Some Cyclic Tetra-amines and Their Metal-ion Complexes. Part VIII.[1] Complexes of Rhodium(III) with *C-rac-* and *C-meso-*5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetra-azacyclotetradecane †

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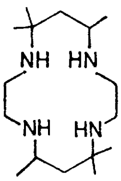
The preparations of complexes of rhodium(III) with the cyclic tetra-amines *C-rac-* and *C-meso-*5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane are reported. For both isomers, *trans*-diacido-derivatives were prepared. For the *C-rac*-isomer a series of derivatives with the amine in folded (*a,b,c,d*) co-ordination, with a chelate or *cis*-unidentate ligands in the two additional co-ordination sites, was also prepared. Configurational isomerism of the complexes arising from the four chiral nitrogen centres present is reported.

PREPARATIONS have been reported of diacido tetra-amine complexes of rhodium, with bis-diaminoethane [2] and *C*-methyl diaminoethanes,[2,3] *N*-methyl diaminoethanes,[4,5] triethylenetetra-amine [3,6] and its analogue 1,4,8,11-tetra-azaundecane,[7] 2,2′,2″-triaminotriethylamine (tren),[3] and the cyclic tetra-amines 1,4,7,10-tetra-azacyclododecane (cyclen),[8] and 1,4,8,11-tetra-azacyclotetradecane (cyclam).[9] Complexes of the isomeric cyclic tetra-amines C-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane = (teta), and the *C-rac*-isomer = (tetb) with nickel(II),[10,11] copper(II),[10,12] and cobalt(III) [13] have been described. In this paper rhodium(III) complexes of these amines are reported.



C-meso-isomer = teta
C-rac - isomer = tetb

Johnson and Basolo [3] prepared a number of dichlorobis(diaminoethane)rhodium(III) derivatives by progressively neutralizing a refluxing solution of the amine hydrochloride and rhodium trichloride; isolating both *cis*- and *trans*-isomers by this procedure for diaminoethane, and 1,1,2,2-tetramethyldiaminoethane, 2,3-dimethyl-2,3-diaminobutane. With *meso*- and *rac*-tetramethylenediamine only the *trans*-isomer was isolated, while for triethylenetetra-amine and 2,2′,2″-triaminotriethylamine only the *cis*-isomer was isolated. Bosnich, Gillard, McKenzie, and Webb [7] isolated only the *trans*-dichloro-derivative of 1,4,8,11-tetra-azaundecane when the amine was treated with *trans*-$[Rh(py)_4Cl_2]Cl$, or $RhCl_3,3H_2O$; this is in contrast to the case with triethylenetetra-amine (1,4,7,10-tetra-azadecane) [3,6] where only the *cis*-isomer was isolated, showing the importance of steric constraints for these ligands. Using a precedure similar to that of Johnson and Basolo, Collman and Schneider [8] were able to prepare only the *cis*-dichlororhodium(III) complex with cyclen. [This amine formed only *cis*, folded macrocycle, derivatives with cobalt(III) also.[8]] Bounsall and Koprich found that cyclam reacts rapidly with $RhCl_3,3H_2O$ to give almost entirely the *cis*-dichloro-complex in water, but 60% *trans*, 30% *cis* dichloro-isomers in methanol.[9] The *cis*-diacido tetra-amine complexes that have been described generally have two unidentate ' additional ' ligands, although the preparation of oxalatobis(diaminoethane)rhodium(III) has been reported.[14]

With cyclam, complexes with cobalt(III),[15] rhodium(III),[9] and chromium(III) [16] have been prepared with the amine in planar (*bcde*) and in folded (*abcd*) co-ordination, generally with unidentate ligands in the remaining sites. The six methyl substituents which distinguish (teta) and (tetb) from cyclam have important stereochemical effects. When co-ordinated to nickel(II) [10] or cobalt(III),[13] complexes of (tetb) with the amine in planar and in folded co-ordination are of comparable stability, the former generally being more stable with unidentate ' additional ' ligands, the latter with chelates; for complexes of (teta), planar co-ordination is much more stable than folded co-ordination. A series of nickel(II) complexes with (teta) in folded co-ordination has recently been

† In Part VII, these compounds (*C-rac-* and *C-meso-*) were incorrectly numbered as 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane and abbreviated to tet *b* and tet *a*.

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[13] P. O. Whimp and N. F. Curtis, *J. Chem. Soc.* (*A*), 1966, 867, 1821.
[14] T. P. Dasgupta, R. M. Milburn, and L. Damrauer, *Inorg. Chem.*, 1970, **9**, 2789.
[15] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102; 1966, **5**, 1515; C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1967, 2069; 1968, 1549.
[16] J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta*, 1970, **4**, 109.

prepared, but these are all much less stable than their (tetb) analogues.[17] With cobalt(III), $[Co(teta)(acac)]^+$ (acac = enolate ion of acetylacetone) is the only *cis*-complex as yet prepared.[17] The stereochemical differences between the isomers in folded co-ordination has been revealed by *X*-ray structural studies on $[Ni(tetb)CH_3CO_2]ClO_4$ [18] and $[Ni(teta)(acac)]ClO_4$.[17] For the (tetb) compound both six-membered chelate rings adopt the optimum chair conformation, with one axial and two equatorial methyl substituents. For the (teta) compound, this conformation would result in 1,3-diaxial methyl substituents on one of the six-membered chelate rings. Strain is relieved by distortion to a twist-boat conformation, which places the methyl substituents in sites very similar to those of the other (chair-conformation) six-membered rings. The strain inherent in this chelate-ring conformation, combined with the reverse situation for planar co-ordination [(teta) less strained than (tetb)] accounts for the differences in co-ordination stereochemistry.[17,18]

Rhodium(III) *Complexes of* (*teta*) *and* (*tetb*).—When rhodium trichloride was heated with the dihydroperchlorates of (teta) or (tetb) in aqueous solution, reaction occurred slowly to yield the *trans*-dichloro-complexes, with some deposition of metallic rhodium. When the reaction with (tetb) was carried out using the amine trihydrochloride, or the dihydroperchlorate in the presence of additional chloride, a sparingly soluble product of stoicheiometry $Rh(tetb)Cl_3$ was formed in *ca.* 40% yield, together with the *trans*-dichloro-complex. The compound $Rh(tetb)Cl_3$ was readily converted into, and reformed from, unambiguously *cis*-compounds, and is considered to have a *cis*, folded amine, structure.

trans-*Diacido-derivatives*.—*trans*-Dibromo-, di-iodo-, and dithiocyanato-rhodium(III) derivatives of (teta) and (tetb) were prepared from the dichloride by anion substitution. The *trans*-diacetato-derivative of (teta) was prepared by reaction with silver acetate. The *trans*-diacido(cyclam)rhodium(III) complexes were reported to undergo easy base hydrolysis, leading to the hydroxo-aquo and various acido-hydroxo and acido-aquo derivatives.[9] Under similar conditions the *trans*-dichloro-complexes of (teta) and (tetb) appeared, from the colour changes, to undergo hydrolysis, but no crystalline derivatives could be isolated. Attempts to prepare ammine derivatives by reaction with aqueous ammonia, as reported for *trans*-dichlorobis(diaminoethane)rhodium(III),[3] were also unsuccessful.

cis-*Derivatives of* (*tetb*).—The low solubility of the compound of composition $Rh(tetb)Cl_3$ suggests that it is not the simple *cis*-dichloro-chloride, *cis*-$[Rh(tetb)Cl_2]Cl$, since salts of these large cations with small anions, such as chloride, are generally very soluble (*cf.* *trans*-$[Rh(teta)Cl_2]Cl$, Experimental section). Moreover, the compound crystallized in the presence of an excess of perchlorate ions, whereas the perchlorate salts of these cations are generally much less soluble than the chlorides. Analogous tribromo- and tri-iodo-compounds were prepared and these also crystallized in the presence of perchlorate. The solubility properties suggest that all three halide ions have specific structural roles in a strongly hydrogen-bonded, or perhaps chloro-bridged polymeric arrangement [*cf.* sparingly soluble $Rh(1,1,2,2\text{-tetramethyldiaminoethane})Cl_3$].[3]

The compound $Rh(tetb)Cl_3$ is readily soluble in aqueous carbonate, and the chelate carbonato-complex cation *cis*-$[Rh(tetb)CO_3]^+$ was isolated with a variety of anions. This complex dissolves in a variety of acids, with evolution of carbon dioxide, to form *cis*-derivatives. With hydrochloric, hydrobromic, or hydroiodic acids, the trihalides were formed.

With oxalic acid the chelated oxalato-complex *cis*-$[Rh(tetb)C_2O_4]^+$ was formed. With nitric acid a sparingly soluble compound of composition $Rh(tetb)(NO_3)_3$ was formed. The i.r. spectra of these two compounds are very similar to their cobalt(III) analogues, and they are assigned analogous structures. Thus the nitrate shows i.r. bands assignable to ionic and bidentate nitrate ions, corresponding with the structure *cis*-$[Rh(tetb)NO_3](NO_3)_2$. When the compound was re-crystallized in the presence of a very large excess of perchlorate ions, a product was obtained which showed bands in the i.r. spectrum assignable to ionic perchlorate, with reduction in relative intensity of the bands assignable to ionic nitrate. Once again the much lower solubility of a nitrate, compared with a perchlorate salt, is unusual and suggests some specific structural role for the ' ionic ' nitrate.

From a solution of $[Rh(tetb)CO_3]ClO_4,H_2O$ in perchloric acid, a compound of composition $Rh(tetb)(ClO_4)_3$,-$2H_2O$ was isolated. This is tentatively formulated as an analogue of the nitrate, $[Rh(tetb)ClO_4](ClO_4)_2,2H_2O$ (see i.r. spectra, below).

The carbonato-complex dissolved readily in acetic acid, and a crystalline tetraphenylborate of composition $[Rh(tetb)(CH_3CO_2)OH]BPh_4,3H_2O$ was isolated. The i.r. spectrum (below) confirmed the presence of hydroxide, and unidentate acetate. The formation of this compound can be rationalized by consideration of the co-ordination properties of the acetate ion. For divalent metal ions, acetate can function as a bidentate ligand, *e.g.* $[Ni(tetb)CH_3CO_2]ClO_4$.[18] For cobalt(III) complexes of (tetb), a variety of chelate oxy-anion derivatives were prepared, *e.g.* $[Co(tetb)NO_3]^+$ and $[Co(tetb)CO_3]^+$.[13] However when the latter species was reacted with acetic acid, only the *trans*-diacetato-derivative was isolated. When $[Rh(tetb)CO_3]^+$ dissolves in acetic acid, congestion in the co-ordination sphere probably prevents formation of the *cis*-diacetato-derivative, while the resistance of rhodium(III) compounds to geometrical isomerization prevents formation of the *trans*-diacetato-complex, as happens for the cobalt(III) case. Therefore a *cis*-aquo-acetato-complex is formed,

[17] N. F. Curtis, T. N. Waters, and D. A. Swann, to be published.

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

but the high acidity of the co-ordinated water, accentuated by crowding in the co-ordination sphere, combined with a higher lattice energy for the tetraphenylborate salt with a large singly charged anion and cation, causes crystallization of the *cis*-hydroxyacetato-complex tetraphenylborate, even from acid solution, or in the presence of an excess of tetraphenylborate.

Addition of thiocyanate to a solution of $[Rh(tetb)CO_3]^+$, prepared by dissolving $Rh(tetb)Cl_3$ in carbonate solution caused precipitation of $[Rh(tetb)CO_3]NCS,H_2O$. If the suspension was heated, rapid conversion to *cis*-$[Rh(tetb)(NCS)_2]CNS,0{\cdot}5H_2O$ occurred. The same compound was formed by addition of thiocyanate to a solution of $[Rh(tetb)CO_3]ClO_2$, in acetic acid. In the presence of an excess of perchlorate the salt *cis*-$[Rh(tetb)(NCS)_2]ClO_4$ crystallized, and recrystallization from hydrochloric acid formed *cis*-$Rh[(tetb)(NCS)_2]Cl$ confirming the ionic structural role of the third thiocyanate ion.

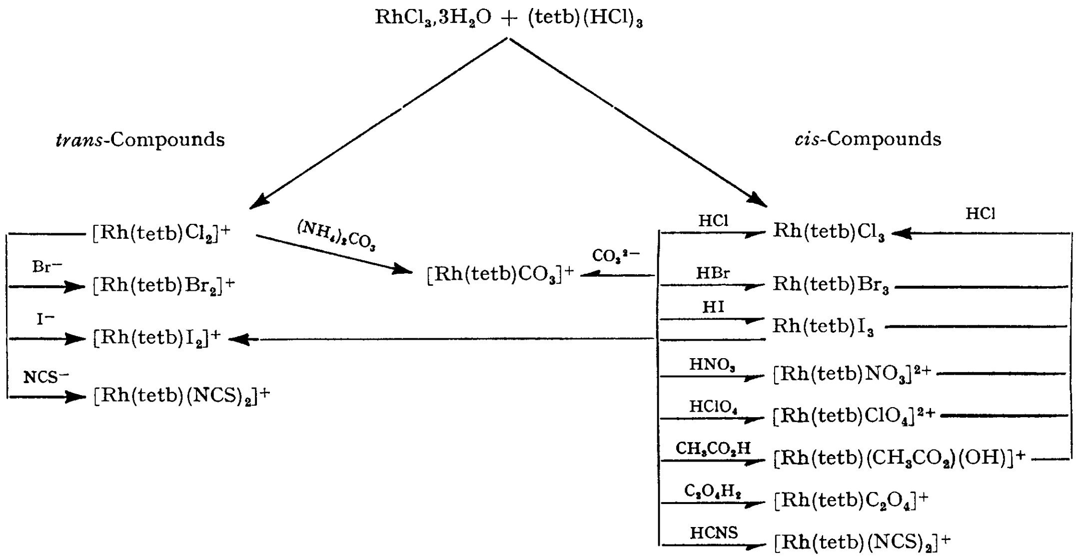
Substitution reactions of the *cis*-complexes are quite rapid, in contrast to the reactions of the *trans*-complexes. Thus when thiocyanate or chloride was added to a solution of the acetato-complex, prepared by dissolving the carbonato-complex in acetic acid, the products *cis*-$[Rh(tetb)(NCS)_2]NCS,0{\cdot}5H_2O$ or $Rh(tetb)Cl_3$ crystallized in seconds, while the reverse reaction with carbonate was equally rapid.

Attempts to prepare chelate acetylacetonato, glycinato, and diaminoethane derivatives were unsuccessful, the carbonato-complex being isolated in each case.

Reactions of *cis*- and *trans*-Rh(tetb) complexes are summarized in the Scheme.

Geometrical Isomerization.—Rhodium(III) complexes are generally much more resistant to geometrical isomerization than their cobalt(III) analogues, and for diacido(tetra-amine)rhodium(III) complexes such transformations are not common. Johnson and Basolo report the conversion of *cis*-$[Rh(en)_2I_2]^+$ into the *trans*-isomer in aqueous solution, $t_{\frac{1}{2}}$ at room temperature *ca.* 3 days.[3] The *cis*-di-iodo cyclam complex also isomerizes slowly to give the *trans*-isomer.[9] Milburn reports the formation of oxalato-bis(diaminoethane)rhodium(III) in low yield by reactions of the *trans*-dichloro-complex with oxalate.[14]

For the tetra-amine complexes, *cis*–*trans* geometrical isomerization involves a planar to folded re-arrangement of the macrocycle and may require inversion at one or more of the secondary amine centres, depending on the particular configuration present (below). One example of *cis* to *trans* isomerism and one of *trans* to *cis* isomerism were observed for the rhodium(III) (tetb) complex. The *cis*-complex $Rh(tetb)I_3$ was slowly converted into *trans*-$[Rh(tetb)I_2]I$ when an aqueous suspension was maintained at 100° for several hours. The low solubility prevented determination of the rate, but it appears to be much slower than for the $[Rh(en)_2I_2]^+$ case (above).



SCHEME

A reverse *trans* to *cis* change occurred when *trans*-$[Rh(tetb)Cl_2]^+$ was heated in a sealed tube in ammonium carbonate solution at 120° for 3 days, *cis*-$[Rh(tetb)CO_3]^+$ being formed in moderate yield, with appreciable decomposition.

Configurational Isomerism.—The cyclic amine 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane has two chiral carbon centres, the configurations of which distinguish (teta), *meso*, from (tetb), *rac*. When co-ordinated to a metal ion, the four secondary amine nitrogen atoms also became chiral centres, and complexes of (teta) and (tetb) can each, in principle, exist in ten non-enantiomorphic configurations. These will, in general, differ in relative energy,[11,18] and different configurations will be optimum for planar and for folded co-ordination.[18] Interconversion of the configurations requires inversion at one or more co-ordinated secondary amino-groups. This process is pH dependent, being virtually inhibited in strongly acidic solution, and rapid under basic conditions. Thus metastable species with non-optimum configuration can be preserved in the solid, or in acidic solution. For nickel(II) and cobalt(III) such metastable species have been prepared, utilizing the fact that different configurations are optimum for planar and folded co-ordination. For example, treatment of *cis*-[Co(α tetb)CO_3]$^+$ with hydrochloric acid yields *trans*-[Co(α tetb)Cl_2]$^+$, metastable with respect to *trans*-[Co(β tetb)Cl_2]$^+$, geometrical isomerization at the cobalt(III) being much more rapid than nitrogen inversion under these conditions.[19] For rhodium(III) the very much slower rate of geometrical isomerization prevented preparation of metastable species by this mechanism. However, with both (teta) and (tetb), reaction of the diprotonated amine with rhodium trichloride in water, essentially acidic conditions, yielded the *trans*-dichloro-complex in a metastable form. These could be retained in acid, but in basic solution were rapidly converted to stable isomeric forms. The isomers differed in their i.r. spectra, particularly in the 1300—650 cm^{-1} region (this was the most convenient method of identification), in colour (stable form paler yellow than the metastable form), details of visible spectra, *X*-ray diffraction patterns, and in solubilities (stable perchlorate salts less soluble than the metastable salts).

The relative stabilities of the possible configurations of the complexes of these amines have been discussed,[11,18] and the structures of a number of the nickel(II) complexes determined by *X*-ray crystallography.[17,18] For folded co-ordination of (tetb), configuration 9 = α * as found for [Ni(α tetb)CH_3CO_2]ClO_4,[18] is optimum, and the *cis*-Rh(tetb) derivatives are assigned this configuration. For planar co-ordination of (teta), configuration 16 = β is optimum, and the stable Rh(teta) derivatives are assigned this configuration. For planar co-ordination of (tetb) the situation is less clear-cut, the stable form of square-planar [Ni(tetb)]$^{2+}$ depending upon the anion present, being 1 = β for [Ni(β tetb)]$ZnCl_4$,H_2O and 7 = γ for [Ni(γ tetb)]$(ClO_4)_2$.[17] For convenience the stable form is designated β, although ' pseudo-centric ' configuration 9 may well be favoured over ' basket ' configuration 1 for *trans*-octahedral co-ordination. In view of the vigorous conditions involved in the anion substitution reactions, the *trans*-diacido-complexes formed from the *trans*-dichloro-complexes will all be in their stable β-configurations.

The metastable forms of *trans*-[Rh(teta)Cl_2]$^+$ and *trans*-[Rh(tetb)Cl_2]$^+$ are formed by reaction of the metal ion (as a chloro-aquo-species) with the amine in acid solution. Analogous metastable species are similarly formed with Pd^{II},[19] Pt^{II},[19] and Cu^{II}.[12,19] Since the chiral nitrogen centres which distinguish these configurations are generated as the metal–nitrogen bond is formed, it seems probable that the initially formed

TABLE 1

Spectroscopic data

trans-Compounds	Infrared spectra (cm^{-1}) ν(OH) of water	ν(NH)	Rhodium(III) *d–d* Spectra (cm^{-1} × 10^{-3}) [a] ν_1 [b]	ν_2 [c]
[Rh(δ teta)Cl_2]ClO_4		3241m,sp; 3199s,sp	24·2 (110)	32·1sh (*ca.* 40)
[Rh(β tetb)Cl_2]ClO_4		3198s,sp; 3190m,sp	24·4 (80)	32·0sh (*ca.* 50)
[Rh(δ teta)Cl_2]Cl,$5H_2O$	3400—3100vs,vbr	3185s,sp		
[Rh(δ tetb)Cl_2]ClO_4,0·$5H_2O$	3575m,br	3198m,br	24·1 (105)	32·1sh (*ca.* 40)
[Rh(β tetb)Cl_2]ClO_4,0·$5H_2O$	3590w,br	3241vw; 3196s,sp; 3182s,sp	24·4 (90)	31·8sh (*ca.* 40)
[Rh(β teta)Br_2]ClO_4		3208w; 3199s,sp; 3187s,sp; 3177s,sp	23·0 (68)	34·3sh (*ca.* 650)
[Rh(β tetb)Br_2]ClO_4		3191m,sp	23·4 (65)	34·7sh (*ca.* 650)
[Rh(β teta)I_2]I,0·$5H_2O$	3562w; 3425w	3186s,sp	21·0 (70)	27·5 (1900)
[Rh(β tetb)I_2]I,$2H_2O$	3582m,sp; 3428m,sp	3180m,sp; 3164s,sp	21·1 (83)	27·5 (1950)
[Rh(β teta)$(NCS)_2$]CNS,0·$5H_2O$	3560br, 3310br	3180m; 3125m; 3083m	28·3 (1075)	36·0 (3800)
[Rh(β tetb)$(NCS)_2$]CNS,0·$5H_2O$	3450br	3100sh; 3077br	28·8 (1470)	32·7 (3030) 38·3 (3230)
[Rh(β teta)$(CH_3CO_2)_2$]ClO_4,$2H_2O$	3531s,sp; 3410s,sp	3243vw; 3156s,sp; 3102sh	27·6 (120)	35·2sh (*ca.* 120)
cis-Compounds				
Rh(α tetb)Cl_3		3168s,sp; 3037s	27·7 (430)	33·2 (330) [e]
Rh(α tetb)Br_3		3158sp; 3043s	*ca.* 30·0 (240) [f,e]	*d*
Rh(α tetb)I_3		3145sp; 3055s	*ca.* 29	*ca* 32·6 [e]
[Rh(α tetb)CO_3]ClO_4,H_2O	3590m,sp; 3452m,sp	3216s,sp; 3090s	28·5 (500)	35·3 (400) [g]
[Rh(α tetb)C_2O_4]ClO_4		3207s,sp; 3112s,sp	29·3 (480)	35·8sh (*ca.* 260)
[Rh(α tetb)NO_3]$(NO_3)_2$		3225s,sp; 3080s,br	28·8 (350)	35·0 (308)
[Rh(α tetb)$(ClO_4)_2$]ClO_4,$2H_2O$	3480s; 3420s	3236m,sp; 3190s		
[Rh(α tetb)OH(CH_3CO_2)]BPh_4,$3H_2O$	3540s, 3420s	3250vw; 3160s; 3110m,sh	27·6 (340)	*ca.* 30·0 (330)
[Rh(α tetb)$(NCS)_2$]CNS,0·$5H_2O$	3525m; 3450m	3112vs,br	28·7 (1380)	33·9 (2600) 38·5 (3200)

[a] In aqueous solution, molecular extinction coefficients in parentheses. [b] $^1T_{1g} \leftarrow {}^1A_{1g}$ in O_h. [c] $^1T_{2g} \leftarrow {}^1A_{1g}$ in O_h. [d] ν_2 obscured by charge-transfer band. [e] Solutions of these very sparingly soluble compounds were prepared by heating, and some hydrolysis may have occurred. [f] The i.r. spectra, apart from anion bands, were virtually identical for other salts of this cation. [g] Spectrum measured for the more soluble chloride salt.

* The configuration numbers are as in ref. 18. The designation α for the configuration optimum for folded co-ordination, β for the configuration optimum for planar co-ordination, is as in refs. 10*a* and 20.

[19] N. F. Curtis, unpublished observations.
[20] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, 1965, **4**, 1091.

complex is in a configuration determined by details of the reaction in which the metal ion is inserted into the macrocyclic ligand. These metastable species are designated ' δ '.

Rhodium(III) d-d *Spectra*.—The visible spectra (Table 1) of these cyclic tetra-amine complexes generally resemble those of previously reported rhodium(III) tetra-amine complexes, and the characteristic differences between *cis*- and *trans*-complexes (higher extinction coefficients and lowest energy band shifted to higher frequency for *cis*-complexes compared with the analogous *trans*-complex) were used for confirmation of the assigned structures. The spectra of the thiocyanato-complexes *cis*- and *trans*-[Rh(tetb)(NCS)$_2$]CNS,$\frac{1}{2}H_2O$ are very similar, unlike the spectra of their cyclam analogues. (The isomers differ in solubilities, details of the i.r. spectra, and in the fact that the *cis*-complex reacts rapidly with carbonate to form the *cis*-carbonato-complex.)

TABLE 2

Metal-ion *d–d* spectra of some *trans*-dichloro(tetra-amine)-rhodium(III) complexes [a]

Amine	1 [b]	2 [c]	Ref.
NNN'N'-Tetramethylethylenediamine	21·7 (63)	27·9 (157), 30·3 (172)	10
NNN'-Trimethylethylenediamine	22·5 (102)	31·1 (150)	10
NN'-Dimethylethylenediamine	23·9 (72)	33·3 (171)	10
δ teta	24·2 (105)	32·1sh	*d*
δ tetb	24·2 (110)	32·2sh	*d*
NH_3	24·3 (66)		8
2,3-Diamino-2,3-dimethylbutane	24·3 (75)		8
β tetb	24·4 (90)	31·8sh	*d*
β teta	24·4 (80)	32·0sh	*d*
1,4,8,11-Tetra-azaundecane	24·4	34·1	12
rac-2,3-Diaminobutane	24·5 (75)	33·4 (120)	8
en	24·6 (75)	34·6 (130)	8
en	24·6 (75)	35·0 (130)	11
cyclam	24·6 (78)	33·2sh (80)	14
1,2-Diaminopropane	24·7 (75)	28·6 (80)	9
(RR)-2,3-Diaminobutane	24·7 (75)	28·6 (82)	9
meso-2,3-Diaminobutane	24·7 (75)	35·3 (120)	8
NN-Dimethylethylenediamine [e]	26·5 (260)	32·1 (200)	10

[a] In $cm^{-1} \times 10^{-3}$, molecular extinction coefficients in parentheses. [b] ${}^1T_{1g} \leftarrow {}^1A_{1g}$ of O_h. [c] ${}^1T_{2g} \rightarrow {}^1A_{1g}$ of O_h. [d] This work. [e] This compound is probably the *cis*-derivative. The other *N*-methylethylenediamines are all below en in ligand-field strength. If compared with spectral data for *cis*-[Rh(en)$_2$Cl$_2$]$^+$, the amine would be placed below en in ligand-field strength. The reported extinction coefficients are more typical of *cis*-complexes.

The *d–d* spectra of a number of *trans*-dichloro(tetra-amine)rhodium(III) cations are listed in Table 2 in order of increasing energy of the ν_1 band, which indicates the order of average ligand-field strength of the complex cations, and thus of the amines in planar co-ordination. The cyclic amines (teta) and (tetb) are comparable to ammonia in ligand-field strength, the stable β-configuration having higher ligand-field strength than the metastable δ-configuration. The ligand-field strength is somewhat lower than for the cyclam complex, an effect probably caused by repulsion in the co-ordination sphere involving the axial methyl substituents (*cf.* the *C*-methyl diaminoethanes with and without axial methyl groups).

Infrared Spectra.—The i.r. spectra (Tables 1 and 3) of the compounds generally resemble those of their cobalt(III) analogues.[13] The spectral bands assignable to the anions support the formulations given.

The spectra of the thiocyanate complexes indicate the presence of *N*-bonded and ' ionic ' thiocyanate ions, as observed for [Rh(en)$_2$Cl(NCS)]NCS [3] and the cyclam thiocyanato-complexes.[9]

The spectrum of [Rh(tetb)NO$_3$](NO$_3$)$_2$ indicates the presence of ionic and bidentate co-ordinated nitrate, closely resembling that of the analogous cobalt(III) compound.[13]

For the *cis*-compound Rh(tetb)(ClO$_4$)$_3$(H$_2$O)$_2$, a variety of structures are possible, with co-ordinated water or perchlorate, the latter unidentate or bidentate. The strong ν_3 perchlorate band in the i.r. spectrum is very much broadened, and partially resolved into three components at 1004, 1080, and 1135 cm^{-1}, and a strong band is present at 853 cm^{-1}, not present for other *cis*-Rh(tetb) complexes. These bands could be assigned as ν_3 of ionic perchlorate (1080 cm^{-1}), ν_3 of co-ordinated perchlorate (1004 and 1135 cm^{-1}), and ν_1 of co-ordinated perchlorate (853 cm^{-1}). Hydrogen bonding by the perchlorate ion could, in principle, produce similar effects, although broadening of the ν_3 band is the usual effect. A number of nickel(II) compounds have been assigned structures with co-ordinated perchlorate, including Ni(*N*-methyldiaminoethane)$_2$(ClO$_4$)$_2$ ($\Delta\nu_3$ = separation between components of ν_3 = 105 cm^{-1}, unidentate), Ni(*NNN'*-trimethyldiaminoethane)(ClO$_4$)$_2$

TABLE 3

Infrared spectral bands assigned to co-ordinated and ionic [a] anions (cm^{-1})

trans-Compounds	
[Rh(β teta)(NCS)$_2$]CNS,0·5H$_2$O	ν(CN): 2122vs; 2105vs; 2052vs; * ν(CS): 836m,sp; 750w *
[Rh(β tetb)(NCS)$_2$]CNS,0·5H$_2$O	ν(CN): 2145vs; 2128vs; 2023vs; * ν(CS): 828m,sp; 760m,sp *
[Rh(β teta)(CH$_3$CO$_2$)$_2$]ClO$_4$,H$_2$O	ν_{as}(OCO) 1595vs; ν_s(OCO) 1390s; δ(OCO) 690m,sp
cis-Compounds	
[Rh(α tetb)CO$_3$]ClO$_4$,H$_2$O	ν_3 1595vs,br; 1266s,sp; ν_2 754m,sp; ν_4 678m,sp
[Rh(α tetb)C$_2$O$_4$]ClO$_4$	ν_{as}(OCO) 1698vs,sp; 1670vs; ν_s(OCO) 1392s,sp; 1257m,sp; δ(OCO) 799m,sp
[Rh(α tetb)NO$_3$](NO$_3$)$_2$ [b]	$\nu_3$1505s, 1283s, 1350s; * ν_1 990s; ν_2 798m; 824m; * ν_4 743w; 710w *
[Rh(α tetb)ClO$_4$](ClO$_4$)$_2$,2H$_2$O	ν_3 1135vs,br; 1004vs; 1080vs,br; * ν_1 852vs
[Rh(α tetb)OH(CH$_3$CO$_2$)]BPh$_4$,3H$_2$O	ν(OH) 3560m,sp; ν_{as}(OCO) 1570vs,br; ν_s(OCO) 1392s,br; δ(OCO) 680m
[Rh(α tetb)(NCS)$_2$]CNS,0·5H$_2$O	ν(CN) 2093s,sp; 2046s,sp; * ν(CS) 829m,sp; 754w *

[a] Bands assigned to ionic anions indicated by *. [b] Overtone and combination bands ($\nu_1 + \nu_3$) 2490, 2250, 2390 *; $2\nu_1$ 1973; ($\nu_2 + \nu_4$) 1762, 1700, 1755.*

($\Delta\nu_3 = 132\ cm^{-1}$, bidentate),[20] $Ni(CH_3CN)_4(ClO_4)_2$ ($\Delta\nu_3 = 123\ cm^{-1}$, unidentate), and $Ni(CH_3CN)_2(ClO_4)_2$ (ν_3 split into three components, overall spread 195 cm^{-1}, bidentate).[21] For co-ordination to a trivalent metal ion, larger separations between the components would be expected, and thus the observed spectrum ($\Delta\nu_3 = 129\ cm^{-1}$) suggests unidentate co-ordination, as for *cis*-$[Rh(tetb)(ClO_4)_2]ClO_4,2H_2O$ or *cis*-$[Rh(tetb)(ClO_4)H_2O](ClO_4)_2,H_2O$. However, no other *cis*-complex of (tetb) with two such bulky anions co-ordinated has been prepared, and the complex shows no tendency to be converted into the hydroxo-species *cis*-$[Rh(tetb)(ClO_4)OH]^+$, as might be expected for the *cis*-perchlorato-aquo-species (*cf.* of the acetato-complex). Attempts to prepare a fluoroborate analogue were unsuccessful, $[Rh(tetb)CO_3]^+$ being recovered unchanged from fluoroboric acid, suggesting that a co-ordinating anion is necessary. All things considered, the structure *cis*-$[Rh(tetb)(ClO_4)](ClO_4)_2,2H_2O$ with chelated perchlorate, analogous to the nitrato-complex, appears most probable.

EXPERIMENTAL

The cyclic tetra-amines *C-rac-* and *C-meso-*5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (tetb and teta respectively, collectively, tet) were prepared as previously described.[10a]

The Amine Dihydroperchlorates, $(teta)(HClO_4)_2$ *and* $(tetb)(HClO_4)_2,0{\cdot}5H_2O$.—The sparingly soluble dihydroperchlorates crystallized when aqueous solutions of the amines were rendered slightly acidic with perchloric acid. For analysis the compounds were recrystallized from hot water [Found for $(teta)(HClO_4)_2$: C, 39·8; H, 7·9; N, 11·7. Calc. for $C_{16}H_{38}Cl_2N_4O_8$: C, 39·6; H, 7·5; N, 11·5%. Found for $(tetb)(HClO_4)_2,0{\cdot}5H_2O$: C, 38·7; H, 8·0; N, 11·4. Calc. for $C_{32}H_{74}Cl_4N_8O_{17}$: C, 38·8; H, 7·5; N, 11·3%].

trans-*Derivatives of* (teta) *and* (tetb) *with Rhodium*(III)

trans-*Dichloro*(*teta*)*rhodium*(III) *Perchlorate,* trans-$[Rh(\delta\ teta)Cl_2]ClO_4$, *and* trans-$[Rh(\beta\ teta)\ Cl_2]ClO_4$.—Rhodium trichloride ($RhCl_3,3H_2O$) (1 g), or an equivalent amount of a $RhCl_6^{3-}$ salt, plus amine dihydroperchlorate (2·1 g, 1 : 1·1 mol) were heated in water (100 ml) on a steam bath for *ca.* 4 h. The colour faded slowly from wine red to yellow, and a small amount of colloidal rhodium separated. The solution was filtered hot through an asbestos pad or fine filter paper, and $NaClO_4$ (2 g) added. The yellow crystalline product (δ-isomer) was filtered from the cold solution, and recrystallized from hot dilute hydrochloric acid, filtering as before. The stable β-isomer was formed when the δ-isomer was recrystallized from hot dilute ammonia. Total yield, including product recovered by evaporation of filtrates *ca.* 90% (Found for δ-isomer: C, 34·6; H, 6·8; Cl, 19·1; Rh, 17·8; for β-isomer: C, 34·9; H, 6·5; N, 10·3. $C_{16}H_{36}Cl_3N_4O_4Rh$ requires C, 34·4; H, 6·5; Cl, 19·1; N, 10·0; Rh, 18·5%).

trans-*Dichloro*(*teta*)*rhodium*(III) *Chloride Pentahydrate,* trans-$Rh(\delta\ teta)Cl_2Cl,5H_2O$.—The previous preparation was followed until after the filtration from the colloidal rhodium, but substituting the amine trihydrochloride[2] (or amine plus two mol of hydrochloric acid) for the amine hydroperchlorate. The filtrate was evaporated to dryness, dissolved in a small volume of hot ethanol, filtered, and an equal volume of concentrated hydrochloric acid was added. The pale yellow crystalline product was filtered off from the cold solution and washed with a little ice-cold ethanol (Found: C, 33·0; H, 7·4. $C_{16}H_{46}Cl_3N_4O_5Rh$ requires C, 32·9; H, 7·9%).

trans-*Dichloro*(*tetb*)*rhodium*(III) *Perchlorate Hemihydrate,* trans-$[Rh(\delta\ tetb)Cl_2]ClO_4,0{\cdot}5H_2O$ *and* trans-$[Rh(\beta\ tetb)Cl_2]ClO_4,0{\cdot}5H_2O$.—The preparations were as for the (teta) analogues, from $RhCl_3,3H_2O$ and $[H_2tetb](ClO_4)_2$ (Found for δ-isomer: C, 34·0; H, 6·8; Cl, 18·7; for β-isomer: C, 33·8; H, 6·6; N, 9·9. $C_{32}H_{74}Cl_6N_8O_9Rh_2$ requires C, 33·9; H, 6·6; Cl, 18·8; N, 9·9%). The formulation as hemihydrates is supported by the presence of weak bands in the i.r. spectra assigned as ν(OH) and δ(HOH).

trans-*Dibromo*(*tet*)*rhodium*(III) *Perchlorate,* trans-$[Rh(\beta\ tet)Br_2]ClO_4$.—*trans*-$[Rh(tet)Cl_2]ClO_4$ (0·2 g) and sodium bromide (0·7 g) were refluxed in water (30 ml) for 3 h, when the yellow colour of the solution deepened and some product crystallized out. The solution was evaporated to half volume and sodium perchlorate was added. The product was filtered off from the cold solution and recrystallized from hot, dilute hydrobromic acid with sodium perchlorate. The orange crystalline product was filtered off from the cold solution and washed with a little cold water and ethanol [Found for (teta) derivative: C, 29·9; H, 5·7; for (tetb) derivative: C, 30·2; H, 5·9. $C_{16}H_{36}Br_2ClN_4O_4$ requires C, 29·7; H, 5·6%].

trans-*Di-iodo*(*tet*)*rhodium*(III) *Iodide Hydrates,* trans-$[Rh(teta)I_2]I,0{\cdot}5H_2O$ *and* trans-$[Rh(tetb)I_2]I_2,2H_2O$.—*trans*-$[Rh(tet)Cl_2]ClO_4$ (0·2 g) and sodium iodide (1 g) were refluxed in water (30 ml) for 2 h, the solution changing to a red-brown colour and crystals of the sparingly soluble product being deposited. The products were recrystallized from hot water with a few drops of hydroiodic acid [Found for (teta) derivative: C, 25·2; H, 5·0. $C_{32}H_{74}I_6N_8ORh$ requires C, 24·7; H, 4·8. Found for (tetb) derivative: C, 23·6; H, 4·8. $C_{16}H_{40}I_3N_4O_2Rh$ requires C, 23·9; H, 5·0%]. The difference in hydration is supported by the relative intensities of the bands assigned to ν(OH) and δ(HOH) in the i.r. spectra.

trans-*Dithiocyanato*(*tet*)*rhodium*(III) *Thiocyanate Hemihydrate,* trans-$[Rh(tet)(NCS)_2]CNS,0{\cdot}5H_2O$.—Aqueous *trans*-$[Rh(tet)Cl_2]ClO_4$ (0·2 g) and NaCNS (0·5 g) were refluxed for 4 h. The pale yellow *products* were filtered off from the cold solution, and recrystallized from hot methanol–propan-2-ol. The (tetb) compound is less soluble than the (teta) compound, which is unusual [Found for (teta) derivative: C, 39·6; H, 6·4; N, 17·0; for (tetb) derivative: C, 40·1; H, 6·7; N, 17·5. $C_{38}H_{52}N_{14}ORh_2S_6$ requires C, 40·0; H, 6·5; N, 17·2%].

trans-*Diacetato*(*teta*)*rhodium*(III) *Perchlorate Dihydrate,* trans-$[Rh(\beta\ teta)(CH_3CO_2)_2]ClO_4,2H_2O$.—*trans*-$[Rh(teta)Cl_2]ClO_4$ and silver acetate (1 : 2 mol ratio) were refluxed in 0·1M acetic acid for four days and the precipitated silver chloride was filtered quantitatively and weighed to ensure precipitation was complete. The filtrate was evaporated to small volume and sodium perchlorate added to the hot solution. The pale yellow product which separated on cooling was filtered off and washed with a small volume of ice-water, followed by propan-2-ol (Found: C, 37·2; H, 7·1. $C_{20}H_{46}ClN_4O_{10}Rh$ requires C, 37·1; H, 7·2%). A similar reaction was attempted using silver nitrate.

[21] A. E. Wickendon and R. A. Krause, *Inorg. Chem.*, 1965, **4**, 404.

Silver chloride was precipitated and products with i.r. spectra showing bands typical of unidentate nitrato-complexes were isolated, but satisfactory analytical results were not obtained.

cis-*Derivatives of* (*tetb*)

(*tetb*)*Rhodium*(III) *Trichloride*, Rh(α tetb)Cl_3.—Rhodium chloride hydrate (1 g), (tetb) trihydrochloride hydrate (1·8 g, 1 : 1·1 mol ratio), and sodium chloride [a] (5 g) were dissolved in water (150 ml) and the mixture was heated on a steam-bath for several hours. The colour slowly changed from wine red to yellow, and the sparingly soluble yellow product and some colloidal rhodium were precipitated. The solution was set aside for 24 h and then filtered; [b] the residue was washed with water. The solid was boiled with dilute aqueous sodium carbonate, when the product dissolved to form the soluble carbonato-complex; the solution was filtered through a pad of asbestos to remove the rhodium metal. The filtrate was acidified with hydrochloric acid and the sparingly soluble pale yellow product was filtered off after 24 h and washed successively with cold water, and propan-2-ol; yield 30—40% [c] (Found: C, 38·9; H, 7·6; Cl, 21·5; Rh, 20·6. $C_{16}H_{36}Cl_3N_4Rh$ requires C, 38·9; H, 7·3; Cl, 21·5; Rh, 20·8%).

Notes. (*a*) The $RhCl_3,3H_2O$ can be replaced by K_3RhCl_6,H_2O and the amine trihydrochloride by amine hydrate plus three mol of HCl or amine tetrahydrochloride plus one mol of NaOH. (*b*) Perchloric acid (1 ml, 60%) was added to the filtrate, when *trans*-Rh(δ tetb)$Cl_2ClO_4,\frac{1}{2}H_2O$ crystallized in *ca.* 50% yield. (*c*) The reaction was carried out under a variety of conditions in an attempt to optimize the yield of *cis*-product. The yield of Rh(*rac* tet)Cl_3 was decreased if the ratio of acid : amine was decreased, or if the total chloride-ion concentration was decreased. Additional acid slowed the reaction, but gave the same final yield of Rh(tetb)Cl_3. Boiling the reacting solution, or the addition of a small volume of ethanol increased the amount of colloidal rhodium deposited, but did not appreciably alter the relative yields of *cis*- and *trans*-products. Reaction of $RhCl_3$ and (tetb)$(HClO_4)_2$ yielded negligible *cis*-product (see above).

Carbonato(*tetb*)*rhodium*(III) *Salts*, cis-[Rh(α tetb)CO_3]ClO_4,H_2O *and* cis-[Rh(α tetb)CO_3]NCS,H_2O.—Rh(tetb)Cl_3 was dissolved in boiling dilute aqueous sodium carbonate and the solution was filtered whilst hot. The carbonato-chloride dihydrate separated from the concentrated solution on cooling. The sparingly soluble perchlorate, thiocyanate, or iodide, all as monohydrates, crystallized when sodium perchlorate, thiocyanate, or iodide was added to the filtrate (Found for perchlorate hydrate: C, 36·1; H, 6·9; Cl, 6·5; Rh, 18·6. $C_{17}H_{38}ClN_4O_8Rh$ requires C, 36·1; H, 6·8; Cl, 6·3; Rh, 18·2%. Found for thiocyanate hydrate: C, 41·3; H, 7·2. $C_{18}H_{38}N_5O_4RhS$ requires C, 41·2; H, 7·3%).

cis-*Oxalato*(*tetb*)*rhodium*(III) *Perchlorate*, *cis*-[Rh(α tetb)C_2O_4]ClO_4.—Rh(tetb)Cl_3 (0·2 g) was dissolved in boiling dilute sodium carbonate solution and oxalic acid (0·2 g) was added to the solution which was then boiled for 10 min and filtered; sodium perchlorate was then added to it. The pale yellow crystalline product which separated on cooling was recrystallized from hot water–methanol (Found: C, 37·2; H, 6·2; N, 9·3. $C_{18}H_{36}ClN_4O_8Rh$ requires C, 37·6; H, 6·3; N, 9·7%).

(*tetb*)*Rhodium*(III) *Tribromide*, Rh(α tetb)Br_3.—[Rh(tetb)CO_3]ClO_4, was treated with hot dilute hydrobromic acid when the sparingly soluble orange product crystallized out (Found: C, 30·7; H, 5·9. $C_{16}H_{36}Br_3N_4Rh$ requires C, 30·6; H, 5·8%).

(*tetb*)*Rhodium*(III) *Tri-iodide*, Rh(α tetb)I_3.—[Rh(tetb)CO_3]ClO_4,H_2O was treated with warm dilute acetic acid–sodium iodide [a] when the sparingly soluble dark orange product crystallized out [b] (Found: C, 25·5; H, 4·9; N, 7·3; I, 48·2. $C_{16}H_{36}I_3N_4Rh$ requires C, 25·0; H, 4·7; N, 7·3; I, 49·6%).

Notes. (*a*) Addition of iodide to a neutral solution of $[Rh(rac\ tet)CO_3]^+$ causes precipitation of sparingly soluble [Rh(*rac* tet)CO_3]I. (*b*) Prolonged heating of the reaction solution causes conversion into *trans*-$[Rh(rac\ tet)I_2]^+$.

cis-*Acetato-hydroxo*(*tetb*)*rhodium*(III) *Tetraphenylborate Trihydrate*, cis-[Rh(α tetb)OH(CH_3CO_2)]$BPh_4,3H_2O$.—[Rh(tetb)CO_3]ClO_4,H_2O (0·5 g) was dissolved in a small volume of hot glacial acetic acid, and the solution was diluted with water and filtered. A filtered solution of sodium tetraphenylborate (0·5 g) in a small volume of ethanol was added to it. The sparingly soluble product was filtered and washed with cold water, and recrystallized from hot methanol–propan-2-ol to give pale yellow needles (Found: two preparations, C, 60·9; 60·6; H, 8·0, 7·7; N, 6·6. $C_{42}H_{66}BN_4O_6Rh$ requires C, 60·6; H, 7·7; N, 6·7%).

Note. The same product was obtained whether one, two, or more molar proportions of $NaBPh_4$ were used.

cis-*Nitrato*(*tetb*)*rhodium*(III) *Nitrate*, [Rh(α tetb)NO_3]$(NO_3)_2$.—[Rh(tetb)CO_3]ClO_4,H_2O was dissolved in a small volume of hot nitric acid (2 : 1 concentrated nitric acid : water). The filtered solution was diluted with several volumes of water when the sparingly soluble *product* crystallized. This was filtered off and washed well with cold water (Found: C, 33·2; H, 6·4. $C_{16}H_{36}N_7O_9Rh$ requires C, 33·5; H, 6·3%).

cis-*Perchlorato*(*tetb*)*rhodium*(III) *Perchlorate Dihydrate*, [Rh(α tetb)$(ClO_4)_2$]$ClO_4,2H_2O$.—[Rh(*rac* tet)CO_3]ClO_4,H_2O was dissolved in a small volume of hot perchloric acid (0·1 g, 5 ml water, 0·5 ml 60% $HClO_4$). The filtered solution was evaporated under reduced pressure and propan-2-ol added. The pale yellow product which crystallized was filtered and washed with propan-2-ol and recrystallized from hot methanol–propan-2-ol (Found: C, 26·4; H, 5·9. $C_{16}H_{40}Cl_3N_4O_{14}Rh$ requires C, 26·6; H, 5·6%).

cis-*Dithiocyanato*(*tetb*)*rhodium*(III) *Thiocyanate Hemihydrate*, cis-[Rh(α tetb)$(NCS)_2$]$NCS,0·5H_2O$.—[Rh(tetb)CO_3]$ClO_4,0·5H_2O$ was dissolved in a small volume of hot 50% acetic acid, filtered, and an equal volume of a hot solution of sodium thiocyanate (10-fold excess) added to the hot filtrate. The yellow crystalline product was filtered from the cold solution and recrystallized from hot water. (Found: C, 39·8; H, 6·5; N, 17·5. $C_{38}H_{73}N_{14}ORh_2S_6$ requires C, 40·0; H, 6·5; N, 17·2%).

Note. The perchlorate salt crystallized when three molar proportions of sodium thiocyanate and an excess of sodium perchlorate was substituted for the excess of sodium thiocyanate. Treatment of the thiocyanate or perchlorate salts with concentrated HCl caused crystallization of the chloride salt.

[0/2192 *Received, 22nd December,* 1970]