Esterification of Amino-acids chelated to Cobalt(III), Molybdenocene, and Platinum(II). Stability of Chelated Esters *versus* Dechelation

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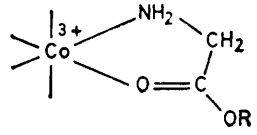
Several complexes of non-functionalized amino-acids, $[Co(en)_2(GlyO)]^{2+}$, $[Co(tren)(aa)]^{2+}$ (en = ethylene-1,2-diamine, GlyO = glycinate), where aa = glycinate, alaninate, or leucinate anion, *trans*-$[Pt(GlyO)_2]$, and $[Mo(\eta\text{-}C_5H_5)_2(GlyO)]^+$ have been esterified either by alkylation with dimethyl sulphate or methyl toluene-*p*-sulphonate or acid-catalyzed esterification in methanol. With the cobalt(III) and molybdenocene complexes, a chelated amino-acid ester is obtained. The reactivity of the complexes is lower than that of the carboxylate salts in the alkylation reactions but comparable to that of the free acids in the acid-catalyzed reactions with methanol. With the cobalt and molybdenocene complexes, a slow dechelation reaction is observed in the presence of chloride ions to give the $[Co(tren)(GlyOCH_3)Cl]^{2+}$ (tren = 2,2′,2″-triaminotriethylamine) and $[Mo(\eta\text{-}C_5H_5)_2(GlyOCH_3)Cl]^+$ ions. With the platinum complex, only a dechelated ester can be isolated.

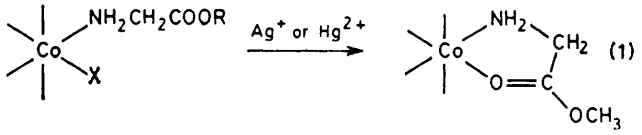
SINCE the initial discovery by Kroll [1] that transition-metal ions catalyze the hydrolysis of amino-acid ester complexes, the reactivity of chelated amino-acid esters has been extensively studied. Because of the inertness of their co-ordination sphere, the cobalt complexes (I) were chosen for detailed mechanistic studies.



(I)

Chelation of the ester has been shown to increase considerably its susceptibility to nucleophilic attack [2] and to stabilize tetrahedral intermediates.[3] This chemistry has been reviewed.[4]

Cobalt(III) complexes of the parent compound (the glycine † derivative) have been prepared by silver(I)- or mercury(II)-catalyzed chelation of monodentate complexes [5] [reaction (1), X = Cl or Br].



(1)

This method, however, is not applicable to the preparation of chelated esters of other more bulky amino-acids because the amino-acid esters do not react with dihalogenotetra-amine complexes of cobalt(III).[6] Furthermore, the choice of solvents for the chelation reaction is very limited: with dimethyl sulphoxide (dmso), dimethylformamide (dmf), or acetonitrile, there is competition between the solvent and the ester function for the free co-ordination position after halogen abstraction so that only poor co-ordinands like acetone, ethyl acetate, or sulpholane (tetrahydrothiophen 1,1-dioxide) can be used; unfortunately, these are relatively poor solvents for the complexes.[7]

On the other hand, the complexes $[Co(N_4)(aa)]^{2+}$ (N_4 = polyamine ligand and aa = amino-acid) can be prepared from essentially all the amino-acids.[8] Moreover, inert amino-acid complexes of several other metals have been described.[9,10] In this work, we have applied the classical methods of esterification to several complexes of non-functionalized amino-acids, with some modification to take into account the change in reactivity compared to normal carboxylic acids. These experiments complement the available information on the change in reactivity of carboxylate functions co-ordinated to transition metals [11–13] and they allow a comparison of the relative stabilities of amino-acid ester chelates of the three systems investigated.

RESULTS AND DISCUSSION

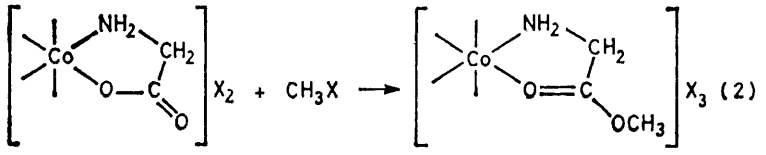
(A) *Alkylation Reactions.*—Three alkylating agents, methyl iodide, methyl toluene-*p*-sulphonate, and dimethyl sulphate have been tested on $[Co(tren)(GlyO)]X_2$ complexes (tren = 2,2′,2″-triaminotriethylamine) in four different solvents, sulpholane, dmso, dmf, and methanol [reaction (2)]. The most significant results are collected in Table 1.

The alkylation reaction can only be run in solvents of poor nucleophilicity contrary to what is observed with sodium, potassium, and tetra-alkylammonium salts of carboxylic acids that are easily alkylated in solvents like dmf, dma (dimethylacetamide), or dmso.[14] In dmso, a very good solvent for these complexes, no alkylation takes place, presumably because the solvent is alkylated faster than the complex and the alkylated solvent [15] is too poor an alkylating agent. In dmf, a reasonable yield of ester can be obtained, but, here again, the solvent competes for the methylating agent and the alkylating power of the alkylated dmf [16] is hardly high enough, as shown by the fact that a much lower yield is obtained if the alkylating agent is first incubated for some time with the solvent. The complexation reduces the nucleophilicity of the carboxylic function so that it becomes comparable to that of an amide. It should be men-

† Throughout this paper, and the following one: Gly = glycine, Ala = alanine, Leu = leucine, Asp = asparagine, Val = valine, His = histidine; deprotonated forms are represented GlyO *etc.* and methylated forms, $GlyOCH_3$ *etc.*

tioned that the pK_a of the protonated complex $[Co(en)_2(GlyO)][SO_4]$ (en = ethylene-1,2-diamine) [17] and oxygen-protonated amides (−0.51 for acetamide and −1.46 for 4-methoxybenzamide) [18] fall in the same range.

(B) *The Acid-catalyzed Esterification.*—In the acid-catalyzed reaction with methanol, it is necessary to dehydrate the medium to drive the reaction to completion [reaction (3)]. The following methods were found satisfactory: dehydration by acid-catalyzed hydrolysis of dimethyl sulphite or of acetone dimethyl acetal. The physical methods of dehydration, like the azeotropic distillation (C_6H_6–EtOH–H_2O or CCl_4–EtOH–H_2O) or reactions in the presence of molecular sieves were not efficient enough.



(2)

TABLE 1

Alkylation of $[Co(tren)(GlyO)]X_2$ with methylating agents [a]

Methylating agent (concentration/ mol dm^{-3})	Solvent	Time/h	Counter ion (concentration/ mol dm^{-3})	Yield of crude ester (%)
$(MeO)_2SO_2$ (0.3)	Sulpholane [b]	2	ClO_4^- (0.12)	≥95
$(MeO)_2SO_2$ (0.2)	dmf	2	ClO_4^- (0.08)	70
$(MeO)_2SO_2$ (0.2)	dmso	2	ClO_4^- (0.08)	<5
$CH_3C_6H_4SO_3Me$-*p* (0.1)	Sulpholane [b]	2 or 24	$CH_3C_6H_4SO_3$-*p*	<5
$CH_3C_6H_4SO_3Me$-*p* (0.3)	dmf	2	$CH_3C_6H_4SO_3$-*p*	70
$CH_3C_6H_4SO_3Me$-*p* (0.3)	dmf [c]	2	$CH_3C_6H_4SO_3$-*p*	30
$CH_3C_6H_4SO_3Me$-*p* (1.0)	MeOH	2	$CH_3C_6H_4SO_3$-*p*	≥95
$CH_3C_6H_4SO_3Me$-*p* (1.0)	Sulpholane [b]	2	$CH_3C_6H_4SO_3$-*p*	<5
$CH_3C_6H_4SO_3Me$-*p* (1.0)	dmso	2	$CH_3C_6H_4SO_3$-*p*	<5

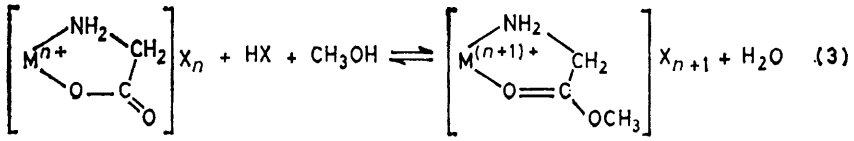
[a] At 60 °C. [b] In sulpholane, the cobalt complex was only moderately soluble. [c] The alkylating agent was first incubated in the solvent for 2 h at 60 °C, then the cobalt complex was added.

Two kinds of acids have been used: sulphuric and toluene-*p*-sulphonic acids whose counter ions are not nucleophilic, and hydrochloric acid. This last one is prepared *in situ* together with the dimethyl sulphite by solvolysis of thionyl chloride.[19] The most significant results are collected in Table 2. The toluene-*p*-sulphonate salts of the cobalt complexes are reasonably soluble in methanol (up to 0.125 mol dm^{-3} for the glycinate complex); in the hydrochloric acid solutions, the chlorides are not very soluble and the esterification takes place under partially heterogeneous conditions.

The esterification of $[Mo(\eta\text{-}C_5H_5)_2(GlyO)]Cl$ is easily followed by n.m.r. spectroscopy because the cyclopentadienyl groups give a sharp signal around 6 p.p.m. for each complex in solution. When D_2SO_4 is added to a solution of the complex in CD_3OD, there is an immediate downfield shift in the position of the CH_2 signal of 0.22 p.p.m. in 1.2 mol dm^{-3} D_2SO_4 and of 0.42 p.p.m. in 4.5 mol dm^{-3} D_2SO_4; similarly, the cyclopentadienyl signal moves downfield by 0.07 and 0.13 p.p.m. respectively but there is no indication of protonation of the cyclopentadienyl ligands even in these strongly acidic solutions. The complex is transformed quickly into an equilibrium mixture of starting material and ester. The addition of sulphite drives the reaction to completion. In CD_3OD and 1.65 mol dm^{-3} DCl (0.82 mol dm^{-3} sulphite) the half-life is 7.5 min at 25 °C ($k = 1.54 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}).

The esterification of $[Co(tren)(GlyO)][CH_3C_6H_4SO_3\text{-}p]_2$ has been followed in the presence of toluene-*p*-sulphonic acid (1 mol dm^{-3}); the rate constants were 2.0×10^{-4} s^{-1} (at 45 °C) and 8×10^{-4} s^{-1} (at 56 °C). It was checked that the dimethyl sulphite does not contribute to the reaction by a direct alkylation mechanism: the rates in the presence and absence of 1 mol dm^{-3} $SO(OMe)_2$ are identical within experimental error.*

In the acid-catalyzed reaction, the reactivity of the complexed carboxylic function is quite similar to that of normal carboxylic acids, as shown by the following comparisons of rates: HCl-catalyzed esterification of benzoic acid, 1.94×10^{-4} dm^3 mol^{-1} s^{-1} (ref. 20); of acetic acid, 6.2×10^{-2} dm^3 mol^{-1} s^{-1} (ref. 21); of diethylacetic acid, 5.0×10^{-4} dm^3 mol^{-1} s^{-1} (ref. 22); toluene-*p*-sulphonic acid-catalyzed esterification of benzoic acid, 2.1×10^{-3} dm^3 mol^{-1} s^{-1} (ref. 23). The slight decrease in reactivity is easily accounted for by the increase in steric hindrance. The carboxylic function in the complex is protonated more easily than the free



(3)

* The kinetics in the absence of sulphite are measured by u.v. spectroscopy at low complex concentration so that in the presence of dry reagents the reaction goes essentially to completion.

TABLE 2

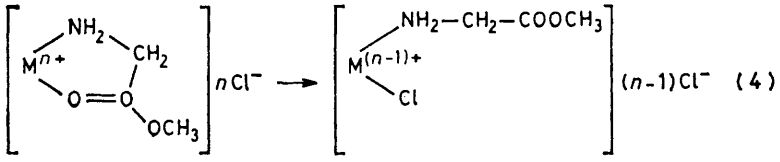
Acid–catalyzed esterifications

Complex	Catalyst	Acid concentration [a]/mol dm^{-3}	T/°C	Time/h	Yield of crude ester (%)
[Co(tren)(GlyO)][$CH_3C_6H_4SO_3$-*p*]$_2$	$CH_3C_6H_4SO_3H$-*p*·H_2O	0.34	52	2.5	50
[Co(tren)(GlyO)][$CH_3C_6H_4SO_3$-*p*]$_2$	$CH_3C_6H_4SO_3H$-*p*·H_2O	0.9	20	72	10
[Co(tren)(GlyO)][$CH_3C_6H_4SO_3$-*p*]$_2$	$CH_3C_6H_4SO_3H$-*p*·H_2O	0.9	65	1	95
[Co(tren)(GlyO)]Cl_2	HCl	2.5	30	10	90 [b]
[Co(tren)(GlyO)]Cl_2	HCl	5.0	45	1	95
[Co(tren)(L-AlaO)][$CH_3C_6H_4SO_3$-*p*]$_2$		1.0	65	2	95
[Co(tren)(L-LeuO)][$CH_3C_6H_4SO_3$-*p*]$_2$	$CH_3C_6H_4SO_3H$-*p*·H_2O	1.0	65	2	95
[Mo(η-C_5H_5)$_2$(GlyO)]Cl	H_2SO_4	1.2	28	10 min	50
[Mo(η-C_5H_5)$_2$(GlyO)]Cl	H_2SO_4	1.2	28	1	95
trans-[Pt(GlyO)$_2$]	H_2SO_4	2.0	40	5	*c*

[a] Acid concentration of the methanolic solution before adding the dehydrating agent. [b] Plus dechelated ester (10%). [c] Only a dechelated ester is obtained.

carboxylic acid, but the reactivity of the complexed protonated substrate is lower than that of R–$COOH_2^+$. The two effects cancel approximately.

(C) *The Dechelation Reaction.*—In hydrochloric acid solutions, a dechelation is observed [reaction (4)]. With the molybdenocene and cobalt complexes, this reaction is slow: for [Mo(η^5-C_5H_5)$_2$(GlyOCH$_3$)]$^{2+}$, $t_{1/2}$ *ca.* 12 h at 25 °C in 1.65 mol dm^{-3} DCl; for [Co(tren)(GlyOCH$_3$)]$^{3+}$, $t_{1/2}$ *ca.* 5 d at 30 °C and 6 h at 65 °C in 2.5 mol dm^{-3} HCl. It is largely suppressed with a more bulky amino-acid; the esterification of [Co(tren)(L-AlaO)]Cl_2 can be conducted in refluxing methanol for 3 h without



(4)

any sign of dechelation. In the absence of a nucleophilic ion, the equilibrium between the chelated and the monodentate ester might favour the former; the chelation of [Co(en)$_2$(H_2O)(GlyOCH$_3$)]$^{3+}$ is believed to take place spontaneously.[12] When the ester function is not part of a chelate, as in [Co(NH_3)$_5$(CH_3COOCH_3)]$^{3+}$, it is extremely labile and easily aquated ($k \geqslant 2 \times 10^{-2}$ s^{-1}).[24] The dechelation, with Cl^- as entering group, is thus at least 1.4×10^4 times slower. The chelate effect appears to be very large here compared for instance to the ring-opening of diaminoalkane complexes of platinum(II).[25]

With the complex *trans*-[Pt(GlyO)$_2$], only a dechelated ester is obtained even when the catalyst is sulphuric acid. We have been unable to detect the accumulation of a chelated ester. The hydrochloric acid-catalyzed esterification with dechelation has been described previously.[26] The difference between this complex and the first two results from the weak affinity of the 'soft' platinum(II) ions for the 'hard' ester ligand.

From a practical point of view, the esterification of an acetate ligand co-ordinated to a transition-metal ion could prove to be as effective as silver-catalyzed halogen abstraction or nitrous acid-catalyzed azide or carbamate abstraction [27] for the preparation of new complexes of weakly nucleophilic ligands.

EXPERIMENTAL

Infrared spectra were recorded as KBr pellets on a Perkin-Elmer model 457 spectrometer. U.v. and visible spectra were recorded on a Unicam SP 1800 spectrophotometer. Proton and ^{13}C n.m.r. spectra were taken on a JEOL FX 60 (60 MHz) in D_2O (0.1% DCl) solutions. The optical rotations were measured in a thermostatted 10-cm cell at 20 °C on a Perkin-Elmer 241 polarimeter.

Materials.—The complex [Co(en)$_2$(GlyO)]Br_2·H_2O was prepared as described previously.[17]

[Co(tren)(GlyO)]Cl_2, was obtained by suspending [Co(tren)Cl_2]Cl (2.8 g, prepared according to Kimura *et al.*[8]) in water (20 cm^3, containing 0.8 g of glycine); the mixture was first stirred for 30 min with gentle warming, then *N*-ethylmorpholine (2 g) was added and the solution kept at 60—70 °C for 5 h. After filtration and evaporation *in vacuo*, the complexes were washed with ethanol to dissolve the red isomer, recrystallized from ethanol–methanol–water (10 : 2 : 1), and dried *in vacuo* at 130 °C (Found: Cl, 20.55. Calc. for $C_8H_{22}Cl_2CoN_5O_2$: Cl, 20.25%); i.r., 1 660—1 650 cm^{-1}; u.v., 472 nm (ε 105 dm^3 mol^{-1} cm^{-1}), 342 (ε 100).

[Co(tren)(GlyO)][$CH_3C_6H_4SO_3$-*p*]$_2$. This was obtained by first transforming [Co(tren)Cl_2]Cl (6 g) into [Co(tren)(OH)$_2$]-OH by passing through an Amberlite IR 401 column (40 cm × 3 cm, OH form). The collected eluate (*ca.* 600 cm^3) was neutralized to pH 7.5 with toluene-*p*-sulphonic acid and glycine (2.1 g) added. The mixture was heated for 7 h at 60 °C. After solvent evaporation, the complex was crystallized from ethanol–methanol–water (13 : 6 : 1) (Found: C, 42.5; H, 6.05; N, 11.0. Calc. for $C_{22}H_{36}$-$CoN_5O_8S_2$: C, 42.5; H, 5.85; N, 11.25%). [Co(tren)-(GlyO)][ClO_4]$_2$ was prepared by a similar method.

[Co(tren)(L-AlaO)][$CH_3C_6H_4SO_3$-*p*]$_2$. The complex [Co-(tren)(L-AlaO)]Cl_2 was prepared as described for [Co(tren)-

(GlyO)]Cl_2 and recrystallized from 2 mol dm^{-3} HCl–methanol (1 : 15). This complex is transformed into the toluene-*p*-sulphonate by passing through an Amberlite IRA 401 column ($CH_3C_6H_4SO_3$-*p* form) and recrystallized from ethanol–methanol–water (13 : 6 : 1) (Found: C, 42.1; H, 6.15; N, 10.65. Calc. for (the monohydrate) $C_{23}H_{40}CoN_5O_9S_2$: C, 42.25; H, 6.1; N, 10.7%); α(589.3 nm, 20 °C, 5 g dm^{-3} in H_2O, 10 cm) (calculated for the non-hydrated complex) −24.7°; ^{13}C n.m.r., δ(p.p.m.) CH_2(tren) 60.9, 58.2, 44.8, 43.9; CO, 183.7; CH_2(GlyO) 45.7; toluene-*p*-sulphonate 141.8, 138.8, 128.8, 124.6, and 19.6.

[Co(tren)(L-LeuO)][$CH_3C_6H_4SO_3$-*p*]$_2$. The complex [Co(tren)(L-LeuO)]Cl_2 was prepared as described for [Co(tren)(GlyO)]Cl_2 and recrystallized from ethanol–methanol–water (13 : 6 : 1). The toluene-*p*-sulphonate was obtained from the chloride by anion-exchange chromatography and recrystallized from a very concentrated solution in water (Found: C, 45.1; H, 6.65; N, 10.05. Calc. for (the monohydrate) $C_{26}H_{46}CoN_5O_9S_2$: C, 44.9; H, 6.65; N, 10.05%), ^{13}C n.m.r., besides signals due to CH_2(tren) and toluene-*p*-sulphonate, δ(p.p.m.) CO 185.0; CH^{α} 55.4; CH^{β}_2 41.1; CH^{γ} 23.3; $CH^{\delta+\delta'}_3$ 21.8 and 19.1; α(589.3 nm, 20 °C, 6.9 g dm^{-3} in H_2O_2 10 cm) (calculated for the non-hydrated complex) −48.1°.

[Co(en)$_2$($GlyOCH_3$)Br]Br_2. This was prepared according to the method of Alexander and Busch [28] (Found: C, 16.25; H, 4.8; Br, 46.4. Calc. for (the monohydrate) $C_7H_{25}Br_3CoN_5O_3$: C, 16.0; H, 4.8; Br, 45.6%). [Co(tren)($GlyOCH_3$)Cl][ClO_4]$_2$ was prepared according to Kimura *et al.*[8] (Found: C, 20.2; H, 4.8; N, 13.0. Calc. for $C_9H_{25}Cl_3CoN_5O_{10}$: C, 20.45; H, 4.75; N, 13.25%). [Co(tren)($GlyOCH_3$)][ClO_4]$_3$ was prepared by chelation of [Co(tren)($GlyOCH_3$)Cl][ClO_4]$_2$ as described by Buckingham *et al.*[5] *trans*-[Pt(GlyO)$_2$] was prepared from $K_2[PtCl_4]$ by a route involving K_2[Pt(GlyO)$_4$] and [Pt(Gly)$_2$$Cl_2$] to avoid the presence of the *cis* isomer; it was characterized by i.r. spectroscopy. [Mo(η-C_5H_5)$_2$(GlyO)]Cl was prepared as described by Gore and Green [10] and characterized as its hexafluorophosphate salt by i.r., n.m.r., and u.v. spectroscopy.

Esterification Methods.—The efficiency of various esterification methods was first determined with cobalt(III) complexes of glycine, because the expected products can be prepared independently by known procedures and their spectra recorded.

The esterification reactions were first followed by two methods: i.r. spectroscopy and synthesis of a dipeptide.

The i.r. spectra of the starting amino-acid complexes [peaks at 1 650s and 1 370s cm^{-1} (both sharp)], the chelated ester [peaks at 1 625s cm^{-1} (sharp) and 1 315m cm^{-1}], and the monodentate ester (peak at 1 740 cm^{-1} (sharp)] are sufficiently different to permit a convenient monitoring of the reaction. When the i.r. spectrum of a crude precipitate of all the cobalt complexes present in solution during esterification is recorded, it gives a good estimate (to an accuracy better than 10%) of the relative percentage of starting material and esters in the mixture.

The chelated ester is a very hygroscopic product whose hydrolysis in the presence of traces of water under neutral or basic conditions is very fast. When the crude yield of ester was high enough, it was felt necessary to measure the yield of ' useful ester ' (the amount of ester that could be transformed into a dipeptide by reaction with an amino-acid ester, glycine methyl ester or preferentially, the more bulky leucine methyl ester). The percentage of dipeptide formed was determined by separation of the products by ion-exchange chromatography. This test is significant because the hydrolysis is faster than the aminolysis.[3]

When the ester yield is >95%, the i.r. spectrum is identical to that of a sample prepared by the chelation method. None of the cobalt(III) chelated esters could be crystallized. Consequently, they were not subjected to elemental analysis. This limitation has been experienced by other workers.[5b]

The Alkylation Reactions.—The complex [Co(tren)(GlyO)]X_2 was suspended or dissolved at a concentration around 0.1 mol dm^{-3} in a dry solvent and incubated at 60 °C for 2 h with the alkylating agent (*ca.* 0.25 mol dm^{-3}). The reaction mixture was cooled down and the complexes precipitated with dry diethyl ether. In dmf, sulpholane, and methanol, it was necessary to add first a small quantity of another solvent to avoid the formation of an oil [chloroform for dmf (1 : 3), Pr^iOH for methanol (1 : 1), and dichloromethane or thf for sulpholane (1 : 1)]. The extent of esterification is then estimated from the i.r. spectrum of the precipitate.

The Acid-catalyzed Reaction with Alcohols.—For the toluene-*p*-sulphonic acid-catalyzed esterification of cobalt complexes, toluene-*p*-sulphonic acid (1 mol dm^{-3}) and the dehydrating agent (2,2-dimethoxypropane, 3 mol dm^{-3}, or dimethyl sulphite, 3.5 mol dm^{-3}) were dissolved in methanol with the complexes [Co(tren)(aa)][$CH_3C_6H_4SO_3$-*p*]$_2$ (0.125 mol dm^{-3}). The mixture was kept for 2 h at 60 °C and precipitated with Pr^iOH and diethyl ether.

For the dipeptide synthesis, instead of precipitating the complex, an amino-acid ester hydrochloride or toluene-*p*-sulphonate (to a concentration of 0.14 mol dm^{-3}) was added with enough *N*-ethylmorpholine (dried over Li[AlH_4]) to neutralize all the acids (about 1.3 mol dm^{-3}). After 30 min, the reaction mixture was diluted with water (1 : 1), poured on an Amberlite IRC 50 resin (sodium form), and eluted with 0.4 mol dm^{-3} NaCl. The excess of the second amino-acid and the *N*-ethylmorpholinium salt come out first followed by eventually some [Co(tren)(aa)]$^{2+}$ complex. The column was washed with water and the dipeptide complex was recovered by elution with 0.1 mol dm^{-3} HCl and characterized by i.r. and ^{13}C n.m.r. spectroscopy.

The kinetics of the esterification of [Co(tren)(GlyO)][$CH_3C_6H_4SO_3$-*p*]$_2$ in the absence of dimethyl sulphite were followed in 10^{-2} mol dm^{-3} solutions at 342 nm {ε for [Co(tren)(GlyO)]$^{2+}$ = 100, ε for [Co(tren)($GlyOCH_3$)]$^{3+}$ ion = 93 dm^3 mol^{-1} cm^{-1}} in a thermostatted cell. For this reaction, the toluene-*p*-sulphonic acid was dried by heating above the melting point on an oil bath at 130 °C under vacuum and the procedure repeated several times. It was recrystallized from ethyl acetate. In the presence of dimethyl sulphite, u.v. spectroscopy cannot be used. An approximate rate constant was obtained by the i.r. spectroscopic method, by assuming that the absorption coefficient for the NH_2 bending peak does not change on esterification.

The sulphuric acid-catalyzed esterification of [Mo(η-C_5H_5)$_2$(GlyO)]Cl was conducted in the same way except that less dimethyl sulphite was used (0.5 mol dm^{-3}) and the chelated ester could be crystallized as an hexafluorophosphate; this last step had to be run in plastic vessels. Spectra: u.v., 364 nm (ε 155) and 568 nm (ε 50); i.r. (KBr disc), 3 240m, 3 135, 3 105m, 1 623s, 1 477m, 1 407m, 1 300m, 1 055m, 1 010m, 760m, 585m, plus the PF_6 peaks at 840s and 560ms cm^{-1}; ^1H n.m.r. [CD_3OD–D_2SO_4(1 mol dm^{-3})], 6.23 (10 H, η-C_5H_5), 5.16 (2 H, br, NH_2), 3.96 (t, 2 H, CH_2), 3.68 (s, 3 H, CH_3).

The hydrochloric acid-catalyzed esterification. The procedure is similar except that the dimethyl sulphite and hydrochloric acid are produced *in situ* by solvolysis of thionyl chloride at −30 °C before adding the complex. The complex $[Mo(\eta\text{-}C_5H_5)(GlyOCH_3)Cl]^+$ can be recovered by precipitation with $[NH_4][PF_6]$. Alternatively, the complex can be purified after solvent evaporation by chromatography on alumina (elution with $CHCl_3$–CH_3OH, 95 : 5) and recrystallized from water by addition of a concentrated solution of $[NH_4][PF_6]$ (Found: C, 31.1; H, 3.4; N, 2.8. Calc. for $C_{13}H_{17}ClF_6MoNO_2P$: C, 31.5; H, 3.45; N, 2.85%). U.v., $\lambda_{max.}$ 402 (ε 167) and 582 (ε 86); i.r. (KBr disc), 3 300m, 3 220m, 3 140m, 1 730s, 1 440m, 1 435m, 1 425m, 1 235s, 1 225s, 1 055s, 390w, and 280w cm^{-1}, plus the PF_6 peaks; n.m.r. (in D_2O), 5.85 (10 H, η-C_5H_5), 3.74 (s, 3 H, CH_3), 3.23 (s, 2 H, CH_2).

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