammine, as for the stable diaquo-complex, is supported by the value of the extinction coefficients for the *d–d* bands, and by the ^1H n.m.r. spectrum (below). Treatment of the carbonato-complex with acid plus thiocyanate or azide yielded initially the *cis*-derivatives, but these were not isolated free of the *trans*-isomers.

These *cis*-compounds could have the amine in the α

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[3] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102; 1966, **5**, 514; C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1967, **2069**; 1968, 1549.

[4] (*a*) J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1970, 2478; (*b*) P. O. Whimp and N. F. Curtis, *J. Chem. Soc.* (*A*), 1966, 867, 1827.

or γ configuration, as preparative conditions would have permitted adoption of the optimum configuration. ^{1}H N.m.r. evidence (below) supports assignment of the α configuration.

Other trans *Derivatives.*—The *trans* β diacido derivatives with azide, thiocyanate, and acetate (as well as the chloride and bromide) were isolated. The *trans*-diacetato-complex was formed by reaction of the *trans*-dichloro-derivative with acetate and also by reaction of the α carbonato-complex with acetic acid and precipitation with ether, in an attempt to prepare a chelated acetato-complex.

Mixed Cobalt(III)-*Cobalt*(II) *Derivatives.*—A number of derivatives of the Co^{III}(tet) system were isolated with complex cobalt(II) anions.[4a] These were paramagnetic (Table 1) and the electronic spectra showed bands assignable to cobalt(II) and cobalt(III) species (Table 2).

Infrared Spectra.—The i.r. spectra show no unusual features. The spectra all show several bands *ca.* 3200 cm^{-1} assigned as ν(NH) and the compounds formulated as hydrates show bands assignable as ν(OH) and δ(HOH). The spectra assignable to co-ordinated and ionic anions are similar to those of analogous compounds with bis(diaminoethane), (tet *b*), *etc.*

Cobalt d–d *Spectra.*—Solution spectra of *trans*- and *cis*-cobalt(III)(tet) derivatives are listed in Table 1. These generally permitted unambiguous assignment of *cis*- or *trans*-configuration. The diammine has extinction coefficients typical of *cis*- rather than *trans*-compounds. Reflectance spectra of the compounds with complex cobalt(II) anions are listed in Table 2.

In Table 3 the spectra of some cobalt(III)(tet) derivatives are compared with those of analogues with other tetra-amines. For such series, the relative ligand field strength of the tetra-amines is given by the order of the lowest energy band [$^1E_g \longleftarrow {}^1A_{1g}$ in D_{4h} for *trans*- and $(^1E + {}^1B_2) \longleftarrow {}^1A_1$ in C_{2v} for *cis*-compounds]. For both planar and folded co-ordination the amine (tet) is above the other cyclic amines (cyclam), (cyclen), and (tet *b*) in ligand field strength, and is comparable in value to trien. This effect must be structural in origin, as the donor atoms are the same for the cyclic amines. For planar co-ordination the stable β configuration is above the metastable γ configuration in ligand field strength, while for folded co-ordination the α configuration is above the γ configuration.

Nuclear Magnetic Resonance Spectra.—The methyl resonance frequencies of a number of the Co^{III}(tet)

TABLE 1

Cobalt(III) *d–d* spectra and ^{1}H n.m.r. spectra of 3,3-dimethyl-1,5,8,11-tetra-azacyclotridecane derivatives

trans-Compounds	Electronic spectra [a]			^{1}H N.m.r. methyl resonances [b]
	(Ia) [c]	(Ib) [d]	(II) [e]	
$[Co(\beta\ tet)Cl_2]^+$	606 (35)	424 (120)		1·00, 1·15 (15)
$[Co(\gamma\ tet)Cl_2]^+$	618 (54)	425 (109)		1·03, 1·17 (14)
$[Co(\beta\ tet)Br_2]^+$	652 (40)			1·02, 1·23 (21)
$[Co(\gamma\ tet)Br_2]^+$	671 (50)			1·06, 1·25 (19)
$[Co(\beta\ tet)(NCS)_2]^+$	511 (257)			
$[Co(\beta\ tet)(N_3)_2]^+$	556 (210)			1·08, 1·28 (20)
$[Co(\beta\ tet)(CH_3CO_2)_2]^+$	532 (19)	412 (24)	355 (32)	
cis-Compounds	(I) [f]	(II) [g]		
$[Co(\alpha\ tet)Cl_2]^+$ [h]	531 (138)			0·95, 1·31 (36)
$[Co(\alpha\ tet)Br_2]^+$ [i]	539 (127)			1·00, 1·68 (68)
$[Co(\alpha\ tet)(C_2O_4)]^+$ [j]	493 (204)	356 (212)		1·00, 1·28 (28)
$[Co(\alpha\ tet)(acac)]^{2+}$	505 (229)			1·00, 1·29 (28) [k]
$[Co(\alpha\ tet)en]^{3+}$ [j]	517 (217)	448 (180)		1·08, 1·48 (40)
$[Co(\alpha\ tet)(NH_3)_2]^{3+}$ [j]	477 (171)	347 (147)		1·06, 1·48 (42)
$[Co(\alpha\ tet)(H_2O)_2]^{3+}$	491 (164)	367 (140)		
$[Co(\gamma\ tet)(H_2O)_2]^{3+}$ [l]	495 (160)	365 (141)		
$[Co(\alpha\ tet)CO_3]^+$ [m]	506 (133)	362 (153)		0·88, 1·71 (29)
$[Co(\gamma\ tet)CO_3]^+$ [m]	520 (127)	374 (152)		0·95

[a] Band maxima in nm. Molecular extinction coefficient (l mol^{-1} cm^{-1}) in parentheses. Solutions in methanol unless otherwise indicated. [b] Measured at 60 MHz in p.p.m. downfield from TMS as internal standard, in formic acid except for the carbonato-complexes, which were in dimethyl sulphoxide. Separation between components of methyl doublet in parentheses (in 0·1 p.p.m.). [c] $^1E_g \longleftarrow {}^1A_{1g}$. [d] $^1A_{2g} \longleftarrow {}^1A_{1g}$. [e] $^1B_{2g} + {}^1E_g \longleftarrow {}^1A_{1g}$, all in D_{4h}. [f] $^1A_2 + {}^1B_1 + {}^1B_2 \longleftarrow {}^1A_1$ in C_{2v} derived from $^1T_{1g} \longleftarrow {}^1A_{1g}$ in O_h. [g] $^1A_1 + {}^1B_1 + {}^1B_2 \longleftarrow {}^1A_1$ in C_{2v} derived from $^1T_{2g} \longleftarrow {}^1A_{1g}$ in O_h. [h] In methanol containing HCl. [i] In methanol containing HBr. [j] In 1M-HCl. [k] acac Methyl resonance at 2·20 p.p.m. [l] From the dichloride, in 1M-HClO$_4$,0·5M Hg(ClO$_4$)$_2$. [m] In dimethyl sulphoxide.

TABLE 2

Cobalt *d–d* spectra and magnetic susceptibilities of cobalt(III)(tet) derivatives with complex cobalt(II) anions

Compound	Reflectance spectrum (nm)			Magnetic susceptibilities	
	Bands assigned to Co^{III}		Bands assigned to Co^{II}	$10^3\chi_M$ [a]	μ_{eff}(B.M.) [b]
trans-$[Co(\beta\ tet)Cl_2]_2CoCl_4,H_2O$	28·9(?)	22·9(sh)	15·5, 14·7, 14·3; 5·9, 5·4, 4·8	9·09	4·60
trans-$[Co(\beta\ tet)Br_2]_2CoBr_4$	26·4	21·5(sh)	15·6(sh), 15·1, 14·2; 5·5, 4·9(sh)	9·42	4·69
trans-$[Co(\beta\ tet)(NCS)_2]_2Co(NCS)_4$	27·1	19·3	17·1(sh), 16·1; 7·6	8·97	4·63

[a] At 298·7 K. [b] Calculated assuming Curie Law, with corrections for diamagnetism and temperature independent paramagnetism.

derivatives are listed in Table 1 (the remainder of the spectrum was poorly resolved). The *trans*-derivatives, β or γ, show two methyl resonances, separation *ca.* 0·15 p.p.m. The *cis*-derivatives, except for $[Co(\gamma\ tet)CO_3]^+$, also show two methyl resonances, separation *ca.* 0·35 p.p.m. (The diammine spectrum resembles that of *cis*-, rather than *trans*-derivatives.) The γ carbonato-complex shows a single methyl resonance.

TABLE 3

Cobalt(III) *d–d* spectra of some tetra-amine derivatives [a]

Amine(N_4)	*trans*- $[Co(N_4)Cl_2]^+$	*cis*- $[Co(N_4)Cl_2]^+$	*cis*- $[Co(N_4)CO_3]^+$	*cis*- $[Co(N_4)C_2O_4]^+$
β tet [b]	606, 424			493, 356
α tet [b]		531	506, 362	
γ tet [b]	618, 425		520, 374	
cyclam [c]	638, 441	558		
cyclen [d]		560, 390	530, 368	520, 355
tet *b* [e]	645, *ca.* 470		552, 383	
trien [f]	615, 450 [g]	535, 395 [h]	507, 358 [i]	498, 357 [j]
$(en)_2$	622, 456 [k]	535, 390 [c]	515, 364 [m]	500, 355 [j]
$(NH_3)_4$	628, 477 [k]	540 [l]	520, 363 [m]	510, 357 [j]

[a] See Table 1 for assignments. [b] This work. [c] Ref. 3. [d] Ref. 6. [e] Ref. 4. [f] Folded trien derivatives in the β (*abcd*) configuration, which is analogous to that of folded cyclic tetra-amines. [g] H. G. Hamilton and D. M. Alexander, *Inorg. Chem.*, 1966, **5**, 2060. [h] A. M. Sargeson and G. M. Searle, *Inorg. Chem.*, 1967, **6**, 787. [i] G. H. Searle, Ph.D. Thesis, Australian National University, 1963. [j] G. R. Brubaker and O. P. Schaefer, *Inorg. Chem.*, 1971, **10**, 968. [k] R. A· Wentworth and T. S. Piper, *Inorg. Chem.*, 1965, **4**, 709. [l] R. C. Brasted and C. Hirayama, *J. Phys. Chem.*, 1959, **63**, 780. [m] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1956, **29**, 311.

The methyl doublet is consistent with the presence of a chair-conformation six-membered chelate ring, with the two methyl groups in equatorial and axial sites (as observed for $[Ni(\beta\ tet)](ClO_4)_2)$.[5] The similarity of the spectra for the *trans*-β and -γ derivatives suggest that the six-membered chelate ring adopts the same conformation in the two series. The similarity of the ^1H n.m.r. spectra of the *cis*-derivatives, except for the γ carbonato-complex, suggest that they have the same, α configuration, which again has the six-membered chelate ring in a chair conformation. The single methyl resonance observed for the γ carbonato-complex is consistent with the presence of a twist-conformation six-membered ring, which places the methyl groups in equivalent sites. These results are discussed in terms of the amine configurations, below.

Magnetic Susceptibility Measurements.—The magnetic susceptibilities of the compounds with complex cobalt(II) anions are listed in Table 2.

STEREOCHEMISTRY

Co-ordination Geometry.—An important property of any cyclic tetra-amine as a ligand is the relative stability of co-ordination compounds with the amine in 'planar' (*bcde*-octahedral, *trans*-disubstituted) and in 'folded' (*abcd*-octahedral, *cis*-disubstituted) co-ordination. This is determined by three main factors: (i) the relative energies of the cyclic amine skeleton in the two arrangements, (ii) interactions involving any substituents on the skeleton, and (iii) interactions involving 'additional' ligands.

(i) The energy difference between different arrangements of the cyclic amine arises from differing strain energy when the donor atoms are constrained to occupy the specified co-ordination sites. Favoured arrangements will permit as many chelate rings as possible to adopt optimum gauche (five-membered) or chair (six-membered) conformations with minimum distortion of the donor atoms from the regular octahedral co-ordination sites. The importance of the latter term will vary with the metal ion, but for cobalt(III) it will be significant. These factors will, in general, differ for the possible configurations arising from the four chiral nitrogen centres, and different configurations will usually be optimum for planar and for folded co-ordination (see below). The reported differences between the co-ordination properties of 1,5,8,11-tetra-azacyclotetradecane (cyclam), with alternating five- and six-membered chelate rings and 1,4,7,10-tetra-azacyclododecane (cyclen),[6] with four linked five-membered chelate rings, arise from these effects. For cyclam with cobalt(III), both planar and folded derivatives have been prepared, the planar arrangement generally being preferred.[3] For cyclen only folded complexes have been reported.[6] 1,5,8,11-Tetra-azacyclotridecane, with the 6–5–5–5-membered chelate ring system would be expected to have properties intermediate to those of cyclam and cyclen.

(ii) Substituents on the carbon skeleton of the amines can have considerable effect on the relative stabilities of planar and folded co-ordination. For the 5,7,7,12,14,14-hexamethyl-derivative of cyclam, the folded arrangement is very much more stable for the *C-rac*-isomer, (tet *b*), than for the *C-meso*-isomer, (tet *a*), the effect essentially arising from non-bonded interactions of the methyl substituents.[7] For (tet) in folded co-ordination in the optimum skeletal configuration, one methyl group is in a 1,3-diaxial relationship to a bridging methylene group (below) and this probably makes folded derivatives relatively less stable than for the unsubstituted tetra-azacyclotridecane.

(iii) The folded arrangement of the amine would be expected to be most stable when the two *cis*-additional co-ordination sites were occupied by a chelate, particularly one such as bidentate CO_3^{2-} which occupies a small volume in the co-ordination sphere.

For Co^{III} with cyclam, a number of *cis*-diacido-derivatives have been prepared from the chelate carbonato-complex, and these isomerise to the stable *trans*-form only with inversion of the nitrogen configuration.[3] With (tet *b*), folded co-ordination to Co^{III} is observed only with chelates; treatment of the carbonato-complex with HCl yields the *cis*-dichloro species as a transient which rapidly isomerises to the

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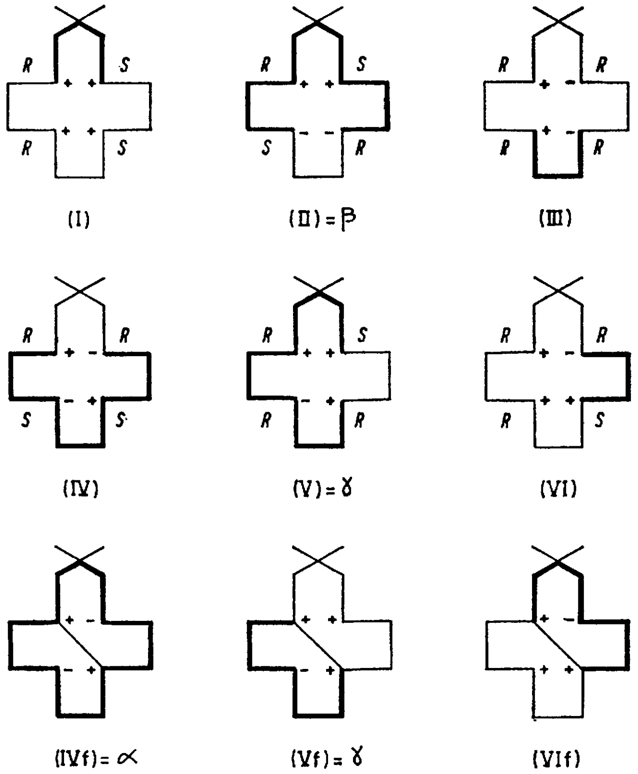
[5] J. M. Waters and K. R. Whittle, *J. Inorg. Nuclear Chem.*, 1972, **34**, 155.

[6] J. P. Collman and P. W. Schneider, *Inorg. Chem.*, 1966, **5**, 1380.

[7] P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc.* (*A*), 1970, 1956.

trans-form, with retention of the nitrogen configuration.[4] The methyl substituents on (tet *b*) have accentuated the preference for chelates in folded co-ordination, compared with cyclam. For unidentate ligands, inter-ligand repulsion would be greater for charged acido-ligands than for small neutral ligands, such as water, and thus the expected order of relative stability of *cis*-complexes would be chelates > small neutral ligands > anions.



Configuration of co-ordinated (tet). A plus sign at a chiral nitrogen centre indicates that the secondary amino-hydrogen atom is above the plane of the (flattened) macrocycle, a minus sign that it is below. Configurations based on the *RS* nomenclature are also indicated. Chelate rings shown in light lines are constrained to adopt the unfavourable twist (six-membered) or eclipsed (five-membered) conformations (see ref. 7). Co-ordination is with the nitrogen atoms in square planar *bcde*-sites ('planar' macrocycle), except where the symbol f indicates *abcd*-co-ordination ('folded' macrocycle) with the *bd*-fold-line indicated

Configurational Isomerism.—With four chiral nitrogen centres, co-ordinated (tet) can, in principle, exist in six configurations (Figure). With cobalt(III), compounds with the amine in three of these configurations were isolated.

The β configuration is stable for *trans*-diacido-derivatives and was not observed in folded co-ordination. From models the symmetrical configuration (II) appears most favoured for planar co-ordination. This configuration is present for [Ni(β tet)](ClO$_4$)$_2$.* [5] and a similar arrangement of the nitrogen centres is present for *trans*-[Ni(cyclam)Cl$_2$] [8] and [Ni(γ tet *b*)](ClO$_4$)$_2$.[9] The β series of compounds is therefore assigned configuration (II).

For folded co-ordination of 1,5,8,11-tetra-azacyclotridecane, configuration (IV) would be preferred. This has the optimum arrangement of the nitrogen centres, the pair of NH groups on the fold-line *cis*, the other pair *cis*, and *trans* to the fold-line pair. However, for the 3,3-dimethyl derivative, (tet), this configuration, in the optimum conformation of the skeleton, would place one of the methyl groups in 1,3-diaxial relationship to a bridging methylene group. This arrangement of the nitrogen centres has been found for the three folded 1,4,8,11-tetra-azacyclotetradecane complexes studies; *cis*[Co(cyclam)Cl$_2$]Cl,[10] [Ni(tet *b*)CH$_3$COO]ClO$_4$,[7] and [Ni(tet *a*)acac]ClO$_4$.[9]

The strain inherent in this arrangement could be reduced by distortion of the six-membered chelate ring to a twist-boat conformation,† but the relative stability of this configuration would still be reduced.

After configuration (IVf), configurations (Vf) and (VIf) are next most favoured for folded co-ordination. These have the fold-line NH groups *cis*, the other pair *trans*. For configuration (Vf), the six-membered chelate ring would be constrained to adopt a twist conformation,‡ which would eliminate the methyl–methylene group interaction. Configuration (VIf) does not have this advantage over (IVf).

Therefore, for folded co-ordination of (tet) the choice of configuration lies between (IVf), with the six-membered chelate ring distorted from the optimum chair conformation to reduce methyl–methylene interactions, and (Vf) with the six-membered chelate ring constrained to adopt a twist conformation.

Two isomeric forms of [Co(tet)CO$_3$]$^+$ were isolated, α and γ, and it is reasonable to conclude that these are in the two preferred configurations (IVf) and (Vf). The α carbonato-complex yielded dichloro- and dibromo-derivatives which were stable in the *cis*-configuration, and no *trans* α derivatives were observed. The γ carbonato-complex gave the *cis*-dichloro- and dibromo-derivatives only as transients which rapidly rearranged to the *trans*-isomers. It can be concluded that the α configuration is much more stable in folded than in planar co-ordination, whereas for the β configuration, the two arrangements are closer in stability. Configuration (IV) would be expected to be relatively strained in planar co-ordination, configuration (V) relatively unstrained, and therefore the assignment α = (IV), γ = (V) is made. This assignment is supported by the observed ^{1}H n.m.r. spectra (above). The

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* The structure of [Ni(β tet)](ClO$_4$)$_2$, determined by *X*-ray crystallography, where the β indicates the configuration of the amine stable for square planar co-ordination to nickel(II), reveals configuration (II), with the six-membered chelate ring

† As observed for [Ni(α tet *a*)acac]ClO$_4$ and [Ni(γ tet *b*)](ClO$_4$)$_2$ in similar circumstances.[9]

‡ As observed for [Ni(α tet *b*)]ClO$_4$)$_2$.[9]

β and γ (planar) and α (folded) configurations show methyl resonance doublets, consistent with chair conformation six-membered chelate rings, while the γ (folded) configuration shows a single methyl resonance, consistent with a twist conformation six-membered chelate ring, as expected for the assignment β = (II), α = (IV), γ = (V).

To summarise; of the three configurations observed, β = (II) occurs only in planar co-ordination, is stable for diacido derivatives; α = (IV) occurs in folded co-ordination, is stable for chelates and with neutral ligands; γ = (V) occurs in folded (carbonato) and planar (diacido) co-ordination.

EXPERIMENTAL

(3,3-*Dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*hydroperchlorate Hydrate*, (Htet)$\mathrm{ClO_4,H_2O}$.—(3,3-Dimethyl-1,5,8,11-tetra-azacyclotridec-1-ene)nickel(II) tetrachlorozincate [11] (4·8 g) was reacted with sodium bicarbonate (2 g, 2·4 mol) and the precipitated zinc carbonate filtered off. The imino-group was reduced by adding sodium borohydride (0·6 g, 1·5 mol) at room temperature. After two hours the solution was slowly heated to boiling, filtered, and sodium cyanide (2·2 g, 4·5 mol) added.* The resulting solution was rendered strongly basic with sodium hydroxide and extracted continuously with diethyl ether until the extractant was no longer basic.† The ether was evaporated, the residue dissolved in a small volume of water and divided into two equal portions. One portion was neutralised with perchloric acid, and the portions recombined, when the product crystallised. This was filtered, sucked dry at the pump, and washed with a small volume of propan-2-ol. Yield *ca.* 85%. Further product was obtained by evaporation of the filtrate, total yield quantitative. Samples for analysis, spectra, *etc.*, were recrystallised from a small volume of hot water (Found: C, 40·2; H, 8·8; N, 16·0. $\mathrm{C_{11}H_{27}ClN_4O_4,H_2O}$ requires C, 39·7; H, 8·8; N, 16·8%).

pH Titration.—A solution of (Htet)$\mathrm{ClO_4,H_2O}$ in 0·1M-KCl at 25° was treated with 0·1M sodium hydroxide in small excess and then titrated with 0·1M hydrochloric acid. The pH at the four ' half neutralisation ' points was 11·6, 10·7, 2·7, and 2·3. The observed equivalent weight was 340 (calc. 333).

Complexes with the Amine in the β *Configuration*

trans-*Dichloro*(β-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Perchlorate*, trans-[Co(β tet)$\mathrm{Cl_2}$]$\mathrm{ClO_4}$.—(Htet)$\mathrm{ClO_4,H_2O}$ (5 g) and $\mathrm{Na_3[Co(CO_3)_3],3H_2O}$ [12] (8 g, 1 : 1·5 mol ratio) were stirred in water for 2 h at room temperature. The solution was slowly heated to boiling, filtered, acidified with hydrochloric acid and heated near boiling for *ca.* 30 min, when the colour changed from red to green. Sodium perchlorate was added and the green product which separated on cooling was filtered and washed with cold 1M perchloric acid. Yield 95%. The product was recrystallised by dissolving in hot very dilute aqueous ammonia, filtering, acidifying the hot solution with hydrochloric acid, boiling for several minutes and adding sodium perchlorate. The *product* was filtered from the cold solution, washed with cold 1M perchloric acid, sucked dry, then washed with propan-2-ol (Found: C, 30·1; H, 6·0; Co, 13·5). $\mathrm{C_{11}H_{26}Cl_3CoN_4O_4}$ requires C, 29·8; H, 5·9; Co, 13·3%).

Note.—This product was also formed in *ca.* 65% yield by hydrogen peroxide, or air, oxidation of cobalt chloride plus amine or amine hydroperchlorate. The solution was then treated as for the previous preparation, after the initial filtration.

Other Salts.—*Fluoroborate*, trans-[Co(β tet)$\mathrm{Cl_2}$]$\mathrm{BF_4}$. This was prepared as for the perchlorate, substituting a solution of amine hydrofluoroborate, prepared by half neutralising a solution of the amine with fluoroboric acid (Found: C, 30·7; H, 6·1; Co, 13·6. $\mathrm{C_{11}H_{26}BCl_2CoF_4}$ requires C, 30·7; H, 6·1; Co, 13·7%).

Tetrachlorocobaltate(II) *hydrate*, trans-[Co(β tet)$\mathrm{Cl_2}$]$_2$-$\mathrm{CoCl_4,H_2O}$. This was prepared by air oxidation of amine plus excess cobalt(II) chloride. The resultant brown solution was acidified with hydrochloric acid and evaporated to small volume on a steam-bath. The dark green crystalline *product* separated on cooling, and was recrystallised from hot methanol–water, using hydrochloric acid plus cobalt chloride to reduce the solubility (Found: C, 29·1; H, 6·0; Cl, 31·0; Co, 19·4. $\mathrm{C_{22}H_{54}Cl_8Co_3N_8O}$ requires C, 29·1; H, 6·0; Cl, 31·3; Co, 19·5%).

Tetrachlorozincate(II) *hydrate*, trans-[Co(β tet)$\mathrm{Cl_2}$]$_2$-$\mathrm{ZnCl_4,H_2O}$. This was prepared as for the fluoroborate, using a solution of amine monohydrochloride, precipitating the *product* by the addition of zinc chloride. Recrystallisation was as for the tetrachlorocobaltate (Found: C, 29·2; H, 6·0; Co, 12·6. $\mathrm{C_{22}H_{54}Co_2Cl_8N_8OZn}$ requires C, 28·9; H, 6·0; Co, 12·9%).

trans-*Dibromo*(β-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Perchlorate*, trans-[Co(β tet)$\mathrm{Br_2}$]$\mathrm{ClO_4}$.—This was prepared and recrystallised as for the chloro-analogue, substituting hydrobromic acid for the hydrochloric acid (Found: C, 25·3; H, 4·9; Co, 10·6. $\mathrm{C_{11}H_{26}Br_2ClN_4O_4}$ requires C, 24·8; H, 4·9; Co, 11·1%).

Other Salts.—*Fluoroborate*, trans-[Co(β tet)$\mathrm{Br_2}$]$\mathrm{BF_4}$. As for the dichloro-analogue, substituting hydrobromic acid for the hydrochloric acid (Found: C, 25·6; H, 5·0; Co, 11·4. $\mathrm{C_{11}H_{26}BBr_2CoF_4}$ requires C, 25·4; H, 5·1; Co, 11·4%).

Tetrabromocobaltate(II) *hydrate*, trans-[Co(β tet)$\mathrm{Br_2}$]$_2$-$\mathrm{CoBr_4,H_2O}$. This was prepared and recrystallised as for the chloro-analogue, substituting cobalt bromide and hydrobromic acid for the cobalt chloride and hydrochloric acid (Found: C, 21·8; H, 4·4; Br, 49·2; Co, 14·0. $\mathrm{C_{22}H_{54}Br_8Co_3N_8O}$ requires C, 21·9; H, 4·3; Br, 49·3; Co, 14·0%).

trans-*Dithiocyanato*(β-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Thiocyanate*, trans-[Co(β tet)$\mathrm{(NCS)_2}$]-CNS.—Air was bubbled for 30 min through a solution containing equivalent amounts of cobalt(II) thiocyanate,

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* Isolated $\mathrm{[Ni(tet)]^{2+}}$ derivatives, *e.g.* $\mathrm{[Ni(tet)](ClO_4)_2}$ or $\mathrm{[Ni(tet)_2C_2O_4](ClO_4)_2}$ may be reacted with cyanide in the same manner.

† The ether extract containing the amine, dried over sodium sulphate, was evaporated to yield the amine, which crystallised as a hydrate, and which was purified by vacuum sublimation at 100°. The free amine absorbed water and/or carbon dioxide from the atmosphere and satisfactory analytical results were not obtained. The amine is very soluble in water and organic solvents. The product obtained by slow evaporation in the atmosphere showed i.r. spectral bands indicative of a carbamate, but again analytical results, although in general agreement, were not satisfactory.

[11] D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1964, **86**, 1331.

[12] H. F. Bauer and W. C. Drinkard, *Inorg. Synth.*, 1966, **8**, 202.

and the tetra-amine neutralised (pH 6) with sulphuric acid. Sodium thiocyanate was added and the solution evaporated, when red crystals of the product separated. These were recrystallised from hot methanol (Found: C, 37·5; H, 5·8; Co, 13·0. $C_{14}H_{26}CoN_7S_3$ requires C, 37·6; H, 5·9; Co, 13·2%).

Another Salt.—Tetrathiocyanatocobaltate(II), trans-$[Co(\beta\ tet)(NCS)_2]_2Co(NCS)_4$. As for the previous preparation, except that 2 mol of cobalt thiocyanate was used. The dark green-black *product* was recrystallised from hot methanol (Found: C, 33·7; H, 4·9; Co, 16·6. $C_{30}H_{52}Co_3N_{16}S_8$ requires C, 33·7; H, 4·9; Co, 16·5%).

trans-*Diazido*(β-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Fluoroborate*, trans-$[Co(\beta\ tet)(N_3)_2]BF_4$.—Sodium azide was added to a solution of *trans*-$[Co(\beta\ tet)Cl_2]BF_4$ in hot dilute aqueous ammonia, and the solution rendered just acid with fluoroboric acid. The dark green product was filtered from the cold solution and recrystallised from hot methanol–water (Found: C, 29·5; H, 6·1; Co, 13·3. $C_{11}H_{26}BCoF_4N_{10}$ requires C, 29·7; H, 5·9; Co, 13·3%). The sparingly soluble perchlorate was prepared analogously.

trans-*Diacetato*(β-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Perchlorate*, trans-$[Co(\beta\ tet)(CH_3CO_2)_2]ClO_4$.—$[Co(\alpha\ tet)CO_3]ClO_4$ was dissolved in a small volume of glacial acetic acid by heating and hot propan-2-ol added to the filtered solution until just turbid. The solution was stoppered and red crystals separated over several days. It was hoped that the product would be the acetato-chelate complex, but the *product* is the *trans*-diacetato complex (Found: C, 36·8; H, 6·6; Co, 11·8. $C_{15}H_{32}ClCoN_4O_8$ requires C, 36·7; H, 6·6; Co, 12·0%). The same product is obtained by reaction of *trans*-$[Co(\beta\ tet)Cl_2]ClO_4$ with sodium acetate in aqueous solution, but was obtained crystalline from water only with difficulty.

Complexes with the Amine in the α Configuration

cis-*Carbonato*(α-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Perchlorate*, cis-$[Co(\alpha\ tet)CO_3]ClO_4$.*—*trans*-$[Co(\beta\ tet)Cl_2]ClO_4$ and $MgCO_3$ were heated together in a small volume of water and the resultant red solution filtered from the excess $MgCO_3$. A vermilion hydrate of the product separated on cooling and was recrystallised from a small volume of hot water. Hydration was variable (*ca.* 2), so the anhydrous *compound* (dehydrated at 100° *in vacuo* over P_2O_5) was analysed (Found: C, 33·1; H, 6·3; N, 12·9. $C_{12}H_{26}ClCoN_4O_4$ requires C, 33·3; H, 6·1; N, 12·95%). This compound crystallises if the solution resulting from the reaction of $(Htet)ClO_4,H_2O$ and $Na_3Co(CO_3)_3,3H_2O$ is evaporated to small volume and allowed to stand.

cis-*Dichloro*(α-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Chloride*, cis-$[Co(\alpha\ tet)Cl_2]Cl$.—$[Co(\alpha\ tet)CO_3]ClO_4$, was dissolved in a small volume of concentrated hydrochloric acid to form a purple solution. The filtered solution was diluted with several volumes of acetone and the purple crystals filtered and washed with acetone after one day. The *product* so obtained was shown by analysis to contain 0·5 mol of acetone, confirmed by the presence of a sharp ν(CO) band at 1720 cm^{-1} in the i.r. spectrum. If propan-2-ol was substituted for the acetone, the *product* was shown by analysis to contain 0·5 mol of propan-2-ol, the ν(CO) band being absent from the i.r. spectrum, but a broad band *ca.* 3600 cm^{-1}, was assigned as ν(OH) of the propan-2-ol. The presence of the acetone or propan-2-ol was supported by the ^1H n.m.r. spectrum (Found, acetone solvate: C, 36·5; H, 7·2; Cl, 26·0; N, 13·9; Co, 14·4. $C_{16}H_{26}Cl_3CoN_4,0{\cdot}5C_3H_6O$ requires C, 36·8; H, 7·2; Cl, 26·1; N, 13·7; Co, 14·4. Found, propan-2-ol solvate: C, 36·6; H, 7·7; N, 13·5. $C_{11}H_{26}Cl_3CoN_4,0{\cdot}5C_3H_8O$ requires C, 36·7; H, 7·4; N, 13·7%).

cis-*Dibromo*(α-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Bromide*, cis-$[Co(\alpha\ tet)Br_2]Br$.—As for the *cis*-dichloro-compound, substituting hydrobromic for the hydrochloric acid. The product is brown. *Solvates* with acetone and propan-2-ol were characterised by analysis and the presence of ν(CO) and ν(OH) bands as for their chloro-analogues (Found, acetone solvate: C, 28·2; H, 5·5; Br, 44·7; N, 10·3; Co, 11·7. $C_{16}H_{26}Br_3CoN_4,0{\cdot}5C_3H_6O$ requires C, 27·7; H, 5·4; Br, 44·3; N, 10·4; Co, 10·9. Found, propan-2-ol solvate: C, 27·9; H, 5·6 $C_{11}H_{26}Br_3CoN_4,0{\cdot}5C_3H_8O$ requires C, 27·7; H, 5·6%).

cis-*Diaminoethane*(α-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Chloride Hydrate*, $[Co(\alpha\ tet)en]Cl_3,H_2O$.—The *cis*-dichloro-chloride was dissolved in a small volume of hot methanol (forming a solution of the green *trans*-dichloro-complex), and a slight excess of diaminoethane was added, followed by several volumes of propan-2-ol. The orange crystalline *product* was filtered off after 24 h and recrystallised from hot methanol (Found: C, 34·2; H, 7·7; Co, 12·7. $C_{13}H_{36}Cl_3CoN_6$ requires C, 34·1; H, 7·9; Co, 12·9%).

cis-*Diammine*(α-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Chloride*, cis-$[Co(\alpha\ tet)(NH_3)_2]Cl_3$.—The *cis*-dichloro-chloride was dissolved in a small volume of warm conc. ammonia and the resultant yellow solution diluted with several volumes of propan-2-ol. The yellow crystalline *product* was filtered and washed well with propan-2-ol (Found: C, 31·4; H, 7·8; Co, 13·9. $C_{11}H_{32}Cl_3CoN_6$ requires C, 31·9; H, 7·8; Co, 14·3%).

cis-*Oxalato*(α-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)-*cobalt*(III) *Perchlorate*, $[Co(\alpha\ tet)C_2O_4]ClO_4$.—$[Co(\alpha\ tet)CO_3]ClO_4,H_2O$ and oxalic acid (1 : 1·2 mol) were heated in a small volume of water near boiling for 30 min, then acidified with $HClO_4$. The vermilion *product* was filtered from the cold solution and recrystallised from a small volume of hot water by the addition of perchloric acid (Found: C, 33·9; H, 5·9; Co, 11·7. $C_{13}H_{26}ClCoN_4O_8$ requires C, 33·9; H, 5·8; Co, 11·4%).

cis-*Acetylacetonato*(α-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Diperchlorate Hydrate*, $[Co(\alpha\ tet)acac](ClO_4)_2,H_2O$.—*trans*-$[Co(\beta\ tet)Cl_2]ClO_4$ was dissolved in a small volume of hot dilute aqueous ammonia, acetylacetone in small excess added, and the solution refluxed for 30 min. The red *product* was isolated and recrystallised as for the oxalato-compound (Found: C, 33·1; H, 6·1; Co, 10·1. $C_{16}H_{35}Cl_2CoN_4O_{11}$ requires C, 32·7; H, 6·0; Co, 10·0%).

Complexes with the Amine in the γ Configuration

cis-*Carbonato*(γ-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Perchlorate*, cis-$[Co(\gamma\ tet)CO_3]ClO_4$.*—The α isomer was recrystallised from hot methanol. Crimson crystals of a variable hydrate of the *product* were filtered after several days, washed with cold ethanol, and dehydrated

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* The α and γ carbonato-perchlorates prepared by these procedures sometimes contained appreciable amounts of the other isomer as impurity. However the preparation of the α *cis*-dichloro-chloride, or γ *trans*-dichloro-perchlorate (or their bromo-analogues) gave isomerically pure products.

at 100° *in vacuo* over P_2O_5 (Found: C, 33·3; H, 6·6; N, 12·9. $C_{12}H_{26}ClCoN_4O_7$ requires C, 33·3; H, 6·1; N, 12·95%).

trans-*Dichloro*(γ-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Perchlorate*, trans-[Co(γ tet)Cl_2]ClO_4.—The γ-carbonato-perchlorate was dissolved in a small volume of concentrated hydrochloric acid, the solution filtered and several volumes of warm 1M perchloric acid added, when the green *product* crystallised. This was filtered from the cold solution and washed with cold 1M perchloric acid, followed by propan-2-ol (Found: C, 30·0; H, 5·9; N, 12·1; Co, 13·2. $C_{11}H_{26}Cl_3CoN_4O_4$ requires C, 29·8; H, 5·9; N, 12·6; Co, 13·3%).

trans-*Dibromo*(α-3,3-*dimethyl*-1,5,8,11-*tetra-azacyclotridecane*)*cobalt*(III) *Perchlorate Dihydrate*, trans-[Co(γ tet)Br_2]-ClO_4,$2H_2O$.—As for the dichloro-analogue (previous preparation) substituting hydrobromic for the hydrochloric acid (Found: C, 23·6; H, 5·2; Co, 10·8. $C_{11}H_{30}Cl_3CoN_4O_5$ requires C, 23·3; H, 5·3; Co, 10·4%).

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