Preparation and Characterization of *trans*-Bis(ethylenediamine)chloro(Boc-L-valine)-Co(III)fluoroborate: an Intermediate in Metal Mediated Peptide Synthesis

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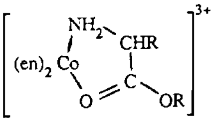
Abstract

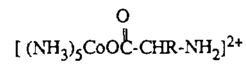
The synthesis, X-ray structure and electronic spectra of the title complex are presented. *trans*-Bis(ethylenediamine)chloro(Boc-L-valine)Co(III)-fluoroborate (Boc = t-butyloxycarbonyl) was prepared from *trans* $[Co(en)_2OHCl]^+$ and an active ester form of Boc-L-valine. Blue crystals of CoCl $(O_4N_5C_{14}H_{34})\cdot BF_4$ are orthorhombic, space group $P2_12_12_1$ with $a = 13.170(2)$, $b = 14.545(2)$, $c = 12.6268(8)$ Å, $Z = 4$ and $R_F(R_{wF}) = 0.040$ (0.042) for 2087 reflections. The structure consists of $[Co(en)_2(Boc\text{-}L\text{-}valine)Cl]^+$ cations and BF_4^- anions linked by an extensive hydrogen bonding network involving the BF_4 F atoms and the N atoms of the cation. Co(III) is coordinated in a distorted octahedral fashion by four en N atoms, a Cl atom, and a carboxylate O atom from the Boc-L-valine ligand. The coordinated Cl and O atoms are *trans* and Boc-L-valine acts as a monodentate ligand. The Co–N bond lengths (1.943(4)–1.955(4) Å) are typical as are the axial Co–Cl (2.248(1) Å) and Co–O(CO$_2$) (1.910(3) Å) distances. The visible absorption spectrum shows two bands (λ = 447, 578 nm) characteristic of *trans* Co(III)-$(en)_2L_2$ complexes.

Introduction

Cobalt(III) complexes of type I (where en = ethylenediamine) have been previously used to activate amino acid esters for peptide synthesis [1]. Binding of amino acid esters to cobalt(III) blocks the amine terminal and activates the carboxyl terminal for peptide formation. More recently, a different role for cobalt(III) in peptide synthesis was demonstrated. Using cobalt(III) complexes of type II where cobalt(III) acts as a C-terminal protecting group [2, 3], several peptide sequences were synthesized in solution. In an attempt to extend the use of cobalt(III) amino acid complexes to solid phase peptide synthesis [3b], we have synthesized bis(ethylenediamine) cobalt(III) amino acid complexes where the amino acid is bound to the cobalt at the carboxyl terminal in a monodentate mode. In this paper we describe the synthesis and X-ray structure of one such complex, *trans*-bis(ethylenediamine)chloro(Boc-L-valine)cobalt(III)fluoroborate.



Type I



$$[(NH_3)_5CoO\overset{O}{\overset{\|}{C}}\text{-}CHR\text{-}NH_2]^{2+}$$

Type II

Experimental

Synthesis of Cobalt(III) Complexes

trans-$[Co(en)_2Cl_2]Cl$ and *trans*-$[Co(en)_2(OH)Cl]Cl$ were prepared using literature methods [4, 5].

trans-[Co(en)$_2$(OH)Cl]BF$_4$

trans-$[Co(en)_2(OH)Cl]Cl$ was converted to *trans*-$[Co(en)_2(OH)Cl]BF_4$ by dissolution in ice water. A saturated $NaBF_4$ solution, 25 ml per g of Co complex, was added. The resulting solution was stirred rapidly while maintaining a temperature of 5 °C. A blue–grey solid precipitated, was collected by filtration and washed with ethanol, then ether. The visible spectrum in 0.1 N TFA showed λ_{max} at 590 and 445 nm.

trans-[Co(en)$_2$Boc-L-valineCl]BF$_4$ (1)

Boc-L-valine (1.37 g, 6.3 mmol) was dissolved in CH_2Cl_2 (4 ml) and cooled in an ice bath. A solution of hydroxybenzotriazole (HOBt) (0.97 g, 6.2 mmol) in 3 ml DMF at 0 °C was added to it. Dicyclohexylcarbodimide (DCC) (1.19 g, 5.8 mmol) in 4 ml CH_2Cl_2 at 0 °C was then added to the above reaction mixture which was left at 0 °C for 2 h. The solution was then filtered and the filtrate was added to a solution of *trans*-$[Co(en)_2(OH)Cl]BF_4$ (2.0 g, 6.3 mmol) in 4 ml DMF. The resulting blue solution was stirred at room temperature for 45 min and stored

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in a refrigerator for 2 h. The solution was then diluted to 25 ml with water and extracted twice with ether to remove unreacted starting materials. The aqueous layer was diluted to 250 ml and loaded on a SP-Sephadex C25 cation-exchange resin column (2 X 60 cm, Na^+ form). After the column was washed thoroughly with deionized water, the blue band was eluted with 0.2 M $NaBF_4$. The resulting solution was concentrated by rotary evaporation, and loaded on a Bio-Gel P2 (Biorad) column, eluted with water, and then concentrated to dryness again. Acetonitrile was added to the dry solid, and the insoluble $NaBF_4$ was removed by filtration. The filtrate was concentrated to dryness by rotary evaporation. The resulting blue solid was recrystallized from $MeOH/H_2O$. Yield: 1.04 g (32%) of *trans*-$[Co(en)_2$Boc-L-valineCl$]BF_4$. The visible spectrum in water showed λ_{max} at 577 and 454 nm. HPLC (20%MeOH/80%H_2O/trace TFA/pH 2.7 with NaOH) gave one peak. ^1H NMR (d_6-DMSO): δ 0.7(d, CH_3 of val), 0.8(d, CH_3 of val), 1.35(s, CH_3 of Boc), 2.5–2.7(broad, CH_2 of en). ^{13}C NMR (d_6-DMSO): δ 17.93, 19.49, 28.16, 30.32, 44.44, 61.39, 77.75, 155.52, 182.30.

X-ray Diffraction Study

Diffraction quality crystals of the title complex were obtained by crystallization from methanol/water, and data were obtained from a single crystal of dimensions 0.15 X 0.25 X 0.5 mm. Crystal data, and additional details of the data collection and refinement, are presented in Table 1. Intensity data were collected and corrected for decay, Lp and absorption (empirical) effects. Diffractometer examination of the reciprocal lattice revealed *mmm* Laue symmetry and systematic absences of $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; and $00l$, $l = 2n + 1$, fixing the space group as $P2_12_12_1$.

The structure was solved by direct methods [6] and refined using full-matrix least-squares techniques [7]. Neutral atom scattering factors, including corrections for anomalous dispersion, were used [8]. An E map based on 350 phases from the starting set with the highest combined figure of merit revealed the Co and Cl atoms. The remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Several cycles of isotropic refinement led to convergence with $R_F = 0.094$. Some hydrogen atoms were located on a difference map prepared at this point; the remaining H atoms were added to the model at calculated positions with N–H and C–H bond lengths taken to be 0.87 and 0.95 Å, respectively. H atom parameters were not refined. The enantiomer was verified by refining both S and I structures; as expected, the L-valine structure gave a significantly lower R factor. Additional refinement, using anisotropic thermal parameters for all non-hydrogen atoms, reduced R_F to 0.040 and R_{wF} to 0.043. For the final cycle, all parameter changes were less than 0.01σ where σ is the e.s.d. obtained from the inverse matrix. A final difference map showed no unusual features; the largest peak was 0.35 e/Å^3.

TABLE 1. Crystal and Refinement Data for 1

Formula	$CoClF_4O_4N_5C_{14}BH_{34}$
Formula weight	*517.65*
a (Å)	13.170(2)
b (Å)	14.545(2)
c (Å)	12.6268(8)
V (Å^3)	2418.8(9)
Space group	$P2_12_12_1$
Z	4
No. reflections used to determine cell constants	25(14.6 $\leq \theta <$ 16.5°)
d_{calc} (g/cm^3)	1.421
d_{obs} (g/cm^3)	1.40(1)[a]
λ (Mo Kα) (Å)	0.71073
Monochromator	graphite
Linear absorption coefficient (cm^{-1})	8.7
Absorption factor range	$0.96 \leq T \leq 1$
Diffractometer	Enraf-Nonius CAD-4
Data collection method	θ-2θ
2θ range (°)	$4 \leq 2\theta \leq 50$
Temperature (K)	297(1)
Scan range (°)	1.20 + 0.35 tan θ
No. standard reflections	3
% variation in standard intensity	±0.4
No. unique data collected	3142
No. data used in refinement $[F_o^2 \geq 3\sigma(F_o^2)]$	2087
Data: parameter ratio	7.7
Final *G.O.F.*[b]	1.23
Final R_F [c]	0.040
Final R_{wF} [d]	0.043
Weighting scheme[e]	$w = 4F_o^2/[\sigma(F_o^2)]^2$

[a] Determined by flotation in mixtures of carbon tetrachloride and cyclohexane. [b] Error in an observation of unit weight, equal to $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables in the least-squares refinement. [c] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. [e] $\sigma(F_o^2) = [S^2(C + R^2B) + (0.04F_o)^2]^{1/2}/\text{Lp}$ where S is the scan rate, C is the total integrated peak count, R is the ratio of scan to background counting time, B is the total background count, and 0.04 is a factor used to downweight intense reflections.

Results and Discussion

Crystal structure

The structure consists of $[Co(en)_2$Boc-L-valineCl$]^+$ and BF_4^- ions. Figure 1 shows a view of the cation with the atom numbering scheme. Final atomic parameters are listed in Table 2. See also 'Supplementary Material'. Selected interatomic distances and bond angles are listed in Table 3.

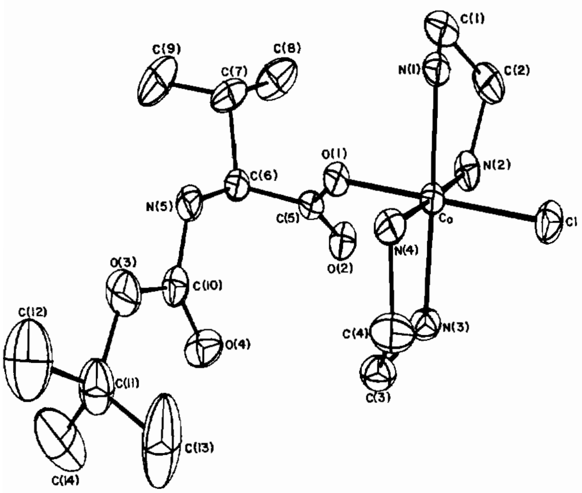


Fig. 1. View of the title complex showing the atom numbering scheme.

TABLE 2. Fractional Atomic Coordinates and Thermal Parameters for 1

	x	y	z	B_{eq} (Å^2)
Co	0.04118(5)	0.29092(4)	0.92570(5)	2.63(1)
Cl	−0.0229(1)	0.39469(9)	0.8120(1)	4.16(3)
F(1)	−0.1274(3)	0.1298(2)	1.1104(2)	5.31(8)
F(2)	−0.0641(2)	0.0923(2)	1.2715(3)	5.67(8)
F(3)	−0.2300(3)	0.1242(3)	1.2537(3)	7.7(1)
F(4)	−0.1106(5)	0.2361(3)	1.2354(3)	9.5(1)
O(1)	0.0904(2)	0.2050(2)	1.0279(2)	2.94(6)
O(2)	0.2517(3)	0.1896(2)	0.9754(3)	3.90(8)
O(3)	0.1410(3)	0.2359(3)	1.3641(3)	5.8(1)
O(4)	0.2635(3)	0.2621(3)	1.2431(3)	4.95(9)
N(1)	−0.0693(3)	0.2049(3)	0.9014(3)	3.08(8)
N(2)	0.1092(3)	0.2297(3)	0.8076(3)	3.8(1)
N(3)	0.1520(3)	0.3755(3)	0.9552(4)	3.66(9)
N(4)	−0.0283(3)	0.3481(3)	1.0444(3)	3.22(8)
N(5)	0.1543(3)	0.1440(3)	1.2280(3)	3.62(9)
C(1)	−0.0325(4)	0.1277(4)	0.8372(5)	4.3(1)
C(2)	0.0357(5)	0.1677(4)	0.7545(4)	4.8(1)
C(3)	0.1360(4)	0.4181(4)	1.0606(5)	4.4(1)
C(4)	0.0245(4)	0.4337(4)	1.0743(5)	5.0(1)
C(5)	0.1814(4)	0.1726(3)	1.0369(4)	2.9(1)
C(6)	0.1984(3)	0.1097(4)	1.1313(4)	3.2(1)
C(7)	0.1582(4)	0.0119(4)	1.1078(5)	4.6(1)
C(8)	0.1966(6)	−0.0237(4)	1.0026(6)	7.3(2)
C(9)	0.1872(6)	−0.0532(5)	1.1987(6)	7.7(2)
C(10)	0.1917(4)	0.2177(4)	1.2758(4)	3.7(1)
C(11)	0.1642(5)	0.3163(4)	1.4300(5)	5.6(1)
C(12)	0.0876(8)	0.3067(8)	1.5185(6)	13.2(3)
C(13)	0.1484(9)	0.4024(5)	1.3735(6)	12.3(3)
C(14)	0.2685(8)	0.3072(6)	1.4750(6)	10.1(2)
B	−0.1328(5)	0.1453(5)	1.2185(6)	4.2(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \text{gamma})B(1,2) + ac(\cos \text{beta})B(1,3) + bc(\cos \text{alpha})B(2,3)]$.

TABLE 3. Bond Lengths (Å) and Angles (°) for 1

Co	Cl	2.248(1)	N(1)	C(1)	1.467(6)
Co	O(1)	1.910(3)	N(2)	C(2)	1.485(8)
Co	N(1)	1.943(4)	N(3)	C(3)	1.483(7)
Co	N(2)	1.955(4)	N(4)	C(4)	1.476(7)
Co	N(3)	1.946(4)	N(5)	C(6)	1.441(6)
Co	N(4)	1.944(4)	N(5)	C(10)	1.325(7)
F(1)	B	1.386(8)	C(1)	C(2)	1.496(8)
F(2)	B	1.363(7)	C(3)	C(4)	1.495(8)
F(3)	B	1.389(8)	C(5)	C(6)	1.519(7)
F(4)	B	1.371(9)	C(6)	C(7)	1.546(7)
O(1)	C(5)	1.292(5)	C(7)	C(8)	1.512(9)
O(2)	C(5)	1.234(5)	C(7)	C(9)	1.535(9)
O(3)	C(10)	1.326(7)	C(11)	C(12)	1.51(2)
O(3)	C(11)	1.466(7)	C(11)	C(13)	1.457(9)
O(4)	C(10)	1.217(6)	C(11)	C(14)	1.49(1)

Cl	Co	O(1)	176.9(2)	N(4)	C(4)	C(3)	107.8(4)
Cl	Co	N(1)	92.9(1)	O(1)	C(5)	O(2)	124.5(4)
Cl	Co	N(2)	89.5(1)	O(1)	C(5)	C(6)	115.2(4)
Cl	Co	N(3)	88.8(1)	O(2)	C(5)	C(6)	120.3(4)
Cl	Co	N(4)	91.6(1)	N(5)	C(6)	C(5)	113.4(4)
O(1)	Co	N(1)	86.5(1)	N(5)	C(6)	C(7)	110.1(4)
O(1)	Co	N(2)	93.5(2)	C(5)	C(6)	C(7)	110.7(4)
O(1)	Co	N(3)	91.8(2)	C(6)	C(7)	C(8)	111.7(5)
O(1)	Co	N(4)	85.3(1)	C(6)	C(7)	C(9)	109.9(5)
N(1)	Co	N(2)	86.0(2)	C(8)	C(7)	C(9)	111.3(5)
N(1)	Co	N(3)	178.0(2)	O(3)	C(10)	O(4)	124.7(6)
N(1)	Co	N(4)	92.6(2)	O(3)	C(10)	N(5)	110.9(5)
N(2)	Co	N(3)	95.2(2)	O(4)	C(10)	N(5)	124.3(6)
N(2)	Co	N(4)	178.2(2)	O(3)	C(11)	C(12)	102.0(6)
N(3)	Co	N(4)	86.3(2)	O(3)	C(11)	C(13)	112.2(6)
Co	O(1)	C(5)	127.8(3)	O(3)	C(11)	C(14)	109.7(5)
C(10)	O(3)	C(11)	122.2(5)	C(12)	C(11)	C(13)	110.2(8)
Co	N(1)	C(1)	109.4(3)	C(12)	C(11)	C(14)	109.0(8)
Co	N(2)	C(2)	108.8(3)	C(13)	C(11)	C(14)	113.2(8)
Co	N(3)	C(3)	109.2(3)	F(1)	B	F(2)	111.0(5)
Co	N(4)	C(4)	109.6(3)	F(1)	B	F(3)	109.1(6)
C(6)	N(5)	C(10)	121.1(4)	F(1)	B	F(4)	107.5(6)
N(1)	C(1)	C(2)	106.7(4)	F(2)	B	F(3)	109.3(5)
N(2)	C(2)	C(1)	108.3(4)	F(2)	B	F(4)	109.1(6)
N(3)	C(3)	C(4)	108.0(5)	F(3)	B	F(4)	111.2(6)

The cation consists of Co(III) coordinated to four ethylenediamine N atoms, a Cl atom and a carboxylate O atom from the Boc-L-valine ligand in a distorted octahedral geometry. The coordinated Cl and O atoms are *trans* and the Boc-L-valine is a monodentate ligand. The Co–N bond lengths (range, 1.943(4)–1.955(4) Å) are normal [9], as are the axial Co–Cl (2.248(1) Å) and Co–O(CO$_2$) (1.910(3) Å) bond lengths [10].

Monodentate coordination of amino acids to metal ions is not common, but is known, as in $[(\text{thrH})\text{Co}(\text{NH}_3)_5]^{3+}$ [11] and $[\text{Fe}(\text{H}_2\text{O})_6][\text{Fe}(\text{glyH})_2(\text{H}_2\text{O})_4](\text{SO}_4)_2$ [12]. Amino acids ordinarily coordinate to metal ions as bidentate ligands through the amino nitrogen and the carboxylate oxygen, as in

$[Co(en)_2(L\text{-glutamate})]\cdot ClO_4$ [13] and $[Co(en)_2(N\text{-Me-ala})]\cdot ClO_4$ [14]. The propensity of amino acids for chelation is demonstrated in $[Co(\alpha Me\text{-}sal_2en)(N\text{-bz-L-ala})]$, where the chelated amino acid forms even when the amino nitrogen is protected with a benzyl group [15]. There has been a recent report of the formation of N-monodentate $t\text{-}[Co(en)_2Cl(NH_2CH_2CO_2H)]^{2+}$ from $t\text{-}[Co(en)_2Cl_2]^+$ and glycine [16]. However, this mode of coordination is not general for other amino acids [1, 2]. For histidine, a trifunctional amino acid, reaction with $t\text{-}Co(en)_2Cl_2$ under similar conditions resulted in the formation of *fac*-$[Co(en)ClhisH]^+$ [10].

The en bite angles, 86.0(2)° and 86.3(2)°, lie within the range reported for other Co–en complexes [17]. Both five-membered Co–en rings show the expected twist conformation but differ slightly in conformational detail (see least-squares planes, Table 4). Bond distances and angles within the Boc-L-valine ligand are similar to those reported for comparable structures. The conformation about C(6)–C(7) is *trans* (see Fig. 1). Amino acids prefer the gauche conformation, but *trans* is also known. For example, L-valine is known to crystallize in two forms, gauche I and *trans* [18] (see Fig. 2), while in the two crystal forms of the pentapeptide Boc-L-Val-L-Pro-Gly-L-Val-Gly, all of the val side chains are in the gauche II form [19]. Thus, while valine appears to have no strong preference for one particular conformation, in the present structure the *trans* conformation may be favored sterically because of the presence of two bulky groups, Boc and $Co(en)_2Cl$.

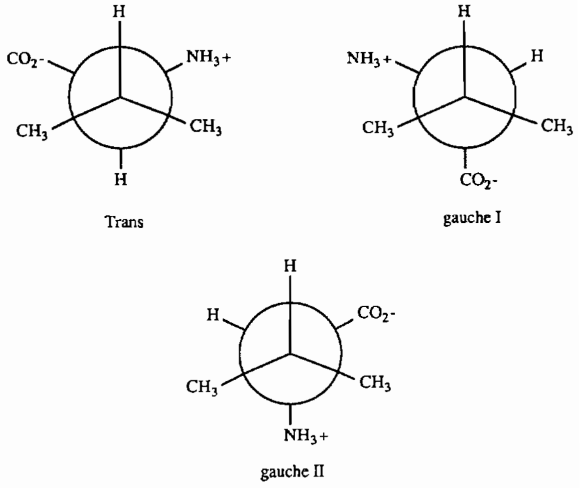


Fig. 2. Three possible rotational isomers of L-valine.

TABLE 4. Least-squares Planes

Atom	Deviation (Å)	Atom	Deviation (Å)	Atom	Deviation (Å)
N(1)[a]	−0.006(4)	Co[a]	0	Co[a]	0
N(2)[a]	0.006(4)	N(1)[a]	0	N(3)[a]	0
N(3)[a]	−0.006(4)	N(2)[a]	0	N(4)[a]	0
N(4)[a]	0.006(4)	C(1)	−0.411(6)	C(3)	−0.325(6)
Co	0.0232(6)	C(2)	0.253(6)	C(4)	0.318(6)
Cl	2.269(1)				
O(1)	−1.880(3)				

[a] Atom used to define the plane.

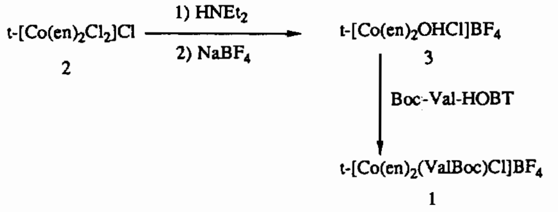
Geometrical features of the BF_4^- ion in this structure are similar to those reported previously [20]. These ions are stabilized in the lattice by hydrogen bonds from the four fluorine atoms to the amino acid nitrogen atom N(5) and to several nitrogen atoms of the ethylenediamine ligands (see Table 5). Additionally, O(2) is intramolecularly hydrogen bonded to N(2) while the keto oxygen atom O(4) forms an interionic H bond with an ethylenediamine ligand of an adjacent cation.

TABLE 5. Hydrogen Bonds

Donor (D)	Hydrogen (H)	Acceptor (A)	Symmetry equivalent of acceptor	Distance (Å)		Angle D–H···A
				D···A	H···A	
N(5)	H(N5)	F(2)	x, y, z	3.023(5)	2.21	154
N(1)	H(N11)	O(4)	$x-\frac{1}{2}, \frac{1}{2}-y, 2-z$	2.901(5)	2.09	153
N(1)	H(N12)	F(1)	x, y, z	2.956(5)	2.08	172
N(2)	H(N21)	O(2)	x, y, z	2.889(5)	2.17	139
N(2)	H(N22)	F(3)	$\frac{1}{2}+x, \frac{1}{2}-y, 2-z$	3.097(6)	2.37	140
N(3)	H(N32)	F(1)	$\frac{1}{2}+x, \frac{1}{2}-y, 2-z$	3.022(5)	2.31	138
N(4)	H(N41)	F(4)	x, y, z	3.105(6)	2.30	152
N(4)	H(N42)	O(2)	$x-\frac{1}{2}, \frac{1}{2}-y, 2-z$	2.959(5)	2.19	146

Synthesis and Characterization

The title compound was prepared from ***trans***-[Co(en)$_2$Cl$_2$]Cl as shown in Scheme 1. The initial step involved the hydrolysis of one inner sphere Cl ion in **2** to the corresponding hydroxy complex using the base diethylamine in a heterogeneous mixture. The resulting solid was rapidly filtered (to prevent the formation of the diaquo complex) and washed with ethanol. The Co(III)–hydroxy complex (**3**) was isolated as the BF_4^- salt. The Co(III)–amino acid complex (**1**) was formed by the reactions of **3** with L-BocNHCH(R)COO(OBt) where OBt is hydroxybenzotriazole and R is isopropyl. The product was characterized by UV–Vis (λ_{max} = 577, 454 nm), ^{1}H and ^{13}C NMR spectroscopy. Evidence for the ***trans*** ethylenediamine configuration was obtained from the UV–Vis spectrum (and compared with other ***trans*** Co(en)$_2$L$_2$ complexes) [21] and ^{13}C NMR (ethylenediamine carbons give only one peak at 44.44 ppm). This ***trans*** structure is confirmed by the X-ray crystal structure analysis (Fig. 1).



Scheme 1.

Supplementary Material

Lists of anisotropic thermal parameters, H atom coordinates, and observed and calculated structure factors are available from the authors on request.

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