The Preparation of the *Trans*-Bis Imidazole and some Carboxylato Bonded *Trans*-Bis Amino Acid Derivatives of the Cobalt(III) Complex of the Macrocyclic Ligand, 5,12-Dimethyl-1,4,8,11-Tetraazacyclotetradeca-4,11-diene

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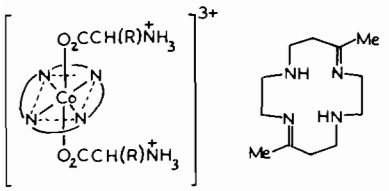
Relatively few examples are known of macrocyclic cobalt(III) complexes in which the *trans*-sites are occupied by amino-acid or amine ligands. Cragel and Douglas [1] have described the preparation of a series of complexes of the type *trans*-$[CoL(\bar{O}_2CCH(R)\overset{+}{N}H_3]^{3+}$ (where L = the macrocyclic ligands cyclam or $Me_4[14]teteneN_4$) containing a variety of carboxylato bonded amino-acids (gly, L-α-ala, L-β-phe and L-leu). The present paper describes the preparation and characterisation of a number of carboxylato-bonded amino acid complexes of the type shown in (I) with gly (R = H), L-α-ala (R = Me), β-ala, L-leu (R = Bu^i), L-val (R = Pr^i) and L-his where the macrocyclic ligand is $Me_2[14]dieneN_4$ (II). Also described is the bis-imidazole derivative which is coordinated via the pyridine nitrogen of the imidazole ring



(I)

(II)

Experimental

The macrocyclic ligand $Me_2[14]dieneN_4$ (5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) as its dihydroperchlorate salt and *trans*-$[CoCl_2(Me_2[14]dieneN_4]ClO_4$ (isomer *a*) were prepared as previously described [2]

Carboxylato-bonded Amino-acid Complexes

The general illustrative procedure is described for the glycine complex. The complex *trans*-$[Co(Me_2[14]dieneN_4)Cl_2](ClO_4)_2$ (0.906 g) was dissolved in the minimum volume of water and the solution heated with AgOH (0.70 g) for *ca.* 15 min on a steam bath. The solution was then cooled and filtered to remove the unreacted AgOH and precipitated AgCl Glycine (0.40 g) was added to the filtrate and the pH adjusted to 5.5 by addition of dilute $HClO_4$. The solution was heated for *ca.* 3 hr at 70 °C and the volume reduced to *ca.* 10 cm^3. Addition of excess ethanol followed by cooling in ice gave a reddish solid. The complex was filtered and washed with ethanol and then ether. The complex was recrystallised by dissolving in the minimum volume of hot water, cooling in ice, followed by the addition of a few cm^3 of 70% $HClO_4$. The red needle-like crystals so obtained were filtered off, washed with ethanol, then ether and dried under vacuum.

The other amino-acid complexes were prepared by a similar procedure using L-α-alanine (0.45 g), β-alanine (0.45 g), L-leucine (0.60 g), L-valine (0.55 g) and L-histidine monohydrochloride (0.84 g). In the case of the β-alanine derivative, addition of ethanol gave an oily product which solidified on trituration with ethanol. Trituration with ethanol was also necessary during the recrystallisation procedure. In the case of the other amino-acid complexes it was necessary to reduce the solution volume to *ca.* 5 cm^3 before the initial precipitation with ethanol. Analytical data for the various complexes are summarised in Table I.

The complex *trans*-$[Co(Me_2[14]dieneN_4)(imidazole)_2](ClO_4)_3$ was prepared as follows. The dichloro-complex *trans*-$[Co(Me_2[14]dieneN_4)Cl_2](ClO_4)$ (0.20 g) was dissolved in acetonitrile (30 cm^3) and heated to *ca.* 60 °C. To the hot solution was added an excess of imidazole (*ca.* 0.60 g) and the solution stirred at *ca.* 60 °C for 10 min To the orange-red solution so obtained was added $NaClO_4$ (0.1 g) followed by methanol (10 cm^3), and the solution allowed to stand overnight at room temperature. The resulting yellow solution was concentrated to *ca.* 15 cm^3 under vacuum, filtered and then further concentrated to give the yellow product which was filtered off and washed with isopropanol. The complex was dissolved in the minimum volume of 90% methanol containing imidazole (40 mg per 10 cm^3) and the solution allowed to stand. The yellow complex so obtained was washed with isopropanol, then ether and dried under vacuum. *Anal.* Calc. for $C_{18}H_{36}N_8O_{14}Cl_3Co$. C, 28.68, H, 4.81; N, 14 86. Found.C, 29.12; H, 4.86; N, 14.84%.

Infrared spectra were determined as KBr discs using a Perkin-Elmer 457 instrument. Visible spectra were determined using a Perkin-Elmer 402 spectrophotometer. Conductivity measurements were made with a Portland Electronics Model P310 conductivity meter using 10^{-3} *M* solutions at 25 °C.

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TABLE I. Analytical Data for the Amino-Acid Complexes.

Amino-acid	Mol. Formula	C[a] (%)	H[a] (%)	N[a] (%)
Glycine	$C_{16}H_{34}N_6O_{16}Cl_3Co$	26.51(26.26)	4.72(4.68)	10.57(11.48)
L-α-Alanine	$C_{18}H_{38}N_6O_{16}Cl_3Co$	28.55(28.45)	5.34(5.04)	11.86(11.06)
β-Alanine	$C_{18}H_{38}N_6O_{16}Cl_3Co$	28.74(28.45)	5 35(5 04)	11.06(11.06)
L-Leucine	$C_{24}H_{50}N_6O_{16}Cl_3Co$	34.83(34.16)	5.82(5.97)	9.93(9.95)
L-valine	$C_{22}H_{48}N_6O_{16}Cl_3Co$	32.83(32.31)	5.78(5.92)	10.73(10.27)
L-Histidine	$C_{24}H_{42}N_{10}O_{16}Cl_3Co$	32.83(32.32)	5.17(4.75)	15.89(15.70)

TABLE II. Spectral Data for the $[Co(Me_2[14]dieneN_4)(L)_2]^{3+}$ Complexes.[a]

L	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	$\nu(COO^-)_{sym}$ (cm^{-1})
gly	490	176	1375
	347	232	
L-α-ala	490	169	1385
	350	228	
β-ala	515	89	1385
	350(sh)	284	
L-leu	487	179	1375
	348	291	
L-val	485	169	1380
	350	271	
L-his	495	75	1390
	350(sh)	213	
imidazole	350(sh)	342	–

[a]Visible spectra determined in aqueous solution.

^1H NMR measurements were made using D_2O or CD_3CN solutions with NaTMS and TMS respectively as reference. Spectra were measured using a Bruker WP-80 instrument

Results and Discussion

The carboxylato-bonded amino-acid derivatives are readily prepared by the reaction of the dichloro-complex *trans*-$[CoCl_2(Me_2[14]dieneN_4]^{2+}$ with AgOH, then the amino acid. Spectroscopic data for the various amino-acid derivatives is summarised in Table II With the exception of the β-alanine derivative all the complexes have the first ligand field band ($^1A_{1g} \rightarrow {}^1T_{1g}$ in O_h) in the range 485–495 nm and the second ligand field band at *ca.* 350 nm. All the amino acid derivatives have $\nu(COO^-)_{sym}$ near 1380 cm^{-1} (KBr disc). For glycine and α-alanine in the solid state these bands occur at 1413 cm^{-1} and 1412 cm^{-1} respectively and fall to 1392 cm^{-1} in $[Cu(gly)_2]$ and 1374 cm^{-1} in $[Pd(gly)_2]$ [3]. All the complexes derived from the amino acids have a strong band near 1650 cm^{-1} assigned to the asymmetric stretching vibration of the coordinated CO_2^- group. Busch and coworkers [4] have shown that the asymmetric stretching vibration of the unionised CO_2H group occurs at 1750–1700 cm^{-1}, whereas the ionised and coordinated CO_2^- stretching band occurs at 1650–1620 cm^{-1} for complexes with Co(III) and Cr(III). All the complexes show the expected broad NH_3^+ stretching band in the 3100–2600 cm^{-1} region.

For the glycine derivative, Λ_M = 439 ohm^{-1} cm^2 mol^{-1} at 25 °C for a 1 × 10^{-3} *M* solution in water, consistent with its formulation as a 3.1 electrolyte (typical values fall in the range 420–480 ohm^{-1} cm^2 mol^{-1} for 3·1 electrolytes in water).

Potentiometric titration of the glycine derivative at I = 0.1 *M* indicates approximate pK_a values of 10.2 and 10.8 at 25 °C for the NH_3^+ ionisation. Values which may be compared with pK 9.78 at 25 °C for the ionisation $NH_3^+CH_2CO_2^- \rightleftharpoons NH_2CH_2CO_2^- + H^+$. The ^1H NMR spectra of the amino-acid derivatives in D_2O display the expected characteristics All the complexes have the imine methyl signal of the macrocycle in the range 2 45–2.50 δ The CH_2 signal of the glycine ligand occurs as a singlet at 3.55 δ and the methyl group of the β-alanine ligand as a doublet at 1.47 δ (J = 7.2 Hz). In the leucine derivative two methyl doublets occur at 0.96 and 1.05 δ (J *ca.* 5 Hz) assigned to the non-equivalent methyl groups.

The bis imidazole derivative is yellow in colour. The i.r spectrum has a strong sharp band at 1640 cm^{-1} assigned to νC=N in the macrocycle and the characteristic ClO_4 bands at *ca.* 1100 cm^{-1} (br) (νOCl asym) and 625 cm^{-1} (δClO_4). The ^1H spectrum (CD_3CN solution) has the imine methyl of the macrocycle at 2.82 δ and signals due to the imidazole protons at 7 15, 7.34 and 7.6 δ

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