Crystal Structure of Tris-(2-aminoethyl)amineglycinatocobalt(III) Ion $[Co(tren)(gly)]^{2+}$, a Peptide Hydrolysis Product from $[Co(tren)(OH)(H_2O)]^{2+}$

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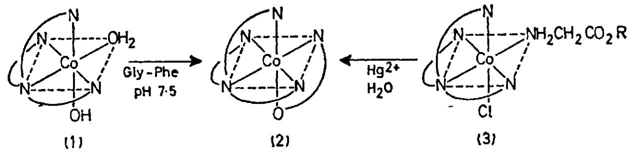
Summary An *X*-ray structure analysis of $[Co(tren)(gly)]Cl{\cdot}ClO_4$ (orange isomer) shows that the glycine is co-ordinated with its nitrogen atom *trans* to the tertiary amine of tren, and that the tren ligand is composed of three ethylenediamine chelate rings with two *k* and one *k'* conformations.

CERTAIN Co^{III} complexes cause the specific hydrolysis of peptides, where the *N*-terminal residue of the peptides becomes attached to the kinetically inert Co^{III} ion.[1] The hydroxoaquotris-(2-aminoethyl)aminocobalt(III) ion (**1**) is one tetramine complex which specifically gives one geometric isomer of $[Co(tren)(aa)]^{n+}$.[2] Hydrolysis of Gly-Phe gave the orange (λ_{max} 470 and 343 nm) glycinato complex (**2**), which was obtained when the glycine ester in $[Co(tren)(GlyOR)Cl]^{2+}$ (**3**) was hydrolysed in the co-ordination sphere of the Co^{3+} ion.



(1) (2) (3)

Since Co(tren) complexes have two nonequivalent reactive sites, two possible structures exist for $[Co(tren)(Gly)]^{2+}$ and $[Co(tren)(GlyOR)Cl]^{2+}$,[3] respectively.† Correct configurational assignments are particularly important as these structures are fundamental not only to peptide hydrolysis but also to other substitution studies in Co(tren) complexes.[4] A detailed knowledge of the conformation of the octahedrally co-ordinated tren will also be of interest in comparison with other six- and five-co-ordinate complexes.[5,6]

The structure of the orange glycinato complex has been established by *X*-ray crystal analysis. Crystals of racemic $[Co(tren)(Gly)]Cl{\cdot}ClO_4$ are monoclinic with $a = 14{\cdot}135$, $b = 9{\cdot}725$, $c = 11{\cdot}544$ Å, $\beta = 98°08'$, $Z = 4$, $D_m = 1{\cdot}76$ g cm^{-3}, space group $P2_1/a$. A total of 2425 reflections were

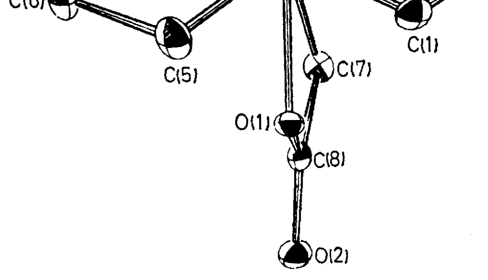


FIGURE. Molecular structure of (**2**) looking down the tertiary nitrogen of the tren N(1)–Co–N(5)(Gly) axis. 50% Probability envelopes for the vibrational ellipsoids of non-hydrogen atoms are shown. The anions are omitted for clarity. Important bond lengths (Å) and angles (deg.) are: N(1)–Co, 1·932; N(2)–Co, 1·963; N(3)–Co, 1·945; N(4)–Co, 1·969; N(5)(gly)–Co, 1·933; O(1)–Co, 1·915 (3); ∠N(2)–Co–N(3), 93·0; N(3)–Co–N(4), 92·7; and N(5)–Co–O(1), 85·3 (1).

† We are currently studying the structure of the red glycinato complex (ref. 2) which may be the configurational isomer of (**2**).

measured in the range $2\theta \leqslant 60°$ using graphite-crystal monochromated Mo-K_α radiation. After five cycles of block diagonal least-squares refinement with isotropic and three cycles with anisotropic thermal parameters, the residual R is 0·039.

As shown in the Figure and structure (**2**), the glycine is co-ordinated with its nitrogen atom *trans* to the tertiary amine nitrogen of the tren ligand. The peptide hydrolysis products, $[\mathrm{Co(tren)(aa)}]^{n+}$, will be more stable in this configuration. The other configuration [N(Gly) *cis* to N (tertiary)] is assumed less stable owing to unfavourable nonbonding interactions between the protons on the amino-acid nitrogen atom and protons on the adjacent tren carbon atoms as well as the primary nitrogen atoms.

Three ethylenediamine chelate rings of the tren ligand are asymmetric with respect to the co-ordination plane and have distorted envelope conformations (Figure). Two rings have the *k* (or *k'*) conformation and the other the *k'* (or *k*) conformation as in the case of octahedral $[\mathrm{Ni(tren)(NCS)_2}]$.[5] The constraints of the tetradentate ligand force some distortion of the co-ordination polyhedron: (i) displacement of the primary amino-groups towards the tertiary nitrogen atom, as reflected in the bond angles N(1)–Co–N(2) 86·1, N(1)–Co–N(3) 86·4, and N(1)–Co–N(4) 85·6(1)° and (ii) compression of the tertiary N–Co bond length (1·923 Å) compared with the primary N–Co bond lengths (mean 1·959 Å). An electronic effect transmitted to the position *trans* to the tertiary nitrogen may be responsible for the unusual short Co–N(Gly) bond distance (1·933 Å) compared with those in analogous trien complexes,[7] and for the resulting out-of-plane deformation of the amino-acid chelate ring.

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