Chiral metal complexes
Part 33*. Coordination stereoselectivity in ternary cobalt(III) complexes of dipeptides and an optically active triamine

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Abstract

A number of complexes of the type $[Co(R,R\text{-benzet})(dipeptidato)]^+$, where *R,R*-benzet is *N*-benzyl-*N'*-(2-picolyl)-1*R*,2*R*-diaminocyclohexane and dipeptidato is the dianion of glygly, gly-*S*-val, gly-*R*-val, gly-*S*-leu, gly-*R*-leu, *S*-leugly, *R*-leugly, *S*-valgly, *S*-leu-*S*-ala and *S*-leu-*S*-phe, where gly = glycine, val = valine, leu = leucine, ala = alanine and phe = phenylalanine have been synthesized and characterized. The complexes were prepared by reacting the peptides with the facially coordinated precursor [*OC*-6-432-*C*]-Co(*R,R*-benzet)Cl_3 in water. All of the ternary complexes containing a peptide are coordinated meridionally, and are formed stereospecifically, except in one case (*S*-valgly). A combination of CD and NMR studies has been used to assign the stereochemistry of the complexes. The assignment was made possible by the low-temperature single-crystal X-ray structure determinations of two of the compounds isolated. Both of these complexes crystallize in the orthorhombic system with space group $P2_12_12_1$ and $Z = 4$; for *C*-[Co(*R,R*-benzet)(gly-*R*-val)]$ClO_4 \cdot H_2O$ $a = 12.520(7)$, $b = 13.954(14)$, $c = 16.594(8)$ Å and for *C*-[Co(*R,R*-benzet)(glygly)]$ClO_4 \cdot 2H_2O$ $a = 9.998(2)$, $b = 19.301(4)$, $c = 13.919(4)$ Å. The structures were refined by full-matrix least-squares procedures to values for *R* of 0.029 and for *R'* of 0.032 for 2014 reflections and for *R* of 0.042 and *R'* of 0.047 for 2150 reflections, respectively. In both structures the complex cations have the configuration [*OC*-6-64-*C*-(*R*),(*R*),(*R*)].

Introduction

Kinetically inert asymmetric cobalt(III) complexes have been used extensively for the resolution and synthesis of optically active amino acids and for examining subtle effects of chiral discriminations between related species [1, 2]. In general, the magnitude of any observed stereoselectivity has been shown to be dependent upon the nature of the secondary ligand(s). In contrast to the largely non-stereoselective bis(diamine)Co(III) complexes, several Co(III)–tetraamine systems have proved to be effective agents for chirality transfer, notably in the synthesis of α-aminoacidates from coordinated α-aminomalonic acids. Appropriate design of chiral tetramine ligands has led to inductions in products with enantiomeric excesses of greater than 75% [3].

More recently, our attention has focussed on less well documented ternary Co(III)–dipeptide complexes containing a chiral triamine. Several workers have reported the synthesis of mono- and bisdipeptidato, tripeptidato and tetrapeptidato complexes of cobalt(III) [4]. However, to our knowledge, no monodipeptide complexes of Co(III) have been synthesised with an asymmetric secondary ligand. Our interest in such systems stems from an effort to develop new resolving agents of high stereospecificity for dipeptides, and to gain an insight into the discriminatory interactions of a chiral kind that are involved. The work was also undertaken with a view to designing viable HPLC systems, via bonding of suitable complexes to stationary phases, for separation of diastereoisomeric mixtures of dipeptides.

We report here studies of the synthesis and characterization of [Co(*R,R*-benzet)(dipeptid-

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ato)]$^+$ complexes, where *R,R*-benzet is *N*-benzyl-*N'*-(2-picolyl)-1*R*,2*R*-diaminocyclohexane and dipeptidato is the dianion of glygly, gly-*S*-val, gly-*R*-val, gly-*S*-leu, gly-*R*-leu, *S*-leugly, *R*-leugly, *S*-valgly, *S*-leu-*S*-ala and *S*-leu-*S*-phe, where gly = glycine, val = valine, leu = leucine, ala = alanine and phe = phenylalanine. In order to be able to assign isomeric configurations in these complexes, we have determined the crystal and molecular structures of [*OC*-6-64-*C*-(*R*), (*R*), (*R*)]-[(*N*-benzyl-*N'*-(2-picolyl)-1,2-diaminocyclohexane)] [(glycylvalinato)(2−)]cobalt(1+) tetraoxochlorate(1−) 1-hydrate (that is, *C*-[Co(*R,R*-benzet)(gly-*R*-val)]$ClO_4 \cdot H_2O$), and of [*OC*-6-64-*C*-(*R*), (*R*), (*R*)]-[(*N*-benzyl-*N'*-(2-picolyl)-1,2-diaminocyclohexane][glycylglycinato)(2−)]-cobalt(1+) tetraoxochlorate(1−) 1-hydrate (that is, *C*-[Co(*R,R*-benzet)(glygly)]$ClO_4 \cdot 2H_2O$). The results of the structure analyses are also given below.

Experimental

N-(2-picolyl)-1R, 2R-diaminocyclohexane

A solution of pyridine-2-carboxaldehyde (37.5 g, 0.35 mol) in dry benzene (150 cm^3) was added dropwise to a stirred solution of 1*R*,2*R*-diaminocyclohexane [5] (39.9 g, 0.35 mol) in dry benzene (500 cm^3) over a period of 1 h. The mixture was allowed to stand for a further 3 h, and then the solvent was removed *in vacuo* to give a pale yellow solid. The imine was dissolved in absolute ethanol (500 cm^3) and hydrogenated over 10% Pd on carbon catalyst at near atmospheric pressure until H_2 uptake had ceased. The catalyst was filtered off with the aid of a celite pad, and the solvent removed *in vacuo* to yield a dark yellow oil. Vacuum distillation gave the title compound as a golden yellow oil (b.p. 135–140 °C, 0.5 mm Hg). Yield = 50 g (70%). ^{1}H NMR ($CDCl_3$): 8.54d (1H), 7.62t (1H), 7.36d (1H), 7.13d (1H), 4.07d (1H), 3.85d (1H), 2.43m (1H), 2.12m (2H), 1.89br (1H), 1.70br (5H), 1.15m (4H).

R,R-benzet trihydrochloride

A solution of freshly distilled benzaldehyde (5.3 g, 0.05 mol) in dry benzene (25 cm^3) was mixed quickly with a solution of *N*-(2-picolyl)-1*R*,2*R*-diaminocyclohexane (10.0 g, 0.049 mol) in dry benzene (25 cm^3), and left to stir for 2 h at room temperature. The solvent was removed *in vacuo*, and the residue azeotroped with dry benzene and finally absolute EtOH. The resultant orange oil was dissolved in absolute EtOH (150 cm^3) and hydrogenated over 10% Pd on C at atmospheric pressure until hydrogen uptake had ceased. The catalyst was filtered off and conc. HCl (25 cm^3) added to the filtrate. The solution was reduced *in vacuo* to a small volume, and crystallization induced by scratching with a glass rod (if no solid is obtained at this stage, the mixture may be diluted with ethanol and added dropwise to a large excess of rapidly stirred diethyl ether). The solid product was filtered, washed with 1:1 EtOH/Et_2O, then Et_2O and air-dried. Yield = 19.0 g (95%). ^{1}H NMR (free ligand, $CHCl_3$): 8.53d (1H), 7.61t (1H), 7.30m (5H), 7.24d (1H), 7.13d (1H), 4.00d (1H), 3.91d (1H), 3.81d (1H), 3.67d(1H), 2.29d (2H), 2.15m (4H), 1.72d (2H), 1.23t (2H), 1.06br (2H).

[Co(R,R-benzet)Cl$_3$]

To a stirred suspension of $Na_3[Co(CO_3)_3] \cdot 3H_2O$ (8.24 g, 0.023 mol) in H_2O (150 cm^3) was added dropwise a solution of *R,R*-benzet·3HCl (9.14 g, 0.023 mol) in H_2O (50 cm^3) over a period of 15 min. After the addition was complete, the mixture was warmed gently for 2 h. The resulting red solution was allowed to cool to room temperature before being filtered through a thick pad of celite. Conc. HCl (20 cm^3) was added dropwise to the filtrate, and the solution left to stir at 50 °C for 1 h, then overnight at room temperature, during which time the product crystallized. The purple–brown compound was filtered off, washed with acetone, 4:1 Et_2O/EtOH and finally Et_2O, and air-dried. Yield = 5.20 g (50%) *Anal.* Calc. for $C_{19}H_{25}N_3Cl_3Co$: C, 49.5; H, 5.5. Found: C, 48.8; H, 5.3%.

C-[Co(R,R-benzet)(glygly)]ClO$_4$·2H$_2$O

The complex was prepared by two methods.

Method A

To a stirred solution of [Co(*R,R*-benzet)Cl_3] (0.30 g, 6.56×10^{-4} mol) and glycylglycine (0.17 g, 1.31×10^{-3} mol) in H_2O (40 cm^3) at 40 °C was added dropwise dilute aqueous NaOH until a pH of 8.0 was obtained. The solution was left stirring at 40 °C for 4 h, then overnight at room temperature. After a two-fold dilution with H_2O, the solution was applied to a CM-Sephadex C-25 column in the Na^+ cycle. Elution with aqueous 0.05 M NaCl led to the development of an initial fast moving faint purple band and a trailing, very intense red–purple band. The two cleanly separated bands were collected in fractions using an LKB Ultrorac II fraction collector. CD and electronic spectral measurements confirmed that each band contained a single isomer. The combined fractions of the slower moving band which contained the bulk of the product were combined and reduced in volume *in vacuo* to about 30 cm^3. Several drops of a saturated

solution of $NaClO_4$ were added. After further evaporation at room temperature over silica gel, the desired product was obtained as a microcrystalline powder. Yield = 300 mg (the yields reported here and elsewhere in this paper refer to the actual amounts of the solid substances isolated; these are lower than the actual yields due to losses associated with the considerable solubilities of the perchlorate salts).

Insufficient material was present in the faster-moving band for any solid to be isolated when treated as above. It was present in but very minor amounts.

Method B

A synthetic procedure similar to that used by Wu and Busch [6] for the preparation of [Co(1,4,7-triaazaheptane)(glygly)]ClO_4 was employed. [Co(*R*,*R*-benzet)Cl_3] (0.6 g, 1.31×10^{-3} mol) and glycylglycine (0.18 g, 1.36×10^{-3} mol) were stirred in H_2O (5 cm^3) for 15 min at 50 °C, during which time most of the solids dissolved. Triethylamine (0.56 cm^3, 4×10^{-3} mol) was then added, and the solution left to stir at 50 °C for 1 h. After cooling, the deep purple solution was diluted five-fold with H_2O and applied to a CM-Sephadex C-25 column (35 × 1.8 cm) in the Na^+ cycle. The column was washed with H_2O, whereupon a yellow–pink by-product was discharged. Development of the column with 0.05 M aqueous NaCl gave a single intense red–purple band, which was collected in fractions. The early fractions possessed CD spectra analogous to those of the faster-moving band in method A, but again these combined fractions contained insufficient material to be isolated. The major isomer was isolated as in A above. Yield = 220 mg. *Anal.* Calc. for $C_{23}H_{35}N_5O_9ClCo$: C, 44.6; H, 5.7; N, 11.3. Found: C, 44.7; H, 5.0; N, 11.0%.

For the following [Co(*R*,*R*-benzet)(dipeptidato)]$^+$ preparations synthetic method A usually gave unsatisfactory results, for unknown reasons, but method B proved suitable in all cases.

C-[Co(R,R-benzet)(gly-R-val)]$ClO_4 \cdot H_2O$

The reaction mixture obtained as described above (method B) was diluted ten-fold and applied to a CM-Sephadex C-25 column (50 × 1.8 cm) in the Na^+ cycle. During early elution (0.05 M aq. NaCl) some yellow–red material was quickly discharged. The main red–purple band was shown to consist of only one isomer. Treatment with saturated $NaClO_4$ solution gave the desired product as deep purple crystals. Yield = 325 mg. *Anal.* Calc. for $C_{26}H_{39}N_5O_8ClCo$: C, 48.5; H, 6.1; N, 10.9. Found: C, 47.9; H, 6.0; N, 10.9%.

C-[Co(R,R-benzet)(gly-S-val)]$ClO_4 \cdot H_2O \cdot NaClO_4$

A single isomer was detected and isolated as outlined above. Yield = 390 mg. *Anal.* Calc. for $C_{26}H_{39}N_5O_{12}Cl_2CoNa$: C, 40.7; H, 5.1; N, 9.1. Found: C, 40.8; H, 5.0; N, 9.2%.

C-[Co(R,R-benzet)(gly-R-leu)]$ClO_4 \cdot 2.5H_2O$

The preparation was similar to those described above, except that 0.30 g (6.56×10^{-4} mol) of Co(*R*,*R*-benzet)Cl_3, 0.12 g (1 mol equiv.) of gly-*R*-leu and 0.28 cm^3 of triethylamine were used. Yield = 150 mg. *Anal.* Calc. for $C_{27}H_{44}N_5O_{9.5}ClCo$: C, 47.3; H, 6.5; N, 10.2. Found: C, 47.6; H, 6.1; N, 9.9%.

C-[Co(R,R-benzet)(gly-S-leu)]$ClO_4 \cdot 2.5H_2O$

The compound was obtained as described immediately above using gly-*S*-leu. Yield = 120 mg. *Anal.* Calc. for $C_{27}H_{44}N_5O_{9.5}ClCo$: C, 47.3; H, 6.5; N, 10.2. Found: C, 47.0; H, 6.1; N, 10.2%.

C-[Co(R,R-benzet)(R-leugly)]$ClO_4 \cdot H_2O \cdot NaClO_4$

The synthesis of this complex was analogous to those of the glyleu complexes. Yield = 140 mg. *Anal.* Calc. for $C_{27}H_{41}N_5O_{12}Cl_2CoNa$: C, 41.5; H, 5.3; N, 9.0. Found C, 42.7; H, 5.5; N, 9.0%.

C-[Co(R,R-benzet)(S-leugly)]$ClO_4 \cdot 2.5H_2O$

The preparation was analogous to those above. Yield = 209 mg. *Anal.* Calc. for $C_{27}H_{44}N_5O_{9.5}ClCo$: C, 47.3; H, 6.5; N, 10.2. Found: C, 47.6; H, 6.3; N, 10.1%.

C-[Co(R,R-benzet)(S-leu-S-ala)]$ClO_4 \cdot 3H_2O$

The complex was similarly obtained. Yield = 100 mg. *Anal.* Calc. for $C_{28}H_{47}N_5O_{10}ClCo$: C, 47.5; H, 6.7; N, 9.9. Found: C, 47.1; H, 6.5; N, 9.9%.

C-[Co(R,R-benzet)(S-leu-S-phe)]$ClO_4 \cdot 4H_2O$

Other minor by-products were observed during chromatography of the reaction mixture, but these were discarded. Yield = 50 mg. *Anal.* Calc. for $C_{34}H_{53}N_5O_{11}ClCo$: C, 50.9; H, 6.7; N, 8.7. Found: C, 51.4; H, 6.0; N, 8.5%.

C- and A-[Co(R,R-benzet)(S-valgly)]ClO_4

The reaction mixture, upon chromatography on CM-Sephadex C-25 gave rise to two red–purple bands, each consisting of a single diastereoisomer as revealed by electronic and CD spectra of separately collected fractions of each. The second eluted isomer had CD and ^1H NMR spectra quite analogous to those of [Co(*R*,*R*-benzet)(*S*-leugly)]$^+$ (*vide infra*), and thus is assigned the *C* stereochemistry. The first eluted species is thus the *A* diastereoisomer. It was isolated as the perchlorate salt in the usual manner. Yield = 90 mg.

Anal. Calc. for $C_{26}H_{45}N_5O_{11}ClCo$: C, 44.7; H, 5.4; N, 10.0. Found: C, 44.3; H, 5.7; N, 10.4%.

Continued elution and treatment with aqueous sodium perchlorate gave crystals of the other isomer as the perchlorate. Yield = 50 mg. *Anal.* Calc. for $C_{26}H_{39}N_5O_8ClCo$: C, 48.5; H, 6.1; N, 10.9. Found: C, 48.7; H, 5.9; N, 10.1%. Only two diastereoisomers are possible for these complexes, aside from stereochemical elaboration associated with coordinated amine nitrogen atoms; the

TABLE 1. Characteristic ^1H NMR data for the complexes[a]

	Complex[b]					
	A[c]	B	C	D	E	F
H(11)	7.74d[d]	7.68d	7.70d	8.28d	7.69d	7.78d
H(12)	7.55t	7.56t	7.62t	7.55t	7.58t	obs
H(13)	8.02t	8.02t	8.05t	8.02t	8.02t	8.04t
H(14)	7.62d	7.60d	7.64d	7.60d	7.64d	7.63d
H(16a)	4.81d	4.90dd	4.78dd	4.80dd	4.91dd	4.81dd
H(16b)	4.42d	4.48dd	4.41dd	4.46dd	4.46dd	4.47dd
H(N1)		[f]	[f]	7.86m	7.52m	7.86m
H(26a)	3.64d	[f]	obs	3.65d[e]	3.80d[e]	3.91d
H(26b)	3.12d	[f]	obs	3.34d[e]	3.73d[e]	3.71dd
Benzene-H	7.2–7.4	7.2–7.4	7.2–7.4	7.2–7.4	7.2–7.4	7.2–7.4
Gly-CH_2	3.81d, 3.46d[h] 3.73d, 2.43d[h]		4.42d, 3.36d[h]	3.70d, 3.18d[e]		3.89d, 3.44d[h]
CH_3		1.00d 0.88d	1.10d, 0.94d	1.00d, 0.47d	1.37d 0.99d, 0.88d	0.85d 0.83d
$J_{16a,\,16b}$	16.2		16.2[e]	15.5	16.3	15.5
$J_{26a,\,26b}$	15.1[h]		15.0[h]	15.5	15.3[e]	14.3[h]
$J_{N1,\,16a}$	4.9[j]		[f]	4.7	4.9	4.8
$J_{N1,\,16b}$	10.0[j]		[f]	10.3	9.7	[f]
	G	H	I[g]	J	K[c]	L[i]
H(11)	8.09d	7.89d	7.74d	7.69d	7.64d	9.80d
H(12)	7.56t	7.46t	7.50t	7.54t	7.54t	7.50t
H(13)	8.02t	8.02t	8.02t	8.02t	8.02t	7.78t
H(14)	7.61d	7.70d	7.62d	7.61d	7.61d	7.35d
H(16a)	4.82dd	4.95d[e]	5.04d	4.92dd	4.88d	5.33d
H(16b)	4.42dd	4.78d[e]	4.63d	4.40obs	4.45d	3.65m
H(N1)	7.94m			7.86m		5.44t
H(26a)	3.85d[g]	3.61d[e]	3.77d	[f]	[f]	4.70m
H(26b)	3.08d[g]	2.98d[e]	3.28d	[f]	[f]	4.09m
Benzene-H	7.2–7.4	7.2–7.4	7.2–7.4	7.2–7.4	7.2–7.4	7.2–7.6
Gly-CH_2	3.77d, 3.65d[g]					
		4.46d, 4.03d	4.09d, 2.97d[g]	3.64d, 2.67d	3.66d, 2.85d[e]	
CH_3	0.78d, 0.72d	0.84d, 0.27d	1.17d, 1.12d[g]	0.99d, 0.87d	0.97d, 0.87d	
$J_{16a,\,16b}$	15.3	16.2[e]	16.3	16.6	16.0	15.3
$J_{26a,\,26b}$	15.3[g]	15.3[e]	15.1	[f]	[f]	14.9
$J_{N1,\,16a}$	[f]	[f]	[f]	5.2	4.9[j]	0.0
$J_{N1,\,16b}$	10.5	[f]	[f]	[f]	9.9[j]	7.3
$J_{N2,\,26a}$						5.1
$J_{N2,\,26b}$						11.0
$J_{N1,\,1}$						11.2
$J_{N2,\,2}$						11.4
$J_{1,\,2}$						11.3
$J_{2,\,3a}$						11.4
$J_{1,\,6b}$						11.2

[a]Data reported as chemical shifts (δ in ppm, coupling constants in Hz). Data were recorded in DMSO-d_6, unless otherwise noted for particular spectral regions for some complexes when certain signals were obscured. [b]A: glygly; B: *S*-leu-*S*-phe; C: gly-*S*-val; D: gly-*R*-val; E: *S*-leu-S-ala; F: gly-*S*-leu; G: gly-*R*-leu; H: *S*-valgly (*A* isomer); I: *S*-valgly (*C* isomer); J: *S*-leugly; K: *R*-leugly; L: [Co(*R*,*R*-benzet)Cl_3]. [c]Added D_2O, except where noted. [d]Symbols: d = doublet, t = triplet, m = multiplet, obs = obscured. [e]In D_2O/DCl. [f]Not assigned. [g]In D_2O/acetone-d_6. [h]In D_2O. [i]In $CDCl_3$. [j]In neat DMSO-d_6.

TABLE 2. CD and electronic spectral data for the complexes[a]

	Complex[b]					
	A	B	C	D	E	F
λ_{max} (nm)[c]	502	519	529	522	521	516
ϵ (M^{-1} cm^{-1})[c]	299	305	355	279	298	320
λ_{max} (nm)[d]	495, 395	515, 400	520, 475	520, 455	510, 365	510
$\Delta\epsilon$ (M^{-1} cm^{-1})[d]	−1.06, +0.16	−1.71, +0.25	−2.30, −1.79	+1.01, +0.79	−2.16, +0.40	−1.71
	G	H	I	J	K	L
λ_{max} (nm)[c]	512	524	514	506	502	545, 662[e]
ϵ (M^{-1} cm^{-1})[c]	274	325	281	273	287	107, 54
λ_{max} (nm)[d]	510, 450	540, 440	495, 400	495, 405	515, 400	665,[e] 540[e]
$\Delta\epsilon$ (M^{-1} cm^{-1})[d]	+0.43, +0.61	+0.21, +0.57	−1.93, +0.40	−1.07, +0.39	−1.09, +0.05	+0.14, −0.16

[a]In H_2O. [b]See Table 1. [c]Electronic spectrum. [d]Extrema in the CD spectrum. [e]In $CHCl_3$.

complex must be the *A* isomer. This is born out by the fact that no equilibration of isomers is observed to occur, as judged by NMR measurements, when all available protons are fully exchanged. This is commented on more fully below.

Electronic spectra and CD were recorded using a Perkin-Elmer Lambda 5 and a Jobin-Yvon CNRS Dichrographe III, respectively. High resolution NMR spectra were recorded on a Bruker WM 360 spectrometer, in several solvents using TSS or DSS, as necessary, as internal standards. ^1H NMR, and electronic and CD spectral data for the complexes are given in Tables 1 and 2, respectively. Analyses were performed by Mrs A. Dams of the School of Chemistry and Applied Chemistry, Cardiff.

X-ray structure analyses

A summary of crystallographic data and refinement parameters for the complex salts is given in Table 3. The structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations. Difference maps yielded the approximate positions for all the hydrogen atoms in the structures. The positions for those of the ligands were optimized assuming the appropriate geometries of the atoms to which they are attached with bond lengths of 1.0 Å.

Calculations were carried out on FACOM M340S and M380S computers using programs written by F.S.S. Neutral atom scattering factors, corrected for anomalous dispersion, were taken from the 'International Tables for X-ray Crystallography' [8]. See also 'Supplementary material'.

Results and discussion

In common with many other linear terdentates, *R,R*-benzet can coordinate to the octahedron facially or meridionally. In ternary complexes, when the secondary ligand(s) is non-discriminatory in its mode of coordination, both *fac* and *mer* isomers may be able to form, but not necessarily in equal amounts; with some ligands, only one arrangement is permitted. In the preparation of trichloro(*R,R*-benzet)cobalt(III), a single isomer was isolated as a purple–brown solid from acidic aqueous media. The complex was soluble in certain organic solvents (DMSO, $CHCl_3$, CH_2Cl_2) giving green/brown dichroic solutions. In H_2O and aqueous MeOH, substitution of the chloride ions by solvent molecules produced red solutions. This solvolysis may be accompanied by geometric isomerization, but this has not been investigaged.

Similar Co(triamine)Cl_3 complexes have been assigned as being facial or meridional through analysis of infrared spectra [9] and on the basis of their colours in the solid state [10, 11]. The contrast between solid *mer*-Co(py)$_3Cl_3$ (green) [12] and *mer*-Co(dien)Cl_3 (brown) would imply that the geometry of Co(*R,R*-benzet)Cl_3 cannot be assigned solely on the basis of its colour. Infrared techniques cannot be used for the assignment in our case, as the ligand is strictly of C_1 symmetry, and is topologically quite different from end to end.

NMR spectroscopy does provide an unambiguous answer. ^1H NMR data and assignments for the complex are presented in Table 1, with respect to the labelling scheme shown in **1**, and the

TABLE 3. Summary of crystallographic data and refinement parameters for the $[Co(R,R\text{-benzet})L]ClO_4 \cdot nH_2O$ complexes

L	gly-*R*-val	glygly
n	1	2
Crystal data		
	$C_{26}H_{39}N_5O_8ClCo$	$C_{23}H_{35}N_5O_9ClCo$
M_r	644.0	620.2
System	orthorhombic	orthorhombic
a (Å)	12.520(7)	9.998(2)
b (Å)	13.954(14)	19.301(4)
c (Å)	16.594(8)	13.919(4)
U (Å^3)	2899.0	2686.0
Z	4	4
D_c (g cm^{-3})	1.475	1.533
F(000)	1352	1296
μ(Mo Kα) (cm^{-1})	7.7	8.3
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
Data collection		
Temperature (°C)	−130	−120
Diffractometer	Nicolet XRD P3 four-circle [7]	
Radiation	graphite-monochromatized Mo Kα	
Crystal size (mm)	0.8 × 0.2 × 0.4	0.27 × 0.35 × 0.11
2θ Range (°)	4.0–46.0	3.0–56.0
Absorption correction	empirical [7]	
T_{min}	0.704	0.624
T_{max}	0.762	0.683
No. reflections	2307	3638
$I > 3\sigma(I)$	2014	2150
Refinement		
Least-squares	full-matrix	
Min. ftn.	$\Sigma w\ \Delta^2$	
Weighting, *w*	1.0	1.0
$(\Delta/\sigma)_{max}$	0.1	0.1
R	0.029	0.042
$R' = (\Sigma w\Delta^2/\Sigma F_o^2)^{1/2}$	0.032	0.047
Final Δ map		
ρ (e Å^{-3})	< |0.4|	< |0.4|

^{1}H spectral region between $\delta = 3.00$ and 6.50 ppm is shown in Fig. 1. The distinction between the H(16a) , H(16b), H(26a) and H(26b) resonances is based on the assumption that the benzyl protons (H(26a) and H(26b)) have a relatively high degree of rotational freedom about the C(26)–N(2) bond, and would show a vicinal coupling with the amine hydrogen (H(N2)), in addition to a geminal coupling. By way of contrast, the pyridyl-methylene carbon, C(16), forms part of a relatively inflexible five-membered chelate ring, in which the positions of its hydrogen atoms are fixed, and coupling with the neighbouring amine hydrogen atom may not be observed for certain vicinal angles. When such coupling is approximately zero, the dihedral angle between the appropriate bonds must be close to 90°. This is only possible when *R,R*-benzet is facially coordinated. The observation of analogous spectral patterns for similarly disposed protons in closely related Co(III)–tetraamine systems [5, 13, 14] provides further evidence in support of these assignments. Since $J_{H(N2),H(2)} = J_{H(1),H(2)} = J_{H(2),H(3a)}$ and $J_{H(N1),H(1)} = J_{H(1),H(2)} = J_{H(1),H(6b)}$, within experimental error, the dihedral angles between the N(1)–H(N1) and C(1)–H(1), N(2)–H(N2) and C(2)–H(2), C(1)–H(1) and C(2)–H(2), C(1)–H(1) and C(6)–H(6b), and C(2)–H(2) and C(3)–H(3a) bond pairs must all be equivalent or differ by approximately 180°. The latter three angles are constrained by the conformation of the cyclohexane ring and the *R* configuration of the chiral carbon atoms to be 170–180°.

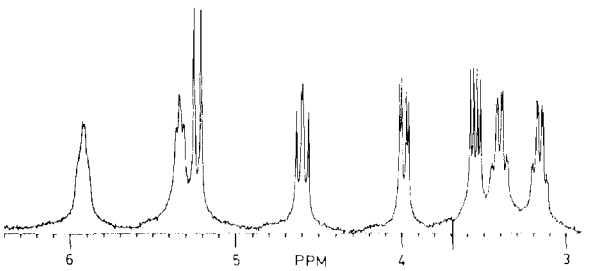
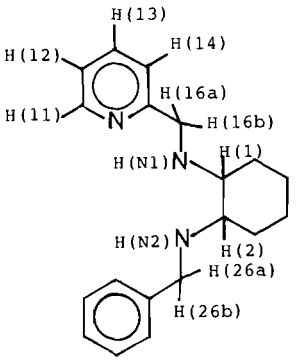


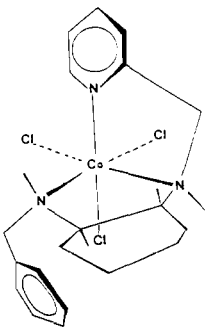
Fig. 1. Relevant portion of the ^{1}H NMR spectrum of $[Co(R,R\text{-benzet})Cl_3$ in $CDCl_3$.

When the secondary nitrogens N(1) and N(2) are coordinated to Co(III), the N–H/C–H dihedral angle cannot be *c.* 0°, and thus they are also close to 180°, and the absolute configurations of the coordinated nitrogens are *S*. The structure of [*OC*-6-423-*C*]-Co(*R*,*R*-benzet)Cl_3 as deduced from the ^{1}H NMR spectrum is shown in **2**.

Electronic and CD spectral data for the complex in $CHCl_3$ are given in Table 2. The progressive shift in λ_{max} for the low energy d–d transition to shorter wavelengths over the series chloroform–methanol–water is consistent with hydrolysis in the protic solvents, as mentioned above.



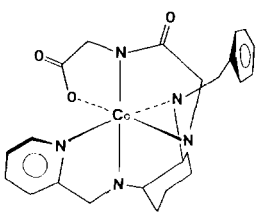
1



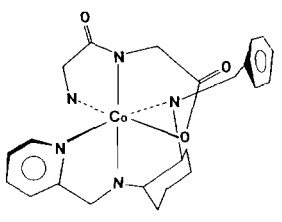
2

The substitution of the three chloride ions by a dianionic dipeptide ligand must however be accompanied by a *fac* to *mer* rearrangement of *R*,*R*-benzet about the metal centre. This change in geometry is enforced by the necessary planarity of the deprotonated amide group of the peptide, and this precludes facial coordination for either ligand [15–18]. In the case of exclusively *mer* topology, coordination of a homochiral or achiral (glygly) dipeptide limits the number of possible diastereoisomeric forms to two if the chiralities of the coordinated secondary nitrogen atoms are fixed. This is actually the case with chiral dipeptides (*vide supra*); when the two isolated isomers of [Co(*R*,*R*-benzet)(*S*-valgly)]$^+$ are equilibrated in H_2O or D_2O, no changes in CD or NMR spectra are observed, respectively, aside from the exchange of protons in the latter. That is to say, differences in these isomers and, *inter alia*, all of the other peptide-containing complexes, must be due solely to the relative orientations of the two terdentate ligands. Under these circumstances, the two possible diastereoisomers that can be formed are those [19] with descriptors [*OC*-6-64-*C*-] and [*OC*-6-64-*A*-], as shown in **3** and **4**, respectively.

A combination of NMR and CD spectroscopic measurements, together with single-crystal X-ray structure determinations of two complex cations as their perchlorate salts permits an unambiguous assignment of topology to all of the complexes that have been synthesized.



3

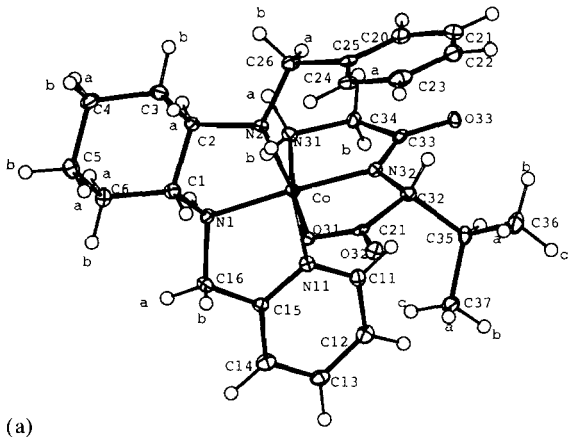


4

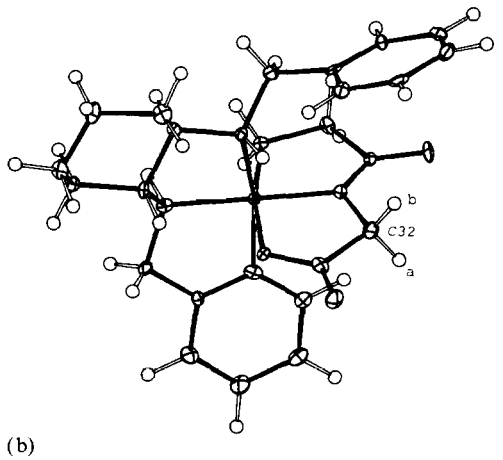
Crystal and molecular structures of C-[Co(R,R-benzet)(gly-R-val)]$ClO_4 \cdot H_2O$ and C-[Co(R,R-benzet)(glygly)]$ClO_4 \cdot 2H_2O$

Final atomic coordinates for the heavy atoms are given in Table 4. Selected bond lengths and angles for the complex cations are given in Table 5.

Perspective views of both complex cations are shown in Fig. 2. The two complex cations are seen



(a)



(b)

Fig. 2. Perspective view of the complex cations (a) *C*-[Co(*R*,*R*-benzet)(gly-*R*-val)]$^+$ and (b) *C*-[Co(*R*,*R*-benzet)(glygly)]$^+$, showing the atomic labelling scheme (the same for both, except for obvious changes to the side chain of the former). Thermal ellipsoids for the non-hydrogen atoms are drawn to include 35% probability.

TABLE 4. Final atomic coordinates (fractional $\times 10^4$) for non-hydrogen atoms for [Co(*R*,*R*-benzet)L]$ClO_4 \cdot nH_2O$ with e.s.d.s in parentheses

	L = gly-*R*-val			L = glygly		
	x	*y*	*z*	*x*	*y*	*z*
Co	157.6(5)	1548.5(4)	1080.0(4)	2537.4(11)	1081.9(4)	569.8(6)
N(11)	262(3)	573(3)	223(2)	2813(6)	1716(3)	1646(4)
N(1)	−1321(3)	1121(3)	1117(3)	4438(6)	856(3)	741(4)
N(2)	−205(3)	2368(3)	2039(2)	2492(7)	288(3)	−344(3)
N(31)	−111(3)	2595(3)	324(2)	2835(5)	1808(3)	−397(4)
N(32)	1598(3)	1900(3)	1013(2)	712(5)	1284(3)	406(4)
O(31)	635(3)	631(2)	1851(2)	1926(4)	427(3)	1510(3)
O(32)	2020(3)	279(2)	2642(2)	95(5)	46(3)	2257(4)
O(33)	2796(3)	2856(2)	304(2)	−844(5)	1974(3)	−341(4)
C(31)	1629(4)	723(3)	2071(3)	640(7)	421(4)	1668(5)
C(32)	2324(4)	1400(3)	1564(3)	−209(8)	912(4)	1036(5)
C(33)	1881(4)	2544(3)	462(3)	346(7)	1778(3)	−187(5)
C(34)	933(4)	2902(4)	−26(3)	1502(7)	2096(4)	−737(5)
C(35)	3250(4)	844(3)	1142(3)			
C(36)	4268(4)	939(4)	1647(3)			
C(37)	3009(4)	−217(3)	998(3)			
C(11)	1036(4)	466(3)	−334(3)	1893(8)	2153(4)	2022(5)
C(12)	1087(4)	−326(4)	−832(3)	2118(8)	2499(4)	2888(6)
C(13)	322(4)	−1029(4)	−758(3)	3321(8)	2391(4)	3361(6)
C(14)	−497(4)	−912(4)	−196(3)	4285(8)	1963(4)	2972(5)
C(15)	−518(4)	−96(3)	280(3)	3988(7)	1620(3)	2112(5)
C(16)	−1357(4)	86(3)	901(3)	4931(7)	1094(4)	1697(5)
C(1)	−1758(4)	1349(4)	1927(3)	4533(6)	90(3)	596(6)
C(2)	−1416(4)	2377(3)	2107(3)	3838(7)	−67(4)	−350(5)
C(3)	−1828(4)	2710(4)	2925(3)	3700(8)	−860(4)	−492(6)
C(4)	−3032(4)	2552(4)	3001(3)	5086(7)	−1199(3)	−444(6)
C(5)	−3344(4)	1504(4)	2820(3)	5885(7)	−994(3)	455(5)
C(6)	−2961(4)	1228(4)	1980(3)	5967(6)	−201(3)	567(5)
C(26)	290(4)	3344(3)	2150(3)	1937(7)	362(4)	−1339(5)
C(25)	1392(4)	3301(3)	2524(3)	457(7)	222(4)	−1401(5)
C(24)	1572(4)	2810(4)	3243(3)	−84(7)	−387(4)	−995(5)
C(23)	2578(5)	2814(4)	3591(3)	−1425(8)	−546(4)	−1157(5)
C(22)	3416(4)	3293(4)	3230(4)	−2231(7)	−97(4)	−1692(6)
C(21)	3244(4)	3776(4)	2508(4)	−1709(8)	513(4)	−2048(5)
C(20)	2233(4)	3780(4)	2163(3)	−362(7)	674(4)	−1912(5)
O(w/w1)	1404(3)	−674(2)	4060(2)	1454(5)	3523(3)	477(4)
O(w2)				−277(5)	3733(3)	2023(4)
Cl	−772(1)	986(1)	4538(1)	−2295(2)	2680(1)	3490(2)
O(a)	−1897(3)	992(4)	4553(3)	−2831(6)	2331(3)	4306(4)
O(b)	−369(5)	1862(3)	4858(3)	−2108(9)	2189(4)	2723(5)
O(c)	−395(3)	874(3)	3716(2)	−3195(6)	3218(3)	3167(4)
O(d)	−368(4)	204(3)	5017(3)	−1043(7)	2995(4)	3762(6)

to be isostructural since their basic molecular frameworks are virtually superimposable with the exception of the pendant phenyl ring of the benzet ligand and even here the difference only involves a small variation in rotation about the N(2)–C(26) bond. The topologies of the cations are as described above and the molecular dimensions within them are as expected. In both molecules the atoms N(1) and N(2) each has *S* absolute configuration.

In both structures a hydrogen bond network serves to link the cations with the lattice water molecule(s) and the perchlorate ions, the details of which are given in Table 6.

Isomeric distributions in the synthesized complexes

With the sole exception of the *S*-valgly reaction, in which the two possible meridional diastereoisomers are both formed in appreciable yield, reactions of dipeptides which have been investigated give a single isolable diastereoisomer. Traces of the other isomer have been detected in several of the syntheses, but the reactions are for all intents and purposes stereospecific. It should be noted, however, that the isomer which is obtained could be of either *C*- or *A*-topology, depending upon the particular peptide involved. However, it transpires that, save for the

TABLE 5. Selected bonding parameters for [Co(*R*,*R*-benzet)L]$ClO_4 \cdot nH_2O$ with e.s.d.s in parentheses

	L = gly-*R*-val	L = glygly		L = gly-*R*-val	L = glygly
Distances (Å)					
Co–N(11)	1.973(4)	1.954(6)	Co–O(31)	1.906(3)	1.919(5)
Co–N(1)	1.946(4)	1.964(6)	Co–N(31)	1.955(4)	1.966(6)
Co–N(2)	2.011(4)	1.992(5)	Co–N(32)	1.872(4)	1.880(6)
O(31)–C(31)	1.303(6)	1.304(8)	C(31)–C(32)	1.535(7)	1.547(10)
O(32)–C(31)	1.234(6)	1.222(9)	C(32)–C(35)	1.561(7)	
O(33)–C(33)	1.253(6)	1.267(8)	C(33)–C(34)	1.521(7)	1.517(10)
N(31)–C(34)	1.492(7)	1.520(9)	C(35)–C(36)	1.531(7)	
N(32)–C(32)	1.467(6)	1.460(9)	C(35)–C(37)	1.529(7)	
N(32)–C(33)	1.331(6)	1.313(8)	C(1)–C(2)	1.526(7)	1.519(9)
N(11)–C(15)	1.354(6)	1.354(8)	C(2)–N(2)	1.520(6)	1.511(9)
C(15)–C(16)	1.493(7)	1.500(9)	N(2)–C(26)	1.508(6)	1.499(8)
C(16)–N(1)	1.489(6)	1.491(8)	C(26)–C(25)	1.514(7)	1.506(10)
N(1)–C(1)	1.485(6)	1.495(8)			
Angles (°)					
N(11)–Co–N(1)	82.8(2)	84.8(2)	O(31)–Co–N(32)	85.1(1)	84.8(2)
N(1)–Co–N(2)	86.2(2)	85.9(3)	N(32)–Co–N(31)	86.1(2)	85.2(2)
N(11)–Co–N(2)	167.8(2)	167.0(2)	N(1)–Co–O(31)	94.1(1)	94.5(2)
N(1)–Co–N(32)	176.9(2)	179.1(3)	N(1)–Co–N(31)	94.9(2)	95.4(2)
O(31)–Co–N(31)	170.6(2)	169.9(2)	N(2)–Co–O(31)	85.5(1)	85.5(2)
N(11)–Co–O(31)	90.0(1)	86.6(2)	N(2)–Co–N(31)	92.6(2)	96.6(2)
N(11)–Co–N(31)	93.6(2)	93.3(2)	N(2)–Co–N(32)	96.7(2)	93.4(3)
N(11)–Co–N(32)	94.2(2)	95.7(2)	O(31)–C(31)–O(32)	123.0(5)	123.9(7)
Co–O(31)–C(31)	114.9(3)	115.8(5)	O(31)–C(31)–C(32)	116.6(4)	116.1(6)
Co–N(31)–C(34)	108.2(3)	110.0(4)	O(32)–C(31)–C(32)	120.3(4)	120.0(6)
Co–N(32)–C(32)	115.8(3)	115.9(5)	N(32)–C(33)–O(33)	128.4(5)	125.9(6)
Co–N(32)–C(33)	118.4(3)	119.8(5)	N(32)–C(33)–C(34)	112.2(4)	113.5(6)
C(32)–N(32)–C(33)	125.8(4)	123.9(6)	O(33)–C(33)–C(34)	119.3(4)	120.5(6)
N(32)–C(32)–C(31)	106.4(4)	107.2(6)	C(32)–C(35)–C(36)	109.3(4)	
N(32)–C(32)–C(35)	114.6(4)		C(32)–C(35)–C(37)	113.9(4)	
C(31)–C(32)–C(35)	111.1(4)		C(36)–C(35)–C(37)	109.4(4)	
N(31)–C(34)–C(33)	112.5(4)	111.2(5)			
Co–N(11)–C(15)	112.1(3)	113.8(5)	N(1)–C(1)–C(2)	106.0(4)	106.6(6)
N(11)–C(15)–C(16)	116.0(4)	116.9(6)	C(1)–C(2)–N(2)	104.9(4)	108.2(5)
C(15)–C(16)–N(1)	108.0(4)	110.1(5)	C(2)–N(2)–Co	106.8(3)	109.4(4)
C(16)–N(1)–Co	108.6(3)	111.1(4)	C(2)–N(2)–C(26)	113.2(4)	111.6(5)
C(16)–N(1)–C(1)	114.5(4)	113.9(6)	C(26)–N(2)–Co	121.1(3)	121.7(4)
Co–N(1)–C(1)	108.3(3)	105.3(4)			
C(1)–C(2)–C(3)	111.4(4)	110.4(6)			

TABLE 6. Proposed hydrogen bonding in the structures of [Co(*R*,*R*-benzet)L]$ClO_4 \cdot nH_2O$ with e.s.d.s. in parentheses

L = gly*R*-val[a]			
N(1)H(N1)...O(33^{I})	2.971(5)	O(w)H(wb)...O(32)	2.812(5)
N(31)H(N31b)...O(33^{I})	2.889(5)	[b]O(w)H(wa)...O(c)	3.172(5)
N(31)H(N31a)...O(w^{II})	3.081(6)	...O(d)	2.991(6)
L = glygly[a]			
N(1)N(N1)...O(w1^{III})	2.895(8)	O(w1)H(w1a)...O(33^{III})	2.872(7)
N(31)H(N31b)...O(33^{III})	2.885(8)	O(w1)H(w1b)...O(w2)	2.791(7)
N(31)H(N31a)...O(w2^{III})	3.127(7)	O(w2)H(w2a)...O(32^{IV})	2.730(7)
		O(w2)H(w2b)...O(d)	2.912(9)

[a]Roman numeral superscripts refer to the following equivalent positions relative to x, y, z: I: $x-\frac{1}{2}, \frac{1}{2}-y, -z$; II: $-x, \frac{1}{2}+y, \frac{1}{2}-z$; III: $\frac{1}{2}+x, \frac{1}{2}-y, -z$; IV: $-x, \frac{1}{2}+y, \frac{1}{2}-z$.
[b]Bifurcated hydrogen bond.

case of *S*-valgly, only the *C*-diasteroisomer is formed.

Electronic absorption and chiroptical data for the complexes are given in Table 2. The electronic spectra consist of a single band in the visible region assignable to the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption of O_h parentage. The broad, slightly asymmetric shape of the band suggests some splitting of the energy levels resulting from the asymmetry of the complexes. The position of the absorbance is 515 ± 15 nm, compared to *c.* 480 nm for $[Co(dien)(glygly)]^+$ [6, 15]. The position of λ_{max} shows some correlation with the structure of the peptide, occurring at shorter wavelength when a glycyl fragment forms the terminal carboxylate.

The CD spectra of the complexes can be grouped into two classes, depending on the sign of the absorption in the region of the long wavelength d–d transition. For the complexes containing gly-*R*-val, gly-*R*-leu and *S*-valgly (the major isomer), two positive maxima are observed between 400 and 600 nm. With all the remaining peptides, only a single broad negative peak is observed, although its shape is also asymmetric, thus indicating the presence of at least two negative contributions. The largest values of $\Delta\epsilon_{max}$ occur when the dipeptide is chiral at the terminal carboxylate, as noted in other similar systems [15, 16]. However, we wish to stress that CD spectral data *cannot* be used to comment on the stereochemistries of the complexes. This is borne out by consideration of the CD spectra of the two complexes whose molecular topologies are unambiguously assigned via crystal structure determinations; dominant bands in their visible CD spectra are of opposite sign. That is to say that vicinal effects are quite significant in these systems, as might be expected on the basis of the underlying structural motif (two terdentates coordinated to the octahedron in the *mer* sense).

^{1}H NMR spectra (Table 1) do provide a means of assigning the stereochemistries of the other species isolated. In the ^{1}H NMR spectrum of *C*-[Co(*R*,*R*-benzet)(gly-*R*-val)]$^+$, a significant downfield shift (0.54 ppm) is observed for the pyridyl H(11) proton, in comparison to *C*-[Co(*R*,*R*-benzet)(glygly)]$^+$. In all other respects, the spectra are quite analogous. The shift may be rationalized in terms of contact deshielding associated with the close proximity of the peptide side chain to the H(11) proton. A similar shift (0.35 ppm) for the gly-*R*-leu complex, when all other spectral characteristics remain constant, is a measure of the magnitude of the deshielding in the two complexes, and hence the distance between the H(11) hydrogen atom and the interacting side chain. This effect is only observed for the gly-*R*-val and gly-*R*-leu complexes, and in view of other spectral analogies, we are confident of assigning the stereochemistry of the latter as *C*.

Such shifts are not expected for either possible diastereoisomer in complexes containing dipeptides composed of *S*-aminoacids. The orientation of the side chain(s) is such that it cannot interact with the pyridyl hydrogen atoms. Thus, except in the case of one of the *S*-valgly isomers, all other ternary complexes of the dipeptides have the same molecular topology, *C*, on the basis of the very close correspondence of their ^{1}H NMR spectra with that of *C*-[Co(*R*,*R*-benzet)(glygly)]$^+$ (Table 1). The remaining *S*-valgly isomer must therefore possess the *A* topology.

The reasons for the stereoselectivity observed in these systems, with the one exception of the *S*-valgly reaction, remain obscure. Kinetic effects probably play a role; molecular models do not suggest any particular steric reason for the observed preferences in the modes of coordination of the various peptides studied. It is true that such preferences do obtain, however, and that this may be employed under some circumstances for the separation of mixtures of peptides via formation of internal diastereoisomers of the kinds reported here. Studies directed towards these separations will be communicated separately in the near future.

Supplementary material

Lists of observed and calculated structure factors, anisotropic temperature factors, atomic coordinates for the hydrogen atoms, proposed hydrogen bond parameters and a comprehensive table of bond lengths and angles are available from the authors on request.

Acknowledgements

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