Structure and Conformation Analyses of Two Isomeric Glycinato[tris(2-aminoethyl)amine]cobalt(III) Complex Ions

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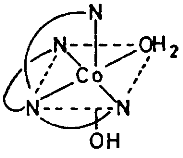
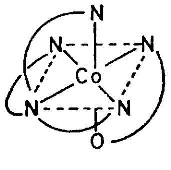
Crystal and molecular structures of the two diastereomeric title complex ions have been determined by *X*-ray diffraction. Crystals of the orange isomer, [Co(taa)(GlyO)]Cl[ClO$_4$], are monoclinic, space group $P2_1/a$, with a = 14.135(4), b = 9.725(4), c = 11.544(4) Å, β = 98.13(13)°, Z = 4, while those of the red isomer, [Co(taa)(GlyO)][ClO$_4$]$_2$, are orthorhombic, space group $P2_12_12_1$, with a = 16.990(4), b = 8.382(4), c = 12.034(4) Å, Z = 4. The structure of the orange isomer has been determined by the heavy-atom method, and of the red isomer by direct methods. The structures have been refined to R 0.039 (orange, 2 425 reflections) and 0.035 (red, 1 708 reflections). The glycine is chelated in the octahedral complex through its NH$_2$ group *trans* to the tertiary amine of taa in the orange isomer, and *cis* in the red isomer. These geometries are adequately reproduced by strain-energy minimization calculations and the latter are correlated with the stability relation. Comparison of the two isomeric complexes shows how the tripod ligand is accommodated in the octahedral structure, and reveals a special steric situation which labilizes a substituent *cis* to N$_{\text{tert}}$ in taa complexes of Co$^{\text{III}}$. The specific reaction path with which [Co(taa)(OH)(OH$_2$)]$^{2+}$ hydrolyzes the *N*-terminal residue of peptides to afford the orange isomeric [Co(taa)L]$^{n+}$ (L = amino-acid anion) is rationalized by the present studies.

CERTAIN cobalt(III) complexes promote the specific hydrolysis of peptides, whereby the *N*-terminal residue of the peptides becomes attached to the kinetically inert cobalt(III) ions.[1-11] The aquahydroxo[tris(2-aminoethyl)amino]cobalt(III) ion, [Co(taa)(OH)(OH$_2$)]$^{2+}$ (1), is one of the effective tetra-amine complexes and yields [6] the hydrolysis products [Co(taa)L]$^{n+}$ (L = amino-acid anion). Since two reactive sites, X and Y, in [Co(taa)XY], are non-equivalent, two geometric possibilities, (2) and (3), exist for these amino-acid complex products. It was demonstrated, however, that the peptide cleavage reactions yielded specifically an orange isomer. On the other hand, when a free amino-acid such as glycine (Gly) or alanine (Ala) was treated with (1) a red complex ion was isolable from the product mixture. In view of similarities in their physical properties, the orange and red complexes were considered to be diastereomeric.

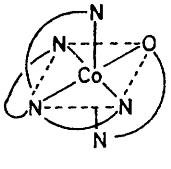
The occurrence of the two diastereomeric cations seemed to provide a unique opportunity for the detailed comparison of molecular geometries differing only in the configuration of the amino-acid chelate. It was expected that *X*-ray crystal-structure analysis of the two isomers would not only remove the uncertainty hitherto attached to their structural assignment but also would



(1)



(2)



(3)

(*i*) afford an explanation for the specific peptide hydrolysis course from a detailed knowledge of their structures, (*ii*) explain the substantial steric differences between the two reactive sites in taa complexes of Co$^{\text{III}}$ which had

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been previously deduced from kinetic studies,[12] and (*iii*) show the peculiar geometric arrangement of the tripod-like taa chelate rings in the octahedral environment of cobalt(III) complexes. Superficially the two isomeric complexes appeared to be electronically equivalent and equally strained, and no undue influence should arise from these sources. It seemed therefore that conformational analysis with some quantification of the steric-strain problems [13] would help to achieve our initial objectives.

We now report the *X*-ray crystallographic studies of the orange glycinato-complex, $[Co(taa)(GlyO)]Cl[ClO_4]$, and the red glycinato-complex, $[Co(taa)(GlyO)][ClO_4]_2$. The structural results are then compared with those obtained from calculations leading to the structures of minimum strain energy. The crystal structure of the former complex was described briefly in a preliminary communication.[14]

EXPERIMENTAL

The complexes $[Co(taa)(GlyO)]^{2+}$ were prepared as described earlier,[6] and recrystallized by slow evaporation of an aqueous solution. The crystals of the orange isomer were rhombic plates with their longer diagonal being the *b* axis, while those of the red isomer were plates elongated along the *c* axis. Crystals used for *X*-ray analysis were *ca.* 0.25 × 0.25 × 0.07 (orange) and 0.2 × 0.3 × 0.07 mm (red). Intensity data were collected by use of a Philips PW 1100 four circle diffractometer with graphite monochromated Mo-K_α radiation. Integrated intensities were obtained by the θ—2θ scan method with a scan speed of 0.0334° min^{-1} with respect to ω and scan width $(1.0 + B\tan\theta)°$ where B was 0.5 (orange) and 0.3 (red). For each reflection, preliminary counts at the peak centre (I_{top}) and at both ends of the scan range (mean I_{bck}) were measured. The intensity measurement was ignored if $I_{top} - 2(I_{top})^{\frac{1}{2}} < I_{bck}$. Background was measured at both ends of the scan range for the time of $\frac{1}{2}t_p(I_{bck}/\bar{I})^{\frac{1}{2}}$ where t_p is the total peak-scanning time and $\bar{I}$ is (total peak count/t_p).

Integrated intensities were obtained for 2 425 (orange isomer; of 3 344 possible) and 1 708 reflections (red isomer; of 2 354 possible) each with $2\theta \leqslant 60°$, and were used for the structure determination.

Crystal Data.—(a) *Orange isomer.* $[Co(C_8H_{22}N_5O_2)]Cl[ClO_4]$, $M = 414$, Monoclinic, $a = 14.135(4)$, $b = 9.725(4)$, $c = 11.544(4)$ Å, $\beta = 98.13(13)°$, $D_m = 1.76$, $Z = 4$. Absent reflections: $0k0$ for k odd and $h0l$ for h odd, indicating space group $P2_1/a$.

(b) *Red isomer.* $[Co(C_8H_{22}N_5O_2)][ClO_4]_2$, $M = 478$, Orthorhombic, $a = 16.990(4)$, $b = 8.382(4)$, $c = 12.034(4)$ Å, $D_m = 1.56$, $Z = 4$. Absent reflections: $h00$ for h odd, $0k0$ for k odd, and $00l$ for l odd, indicating space group $P2_12_12_1$. For both isomers, intensities were corrected for Lorentz-polarization factors but not for absorption effects.

Determination and Refinement of the Structure.—The structure of the orange isomer was solved by the heavy-atom method. The electron-density map, synthesized with the phases calculated by the contributions of cobalt and chlorine atoms, revealed all non-hydrogen atom positions. Refinement of the structure was carried out by the method of least squares with block-diagonal approximations. *R* was steadily decreased to 0.052 when the anisotropic thermal parameters were included. A subsequent difference-Fourier synthesis revealed all hydrogen-atom positions. When these atoms were added with isotropic temperature factors, *R* was reduced to 0.039.

The structure of the red isomer was solved by a direct method by use of the program MULTAN. Refinement of the parameters of all non-hydrogen atoms carried out as before resulted in *R* 0.060. When all the hydrogen-atom positions deduced from a subsequent difference-Fourier synthesis were added, *R* was reduced to 0.044. In this refinement, the anomalous-dispersion correction terms for cobalt ion and neutral chlorine were taken into consideration.[15] However when the resulting atomic co-ordinates were inverted and used as input to the same program with all the other parameters unchanged, *R* was reduced to 0.035 without any further refinement. All the co-ordinates and drawings of the red isomer are based on this latter configuration, although no further elaboration was made to establish clearly the enantiomorph.

In the least-squares refinement, unit weights were used for both isomers. Atomic scattering factors for non-hydrogen atoms were taken from ref. 16 and for hydrogen atoms from ref. 17. Final atomic parameters are given in Table 1 for both isomers. Final observed and calculated structure factors, anisotropic thermal parameters, and calculated atom co-ordinates for each isomer are listed in Supplementary Publication No. SUP 21752 (28 pp., 1 microfiche).*

TABLE 1

Final atomic parameters for non-hydrogen atoms (× 10^4), with estimated standard deviations, here and in succeeding Tables, in parentheses

Atom	*x*	*y*	*z*
(*a*) Orange isomer			
Co	4 026(0)	2 437(0)	1 721(0)
Cl(1)	2 650(1)	1 839(1)	6 709(1)
Cl(2)	1 594(1)	562(1)	619(1)
O(1)	5 227(2)	1 678(2)	1 466(2)
O(2)	6 034(2)	930(3)	71(3)
O(3)	1 912(3)	1 813(5)	5 765(3)
O(4)	2 338(3)	1 243(4)	7 715(3)
O(5)	3 432(4)	1 051(5)	6 429(5)
O(6)	2 942(3)	3 208(4)	6 935(4)
N(1)	4 397(2)	2 602(3)	3 397(2)
N(2)	4 573(2)	4 281(3)	1 624(3)
N(3)	2 787(2)	3 154(3)	1 965(3)
N(4)	3 670(2)	535(3)	2 049(3)
N(5)	3 666(2)	2 273(3)	42(3)
C(1)	5 202(2)	3 620(4)	3 588(3)
C(2)	4 931(3)	4 834(4)	2 803(3)
C(3)	3 568(3)	3 124(4)	3 962(3)
C(4)	2 639(3)	2 856(4)	3 170(4)
C(5)	4 715(3)	1 208(4)	3 818(4)
C(6)	3 987(3)	166(4)	3 288(4)
C(7)	4 541(3)	2 046(4)	−512(3)
C(8)	5 332(2)	1 500(3)	387(3)

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* For details see Notices to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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TABLE 1 (*Continued*)

Atom	*x*	*y*	*z*	*B*/Å²
(*b*) Red isomer				
Co	4 207(0)		−1 352(1)	9 604(1)
Cl(1)	4 279(1)		−893(2)	5 044(1)
Cl(2)	1 940(1)		−4 375(2)	7 842(1)
O(1)	4 727(2)		−2 612(5)	8 522(3)
O(2)	5 765(3)		−2 723(6)	7 411(4)
O(3)	5 108(3)		−742(7)	4 831(5)
O(4)	4 142(4)		−1 168(8)	6 181(4)
O(5)	3 991(4)		−2 235(6)	4 433(5)
O(6)	3 903(3)		540(6)	4 996(6)
O(7)	2 229(4)		−2 814(7)	7 633(5)
O(8)	1 474(3)		−4 338(8)	8 843(4)
O(9)	1 455(4)		−4 896(9)	6 934(5)
O(10)	2 578(4)		−5 404(9)	8 008(7)
N(1)	3 612(3)		−134(6)	10 691(4)
N(2)	4 876(3)		−2 041(7)	10 835(4)
N(3)	3 483(3)		−3 093(6)	9 882(4)
N(4)	3 488(3)		−442(6)	8 493(4)
N(5)	4 993(3)		286(6)	9 225(4)
C(1)	4 169(4)		239(8)	11 628(5)
C(2)	4 614(4)		−1 295(10)	11 903(5)
C(3)	2 931(3)		−1 131(9)	11 141(5)
C(4)	2 731(3)		−2 477(8)	10 352(5)
C(5)	3 314(3)		1 318(8)	10 099(5)
C(6)	2 966(3)		798(7)	9 006(5)
C(7)	5 618(3)		−422(8)	8 536(5)
C(8)	5 365(3)		−2 023(7)	8 111(5)

Final atomic (× 10^3) and isotropic thermal parameters (× 10) for hydrogen atoms

Atom	*x*	*y*	*z*	*B*/Å²
(*i*) Orange isomer				
H[N(2)]	501(3)	418(4)	128(4)	41(10)
H′[N(2)]	419(3)	496(4)	119(3)	39(9)
H[N(3)]	236(3)	278(4)	146(3)	39(9)
H′[N(3)]	273(3)	405(4)	186(3)	32(9)
H[N(4)]	396(3)	0(4)	149(3)	34(9)
H′[N(4)]	311(3)	39(4)	186(3)	36(9)
H[N(5)]	330(3)	162(4)	−11(4)	41(10)
H′[N(5)]	337(3)	298(4)	−18(4)	37(9)
H[C(1)]	575(3)	317(4)	333(3)	38(9)
H′[C(1)]	535(3)	383(4)	447(3)	32(9)
H[C(2)]	451(3)	536(4)	303(3)	30(8)
H′[C(2)]	544(3)	540(4)	272(3)	29(8)
H[C(3)]	363(3)	415(4)	405(3)	33(9)
H′[C(3)]	361(3)	269(4)	474(3)	35(9)
H[C(4)]	248(3)	197(4)	328(4)	42(10)
H′[C(4)]	219(3)	343(4)	344(3)	36(9)
H[C(5)]	492(3)	119(4)	465(3)	32(9)
H′[C(5)]	531(3)	100(4)	349(3)	37(9)
H[C(6)]	341(3)	19(4)	375(4)	40(9)
H′[C(6)]	428(3)	−71(4)	329(4)	42(10)
H[C(7)]	443(3)	143(4)	−119(3)	30(8)
H′[C(7)]	477(3)	289(4)	−83(3)	23(8)
(*ii*) Red isomer				
H[N(2)]	529(5)	−219(10)	1 057(7)	68(23)
H′[N(2)]	487(3)	−316(7)	1 089(5)	27(14)
H[N(3)]	343(3)	−361(7)	927(6)	24(12)
H′[N(3)]	357(4)	−387(8)	1 026(5)	38(15)
H[N(4)]	374(4)	20(10)	803(6)	50(20)
H′[N(4)]	313(4)	−145(10)	820(6)	58(20)
H[N(5)]	478(3)	95(6)	890(4)	11(10)
H′[N(5)]	518(3)	81(6)	976(4)	18(11)
H[C(1)]	448(4)	117(9)	1 150(5)	42(16)
H′[C(1)]	388(4)	47(8)	1 234(6)	44(17)
H[C(2)]	504(3)	−99(7)	1 231(4)	17(11)
H′[C(2)]	428(4)	−228(8)	1 231(5)	39(15)
H[C(3)]	252(4)	−41(8)	1 136(5)	33(15)
H′[C(3)]	310(3)	−140(8)	1 192(5)	28(13)
H[C(4)]	233(3)	−207(7)	969(5)	32(14)
H′[C(4)]	250(3)	−325(6)	1 073(4)	18(12)
H[C(5)]	382(3)	201(7)	1 002(5)	24(13)
H′[C(5)]	282(4)	164(9)	1 065(6)	48(18)
H[C(6)]	289(4)	177(8)	848(5)	38(16)
H′[C(6)]	247(4)	14(9)	917(5)	39(16)
H[C(7)]	567(5)	27(11)	795(7)	78(24)
H′[C(7)]	610(6)	−9(13)	901(8)	83(31)

RESULTS

Description of the [Co(taa)(GlyO)]$^{2+}$ *Cations*.—The glycine chelates with its nitrogen atom, N(5), *trans* in the orange and *cis* in the red isomer, to the tertiary amine, N(1), of the ligand taa. Hence, the configurations of the orange and red complexes are assigned as (2) and (3), respectively.

TABLE 2

Intramolecular bond distances (Å) within the [Co(taa)(GlyO)]$^{2+}$ cations

	Orange		Red	
Atoms	Found	Calc.*	Found	Calc.*
Co–O(1)	1.915(2)	1.908	1.894(4)	1.893
Co–N(1)	1.932(3)	1.942	1.943(5)	1.947
Co–N(2)	1.963(3)	1.967	1.955(5)	1.962
Co–N(3)	1.945(3)	1.951	1.938(5)	1.950
Co–N(4)	1.969(3)	1.971	1.965(5)	1.968
Co–N(5)	1.933(3)	1.949	1.968(5)	1.975
O(1)–C(8)	1.288(4)	1.268	1.290(7)	1.269
O(2)–C(8)	1.239(4)	1.238	1.231(7)	1.235
N(1)–C(1)	1.499(5)	1.501	1.505(7)	1.503
N(1)–C(3)	1.513(5)	1.508	1.527(8)	1.519
N(1)–C(5)	1.487(5)	1.493	1.499(8)	1.499
N(2)–C(2)	1.480(5)	1.489	1.497(8)	1.498
N(3)–C(4)	1.467(6)	1.477	1.490(8)	1.491
N(4)–C(6)	1.477(5)	1.489	1.500(8)	1.500
N(5)–C(7)	1.494(5)	1.491	1.473(8)	1.483
C(1)–C(2)	1.502(5)	1.506	1.528(10)	1.521
C(3)–C(4)	1.504(5)	1.511	1.514(9)	1.510
C(5)–C(6)	1.505(6)	1.510	1.506(8)	1.508
C(7)–C(8)	1.501(5)	1.508	1.499(9)	1.501

* From strain-energy minimization calculations.

TABLE 3

Intramolecular bond angles (°) within the [Co(taa)(GlyO)]$^{2+}$ cations

	Orange		Red	
Atoms	Found	Calc.	Found	Calc.
O(1)–Co–N(1)	94.3(1)	93.9	176.3(2)	
O(1)–Co–N(2)	88.7(1)	88.3	94.9(2)	94.0
O(1)–Co–N(3)	178.2(1)		89.7(2)	89.6
O(1)–Co–N(4)	85.8(1)	86.1	92.3(2)	92.2
O(1)–Co–N(5)	85.3(1)	86.0	85.1(2)	85.5
N(1)–Co–N(2)	86.1(1)	87.0	87.0(2)	87.5
N(1)–Co–N(3)	86.4(1)	87.2	87.1(2)	87.1
N(1)–Co–N(4)	85.6(1)	86.3	86.0(2)	86.5
N(1)–Co–N(5)	179.5(1)		98.2(2)	97.8
N(2)–Co–N(3)	93.0(1)	92.9	90.9(2)	91.2
N(2)–Co–N(4)	169.7(1)		172.7(2)	
N(2)–Co–N(5)	93.6(1)	93.1	89.2(2)	88.9
N(3)–Co–N(4)	92.7(1)	92.9	90.9(2)	91.4
N(3)–Co–N(5)	94.0(1)	92.8	174.8(2)	
N(4)–Co–N(5)	94.5(1)	93.6	89.6(2)	89.0
C(8)–O(1)–Co	115.9(2)		116.3(4)	
C(1)–N(1)–Co	106.6(2)	106.1	106.7(3)	106.1
C(1)–N(1)–C(3)	109.6(3)	110.3	108.9(4)	109.6
C(1)–6(1)–C(5)	111.6(3)	111.9	113.5(4)	111.5
Co–N(1)–C(3)	110.5(2)	110.1	110.3(3)	110.3
Co–N(1)–C(5)	105.9(2)	105.6	106.4(3)	105.9
C(3)–N(1)–C(5)	112.4(3)	112.5	110.9(4)	111.5
C(2)–N(2)–Co	111.2(2)	110.0	110.8(4)	109.8
C(4)–N(3)–Co	109.2(2)	108.0	110.4(4)	109.3
C(6)–N(4)–Co	111.5(2)	110.6	110.9(3)	110.3
C(7)–N(5)–Co	109.5(2)	108.2	109.8(4)	109.0
C(2)–C(1)–N(1)	108.2(3)	108.1	107.3(5)	107.9
C(4)–C(3)–N(1)	110.1(3)	110.1	110.8(5)	110.7
C(6)–C(5)–N(1)	109.1(3)	108.9	108.2(5)	108.5
C(8)–C(7)–N(5)	109.5(3)	109.3	110.2(5)	110.1
O(1)–C(8)–O(2)	124.1(3)	122.3	123.0(5)	121.7
O(1)–C(8)–C(7)	115.9(3)	117.3	116.9(5)	118.0
O(2)–C(8)–C(7)	120.0(3)	120.4	120.1(5)	120.3
N(2)–C(2)–C(1)	106.8(3)	107.8	108.2(5)	108.9
N(4)–C(4)–C(3)	107.7(3)	108.6	107.7(5)	108.3
N(4)–C(6)–C(5)	108.5(3)	109.2	109.1(5)	109.7

Intramolecular bond distances and angles with their estimated standard deviations are given in Tables 2 and 3. Figure 1 compares the two isomers viewed in projection along the N_{tert}–Co axis. The conformation of the orange isomer can be inverted since the crystal belongs to centrosymmetric space group $P2_1/a$. The conformations shown are consistent with the numerical descriptions in the text for both isomers. Clearly the ligands are arranged in a near-octahedral geometry, the taa ligand co-ordinating to the cobalt ion with the donor atoms occupying one apical (N_{tert}) and three equatorial positions (N_{prim}) in each isomer. Obviously the geometries of the taa ligand in the present six-co-ordinate complexes deviate from the three-fold axial symmetry which seems to be favoured by its tripod-like arrangement, as indicated in five-co-ordinate complexes such as [Zn(taa)(NCS)][SCN] [18] and [Cu(taa)(NCS)][SCN].[19]

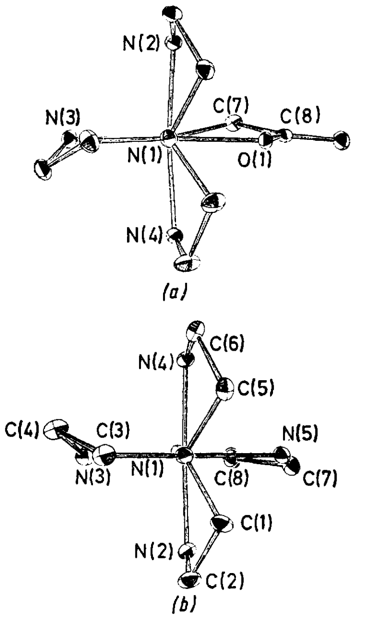


FIGURE 1 Projection of the $[Co(taa)(GlyO)]^{2+}$ cations of (a) the orange and (b) the red isomer, on a plane perpendicular to the N_{tert}–Co axis

However, careful examination of the bond angles at Co reveals that there is a significant, although small, difference in the deviation from the four-fold axial symmetry between the two cobalt complexes: N(2)–Co–N(3), 93.0(1) (orange) and 90.9(2)° (red); N(4)–Co–N(3), 92.7(1) (orange) and 90.9(2)° (red) (Figure 2 and Table 3, see later). Other co-ordination angles differing significantly from 90° are: N(1)–Co–O(1) 94.5(1) (orange) and N(1)–Co–N(5) 98.2(2)° (red).

The mean of the Co–N(taa) bond distances is 1.952 (orange) and 1.950 Å (red) and is comparable with corresponding values in the taa analogues: 1.963 in Δ-β_1-(*R*,*R*)-(4) and 1.951 Å in Δ-β_1-(*R*,*S*)-$[Co(3,6\text{-}NH\text{-}od)(GlyO)]I_2$, (5) (3,6-NH-od = 3,6-diazaoctane-1,8-diamine).[20] However, the bonds Co–N(1) and Co–N(3) are significantly shorter than Co–N(2) and Co–N(4) in both taa isomers. Interestingly, the Co–N(GlyO) bond length [1.933(3) Å] in the orange isomer is much smaller than that in the red [1.968(5) Å], the latter value being comparable with that of 1.960(7) Å in (5).[20] Also significant is the increase in Co–O(GlyO) distance [1.915(2) Å] in the orange isomer over that [1.894(4) Å] in the red; *cf.* 1.906(5) in (4) and 1.914(6) Å in (5).[20]

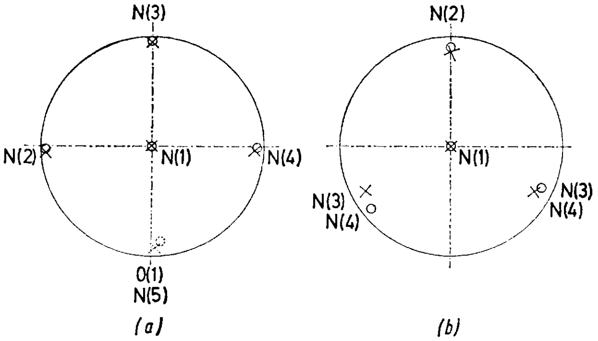
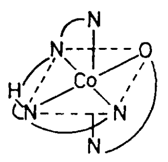


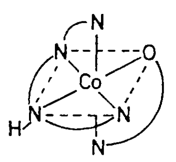
FIGURE 2 (a) Stereographic projection showing arrangement of ligand atoms around the cobalt ion in the orange (X) and the red isomer (○). The direction of the Co–N(1) bond is taken as a polar axis. Broken lines indicate that the ligand atom is oriented toward the southern hemisphere [opposite to N(1)]. (b) The same projection for the two five-co-ordinate complexes, [Zn(taa)(NCS)][SCN] (ref. 18) (X) and [Cu(taa)(NCS)]-[SCN] (ref. 19) (○). The atom numbering in parentheses corresponds to the latter complex

Table 4 shows the results of calculation of the least-squares planes containing the Co and the four ligand atoms. Clearly plane (1) [Co, O(1), N(1), N(3), and N(5)] has an exceedingly good planarity for both isomers.

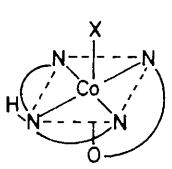
Conformation of the Chelate Rings.—Since the angles subtended at the cobalt atom by the taa chelate rings are all close to 86° [means: 86.0° (orange) and 86.4° (red)], the co-ordination plane [plane (3) of Table 4] deviates significantly from coplanarity.



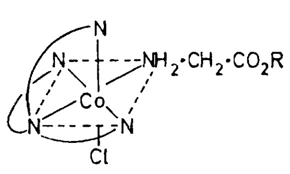
(4)



(5)



(6)



(7)

All the five-membered ring moieties have unsymmetrical envelope conformations with the exception of the ring containing C(2) in the orange isomer (see Table 5). Torsion

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[18] G. D. Andreetti, P. C. Jain, and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1969, **91**, 4112.

[19] P. C. Jain and E. C. Lingafelter, *J. Amer. Chem. Soc.*, 1967, **89**, 6131.

[20] D. A. Buckingham, P. J. Cresswell, R. J. Dellaca, M. Dweyer, G. J. Gainsford, L. G. Marzilli, I. E. Maxwell, W. T. Robinson, A. M. Sargeson, and K. R. Trunbull, *J. Amer. Chem. Soc.*, 1974, **96**, 1713.

TABLE 4

Details of least-squares planes containing the cobalt ion. Equations are in the form $lX + mY + nZ = D$, where X, Y, and Z are orthogonal (Å) co-ordinates along the crystallographic a^*, b, and c axes. Deviations (Å) of atoms from the planes are given in square brackets. Data for orange isomer precedes that for the red

Plane (1): Co, O(1), N(1), N(3), N(5)

$$0.3346X + 0.9266Y - 0.1718Z = 3.8735$$
$$0.6046X - 0.3480Y + 0.7165Z = 10.0660$$

[Co 0.012, 0.013; O(1) −0.016, 0.018; N(1) 0.015, −0.016; N(3) −0.015, 0.017; N(5) 0.016, −0.016]

Plane (2): Co, N(1), N(2), N(4), N(5) (orange); Co, O(1), N(1), N(2), N(4) (red)

$$0.9081X - 0.3559Y - 0.2208Z = 4.0733$$
$$0.0959X + 0.9285Y + 0.3586Z = 12.2547$$

[Co −0.057, 0.010; N(1) −0.053, −0.046; N(2) 0.050, 0.043; N(4) 0.049, 0.044; N(5) −0.046, O(1) −0.041]

Plane (3): Co, O(1), N(2)—(4) (orange); Co, N(2)—(5) (red)

$$0.3288X + 0.0630Y + 0.9423Z = 3.1183$$
$$0.1358X + 0.9388Y + 0.3164Z = 10.8070$$

[Co −0.068, −0.017; O(1) 0.085; N(2) 0.079, 0.106; N(3) −0.076, −0.105; N(4) 0.081, 0.106; N(5) −0.106]

TABLE 5

Deviations of carbon atoms from their respective N_{tert}–Co–N_{prim} or N(GlyO)–Co–O(GlyO) planes

		Deviation*/Å	
Plane	Atom	Orange	Red
N(1)–Co–N(2)	C(1)	−0.588	0.640
	C(2)	0.046	0.030
N(1)–Co–N(3)	C(3)	0.040	−0.017
	C(4)	0.579	−0.528
N(1)–Co–N(4)	C(5)	0.728	−0.717
	C(6)	0.204	−0.177
N(5)–Co–O(1)	C(7)	0.365	0.276
	C(8)	0.111	0.134

* The deviation is positive if the atom is displaced from the plane of reference in the direction of a right-hand screw rotating in the manner N(1)→Co→N(i) (i = 2, 3, or 4) or N(5)→Co→O(1).

TABLE 6

Torsion angles (°) about the bond involved in the chelate rings

	Orange		Red	
	Found	Calc.	Found	Calc.
C(1)–C(2)–N(2)–Co	27.5	27.4	−24.0	−23.8
N(2)–C(2)–C(1)–N(1)	−47.8	−48.1	45.4	45.5
C(2)–C(1)–N(1)–Co	46.0	45.8	−45.6	−45.3
Co–N(1)–C(3)–C(4)	21.2	20.6	−20.7	−20.7
N(3)–C(4)–C(3)–N(1)	−40.7	−40.5	37.8	38.8
C(3)–C(4)–N(3)–Co	41.7	41.3	−38.2	−39.0
Co–N(1)–C(5)–C(6)	−47.3	−47.1	46.8	46.6
N(4)–C(6)–C(5)–N(1)	41.2	41.4	−41.7	−41.3
C(5)–C(6)–N(4)–Co	−15.8	−15.9	17.3	16.4
C(8)–C(7)–N(5)–Co	21.1	21.1	13.9	11.6
O(1)–C(8)–C(7)–N(5)	−18.2		−9.7	
O(2)–C(8)–O(1)–Co	−174.6		179.2	
C(7)–C(8)–O(1)–Co	6.1		0.1	

angles about the C–C bonds and chiralities of the five-membered rings of the taa ligand are: C(1)–C(2) 47.8 λ, C(3)–C(4) 40.7 λ, C(5)–C(6) 41.2 δ (orange isomer), 45.4 δ, 37.8 δ, 41.7 λ (red isomer) (Table 6). The signs of the torsion angles and chiralities can be reversed for the orange isomer. Apparently the chelating mode of the glycine has little effect on torsional strain in the taa ligand. The envelope conformation of the central chelate ring clearly disturbs the symmetry of the *mer*-$NH_2[CH_2]_2NH[CH_2]_2NH_2$ residue in both complexes.* Within the ethylenediamine rings the three C–C, C–N_{prim}, and C–N_{tert} bond-length values are very close, means 1.503, 1.475, and 1.500 Å (orange) and 1.506, 1.496, and 1.511 Å (red). In the orange isomer the C–N distances are significantly greater for N_{tert} than for N_{prim}, as in taa·3HCl where C–N_{tert} is 1.492 and C–N_{prim} 1.474 Å.[21] Considerable angular distortion occurs in the red cation at N_{tert} [C(1)–N(1)–C(5), 113.5(4)°] whereas the corresponding angle in the orange cation reflects less strain [111.6(3)°].

The glycine chelate [mean N(GlyO)–Co–O(GlyO) 85.2°] in the taa complexes is not coplanar (see Figure 1) as it is in the structurally similar *mer*-[Co(3NH-pd)(GlyO)X]$^+$ (6) (X = NO_2 or Cl; 3NH-pd = 3-azapentane-1,5-diamine).[22] Polarization of the co-ordinated carboxy-group is evident in both isomers. Thus, the distances C(8)–O(2) and C(8)–O(1) are 1.239(4) and 1.288(4) Å for the orange isomer, and 1.231(4) and 1.290(4) Å for the red. A similar effect was found in the 3,6-NH-od counterparts, (4) [1.205(9) and 1.304(9) Å] and (5) [1.223(9) and 1.276(9) Å].[20]

Description of the Crystal Structure.—All interionic contacts less than <3.25 Å are listed in Table 7. Projections of the crystal structures are presented in Figure 3.

TABLE 7

Important interionic contacts (<3.25 Å) between non-hydrogen atoms

		Symmetry operation [a]	Translation
(*a*) Orange isomer			
Cl(2) ··· N(4)	3.139(5) [b]	I	(000)
N(2) ··· Cl(2)	3.110(3)	II	$(00\bar{1})$
N(5) ··· O(4)	3.194(4)	I	
Cl(2) ··· N(2)	3.247(3)	IV	$(\bar{1}00)$
O(3) ··· C(1)	3.237(5)	IV	
N(3) ··· O(2)	3.170(4)	IV	
O(2) ··· N(4)	2.917(4) [b]	III	$(0\bar{1}\bar{1})$
O(2) ··· N(5)	3.149(4)	III	
O(2) ··· C(7)	3.069(5)	III	
O(2) ··· C(8)	3.046(4)	III	
C(8) ··· C(8)	3.151(5)	III	
O(4) ··· N(3)	3.035(5) [b]	II	$(0\bar{1}0)$
(*b*) Red isomer			
N(4) ··· O(4)	3.057(8)	I	(000)
N(4) ··· O(7)	3.098(8)	I	
O(8) ··· O(5)	3.062(8)	II	(001)
N(3) ··· O(9)	2.991(8) [b]	II	
C(4) ··· O(9)	3.223(9)	II	
N(2) ··· O(8)	2.976(7)	III	
O(3) ··· N(2)	3.204(8) [b]	IV	(010)
O(6) ··· N(2)	2.970(7) [b]	IV	
N(4) ··· O(2)	2.826(7) [b]	IV	
N(5) ··· O(2)	2.885(7) [b]	IV	
N(5) ··· O(5)	3.148(8) [b]	IV	
C(6) ··· O(2)	3.016(7)	IV	

[a] Symmetry operation on second atom only: for orange isomer, I x, y, z, II $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$, III $1 - x, 1 - y, 1 - z$, IV $\frac{1}{2} + x, \frac{1}{2} - y, z$; for red isomer, I x, y, z, II $\frac{1}{2} - x, -1 - y, -\frac{1}{2} + z$, III $\frac{1}{2} + x, -\frac{1}{2} - y, 1 - z$, IV $1 - x, -\frac{1}{2} + y, \frac{3}{2} - z$. [b] Suggested H bond based on crystal-packing considerations.

Orange isomer. As shown in Figure 3(*a*), each of the

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* The deviation of C(4) from the pseudo-mirror plane [plane (1) in Table 5] is mostly responsible for the enantiomorphism of glycinato-complexes.

[21] C. Nave and M. R. Truter, *J.C.S. Dalton*, 1974, 2351.

[22] H. Kuroya, *J. Chem. Soc. Japan*, 1971, **92**, 905.

three N_{prim} atoms of the taa ligand is connected to either the chloride anion or the oxygen atom of the perchlorate anion, or the oxygen atom of the glycine ligand, by two hydrogen bonds which, together with one covalent and one co-ordinate bond to cobalt ion, form roughly tetrahedral bonding arrangements around each N_{prim} atom. These hydrogen bonds tightly connect the molecule I to the molecules II_{001} and III_{001} forming a chain of molecules extending in both the *a* and *b* direction. The packing between the molecules I and II, however, is rather loose with the only one short contact <3.5 Å [3.237 Å between C(1) of molecule IV_{100} and O(3) of molecule II]. Oxygen atoms other than O(4) of the perchlorate ion seem to fill space in the crystal.

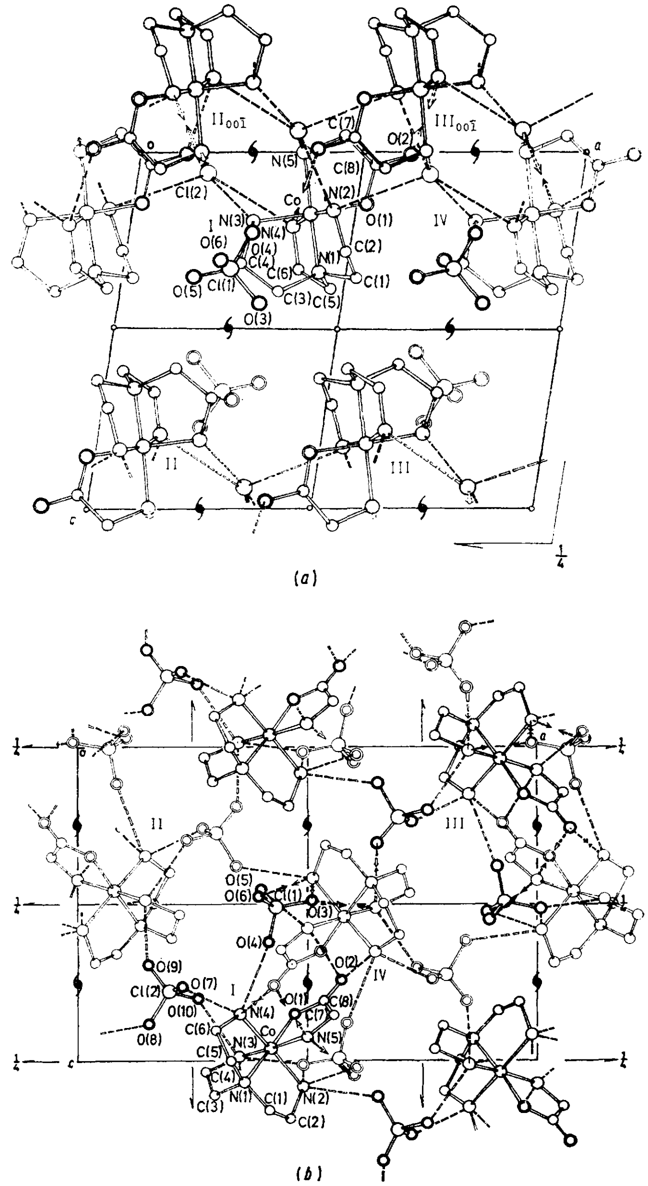

FIGURE 3 Projection of the crystal structure of (*a*) the orange and (*b*) the red isomer along the *b* axis. Hydrogen bonds are indicated by double broken lines. Symmetry operations are defined in Table 7

Red isomer. Figure 3(*b*) shows that each of the three N_{prim} atoms of the taa ligand is connected to either O(2) of the adjacent complex or oxygen atoms of the two perchlorate ions by three (in place of the two for the orange isomer) hydrogen bonds (presumably one single and one bifurcated hydrogen bond for each N_{prim} atom). Each of the eight oxygen atoms of the two perchlorate ions is hydrogen bonded to one atom of the complex ion. This network of hydrogen bonds links the complex ions together in all directions.

Strain-energy Minimization Calculations.—The crystal-structure analysis seems to verify the supposition that the two diastereomers are almost equally strained and electronically similar, thus permitting meaningful comparison based on conformation analysis. Based on the same assumption, Buckingham *et al.* calculated the structure of minimum strain energy for two isomeric $[CoCl(taa)(NH_3)]^{2+}$ cations (see later). The strain-energy minimization procedure has been described in detail elsewhere.[13] In summary, the total molecular strain energy is expressed as a sum of four terms [equation (1)] where $U(r_{ij})_B$ is the

$$U = \Sigma U(r_{ij})_B + \Sigma U(\theta_{ijk}) + \Sigma U(\phi_{ijkl}) + \Sigma U(r_{ij})_{NB} \quad (1)$$

potential energy for bond deformation between bonded atoms *i* and *j*, $U(\theta_{ijk})$ is the potential energy for valence-angle deformation between bonded atoms *i*, *j*, and *k*, $U(\phi_{ijkl})$ is the potential energy for torsional strain about the bond *jk* as defined by bonded atoms, *i*, *j*, *k*, and *l*, and $U(r_{ij})_{NB}$ is the non-bonded potential energy between two atoms *i* and *j*. The terms used in the force field are analogous to those used for minimization calculations on the β_2-[Co(3,6-NH-od){(*S*)-ProO}]$^{2+}$ complexes (ProO = prolinato).[23] Minimization of the total molecular-strain energy was achieved by a modified Newton–Raphson method of optimization due to Boyd.[24]

Trial co-ordinates for the orange and red isomers were obtained from the crystal-structure analysis, and hydrogen atoms were placed at calculated positions by approximating to C_{2v} symmetry at each carbon and nitrogen centre (N–H 1.03, C–H 1.09 Å). Calculations were carried out for the orange and red isomers by use of 257 (41 bonded, 88 angular, 118 non-bonded, 10 torsional) and 258 (41 bonded, 88 angular, 119 non-bonded, 10 torsional) interactions, respectively. For each isomer a total of 108 independent co-ordinates was varied during the minimization procedure and no new non-bonded interactions of any significance were produced during refinement.

TABLE 8

Minimized strain-energy terms (kcal mol^{-1}) for the two structures

Term	Structure (2)	Structure (3)
Bond deformation	1.0	1.5
Valence-angle deformation	3.4	3.3
Torsional interaction	6.5	7.2
Non-bonded interaction	5.0	6.7
Total strain energy	16.0	18.8

The minimization was considered to have converged when the root-mean-square displacement was <0.02 Å for the orange and <0.04 Å for the red isomer. Convergence from trial co-ordinates was quite rapid (6—7 cycles).

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[23] D. A. Buckingham, I. E. Maxwell, A. M. Sargeson, and M. R. Snow, *J. Amer. Chem. Soc.*, 1970, **92**, 3617.

[24] R. H. Boyd, *J. Chem. Phys.*, 1967, **47**, 3736.

During refinement it was necessary to introduce a damping factor (0.2) to maintain convergence toward a minimum-energy molecular geometry. Figure 4 gives perspective views of the cations plotted from the minimized co-ordinates (see Supplementary Publication). A breakdown of the final energy terms is given in Table 8 which gives a comparison of the minimized and crystal structures in terms of bond lengths, and bond and torsion angles.

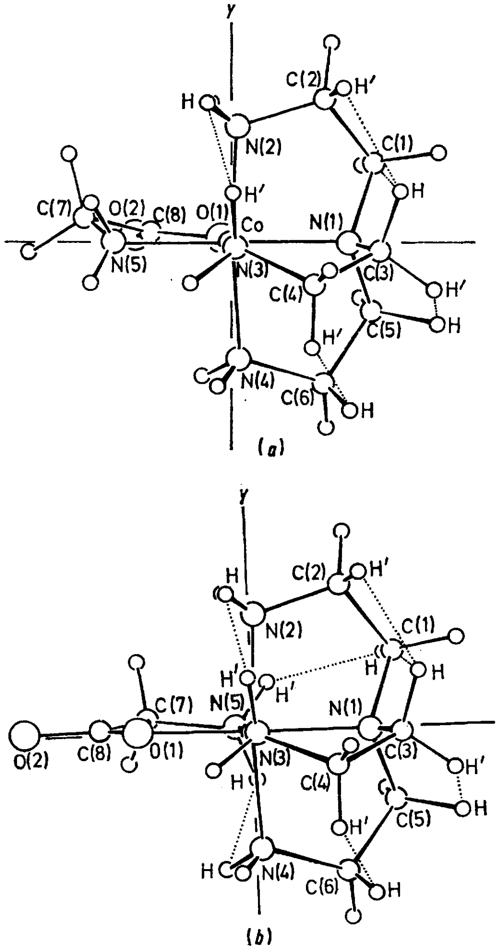

FIGURE 4 The orange (*a*) and red isomers (*b*) of $[Co(taa)(GlyO)]^{2+}$ drawn by use of minimized co-ordinates, and showing major non-bonded interactions. The red isomer here is enantiomeric to that obtained by crystal-structure analysis

DISCUSSION

Structure Assignment.—The present *X*-ray study has established the structures (2) for the orange and (3) for the red glycinato-complex cations, the reverse of an earlier tentative assignment.[6] The same configuration as (2) is now assignable to other amino-acid complexes obtained from peptide hydrolysis by (1), since all have the common visible absorptions at 470 and 343 nm.[6]

The recent proton-exchange studies by Buckingham *et al.*[25] distinguished the structure of two isomeric $[CoCl(taa)(NH_3)]^{2+}$ complexes; the purple isomer (ε_{530} 136, ε_{363} 126 dm^3 mol^{-1} cm^{-1}) with the NH_3 group *cis* to N_{tert} of the taa and the red isomer (ε_{512} 94, ε_{367} 99 dm^3 mol^{-1} cm^{-1}) with the NH_3 group *trans*. Their characteristic visible absorptions allow us to assign the hitherto uncertain geometry[5] of $[CoCl(taa)(GlyOR)]^{2+}$ as (7), since this glycine ester complex has the same visible pattern (ε_{514} 99, ε_{370} 102 dm^3 mol^{-1} cm^{-1}) as the latter monoammine complex. One can, then, visualize the reaction in which (7) affords the glycinato-product (2) in the presence of mercury(II) ion,[6] by assuming ester hydrolysis in the cobalt co-ordination sphere in the position *cis* to N_{tert}.

Comparison of Orange and Red $[Co(taa)(GlyO)]^{2+}$ *Cations.*—The total strain-energy difference between the orange and red isomers is calculated at 2.8 kcal mol^{-1} in favour of the former cation (Table 8). This difference is sufficiently large[25] to permit a prediction of the correct stability relation. The non-bonded interaction term makes the most significant contribution to the energy difference. Agreement between crystal and minimized torsion angles about the C–C, C–N, and C–O bonds (Table 6), which are primary parameters in the energy summation, is excellent indicating the calculations have adequately reproduced the observed chelate-ring conformations.

The major steric repulsions for both isomers occur within the taa ligand (see Table 9). The corresponding non-bonded distance between the two isomers is similar, showing that the taa geometry is almost unaffected by the orientation of the chelate ring. Further, the agreement between crystal and minimized geometry indicates that intermolecular crystal forces have not significantly perturbed the taa molecular geometry. The evidence from crystal-structure analyses, molecular models, and minimization calculations on the taa complexes is consistent with a rigid arrangement of the conformations.

TABLE 9

Intramolecular non-bonded interactions[a] (>0.4 kcal mol^{-1})

	Orange		Red	
Atoms	Found[b]	Calc.	Found[b]	Calc.
N(2)H · · · H′N(3)	2.16 (0.5)	2.19 (0.4)	2.04 (0.9)	2.09 (0.7)
C(1) · · · HC(3)	2.43 (0.6)	2.46 (0.5)	2.43 (0.6)	2.45 (0.5)
C(2)H′ · · · HC(3)	2.02 (1.0)	2.07 (0.8)	2.03 (1.0)	2.08 (0.7)
C(3)H′ · · · HC(5)	2.22 (0.4)	2.24 (0.3)	2.20 (0.4)	2.22 (0.4)
C(4)H′ · · · HC(6)	2.10 (0.7)	2.13 (0.6)	2.07 (0.8)	2.11 (0.7)
N(4)H · · · HN(5)			2.13 (0.6)	2.16 (0.5)
N(5)H′ · · · HC(1)			2.08 (0.8)	2.09 (0.7)
N(5)H · · · H′C(5)			2.25 (0.3)	2.22 (0.4)
N(5)H′ · · · H′C(7)			2.20 (0.4)	2.20 (0.4)

[a] Energy of interaction in kcal mol^{-1} in parentheses follows distance (Å). [b] Hydrogen-atom positions for crystal structure based on local tetrahedral C_{2v} symmetry around nitrogen and carbon, assuming N–H 1.03, C–H 1.09 Å.

The red complex cation is less stable owing to extra unfavourable non-bonded interactions between the protons on the glycine nitrogen atom, N(5), and the adjacent protons on the taa carbon and nitrogen atoms (Figure 4, Table 9). The steric crowding at the N(5) position in (3) is also evident in the bond angles: N(1)–Co–N(5) 98.2°, 1.0 kcal mol^{-1} (crystal); 97.8°, 0.9 kcal mol^{-1} (minimized); and C(1)–N(1)–C(5) 113.6°,

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[25] D. A. Buckingham, P. J. Cresswell, and A. M. Sargeson, *Inorg. Chem.*, 1975, **9**, 1485.

0.4 kcal mol^{-1} (crystal); 113.3°, 0.3 kcal mol^{-1} (minimized); corresponding values for the orange isomer are: N(1)–Co–O(1) 93.7, 0.2 kcal mol^{-1} (crystal); 93.9°, 0.2 kcal mol^{-1} (minimized); and C(1)–N(1)–C(5) 111.4°, 0.1 kcal mol^{-1} (crystal); 111.9°, 0.1 kcal mol^{-1}. Another effect of the steric crowding *cis* to N_{tert} is manifested in the arrangements of the tetra-amine around the cobalt ion (Figures 1 and 2). Thus, as mentioned earlier, in the red isomer (3), both N(2) and N(4) of the taa ligand are bent toward N(3) compared with the orange isomer (2). From another point of view, one can state that without countering forces such as the non-bonded interactions from the *cis* substituent, octahedrally co-ordinated taa would tend to have tripod geometry to some extent, in order to relieve the internal non-bonded strain.

The glycinato-groups show significant differences in terms of planarity (Figure 4, Table 5). In the red isomer, C(7) is apparently forced to deviate to twist the C(7)–N(5) axis so that the protons attached to N(5) suffer the least intramolecular non-bonded repulsion. However, the deviation of C(7) from planarity in the orange isomer seems to be required by the unusual short Co–N(5) bond distance, which serves to maintain optimum bond angles within the five-membered chelate ring.

Chemical Significance of these Structures.—It is now clear that the position *cis* to N_{tert} in the octahedral taa complexes is sterically hindered. As a result, the *cis* substituent should be labile relative to the *trans*, and this may explain several experimental observations. For instance, Buckingham *et al.*[25] found that in base hydrolysis of the two isomeric $[CoCl(taa)(NH_3)]^+$, 85% isomerization of the *cis*-NH_3 group occurred, while the *trans*-NH_3 retained the same configuration. Zipp *et al.*[12] showed that the first aquation rate of $[CoBr_2(taa)]^+$ was 30 times as rapid as that of *cis*-$[CoBr_2(en)_2]^+$ (en = ethylenediamine), and this was attributed to the labile nature of the bromide ion *cis* to N_{tert}.[12]

As noted, the bond distances between the metal and the ligand *trans* to N_{tert} are significantly shorter than the other Co–N_{prim} and Co–O bond lengths. This may be accounted for by a special electronic effect transmitted by N_{tert} to the *trans* position. The same effect may prevail for a unidentate ligand and contribute to the slower aquation rate of the second halide ion in $[CoX_2(taa)]^+$,[12] or the thermodynamic stability of *trans*-NH_3 in $[CoCl(taa)(NH_3)]^{2+}$.[25]

One could rationalize the specific formation of the orange amino-acid complexes in peptide hydrolysis with (1) by assuming similar steric effects in the initial rate-determining step which involves replacement of the *trans*-aqua-molecule by the terminal amino-group of the peptide before its chelation. For the reaction of free glycine, the basic group (either amino or carboxy depending on the pH) would first attack at the *trans* position, followed by rapid chelation. Thus, a mixture of orange and red cationic products would result.[6]

The geometrical assignment of the two isomers now permits an explanation for the difference in visible spectrum between (2) (ε_{472} 100, ε_{343} 97) and (3) (ε_{500} 90, ε_{347} 75 dm^3 mol^{-1} cm^{-1}),[6] which is unusually large for CoN_5O complexes. In the spectra of octahedral CoN_4(a)(b) complexes, the *trans* isomers invariably display the band *I* at higher wavelengths than do the *cis* isomers, provided that both a and b are weaker than N in ligand-field strength, *e.g.* CoN_4O_2, CoN_4ClO, or CoN_4Cl_2.[26] When (2) and (3) are regarded as *cis*- and *trans*-CoN_4XO (N for N_{prim}, X for N_{tert}), a close similarity between CoN_4XO and CoN_4(a)(b) is evident. This suggests that N_{tert} should be placed below N_{prim} in the spectrochemical series. A similar argument is applied to the two isomeric $[CoCl(taa)(NH_3)]^{2+}$ of which the purple isomer (Cl *trans* to N_{tert}) has the band *I* at higher wavelength (530 compared with 512 nm) than the red isomer (Cl *cis* to N_{tert}). It is then significant that despite the fact that N_{tert} may exert a weaker ligand-field strength than N_{prim}, the bond distance is shorter for Co–N_{tert} than for Co–N_{prim}, which may be a result of the unique co-ordination bond angles at N_{tert}. The relative polarities of the orange and red isomers are also consistent with that of *cis*- and *trans*-CoN_4X_2, as shown, for instance, by the R_F value on silica gel t.l.c. [0.3 for (2), 0.8 for (3), with eluant BuOH : H_2O : $HClO_4$ 5 : 5 : 1]; (3) is as non-polar as the orange $[Co(taa)(LeuO)]^{2+}$ complex (LeuO = leucinato).

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[26] See *e.g.*, Y. Shimura, 'Co-ordination Stereochemistry,' (in Japanese), Baifu-kan, Tokyo, 1972, p. 131.