Reactions of Complex Compounds of Cobalt. Part 10.[1] Mixed Complexes of Cobalt(III) containing 3-Azapentane-1,5-diamine and an Amino-acid

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Several new complexes of 3-azapentane-1,5-diamine (apd) are described: [Co(apd)(GlyO)(OH_2)]$^{2+}$, [Co(apd)(Gly)(OH_2)]$^{3+}$ (Gly = glycine, GlyO = glycinate) with a protonated co-ordinated carboxyl group, and [Co(apd)(PheO)(OH)]$^{+}$ (PheO = phenylalaninate). These are unexpectedly obtained as the major products from the reaction at low temperature of [Co(apd)$(OH)_3$] with glycylglycylglycine or L-phenylalanylglycylglycine. The ion [Co(apd)(C_2O_4)(OH_2)]$^{+}$ has also been prepared for comparison, and the acidity constants for these and for several other aqua(3-azapentane-1,5-diamine)cobalt(III) complexes are given.

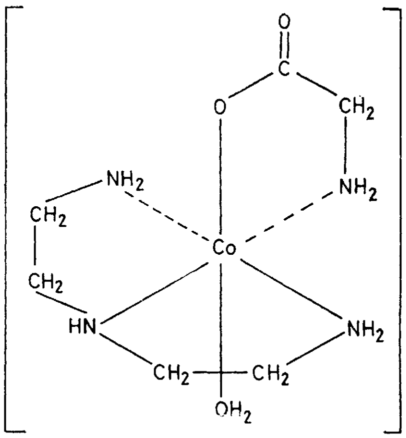
THE mononuclear complexes of cobalt(III) with 3-azapentane-1,5-diamine (apd) can be classified into three groups, of the types [Co(apd)L] (L being a terdentate ligand such as a dipeptide [2,3]), [Co(apd)(L–L)X] {L–L being bidentate and X unidentate, *e.g.*[4,5] [Co(apd)(GlyO)Cl]$^{+}$}, and [Co(apd)X(Y)Z] (X, Y, and Z being unidentate).

In our work on the peptide complexes of cobalt, and on their selective hydrolysis, we have obtained new apd complexes and measured a number of properties of them and of related known compounds. We report these findings here, with some comments on other aspects of the Co–apd system. In particular, from the mild reaction at 5 °C of glycylglycylglycine with (3-azapentane-1,5-diamine)trihydroxocobalt(III) a major product is the complex [Co(apd)(GlyO)(OH)]$^{+}$. We describe the syntheses of this complex and of some analogues, but postpone general discussion of our extensive work on peptide hydrolysis by the Co^{III}(apd) fragment.

RESULTS AND DISCUSSION

Complexes of the type [Co(apd)(GlyO)X]$^{+}$ (X = Cl, NO_2, or CN) are known: [4,5] on dissolution in 0.2 mol dm^{-3} sodium hydroxide, or on standing in aqueous solution, the chloro-complex was found [6] to give [Co(apd)(GlyO)(OH)]$^{+}$. Reaction under mild conditions of [Co(apd)$(OH)_3$] with glycine or with glycylglycylglycine, followed by chromatography and acidification with perchloric acid, gave the new crystalline products [Co(apd)(GlyO)(OH_2)][ClO_4]$_2$·H_2O (1) and [Co(apd)(Gly)(OH_2)][ClO_4]$_3$ (2). In a similar reaction with L-phenylalanylglycylglycine, [Co(apd)(PheO)(OH)][ClO_4] was isolated without acidification.

In the i.r. spectrum of the triperchlorate (2) the peak at *ca.* 1 600 cm^{-1} is split † relative to that in the diperchlorate (1), suggesting that the 'extra' proton is attached to the carbonyl group of co-ordinated glycinate. Although in neutral solution the proton magnetic resonance of [Co(apd)(GlyO)(OH)]$^{+}$ shifts only very slightly as the co-ordinated hydroxo-group is protonated, a much larger downfield shift (*ca.* 0.5 p.p.m.) occurs in strongly acidic solution which is typical of protonation of a carbonyl group of a co-ordinated glycinate residue.[2] The visible spectrum of the acidic solution shows a clear splitting of the longest-wavelength spin-allowed absorption band in the 500-nm region, so that the oxygen ligands are probably mutually *trans*, suggesting the *mer* structure shown for (1).



Although it is possible that the [Co(apd)(GlyO)(OH)]$^{+}$ formed in the reaction of [Co(apd)$(OH)_3$] with L-alanylglycylglycine and with L-phenylalanylglycylglycine results from the attack of [Co(apd)$(OH)_3$] on the *C*-terminal end of the peptide, an alternative explanation, that [Co(apd)$(OH)_3$] reacted with glycylglycine formed by the initial cleavage of the tripeptide, is more likely. The proportions of [Co(apd)(AlaO)(OH)]$^{+}$ and [Co(apd)(GlyO)(OH)]$^{+}$ are consistent with *N*-terminal attack as the sole mechanism if the reaction rates of [Co(apd)-

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† A similar splitting is found for [Co(Gly)(en)$_2$][ClO_4]$_3$ made by freeze-drying a solution of [Co(GlyO)(en)$_2$]$^{2+}$ in perchloric acid or [Co(en)$_2$(Gly)]$^{3+}$ (en = ethylenediamine).

[1] Part 9; I. G. Browning, R. D. Gillard, J. R. Lyons, and P. R. Mitchell, *J.C.S. Dalton*, 1974, 373.

[2] I. G. Browning, R. D. Gillard, J. R. Lyons, P. R. Mitchell, and D. A. Phipps, *J.C.S. Dalton*, 1972, 1815.

[3] I. G. Browning, Ph.D. Thesis, University of Kent at Canterbury, 1973.

[4] Y. Wu and D. H. Busch, *J. Amer. Chem. Soc.*, 1972, **94**, 4115.

[5] K. Ohkawa, J. Fujita, and Y. Shimura, *Bull. Chem. Soc. Japan*, 1972, **45**, 161.

[6] Y. Wu, Ph.D. Dissertation, Ohio State University, 1968.

$(OH)_3]$ with L-alanylglycylglycine and with glycylglycine are the same.

The electronic spectra in aqueous solutions of (1) and of its oxalato-analogue (made by a similar synthesis) are given in Table 1. In each case, the spectrum varies reversibly with pH, confirming the presence of co-ordinated water; the pK value for the aqua-ligand in the glycinato-complex derived from changes in the visible absorption spectra agrees with that from potentiometric titration.

The potentiometric pK_a values obtained at 25 °C during this work are as follows: *fac*-$[Co(apd)(OH_2)_3]^{3+}$, pK_1 5.0, pK_2 7.4, pK_3 9.7 * {the accuracy of these values is limited because in the higher range of pH there will be some isomerization to the *mer* isomer of $[Co(apd)(OH)_3]$, which we found to be more stable}; *mer*-$[Co(apd)(OH_2)_3]^{3+}$ pK_1 5.5, pK_2 7.7, pK_3 9.8; $[Co(apd)(GlyO)(OH_2)]^{2+}$, 5.9, p$K$ (spectrophotometric) 5.8; and $[Co(apd)(C_2O_4)(OH_2)]^+$, p$K$ 7.2.

As expected, for both isomers of $[Co(apd)(OH_2)_3]^{3+}$, the values of the acidity constants of the co-ordinated water increase as the charges on the complex decrease. The same trend is found for the complex ions $[Co(apd)(L-L)(OH_2)]^{n+}$ with only one co-ordinated water: in the series L–L = en, GlyO⁻, and $[C_2O_4]^{2-}$ the values of pK are 5.14,[8] 5.9, and 7.2 respectively.

The *facial* isomers of $[Co(apd)(OH_2)_2(OH)]^{2+}$ and of $[Co(apd)(OH_2)_3]^{3+}$ are known [9,10] to be more stable than the *meridional* isomers: favourable hydrogen bonding between the water ligands was said [11] to be a possible reason. In an attempt to prepare *fac*-$[Co(apd)_2]^{3+}$, Keene and Searle [11] treated *fac*-$[Co(apd)(OH_2)_3]^{3+}$ with apd in alkaline solution: however, they unexpectedly obtained almost isomerically pure *mer*-$[Co(apd)_2]^{3+}$, and thus they suspected the identity of the starting material *fac*-$[Co(apd)(OH_2)_3]^{3+}$ as this complex had never been isolated but only obtained in solution. By freeze-drying a solution of *fac*-$[Co(apd)(OH_2)_3]^{3+}$ in $HClO_4$ we obtained for the first time crystalline *fac*-$[Co(apd)(OH_2)_3]^{3+}$ as the perchlorate salt, and characterized it by analysis and by ^1H n.m.r. on a redissolved sample. However, a solution of *fac*-$[Co(apd)(OH)_3]$, prepared by adding base to *fac*-$[Co(apd)(OH_2)_3]^{3+}$, isomerized to *mer*-$[Co(apd)(OH)_3]$, identified by ^1H n.m.r. and visible spectroscopy. Freeze-drying *fac*-$[Co(apd)(OH_2)_3]^{3+}$ in HCl gave only the known [9] *mer* isomer of $[Co(apd)Cl_3]$, identified by i.r. spectroscopy; thus complete isomerization occurred even at the very low temperature of freeze-drying.

TABLE 1

Electronic spectra * of *mer*-$[Co(apd)(L-L)(OH_2)]^{n+}$

Complex	pH	λ	ε	λ	ε
$[Co(apd)(GlyO)(OH_2)]^{2+}$	acid	520, 452	61, 78	356	103
$[Co(apd)(GlyO)(OH)]^+$	Alkaline	500	95	363	132
$[Co(apd)(C_2O_4)(OH_2)]^+$	4.0	506	96	366	144
$[Co(apd)(C_2O_4)(OH)]$	10.6	522	106	365	133

* λ in nm, ε in $dm^3 mol^{-1} cm^{-1}$.

As *fac*-$[Co(apd)(OH_2)_3]^{3+}$ and *fac*-$[Co(apd)(OH_2)_2(OH)]^{2+}$ are the *more* stable [9,10] and *fac*-$[Co(apd)_2]^{3+}$,[11] *fac*-$[Co(apd)(OH)_3]$, and *fac*-$[Co(apd)Cl_3]$ (which was too unstable even to be isolable) are the *less* stable isomers, it seems that, as suggested by Keene and Searle,[11] hydrogen bonding between at least two water ligands is required to stabilize the *facial* configuration.

EXPERIMENTAL

General Methods.—Electronic spectra were recorded using a Unicam SP 800 spectrometer, and optical densities at particular wavelengths were determined with a Unicam SP 600 spectrophotometer. Hydrogen-1 n.m.r. spectra were recorded at 60 MHz using a Perkin-Elmer R10 instrument. For potentiometric titrations, a Radiometer automatic titrator was used (type 25 pH meter, TTT11 titrator, and TTA 31 burette fitted with a 0.5-cm^3 syringe burette and SBR2 titrigraph recorder).

Cobalt Analysis.—Results of atomic absorption (using a Unicam SP 90 spectrometer and an acetylene–air flame) did not agree with those obtained by absorptiometry as the ligands interfere. The use of a hotter (dinitrogen oxide–acetylene) flame has been recommended [12] for this reason. In order to avoid this difficulty, we used the absorptiometric method, and attempted to convert the cobalt(III) complex into Co^{2+} in various ways. Chemical routes were favoured after we had established that complete photochemical destruction of our complexes was incomplete even after long irradiation.

We tried: (*i*) ignition in a silica crucible followed by dissolution of the cobalt oxide in HCl; (*ii*) decomposition of the complex in boiling *aqua regia*; (*iii*) destruction of the complex by boiling in a mixture of sulphuric and nitric acids; and (*iv*) oxidation with a 2% solution of ammonium peroxodisulphate. The last method was chosen since the others were not only very tedious but unreliable

A sample of a solution containing cobalt (*ca.* 0.2 mg) was treated with a solution of $[NH_4]_2[S_2O_8]$ (2%, *ca.* 1 cm^3) and the mixture was heated on a steam-bath for at least 2 h. After cooling, $HClO_4$ (2 mol dm^{-3}, 1 cm^3), ammonium thiocyanate solution (6 mol dm^{-3}, 1 cm^3), and acetone (12 cm^3) were added. The volume was made up to 25 cm^3 with water, and the absorbance was measured at 620 nm and compared with a calibration curve.

Analytical results for C, H, and N are collected in Table 2; combustion analysis of the di- and tri-perchlorate salts, particularly on the scale required for a Cl analysis, is hazardous.

Preparations for starting materials followed standard methods, and we comment only on points of discrepancy.

‘ *Diaqua*(3-*azapentane*-1,5-*diamine*)*perchloratocobalt*(III)

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* These values for the triaqua-complexes are very similar to those known [7] for *fac*-$[Co(NH_3)_3(OH_2)_3]^{3+}$ and triaqua(triaminocyclohexane)cobalt(III).

[7] G. Schwarzenbach, J. Boesch, and H. Egli, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2141.

[8] R. C. Beaumont, *Inorg. Chem.*, 1969, **8**, 1805.

[9] S. H. Caldwell and D. A. House, *J. Inorg. Nuclear Chem.*, 1969, **31**, 811.

[10] P. Wilairat and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2293.

[11] F. R. Keene and G. H. Searle, *Inorg. Chem.*, 1972, **11**, 148.

[12] K. Fujiwara, H. Haraguchi, and K. Fuwa, *Analyt. Chem.*, 1972, **44**, 1895.

Perchlorate.'—Hoping to use this complex [13] in syntheses, and wishing to check the reality of the very low molar absorption coefficient reported [13] (ε ≈ 11 dm^3 mol^{-1} cm^{-1}) and the co-ordination of perchlorate ion, we repeated Crayton's procedure. The complex $[Co(apd)(NO_2)_3]$ (7.1 g, 24 mmol) was stirred with water (35 cm^3) and concentrated $HClO_4$ (63 cm^3, 73 mmol). The mixture was heated (steam-bath) until evolution of NO_2 ceased, then concentrated to *ca.* 5 cm^3. Ethanol (10 cm^3) was added, and the solution was cooled with continuous stirring. The resulting pale orange crystals were collected and washed with ethanol, yield 1.4 g (*ca.* 11%) (Found: C, 15.0; H, 4.50; Co, 3.2; N, 17.05. Calc. for $C_4H_{17}Cl_3CoN_3O_{14}$: C, 9.70; H, 3.45; Co, 11.85; N, 8.45%). The product contained no Co^{II}. A sample (156.4 mg) was dissolved in water and the solution was chromatographed on a column (40 × 1.5 cm) of SP-Sephadex-C25. With water as eluant, a red band separated, which had λ 485 and 335 nm (ε 134 and 726 dm^3 mol^{-1} cm^{-1}). With sodium chloride as a stepwise eluant two more bands separated, a brown one with λ 490 and 350 (ε 59 and 945) and an orange one with λ 482 (ε 85 dm^3 mol^{-1} cm^{-1}). These observations, with the low cobalt content, suggest that the product is not as named, but is a mixture of ligand perchlorate and nitro-complexes of Co^{III}. The high N : C ratio of 0.97 : 1 (calc. 0.75 : 1) supports this.

TABLE 2

Analytical results for the cobalt complexes

Complex	Stoicheiometry	Analysis (%) Calc. C	Calc. H	Calc. N	Found C	Found H	Found N	Notes
$[Co(apd)Cl_3]$	$C_4H_{13}Cl_3CoN_3$	17.9	4.90	15.65	18.3	5.20	17.55	*a*
					17.8	5.00	15.5	*b*
fac-$[Co(apd)(OH_2)_3][ClO_4]_3\cdot 3H_2O$	$C_4H_{25}Cl_3CoN_3O_{18}$	8.45	4.45	7.40	8.30	3.75	7.75	*c, d*
$[Co(apd)(GlyO)(OH_2)][ClO_4]_2\cdot H_2O$ (1)	$C_6H_{21}Cl_2CoN_4O_{12}$	15.3	4.50	11.9	15.3	4.10	12.1	*c, d*
$[Co(apd)(Gly)(OH_2)][ClO_4]_3$ (2)	$C_6H_{20}Cl_3CoN_4O_{15}$	13.0	3.65	10.1	13.25	3.90	10.15	*c*
$[Co(apd)(C_2O_4)(OH_2)][ClO_4]\cdot H_2O$	$C_6H_{17}ClCoN_3O_{10}$	18.7	4.45	10.9	18.55	4.55	10.6	*c*

[a] $[Co(apd)(NO_2)_3]$ (10 g, 36 mmol), heated on steam-bath with concentrated HCl (250 cm^3) until NO_2 evolution stopped, cooled, brown precipitate washed with acetone, yield 4.3 g (45%). [b] Following ref. 9: see Experimental section. [c] Preparation in text. [d] Low values are often obtained with our automatic C, H, and N analyser for compounds with loosely held water of crystallization, corresponding to the loss of all of the loosely held water during the purging stage: in this case, for $[Co(apd)(OH_2)_3][ClO_4]_3\cdot H_2O$, H(calc.) = 3.70% (two mol of hydrate water lost), and, for anhydrous $[Co(apd)(GlyO)(OH_2)][ClO_4]_2$, H (calc.) 4.05% (one mol of hydrate water lost).

(3-*Azapentane*-1,5-*diamine*)*trichlorocobalt*(III).—As implied in Table 2, we found the direct method [9] from cobalt(II) chloride more convenient, giving a purer product. However, since our yield (*ca.* 26%) was only half that (50%) reported,[9] we investigated the fate of the remaining apd. (Our yield increased only to 30% by concentrating the aerated solution cold rather than, as directed,[9] at 80—90 °C.) After removing $[Co(apd)Cl_3]$, ethanol was added to the filtrate, giving a light green precipitate, which was collected and washed with ethanol and diethyl ether. This, which accounts for *ca.* 70% of the apd used, had approximately the composition of the mixed complex $2[Co(apd)_2]Cl_3$–$[Co(apd)_2]_2[CoCl_4]_3$ (Found: C, 21.5; H, 6.35; Co, 19.6; N, 17.55. Calc. for $C_{32}H_{104}Cl_{18}Co_7N_{24}$: C, 20.5; H, 5.60; Co, 22.0; N, 17.9%). A sample (320.8 mg) dissolved in water (250 cm^3) to give a yellow solution, which was chromatographed on an SP-Sephadex-C25 column (70 × 2 cm). The ions $[Co(apd)_2]^{3+}$ and $[Co(OH_2)_6]^{2+}$ were separated, in the ratio 1.3 : 1. [Two minor red bands accounting for *ca.* 3% of the total cobalt probably contained chlorocobalt(III) complexes.]

The thermal decomposition of $[Co(apd)Cl_3]$ was observed. It was heated in a sublimer at *ca.* 10^{-3} mmHg.* At 202.5 °C a white sublimate of ethylenediammonium chloride formed [single sharp proton resonance peak in D_2O at 6.53 (Found: C, 18.55; H, 7.90; N, 20.75. Calc. for $C_2H_{10}Cl_2N_2$: C, 18.05; H, 7.60; N, 21.05%). At 203 °C the residual solid melted (changing to dark green); it was kept at 204 °C for 1 h, but no further change occurred, and, on cooling, gave a dark green solid. This dissolved in water to give a ratio of 39 : 11 for Co^{II} : Co^{III}. Chromatography of the solution on SP-Sephadex-C25 gave seven components which in order of elution were: (1) yellow; (2) red $[Co(OH_2)_6]^{2+}$; (3) yellow; (4) yellow; (5) yellow $[Co(apd)_2]^{3+}$; (6) brown; and (7) strongly adsorbed brown. The yellow bands (1), (3), and (4) had unusual absorption spectra, with several bands in the 370—460 nm region. These probably involve oxidation products of apd similar to the yellow cation mentioned [14] by Wilairat and Garner from $[Co(apd)(OH_2)_3]^{3+}$. It seems that, as in the thermolysis [15] of $[Co(NH_3)_3Cl_3]$, it is the amine and not the chloride which is finally oxidised.

fac-*Triaqua*(3-*azapentane*-1,5-*diamine*)*cobalt*(III) *Perchlorate Trihydrate*.—This species was already known [9,10] in solution. First, a solution of *mer*-$[Co(apd)(OH)_3]$ was made by the following modification of the method given by Caldwell and House.[9] Powdered $[Co(apd)Cl_3]$ (1.34 g, 5 mmol) was mixed with boiled water (35 cm^3) and Deacidite FFIP ($[OH]^-$ form, 20 cm^3, 24 mequiv.) and kept for 20 min, then filtered. The filtrate was passed slowly through a column (60 × 2.7 cm) of Deacidite FFIP ($[OH]^-$ form), and the eluate was acidified with $HClO_4$ (2 mol dm^{-3}, 10 cm^3). Isomerization was achieved by keeping the solution on the steam-bath for 1 h; concentration (freeze-drying) gave crystals which were washed with concentrated $HClO_4$ and dried *in vacuo*. No attempt was made to dry this complex by heating since $[Co(NH_3)_3(OH_2)_3][ClO_4]_3$ is said [15] to explode on losing water.

Aqua(3-*azapentane*-1,5-*diamine*)*glycinatocobalt*(III) *Per-*

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

[13] P. H. Crayton, Ph.D. Dissertation, University of Buffalo, 1956.

[14] P. Wilairat and C. S. Garner, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1833.

[15] J. P. Smith and W. W. Wendlandt, 'The Thermal Properties of Transition-metal Ammine Complexes,' Elsevier, London, 1967.

chlorate. The Reaction of [Co(apd)(OH)$_3$] *with Glycylglycylglycine at* 5 °C.—In most of our experiments on the hydrolysis of peptides promoted by metal ions, we had used fairly forcing conditions. However, in the case of glycylglycylglycine we carried out some experiments under mild conditions, and the complex named is a major product.

Glycylglycylglycine (0.75 g, 5 mmol) was dissolved in a solution of (3-azapentane-1,5-diamine)trihydroxocobalt(III) (160 cm^3) made from [Co(apd)Cl$_3$] (1.34 g, 5 mmol). The solution was kept at 5 °C for 3 d, then concentrated and chromatographed on SP-Sephadex-C25 (25 × 2.2 cm column). Only four separate fractions were obtained. The first, which was eluted with water, was pale pink but contained very little cobalt, and indeed consisted mainly of free peptides and glycine. The second, which was eluted with sodium chloride solution (0.5 mol dm^{-3}) contained the substance of interest in this paper. It contained *ca.* 40% of the total cobalt in the preparation. The third fraction, which was a magenta colour and eluted with NaCl, was almost certainly *mer*-[Co(apd)(OH$_2$)$_2$(OH)]$^{2+}$ which isomerized, at least according to its final visible and proton resonance spectra, to the *facial* isomer. The *meridional* isomer is known [10] to isomerize under these conditions. The fourth fraction, also magenta and also eluted with NaCl, was identified as the *facial* isomer of the diaqua(3-azapentane-1,5-diamine)hydroxocobalt(III) ion, by its visible and proton resonance spectra. The plot of proton magnetic resonance against pH showed a small change at pH *ca.* 7 and a much larger downfield shift in strongly acidic solution, corresponding to protonation of the hydroxo-ligand and the carbonyl group of the glycinate ligand respectively.

In a similar experiment, the solution of glycylglycylglycine and [Co(apd)(OH)$_3$] was kept at 5 °C for 1 week. The first band separated by chromatography on SP-Sephadex-C25 by elution with 0.1 mol dm^{-3} sodium perchlorate was desalted (using Sephadex G10), acidified with HClO$_4$, and concentrated in a rotatory evaporator. The crystals were collected and dried. The yield, estimated by cobalt analysis, was *ca.* 30% (Found: C, 12.25; H, 4.15; N, 9.30. Calc. for $C_6H_{24}Cl_3CoN_4O_{17}$: C, 12.2; H, 4.10; N, 9.50%).

Synthesis. Glycine (0.85 g, 11 mmol) was dissolved in a solution of *mer*-[Co(apd)(OH)$_3$] prepared from [Co(apd)Cl$_3$] (2.68 g, 10 mmol) by the ion-exchange method already described and the mixture was kept at 5 °C for 3 weeks. It was then chromatographed on SP-Sephadex-C25 (25 × 2.5 cm column) and the first band eluted with Na[ClO$_4$] (0.1 mol dm^{-3}) was concentrated, desalted by gel chromatography (Sephadex G10, 90 × 2 cm column), and divided into two parts: one part was merely acidified with HClO$_4$ and the other was made strongly acidic; both were then concentrated. The two crops of crystals (I and II respectively), obtained from the two solutions, were filtered off and dried. The yield of the reaction was estimated by measuring the amount of cobalt in the band initially collected (82%).

This complex was also prepared in solution by adding sodium hydroxide to a solution of [Co(apd)(GlyO)Cl]Cl prepared according to the procedure [6] of Wu and acidifying with HClO$_4$ after the hydrolysis of the chloride was complete.

(3-*Azapentane*-1,5-*diamine*)*hydroxo*(*phenylalaninato*)-*cobalt*(III) *Perchlorate.*—L-Phenylalanylglycylglycine (0.5 g, 2.2 mmol) was dissolved in a solution of [Co(apd)(OH)$_3$] (350 cm^3) prepared from [Co(apd)Cl$_3$] (0.6 g, 2.2 mmol). The solution was kept at 5 °C for 40 h, concentrated, and chromatographed on SP-Sephadex-C25 (65 × 4 cm column). Elution with Na[ClO$_4$] (0.05 mol dm^{-3}) gave two red bands, [Co(apd)(GlyO)(OH)]$^+$, 6% based on cobalt content: identified by ^{1}H n.m.r.; [Co(apd)(PheO)(OH)]$^+$, 22% based on cobalt content, and identified by ^{1}H n.m.r. On concentration, a small quantity of red crystals of the latter complex was obtained (Found: C, 33.1; H, 5.00. $C_{12}H_{22}ClCoN_4O_7$ requires C, 33.6; H, 5.15%).

The reaction of [Co(apd)(OH)$_3$] with L-alanylglycylglycine at 5 °C, worked up in a similar way, gave a red band (42% based on cobalt content) which was shown by ^{1}H n.m.r. to be a mixture of [Co(apd)(AlaO)(OH)]$^+$ and [Co(apd)(GlyO)(OH)]$^+$ in the ratio 4 : 1, which were not easily separated.

Aqua(3-*azapentane*-1,5-*diamine*)*oxalatocobalt*(III) *Perchlorate Monohydrate.*—The complex [Co(apd)Cl$_3$] (2.68 g, 10 mmol) and sodium oxalate (1.34 g, 10 mmol) were mixed with water (50 cm^3) and kept at room temperature with stirring for 1 d. The solution was chromatographed on SP-Sephadex-C25 (70 × 2.5 cm column). On elution with 0.1 mol dm^{-3} Na[ClO$_4$] a broad red band was collected. It was concentrated in a rotary evaporator and the resulting crystals were filtered off, yield 2.9 g (75%).

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