Metal-ion Complexes of 5,12-Dimethyl-7,14-diphenyl-1,4,8,11-tetra-aza-cyclotetradeca-4,11-diene. Part II.[1] Some Compounds of Cobalt(III)

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The preparation and properties of the cobalt(III) compounds of the macrocycle, 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4 11-diene (**1**), *trans*-[Co(**1**)Cl_2]ClO_4, *trans*-[Co(**1**)Br_2]ClO_4, *trans*-[Co(**1**)-$(NCS)_2$]CNS,H_2O, *trans*-[Co(**1**)$(CH_3CO_2)_2$]ClO_4, *cis*-[Co(**1**)en]$(ClO_4)_3$, *cis*-[Co(**1**)acac]$(ClO_4)_2$, [Co(**1**)-$(NH_3)_2$]$(ClO_4)_3$, and [Co(**1**)(H_2O)(NH_3)]$(ClO_4)_3$,H_2O are reported. Also reported are the preparation of the new compounds of the related macrocycle, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (**2**), *cis*-[Co(**2**)acac]$(ClO_4)_2$, *cis*-[Co(**2**)en]Cl$(ClO_4)_2$, and [Co(**2**)$(NH_3)_2$]$(ClO_4)_3$.

COMPLEXES of 5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradecadiene[2] (**1**) with nickel(II) and copper(II) have been described,[1] and in this paper some compounds with cobalt(III) are reported. For comparison purposes, some new cobalt(III) compounds of the related macrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (**2**) were prepared.[3] The ligand (**1**) could have the 4,11-diene structure (**1a**) or the 4,14-diene structure (**1b**), the former being considered most likely.[1]

Cobalt(III) compounds of (**1**) were prepared by two procedures, reaction of (**1**) with $Na_3Co(CO_3)_2,3H_2O$ in methanol and reaction of (**1**) with a cobalt(II) salt in methanol followed by air or hydrogen peroxide oxidation; in each case followed by acidification to give the *trans*-di-acido-complex. Yields were higher for the first method. The *trans*-dichloro- and dibromo-compounds were prepared by these procedures, and the *trans*-di-isothiocyanato- and diacetato-compounds were prepared from the chloro-complex by anion substitution. Also prepared from the chloro-complex were the diammine (presumably *trans*) and folded macrocycle compounds with the chelates acetylacetonate and diaminoethane. The ammine and diaminoethane compounds were stable in acid solution. The aquo-ammine was isolated by acidification of a boiled solution of the diammine in water–methanol. Attempts to prepare a chelate carbonato-compound for comparison with [Co(2)CO_3]ClO_4, the only previously reported cobalt(III) compound with (2) in folded co-ordination[3] were not successful. However, the new compounds *cis*-[Co(**2**)acac]ClO_4 and *cis*-[Co(**2**)en]Cl$(ClO_4)_2$ were prepared for comparison, as was [Co(**2**)$(NH_3)_2$]$(ClO_4)_3$ (presumably *trans*). The amine compounds with (**2**) are stable in acid, but in neutral solution are more rapidly hydrolysed than their analogues with (**1**). For the diammine the hydrolysis proceeded to the dihydroxo-compound.

The di-imine (**1**) when co-ordinated to cobalt(III) is resistant to acid hydrolysis, but is rapidly hydrolysed under basic conditions, with release of benzaldehyde. This susceptibility to base hydrolysis is much more noticeable than for the compounds of (**1**) with nickel(II) or copper(II),[1] or for the compounds of the related di-imine (**2**) with cobalt(III).[3]

Cobalt(III) d–d *Spectra*.—Spectra are reported (Table) for compounds of (**1**) and of some of their analogues with (**2**). In general only the lowest energy transition, $^1E_g \longleftarrow {}^1A_{1g}$ in D_{4h} for the *trans*-compounds and

Cobalt(III) *d–d* spectra [a]

Compound	Band maximum [b]	ε [c]
trans-[Co(β**1**)Cl_2]ClO_4	620	64
trans-[Co(β**1**)Br_2]ClO_4	652	53
trans-[Co(β**1**)$(CH_3CO_2)_2$]ClO_4	551	47
trans-[Co(β**1**)$(NCS)_2$]CNS,H_2O	548	480
[Co(**1**)$(NH_3)_2$]ClO_4,H_2O [d]	456	93
cis-[Co(α**1**)en]$(ClO_4)_3$ [d]	478	166
cis-[Co(α**1**)acac]$(ClO_4)_2$	512	238
trans-[Co(β**2**)Br_2]ClO_4	672	54
trans-[Co(β**2**)$(CH_3CO_2)_2$]ClO_4	559	41
cis-[Co(α**2**)en]Cl$(ClO_4)_2$ [d]	495	133
cis-[Co(α**2**)acac]$(ClO_4)_2$	522	181

[a] Unless otherwise stated, in methyl cyanide solution. [b] In nm, see text for assignment. [c] Molar extinction coefficient, in l mol^{-1} cm^{-1}. [d] In 10 : 1 dimethyl sulphoxide : 20% aqueous perchloric acid.

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[1] Part I, D. F. Cook, N. F. Curtis, and R. W. Hay, *J.C.S. Dalton*, 1973, 1160.

[2] K. Hideg and D. Lloyd, *Chem. Comm.*, 1970, 929; *J. Chem. Soc.* (*C*), 1971, 3441.

[3] N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 1967, **6**, 770.

$({}^1E + {}^1B_2) \longleftarrow {}^1A_1$ in C_{2v} for the *cis*-compounds was observed clear of charge transfer or ligand absorption. Energies and intensities observed support the assignment of *trans*-structures to the di-acido-compounds, and *cis*-structure to the compounds with chelates. Distortions from octahedral symmetry are too small to permit assignment of a structure to the di-ammine.

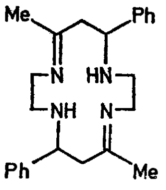
In all cases the band observed was at higher energy for the compounds of (**1**) compared with their analogues with (**2**), indicating a higher ligand field strength for (**1**) than for (**2**) in both planar and folded co-ordination. A similar effect was observed for compounds of (**1**) and (**2**) with nickel(II).[1] Replacement of the *gem* methyl groups of (**2**) by the phenyl groups of (**1**) would be expected to cause a decrease in base strength and hence donor ability.[4] The reversal of the order of base strength and effective ligand field strength for (**1**) and (**2**) probably arises from greater repulsion between the ' additional ' ligands and the macrocycle for (**2**), where axial methyl substituents are present.

Infrared Spectra.—The i.r. spectra of the compounds show bands assignable to ν(NH) *ca.* 3200 cm^{-1}, ν(C:N) *ca.* 1660 cm^{-1} and the aromatic groups of (**1**). The compounds with additional ligands which have i.r. spectra show bands at frequencies similar to those of analogous cobalt(III) tetra-amine derivatives. The complexes formulated as hydrates show ν(OH) and δ(HOH) absorptions.

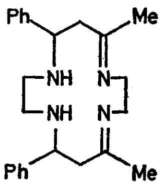
^1H *Nuclear Magnetic Resonance Spectra*.—The ^1H n.m.r. spectra * of *trans*-$[Co(\mathbf{1})Br_2]ClO_4$ and *trans*-$[Co(\mathbf{1})(CH_3CO_2)_2]ClO_4$ show single methyl and unresolved phenyl resonances (bromide: σ_{Me} 2·52, σ_{Ph} 7·47; acetate: $\sigma_{Me(acetate)}$ 2·10, σ_{Me} 2·63, σ_{Ph} 7·52 p.p.m.). The spectra are similar to those of square planar nickel(II) compounds of (**1**) in the β configuration.[1] The methyl resonance has a chemical shift similar to that of the imine methyl group of *trans*-cobalt(III) compounds of (**2**).[5] The spectrum of the acetylacetonato-compound also shows a single methyl resonance (σ_{Me} 2·59 p.p.m.) but the phenyl resonance is more complex, and could be interpreted as one unresolved phenyl resonance (7·48 p.p.m.) overlying a partially resolved phenyl resonance. The acetylacetone methyl resonance is a doublet (2·42, 2·32 p.p.m.), although for the analogue with (**2**) it is a singlet (2·20 p.p.m.), as are the resonances of the imine (2·51 p.p.m.), axial (1·35 p.p.m.) and equatorial (1·73 p.p.m.) methyl groups. In deuteriomethyl cyanide the imine methyl resonance of $[Co(\mathbf{1})acac]^{2+}$ is a doublet (2·43, 2·49 p.p.m.) as well as the acetylacetone methyl resonance (2·15, 2·24 p.p.m.), with the phenyl resonance again complex at *ca.* 7·49 p.p.m. The methyl resonances remain singlet for the compound of (**2**) in this solvent.

The spectra indicate that for $[Co(\mathbf{2})acac]^{2+}$ the cation possesses twofold symmetry, with the methyl substituents on the two six-membered chelate rings, and the two methyl groups of the acetylacetone in equivalent sites. For $[Co(\mathbf{1})acac]^{2+}$ the spectra indicate the absence of this twofold symmetry, supporting the assignment of configuration made for the nickel(II) compounds of (**1**).[1] For the *C-meso*-configuration of both (**1**a) and (**1**b), the optimum folded conformation has one six-membered chelate ring in a half-chair, and the other in a half-boat conformation, which would place the substituents on the two six-membered chelate rings, and possibly also the acetylacetone methyl groups, in dissimilar sites and thus account for the observed spectra.[1]

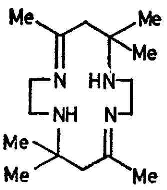
Co-ordination Stereochemistry.—Compounds of cobalt(III) with (**1**) were prepared in planar (*bcde*) co-ordination with unidentate additional ligands, and in folded (*abcd*) co-ordination with chelates. The latter were prepared similarly to, and had properties similar to those of, their analogues with (**2**).



(**1**a)



(**1**b)



(**2**)

The ^1H n.m.r. spectra of the acetylacetonato-compounds of (**1**) suggest that the two six-membered chelate rings are not equivalent, as expected for the *C-meso-N-rac*-configurations of both (**1**a) and (**1**b) in folded co-ordination. The ease of preparation of cobalt(III) compounds of (**1**) with chelates indicates that the macrocycle cannot be too strained in folded co-ordination, relative to planar co-ordination. Models suggest that the macrocycle (**1**b) would be much more strained in folded co-ordination than (**1**a), supporting the assignment of the structure (**1**a).[1]

For co-ordinated (**2**), the *N-rac* (α) and *N-meso* (β) configurations are of comparable stability in planar co-ordination, and the α and β isomers were both isolated for compounds such as $[Ni(\mathbf{2})](ClO_4)_2$ [6,7] and *trans*-$[Co(\mathbf{2})Cl_2]ClO_4$.[3] For (**1**a) and for (**1**b) the *N-rac* (α) configuration is expected to be highly strained in planar co-ordination.[1] Metastable planar α configuration compounds of (**1**) were prepared for nickel(II) by unfolding α configuration compounds with chelates under acid conditions which preserved the nitrogen configuration.[1] Treatment of $[Co(\alpha\mathbf{2})CO_3]ClO_4$ with acid HX provides a convenient method of preparation of isomerically pure *trans*-$[Co(\alpha\mathbf{2})X_2]^+$ (co-ordinating anion) and *trans*-$[Co(\alpha\mathbf{2})(H_2O)_2]^{3+}$ (nonco-ordinating anion) compounds. Attempts to use a similar procedure to prepare metastable α-planar compounds of (**1**) with cobalt(III) were foiled by the resistance to acid hydrolysis of the diaminoethane and acetylacetone compounds and the inability to prepare the carbonato-compound.

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* In deuteriotrifluoroacetic acid, chemical shifts from TMS as internal standard, measured at 100 MHz.

[4] *Chem. Soc. Special Publications*., Nos. 17 and 25.

[5] R. E. Ball and J. F. Endicott, *Chem. Comm*., 1968, 51.

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

[7] M. F. Bailey and I. E. Maxwell, *J.C.S. Dalton*, 1972, 938.

EXPERIMENTAL

The ligand (**1**) was prepared by the method of Hideg and Lloyd.[2]

trans-*Dichloro-(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, trans-*$[Co(\mathbf{1})Cl_2]ClO_4$.—The ligand (5 g) was stirred with $Na_3Co(CO_3),3H_2O$ [8] (5 g, 1 : 1·06 mol ratio) in methanol (50 ml) for 1 h. Concentrated hydrochloric acid (5 ml) was added and the solution heated on a steam-bath for 30 min. Hot aqueous perchloric acid (50 ml, 1M) was added to the hot, filtered, reaction solution, and the methanol slowly evaporated. The green crystalline *product* was filtered off from the cold solution and recrystallised by dissolution in the minimum volume of hot methanol, adding hot aqueous perchloric–hydrochloric acid (1M in each) until crystallisation commenced, and allowing the solution to cool slowly. Yield *ca.* 40% (Found: C, 47·7; H, 5·4; Co, 9·8. $C_{24}H_{34}Cl_3CoO_4$ requires C, 47·4; H, 5·6; Co, 9·7%).

trans-*Dibromo(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, trans-*$[Co(\mathbf{1})Br_2]ClO_4$.—As for the previous preparation, substituting hydrobromic for the hydrochloric acid (Found: C, 41·9; H, 4·9; N, 8·0. $C_{24}H_{34}Br_2ClCoO_4$ requires C, 41·6; H, 4·9; N, 8·1%).

trans-*Di-isothiocyanato(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Thiocyanate Hydrate, trans-*$[Co(\mathbf{1})(NCS)_2]CNS,H_2O$.—The dichloro-complex (1 g) was dissolved in hot methanol (20 ml) containing a few drops of acetic acid, sodium thiocyanate (2 g) was added, and the solution heated on a steam-bath for 30 min. Hot dilute acetic acid (0·1M) was added to the solution until crystallisation commenced, and the red-brown crystals filtered off from the cold solution. The *product* was recrystallised by dissolution in hot methanol and precipitation with hot dilute acetic acid as before (Found: C, 51·4; H, 5·6; Co, 9·7; N, 15·7. $C_{27}H_{36}CoN_7OS_3$ requires C, 51·5; H, 5·8; Co, 9·4; N, 15·6%).

trans-*Diacetato(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, trans-*$[Co(\mathbf{1})(CH_3CO_2)_2]ClO_4$.—The dichloro-complex (1 g) was dissolved in hot methanol (20 ml) containing a few drops of acetic acid, sodium acetate (2 g) was added and the solution heated on a steam-bath for 30 min. Hot dilute perchloric acid 0·1M containing sodium perchlorate (2M) was added until crystallisation commenced. The pink *product* was recrystallised from hot methanol with hot aqueous sodium perchlorate (Found: C, 51·4; H, 6·2; N, 8·1. $C_{28}H_{38}ClCoN_4O_8$ requires C, 51·3; H, 6·2; N, 8·6%).

cis-*Acetylacetonato(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, cis-*$[Co(1)acac]ClO_4$.—The dichloro-complex (1 g) was dissolved in hot methanol (20 ml) and then acetylacetone (0·5 g) and a few drops of concentrated aqueous ammonia added. The solution was heated on a steam-bath for 30 min and the product crystallised by the addition of hot dilute perchloric acid. The dark red *product* was recrystallised by dissolving in hot methanol and precipitation with hot dilute perchloric acid (Found: C, 47·3; H, 6·2; N, 7·8. $C_{29}H_{41}Cl_2CoN_4O_6$ requires C, 47·4; H, 5·6; N, 7·6%).

cis-*Diaminoethane-(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, cis-*$[Co(\mathbf{1})en](ClO_4)_3$.—One mol of diaminoethane was added to a solution of the dichloro-compound in the minimum volume of hot methyl cyanide. After a few minutes a propan-2-ol solution of lithium perchlorate was added. The orange *product* was filtered from the cold solution, washed with propan-2-ol, and recrystallised from hot dilute perchloric acid–methanol (Found: C, 39·5; H, 5·0; N, 10·6. $C_{26}H_{40}Cl_3CoN_6O_{12}$ requires C, 39·4; H, 5·1; N, 10·6%).

Diammine(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate Hydrate, $[Co(\mathbf{1})(NH_3)_2](ClO_4)_3,H_2O$.—As for the previous preparation, substituting a few drops of conc. aqueous ammonia for the diaminoethane. The *product* was orange in colour (Found: C, 39·4; H, 5·1; N, 10·9. $C_{24}H_{42}Cl_3CoN_6O_{13}$ requires C, 39·7; H, 5·4; N, 10·7%).

Aquoammine(5,12-dimethyl-7,14-diphenyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate Hydrate, $[Co(\mathbf{1})(H_2O)(NH_3)](ClO_4)_3,H_2O$.—A solution of the diammine in water–methanol was heated in a boiling water bath for 10 min, then acidified with perchloric acid. The red-orange *product* was filtered off from the cold solution (Found: C, 36·8; H, 4·5; N, 8·6. $C_{24}H_{39}Cl_3CoN_5O_{14}$ requires C, 36·7; H, 4·6; N, 8·9%).

The new compounds of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (**2**) were prepared by procedures similar to those used for the analogous compound of (**1**).

cis-*Acetylacetonato-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, cis-*$[Co(\mathbf{2})acac](ClO_4)_2$.—(Found: C, 39·9; H, 6·4; N, 8·6. $C_{19}H_{39}CoCl_2N_4O_{10}$ requires C, 39·6; H, 6·2; N, 8·8%.)

cis-*Diaminoethane-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Chloride Diperchlorate, cis-*$[Co(\mathbf{2})en]Cl(ClO_4)_2$.—This compound crystallised as the chloride diperchlorate even from dilute perchloric acid (Found: C, 34·0; H, 6·0; N, 13·5. $C_{18}H_{40}Cl_3CoN_6O_8$ requires C, 34·1; H, 5·7; N, 13·3%).

Diammine(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Perchlorate, $[Co(\mathbf{2})(NH_3)_2](ClO_4)_3$.—(Found: C, 28·2; H, 5·6; N, 12·2. $C_{16}H_{38}Cl_3CoN_6O_{12}$ requires C, 27·9; H, 5·6; N, 12·2%.)

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[8] G. L. Johnson, *Inorg. Synth.*, 1966, **8**, 242.